SYNTHESIS AND CRYSTAL STRUCTURE OF SOME
NOVEL PHASES INVOLVING METAL-METAL BONDING

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Ph.D. Thesis Submitted to Iowa State University

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Synthesis and crystal structure of some
novel phases involving metal-metal bonding[†]

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Crystal growth and X-ray diffraction studies have been carried out for zirconium monochloride and (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)sodium heptantimonide(-3). Single crystals of ZrCl were grown via the reaction of gaseous zirconium tetrachloride with electropolished strips of zirconium metal in a sealed tantalum tube in a 750+500° temperature gradient. The crystal structure was determined from three-dimensional X-ray data collected on an automated diffractometer using MoK_α radiation. Zirconium monochloride crystallizes in the monoclinic system with four molecules in a unit cell of symmetry C2 and dimensions $a = 5.943$, $b = 3.419$, $c = 9.087\text{\AA}$ and $\beta = 102.50^\circ$. The structure was solved by Patterson methods. Full matrix least squares refinement on all 203 observed reflections using anisotropic thermal parameters resulted in final converged

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atomic parameters with $R = 0.081$ and $R_w = 0.087$. The crystal structure involves sheets of metal or chlorine atoms in the sequence Cl-Zr-Zr-Cl and is consistent with the graphitic character of the compound. Intralayer Zr-Zr and Cl-Cl interatomic distances are both $3.43\text{\AA}$. The interlayer Cl-Cl interatomic distance is $3.61\text{\AA}$ while that for Zr-Zr is $3.09\text{\AA}$. The latter compares with $3.149\text{\AA}$ in the metal and is indicative of a strong metal-metal interaction.

The dark brown crystalline (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)sodium heptantimonide(-3), $(C_{18}H_{36}N_2O_6 \cdot Na^+)_3Sb_7^{3-}$, was prepared from the reaction of a 1:1 alloy of sodium and antimony with $C_{18}H_{36}N_2O_6$, a 2,2,2-crypt, in ethylenediamine. Lattice constants $a = 23.292$, $b = 13.791$, $c = 25.355\text{\AA}$ and $\beta = 108.56^\circ$ for the monoclinic space group $P2_1/n$ and four molecules per unit cell were deduced from three dimensional X-ray data collected from a single crystal of the compound on a four-circle diffractometer using MoK_α radiation. The problem was phased using direct methods. A block diagonal least squares refinement of the 88 independent nonhydrogen atoms with isotropic temperature factors on all 4662 observed reflections resulted in converged atomic parameters with a residual of 0.172. After converting the temperature factors of the heavy atoms to anisotropic values, further block least squares refinement resulted in a residual of 0.130. Stepwise full matrix least squares refinement of the heavy atoms and the light atoms of the crypts in turn

resulted in converged atomic parameters with $R = 0.111$ and $R_w = 0.134$. Further refinement after conversion of the temperature factors of the light atoms to anisotropic values did not result in a statistically significant improvement in the weighted residual. This structure demonstrates the first example of a well-characterized polyatomic anion for a metallic element. Three cryptated sodium cations in which the sodium ion occupies the central cavity of the macrobicycle occur with the Sb_7^{3-} cluster anion. The arrangement of the oxygen atoms of the crypt around sodium approximates a trigonal antiprism. The seven antimony atoms in the anion cluster are coordinated in an end-capped trigonal prism having approximate C_{3v} symmetry.

INTRODUCTION

Much attention in recent years has been focused on compounds involving metal-metal bonding. While very few examples were known only a few years ago, it now appears that catenation is an important facet of the chemistry of the metallic elements.¹ In approximately the last decade it has been demonstrated that many metals, particularly the heavier ones in lower than normal oxidation states, show a propensity toward forming homonuclear metal to metal bonds. The occurrence of metal-metal bonds in compounds of the transition metals have been reviewed by several authors.²⁻⁵ Recently, Corbett has reviewed the homopolyatomic ions known for the post-transition elements,^{6a} and Gillespie and Passmore have presented a general review of the homopolyatomic cations of the elements.^{6b} Among the reasons for neglect of this field of chemistry until recently have been the nonexistence of good solvent systems for metallic systems, the range of composition that many such compounds exhibit, and the lack of a theory of valence to adequately describe such compounds.⁷ Cotton has emphasized that the surest indication of the existence of a metal-metal interaction is provided by the determination of the molecular structure.⁸ In this research X-ray crystallography was chosen as the method of structural elucidation.

The reduction of several of the rare earth metal halides by the respective metal has resulted in several unexpected and unusual compounds.⁹ The preparation and subsequent determination of the structure of gadolinium sesquichloride^{10,11} represents a rewarding investigation in this area. The overriding feature of the structure is the occurrence of chains of gadolinium atoms involving elongated octahedra sharing edges running parallel to the fiber axis. The chains dictate the structural arrangement and are separated by sheaths of chlorine atoms all of which occupy faces of metal atom triangles.

Research techniques developed in the study of the rare earth-rare earth metal halide systems have proven applicable to the investigation of other systems of experimental interest. A scarcity of information concerning the lower halides of zirconium and hafnium led to the study of the reduction characteristics of halides of the two elements by Struss and Corbett.^{12,13} The reaction of gaseous HfCl_4 from a reservoir at $450\text{--}550^\circ$ with a large area of hafnium foil at $610\text{--}650^\circ$ in a sealed tantalum tube gives a very small amount of metallic product HfCl_{1+x} ($0 < x < .2$). The analogous reaction for ZrCl_4 at 600° produces ZrCl_3 and a small amount of ZrCl_{1+x} mixed with ZrCl_2 . Equilibration of either metallic product with the respective metal at 625 to 650° in a tantalum container gives the pure monochloride. While the reduction to zirconium monochloride is more facile, the two monochlorides are apparently

isostructural and metallic conductors.¹³ A previous preparation of zirconium(III) chloride, bromide and iodide resulted in better yields than for the corresponding hafnium(III) halides.¹⁴ Apparently the facility of the reduction of zirconium halides relative to those of hafnium is one of the few differences in the chemistry of the two elements. Larsen has proposed a separation scheme involving the reduction of zirconium tetrahalides containing hafnium in natural abundance to the appropriate zirconium trihalide by either metallic zirconium or aluminum in molten 76 mole percent aluminum trihalide at 260-310°.¹⁵ Under the same time and temperature conditions, the respective hafnium tetrahalide remains substantially unreduced and can be separated along with the aluminum halide solvent by sublimation from the nonvolatile zirconium trihalide. It remains to be seen if this approach is practicable, but the separation of zirconium and hafnium is of commercial significance as the disparate thermal neutron capture cross sections of the two elements enjoins the use of zirconium for cladding nuclear fuel and hafnium for control rods in nuclear reactors.¹⁶

The purity of several of the reported trihalide phases is questionable because of the use of powdered zirconium metal as the reducing agent or because of side reactions with silica containers.^{14,17,18} Newham and Watts reported the preparation of pure anhydrous zirconium trichloride, tribromide and

triiodide from passage of the appropriate tetrahalide vapor mixed with hydrogen through a glow discharge.¹⁹ Afterwards the product was freed from absorbed or unreduced contaminants by heating in vacuo. Struss and Corbett carried out their reactions between gaseous tetrahalide and the appropriate metal foil in sealed tantalum containers.^{12,13} Thus, side reactions with the container and cessation of the reaction by blockage of the surface of the metal particles were obviated. Zirconium dihalides of uncertain purity have been obtained from the disproportionation of the trihalides.^{20,21} Heating zirconium trichloride and metallic zirconium in a quartz tube lined with platinum foil resulted in zirconium dichloride of 95-99% purity.²² The homogeneity range of zirconium(II) chloride is presently being investigated in this laboratory.²³

The patent literature contains a reference to a product called "Zirklor"²⁴ made by electrolytic reduction of a $\text{SrCl}_2\text{-NaCl-ZrCl}_4$ melt (63:34:3) onto graphite. Its color, softness, graphitic character and analysis correspond to the properties of ZrCl , but the powder pattern data given in the patent are in poor agreement with the data reported by Struss and Corbett.¹³ Surprisingly, a sample of the material "Zirklor" was found to have substantially the same pattern as did ZrCl .¹³ A report of the synthesis of ZrCl and its powder pattern by Troyanov and T'sirelnikov²⁵ agrees generally with that of Struss and Corbett with the exception of the omission of the lowest angle line in the powder pattern by the former

authors. A subsequent crystal structure determination for ZrCl by Troyanov²⁶ is poorly refined and in error. The preparation of a suitable single crystal of ZrCl will be described in Chapter II of this thesis and the structure determination of ZrCl will be described in Chapter III.

Several years ago the X-ray investigation of the product of the reduction of molten bismuth chloride by bismuth metal revealed that the phase corresponded to the stoichiometry $\text{BiCl}_{1.167}$.²⁷ The structure determination resulted in the discovery of the homopolyatomic cation Bi_9^{5+} associated with the large complex anions $[\text{BiCl}_5]^{2-}$ and $[\text{Bi}_2\text{Cl}_8]^{2-}$ in the ratio 2:4:1. When the reduction is carried out in the aluminum chloride solvent system, two compounds $\text{Bi}_5^{3+}(\text{AlCl}_4^-)_3$ and $(\text{Bi}^+\text{AlCl}_4^-)_n$ crystallize following reduction of the composition $\text{BiCl}_3 \cdot \text{AlCl}_3$ by a stoichiometric or excess quantity of bismuth, respectively.²⁸ Attempts to obtain a single crystal of either compound suitable for an X-ray structure determination were thwarted by the tendency to supercool and produce twinned crystals.²⁹ During the course of this research several attempts were made to prepare the compound $\text{Bi}_5^{3+}(\text{AlBr}_4^-)_3$ and isolate a single crystal suitable for a structural determination.

Over forty years ago, Zintl reported potentiometric evidence for solutions of polyatomic anions of antimony, bismuth, lead, tin and arsenic, among others, after reduction of a salt of the respective heavy metal with sodium metal in

liquid ammonia.³⁰⁻³³ The compounds indicated for Group IV and V elements are listed in Table 1. These unusual phases were

Table 1. Zintl phases

Na_3As	Na_4Sn_9	Na_4Pb_7
Na_3As_3	Na_3Sb	Na_4Pb_9
Na_3As_5	Na_3Sb_3	Na_3Bi
Na_3As_7	Na_3Sb_7	Na_3Bi_3

not further characterized because it was not possible to isolate them from the ammoniacal solutions in crystalline form. It is significant that two of the reported products, Na_4Sn_9 and Na_4Pb_9 , contain anions that are isoelectronic and presumably isostructural with the Bi_9^{5+} cation in $\text{BiCl}_{1.167}$.⁶ Attempts to prepare solid phases containing these anions have been frustrated by their tendency to form the known and more stable intermetallic phase involving the heavy metal and the sodium counter cation. Some effort has been made to generate such species in molten salts, and the cryogenic evidence for Sb_3^{3-} in NaI is encouraging.³⁴ Exploratory work in this laboratory seeking to isolate stable cluster anions by varying the conditions, solvent and cation from those used by Zintl have been unsuccessful.³⁵ However, Kummer and Diehl have

recently reported isolation of a crystalline compound $\text{Na}_4\text{Sn}_9 \cdot 6\text{-}8$ ethylenediamine.³⁶ They present Mössbauer data, magnetic data and preliminary X-ray data, but they have yet to report a complete X-ray structure determination.

Recently, Dye has reported the preparation and crystal structure of a compound $\text{Na}_2\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6$ which contains a cryptated sodium cation and a sodium anion.^{37,38} Cryptates are a new type of complexing agent that wrap themselves around metal ions in solution thereby effectively hiding the metal ion from the solvent.³⁹ The compound $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6[\text{I}]$ is one of

I

a series of polyoxamacrobicycles synthesized by Lehn⁴⁰ consisting of a bicyclic ring system with two nitrogen bridgeheads and a defined number of ether-oxygen atoms in the bridges. The systematic designation is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane. While the shorter designation 2,2,2-crypt has the feature of specifying the number of ether oxygens in each bridge, in many cases it will be convenient to simply use the abbreviation C. Dye exploited 2,2,2-crypt to encapsulate the sodium cation in solutions of sodium in ethylamine which ultimately allowed

isolation of solid NaC^+Na^- .³⁷ One sodium cation was found to occupy the central cavity of the macrobicycle[I] as has been found for all of its complexes with alkali, alkaline earth and other metal ions so far studied.⁴¹ The sodium anion was found to be located outside of the cryptated cation at a large distance from all other atoms.³⁸ By comparison with the known crystal structure of (cryptated sodium) iodide⁴² the outside sodium is similar to the iodide ion in its placement, but distance comparisons suggest it is somewhat larger than the iodide ion.³⁸

Don Merryman and Frank Armatis have been involved in a series of synthetic attempts to prepare stable compounds containing homopolyatomic anions.⁴³ Typically, 18-crown-6 ether or the 2,2,2-crypt[I] was allowed to react with sodium alloys of heavy metals in amines to stabilize a salt containing the cryptated sodium cation and a presumed polyatomic anion. In the case of a 1:1 alloy of sodium and antimony, reaction with 2,2,2-crypt in ethylenediamine lead to the isolation of a dark brown crystalline solid on evaporation of the solvent. The X-ray structure determination reported here confirms that the compound involves three cryptated sodium cations and a Sb_7^{3-} cluster anion. The synthesis of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ will be described in Chapter II of this thesis. The details of the structure determination will be given in Chapter IV.

During the course of this work the goal of synthesizing a single crystal of zirconium monochloride suitable for a structure determination and solving the crystal structure has been realized. Now that the structure is known, the physical properties can be correlated with it. In fact, the layer structure determined for zirconium monochloride explains why it was so difficult to find a suitable single crystal. The synthetic work on the $\text{Bi-BiBr}_3\text{-AlBr}_3$ system did not produce such satisfactory results. While apparently crystalline material was obtained from two preparations and X-ray data sets were recorded for two different crystals, it has not been possible to solve the structure. Reasonable positions for the tetrabromoaluminate groups could be chosen by inspection of the Patterson map, but the positions of the bismuth atoms were more elusive. One interpretation of the problem involves packing of the Bi_5^{3+} units in alternative orientations. Despite the disappointment of not having solved the structure, the structure solution of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ has provided the opportunity to extend the idea of catenation of metal atoms to anions and to demonstrate the first example of a stable solid containing a well-characterized homopolyatomic cluster anion for a metallic element.

EXPERIMENTAL PROCEDURE

Preparation and Handling of Compounds

Preparation of zirconium monochloride

Struss and Corbett reported the formation of stable zirconium monochloride from the reaction of a partially reduced sample of zirconium chloride with zirconium metal at 625° in a closed tantalum container.¹³ The purpose of this research was to prepare a single crystal of ZrCl suitable for a structure determination. While the preparation of ZrCl was quite straightforward, the first several reactions resulted in polycrystalline products. The metal strips used had been cold-rolled to a 15-20 mil fold from crystal bar zirconium containing less than 0.05% hafnium. Typically two strips of foil about 8 cm long were reacted with 0.05 g of zirconium tetrachloride in a closed tantalum container. The tetrachloride had been prepared by treating the metal with HCl (Precision Gas Products) at an initial temperature of 300° and increasing to 500° followed by vacuum sublimation through a coarse frit.¹³ In order to determine the optimum temperature conditions, several preparations were carried out at various temperatures between 650 and 900°. The use of a 700-900° temperature gradient gave somewhat better results, but the reaction period of one week was apparently too short as the crystals were too small. A subsequent preparation was

carried out under similar conditions for 30 days. The half of a metal strip that had been at the cool end of the reaction tube was covered with gleaming black zirconium monochloride platelets while a dull grey powder clung to the other half of the strip. The powder pattern of the ZrCl platelets compared favorably with that of Struss and Corbett,¹³ and the powder pattern of the grey powder established it as zirconium metal. It is reasonable that ZrCl would disproportionate to ZrCl_4 and the metal at 900° . Several platelets of ZrCl from this preparation were mounted and exposed to X-rays. Most were polycrystalline, but a few gave streaked spots. The layer line separation in these photographs gave a spindle axis of $3.42\text{\AA}$. The idea that the streaking indicated a disordering problem prompted the construction of a device capable of producing a continuously increasing potential that could be attached to the thermocouple input of a Brown temperature controller to enable the reaction tube to be cooled very slowly. The effect of electropolishing the metal was also contemplated, and a series of preparations was carried out to assess the merit of these proposals. The best crystals obtained from this series of reactions were grown on electropolished metal in a $700\text{--}900^\circ$ temperature gradient. Evidently electropolishing the metal does help to prevent nucleation, and electropolishing is the method of choice for cleaning zirconium because the high affinity of zirconium for oxygen

precludes cleaning it in oxidizing acid solutions or by induction heating. Finally, a preparation was undertaken in which electropolished strips of zirconium metal were heated with a small amount of zirconium tetrachloride in a sealed tantalum container in a 600-800° gradient for 24 days. The furnace was then cooled at an initial rate of $1.25^{\circ} \text{ day}^{-1}$ for four days. At this point the rate was increased to $5^{\circ} \text{ day}^{-1}$. The scheme of slowly cooling the furnace was thwarted the next day by a power failure. Nonetheless, when the tube was taken into the dry box and cut open, bright, well-formed hexagonal platelets were found clinging to the center portions of the metal strips. No reaction had occurred at the cool end of the tube. As before, powdered zirconium metal was found on the surface of the strips at the hot end of the tube. Of the dozen crystals that were mounted, two gave sufficiently promising oscillation patterns that they were considered good enough to align. Oscillation photographs established that the spindle axis was $3.42\text{\AA}$ as before. However, the zero-level and first-level Weissenberg photographs of these two crystals were now of sufficient quality to allow construction of the reciprocal lattice. Plotting the spots from the two films on polar graph paper resulted in a primitive monoclinic cell having $a=9.19$, $b=3.42$, $c=5.92\text{\AA}$ and $\beta=103^{\circ}$. Unfortunately, by the time that priority for the diffractometer could be established, neither crystal diffracted

X-radiation. Since a search of the reaction product from which these two crystals had originally been obtained failed to produce a suitable crystal, the reaction was repeated using the same conditions. This reaction was apparently defeated by power failures during both the equilibration and cooling periods. After an appeal for an emergency power circuit had been heeded by the lab electricians, the reaction was repeated yet again. Following two sessions of mounting crystals from this reaction, capillary No. 215 was confirmed to contain a single crystal of zirconium monochloride.

Preparation of (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) sodium heptantimonide(-3)

Preliminary X-ray investigations were carried out on several phases expected to contain polyanions. In their synthetic work, Don Merryman and Frank Armatis employed the bicyclic amine 2,2,2-crypt or 18-crown-6 ether with sodium alloys of bismuth, lead and antimony in a solvent such as ethylenediamine or liquid ammonia to obtain a solid presumably containing a polyanion.⁴³ The first such solid investigated resulted from the reaction of NaSb and 2,2,2-crypt in ethylenediamine. Microscopic examination of the resultant solid product revealed dark brown crystals possessing regular external morphology in the form of needles on the order of tenths of millimeters in diameter and a millimeter in length. The first crystals that were mounted in capillaries in the

dry box were picked up with a wand greased with Vaseline. Two of six crystals mounted initially exhibited a diffraction pattern, but after several days they no longer diffracted X-rays. Crystals from a second preparation of this compound were mounted on another occasion using silicone lubricant rather than Vaseline. Several of these crystals gave good diffraction patterns. The reaction of NaSb_3 with 2,2,2-crypt in ethylenediamine produced a solid of similar morphology. Diffraction photographs obtained from these crystals had the same pattern as those obtained from the material prepared from the 1:1 alloy. Powder patterns of the two solids confirmed that they were the same compound. Several other compounds were examined with less success. A grey solid made by mixing NaBi and 2,2,2-crypt in ethylenediamine occurred as diamond shaped crystals adhering to the walls of the reaction tube. Once the tube was cracked open in the dry box, it was discovered the crystals had the consistency of Philadelphia cheese. None was successfully mounted in a capillary. A dark brown solid made from Na_4Pb_9 and 18-crown-6 ether occurred as large needles. While these crystals were easily scraped from the tube and mounted, most were found to be amorphous upon exposure to X-rays. A second preparation involving Na_4Pb_9 and 2,2,2-crypt in liquid ammonia gave slightly better formed crystals. However, these too were shown to be amorphous upon X-ray examination.

Since the antimony system seemed the most promising, further effort was concentrated on that system. Good crystals were readily obtained by reacting powdered NaSb with 2,2,2-crypt in ethylenediamine at room temperature for 12 hours.⁴³ The reaction was carried out in a Y-shaped reaction vessel which could be evacuated. Afterwards, the side arm was immersed in an ice bath and the ethylenediamine solvent was slowly distilled off over a twelve hour period. A deficiency of crypt was used to favor cryptation of sodium ions. The 1:3 alloy which was found to give the same product dissolved more slowly. Letting the solution stand longer or gently heating it to 40-50° was found to be equally satisfactory. The 2,2,2-crypt used in these syntheses was purchased from EM Laboratories, Inc. Its synthesis has been outlined by Truter and Pedersen³⁹ as follows:

Dye, et al. have published a modification⁴⁴ of the original procedure of Lehn.⁴⁵

Mounting of crystals

A dry box designed primarily for mounting crystals was obtained from Blickman, Inc. It differs from the other dry boxes in the group in having a nearly horizontal window to facilitate the use of an external Bausch and Lomb "Stereozoom" microscope with a 7 inch focal length. To avoid the inconvenience of focusing the microscope from outside of the box, crystals to be mounted are placed on a lab jack which can be raised or lowered as needed to bring them into focus. This dry box has been equipped with a hot wire for sealing off capillaries which is operated by a foot switch. The moisture content of the box is monitored with a Beckman electrolytic hygrometer. Like the other dry boxes in the group, entrance is gained through an evacuable port. The box is flushed with dry nitrogen. An internal recirculating system consisting of a squirrel cage fan which pulls the incoming gas stream and the box atmosphere through a Molecular Sieve is capable of keeping the moisture content in the box below 30 ppm under most circumstances.

After crystals were sorted in the dry box, candidates for mounting were picked up on the end of a thin glass stalk tipped with Vaseline (ZrCl) or silicone lubricant ($[\text{NaC}^+]_3\text{Sb}_7^{3-}$) and gently inserted into 0.2 mm i.d. Lindemann

(LiBeBO_3) glass capillaries. Once the stalk was inserted into the capillary, it was twisted to coat the walls with lubricant so that it could be removed leaving the crystal lodged in the capillary. The end of the capillary was then sealed off using the resistance wire inside the dry box, and the seal-off was checked visually with the microscope for the absence of pin-holes. When enough crystals had been mounted, the capillaries were removed from the dry box and sealed off to a length of about one cm on either side of the crystal using a fine tipped gas-oxygen flame. These shortened capillaries were then held in a brass pin 7 mm long by 3 mm o.d. with Apiezon W. Finally, the pin was placed in a goniometer head which could be attached to either X-ray cameras or the full-circle diffractometer.

X-Ray Diffraction Techniques

Camera techniques

Prior to the collection of intensity data, oscillation photographs were taken on a Weissenberg camera⁴⁶ in order to assess the diffraction characteristics of the crystal. If it is desired to proceed with further film work, the crystal is aligned so that the spindle axis is perpendicular to the X-ray beam. It is then possible to take Weissenberg photographs from which the reciprocal lattice can be constructed. The Weissenberg method involves translating the camera back and forth while the crystal oscillates. A screen with a

slit in it allows only one predetermined level of diffraction maxima to expose the film. In this manner the spots of the given diffracted cone are spread out over the film in a series of pinacoids which can be readily indexed. If, for example, the spindle axis corresponds to the b-axis, then the zero-level photograph contains all the $h0l$ reflections, the first level the $h1l$, the second level the $h2l$, and so forth. In order to examine the extinctions along the spindle axis it is either necessary to realign the crystal along another axis or to obtain photographs using a precession camera. The precession technique allows undistorted reproduction of the reciprocal lattice.⁴⁷ For a crystal having the b axis corresponding to the spindle axis, this is accomplished by aligning the crystal so that the $hk0$ or $Ok l$ plane is normal to the X-ray beam. A flat piece of film opposite the beam from the crystal precesses while the crystal is slowly precessed. A screen with a circular slit enables diffraction maxima from a given layer to be recorded on the film. The spindle axis is then rotated by the angle β^* in order to record the diffraction maxima from the other plane.

Data collection

Intensity data for the reflections observed within one asymmetric unit of reciprocal space for a given crystal system can be obtained either by estimating intensities of spots on film or by using an automated diffractometer. X-ray data for

both of these compounds were taken at ambient temperature using a four-circle diffractometer interfaced with a PDP-15 computer.⁴⁸ The computer is programmed to control the diffractometer such that it is possible to take data from an unaligned crystal.⁴⁹ Several photographs are taken at arbitrary values of χ and ϕ . A few spots are chosen on each photograph, and their coordinates become input to the computer. The computer indexes these ten to fifteen reflections based on the fact that the indices must be whole small numbers. It then outputs a tentative unit cell and cell scalars which the user may transform if it is necessary. This unit cell assignment is verified by taking "oscillation" photographs aligned along the three crystallographic axes. Finally, three strong noncoplanar reflections are chosen as standard reflections. The instrument tunes on these reflections prior to undertaking data collection, and it checks these standards periodically while data are being collected. The X-radiation employed is Mo K_{α} ($\lambda=7.0954\text{\AA}$) obtained using a graphite monochromator. Reflections are measured with a scintillation counter using a step scan technique⁵⁰ to obtain integrated intensities.

ZrCl Diffraction data for ZrCl were collected from a shiny black hexagonal platelet measuring 0.14 x 0.11 x 0.02 mm. The dataset was recorded on the basis of a monoclinic unit cell having $a=5.95$, $b=3.43$, $c=9.09\text{\AA}$ and $\beta=102.43^{\circ}$. This

compares with lattice constants $a=9.19$, $b=3.42$, $c=5.92$ and $\beta=103^\circ$ estimated from film work with a previous crystal that proved to be unsuitable for a complete structure determination. A total of 230 integrated intensities were obtained out of 416 reflections checked in the two octants hkl and $hk\bar{l}$. Refined unit cell parameters and their standard deviations were obtained by a least squares fit⁵¹ to twice the Ω angles of 16 independent reflections which were tuned by the diffractometer after the dataset had been recorded. Any error in the instrumental zero was eliminated by centering the reflection at $+\Omega$ and $-\Omega$. The final cell constants with errors for the last significant digits in parentheses are $a=5.943$ (6), $b=3.419$ (3), $c=9.087$ (18) Å, $\alpha=\gamma=90.00$ (0) and $\beta=102.50$ (12)°.

$(NaC^+)_3Sb_7^{3-}$ The needle used for data collection was an approximately regular rectangular prism having dimensions 0.1 x 0.2 x 0.6 mm. The compound crystallizes with monoclinic symmetry: $a=23.45$, $b=13.93$, $c=25.52$ Å and $\beta=108.73^\circ$. A total of 6717 integrated intensities were measured for reflections hkl and $hk\bar{l}$ out of 11,263 reflections scanned. Since a thirty per cent decrease in the intensities of the standards occurred during data collection, a dataset scaled linear in time to the initial sum of the intensities of the standards was prepared. Lattice constant refinement in the same manner as for $ZrCl$ resulted in final cell constants $a=23.263$ (43), $b=13.776$ (4), $c=25.344$ (73) Å, $\alpha=\gamma=90.00$ (0) and $\beta=108.57$ (19)°.

Data reduction

After data collection, a series of steps collectively referred to as data reduction are carried out. Initially the data tape was read, and cards were punched with a record of the indices, theta, chi, phi, background count, total count and net count for each reflection. At this point the raw intensities were corrected for absorption. The extent to which an X-ray is absorbed in passing through a crystal of thickness t is given by⁵²

$$I = I_0 \exp(-\mu t) .$$

In this expression μ , the linear absorption coefficient, is defined as

$$\mu = \frac{n}{V} \sum_i (\mu_a)_i$$

where μ_a is the atomic absorption coefficient and n is the number of molecules in the unit cell with volume V . The absorption by a given crystal is thus a function of its shape and its orientation. No fully satisfactory method of evaluating the absorption correction for the general case has so far been described. The difficulty in making absorption corrections arises from having to calculate the absorption for the actual path length traveled within a crystal by the incident and diffracted beams for each infinitesimal volume element of the crystal dV and then to integrate these results

over the entire volume of the crystal.⁵³ While the linear absorption coefficients for ZrCl and $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ were both small, 66 and 25, respectively, the dimensions of both crystals were sufficiently different that it seemed appropriate to apply an absorption correction. The program TALABS⁵⁴ which was used calculates the absorption coefficient⁵⁵

$$A = \int \exp(-\mu L) dV .$$

The total path length L is equal to the sum of l_1 and l_2 where l_1 is the length of the path of the incident ray from its point of entry into the crystal up to the volume element dV and l_2 is the corresponding length of the path of the beam diffracted in dV . The integration is carried out over the volume V of the crystal. The program bases this calculation on the contribution to the diffracted intensity from a tetrahedron in which the path length of the rays is a linear function of the coordinates of the diffracting element.

After the absorption correction is carried out, each dataset was reduced using the program DATRED. This program divides each integrated intensity by its absorption coefficient, A , and also by a Lorentz and polarization factor⁵⁶ given by

$$L_p = \frac{\cos^2 2\theta_m + \cos^2 2\theta}{(1 + \cos^2 2\theta_m) \sin 2\theta} .$$

These corrected intensities are proportional to the square of the structure factor, F_o^2 . The estimated error in each intensity measurement is calculated by

$$(\sigma_I)^2 = [TC + BK + (K_T TC)^2 + (K_B BK)^2 + (KI)^2]/A^2$$

where TC is the total count, BK is the background count, I is the net intensity, A is the transmission factor, and K_T , K_B and K are fractional random errors in TC, BK and I, respectively.⁵⁷ The arbitrary value 0.03 was assigned to K_T , K_B and K. The estimated standard deviation in each structure factor is based on the finite difference method. The function used is

$$\sigma_F = \left| \frac{I/A + \sigma_I}{L_P} \right|^{\frac{1}{2}} - |F_o|$$

where all terms are as defined above.⁵⁷ In the case of ZrCl₂ 203 reflections of the 230 integrated intensities collected were found to be statistically above background by more than $3\sigma_I$. Of the 6717 integrated intensities recorded for $(NaC^+)_3Sb_7^{3-}$, 4662 were more than $3\sigma_I$ above background.

Space group determination

Each reduced dataset was inspected for systematic conditions for reflection. For ZrCl₂ the condition $h+k=2n$ for all reflections hkl was observed. This condition requires the cell to be C-centered. Since no other conditions were

noted, the space group choice included C2 No.5, Cm No.8 and C2/m No.12. In the case of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ no conditions were found for hkl reflections. The condition $k=2n$ found for Ok0 reflections requires a 2-fold screw axis and the condition $h+l=2n$ for h0l reflections requires an n-glide. These conditions serve to uniquely fix the space group as $P2_1/n$ (a non-standard setting of $P2_1/c$).

THE CRYSTAL STRUCTURE OF ZIRCONIUM MONOCHLORIDE

Structure Determination

Structure solution

The solution of a crystal structure from the intensities of a set of X-ray diffraction maxima depends upon recovering the phase relationships among the maxima. The intensity of scattered radiation is proportional to the absolute value of the square of the amplitude $|F(hkl)|^2$. The structure factor $F(hkl)$ represents the resultant amplitude of the waves scattered in the direction of the reflection hkl by the j atoms in the unit cell:

$$F(hkl) = \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)].^1$$

The value of the structure factor is determined by the atomic scattering factors f_j , which are a function of the number and distribution of electrons in the atoms and on the scattering angle θ , and by the exponential terms, which depend on the positions of the atoms. Since X-rays are scattered by electrons, solution of a crystal structure is equivalent to finding the electron density. The electron density is given

¹A more complete discussion can be found in any standard crystallographic text such as Buerger.⁴⁶

by the Fourier transform of the structure factors:

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + lz)].$$

As stated earlier, it is necessary to devise a way to determine the phases of the structure factors in order to solve the crystal structure. No general solution to the phase problem exists. It has been found, however, that structures containing one or a few atoms that are markedly heavier than the remainder can be solved by locating the heavy atoms by methods which do not require a prior knowledge of the phases. The heavy atoms can then provide the principal phasing from which the lighter atom positions can be developed. Patterson pointed out that a Fourier calculation using the phaseless quantities $|F|^2$ results in peaks corresponding to all the interatomic vectors, with magnitudes proportional to the atomic numbers of the atoms involved.⁵⁸

A three dimensional Patterson map was calculated from the 203 observed structure factors for ZrCl using the program ALFF.⁵⁹ Interpretation of the Patterson map was very straightforward. Four strong peaks of equal intensity were located at $\frac{3}{4}, 0, \frac{1}{4}$, $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$, $\frac{1}{4}, 0, \frac{3}{4}$ and $\frac{3}{4}, \frac{1}{2}, \frac{3}{4}$. Inspection of the interatomic vectors for the general positions of the three possible space groups prompted the choice of C2 No.5 because of its intraset vectors $\pm(2x, 0, 2z; \frac{1}{2}+2x, \frac{1}{2}, 2z)$. The

peak at $\frac{3}{4}, 0, \frac{1}{4}$ was assigned as corresponding to a fourfold zirconium position. Three cycles of full matrix least squares refinement on the x and z coordinates of one zirconium at $\frac{3}{8}, 0, \frac{1}{8}$ using the program ORFLS⁶⁰ resulted in an unweighted residual¹ of 0.384. The chlorine position was located from an electron density map calculated using the program ALFF.⁵⁹ Other than the zirconium peak at $\frac{3}{8}, 0, \frac{1}{8}$ and the peak at $\frac{1}{8}, 0, \frac{3}{8}$ assigned as chlorine, the map was flat. Three cycles of refinement on the x and z coordinates of these two atom positions resulted in unweighted residual of 0.283.

Refinement

Refinement of the structure was carried out using the full matrix least squares program ORFLS.⁶⁰ The scattering factors used are those of Hanson et al.⁶¹ with corrections for both real and imaginary parts of anomalous dispersion.⁵² The reflections were weighted by σ_F^{-2} to account for the reliability of each measurement. A reduced dataset that had

¹The unweighted residual R and the weighted residual R_w used are defined by

$$R = \sum \left| |F_O| - |F_C| \right| / \sum |F_O|$$

and

$$R_w = \left[\sum_w (|F_O| - |F_C|)^2 / \sum_w |F_O|^2 \right]^{1/2}.$$

not been corrected for absorption was used in the initial stages of the refinement. A total of five cycles of refinement on the x and z coordinates of the two atom positions resulted in a residual of 0.146. Since the space group does not fix y, the y coordinate of one atom must be held constant. However, it was found to be necessary to constrain the y coordinates of both atoms in order to carry out the refinement using this dataset. The refinement of the x and z positional coordinates and the isotropic temperature factors of the two atoms converged in two cycles with $R=0.120$ and $R_w=0.150$. Final positional parameters and isotropic temperature factors are listed in Table 2. The specter of partial occupancy was

Table 2. Atomic parameters^a from isotropic refinement of ZrCl

	Positional parameters			Isotropic thermal parameters B($\times 10^3$)
	x	y	z	
Zr	0.3780(6)	0.0000(0)	0.1339(4)	893(123)
Cl	0.1100(17)	0.0000(0)	0.3295(10)	995(183)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

ruled out after varying the atom multiplier for zirconium. In two cycles of refinement the atom multiplier for zirconium

converged at 0.987(25) with $R=0.121$ and $R_w=0.150$. A difference electron density map was flat to ± 2 electrons/ $\text{\AA}^3$. When the refinement was repeated using the absorption-corrected dataset it was possible to vary the y coordinate for the chlorine atom. However, since the same weighted residual of 0.165 for the converged positional and isotropic thermal parameters was obtained as in the case where y for chlorine was constrained to zero, the latter case is the preferable one according to the statistical test of Hamilton.⁶²

Conversion of the isotropic temperature factors to anisotropic temperature factors brought even more headaches. It was not possible to vary the anisotropic temperature factors¹ for either atom without their becoming not positive-definite. Refinement of the x and z positional parameters and the components of the anisotropic temperature factors β_{11} , β_{33} and β_{13} while damping the shifts in β_{22} and holding β_{23} and β_{12} identically zero using the original reduced dataset resulted in the parameters shown in Table 3 and $R=0.081$, $R_w=0.109$. The observed and calculated structure factors are listed in Table 4. In the refinement using the dataset that

¹The anisotropic temperature factors have the general form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table 3. Atomic parameters^a from anisotropic refinement of ZrCl

	Positional parameters			Anisotropic thermal parameters ($\times 10^4$)			
	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}
Zr	0.3779(5)	0.0000(0)	0.1339(3)	58(10)	8 ^b	68(5)	11(5)
Cl	0.1104(14)	0.0000(0)	0.3306(9)	72(23)	5	69(10)	20(12)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

^bErrors indeterminate since shifts were damped.

had been corrected for absorption, the anisotropic temperature factors again became not positive-definite. For the case where the y coordinate for chlorine as well as β_{12} and β_{23} were constrained at zero and where the shifts in β_{22} were damped, residuals $R=0.081$ and $R_w=0.111$ were obtained.

Improving the refinement

Inquiry concerning the peculiarities encountered in the refinement of the dataset collected from this crystal disestablished their uniqueness. Apparently, the program controlling the data-taking procedure of the diffractometer contained a statistical error for the larger reflections which are normally counted for a shorter period of time than the

Table 4. . . Observed and calculated structure factors^a for ZrCl₄

L = 0

H K FO FC

2 0 60 71

4 0 583 606

6 0 111 103

1 1 237 230

3 1 257 357

5 1 153 140

0 2 1136 890

4 2 486 505

6 2 75 94

1 3 170 161

3 3 179 166

0 4 570 459

L = 1

H K FO FC

0 0 353 316

2 0 209 206

4 0 221 235

6 0 135 128

1 1 812 817

3 1 174 165

5 1 428 439

0 2 342 363

2 2 180 175

4 2 267 201

1 3 536 525

3 3 102 112

0 4 177 151

L = 2

H K FO FC

0 0 258 232

2 0 695 656

4 0 210 197

6 0 351 329

1 1 291 292

3 1 211 209

5 1 221 211

0 2 184 168

2 2 502 534

4 2 164 172

1 3 223 206

3 3 147 135

0 4 115 105

L = 3

H K FO FC

0 0 247 217

2 0 314 363

4 0 190 182

6 0 211 192

1 1 261 261

3 1 506 450

5 1 185 193

0 2 151 208

2 2 230 252

4 2 147 157

L = 4

H K FO FC

0 0 667 553

2 0 267 304

4 0 338 315

1 1 238 372

3 1 294 255

5 1 176 172

0 2 471 452

2 2 218 227

4 2 264 280

1 3 138 159

3 3 202 203

L = 5

F K FO FC

0 0 381 382

2 0 224 232

4 0 221 215

1 1 357 384

3 1 218 226

5 1 200 196

0 2 269 254

2 2 169 198

4 2 189 194

1 3 266 283

L = 6

H K FO FC

0 0 313 275

2 0 228 254

4 0 208 186

1 1 241 247

3 1 228 216

0 2 228 227

2 2 181 222

1 3 177 196

L = 7

H K FO FC

0 0 296 244

2 0 177 196

4 0 227 208

1 1 210 211

3 1 163 151

0 2 243 212

2 2 157 177

L = 8

H K FO FC

0 0 206 167

2 0 147 163

1 1 231 229

3 1 135 132

0 2 158 147

2 2 120 148

L = 9

H K FO FC

0 0 149 143

2 0 202 214

1 1 98 101

0 2 146 130

L = 10

H K FO FC

0 0 123 117

L = -1

H K FO FC

2 0 237 229

4 0 177 206

6 0 156 155

1 1 55 72

3 1 780 886

0 2 374 363

2 2 198 213

4 2 150 154

6 2 135 139

3 3 492 493

0 4 199 151

L = -2

H K FO FC

0 0 238 232

2 0 834 804

6 0 460 454

1 1 211 206

3 1 271 349

5 1 155 151

0 2 200 169

2 2 585 619

4 2 63 42

6 2 407 412

1 3 162 147

3 3 152 162

0 4 115 105

L = -3

H K FO FC

0 0 234 217

2 0 292 284

4 0 159 166

6 0 144 148

1 1 748 655

3 1 169 164

5 1 485 481

0 2 199 212

2 2 241 235

4 2 137 140

6 2 133 133

1 3 478 460

3 3 88 111

L = -4

H K FO FC

0 0 627 553

2 0 274 256

4 0 453 501

6 0 97 101

1 1 334 359

3 1 211 200

5 1 180 185

0 2 484 454

2 2 213 200

4 2 396 433

6 2 83 92

1 3 226 217

3 3 121 129

L = -5

H K FO FC

0 0 363 382

2 0 243 358

4 0 222 231

6 0 115 117

1 1 274 301

3 1 494 432

5 1 154 162

0 2 272 255

2 2 194 177

4 2 203 202

1 3 189 201

3 3 309 334

L = -6

H K FO FC

0 0 295 275

2 0 388 369

4 0 194 211

6 0 257 301

1 1 220 225

3 1 272 240

5 1 137 140

0 2 233 228

2 2 321 307

4 2 176 188

1 3 165 171

3 3 179 192

L = -7

H K FO FC

0 0 277 244

2 0 251 237

4 0 184 177

6 0 187 171

1 1 213 246

3 1 226 215

5 1 255 249

0 2 218 213

2 2 207 208

4 2 159 157

1 3 161 194

L = -8

H K FO FC

0 0 181 167

2 0 205 202

4 0 209 197

1 1 171 191

3 1 205 198

5 1 194 171

0 2 136 147

2 2 171 181

4 2 166 177

L = -9

H K FO FC

0 0 158 143

2 0 210 216

4 0 173 158

1 1 147 158

3 1 137 136

0 2 138 130

2 2 192 195

L = -10

H K FO FC

0 0 131 117

2 0 87 93

4 0 132 131

1 1 175 204

3 1 112 121

^aStructure factors have been multiplied by 10.

smaller ones and rescaled. When this problem was investigated it was also found that a set of parentheses missing in the program declaring the orientation matrix had the result of equating θ and Ω . A nonuniformity in the steps of the Ω scan was also discovered.⁶³ While the quantitative effect of these problems is difficult to assess precisely, it is considered fortunate that the refinement of this dataset went as well as it did. Particularly in view of the fact that the counting statistics were in question for the larger reflections it seemed appropriate to reweight the dataset. New weights were assigned to each reflection of the original reduced dataset using the program Omega.¹ All positional and thermal parameters converged after two cycles of refinement using the new weighting scheme. The final residual indices were $R=0.080$ and $R_w=0.087$. The parameters from this refinement are given in Table 5. The positional parameters for both zirconium and chlorine are within one standard deviation of those reported in Table 3 for the refinement using the original weighting scheme. However, the errors in these parameters

¹Omega is a local program written by C. R. Hubbard which calculates new weights for structure factors after refinement of a structure using ORFLS.⁶⁰

Table 5. Final parameters^a from the refinement of ZrCl using new weights

	Positional parameters			Anisotropic thermal parameters ($\times 10^4$)			
	x	y	z	β_{11}	β_{22}	β_{33}	β_{13}
Zr	0.3779(2)	0.0000(0)	0.1341(2)	31(7)	3(22)	63(3)	11(3)
Cl	0.1098(7)	0.0000(0)	0.3296(6)	43(13)	21(38)	67(5)	17(6)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

are improved by reweighting, as expected. Happily, the thermal parameters converged in this refinement without anomalous behavior on the part of β_{22} . Reweighting the reflections of the dataset that had been corrected for absorption and carrying out one cycle of least squares refinement resulted in the residuals $R=0.082$ and $R_w=0.098$.

A projection of the structure along the unique b-axis is presented in Figure 1. An alternate projection on the (001) plane is shown in Figure 2. The thermal ellipsoid plot program ORTEP⁶⁴ was used to prepare these drawings.

Interatomic distances and angles

Interatomic distances and angles were calculated using the function and error program ORFFE.⁶⁵ The estimated

Figure 1. Projection of the structure of ZrCl on the (010) plane. Atoms at $y=0.0$ are represented by open circles while those at $y=0.5$ are shaded.

Figure 2. Projection of the structure of ZrCl_2 on the (001) plane. Zirconium atoms at $z=0.1341$ are shaded while those at $z=-0.1341$ are represented by open circles. Chlorine atoms at $z=\pm 0.3296$ are superimposed.

standard deviations were calculated using the variance-covariance matrix from the final least squares cycle. These are tabulated for the anisotropic refinement using new weights in Table 6.

Table 6. Interatomic distances and angles^a from anisotropic refinement of ZrCl

Interatomic Distances ^b		Interatomic Angles ^c			
		Atom 1	Atom 2	Atom 3	Degrees
Intralayer			(Vertex)		
Zr-Zr	3.419(3) Å	Zr(1,1)	Zr(1,4)	Zr(1,103)	67.30(15)
	3.428(3)	Zr(1,204)	Zr(1,4)	Zr(1,2)	60.09(3)
Cl-Cl	3.419(3)	Zr(1,4)	Zr(1,2)	Zr(1,104)	120.18(7)
	3.428(3)	Zr(1,4)	Zr(1,2)	Zr(1,101)	124(4)
		Zr(1,4)	Zr(1,2)	Zr(1,103)	56(4)
Interlayer		Zr(1,101)	Zr(1,2)	Zr(1,103)	67.30(15)
Zr-Zr	3.09(14)	Zr(1,104)	Zr(1,2)	Zr(1,103)	90(5)
	3.09(14)	Zr(1,104)	Zr(1,2)	Zr(1,101)	56(4)
Cl-Cl	3.61(13)	Cl(2,2)	Zr(1,2)	Zr(1,104)	131(3)
	3.61(17)	Cl(2,2)	Zr(1,2)	Zr(1,101)	171(1)
		Cl(2,2)	Zr(1,2)	Zr(1,103)	105(1)
Zr-Cl	2.63(13)	Cl(2,2)	Zr(1,2)	Zr(1,4)	49(3)
	2.63(11)	Cl(2,2)	Zr(1,2)	Cl(2,104)	81.3(4)
		Zr(1,2)	Cl(2,2)	Zr(1,4)	81.3(4)

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

^bDifferences of pairs of distances are statistically insignificant.

^cReference numbers correspond to those shown in Figures 1 and 2.

Discussion

The remarkable layer structure found for ZrCl consists of approximately cubic-close-packed layers of either metal or chlorine in the sequence Cl-Zr-Zr-Cl . Each zirconium has three metal neighbors in the next layer at $3.09 \text{ \AA}$, six metal neighbors in the same layer at $3.43 \text{ \AA}$ and three chlorine neighbors in the opposite layer at $2.63 \text{ \AA}$. In zirconium metal there are twelve equal metal-metal distances of $3.19 \text{ \AA}$. In Zr-Cl intralayer interatomic distances for chlorine are also $3.43 \text{ \AA}$. Interlayer chlorine-chlorine distances are $3.61 \text{ \AA}$. The sum of the usual atomic radii⁷ is $3.62 \text{ \AA}$, but chlorine-chlorine approaches as close as $3.22 \text{ \AA}$ have been reported in GdCl_3 and Gd_2Cl_3 .¹¹ The zirconium chlorine distances of $2.63 \text{ \AA}$ compare with three zirconium-chlorine distances 2.498 , 2.655 and $2.307 \text{ \AA}$ found for ZrCl_4 ⁶⁶ and a zirconium-chlorine distance of $2.44 \text{ \AA}$ in Rb_2ZrCl_6 .⁶⁷

The short zirconium-zirconium interlayer distance suggests a strong interaction between zirconium sheets. Another measure of bond formation suggested by Pauling⁶⁸ involves calculating the bond order n from the equation

$$D(n) = D(1) - 0.60 \log n$$

where $D(1)$ is twice the single bond radius. Using a single bond radius of $1.454 \text{ \AA}$ for zirconium,⁷ a bond order of 0.50 is obtained for the $3.09 \text{ \AA}$ interlayer distance while that for $3.43 \text{ \AA}$ intralayer distance is 0.13 . For a chlorine

single bond radius of $0.99 \text{ \AA}$ ⁷ a bond order of 0.023 is obtained for the $3.43 \text{ \AA}$ chlorine-chlorine intralayer distance and 0.005 for the $3.62 \text{ \AA}$ interlayer distance. The bond order for the zirconium-chlorine distance is 0.48. The sum of bond orders to a particular atom is given by $\sum N_i n_i$ where N_i is the number of bonds and their bond order is n_i . Thus, the sum of all bond orders to zirconium is 3.7 and to chlorine is 1.4.

Similar bond orders and distances were found for Hf and S in Hf_2S by Franzen and Graham.⁶⁹ In Hf_2S each S atom is surrounded by six Hf atoms in trigonal prismatic coordination. The coordination polyhedron around each Hf is a distorted octahedron of three S and three Hf atoms. Around each S atom there are six equivalent Hf-S distances of $2.63 \text{ \AA}$ with a bond order of 0.56 and six S-S distances of $3.37 \text{ \AA}$ with bond order 0.008. Around each Hf atom there are three Hf-Hf distances of $3.06 \text{ \AA}$ with bond order 0.50 and six Hf-S distances of $3.37 \text{ \AA}$ with bond order 0.15. The sum of the bond orders to Hf is 4.08. A sum of bond orders of 3.36 to sulfur indicates substantial participation of 3d orbitals in bonding. It has been pointed out that the similar metal-metal and nonmetal-nonmetal nonbonded distances found in both structures may be dictated by close packing of the larger anions and may thus not necessarily be indicative of bond order.⁷⁰

During the course of this structural investigation a structure for ZrCl was published by Troyanov.²⁶ Troyanov and

T'sirelnikov²⁵ had previously reported the synthesis of ZrCl and a powder pattern which agreed with that of Struss and Corbett¹³ except for the omission of a weak line with $d=9.73 \text{ \AA}$. Troyanov and T'sirelnikov indexed the powder pattern of ZrCl on the basis of a rhombohedral lattice having $a=9.12 \text{ \AA}$, $\alpha=21.62^\circ$ and $Z=2$. Troyanov proceeded with a single crystal structural determination using film methods. The choice of the space group $R\bar{3}m$ based on the improper indexing of the powder pattern is more likely the reason for the poor refinement he obtained than errors made in measuring the intensities from the films as he suggested. In any case the R factor did not drop below 0.29. Surprisingly enough the basic ordering and packing of layers Cl-Zr-Zr-Cl was properly deduced. The interatomic distances found of $3.41 \text{ \AA}$ for either Zr-Zr or Cl-Cl within a layer are reasonable, but interlayer distances of $2.87 \text{ \AA}$ for Zr-Zr, $2.81 \text{ \AA}$ for Cl-Cl and $3.10 \text{ \AA}$ for Zr-Cl are certainly unreasonable.

The layer structure found for ZrCl accounts well for the physical properties of the compound. Zirconium monochloride occurs as shiny black hexagonal platelets which are graphitic in character. Dean²⁴ has suggested the use of "Zirklor" as a lubricant; however, the use of a reduced compound for such a purpose is questionable. The reason for the difficulty encountered in finding a single crystal of ZrCl suitable for a structure determination is also apparent now that the

structure is known. The broad faces of the hexagonal platelets are parallel to the (001) planes whereas the thin dimension is roughly coincident with the c-axis. While there are strong interactions between Zr-Zr planes and Zr-Cl planes, the Cl-Cl interplanar distance of 3.62 Å indicates only weak van der Waals contacts. Therein lies the basis for the graphitic character of the compound and its propensity toward polycrystallinity.

Recently, ZrBr has been prepared in this laboratory from the reaction of ZrBr_4 and Zr turnings in a tantalum container heated in the final stages to 800° for 12 days.²³ ZrBr occurs as dark shiny platelets much like those of ZrCl although some needles of ZrBr have been observed. The powder pattern of ZrBr has been indexed by comparison with the powder pattern and the structure determined for ZrCl. Reasonable agreement between calculated and observed powder patterns has been obtained for ZrBr in the case where the coordination polyhedron around zirconium is a trigonal antiprism as in ZrCl; but the Br-Zr-Zr-Br four-layer sheets adopt an alternate packing to that of the Cl-Zr-Zr-Cl four-layer sheets in ZrCl.²³

Preliminary measurements have shown that ZrCl reacts reversibly with hydrogen even at room temperature to form a golden phase approximating $\text{ZrClH}_{0.5}$.⁷¹ Perhaps hydrogen enters the lattice filling the interstices between planes of

chlorines. No structural work has as yet been done, however, to confirm the hydrogen sites.

THE CRYSTAL STRUCTURE OF
(4,7,13,16,21,24-HEXA-OXA-1,10-DIAZABICYCLO[8.8.8]HEXACOSANE)
SODIUM HEPTANTIMONIDE(-3)

Structure Determination

Structure solution

The heavy atoms were located using the program package MULTAN⁷² which is a system for solving crystal structures using direct methods. In this approach an attempt is made to determine the phases of the structure factors without first deriving a set of atomic positions. Any structure determination involves many more observations than there are parameters. Thus all the structure factors cannot be independent. In 1948 Harker and Kasper showed that inequality relationships existed between the structure factors and could occasionally lead to definite information about the phases of structure factors.⁷³

The Cauchy inequality

$$\left| \sum_{j=1}^N a_j b_j \right|^2 \leq \left(\sum_{j=1}^N |a_j|^2 \right) \left(\sum_{j=1}^N |b_j|^2 \right)$$

was applied to the unitary structure factor

$$U(hkl) = \sum_{j=1}^n n_j \exp\{2\pi i(hx_j + ky_j + lz_j)\}$$

by letting $a_j = \sqrt{n_j}$ and $b_j = \sqrt{n_j} \exp\{2\pi i(hx_j + ky_j + lz_j)\}$. By taking the symmetry elements of a given space group into account, relationships among the larger unitary structure

factors can be deduced. For a centric cell, the signs of a number of structure factors can be chosen arbitrarily because of the existence of a number of nonequivalent centers of symmetry which may be chosen as the origin. With three-dimensional data the selection and arbitrary assignment of signs to three strong reflections amounts to fixing the origin of the cell. Once progress in sign determination breaks down because of the inability to relate fresh signs to ones already determined, sign symbols are introduced. At the end of the sign-determining process the signs of the largest U 's should have been determined in terms of a few sign symbols. If the number of symbols is n , there are 2^n possible sets of signs. The structure is sought by calculating Fourier syntheses for each of these sets and evaluating the respective electron density maps. In general, inequality relationships can be used only to solve simple structures. By definition the maximum value of the unitary structure factor $U(hkl)$ is 1. For N equal atoms in a centrosymmetric unit cell the average value of $|U(hkl)|^2$ is $1/N$. As the complexity of the structure increases, the fraction of the structure factors for which the inequality relationships are applicable declines.

In 1952 Sayre,⁷⁴ Cochran⁷⁵ and Zachariasen⁷⁶ independently showed that even when the $|U|$ values were smaller than necessary to satisfy the inequality relationships, the relationship

$$S(h)S(h')S(h-h') = +1$$

was probably true. Thus the sign S of $U(h+h', k+k', l+l')$ can be deduced from the known signs of $U(hkl)$ and $U(h'k'l')$ by taking the product of the signs of the latter two unitary structure factors. MULTAN⁶⁰ uses this relationship to develop a set of signs for the structure factors after first assigning arbitrary signs to a specified number of large $|U|$'s and relating the larger $|U|$'s using inequalities. A probability of correctness is given to each of the 2^n subsets arising from the n symbols used to relate the reflections. In the final step a Fourier synthesis is carried out on the most probable subset. The resulting electron density map is scanned automatically and the positional coordinates of the peaks are listed. Distances and angles among peaks within $1.9\text{\AA}$ of each other are printed out in order to facilitate assessment of the reasonableness of the model. Each time the Fourier step is repeated a Fourier synthesis is carried out on the next most probable subset.

In the present structure solution the seven strongest peaks output from the Fourier step of MULTAN⁶⁰ were located in a cluster having interpeak distances on the order of $2.8\text{\AA}$. Following the assignment of these seven peaks as antimony atoms, three cycles of least squares refinement using ORFLS⁶⁰ resulted in a residual of 0.398. An electron density map calculated using the program ALFF⁵⁹ contained, in addition to the seven antimony atoms, three peaks of appropriate height for sodium atoms with smaller peaks appropriate to the

constituent carbon nitrogen and oxygen atoms of 2,2,2-crypt clustered about them. The 26 independent nonhydrogen atoms of the first crypt were readily located from a difference electron density map¹ phased by the seven antimony and three sodium atoms. The complete sets of atoms making up the other two independent crypts proved to be much more difficult to locate. Three cycles of least squares refinement of the 10 heavy atoms and the 26 atoms of the first crypt resulted in an agreement factor of 0.233. From a difference map phased with these 36 atoms, plausible positions for the 26 atoms of the second crypt were assigned. This turned out to be painstaking work as the programs used do not accommodate such a large problem well. After a cycle of least squares refinement was carried out on these 62 atoms, an agreement factor of 0.231 was obtained. Finally a third difference map was computed in order to locate the 26 independent atom positions of the third crypt. Locating the atoms of the final crypt proved to be even more difficult than for the second one. Only two thirds of the atoms comprising the molecule emerged in the difference map output by ORFURER.⁷⁷ Nitrogen and

¹Light atoms were located from electron density maps calculated using the program ORFURER.⁷⁷ ORFURER is an adaptation of the Fourier step from MULTAN⁷⁰ by M. Gifkins which calculates and searches electron density maps from the structure factors output from ORFLS.⁶⁰

oxygen atom positions were assigned after comparing the peaks in the difference map with those in the electron density map phased by only the heavy atoms and calculated using ALFF.⁵⁹ Carbon atom positions were less readily assigned as the peaks were broad and not very large, and in some cases there was evidence for disordering of the ethylene bridges.

Refinement

The initial stages of the refinement were carried out using the block-diagonal least squares program FBLS.⁷⁸ The calculation time for FBLS is about one fourth of that required for the full matrix least squares program ORFLS,⁶⁰ and the refined parameters obtained from FBLS normally agree with those from ORFLS within the respective estimated standard deviations. Pertinent to this refinement of 88 independent atoms is the fact that FBLS can accept 100 atoms while the maximum number of atoms that can be accommodated by ORFLS is 83. The scattering factors used in either program were those of Hanson et al.⁶¹ Scattering factors for antimony and sodium were corrected for both the real and imaginary components of anomalous dispersion.⁵² In either program the reflections were weighted by σ_F^{-2} to account for the reliability of each measurement. In the initial stages of refinement a reduced dataset which had not been corrected for absorption was used. Refinement of all 88 atoms with isotropic temperature factors using FBLS resulted in converged

positional and thermal parameters with an unweighted residual of 0.172. After converting the isotropic temperature factors of the heavy atoms to anisotropic temperature factors, three cycles of block-diagonal least squares using FBLS with the dataset that had been corrected for absorption resulted in well-behaved positional and thermal parameters with weighted and unweighted residuals 0.1304 and 0.1676, respectively. A refinement of the parameters from FBLS using ORFLS⁶⁰ was attempted by refining only a part of the structure at a time after removing 5 carbon atoms from the atom list. Two cycles were carried out on the heavy atoms followed by two cycles on the first crypt, then two cycles on the second crypt and finally two cycles on the third crypt. Such a procedure is quite laborious as each cycle requires about 40 minutes of computer time, and jobs of this size do not enjoy daily turnaround at the computer center. This stepwise refinement resulted in converged parameters with $R = 0.113$ and $R_w = 0.139$. Conversion of the isotropic temperature factors of the light atoms of the first crypt to anisotropic temperature factors followed by two cycles of refinement using ORFLS did not produce a change in the unweighted residual. Thus the use of anisotropic temperature factors for the light atoms is unwarranted according to the statistical test of Hamilton.⁶²

Improving the refinement

Since it was considered imperative to use all 88 independent nonhydrogen atoms in the final refinement, a Fortran version of ORFLS was recompiled with atom arrays dimensioned at 120. After this had been done it was discovered that a 95 atom version of ORFLS was resident on disk under the program name ORFLSA.⁷⁹ Thereafter, the final refinement cycles were carried out using ORFLSA with all 88 independent nonhydrogen atoms in the atom list.

The dataset being used in this structure solution was collected just prior to that collected from the crystal of ZrCl so it is probable that the same instrumental problems affect both datasets. However, when the dataset was reweighted using OMEGA,⁶⁴ two cycles of full matrix least squares refinement using ORFLSA on the 10 heavy atoms with all 78 light atoms in the atom list resulted in converged parameters for the heavy atoms with a residual of 0.121 and a weighted residual of 0.161. Since this represents an increase of 0.02 in the weighted agreement factor, the absorption-corrected dataset with original weights was used in the final steps of refinement.

Estimated standard deviations for bond distances and angles calculated using the converged parameters from ORFLS contained significant contributions from errors in the lattice constants. Therefore the lattice constants were redetermined prior to the final refinement. The crystal from which the

X-ray reflection dataset had been collected was reoriented on the diffractometer and tuned values of the angles 2θ , Ω , χ and ϕ were measured on both sides of the instrumental zero for 24 strong reflections with $17.5 < 2\theta < 25^\circ$. A least squares fit to twice the average Ω angle using the program LCR2⁵¹ resulted in converged cell constants of $a=23.292(7)$, $b=13.791(6)$, $c=25.355(6)\text{\AA}$ and $\beta=108.56(2)^\circ$. These compare with $a=23.263(43)$, $b=13.776(4)$, $c=25.344(73)\text{\AA}$ and $\beta=108.57(19)$ obtained previously. One cycle of least squares refinement using ORFLSA with the more precise lattice constants was carried out on the ten heavy atoms with anisotropic temperature factors and on the nonhydrogen atoms of the first crypt with isotropic temperature factors. A file of the final parameters and the variance-covariance matrix was created in order to calculate bond distances and angles and their standard deviations. Two cycles of refinement on the nonhydrogen atoms of the second crypt with isotropic thermal parameters using ORFLSA resulted in converged parameters, and a file containing the final parameters and the variance-covariance matrix was created. It was not considered worthwhile to spend more time refining the third crypt since earlier refinements of this crypt using ORFLS had not resulted in improved standard deviations for the atomic parameters over those obtained from FBLS. Finally two cycles of refinement on the heavy atoms using ORFLSA with the refined light atom parameters as described above in the atom list resulted in

converged positional parameters for the heavy atoms with a conventional R of 0.111 and a weighted R of 0.134. The ratio of the largest shift to standard deviation in coordinate in the last refinement cycle was 0.07. A final calculation of structure factors was carried out after the last cycle. A difference Fourier map showed no features other than two ripples of less than 3 and 5 $e^-/\text{\AA}^3$, respectively, in the vicinity of Sb(5) and one ripple of less than 3 $e^-/\text{\AA}^3$ near Sb(6). This is not unreasonable since scattering factors for Sb^0 were used. Otherwise, the map showed only a randomly fluctuating background of $\leq \pm 1 e^-/\text{\AA}^3$. Since no discernable hydrogen peaks appeared in the difference map, these atoms were not included in the refinement. The calculated and observed structure factors for all 4662 observed reflections are tabulated in Table 7.¹ The final atomic and thermal parameters for the 88 independent nonhydrogen atoms are listed in Table 8.

Interatomic distances and angles

Interatomic distances and angles for the Sb_7^{3-} anion and the first two crypts were calculated using the function and error program ORFFE.⁶⁶ Standard deviations were estimated using the variance-covariance matrix from the appropriate

¹Structure factors shown in Table 7 have been multiplied by 10.

Table 7. Observed and calculated structure factors for $(\text{NaC}^+)_{3}\text{Sb}_7^{3-}$

L	K	FC	FC	1	4	1530	1054	1	8	783	665	2	1	3198	2931	15	4	575	493	6	10	1422	1410	8	2	619	766
M	K	FC	FC	2	4	1383	1221	2	8	1072	1118	4	1	670	789	0	5	416	350	7	10	560	565	9	2	1892	1589
4	4	1537	1438	4	4	375	362	4	8	459	528	5	1	970	929	2	5	541	791	8	10	613	880	11	2	1885	1768
6	0	1346	1369	5	4	507	561	5	8	361	471	6	1	343	207	3	5	1351	1366	13	10	460	539	12	2	576	531
8	0	455	384	6	4	1128	993	7	8	893	749	7	1	1344	1717	4	5	3095	3128	5	11	1064	917	19	2	467	415
10	0	638	401	7	4	666	560	8	8	451	291	8	1	1002	1164	5	5	2319	2118	1	11	392	417	20	2	345	248
14	0	757	752	8	4	1120	952	9	8	1089	1084	9	1	980	1277	6	5	518	554	2	11	681	448	23	2	429	320
16	0	552	393	9	4	1315	1424	10	8	422	381	10	1	854	944	7	5	1235	1106	5	11	369	429	0	3	2353	1904
18	0	456	497	10	4	515	483	11	8	367	303	11	1	779	1008	8	5	892	877	7	11	536	641	1	3	1873	1913
20	0	1053	1189	11	4	1325	1131	13	8	331	138	12	1	1466	1439	10	5	963	884	10	11	396	416	2	3	652	604
22	0	334	374	12	4	1089	1005	14	8	386	300	13	1	410	462	11	5	725	836	12	11	440	383	3	3	4606	4316
24	0	332	147	13	4	949	816	15	8	542	513	18	1	722	673	12	5	936	863	13	11	483	361	4	3	2134	1816
1	1	761	689	15	4	1006	924	1	9	381	447	19	1	467	558	13	5	975	1079	1	12	326	244	5	3	4776	4743
2	1	244	437	16	4	661	531	2	9	782	724	20	1	597	593	14	5	1560	1600	1	12	466	339	6	3	519	470
3	1	577	602	18	4	377	430	3	9	964	987	0	2	2264	2037	15	5	462	516	2	12	398	362	7	3	4215	4049
4	1	957	1295	19	4	384	531	4	9	1764	1741	1	2	568	663	16	5	1017	1032	11	12	500	486	8	3	3314	3100
5	1	2558	3023	21	4	527	578	5	9	717	687	2	2	2049	2210	20	5	364	365	1	13	660	544	9	3	2744	2486
6	1	3917	3476	1	5	552	613	6	9	1546	1518	3	2	1079	990	21	5	502	461	3	13	388	302	10	3	2926	2891
7	1	687	816	2	5	741	737	7	9	834	754	4	2	5372	6047	0	6	462	511	11	13	375	285	11	3	1351	1603
8	1	829	664	3	5	1808	1681	8	9	736	613	5	2	478	438	1	6	398	463	2	15	378	196	13	3	748	763
9	1	2356	2260	4	5	1617	1602	9	9	1076	914	6	2	3866	3815	2	6	712	723	1	12	466	339	14	3	879	925
10	1	1124	887	5	5	424	461	10	9	363	355	7	2	3158	3083	3	6	747	680					16	3	539	578
11	1	2001	1914	6	5	1191	1193	11	9	402	368	8	2	1762	1717	4	6	700	718	M	K	FC	FC	35	3	299	63
13	1	493	395	8	5	287	318	14	9	507	631	9	2	4079	3859	5	6	1139	1289	0	0	6350	6599	0	4	539	643
15	1	512	525	9	5	1569	1367	16	9	450	517	10	2	625	564	7	6	518	542	2	0	7184	6698	2	4	1619	1648
16	1	661	679	10	5	515	502	1	10	554	555	11	2	2792	2544	11	6	414	552	4	0	1434	974	3	4	2103	2120
18	1	716	727	11	5	924	1090	2	10	355	143	12	2	835	874	12	6	536	525	6	0	1190	1341	4	4	604	744
0	2	2353	2361	13	5	527	468	3	10	418	359	14	2	811	988	13	6	1267	1360	8	0	963	1094	5	4	1287	1477
1	2	4563	4376	14	5	443	286	5	10	1073	1018	15	2	945	843	15	6	1078	1120	10	0	2314	2369	5	4	1786	1668
2	2	1472	1416	15	5	625	567	6	10	412	333	17	2	781	775	17	6	357	445	12	0	841	1670	8	4	1619	1609
3	2	1515	1091	16	5	415	358	7	10	511	899	19	2	375	309	0	7	1447	1535	14	0	381	270	9	4	834	573
4	2	1542	1361	0	6	478	647	9	10	605	684	0	3	803	559	1	7	1536	1617	16	0	365	461	11	4	807	644
5	2	2990	2840	1	6	2471	2328	11	10	357	265	1	3	1715	1450	3	7	2285	2383	18	0	1394	1529	12	4	473	456
6	2	775	792	2	6	2505	2584	12	10	545	497	2	3	346	397	4	7	346	237	20	0	733	964	13	4	1053	1069
7	2	1415	1216	3	6	2361	2226	17	10	352	212	4	3	265	212	5	7	1438	1381	24	0	345	245	15	4	984	850
8	2	1223	1363	4	6	4217	4094	5	11	703	694	5	3	1478	1415	8	7	715	714	0	1	1059	1550	16	4	458	532
9	2	864	731	5	6	1410	1464	7	11	696	667	7	3	582	361	9	7	498	441	1	1	1482	1292	19	4	559	679
11	2	1707	1367	6	6	3307	3052	0	12	1066	1058	8	3	1110	972	11	7	726	688	2	1	3156	3095	21	4	376	394
12	2	867	668	8	6	754	723	1	12	1069	889	10	3	1411	1238	13	7	1189	1126	4	1	1322	916	0	5	417	292
13	2	787	815	9	6	349	220	2	12	735	646	11	3	432	365	15	7	888	964	5	1	1951	1710	1	5	829	723
14	2	254	372	12	6	414	353	3	12	605	589	12	3	1584	1550	16	7	372	389	6	1	976	1677	3	5	282	520
18	2	367	269	14	6	1780	1045	5	12	527	466	14	3	370	256	0	8	342	200	8	1	302	309	4	5	534	530
19	2	439	357	15	6	555	409	8	13	329	9	15	3	606	703	1	8	941	982	9	1	1718	1564	6	5	288	141
1	3	1397	1372	16	6	655	760	3	16	355	126	19	3	510	455	2	8	611	671	10	1	282	155	7	5	1314	1230
2	3	656	589	20	6	427	426					20	3	527	469	3	8	2126	2041	11	1	932	870	9	5	1987	1910
3	3	4682	4056	1	7	368	518	L = 1				0	4	979	827	4	8	323	367	12	1	483	521	11	5	904	965
4	3	1475	1511	2	7	1497	1491	M	K	FC	FC	2	4	3092	2895	5	8	1928	1973	13	1	552	698	12	5	371	414
5	3	4556	4215	3	7	1016	1002	1	0	2621	2188	5	4	2607	2286	7	8	1101	1053	14	1	514	371	13	5	485	514
6	3	1519	1339	4	7	1811	1749	5	0	3267	2496	4	4	1281	1162	9	8	653	630	15	1	409	501	14	5	503	1029
7	3	2396	2586	5	7	1294	1206	7	0	1591	1307	5	4	2907	2816	10	8	570	673	16	1	888	902	16	5	577	560
8	3	2048	1937	6	7	373	228	9	0	1727	1945	6	4	1868	1881	14	8	256	379	18	1	350	549	0	6	630	550
9	3	2471	2601	7	7	543	563	11	0	1846	1741	7	4	800	976	6	9	1226	1393	0	2	1389	1294	1	6	1711	1658
10	3	3673	3436	8	7	654	663	13	0	520	556	8	4	3978	4047	9	9	1090	1079	1	2	1642	1770	2	6	1922	1814
11	3	1838	1786	11	7	726	617	15	0	977	928	9	4	1865	1757	11	9	372	282	2	2	882	1010	3	6	1302	1153
12	3	1748	1570	12	7	754	645	17	0	1354	1461	10	4	3306	3115	13	9	360	359	3	2	3503	2567	4	6	2569	2504
13	3	953	1016	13	7	531	493	19	0	574	533	11	4	995	1037	2	10	654	789	4	2	2116	1708	5	6	461	557
14	3	725	804	14	7	728	671	6	1	3364	3197	12	4	1110	1149	3	10	506	459	5	2	2155	1532	5	6	1212	1100
15	3	452	615	15	7	684	709	1	1	4519	4096	13	4	342	405	5	10	1298	1432	6	2	827	831	7	6	869	776
16	3	775	772	0	8	959	1142	2	1	1680	1666	14	4	359	151	5	10	826	860	7	2	330	314	9	6	311	270

Table 7. (Continued)

10 6 930 875	L = 3	3 4 1728 1691	8 8 1063 1067	2 2 964 727	6 6 483 375	4 13 314 282
11 6 552 506	H K FO FC	4 4 1369 1206	10 8 893 765	3 2 1332 1758	7 6 546 656	
12 6 1422 1382	1 0 3220 2742	5 4 2337 2347	11 8 448 493	4 2 1182 1139	8 6 236 79	L = 5
13 6 736 691	3 0 297 904	6 4 1037 1742	12 9 343 335	5 2 624 754	9 6 337 295	H K FO FC
14 6 1452 1666	5 0 729 719	7 4 686 666	1 9 493 359	7 2 429 851	10 6 296 445	1 0 1212 1541
15 6 511 583	7 0 3142 2733	8 4 3102 2974	2 9 475 526	9 2 371 96	11 6 399 486	3 0 806 511
16 6 511 578	9 0 673 557	9 4 1349 1484	3 9 619 545	10 2 555 398	12 6 1442 1546	5 0 546 452
20 6 352 412	13 0 694 741	10 4 2370 2406	10 9 464 521	11 2 476 376	13 6 582 610	7 0 3010 2839
0 7 418 622	15 0 316 254	11 4 948 994	12 9 376 368	13 2 676 739	14 6 1414 1571	9 0 916 868
1 7 592 825	17 0 853 896	12 4 402 260	0 10 467 478	15 2 441 594	16 6 477 573	11 0 1755 1872
3 7 1464 1419	0 1 2957 2884	14 4 490 455	1 10 321 269	17 2 675 574	20 6 376 281	13 0 1299 1425
5 7 1364 1435	1 1 1935 1771	16 4 441 309	2 10 471 535	0 3 1256 1180	0 7 683 669	15 0 519 463
7 7 377 397	2 1 363 551	18 4 405 427	3 10 560 632	1 3 3575 3307	1 7 409 461	17 0 367 287
9 7 665 792	3 1 963 692	0 5 1151 1049	4 10 970 1081	2 3 1822 1985	2 7 1100 1141	0 1 636 533
11 7 452 438	4 1 2032 1748	1 5 1696 1909	5 10 688 719	3 3 1765 1600	3 7 1141 1122	1 1 4551 3941
12 7 651 796	5 1 2147 1955	2 5 1298 1122	6 10 762 826	4 3 3166 3150	4 7 1051 1034	2 1 4454 3918
13 7 408 430	6 1 1159 1027	3 5 758 752	11 10 319 215	5 3 1302 1436	5 7 836 708	3 1 2754 2641
14 7 362 447	7 1 2071 1997	4 5 442 417	13 10 314 357	7 3 1752 1817	6 7 379 458	4 1 3321 2811
15 7 472 682	8 1 1392 1147	5 5 2299 2029	0 11 362 329	8 3 3344 3238	7 7 779 812	5 1 3735 3292
21 7 319 85	9 1 1535 1597	7 5 1531 1353	1 11 608 610	9 3 1238 1258	8 7 292 137	6 1 300 110
0 8 370 317	10 1 1488 1478	8 5 946 934	2 12 670 505	10 3 1925 1901	9 7 876 844	7 1 2265 2151
1 8 622 363	11 1 1326 1412	10 5 390 415	1 12 803 765	11 3 962 859	12 7 368 432	8 1 1750 1561
2 8 636 550	17 1 659 770	11 5 560 577	2 12 654 549	12 3 613 557	0 8 778 867	9 1 1229 1281
3 8 315 305	18 1 682 735	12 5 1069 1196	3 12 494 466	14 3 601 588	1 8 292 451	10 1 735 597
5 8 459 435	19 1 619 773	13 5 842 873	5 12 349 258	15 3 471 414	2 8 469 507	12 1 825 830
7 8 655 650	0 2 311 311	14 5 1704 1712	7 12 425 293	16 3 517 464	3 8 600 630	13 1 775 777
12 8 539 575	1 2 570 643	15 5 718 735	9 12 453 363	17 3 518 567	5 8 294 356	14 1 754 792
13 8 389 465	2 2 1731 1626	16 5 618 718	9 13 394 323	18 3 421 376	7 8 390 395	17 1 813 860
15 8 480 496	3 2 1371 1213	0 6 270 78		0 4 362 686	8 9 576 516	18 1 418 500
1 9 1102 1241	4 2 4230 3973	1 6 1343 1758	L = 4	1 4 1457 1278	9 8 328 434	19 1 505 582
2 9 1468 1543	5 2 323 396	2 6 320 219	H K FO FC	2 4 646 658	11 8 494 466	0 2 489 470
3 9 938 887	6 2 1750 1948	3 6 1347 1467	0 0 293 261	3 4 2622 2529	0 9 476 474	1 2 687 773
4 9 1598 2151	7 2 1501 1219	5 6 1813 1810	0 0 2473 2850	4 4 952 766	1 9 882 943	2 2 2543 2313
5 9 717 751	8 2 778 785	9 6 561 355	4 0 4273 3728	5 4 1857 1965	2 9 1084 1068	3 2 3268 3242
6 9 1558 1563	9 2 3037 3163	11 6 324 529	6 0 2617 2320	6 4 1907 1901	3 9 370 448	4 2 2117 1790
7 9 1072 1082	10 2 284 94	13 6 867 986	8 0 3092 3055	7 4 1340 1303	4 9 1551 1501	5 2 1384 1410
8 9 316 281	11 2 1568 1517	15 6 343 330	10 0 1747 1754	8 4 1071 926	5 9 398 401	6 2 807 834
9 9 859 901	12 2 1131 1142	16 6 462 410	16 0 456 607	9 4 1066 1249	6 9 490 422	8 2 1975 1888
11 9 456 353	13 2 409 432	19 6 338 243	18 0 1121 1344	10 4 450 495	7 9 556 602	9 2 675 649
1 10 576 505	14 2 739 836	2 7 500 499	20 0 516 618	13 4 802 817	8 9 576 558	10 2 653 723
2 10 336 336	15 2 947 912	1 7 432 227	0 1 2321 2456	14 4 356 333	10 9 535 426	12 2 1066 1047
3 10 333 405	17 2 917 876	2 7 278 223	1 1 827 832	15 4 545 582	0 10 704 683	13 2 874 822
5 10 426 457	19 2 405 519	3 7 449 376	2 1 4420 3971	19 4 522 514	1 10 309 415	15 2 769 814
6 10 446 484	0 3 2475 1957	4 7 870 663	3 1 2140 1910	0 5 1356 1275	2 10 617 589	17 2 455 544
10 10 486 432	1 3 1028 1010	5 7 343 262	4 1 3336 3310	2 5 456 572	6 10 507 621	0 3 1311 1123
12 10 558 570	3 3 2810 2873	7 7 390 508	5 1 611 666	3 5 2094 2169	7 10 350 394	1 3 826 778
14 10 314 97	4 3 1444 1670	8 7 290 139	6 1 487 491	4 5 977 881	9 10 515 514	2 3 303 119
1 11 222 160	5 3 477 343	9 7 680 732	7 1 1291 1229	5 5 944 1051	10 10 404 326	3 3 1455 1313
5 11 324 493	6 3 1523 1845	11 7 732 779	8 1 622 529	7 5 1306 1223	12 10 427 281	5 3 656 607
0 12 842 741	7 3 1142 1203	13 7 1367 1544	9 1 940 935	8 5 322 266	16 10 316 129	6 3 2148 2279
1 12 514 356	8 3 1215 1324	15 7 1012 1066	10 1 285 485	9 5 1738 1569	1 11 551 384	7 3 575 862
2 12 448 234	9 3 950 907	20 7 356 325	11 1 735 731	12 5 355 398	6 11 541 269	8 3 1229 1494
11 12 413 449	10 3 363 518	0 8 391 274	12 1 542 655	14 5 395 432	10 11 441 369	9 3 376 349
0 13 483 441	11 3 931 908	1 8 867 701	13 1 1032 1051	16 5 304 263	3 12 420 360	10 3 1107 1146
2 13 646 543	13 3 544 578	2 8 499 494	14 1 290 211	0 6 3076 2349	9 12 457 304	12 3 957 1003
4 13 460 358	15 3 546 652	3 8 1518 1533	15 1 416 570	1 6 881 1035	0 13 672 530	13 3 555 500
	19 3 463 440	4 8 859 862	16 1 800 610	2 5 376 774	1 13 309 298	0 4 1766 1531
	0 4 3129 2563	5 8 1074 999	0 2 1770 1540	4 5 767 476	2 13 624 484	2 4 653 614
	2 4 932 784	7 8 628 480	1 2 579 507	5 6 1002 1019	3 13 442 377	3 4 2079 1872

Table 7. (Continued)

4	4	1551	1949	8	9	841	809	15	2	431	438	1	7	757	740	2	1	1510	1234	8	5	899	921	17	11	352	208
7	4	1402	1400	10	9	744	826	17	2	355	355	2	7	640	504	1	1	3001	3152	9	5	497	496	12	11	354	409
8	4	450	340	13	9	359	331	19	2	345	229	3	7	877	911	2	1	2620	2431	10	5	375	212	12	12	333	255
9	4	1223	1376	0	10	747	723	1	7	720	704	4	7	813	659	3	1	1569	1813	11	5	419	516	1	13	583	482
12	4	465	556	2	10	433	359	2	3	3109	2964	5	7	373	338	4	1	736	793	13	5	565	670	3	13	326	222
14	4	705	709	3	10	664	740	3	3	938	763	7	7	1234	1277	5	1	1997	1543	15	5	359	359				
15	4	328	378	5	10	388	394	4	3	3478	3315	8	7	358	260	6	1	273	756	16	5	852	832				
18	4	333	375	6	10	358	275	5	3	2267	2283	9	7	1048	1278	7	1	1320	1333	18	5	370	444				
0	5	1266	1410	8	10	609	551	7	3	2303	2260	10	7	546	572	10	1	551	551	1	6	1237	1239				
1	5	1275	1502	0	11	350	233	8	3	1226	1354	14	7	516	558	11	1	1025	912	2	6	460	330				
2	5	528	675	1	11	469	451	9	3	1170	1178	16	7	578	562	12	1	1534	1580	3	6	1273	969				
4	5	761	822	2	11	712	635	10	3	354	441	0	8	995	1026	13	1	1541	1526	6	6	379	383				
5	5	1054	828	0	12	519	426	11	3	794	829	1	8	813	849	14	1	995	1088	7	6	969	1160				
6	5	1011	1035	2	12	634	528	12	3	490	462	2	8	1185	1185	15	1	524	465	8	6	359	369				
7	5	1468	1315	3	12	525	376	13	3	605	648	3	8	325	445	0	2	1178	1047	10	6	604	692				
11	5	437	564	5	12	354	273	14	3	494	492	4	8	655	697	1	2	1920	1923	13	6	516	555				
12	5	911	1036	7	12	481	408	16	3	436	457	7	8	313	325	2	2	2104	1892	18	6	700	673				
13	5	758	1012	1	13	506	493	18	3	558	511	8	8	543	398	3	2	4175	2907	17	6	415	368				
14	5	612	686	3	13	411	434	0	4	1443	1441	9	8	765	740	4	2	963	1017	0	7	359	387				
15	5	618	601	3	14	362	238	1	4	837	756	10	8	575	530	5	2	2912	2847	1	7	2226	2197				
18	5	410	422	2	4	1040	1040	11	8	415	501	5	2	2760	2659	2	7	456	495	4	1	1067	1070				
1	6	1504	1314					3	4	403	423	17	8	387	403	8	2	1912	2103	3	7	1410	1674				
3	6	2660	2307					4	4	1396	1287	2	9	704	749	10	2	335	348	4	7	352	350				
4	6	297	280					5	4	1208	1307	3	9	397	412	11	2	470	518	5	7	991	998				
5	6	973	1197					6	4	1414	1337	6	9	824	791	13	2	535	669	7	7	458	435				
7	6	288	364					7	4	1799	1714	7	9	391	265	15	2	455	491	9	7	723	646				
8	6	334	364					8	4	565	483	8	9	1254	1353	18	2	367	330	12	7	347	290				
14	6	513	588					9	4	1553	1459	9	9	489	505	0	3	450	324	15	7	444	325				
16	6	375	375					10	4	351	387	10	9	573	672	1	3	1492	1340	17	7	311	344				
17	6	426	372					11	4	757	717	11	9	432	447	3	3	885	900	1	8	273	336				
0	7	554	594					12	4	455	383	0	10	983	893	4	3	1643	1679	2	8	642	634				
1	7	1733	1324					13	4	329	427	2	10	924	821	5	3	584	584	4	8	368	392				
2	7	504	614					16	4	348	422	6	10	409	451	6	3	1556	1614	5	8	683	692				
3	7	1400	1552					17	4	527	616	9	10	503	537	7	3	355	252	6	9	856	761				
5	7	1051	1329					0	5	855	804	11	10	724	652	8	3	960	1087	7	8	1223	1079				
6	7	314	368					1	5	1176	1038	13	10	446	521	10	3	957	916	8	8	568	639				
8	7	435	345					2	5	1409	1318	1	11	332	424	11	3	637	580	9	8	1288	1337				
9	7	307	54					3	5	1798	1697	5	11	372	454	12	3	682	633	11	8	636	646				
11	7	369	538					4	5	714	755	7	11	597	581	13	3	531	647	15	8	354	196				
12	7	339	219					5	5	1671	1489	1	12	761	674	14	3	325	446	0	9	847	879				
13	7	721	930					6	5	1087	922	2	12	332	344	17	3	444	559	1	9	757	767				
15	7	320	447					7	5	398	361	3	12	605	508	0	4	848	748	2	9	437	525				
0	8	556	576					10	5	489	510	4	12	488	314	1	4	1156	1227	3	9	434	372				
1	8	836	825					11	5	359	410	5	12	350	210	2	4	3424	3376	8	9	821	859				
2	8	933	852					12	5	477	601	1	13	757	284	3	4	1132	977	10	9	625	704				
3	8	515	594					15	5	368	409	3	13	384	338	4	4	2989	2734	11	9	347	357				
4	8	1030	1021					16	5	350	266					5	4	628	663	12	9	361	406				
6	8	397	377					0	6	3319	3401					6	4	928	929	3	10	444	425				
7	8	602	602					1	6	1109	1323					7	4	1713	1681	4	10	541	577				
8	8	1062	1071					2	6	2237	2193					8	4	604	591	6	10	966	1014				
9	8	953	1085					3	6	1747	1753					9	4	1009	966	7	10	332	378				
10	8	479	568					4	6	1193	1472					10	4	1266	1284	8	10	774	852				
11	8	566	574					5	6	1164	1262					12	4	925	973	10	10	476	446				
0	9	526	605					7	6	475	596					0	5	2325	2214	0	11	643	561				
1	9	782	755					8	6	385	214					1	5	2195	2326	1	11	392	291				
2	9	432	368					12	6	652	942					2	5	663	740	2	11	602	530				
3	9	610	537					14	6	627	673					4	5	855	1005	3	11	322	215				
5	9	372	286					18	6	407	462					5	5	484	351	4	11	346	228				
7	9	526	586					0	7	473	325					7	5	966	720	5	11	320	378				

Table 7. (Continued)

3	4	445	290	5	9	451	396	3	4	2085	1994	L = 10	17	4	338	353	3	1	1334	1032	1	7	781	827			
4	4	319	336	6	9	1244	1265	1	4	568	526	H	K	FC	FC	1	5	660	620	4	1	590	537	3	7	421	561
5	4	359	451	7	9	726	654	2	4	2781	2613	0	0	815	623	4	5	805	663	5	1	474	263	5	7	754	813
6	4	1010	896	8	9	1153	1236	3	4	1162	1214	2	C	1669	1293	5	5	1062	1091	6	1	274	93	7	7	696	872
7	4	1111	1122	9	9	567	611	4	4	1655	1495	4	C	369	286	6	5	937	1176	6	1	745	632	10	7	325	379
8	4	755	821	10	9	507	578	5	4	632	679	6	0	614	835	7	5	341	388	10	1	1369	1424	9	8	759	839
11	4	307	189	11	9	335	355	6	4	592	448	8	0	799	465	8	5	501	499	11	1	1092	1034	1	8	513	419
14	4	454	524	0	10	654	789	7	4	809	850	10	C	2113	1964	9	5	456	573	12	1	577	760	2	8	399	460
16	4	455	532	2	10	476	737	8	4	504	524	12	0	2319	2257	C	6	266	173	16	1	313	340	3	8	625	779
17	4	410	523	11	10	353	390	10	4	1126	1048	14	0	981	889	1	6	386	361	0	2	999	855	4	8	478	538
C	5	311	391	13	10	392	390	12	4	493	509	0	1	1412	1414	4	6	455	544	1	2	1734	1655	6	8	486	505
1	5	1056	725	5	11	334	497	15	4	331	323	1	1	3772	2991	5	6	321	405	2	2	1140	1125	0	9	554	535
2	5	471	369	7	11	371	421	17	4	493	472	2	1	1021	1185	6	6	1211	1236	3	2	885	774	4	9	453	438
3	5	1329	1125	0	12	340	304	0	5	323	114	3	1	1136	1104	7	6	435	441	4	2	910	870	6	9	425	416
4	5	387	247	1	12	487	486	1	5	789	844	4	1	744	682	8	6	702	940	5	2	416	368	8	9	423	399
7	5	300	52	2	12	419	363	6	5	897	932	5	1	741	571	11	6	318	349	6	2	862	969	2	11	326	195
9	5	575	623	6	12	307	178	7	5	536	493	6	1	341	381	16	6	434	594	7	2	692	732	5	11	384	334
10	5	378	166					8	5	719	764	7	1	767	714	0	7	526	641	8	2	461	460	1	12	498	410
11	5	558	664	L = 9				11	5	427	470	8	1	313	315	1	7	545	606	9	2	655	784	6	12	325	305
15	5	321	291	H	K	FC	FC	13	5	453	588	10	1	684	577	2	7	855	681	11	2	492	476	1	13	370	274
16	5	455	492	1	0	2835	2429	14	5	463	534	C	2	1785	1491	4	7	1284	1342	0	3	885	1002				
18	5	374	275	3	0	1945	2025	16	5	814	826	2	2	1124	968	5	7	777	761	1	3	900	865	L = 12			
C	6	2133	2069	5	0	1227	1253	0	6	593	512	3	2	900	965	6	7	753	1020	2	3	624	712	H	K	FC	FC
1	6	508	891	7	0	1118	1097	3	6	1036	992	4	2	523	693	7	7	773	746	4	3	359	219	0	0	2881	2574
2	6	1792	1896	9	0	1189	1589	5	6	1473	1516	5	2	287	293	9	7	354	368	5	3	263	270	2	0	3683	3314
3	6	1130	1114	11	0	779	737	7	6	1080	1248	6	2	473	470	10	7	516	459	6	3	410	412	4	0	1055	847
4	6	1388	1042	13	0	456	416	8	6	644	592	7	2	741	650	12	7	276	144	8	3	807	794	6	0	253	139
5	6	902	796	15	0	421	280	10	6	374	367	8	2	596	669	14	7	311	165	9	3	689	737	8	C	474	473
6	6	350	427	17	0	417	438	11	6	385	208	9	2	481	453	1	8	318	455	10	3	730	613	10	0	1158	1246
8	6	742	820	0	1	1348	1301	15	6	392	374	10	2	597	640	7	8	480	489	11	3	674	650	12	0	649	747
9	6	411	341	1	1	1027	1243	0	7	581	588	11	2	824	945	11	8	343	352	12	3	707	570	0	1	846	1045
10	6	360	175	3	1	256	372	1	7	701	651	12	2	357	251	1	9	461	446	14	3	374	387	1	1	1773	1743
12	6	346	424	5	1	694	866	2	7	554	591	13	2	365	494	2	9	307	256	15	3	512	580	2	1	855	920
13	6	549	557	6	1	517	397	3	7	835	792	14	2	402	279	4	9	375	397	0	4	2020	1939	3	1	624	684
15	6	533	481	7	1	1554	1291	7	7	843	869	16	2	321	367	5	9	365	332	1	4	876	885	5	1	1075	1032
16	6	705	625	8	1	310	349	8	7	322	228	17	2	337	229	6	9	665	609	2	4	658	718	6	1	561	664
0	7	738	808	9	1	692	568	9	7	620	664	0	3	2462	2245	8	9	416	390	3	4	657	559	7	1	327	181
1	7	744	766	10	1	1455	1608	15	7	451	555	1	3	1355	1253	9	9	340	423	4	4	686	642	9	1	1257	1362
3	7	536	547	11	1	1590	1585	C	8	498	419	2	3	2743	2456	12	9	294	27	6	4	861	910	10	1	456	572
4	7	583	772	12	1	1560	1651	1	8	464	524	3	3	2037	1767	C	10	340	378	11	4	299	9	11	1	360	302
5	7	685	700	13	1	1204	1132	2	8	396	416	4	3	465	385	3	10	480	472	17	4	317	320	13	1	261	70
6	7	536	608	15	1	331	369	5	8	398	391	5	3	1202	1139	4	10	458	421	0	5	1740	1741	0	2	1273	1205
7	7	1261	1428	C	2	1047	991	6	8	684	732	6	3	759	745	5	10	628	547	1	5	255	171	1	2	1012	1120
9	7	815	524	1	2	2578	2386	7	8	948	975	7	3	1157	1123	6	10	277	188	2	5	710	852	2	2	1171	1029
14	7	455	507	2	2	860	754	9	8	782	779	8	3	443	373	7	10	355	356	4	5	635	806	3	2	605	645
16	7	397	379	3	2	3111	2918	10	8	482	393	9	3	731	722	1	11	354	181	5	5	514	553	4	2	454	347
C	8	602	532	4	2	965	924	0	9	942	1015	11	3	548	533	C	13	484	443	6	5	1053	1172	5	2	636	572
1	8	553	608	5	2	710	767	1	9	368	382	16	3	467	383	2	13	435	305	10	5	567	425	7	2	575	388
2	8	934	908	6	2	2652	2562	4	10	455	528	17	3	328	276					11	5	482	554	8	2	755	851
4	8	374	366	7	2	405	352	6	10	727	740	0	4	1521	1505	L = 11				13	5	340	326	10	2	893	906
7	8	607	642	8	2	1202	1303	7	10	330	305	1	4	578	680	H	K	FC	FC	17	5	329	288	13	2	575	538
8	8	503	529	10	2	326	328	8	10	719	636	2	4	856	943	1	0	4402	4190	C	6	699	712	15	2	498	531
9	8	393	538	C	3	362	494	5	11	369	464	3	4	562	691	3	0	670	671	1	6	475	339	16	2	384	265
10	8	423	441	1	3	1447	1344	7	11	386	417	4	4	382	255	7	0	578	598	2	6	844					

Table 7. (Continued).

7	3	1153	1244		L = 13	7	6	394	464	3	4	592	569	8	3	466	438	3	3	687	564	5	6	419	321		
7	3	1209	1269	H	K	FO	FC	13	6	387	327	5	4	520	638	9	3	907	912	4	3	581	501	6	6	479	400
8	3	328	615	1	0	1645	1705	1	7	1079	933	7	4	410	428	10	3	422	394	5	3	672	714	7	6	512	454
9	3	542	674	3	0	355	237	3	7	941	847	9	4	1014	1082	0	4	336	245	6	2	367	279	1	7	530	671
10	3	474	456	5	0	331	128	5	7	913	976	10	4	426	275	1	4	325	372	7	3	437	466	1	9	376	410
0	4	1023	1139	7	0	300	412	7	7	651	496	11	4	785	785	2	4	1056	949	9	3	384	280	0	10	326	199
1	4	415	489	9	0	363	497	10	7	454	507	13	4	313	212	4	4	1403	1358	14	3	366	340				
2	4	295	556	0	1	775	915	11	7	329	314	14	4	215	136	6	4	1126	1735	0	4	372	379				
3	4	638	870	1	1	3233	2547	0	8	644	723	0	5	487	384	8	4	703	669	5	4	401	296	H	K	FO	FC
4	4	667	663	2	1	1280	1213	1	8	463	456	2	5	551	564	10	4	394	339	6	4	472	601	0	0	876	841
5	4	789	855	3	1	1777	1510	2	8	307	293	3	5	1322	1211	2	5	621	564	8	4	753	674	2	0	1327	1287
6	4	910	501	6	1	532	526	3	8	759	650	4	5	1225	1309	3	5	626	454	9	4	452	645	4	0	1140	1164
7	4	500	357	9	1	382	362	5	8	389	378	5	5	895	834	4	5	972	906	1	5	292	254	6	0	482	410
9	4	1256	1218	10	1	345	548	7	8	338	246	6	5	854	932	5	5	748	633	3	5	349	393	8	0	379	280
10	4	318	203	14	1	524	537	11	8	313	239	0	6	1181	1006	7	5	329	304	8	5	290	51	1	1	465	531
11	4	1278	1224	16	1	356	372	2	9	667	419	1	6	614	453	8	5	640	682	10	5	309	286	2	1	976	919
13	4	450	421	0	2	1357	1280	4	9	630	566	2	6	1030	950	10	5	738	756	4	6	581	443	3	1	772	822
15	4	305	289	3	2	603	715	6	9	439	395	2	6	413	303	12	5	336	244	6	6	318	159	4	1	911	899
0	5	414	421	5	2	954	1187	8	9	434	429	4	6	1305	1205	1	6	452	327	8	6	449	518	6	1	426	433
2	5	904	827	7	2	1146	1286	6	10	291	241	5	6	330	301	3	5	424	456	10	6	423	480	9	1	346	333
3	5	1017	1053	8	2	364	390					6	6	844	702	11	6	326	311	0	7	327	280	9	1	354	151
4	5	1247	1234	9	2	762	891	L = 14				10	6	561	640	1	7	277	55	1	7	631	685	1	2	969	949
5	5	1437	1328	11	2	572	495	H	K	FO	FC	1	7	919	845	3	7	551	404	0	8	447	501	3	2	1011	959
6	5	1230	1179	1	2	967	1028	0	0	3374	3157	2	7	623	671	5	7	452	249	2	8	585	514	9	2	366	348
7	5	551	518	3	3	299	287	2	0	1587	1590	4	7	911	863	8	7	374	309					0	3	330	142
9	5	612	617	4	3	594	497	8	0	524	372	7	8	407	411	11	7	325	265	L = 17				1	3	521	426
13	5	287	116	5	3	280	432	14	0	677	729	9	8	495	531	0	8	512	567	H	K	FO	FC	1	4	381	218
0	6	567	911	6	3	787	747	16	0	463	396	11	8	332	171	1	8	414	462	1	0	1326	1197	6	4	462	731
1	6	474	552	7	3	394	350	0	1	1331	1244	0	9	486	433	3	8	394	346	3	0	1936	1804	8	4	543	568
2	6	1028	981	8	3	782	623	1	1	475	541	2	9	321	288	1	9	374	315	5	0	1297	1183	5	5	463	425
3	6	782	704	5	3	853	909	3	1	533	470	5	10	461	434	2	9	531	466	7	0	594	598	7	5	322	255
4	6	1154	1467	10	3	980	968	5	1	643	769	0	12	385	235	4	9	336	299	0	1	465	302	10	5	336	244
5	6	760	828	11	3	308	433	6	1	504	537	1	12	474	401	6	9	317	323	1	1	563	701	0	6	622	640
6	6	1195	1324	12	3	598	633	8	1	833	862					0	10	362	396	2	1	903	947	1	6	453	422
7	6	399	429	0	4	862	835	10	1	529	583	L = 15				0	12	332	141	3	1	867	966	0	7	329	133
10	6	405	461	1	4	459	512	0	2	572	562	H	K	FO	FC					4	1	1056	998	4	7	454	304
1	7	733	806	2	4	549	487	1	2	451	603	1	0	592	553	L = 16				5	1	394	482	6	7	410	393
2	7	677	1092	4	4	1829	1691	2	2	417	370	3	0	1730	1509	H	K	FO	FC	0	2	323	246	0	8	575	684
4	7	1338	1330	5	4	327	374	4	2	391	300	5	0	1048	1015	0	0	954	980	1	2	306	75	2	8	464	495
5	7	424	379	6	4	1322	1469	5	2	671	568	0	1	290	337	4	0	1087	1164	2	2	327	453				
6	7	705	614	7	4	469	509	7	2	312	234	1	1	1123	1078	6	0	446	501	4	2	404	357				
11	7	371	318	8	4	766	816	8	2	463	553	3	1	319	251	8	0	317	249	12	2	338	232	H	K	FO	FC
0	8	369	431	10	4	358	454	9	2	306	313	4	1	780	672	12	0	392	474	0	3	893	768	1	0	955	908
9	8	416	390	0	5	1434	1268	10	2	550	607	12	1	482	488	14	0	546	570	2	3	319	369	3	0	1016	1253
11	8	338	376	2	5	1274	1300	11	2	384	276	14	1	587	551	0	1	297	337	3	3	530	426	5	0	826	855
0	9	354	312	3	5	765	717	13	2	613	631	0	2	809	774	1	1	475	457	6	3	342	263	7	0	353	528
1	9	269	143	4	5	1264	1205	15	2	506	473	3	2	454	390	2	1	641	658	7	3	449	545	0	1	785	749
2	9	342	373	5	5	820	464	0	3	804	847	5	2	998	1012	3	1	957	1019	9	3	365	520	1	1	825	626
10	9	329	339	6	5	668	831	1	3	531	405	6	2	396	466	4	1	498	437	11	3	382	83	2	1	1032	997
3	10	445	426	7	5	436	488	3	3	910	940	7	2	893	1072	5	1	420	405	0	4	286	181	3	1	1116	1073
5	10	513	569	9	5	386	413	4	3	868	865	8	2	606	459	1	2	645	575	2	4	475	416	4	1	816	755
7	10	526	529	10	5	778	816	5	3	1535	1453	9	2	614	713	2	2	427	407	4	4	366	382	5	1	467	439
1	11	328	323	11	5	470	607	6	3	473	470	11	2	309	328	3	2	879	804	0	5	792	759	2	2	362	434
1	12	567	357	12	5	360	248	7	3	1264	1209	15	2	343	241	5	2	650	773	3	5	450	399	3	2	434	396
2	12	302	204	0	6	555	500	8	3	506	604	0	3	1005	829	10	2	291	184	5	5	479	470	5	2	366	488
3	12	359	301	2	6	998	866	9	3	1013	1050	2	2	374	205	11	2	304	171	8	5	656	661	6	2	382	451
				3	6	1260	1234	10	3	431	597	3	3	652	717	0	3	347	341	10	5	339	301	7	2	492	384
				4	6	649	509	11	3	677	526	5	3	591	502	1	3	616	510	1	6	595	408	0	3	430	442
				5	6	1405	1320	12	4	398	369	7	3	639	631	2	3	666	481	3	6	355	34	1	3	344	323

Table 7. (Continued)

3 3 446 372	3 2 437 379	13 1 1508 1535	1 5 1215 1257	5 9 805 647	2 2 822 902	10 6 765 680
6 3 434 424	1 3 461 489	15 1 1376 1431	2 5 1460 1403	6 9 1540 1440	12 2 439 525	11 6 569 571
7 3 522 565	7 3 329 343	16 1 640 615	3 5 275 270	7 9 351 145	13 2 741 497	12 6 414 336
8 3 492 342	4 4 314 299	17 1 740 846	4 5 2980 2952	8 9 1605 1474	14 2 569 740	13 6 766 706
10 3 348 249		20 1 560 672	5 5 2082 1815	10 9 842 701	15 2 365 531	14 6 459 287
6 4 442 427	L = 22	22 1 410 445	6 5 1816 1822	13 9 415 499	17 2 674 724	20 6 405 462
8 4 434 400	H K FO FC	C 2 1881 2037	7 5 2387 2247	17 9 378 377	22 2 414 291	1 7 328 622
0 5 645 551	C 0 310 274	1 2 353 552	9 5 633 538	2 10 338 251	0 3 2026 1904	1 7 479 578
2 5 409 335	2 0 566 432	2 2 1258 1066	11 5 324 331	4 10 485 268	1 3 2523 2743	2 7 2764 2842
4 5 285 240	6 0 365 399	3 2 620 765	13 5 334 397	5 10 530 486	2 3 1899 1930	4 7 2491 2557
6 5 358 480	0 2 388 457	4 2 551 721	16 5 463 504	6 10 1002 804	3 3 3704 3225	5 7 717 651
4 6 455 359	1 4 493 470	5 2 556 494	19 5 561 531	7 10 524 517	4 3 2629 2137	7 7 428 443
6 6 341 335	2 4 276 49	6 2 3677 3055	21 5 477 497	8 10 617 535	5 3 808 474	8 7 680 612
7 6 388 260	1 6 358 103	7 2 1564 1413	0 6 526 512	11 10 440 243	6 3 3498 3228	10 7 387 338
8 6 318 222	0 7 334 214	8 2 976 992	1 6 2008 2351	0 11 976 917	7 2 602 580	11 7 773 707
1 7 709 631	1 7 324 187	9 2 2924 2613	2 6 1023 1008	1 11 556 547	10 3 3085 2991	12 7 565 432
3 7 447 439		10 2 1761 1675	3 6 1312 1353	2 11 735 543	12 3 1972 1955	15 7 667 546
4 7 298 102	L = 23	11 2 2125 2160	4 6 344 414	7 11 614 619	13 2 659 665	17 7 375 390
5 7 357 327	H K FO FC	12 2 964 808	5 6 389 330	13 11 413 327	14 3 525 566	18 7 416 309
5 8 377 275	C 3 472 765	13 2 571 415	7 6 923 824	1 13 845 719	15 3 656 792	0 8 310 317
1 9 442 324	1 3 452 513	14 2 484 628	8 6 863 709	3 13 456 312	16 3 1027 990	1 8 704 700
3 9 331 242	2 3 381 366	15 2 504 658	9 6 665 644		17 3 503 546	3 9 411 331
	C 5 379 338	16 2 754 700	10 6 663 620	L = -2	19 3 421 604	6 8 741 630
	1 6 368 290	17 2 421 455	11 6 425 158	H K FO FC	20 3 358 349	7 8 653 493
L = 20		21 2 378 342	12 6 714 666	0 0 6436 6599	21 3 634 667	9 8 1055 911
H K FO FC		23 2 357 210	13 6 861 809	2 0 6312 5926	0 4 520 643	12 8 337 167
0 0 979 1059	L = 24	C 3 704 559	14 6 615 618	4 0 2015 1670	1 4 3974 4017	17 8 515 576
2 0 1223 1181	H K FO FC	1 3 1934 1897	15 6 1131 1077	6 0 1066 857	2 4 535 557	1 9 385 557
4 0 590 532	2 0 311 249	2 3 2960 2424	17 6 372 333	10 0 3505 3216	3 4 1870 1720	4 9 428 396
0 1 588 501	4 0 465 399	3 3 2061 2049	0 7 1428 1540	12 0 2105 2218	6 4 559 684	6 9 638 603
2 1 954 652	0 2 546 477	4 3 2565 2082	1 7 717 708	14 0 1685 1740	9 4 1314 1268	10 5 580 610
4 1 553 560	2 2 326 261	5 3 1517 1324	2 7 967 828	16 0 1772 1913	11 4 873 755	12 9 458 475
6 1 563 524	1 4 504 486	6 3 1738 1365	3 7 2021 1925	18 0 547 444	12 4 1104 1168	14 9 509 556
0 2 435 275		7 3 1048 874	5 7 2835 2628	20 0 556 525	13 4 505 308	15 9 311 168
1 2 687 753	L = 25	8 3 1529 1469	7 7 1461 1460	22 0 510 529	14 4 359 511	16 9 701 728
2 2 373 345	H K FO FC	9 3 1425 1334	9 7 365 433	0 1 1494 1550	15 4 482 428	19 9 425 365
3 2 341 356	1 1 317 281	10 3 2427 2242	10 7 498 494	1 1 205 293	16 4 431 381	1 10 329 459
7 2 502 461		12 3 1490 1402	11 7 394 339	2 1 1816 1562	18 4 437 364	3 10 376 344
4 3 379 273	L = -1	13 3 623 755	14 7 434 400	3 1 2638 2508	21 4 384 424	5 10 1078 954
7 3 454 453	H K FO FC	14 3 431 323	16 7 521 566	5 1 1940 1837	0 5 331 262	7 10 1514 1417
9 3 420 312	1 0 167 593	17 3 573 514	18 7 375 300	6 1 3245 2276	1 5 974 1141	9 10 484 579
4 4 306 316	3 0 2840 2790	21 3 370 418	19 7 373 395	7 1 1602 1454	2 5 1223 1161	9 10 753 679
6 4 460 455	5 0 637 497	0 4 820 827	0 8 276 200	8 1 2015 1537	3 5 952 1297	5 11 368 224
2 5 279 86	7 0 874 902	1 4 1100 1000	1 8 581 625	9 1 1247 1269	4 5 1760 1936	7 11 363 370
0 6 625 508	9 0 845 1037	3 4 1332 1338	2 8 477 499	10 1 385 430	5 5 464 303	10 11 379 153
1 6 408 336	11 0 3105 3372	5 4 1650 1562	3 8 1604 1570	11 1 3171 2030	7 5 2081 1868	0 12 737 741
3 6 353 261	13 0 1074 1327	6 4 503 348	5 8 1301 1256	12 1 713 556	13 5 414 361	1 12 753 646
4 6 235 152	15 0 577 765	7 4 602 563	6 8 962 892	13 1 632 568	14 5 369 275	2 12 613 551
4 7 343 269	17 0 614 514	8 4 1397 1565	7 8 753 714	15 1 408 502	15 5 734 699	3 12 519 443
0 8 387 358	C 1 3170 3197	9 4 900 1038	8 8 432 240	17 1 334 268	17 5 370 325	12 12 400 213
2 8 326 325	1 1 5861 5550	10 4 1847 1648	10 8 647 621	22 1 390 363	0 6 633 580	0 13 475 441
	2 1 4364 3906	11 4 1241 1073	11 8 425 286	0 2 1271 1294	1 6 744 735	
	3 1 5626 5410	12 4 1251 1270	12 8 450 394	1 2 2023 2079	3 6 1140 1129	L = -3
L = 21		13 4 528 482	14 8 471 462	2 2 422 997	4 6 2478 2275	H K FO FC
H K FO FC		14 4 445 282	17 8 620 624	3 2 1531 1369	5 6 1052 981	1 0 2453 2541
3 0 413 335	4 1 2180 1982	15 4 640 678	0 9 292 194	4 2 1532 1159	6 6 3172 3046	3 0 447 455
0 0 327 111	7 1 377 676	16 4 462 440	1 9 541 586	5 2 3451 3535	7 6 375 346	7 0 3801 2973
0 1 497 521	8 1 526 450	17 4 435 488	2 9 466 239	6 2 1848 1639	8 6 2127 1709	11 0 1420 1697
2 1 571 516	9 1 445 775	0 5 444 350	4 9 1147 896	7 2 1505 1473	9 6 478 380	13 0 1741 1575
3 1 318 293	10 1 485 561					
6 1 425 277	12 1 585 484					

Table 7. (Continued)

15	5	854	690	6	4	2552	2246	6	8	972	805	4	1	1022	1312	10	4	476	373	19	8	490	411	19	1	542	570
17	0	564	537	7	4	970	915	7	8	460	354	5	1	1634	1547	11	4	278	136	0	9	473	474	22	1	432	412
0	1	2836	2884	8	4	2819	2925	8	8	751	701	7	1	294	129	12	4	784	217	1	9	815	974	0	2	509	470
1	1	5918	5292	9	4	432	593	9	8	946	921	11	1	1971	2068	14	4	623	850	2	9	414	458	1	2	4283	3894
2	1	2581	2290	10	4	440	363	10	9	629	726	12	1	309	269	17	4	364	499	3	9	668	659	2	2	901	937
3	1	820	703	11	4	862	868	11	8	907	811	13	1	1012	1090	18	4	441	400	4	9	663	687	3	2	4173	4066
4	1	1626	1587	12	4	418	512	13	8	327	237	15	1	580	521	0	5	1056	1275	5	9	856	765	4	2	4569	4651
5	1	3836	3214	15	4	1290	1186	15	8	399	439	16	1	405	256	1	5	640	544	6	9	503	615	5	2	3809	3822
6	1	2717	2514	17	4	860	934	15	8	428	415	17	1	601	645	2	5	1207	1499	7	9	1150	1073	6	2	2721	2819
7	1	759	515	18	4	439	368	17	8	904	854	18	1	413	499	5	5	1225	1165	8	9	369	488	7	2	3687	3606
9	1	1040	928	20	4	408	531	19	8	496	492	21	1	453	326	7	5	1544	1865	9	9	969	957	8	2	811	852
10	1	1738	1854	0	5	1009	1100	1	9	297	300	22	1	364	252	8	5	664	556	10	9	974	998	9	2	830	831
11	1	2752	2643	1	5	1127	1246	2	9	692	503	24	1	293	153	9	5	1736	1607	12	9	769	832	10	2	1564	1932
12	1	585	587	2	5	765	800	4	9	891	763	0	2	1504	1538	12	5	458	471	16	9	752	628	11	2	504	422
13	1	2630	2613	3	5	899	1051	5	9	1225	1020	1	2	2140	2385	13	5	471	322	18	9	594	484	12	2	2471	2424
14	1	668	704	5	5	1753	1386	6	9	1022	842	3	2	846	735	14	5	1139	1120	0	10	590	682	13	2	465	459
15	1	1772	1908	6	5	2474	2333	7	9	542	614	4	2	3483	2995	16	5	620	504	5	10	612	513	14	2	269	306
16	1	826	845	7	5	2152	1691	8	9	1232	931	5	2	1566	1606	17	5	363	387	7	10	1005	879	16	2	915	830
17	1	858	1018	8	5	1236	1231	9	9	405	327	6	2	406	489	19	5	388	248	9	10	500	341	17	2	561	534
18	1	454	511	9	5	1299	1128	10	9	893	728	7	2	1987	1530	0	5	2542	3349	14	10	433	321	18	2	543	533
20	1	429	462	10	5	450	300	14	9	311	69	8	2	493	661	1	6	725	912	1	11	325	274	21	2	477	455
21	1	584	558	11	5	369	173	16	9	379	277	9	2	937	1004	2	5	2704	3042	5	11	405	530	0	3	1202	1123
22	1	622	635	12	5	1276	1352	18	9	350	265	10	2	282	57	3	6	483	685	6	11	356	292	1	3	825	761
1	2	616	776	14	5	1123	1142	0	10	406	478	11	2	876	931	6	5	3151	2825	13	11	318	194	2	3	1987	1589
3	2	2271	3012	17	5	456	781	2	10	564	741	12	2	581	729	7	6	554	436	2	12	502	462	3	3	2267	2298
5	2	3769	3506	19	5	424	476	6	10	572	622	13	2	439	564	8	6	2742	2521	9	12	582	536	4	3	744	563
7	2	1325	1330	1	6	1690	2019	8	10	355	293	14	2	829	872	10	6	857	740	10	12	376	371	5	3	1298	945
8	2	961	1191	2	6	323	599	9	10	540	535	17	2	590	554	11	6	849	671	11	12	464	487	6	3	1144	1270
9	2	605	622	3	6	1715	1939	11	10	753	727	21	2	651	663	12	6	1055	878	12	12	453	386	7	3	384	428
10	2	2200	2285	4	6	1343	1364	16	10	416	365	23	2	585	512	13	6	914	805	0	13	507	530	8	3	509	719
11	2	1442	1196	5	6	1506	1572	18	10	426	394	0	3	1130	1180	14	6	1146	1050	2	13	327	251	10	3	1324	1339
12	2	2286	2262	6	6	686	550	1	11	429	457	1	3	2616	2622	15	6	842	830	13	3	700	642	13	3	700	642
13	2	471	623	7	6	958	829	2	11	375	474	2	3	2301	2263	16	6	414	341	14	3	521	491	14	3	521	491
14	2	357	266	8	6	998	899	6	11	440	372	3	3	4908	4767	19	6	347	247	15	3	466	447	15	3	466	447
16	2	1228	1257	9	6	1088	923	7	11	476	303	4	3	3249	2934	22	6	345	370	1	0	3257	3473	16	3	423	263
18	2	479	375	10	6	777	904	12	11	443	235	5	3	4854	4314	0	7	637	669	3	0	410	919	17	3	600	614
19	2	527	505	11	6	604	796	0	12	552	505	6	3	1868	1812	2	7	1446	1556	5	0	2524	2379	19	3	512	625
21	2	525	534	12	6	628	611	1	12	612	479	7	3	3293	3309	4	7	1573	1721	7	0	1218	1194	20	3	390	431
23	2	346	361	14	6	508	479	3	12	332	173	8	3	1041	903	6	7	327	303	9	0	2798	2592	0	4	1553	1531
0	3	2304	1557	19	6	342	304	7	12	462	382	9	3	2494	2443	7	7	565	436	15	0	1096	894	2	4	2734	2850
1	3	3041	2593	0	7	446	499	9	12	371	412	10	3	1132	1050	8	7	983	875	17	0	1080	1100	3	4	516	428
2	3	1635	1590	1	7	897	1240	11	3	1637	1582	11	3	1637	1582	9	7	387	317	19	0	326	162	4	4	3214	3219
3	3	3119	2470	2	7	1480	1515	12	3	1926	2026	10	7	781	780	10	7	781	780	0	1	643	534	5	4	637	680
4	3	2903	2594	3	7	466	370	14	3	336	249	11	7	850	1003	11	7	850	1003	1	1	1621	1210	6	4	4615	4642
6	3	2563	2530	5	7	2385	2230	16	3	1187	1222	12	7	333	406	12	7	333	406	2	1	1347	1472	8	4	4334	4248
7	3	1163	1017	6	7	638	616	2	0	1605	1665	17	3	695	599	13	7	805	973	3	1	1726	1852	10	4	2139	2101
8	3	2394	2227	7	7	1732	1487	4	0	524	616	18	3	426	433	14	7	362	430	4	1	1227	950	11	4	1052	1114
9	3	1010	827	8	7	401	372	6	0	5787	5770	19	3	571	576	16	7	326	316	5	1	2426	2333	14	4	424	348
10	3	934	1041	9	7	892	834	8	0	1087	1012	20	3	386	432	17	7	618	467	6	1	1032	1041	15	4	964	853
12	3	798	734	11	7	1313	1133	10	0	2997	2953	22	3	381	388	18	7	487	491	7	1	2068	1954	17	4	1115	1120
13	3	1326	1326	12	7	536	505	12	0	3521	3632	0	4	302	686	20	7	383	271	8	1	942	780	0	5	1218	1410
14	3	504	408	13	7	1369	1287	14	0	3117	2872	1	4	1788	3909	0	8	761	867	10	1	1593	1725	1	5	2855	3510
17	3	498	487	14	7	317	264	16	0	2048	2180	2	4	361	73	1	8	754	710	11	1	3126	2940	2	5	3822	4124
0	4	2723	2563	15	7	562	528	18	0	1090	1154	3	4	2361	2117	3	8	375	398	12	1	1589	1612	3	5	1045	1302
1	4	459	554	16	7	423	488	22	0	687	624	4	4	825	606	4	8	417	445	13	1	2009	1954	4	5	1208	1237
2	4	1848	1493	18	7	419	382	0	1	2204	2456	6	4	670	775	12	8	358	320	14	1	620	555	5	5	950	616
3	4	673	840	3	8	606	787	1	1	2146	2218	7	4	1524	1568	13	8	535	640	15	1	1024	992	6	5	1429	1151
4	4	1639	952	4	8	395	278	2	1	719	780	8	4	1037	999	14	8	334	356	16	1	563	790	7	5	2517	2444
5	4	628	626	5	8	607	684	3	1	1081	1136	9	4	744	731	17	8	50									

Table 7. (Continued)

9	5	1864	1526	4	10	1119	1183	20	2	573	624	2	7	541	383	L = -7	0	4	737	742	12	8	369	453			
10	5	1342	1397	5	10	666	724	21	2	488	448	3	7	371	374	H	K	FC	FC	1	4	1579	1422	14	8	418	639
11	5	561	473	6	10	1256	1217	23	2	419	448	4	7	691	630	3	0	897	857	2	4	1846	1967	0	9	735	979
12	5	1017	1043	8	10	760	780	1	3	1445	1329	5	7	634	545	5	0	2944	3005	3	4	552	639	1	9	390	351
13	5	589	493	10	10	560	524	2	3	2806	2566	6	7	351	13	7	0	1064	1003	4	4	2326	2572	2	9	911	1714
14	5	1245	1242	11	10	550	585	3	3	3247	3291	8	7	1060	1206	9	0	3203	3396	5	4	494	547	3	9	617	769
16	5	415	377	12	10	616	608	4	3	2731	2690	10	7	475	470	11	0	1603	1596	6	4	1784	1695	4	9	703	725
1	6	722	773	13	10	461	498	5	3	3730	3829	11	7	904	1028	13	0	746	711	8	4	2777	2173	5	6	703	844
2	6	862	924	1	11	512	473	6	3	1895	1607	12	7	639	739	15	0	417	367	9	4	1673	1947	6	9	450	599
3	6	1875	1874	3	11	347	302	7	3	3237	3536	13	7	820	939	17	0	813	629	10	4	835	865	8	9	423	450
4	6	704	766	7	11	364	330	8	3	1295	1223	14	7	909	958	19	0	787	769	11	4	680	806	12	9	453	428
5	6	1112	1192	10	11	524	534	9	3	2654	2511	16	7	497	506	0	1	1434	1234	12	4	343	283	14	9	562	519
6	6	652	636	12	11	537	484	10	3	378	44	17	7	571	501	1	1	1765	1720	13	4	723	792	15	6	395	299
7	6	915	997	0	12	357	426	11	3	2201	1345	18	7	381	373	3	1	773	838	14	4	510	623	17	9	415	213
8	6	755	856	7	12	444	453	12	3	1680	1052	19	7	477	364	4	1	853	799	15	4	425	413	2	10	362	262
9	6	535	514	9	12	663	555	13	3	1179	1186	0	8	840	1036	5	1	2815	2784	17	4	654	665	4	10	766	624
10	6	427	463	11	12	393	266	16	3	1949	1095	2	8	492	667	6	1	1477	1731	18	4	801	749	5	10	349	410
11	6	1148	1074	11	13	476	242	18	3	793	795	3	8	1101	1224	7	1	3174	3224	20	4	385	374	6	10	755	590
13	6	1553	1618	5	14	361	277	0	4	1385	1441	7	8	1021	1062	8	1	1472	1271	0	5	2776	2214	7	10	368	397
15	6	1013	561					1	4	1575	1546	9	8	797	753	11	1	1211	947	1	5	276	522	12	10	472	300
16	6	336	159					2	4	1239	1276	10	8	324	239	12	1	1220	1204	2	5	3370	3736	13	10	347	347
19	6	334	255	H	K	FO	FC	3	4	3135	3268	13	8	490	301	13	1	704	684	3	5	1885	1040	0	11	519	561
0	7	570	553	0	0	5459	5292	4	4	622	403	1	9	641	622	14	1	442	408	4	5	2011	2191	1	11	544	536
1	7	2071	2649	2	0	4225	3931	5	4	543	462	3	9	952	824	18	1	388	483	5	5	771	824	3	11	345	317
2	7	652	639	6	0	4174	4308	6	4	1937	814	4	9	312	334	20	1	341	330	6	5	396	590	4	11	363	314
3	7	1886	2247	8	0	3776	3549	7	4	2868	2781	5	9	954	805	21	1	424	286	7	5	1159	1099	7	11	353	242
4	7	254	25	10	0	1157	1147	8	4	461	418	6	9	823	906	0	2	1100	1047	8	5	1616	1497	10	11	222	273
5	7	428	86	12	0	2757	2462	9	4	1191	1211	7	9	1307	1203	1	2	882	870	9	5	1634	1442	12	11	429	431
6	7	893	952	14	0	2138	2234	10	4	407	457	8	9	623	696	2	2	350	260	10	5	635	615	3	12	298	52
7	7	1111	1009	16	0	943	864	14	4	1139	1073	9	9	1081	994	3	2	3050	3078	11	5	432	365	7	12	338	252
8	7	512	708	18	0	407	515	16	4	523	366	10	9	924	947	4	2	1937	1934	13	5	958	812	10	12	292	334
9	7	1368	1128	22	0	406	423	17	4	378	477	12	9	1003	986	5	2	3267	2995	15	5	530	596	1	13	434	372
11	7	942	766	0	1	1823	1869	19	4	572	550	14	9	388	424	6	2	1165	1099	17	5	369	357	7	13	333	307
13	7	1026	764	1	1	635	784	0	5	792	804	18	9	439	444	7	2	1530	1565	22	5	377	348				
15	7	892	925	2	1	1654	1457	1	5	521	671	0	10	870	893	8	2	517	489	4	6	928	920				
0	8	456	576	3	1	1077	1053	2	5	985	814	1	10	390	567	10	2	416	495	5	6	691	449	H	K	FO	FC
2	8	416	654	4	1	2355	2435	3	5	808	959	3	10	507	622	11	2	334	515	6	6	705	532	0	0	3075	3423
4	8	475	392	6	1	639	724	4	5	214	460	6	10	392	254	12	2	1670	1021	7	6	693	434	2	0	721	926
5	8	365	411	7	1	1055	970	6	5	435	732	13	10	444	466	13	2	758	844	8	6	578	390	4	0	1536	1819
6	8	586	556	8	1	941	1096	7	5	1331	1775	3	11	508	475	14	2	829	773	11	6	611	576	6	0	4819	4488
7	8	1225	1162	10	1	1301	1390	8	5	1292	1182	5	11	596	567	17	2	971	972	12	6	459	490	9	0	4419	4807
9	8	556	496	13	1	1252	1243	9	5	1170	1305	10	11	337	333	19	2	491	448	13	6	1842	1894	10	0	2174	2429
0	8	1374	1413	16	1	868	794	10	5	572	767	12	11	399	237	22	2	558	537	14	6	497	389	12	0	531	444
10	8	332	129	17	1	929	979	12	5	808	780	16	11	333	51	0	3	471	325	15	6	1395	1398	16	0	592	713
11	8	561	813	18	1	795	593	13	5	851	817	1	12	580	664	2	3	822	596	0	7	343	387	18	0	433	541
13	8	416	392	21	1	414	309	14	5	878	808	3	12	352	388	3	3	1922	1779	1	7	2574	2958	0	1	909	984
15	8	507	450	0	2	849	903	16	5	700	626	6	12	349	318	4	3	2260	2465	3	7	1808	2172	1	1	699	713
16	9	413	324	1	2	886	933	0	6	2977	3401	9	12	339	278	5	3	2084	2268	5	7	1627	1140	2	1	1486	1422
17	8	644	650	2	2	4147	4164	1	6	1689	1867	11	12	403	372	6	3	1198	1602	7	7	743	623	3	1	608	644
19	8	445	488	3	2	974	1165	2	6	4308	4837	13	12	362	206	7	3	1676	1580	8	7	906	894	6	1	1067	1045
0	9	454	604	4	2	2323	2124	3	6	1185	1335	14	12	329	94	8	3	1855	2352	9	7	337	75	7	1	509	399
1	9	295	178	5	2	448	142	4	6	2222	2849	0	13	402	333	9	3	1106	1110	11	7	493	588	8	1	919	989
3	9	302	175	7	2	724	477	5	6	833	1076	4	13	358	233	10	3	2115	2301	2	8	925	1050	9	1	1683	1841
5	9	361	155	9	2	671	604	6	6	973	908	10	13	420	416	12	3	307	306	4	8	347	364	10	1	2172	2233
7	9	591	651	11	2	1365	1423	8	6	1733	1532	12	13	409	205	14	3	414	26	7	8	552	559	12	1	1123	1007
14	9	371	474	12	2	752	543	10	6	656	540	6	14	284	118	16	3	816	614	8	8	494	433	13	1	533	459
18	9	518	372	13	2	559	769	13	6	659	768					19	3	726	942	9	8	550	991	15	1	368	289
0	10	681	723	14	2	502	428	15	6	720	692					20	3	385	212	10	8	341	355	17	1	640	669
2	10	740	809	18	2	682	705	0	7	457	325					24	3	318	119	11	8	762	853	19	1	435	449

Table 7. (Continued)

3	2	508	743	15	5	665	719	5	11	444	278	5	3	1249	1290	5	7	972	952	17	1	297	26	5	6	412	456
1	2	1301	913	15	5	356	294	9	11	514	462	6	3	2565	2765	6	7	363	313	18	1	587	545	6	6	834	741
3	2	1597	1506	19	5	459	539	11	11	480	427	8	3	1863	1978	9	7	575	644	19	1	545	569	9	6	582	565
4	2	733	814	0	6	1873	2069	0	12	325	304	9	3	1442	1243	10	7	556	579	0	2	1700	1491	10	6	509	475
5	2	1361	1573	1	6	487	605	1	12	522	617	10	3	550	643	11	7	1344	1522	1	2	571	726	11	6	748	685
6	2	580	634	2	6	2664	3096	5	12	335	179	14	3	386	295	13	7	1346	1397	2	2	884	896	12	6	1651	1844
7	2	689	774	3	6	1417	1272	8	12	504	423	16	3	565	449	15	7	667	733	3	2	1847	1938	13	6	829	894
8	2	477	223	4	6	2374	2432	10	13	469	375	19	3	563	645	0	8	295	419	4	2	322	125	14	6	1679	1732
9	2	663	481	5	5	799	967					21	3	411	416	2	8	442	459	5	2	2593	2793	15	6	428	565
10	2	812	610	7	6	433	418	L = -9				0	4	1824	1894	4	8	410	413	6	2	707	778	16	6	678	673
11	2	474	521	8	6	675	798	H K F0 FC				1	4	403	591	5	8	872	966	8	2	1005	923	19	6	318	123
12	2	419	312	9	6	574	563	1	0	2871	2641	2	4	591	514	7	9	317	196	9	2	1151	1214	0	7	546	640
15	2	452	601	11	6	379	330	3	0	2801	2467	3	4	1985	2121	14	8	418	455	10	2	791	853	2	7	385	347
16	2	390	532	12	6	1237	1400	7	0	2451	2434	5	4	537	428	18	8	468	455	11	2	606	586	3	7	756	865
18	2	758	787	13	6	349	276	9	0	2789	2723	6	4	1396	1316	0	9	891	1015	18	2	396	431	5	7	861	881
20	2	428	640	14	6	1147	1156	11	0	2255	2327	7	4	545	495	2	9	1206	1216	19	2	474	390	6	7	527	373
2	3	583	1123	16	6	212	223	15	0	796	903	8	4	980	1205	3	9	854	990	20	2	352	314	7	7	325	383
3	3	1383	1564	0	7	617	806	17	0	427	263	9	4	828	677	4	9	573	590	21	2	542	508	8	7	372	244
4	3	1512	1498	3	7	914	968	19	0	619	501	12	4	420	649	5	9	1324	1438	0	3	2272	2245	10	7	553	697
5	3	635	812	4	7	480	256	0	1	1398	1700	13	4	569	611	6	9	476	299	1	3	2013	2075	14	7	404	466
7	3	1713	1595	5	7	668	682	1	1	839	472	14	4	359	351	7	9	477	416	2	3	755	859	1	8	668	830
8	3	647	549	6	7	612	456	2	1	942	936	15	4	634	533	8	9	433	471	3	3	2231	2451	2	9	662	821
9	3	348	253	7	7	345	347	3	1	964	855	16	4	340	191	3	10	338	424	4	3	946	1162	4	8	827	1046
10	3	561	556	10	7	427	524	4	1	1399	1497	17	4	363	320	14	10	385	326	5	3	1845	2156	5	8	489	354
11	3	584	545	11	7	343	273	7	1	1479	1314	18	4	1005	906	15	10	553	446	7	3	1940	2098	6	8	787	803
12	3	1132	956	12	7	559	541	8	1	2045	1973	20	4	755	754	1	11	384	334	8	3	841	715	10	8	495	572
13	3	746	815	13	7	415	462	9	1	2719	2800	0	5	379	113	4	11	419	360	9	3	1317	1390	12	8	652	622
14	3	652	675	14	7	692	774	10	1	1596	1588	1	5	1354	1431	1	12	324	298	10	3	1357	1325	17	8	385	330
15	3	856	748	16	7	473	470	11	1	1062	1242	2	5	806	665	17	12	448	486	11	3	920	1109	1	9	383	341
17	3	790	844	0	8	421	532	13	1	301	336	3	5	1022	1140	12	12	475	392	12	3	798	669	2	9	645	838
18	3	1135	1236	1	8	338	367	15	1	703	752	4	5	1674	1669	1	13	345	216	14	3	566	654	3	9	395	368
19	3	671	661	3	8	531	555	16	1	416	401	5	5	451	394	7	13	444	311	15	3	607	489	4	9	964	1087
20	3	400	307	6	8	445	519	17	1	704	808	6	5	717	719	9	13	433	273	17	3	901	865	5	9	565	683
21	3	673	641	7	8	656	609	19	1	415	450	7	5	1196	1052					18	3	937	906	6	9	539	519
0	4	1602	1839	9	8	422	461	0	2	1018	990	8	5	1036	1170	L = -10				19	3	741	607	7	9	813	848
1	4	536	367	10	8	457	509	1	2	543	651	10	5	298	190	H K F0 FC				20	3	552	585	9	9	522	499
2	4	735	234	12	8	459	531	2	2	1206	1417	11	5	467	431	0	0	844	623	21	3	491	481	15	9	352	153
3	4	1052	831	14	8	771	350	3	2	1107	1030	12	5	1375	1314	2	0	660	555	0	4	1405	1505	17	9	501	366
4	4	1687	1524	15	8	463	423	4	2	1143	1148	13	5	1385	1460	4	0	552	298	1	4	897	1009	1	10	358	343
6	4	1650	2056	16	8	346	229	5	2	676	760	14	5	972	953	6	0	1321	1545	2	4	451	238	3	10	987	978
7	4	1901	1950	1	9	374	246	6	2	1096	1144	15	5	989	974	8	0	3747	2949	4	4	1516	1633	5	10	721	689
8	4	764	867	2	9	543	651	7	2	1231	1170	16	5	421	403	10	0	3765	3758	6	4	1477	1522	6	10	473	708
9	4	1662	1448	3	9	405	387	8	2	1233	1352	17	5	455	321	12	0	1311	1587	7	4	593	1205	14	10	409	265
11	4	829	951	6	9	367	453	9	2	887	853	0	6	595	512	14	0	882	987	9	4	2095	2085	16	10	444	272
13	4	636	612	7	9	358	217	10	2	1223	1345	1	6	391	480	16	0	1303	1340	10	4	312	485	2	11	323	295
14	4	863	854	8	9	383	289	11	2	808	829	3	6	414	588	18	0	863	864	11	4	295	390	9	11	599	585
15	4	657	667	9	9	392	318	13	2	428	361	4	6	530	447	0	1	1350	1414	13	4	1224	1068	11	11	351	463
16	4	450	276	10	9	388	313	14	2	1215	1253	5	6	375	135	1	1	1397	1365	15	4	602	505	12	11	345	277
1	5	316	391	12	9	756	611	15	2	593	701	6	6	1213	1172	3	1	1302	1183	16	4	380	295	16	11	393	260
1	5	277	490	14	9	733	617	16	2	485	390	7	6	305	10	7	1	384	438	18	4	328	188	7	12	351	326
3	5	405	380	17	9	600	417	17	2	1034	1060	8	6	617	651	8	1	1638	1618	2	5	358	615	8	12	473	395
5	5	787	666	0	10	762	789	19	2	854	870	9	6	456	404	9	1	443	671	7	5	1138	1261	9	12	382	424
6	5	893	884	1	10	613	612	21	2	354	335	13	6	979	928	10	1	2531	2559	9	5	594	592	10	12	521	450
7	5	481	445	3	10	942	929	22	2	462	401	14	6	495	556	11	1	655	847	10	5	428	520	11	12	359	277
8	5	399	650	5	10	834	981	0	3	297	493	15	6	950	835	12	1	916	836	13	5	693	603	2	13	371	332
9	5	836	810	11	10	380	236	1	3	1416	1396	0	7	548	583	13	1	330	327	15	5	633	757	4	13	346	275
11	5	357	315	14	10	401	271	2	3	1511	1840	1	7	540	495	14	1	547	702	19	5	449	484	6	13	370	260
13	5	1132	1126	16	10	395	265	3	3	1029	984	3	7	1028	1078	15	1	552	525	2	6	390	437				
14	5	575	562	2	11	316	354	4	3	1432	1732	4	7	785	850	16	1	843	1037	4	6	922	814				

Table 7. (Continued)

L = -11				L = -12				L = -13				L = -14			
H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
1	0	3255	3796	1	0	2698	2574	1	0	1615	1742	1	0	3199	3156
5	0	2229	1939	5	0	2543	2462	5	0	962	741	5	0	2647	2713
7	0	361	374	7	0	2648	2649	7	0	615	463	7	0	2253	2335
9	0	1356	1362	9	0	353	372	9	0	503	286	9	0	332	478
11	0	1109	1274	11	0	552	503	11	0	532	631	11	0	414	486
13	0	577	544	13	0	605	723	13	0	1541	1580	13	0	1280	1367
15	0	1389	1478	15	0	822	834	15	0	1124	1212	15	0	1151	1348
17	0	829	826	17	0	431	409	17	0	447	542	17	0	317	125
19	0	1193	1296	19	0	1358	1378	19	0	375	248	19	0	563	829
21	0	3145	2580	21	0	618	741	21	0	830	916	21	0	282	78
23	0	444	433	23	0	812	839	23	0	2972	2862	23	0	5403	449
25	0	2146	2052	25	0	1059	1086	25	0	727	820	25	0	358	585
27	0	1751	1935	27	0	308	386	27	0	1540	1627	27	0	863	845
29	0	1331	1226	29	0	1181	1745	29	0	1341	1355	29	0	5440	404
31	0	1740	746	31	0	1055	1015	31	0	935	892	31	0	369	414
33	0	1153	1273	33	0	393	273	33	0	1260	1332	33	0	498	499
35	0	1339	1425	35	0	982	961	35	0	552	483	35	0	517	626
37	0	1802	2132	37	0	352	225	37	0	1034	988	37	0	304	465
39	0	1934	1807	39	0	1007	1042	39	0	1107	1166	39	0	305	249
41	0	1428	1420	41	0	857	977	41	0	967	999				
43	0	1055	1028	43	0	1422	1447								
45	0	582	525	45	0	438	411								
47	0	435	507	47	0	392	444								
49	0	343	426	49	0	2146	2052								
51	0	925	856	51	0	1177	1276								
53	0	1062	1152	53	0	307	250								
55	0	838	829	55	0	573	706								
57	0	404	164	57	0	857	778								
59	0	2684	2700	59	0	288	235								
61	0	546	342	61	0	565	551								
63	0	2464	2603	63	0	568	611								
65	0	1358	1378	65	0	422	458								
67	0	813	890	67	0	1124	1162								
69	0	2259	2172	69	0	1458	1552								
71	0	1507	1744	71	0	618	741								
73	0	845	795	73	0	812	839								
75	0	326	276	75	0	1059	1086								
77	0	852	793	77	0	308	386								
79	0	643	750	79	0	1181	1745								
81	0	742	842	81	0	1007	1042								
83	0	665	734	83	0	857	977								
85	0	855	1002	85	0	1422	1447								
87	0	1975	2152	87	0	438	411								
89	0	655	903	89	0	392	444								
91	0	422	328	91	0	2146	2052								
93	0	1377	1618	93	0	1177	1276								
95	0	1524	1416	95	0	307	250								
97	0	1041	1161	97	0	573	706								
99	0	511	550	99	0	857	778								
101	0	379	484	101	0	288	235								
103	0	519	638	103	0	565	551								
105	0	1281	1479	105	0	568	611								
107	0	322	46	107	0	422	458								
109	0	475	487	109	0	1124	1162								
111	0	498	444	111	0	1458	1552								
113	0	551	455	113	0	618	741								
115	0	1859	1938	115	0	812	839								
				115	0	1059	1086								
				115	0	308	386								
				115	0	1181	1745								
				115	0	1007	1042								
				115	0	857	977								
				115	0	1422	1447								
				115	0	438	411								
				115	0	392	444								
				115	0	2146	2052								
				115	0	1177	1276								
				115	0	307	250								
				115	0	573	706								
				115	0	857	778								
				115	0	288	235								
				115	0	565	551								
				115	0	568	611								
				115	0	422	458								
				115	0	1124	1162								
				115	0	1458	1552								
				115	0	618	741								
				115	0	812	839								
				115	0	1059	1086								
				115	0	308	386								
				115	0	1181	1745								
				115	0	1007	1042								
				115	0	857	977								
				115	0	1422	1447								
				115	0	438	411								
				115	0	392	444								
				115	0	2146	2052								
				115	0	1177	1276								
				115	0	307	250								
				115	0	573	706								
				115	0	857	778								
				115	0	288	235								
				115	0	565	551								
				115	0	568	611								
				115	0	422	458								
				115	0	1124	1162								
				115	0	1458	1552								
				115	0	618	741								
				115	0	812	839								
				115	0	1059	1086								
				115	0	308	386								
				115	0	1181	1745								
				115	0	1007	1042								
				115	0	857	977								
				115	0	1422	1447								
				115	0	438	411								
				115	0	392	444								
				115	0	2146	2052								
				115	0	1177	1276								
				115	0	307	250								
				115	0	573	706								
				115	0	857	778								
				115	0	288	235								
				115	0	565	551								
				115	0	568	611								
				115	0	422	458								
				115	0	1124	1162								
				115	0	1458	1552								
				115	0	618	741								
				115	0	812	839								
				115	0	1059	1086								
				115	0	308	386								
				115	0	1181	1745								
				115	0	1007	1042								
				115	0	857	977								
				115	0	1422	1447								
				115	0	438	411								

Table 7. (Continued).

1	2	538	563	10	6	744	632	7	2	470	282	12	10	298	138	8	4	683	696	8	1	763	888	10	7	379	247
1	2	444	548	12	6	576	482	10	2	523	580	11	4	645	792	9	1	556	511	11	7	760	640	11	7	760	640
2	2	562	612	1	7	930	1790	11	2	465	569	12	4	640	710	11	1	826	700	12	7	351	265	12	7	351	265
4	2	777	762	2	7	519	669	14	2	351	254	13	4	583	678	13	1	918	832	13	7	789	738	13	7	789	738
5	2	737	601	5	7	451	331	20	2	433	527	14	5	337	239	15	1	1019	960	16	7	374	232	16	7	374	232
6	2	1142	1232	7	7	544	530	22	2	417	413	15	5	670	580	16	1	396	447	17	8	350	353	17	8	350	353
7	2	393	826	10	7	747	652	3	3	957	830	16	5	576	413	17	1	611	496	18	8	328	479	18	8	328	479
8	2	637	653	12	7	941	858	2	3	1352	1256	17	5	545	430	18	2	416	246	19	8	343	290	19	8	343	290
9	2	538	561	14	7	416	397	4	3	1468	1469	18	5	365	476	19	2	1160	1163	20	8	424	316	20	8	424	316
11	2	787	797	13	7	382	251	5	2	698	725	19	5	576	927	20	2	821	821	21	9	585	421	21	9	585	421
12	2	874	954	4	8	372	457	6	3	1068	1794	20	5	877	993	21	2	956	914	22	9	452	308	22	9	452	308
14	2	549	702	5	8	562	352	7	3	1458	1557	21	5	496	687	22	2	1334	1262	23	9	334	178	23	9	334	178
15	2	501	559	6	8	561	541	11	3	1282	1140	22	5	655	610	23	2	285	83	24	9	377	363	24	9	377	363
17	2	338	400	7	8	628	624	13	3	500	670	23	5	514	546	24	2	1212	1128	25	9	319	156	25	9	319	156
18	2	343	376	16	8	352	490	2	4	474	440	24	5	640	570	25	2	368	311	26	9	364	235	26	9	364	235
19	3	782	847	13	8	506	440	3	4	308	152	25	5	640	705	26	2	387	405	27	10	566	511	27	10	566	511
2	3	422	401	0	9	332	433	4	4	721	733	26	5	325	353	27	2	598	451	28	10	493	509	28	10	493	509
3	3	610	676	4	9	602	616	5	4	740	779	27	5	363	471	28	2	403	291	29	10	329	265	29	10	329	265
4	3	847	836	6	9	692	627	6	4	840	969	28	5	366	378	29	3	828	769	30	10	329	265	30	10	329	265
5	3	1181	1164	7	9	379	287	7	4	303	148	29	5	327	55	30	3	1236	1108	31	10	329	265	31	10	329	265
6	3	926	824	9	9	459	441	8	4	615	506	30	5	552	488	31	3	1313	1253	32	10	329	265	32	10	329	265
7	3	851	950	11	9	458	270	10	4	326	415	31	5	526	395	32	3	677	765	33	10	329	265	33	10	329	265
8	3	624	841	5	10	345	207	13	4	366	428	32	5	580	546	33	3	672	603	34	10	329	265	34	10	329	265
9	3	502	672	6	10	358	480	16	4	604	584	33	5	592	458	34	3	852	966	35	10	329	265	35	10	329	265
10	3	625	705	9	10	544	544	13	4	614	574	34	5	524	468	35	3	387	102	36	10	329	265	36	10	329	265
11	3	705	659	1	12	435	292	1	5	292	427	35	5	1254	1135	36	3	496	569	37	10	329	265	37	10	329	265
13	3	366	345	6	12	290	94	2	5	359	302	36	5	1157	1057	37	3	513	448	38	10	329	265	38	10	329	265
15	3	479	355					9	5	578	374	37	5	730	443	38	3	691	676	39	10	329	265	39	10	329	265
17	3	675	539					10	5	694	752	38	5	410	519	39	3	363	301	40	10	329	265	40	10	329	265
19	3	504	565					12	5	852	900	39	5	1046	962	40	3	333	362	41	10	329	265	41	10	329	265
21	3	429	376					20	5	335	179	40	5	780	803	41	3	778	801	42	10	329	265	42	10	329	265
0	4	288	516					1	6	1075	1123	41	5	488	379	42	3	1300	1317	43	10	329	265	43	10	329	265
2	4	1001	1153					3	6	725	796	42	5	1071	1203	43	3	1346	1373	44	10	329	265	44	10	329	265
3	4	367	305					5	6	435	333	43	5	274	325	44	3	617	685	45	10	329	265	45	10	329	265
5	4	698	743					7	6	729	941	44	5	634	768	45	3	660	629	46	10	329	265	46	10	329	265
6	4	789	644					9	6	825	887	45	5	1081	1137	46	3	602	498	47	10	329	265	47	10	329	265
7	4	780	854					10	6	692	594	46	5	922	782	47	3	488	430	48	10	329	265	48	10	329	265
8	4	526	361					11	6	972	943	47	5	577	646	48	3	619	619	49	10	329	265	49	10	329	265
11	4	475	449					12	6	895	746	48	5	961	949	49	3	721	758	50	10	329	265	50	10	329	265
0	5	366	384					13	6	708	632	49	5	450	566	50	3	523	539	51	10	329	265	51	10	329	265
1	5	354	440					14	6	561	612	50	5	799	692	51	3	559	498	52	10	329	265	52	10	329	265
2	5	612	652					17	6	377	403	51	5	954	952	52	3	332	256	53	10	329	265	53	10	329	265
8	5	719	787					3	7	711	689	52	5	1186	1113	53	3	550	361	54	10	329	265	54	10	329	265
10	5	457	475					5	7	551	482	53	5	910	892	54	3	597	590	55	10	329	265	55	10	329	265
11	5	614	540					6	7	336	318	54	5	623	522	55	3	583	418	56	10	329	265	56	10	329	265
12	5	365	372					7	7	322	257	55	5	887	836	56	3	998	1021	57	10	329	265	57	10	329	265
13	5	802	777					9	7	439	501	56	5	572	464	57	3	444	313	58	10	329	265	58	10	329	265
16	5	376	397					11	7	431	543	57	5	631	621	58	3	529	545	59	10	329	265	59	10	329	265
17	5	428	532					12	7	357	481	58	5	567	564	59	3	1118	951	60	10	329	265	60	10	329	265
0	6	1103	1006					13	7	374	391	59	5	543	492	60	3	827	780	61	10	329	265	61	10	329	265
1	6	672	687					0	8	462	567	60	5	485	421	61	3	580	795	62	10	329	265	62	10	329	265
2	6	962	934					2	8	430	593	61	5	389	379	62	3	522	649	63	10	329	265	63	10	329	265
3	6	577	1007					5	8	319	240	62	5	943	782	63	3	336	391	64	10	329	265	64	10	329	265
4	6	654	623					17	8	361	292	63	5	449	535	64	3	507	588	65	10	329	265	65	10	329	265
5	6	718	524					1	9	397	377	64	5	1064	1068	65	3	468	473	66	10	329	265	66	10	329	265
6	6	662	530					3	9	509	321	65	5	365	362	66	3	372	426	67	10	329	265	67	10	329	265
7	6	453	356					6	9	723	481	66	5	1088	1109	67	3	354	238	68	10	329	265	68	10	329	265
8	6	756	545					8	9	776	645	67	5	616	511	68	3	594	698	69	10	329	265	69	10	329	265
9	6	321	190					10	9	479	313	68	5	941	983	69	3	375	397	70	10	329	265	70	10	329	265

Table 7. (Continued).

3	4	891	652	13	1	352	214	10	1	747	572	5	6	581	428	3	4	311	227
5	4	740	657	15	1	327	275	12	1	528	405	6	6	328	252	4	4	457	581
7	4	365	361	18	1	318	222	13	1	251	35	10	6	353	272	6	4	424	591
8	4	499	640	2	2	1707	937	3	2	317	284	1	7	341	309	0	5	352	338
11	4	519	726	3	2	444	504	9	2	467	394	14	7	324	234	9	5	312	137
12	4	512	500	4	2	918	702	12	2	336	87	16	7	362	135	11	7	436	480
13	4	418	574	5	2	729	827	13	2	451	431	6	9	339	235				
15	4	302	67	6	2	563	445	16	2	417	325	19	9	297	139				
17	4	477	416	7	2	512	934	18	2	454	437								
0	5	362	392	9	2	452	466	3	3	529	508								
1	5	486	404	10	2	550	254	5	3	595	606								
2	5	388	365	12	2	482	199	6	3	397	385								
3	5	499	510	20	2	706	159	7	3	462	399								
5	5	375	352	0	3	454	442	8	3	462	404								
7	5	623	678	2	3	564	574	9	3	629	435								
8	5	480	520	4	3	489	529	1	4	340	279								
10	5	305	333	7	3	723	697	14	4	372	391								
14	5	520	435	9	3	547	533	17	4	507	453								
16	5	454	368	13	3	710	656	18	4	324	42								
17	5	375	194	14	3	517	177	2	5	354	410								
0	6	596	640	16	3	391	305	3	5	400	330								
1	6	483	482	18	2	442	382	4	5	407	307								
2	6	471	577	1	4	344	151	5	5	337	421								
2	6	412	381	5	4	364	374	0	6	517	508								
10	6	721	631	6	4	913	959	1	6	651	556								
11	6	362	270	8	4	999	1025	2	6	612	577								
12	6	735	710	10	4	538	484	3	6	426	344								
14	6	599	452	12	4	333	304	10	6	330	180								
1	7	356	458	14	4	324	151	4	7	441	341								
2	7	581	533	0	5	523	551	6	7	334	209								
18	7	393	357	1	5	737	388	8	8	326	91								
0	8	666	684	2	5	773	767	4	9	360	274								
2	8	356	484	3	5	319	280												
13	8	333	366	4	5	423	389												
2	9	368	389	12	5	427	472												
3	9	515	386	14	5	363	458												
4	9	449	476	1	6	516	411												
5	9	568	479	3	6	769	685												
10	9	430	379	6	6	267	171												
5	11	360	327	1	7	709	770												
				3	7	439	505												
				6	8	423	236												
				12	9	265	38												
				4	10	551	511												
				6	10	462	393												

Table 8. Final parameters^a for (NaC⁺)₃Sb₇³⁻

Positional parameters for heavy atoms

	x	y	z
Sb(1)	0.22558(15)	0.18851(22)	0.41768(10)
Sb(2)	0.17610(12)	0.07328(20)	0.47838(10)
Sb(3)	0.32617(13)	0.25736(22)	0.50100(12)
Sb(4)	0.37464(11)	0.09264(20)	0.55983(10)
Sb(5)	0.26285(14)	0.33736(20)	0.56892(13)
Sb(6)	0.27292(12)	0.01810(20)	0.57388(10)
Sb(7)	0.19929(12)	0.18028(21)	0.58058(10)
Na(1)	0.66271(59)	0.28473(89)	0.61846(50)
Na(2)	0.53016(61)	0.3711(10)	0.28429(51)
Na(3)	0.57729(59)	0.8286(11)	0.13623(53)

Anisotropic thermal parameters (x10³)^b for heavy atoms

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	5.9(1)	12.7(2)	2.22(5)	3.9(1)	0.36(6)	0.34(9)
Sb(2)	3.27(7)	11.3(2)	3.26(6)	0.4(1)	-0.14(5)	-1.88(9)
Sb(3)	3.91(8)	11.6(2)	4.46(8)	0.3(1)	1.39(6)	2.2(1)
Sb(4)	2.68(6)	10.9(2)	3.64(6)	1.8(1)	0.57(5)	0.7(1)
Sb(5)	4.50(9)	8.5(2)	5.32(9)	0.5(1)	1.15(7)	-1.9(1)
Sb(6)	3.95(8)	10.2(2)	3.05(6)	0.5(1)	0.55(5)	0.92(9)
Sb(7)	3.78(8)	11.3(2)	3.43(6)	1.0(1)	1.57(6)	-0.2(1)
Na(1)	3.8(3)	6.8(8)	2.8(3)	2.0(4)	1.0(2)	0.7(4)
Na(2)	3.5(3)	12(1)	2.8(3)	2.0(5)	1.1(2)	1.0(4)
Na(3)	3.0(3)	13(1)	3.1(3)	-1.6(6)	0.8(2)	0.1(5)

^aEstimated standard deviations in parameters from ORFLS⁶⁰ are in parentheses.

^bThe anisotropic temperature factors have the general form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table 8. (Continued)

Positional and thermal parameters for the first crypt

	x	y	z	B
N(101)	0.6057(14)	0.0948(22)	0.6186(12)	8.8(8)
C(102)	0.6020(21)	0.0839(34)	0.6771(18)	10.6(13)
C(103)	0.5829(19)	0.1808(32)	0.6954(16)	9.9(11)
O(104)	0.6282(11)	0.2516(17)	0.7031(9)	8.6(6)
C(105)	0.6810(21)	0.2450(34)	0.7536(18)	10.6(12)
C(106)	0.7205(21)	0.3245(35)	0.7619(19)	10.9(13)
O(107)	0.7373(12)	0.3329(20)	0.7122(11)	10.4(7)
C(108)	0.7718(23)	0.4239(39)	0.7184(21)	12.8(15)
C(109)	0.7704(26)	0.4627(41)	0.6716(24)	15.2(16)
N(110)	0.7186(16)	0.4677(24)	0.6220(14)	9.2(8)
C(111)	0.7298(22)	0.4807(35)	0.5721(18)	9.9(13)
C(112)	0.7611(19)	0.3989(33)	0.5577(16)	10.0(11)
O(113)	0.7277(11)	0.3151(20)	0.5559(9)	8.3(6)
C(114)	0.7573(21)	0.2276(36)	0.5483(18)	9.6(12)
C(115)	0.7250(18)	0.1441(28)	0.5582(15)	7.7(10)
O(116)	0.7270(9)	0.1506(15)	0.6150(8)	6.9(5)
C(117)	0.7136(17)	0.0599(27)	0.6351(14)	7.8(9)
C(118)	0.6499(17)	0.0237(28)	0.6100(14)	7.8(9)
C(119)	0.5465(18)	0.0930(28)	0.5779(16)	9.4(10)
C(120)	0.5495(20)	0.1347(34)	0.5232(18)	11.6(12)
O(121)	0.5624(13)	0.2400(21)	0.5323(11)	9.0(7)
C(122)	0.5170(22)	0.2992(36)	0.5446(19)	12.5(14)
C(123)	0.5356(17)	0.4039(28)	0.5468(14)	8.8(9)
O(124)	0.5881(13)	0.4238(21)	0.5892(11)	10.4(7)
C(125)	0.6142(28)	0.5203(44)	0.5952(22)	14.2(16)
C(126)	0.6690(27)	0.5316(38)	0.6289(21)	13.4(15)

Table 8. (Continued)

Positional and thermal parameters for the second crypt

	x	y	z	B
N(201)	0.6393(16)	0.3287(27)	0.3723(14)	10.8(9)
C(202)	0.6877(23)	0.3230(36)	0.3491(19)	12(1)
C(203)	0.6834(27)	0.3905(42)	0.3088(25)	15(2)
O(204)	0.6323(16)	0.3958(25)	0.2572(14)	13.8(9)
C(205)	0.6375(22)	0.3237(35)	0.2169(20)	12(1)
C(206)	0.5836(27)	0.3316(37)	0.1777(21)	13(1)
O(207)	0.5366(21)	0.2890(29)	0.1940(16)	17(1)
C(208)	0.4652(38)	0.2839(55)	0.1526(30)	20(2)
C(209)	0.4262(50)	0.3642(89)	0.1543(43)	28(4)
N(210)	0.4335(29)	0.4466(52)	0.1871(24)	18(2)
C(211)	0.4528(35)	0.5520(62)	0.1852(31)	20(2)
C(212)	0.4652(72)	0.569(11)	0.2380(68)	38(8)
O(213)	0.5142(19)	0.5571(29)	0.2652(18)	16(1)
C(214)	0.5175(22)	0.6048(34)	0.3097(21)	11(1)
C(215)	0.5612(23)	0.5790(38)	0.3566(20)	13(1)
O(216)	0.5505(13)	0.4818(21)	0.3663(11)	10.7(7)
C(217)	0.5906(24)	0.4515(35)	0.4175(20)	13(1)
C(218)	0.6450(23)	0.4133(36)	0.4138(19)	13(1)
C(219)	0.6232(23)	0.2358(39)	0.3994(21)	13(1)
C(220)	0.5872(33)	0.1727(47)	0.3612(27)	18(2)
O(221)	0.5265(15)	0.2052(22)	0.3307(11)	12.0(8)
C(222)	0.4756(29)	0.2090(41)	0.3359(23)	15(2)
C(223)	0.4266(33)	0.2429(56)	0.3189(30)	18(2)
O(224)	0.4168(22)	0.3193(37)	0.2889(22)	20(2)
C(225)	0.3742(36)	0.3351(60)	0.2292(35)	21(3)
C(226)	0.3866(36)	0.4153(58)	0.2034(29)	19(2)

Table 8. (Continued)

Positional and thermal parameters for the third crypt^c

	x	y	z	B
N(301)	0.5912(19)	0.9531(29)	0.2287(16)	12(1)
C(302)	0.5654(25)	0.9192(40)	0.2671(21)	12(2)
C(303)	0.4978(27)	0.9655(44)	0.2184(22)	14(2)
O(304)	0.4822(16)	0.8642(25)	0.1816(13)	12(1)
C(305)	0.4581(32)	0.9486(49)	0.1420(25)	17(2)
C(306)	0.4244(24)	0.8824(37)	0.1043(20)	11(1)
O(307)	0.4695(17)	0.8624(27)	0.0658(14)	13(1)
C(308)	0.4409(27)	0.7681(42)	0.0576(22)	14(2)
C(309)	0.4797(26)	0.7426(40)	0.0036(23)	13(2)
N(310)	0.5493(19)	0.6942(28)	0.0310(15)	11(1)
C(311)	0.5997(24)	0.7262(36)	0.0157(20)	11(1)
C(312)	0.5872(27)	0.8393(39)	0.0014(22)	13(2)
O(313)	0.6304(18)	0.8426(28)	0.0541(15)	14(1)
C(314)	0.6559(25)	0.9532(39)	0.0603(20)	12(2)
C(315)	0.6097(26)	0.0060(42)	0.0657(21)	13(2)
O(316)	0.5990(18)	0.0174(28)	0.1238(14)	14(1)
C(317)	0.6508(24)	0.0092(38)	0.1780(19)	11(2)
C(318)	0.6294(22)	0.0299(35)	0.2191(18)	10(1)
C(319)	0.6555(33)	0.8977(52)	0.2578(27)	18(2)
C(320)	0.6207(28)	0.7667(45)	0.2542(23)	14(2)
O(321)	0.6721(20)	0.7624(32)	0.2240(17)	16(1)
C(322)	0.6907(31)	0.6851(45)	0.2042(25)	16(2)
C(323)	0.6526(31)	0.6332(46)	0.1660(29)	16(2)
O(324)	0.5958(18)	0.6157(29)	0.1411(15)	14(2)
C(325)	0.5819(26)	0.5787(40)	0.0813(21)	13(2)
C(326)	0.5282(26)	0.6252(40)	0.0589(21)	12(2)

^cEstimated standard deviations in parameters from FBLs⁷⁸ are in parentheses.

Table 9. Interatomic distances and angles^a for the Sb₇³⁻ anion

Distances (Å)						
	Sb(2)	Sb(3)	Sb(4)	Sb(5)	Sb(6)	Sb(7)
Sb(1)	2.711(16)	2.776(43)	4.339(69)	4.190(19)	4.432(24)	4.365(14)
Sb(2)		4.209(12)	4.432(52)	4.434(25)	2.838(46)	2.880(12)
Sb(3)			2.755(15)	2.824(22)	4.159(14)	4.211(34)
Sb(4)				4.313(5)	2.708(8)	4.448(12)
Sb(5)					4.409(4)	2.693(6)
Sb(6)						2.856(5)

Bonded Angles							
Atom 1	Atom 2	Atom 3	Degrees	Atom 1	Atom 2	Atom 3	Degrees
	(Vertex)				(Vertex)		
Sb(1)	Sb(3)	Sb(4)	103.4(8)	Sb(5)	Sb(7)	Sb(2)	105.4(6)
Sb(4)	Sb(3)	Sb(5)	101.3(1)	Sb(5)	Sb(7)	Sb(6)	105.2(2)
Sb(1)	Sb(3)	Sb(5)	96.9(2)	Sb(1)	Sb(2)	Sb(6)	106.0(1)
Sb(2)	Sb(6)	Sb(7)	60.8(3)	Sb(1)	Sb(2)	Sb(7)	102.6(4)
Sb(6)	Sb(7)	Sb(2)	59.3(9)	Sb(4)	Sb(6)	Sb(2)	106.1(7)
Sb(7)	Sb(2)	Sb(6)	59.9(7)	Sb(4)	Sb(6)	Sb(7)	106.1(2)
Sb(3)	Sb(5)	Sb(7)	99.5(5)				
Sb(3)	Sb(1)	Sb(2)	100.2(3)				
Sb(3)	Sb(4)	Sb(6)	99.2(6)				

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

Table 10. Interatomic distances and angles^a for the first cryptated sodium cation

Bonded Distances			Nonbonded Distances		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
N(101)	C(102)	1.52(5)	N(101)	N(110)	5.76(4)
C(102)	C(103)	1.52(5)	N(101)	O(104)	2.97(4)
C(103)	O(104)	1.40(4)	N(101)	O(116)	2.96(4)
O(104)	C(105)	1.47(5)	N(101)	O(121)	2.90(4)
C(105)	C(106)	1.40(5)	N(110)	O(107)	2.87(4)
C(106)	O(107)	1.44(5)	N(110)	O(113)	2.74(4)
O(107)	C(108)	1.47(5)	N(110)	O(124)	2.95(5)
C(108)	C(109)	1.29(6)	O(104)	O(107)	2.72(4)
C(109)	N(110)	1.44(6)	O(104)	O(113)	5.06(5)
N(110)	C(111)	1.38(5)	O(104)	O(116)	3.94(4)
N(110)	C(126)	1.51(5)	O(104)	O(121)	4.11(5)
C(111)	C(112)	1.45(5)	O(104)	O(124)	3.62(4)
C(112)	O(113)	1.39(4)	O(107)	O(113)	3.91(3)
O(113)	C(114)	1.43(5)	O(107)	O(116)	3.47(3)
C(114)	C(115)	1.44(5)	O(107)	O(121)	5.22(9)
C(115)	O(116)	1.43(4)	O(107)	O(124)	4.06(7)
O(116)	C(117)	1.42(4)	O(113)	O(116)	2.72(3)
C(117)	C(118)	1.50(5)	O(113)	O(121)	3.85(4)
C(118)	N(101)	1.49(4)	O(113)	O(124)	3.91(4)
N(101)	C(119)	1.43(5)	O(116)	O(121)	3.94(6)
C(119)	C(120)	1.52(5)	O(116)	O(124)	4.87(4)
C(120)	O(121)	1.49(5)	O(121)	O(124)	2.88(4)
O(121)	C(122)	1.45(5)	Na(1)	C(102)	3.64(5)
C(122)	C(123)	1.50(5)	Na(1)	C(103)	3.41(5)
C(123)	O(124)	1.37(4)	Na(1)	C(105)	3.36(5)
O(124)	C(125)	1.45(6)	Na(1)	C(106)	3.50(6)
C(125)	C(126)	1.30(6)	Na(1)	C(108)	3.53(7)
Na(1)	N(101)	2.94(3)	Na(1)	C(109)	3.46(6)
Na(1)	N(110)	2.83(3)	Na(1)	C(111)	3.51(5)
Na(1)	O(104)	2.56(3)	Na(1)	C(112)	3.51(5)
Na(1)	O(107)	2.55(5)	Na(1)	C(114)	3.34(6)
Na(1)	O(113)	2.55(4)	Na(1)	C(115)	3.10(4)
Na(1)	O(116)	2.40(2)	Na(1)	C(117)	3.30(4)
Na(1)	O(121)	2.71(5)	Na(1)	C(118)	3.61(4)
Na(1)	O(124)	2.54(3)	Na(1)	C(119)	3.69(5)
			Na(1)	C(120)	3.61(6)
			Na(1)	C(122)	3.32(7)
			Na(1)	C(123)	3.37(5)
			Na(1)	C(125)	3.43(6)
			Na(1)	C(126)	3.41(5)

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

Table 10. (Continued)

Bonded Distances

Atom 1 Atom 2 Distance (Å)

Nonbonded Distances

Atom 1 Atom 2 Distance (Å)

C(119)	Sb(4)	3.88(4)
C(120)	Sb(4)	4.49(5)
C(122)	Sb(3)	4.26(6)
C(122)	Sb(4)	4.48(5)

Bonded Angles

Atom 1 Atom 2 Atom 3 Degrees
(Vertex)

N(101)	C(102)	C(103)	109(3)
C(102)	C(103)	O(104)	112(4)
C(103)	O(104)	C(105)	117(3)
O(104)	C(105)	C(106)	114(4)
C(105)	C(106)	O(107)	106(4)
C(106)	O(107)	C(108)	105(3)
O(107)	C(108)	C(109)	114(5)
C(108)	C(109)	N(110)	126(6)
C(109)	N(110)	C(111)	117(4)
C(109)	N(110)	C(126)	113(4)
C(111)	N(110)	C(126)	114(4)
N(110)	C(111)	C(112)	113(4)
C(111)	C(112)	O(113)	110(4)
C(112)	O(113)	C(114)	115(3)
O(113)	C(114)	C(115)	110(4)
C(114)	C(115)	O(116)	106(3)
C(115)	O(116)	C(117)	111(2)
O(116)	C(117)	C(118)	116(3)
C(117)	C(118)	N(101)	111(3)
C(118)	N(101)	C(102)	110(3)
C(118)	N(101)	C(119)	116(3)
C(119)	N(101)	C(102)	111(3)
N(101)	C(119)	C(120)	110(4)
C(119)	C(120)	O(121)	107(3)
C(120)	O(121)	C(122)	117(3)
O(121)	C(122)	C(123)	109(4)
C(122)	C(123)	O(124)	113(3)

Atom 1 Atom 2 Atom 3 Degrees
(Vertex)

C(123)	O(124)	C(125)	120(4)
O(124)	C(125)	C(126)	118(5)
C(125)	C(126)	N(110)	119(5)
N(101)	Na(1)	N(110)	178.2(10)
N(101)	Na(1)	O(104)	65.0(9)
N(101)	Na(1)	O(116)	66.4(9)
N(101)	Na(1)	O(121)	61.6(9)
N(110)	Na(1)	O(107)	64.4(10)
N(110)	Na(1)	O(113)	61.0(10)
N(110)	Na(1)	O(124)	66.4(11)
O(104)	Na(1)	O(107)	64.3(9)
O(104)	Na(1)	O(113)	163.1(10)
O(104)	Na(1)	O(116)	105.0(10)
O(104)	Na(1)	O(121)	102.3(11)
O(104)	Na(1)	O(124)	90.6(11)
O(107)	Na(1)	O(113)	100.1(10)
O(107)	Na(1)	O(116)	89.2(11)
O(107)	Na(1)	O(121)	165.4(11)
O(107)	Na(1)	O(124)	106.0(13)
O(113)	Na(1)	O(116)	66.6(9)
O(113)	Na(1)	O(121)	93.8(9)
O(113)	Na(1)	O(124)	100.4(10)
O(116)	Na(1)	O(121)	100.6(10)
O(116)	Na(1)	O(124)	161.9(9)
O(121)	Na(1)	O(124)	66.6(11)

Table 11. Interatomic distances and angles^a for the second cryptated sodium cation

Bonded Distances			Nonbonded Distances		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
N(201)	C(202)	1.43(5)	N(201)	N(210)	5.77(11)
C(202)	C(203)	1.36(6)	N(201)	O(204)	3.02(5)
C(203)	O(204)	1.46(6)	N(201)	O(216)	2.93(5)
O(204)	C(205)	1.46(5)	N(201)	O(221)	3.02(5)
C(205)	C(206)	1.33(6)	N(210)	O(207)	3.20(8)
C(206)	O(207)	1.41(6)	N(210)	O(213)	2.72(9)
O(207)	C(208)	1.66(8)	N(210)	O(224)	3.24(8)
C(208)	C(209)	1.44(11)	O(204)	O(207)	2.73(6)
C(209)	N(210)	1.39(11)	O(204)	O(213)	3.59(5)
N(210)	C(211)	1.53(8)	O(204)	O(216)	4.01(5)
N(210)	C(226)	1.35(8)	O(204)	O(221)	4.40(5)
C(211)	C(212)	1.30(15)	O(204)	O(224)	5.43(6)
C(212)	O(213)	1.14(15)	O(207)	O(213)	4.22(6)
O(213)	C(214)	1.29(5)	O(207)	O(216)	5.04(5)
C(214)	C(215)	1.34(6)	O(207)	O(221)	3.73(5)
C(215)	O(216)	1.40(5)	O(207)	O(224)	4.25(8)
O(216)	C(217)	1.40(5)	O(213)	O(216)	2.64(5)
C(217)	C(218)	1.40(6)	O(213)	O(221)	5.11(5)
C(218)	N(201)	1.55(5)	O(213)	O(224)	4.14(6)
N(201)	C(219)	1.55(5)	O(216)	O(221)	3.92(4)
C(219)	C(220)	1.37(7)	O(216)	O(224)	2.83(7)
C(220)	O(221)	1.45(7)	O(221)	O(224)	2.90(6)
O(221)	C(222)	1.52(6)			
C(222)	C(223)	1.31(8)	Na(2)	C(202)	3.56(6)
C(223)	O(224)	1.28(7)	Na(2)	C(203)	3.42(6)
O(224)	C(225)	1.54(8)	Na(2)	C(205)	3.50(6)
C(225)	C(226)	1.36(9)	Na(2)	C(206)	3.36(6)
			Na(2)	C(208)	3.42(8)
Na(2)	N(201)	2.85(6)	Na(2)	C(209)	3.42(12)
Na(2)	N(210)	2.95(7)	Na(2)	C(211)	3.59(8)
Na(2)	O(204)	2.69(4)	Na(2)	C(212)	3.16(16)
Na(2)	O(207)	2.60(4)	Na(2)	C(214)	3.32(5)
Na(2)	O(213)	2.61(4)	Na(2)	C(215)	3.34(5)
Na(2)	O(216)	2.50(3)	Na(2)	C(217)	3.40(6)
Na(2)	O(221)	2.59(3)	Na(2)	C(218)	3.55(8)
Na(2)	O(224)	2.78(5)	Na(2)	C(219)	3.56(7)

^aEstimated standard deviations from ORFFE⁶⁵ are in parentheses.

Table 11. (Continued)

Bonded Distances

Atom 1 Atom 2 Distance (Å)

Nonbonded Distances

Atom 1 Atom 2 Distance (Å)

Na(2)	C(220)	3.38(7)
Na(2)	C(222)	3.38(6)
Na(2)	C(223)	3.33(7)
Na(2)	C(225)	3.50(9)
Na(2)	C(226)	3.38(9)

Bonded Angles

Atom 1 Atom 2 Atom 3 Degrees
(Vertex)

N(201)	C(202)	C(203)	113(5)
C(202)	C(203)	O(204)	123(5)
C(203)	O(204)	C(205)	112(4)
O(204)	C(205)	C(206)	101(4)
C(205)	C(206)	O(207)	112(5)
C(206)	O(207)	C(208)	123(5)
O(207)	C(208)	C(209)	118(7)
C(208)	C(209)	N(210)	134(10)
C(209)	N(210)	C(211)	138(8)
C(209)	N(210)	C(226)	88(7)
C(211)	N(210)	C(226)	126(7)
N(210)	C(211)	C(212)	96(9)
C(211)	C(212)	O(213)	116(15)
C(212)	O(213)	C(214)	103(10)
O(213)	C(214)	C(215)	117(5)
C(214)	C(215)	O(216)	106(4)
C(215)	O(216)	C(217)	110(4)
O(216)	C(217)	C(218)	113(4)
C(217)	C(218)	N(201)	116(4)
C(218)	N(201)	C(202)	114(4)
C(218)	N(201)	C(219)	107(3)
C(219)	N(201)	C(202)	118(4)
N(201)	C(219)	C(220)	113(5)
C(219)	C(220)	O(221)	117(6)
C(220)	O(221)	C(222)	123(4)
O(221)	C(222)	C(223)	109(5)
C(222)	C(223)	O(224)	132(8)

Atom 1 Atom 2 Atom 3 Degrees
(Vertex)

C(223)	O(224)	C(225)	130(6)
O(224)	C(225)	C(226)	115(7)
C(225)	C(226)	N(210)	136(8)
N(201)	Na(2)	N(210)	168(2)
N(201)	Na(2)	O(204)	66(1)
N(201)	Na(2)	O(216)	66(1)
N(201)	Na(2)	O(221)	67(1)
N(210)	Na(2)	O(207)	70(2)
N(210)	Na(2)	O(213)	58(2)
N(210)	Na(2)	O(224)	69(2)
O(204)	Na(2)	O(207)	62(2)
O(204)	Na(2)	O(213)	85(1)
O(204)	Na(2)	O(216)	101(1)
O(204)	Na(2)	O(221)	113(1)
O(204)	Na(2)	O(224)	166(1)
O(207)	Na(2)	O(213)	108(1)
O(207)	Na(2)	O(216)	162(1)
O(207)	Na(2)	O(221)	92(1)
O(207)	Na(2)	O(224)	104(2)
O(213)	Na(2)	O(216)	62(1)
O(213)	Na(2)	O(221)	158(1)
O(213)	Na(2)	O(224)	100(1)
O(216)	Na(2)	O(221)	101(1)
O(216)	Na(2)	O(224)	93(2)
O(221)	Na(2)	O(224)	65(1)

Table 12. Interatomic distances and angles^a for the third
cryptated sodium cation

Bonded Distances			Nonbonded Distances		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
N(301)	C(302)	1.38(8)	N(301)	N(310)	5.98(7)
C(302)	C(303)	1.78(8)	N(301)	O(304)	2.73(7)
C(303)	O(304)	1.65(7)	N(301)	O(116)	2.86(7)
O(304)	C(305)	1.52(8)	N(301)	O(121)	3.26(7)
C(305)	C(306)	1.37(9)	N(310)	O(307)	3.26(6)
C(306)	O(307)	1.67(7)	N(310)	O(313)	2.72(6)
O(307)	C(308)	1.45(7)	N(310)	O(324)	2.87(6)
C(308)	C(309)	1.90(9)	O(304)	O(307)	2.86(5)
C(309)	N(310)	1.68(7)	O(304)	O(313)	5.44(5)
N(310)	C(311)	1.42(7)	O(304)	O(316)	4.07(5)
N(310)	C(326)	1.37(7)	O(304)	O(321)	4.43(6)
C(311)	C(312)	1.61(8)	O(304)	O(324)	4.64(5)
C(312)	O(313)	1.39(7)	O(307)	O(313)	3.86(6)
O(313)	C(314)	1.63(7)	O(307)	O(316)	3.61(6)
C(314)	C(315)	1.34(8)	O(307)	O(321)	5.31(6)
C(315)	O(316)	1.58(7)	O(307)	O(324)	4.50(6)
O(316)	C(317)	1.52(7)	O(313)	O(316)	3.21(6)
C(317)	C(318)	1.32(8)	O(313)	O(321)	4.25(6)
C(318)	N(301)	1.45(8)	O(313)	O(324)	4.05(6)
N(301)	C(319)	1.63(9)	O(316)	O(321)	4.36(6)
C(319)	C(320)	1.97(10)	O(316)	O(324)	5.56(6)
C(320)	O(321)	1.61(8)	O(321)	O(324)	3.05(6)
O(321)	C(322)	1.31(8)			
C(322)	C(323)	1.30(9)	Na(3)	C(302)	3.63(6)
C(323)	O(324)	1.29(8)	Na(3)	C(303)	3.71(6)
O(324)	C(325)	1.53(7)	Na(3)	C(305)	3.27(6)
C(325)	C(326)	1.36(8)	Na(3)	C(306)	3.47(6)
			Na(3)	C(308)	3.27(6)
Na(3)	N(301)	2.84(6)	Na(3)	C(309)	3.61(6)
Na(3)	N(310)	3.14(5)	Na(3)	C(311)	3.56(6)
Na(3)	O(304)	2.84(4)	Na(3)	C(312)	3.51(6)
Na(3)	O(307)	2.62(4)	Na(3)	C(314)	3.51(6)
Na(3)	O(313)	2.76(4)	Na(3)	C(315)	3.27(6)
Na(3)	O(316)	2.70(4)	Na(3)	C(317)	3.02(6)
Na(3)	O(321)	2.74(5)	Na(3)	C(318)	3.46(6)
Na(3)	O(324)	2.96(4)	Na(3)	C(319)	3.19(7)

^aEstimated standard deviations from FBOND⁷⁸ are in parentheses.

Table 12. (Continued)

Bonded Distances

Atom 1 Atom 2 Distance (Å)

Nonbonded Distances

Atom 1 Atom 2 Distance (Å)

Na(3)	C(320)	2.96(7)
Na(3)	C(322)	3.31(7)
Na(3)	C(323)	3.17(7)
Na(3)	C(325)	3.73(6)
Na(3)	C(326)	3.40(6)

Bonded Angles

Atom 1	Atom 2 (Vertex)	Atom 3	Degrees
N(301)	C(302)	C(303)	83(4)
C(302)	C(303)	O(304)	94(4)
C(303)	O(304)	C(305)	72(4)
O(304)	C(305)	C(306)	88(5)
C(305)	C(306)	O(307)	101(4)
C(306)	O(307)	C(308)	83(4)
O(307)	C(308)	C(309)	88(4)
C(308)	C(309)	N(310)	113(4)
C(309)	N(310)	C(311)	122(4)
C(309)	N(310)	C(326)	92(4)
C(311)	N(310)	C(326)	145(5)
N(310)	C(311)	C(312)	105(4)
C(311)	C(312)	O(313)	78(4)
C(312)	O(313)	C(314)	105(4)
O(313)	C(314)	C(315)	104(5)
C(314)	C(315)	O(316)	121(5)
C(315)	O(316)	C(317)	121(4)
O(316)	C(317)	C(318)	108(5)
C(317)	C(318)	N(301)	112(5)
C(318)	N(301)	C(302)	142(5)
C(318)	N(301)	C(319)	84(4)
C(319)	N(301)	C(302)	94(5)
N(301)	C(319)	C(320)	96(5)
C(319)	C(320)	O(321)	73(5)
C(320)	O(321)	O(322)	127(5)
O(321)	C(322)	C(323)	120(6)
C(322)	C(323)	O(324)	145(7)
C(323)	O(324)	C(325)	114(5)
O(324)	C(325)	C(326)	98(5)
C(325)	C(326)	N(310)	96(5)

final least squares cycle. Interatomic distances and angles for the Sb_7^{3-} anion are given in Table 9 while distances and angles for the first and second crypts are given in Table 10 and 11, respectively. The program FBOND⁷⁸ was used to obtain bond distances and angles for the third crypt, and these are listed in Table 12.

Discussion

The packing of three cryptated sodium cations per Sb_7^{3-} cluster anion is shown in a projection of the unit cell on the (010) plane in Figure 3.¹ For clarity the cryptated sodium cations are represented simply as a N-Na-N linkage, and the three independent cryptated cations are identified by numerals.

The anion

The Sb_7^{3-} anion is not only the first well-characterized homopolyatomic anion for a metallic element, but it is also apparently one of only a few rigorously established examples of a seven atom polyhedron.⁶ The geometry of the anion is shown in Figure 4. The seven antimony atoms are clustered in an end-capped trigonal prism having approximate C_{3v} symmetry.

¹The projection of the unit cell on the (010) plane and plots of the Sb_7^{3-} anion and cryptated sodium cations that follow were plotted using the thermal ellipsoid plotting program ORTEP.⁶⁴

Figure 3. Projection of the structure of $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ on the (010) plane.

Figure 4. Geometry of the Sb_7^{3-} anion in $(\text{NaC}^+)_3\text{Sb}_7^{3-}$.

Least squares planes have been calculated¹ for the three four-atom faces: 1,2,6,4; 1,2,7,5; and 5,7,6,4. The perpendicular distance of each of the four atoms from the respective plane is given in Table 13. The angle between the normals to the planes determined by atoms 4,5,1 and 6,7,2 is $0.5(7)^\circ$.⁶⁵

Table 13. Deviations from least squares planes

Atom Distance, Å		Atom Distance, Å		Atom Distance, Å	
Sb(4)	0.0042	Sb(1)	-0.0189	Sb(1)	0.0287
Sb(5)	-0.0042	Sb(2)	0.0276	Sb(2)	-0.0439
Sb(6)	-0.0063	Sb(5)	0.0193	Sb(4)	-0.0288
Sb(7)	0.0063	Sb(7)	-0.0280	Sb(6)	0.0440

A few years ago Muetterties and Wright reviewed the literature concerning molecular polyhedra of high coordination number.⁸⁰ Important polyhedra for the seven-atom family included the capped octahedron (C_{3v}), the pentagonal bipyramid (D_{5h}) and the face-capped trigonal prism (C_{2v}). A fourth basic geometry for seven-coordination which has been rigorously

¹Least squares planes were calculated using the local program LSP2 written by Wayne Rohrbaugh.

established for complexes, metal clusters and polymeric oxides is the tetragonal base-trigonal base (C_s) polyhedron. It is important to note that these polyhedra have been proposed for ML_7 complexes rather than for a homopolyatomic noncentered cluster as is under consideration here. The C_{3v} , D_{5h} and C_{2v} idealized polyhedra represent limiting symmetry forms as opposed to energetically favored or experimentally established geometries. Conformational interconversions require only slight bending modes, and the energy differences between these idealized geometries should be small with respect to intermolecular forces generated by ordering or by solvation phenomena in the solid, liquid or solution states.⁸¹

Gillespie, among others, has evaluated the relative stabilities of the MX_7 models simply by considering repulsive forces generated from interactions of like ligands constrained to a spherical surface.⁸² The analysis has limited predictive value, however, as the energy differences are very small, attractive forces are ignored and calculations are limited to spherical models.

Recently Muetterties and Guggenberger have emphasized that there is a paucity of available structural data for the seven atom family.⁸³ While there are no good observed C_{3v} -type structures, in $Rb_5Zr_4F_{21}$ there are two independent ZrF_7 polyhedra with the same structure which is midway between the C_{3v} and D_{5h} geometries.⁸⁴ Among several complexes which

have been reported which are close to the pentagonal bipyramidal structure are ZrF_7^{3-} ,⁸⁵ ReF_7 ,⁸⁶ IF_7 ⁸⁷ and $\text{V}(\text{CN})_7^{4-}$.⁸⁸ Two compounds $\text{Na}_5\text{Zr}_2\text{F}_{13}$ ⁸⁹ and K_2NbF_7 ⁹⁰ have been reported which adopt the C_{2v} structure. The structure found for the Sb_7^{3-} anion does not approach any of these idealized polyhedra. It is similar, however, to the structure of P_4S_3 . Here phosphorus atoms form a tetrahedron and sulfur atoms bridge along three adjacent edges of the tetrahedron.⁸ If outer shell p electrons are considered, the two clusters are isoelectronic. Using a Lewis electron-pair scheme one has a cluster with nine electron-pair bonds and a lone pair on each bridging atom.

The cations

For each of the three independent cryptated cations the sodium ion occupies the central cavity of the macrobicycle. The coordination polyhedron about sodium is bicapped trigonal antiprismatic. The geometry of the first and second cryptated sodium cations is illustrated in Figures 5 and 6, respectively. The bond distances indicated in the figures were calculated prior to the final lattice constant refinement. The numbering system for the third crypt which is not illustrated parallels that of the other two. Moras, Metz and Weiss noted that as the size of the alkali cation decreases from cesium to sodium, the oxygen coordination changes from approximately trigonal prismatic in the case

of CsC^+I^- and RbC^+I^- ⁹¹ and KC^+I^- ⁹² to very nearly trigonal antiprismatic in the case of NaC^+I^- .⁴² The conformational flexibility of 2,2,2-crypt was also noted by Dye et al. who likewise found trigonal antiprismatic coordination about sodium in NaC^+Na^- ³⁸ and confirmed the ability of the strands to twist. While free 2,2,2-crypt exists in solution as an equilibrium mixture of three conformations having the bridge-head nitrogens either out-out, in-out, or in-in,⁹³ all crystal structures so far determined for cryptated metal ions logically have contained crypt in the in-in conformation.⁴¹ The N(101)-N(110) distance of 5.76 Å found here compares with 6.87 Å in free crypt.⁹⁴

A convenient way to consider the atom placements in the present structure is by comparison with the known structures of NaC^+Na^- ³⁸ and NaC^+I^- .⁴² The former compound crystallizes in the space group R32 while the latter one crystallizes in the space group P31c. Although P31c does not have the two-fold rotation axes of R32, both space groups have three-fold symmetry. Interatomic distances and angles found for the two compounds are compared with averages for the first crypt in Table 14.

The refinement reported here is more satisfactory for the first crypt than for the other two. That of the second crypt is reasonably satisfactory with the exception of the atoms near the N(210) bridgehead. While the refinement of the third crypt is much less satisfactory than for the other

Table 14. Interatomic distances and angles for cryptated sodium cations

Bonded Distances ($\text{\AA}$)	$\text{NaC}^+\text{Na}^-^a$	NaC^+I^-^b	Crypt 1 ^b
Na-N	2.72(1)	2.75(2)	2.88(8)
Na-O	2.57(1)	2.58(2)	2.55(10)
N-Cl	1.48(2)	1.47(2)	1.46(5)
Cl-C1	1.29(2)	1.44(3)	1.43(11)
C2-O	1.41(1)	1.44(2)	1.44(4)
O-C3	1.40(2)	1.40(5)	1.43(3)
C3-C3(2)	1.31(3)	1.40(4)	1.45(5)
Nonbonded Distances ($\text{\AA}$)			
Na-Cl	3.45(2)	3.53(2)	3.55(11)
Na-C2	3.46(2)	3.46(2)	3.46(11)
Na-C3	3.34(3)	3.39(2)	3.33(13)
O-O(2)	2.86(2)	2.79(2)	2.77(9)
O-O(3)	4.09(2)	4.07(2)	3.98(9)
O-O(3 ¹ 2)	5.13(2)	5.12(2)	5.05(17)
O-O(3 ² 2)	3.38(2)	3.53(2)	3.65(19)
N-N(2)	5.44(2)	5.50(2)	5.76
Angles (deg)			
Na-N-Cl	107(1)	110(1)	105(4)
Cl-N-Cl(3)	112(1)	109(1)	113(3)
N-Cl-C2	128(1)	113(2)	115(7)
Cl-C2-O	120(1)	117(3)	113(4)
C2-O-C3	107(1)	100(2)	114(5)
O-C3-C3(2)	121(2)	116(3)	110(3)
O-Na-O(2)	67.6(3)	65.7(4)	66(1)
O-Na-O(3)	105.4(3)	104.4(4)	102(2)
O-Na-O(3 ¹ 2)	171.2(3)	167.0(4)	163(2)
O-Na-O(3 ² 2)	82.0(3)	86.6(4)	91(2)

^aEstimated standard deviation of the least significant digit is given in parentheses.

^bEstimated standard deviation of the average of distances from Table 10 is given in parentheses.

two, inspection of the Na-N, Na-O and Na-C distances in Table 12 assures that the ligand complexing Na(3) is indeed 2,2,2-crypt. The specter of disorder at the bridgeheads N(210), N(301) and N(310) in this structure determination was indicated by multiple carbon positions in the difference maps phased on the basis of only the heavy atom positions. Block least squares refinement of judiciously chosen positions for the atoms of the second and third crypts followed by refinement of the positions and isotropic thermal parameters resulted in considerably larger thermal parameters than obtained in the case of the first crypt. Stout and Jensen have discussed the difficulties arising from disorder which is limited to a given portion of a molecule.⁹⁵ They suggest that this type of disorder is indicated by abnormally high thermal parameters for whole atoms located at sites having partial occupancy. The introduction of fractional atom positions for carbon atoms surrounding the N(210) bridgehead of the second crypt and for C(305), C(308), C(309), C(319), C(320), O(321), C(322) and C(323) in the third crypt did result in smaller converged isotropic thermal parameters for those atoms but did not provide a statistically significant⁶² improvement in the weighted agreement factor.

It may be noted that in the block least squares refinement of the second crypt more reasonable distances and angles were found than with the full matrix one. For the former

refinement estimated standard deviations for the distances between 0.06 and 0.08Å and for the angles 3.7 and 5.2° were obtained. Apparently to the extent that the block diagonal approach is a rougher approximation than the full-matrix one, errors are distributed over the macrobicycle as a whole. In view of this experience with the second crypt it seemed appropriate to report the block least squares refinement for the third crypt rather than carry out a full-matrix refinement of dubious value. Some consolation is derived from the fact that Dye et al.³⁸ observed abnormally high thermal parameters for carbon, nitrogen and oxygen atoms of 2,2,2-crypt in NaC^+Na^- plus unusually short C-C distances of 1.29 and 1.31Å and bond angles at carbon of 128, 120 and 122°. They noted that artificial shortening of interatomic distances and opening of bond angles often occur in structures with high thermal parameters. Among the factors presumably contributing to the difficulties experienced in the refinement reported here is the fact that a thirty per cent decay in the intensities of the standards occurred during data collection. Dye et al. reported observing thermal decomposition during data collection for NaC^+Na^- .³⁸ However, final atomic parameters obtained from data they collected from a second crystal agreed within 3σ of those determined from the original data. In view of the fact that the goniometer stage conducts heat from the motors driving the four circles of the

diffractometer used here, the $(\text{NaC}^+)_3\text{Sb}_7^{3-}$ crystal may have suffered some thermal decomposition during data collection. The effect of instrumental intemperance⁶³ at the time of data collection is unknown. All of these problems and details are, of course, less significant and interesting than the anion discovered.

Conclusion

The solution of the crystal structure of (cryptated sodium) heptantimonide(-3) provides the first example of a stable solid containing a well-characterized homopolyatomic cluster anion for a metallic element. Only recently Corbett indicated that there is no evidence for solid compounds containing Sb_7^{3-} .⁶ The demonstrated success of this synthetic approach as well as the preliminary results of Kummer and Diehl who achieved the isolation of Sn_9^{4-} in salts with sodium complexed with ethylenediamine³⁶ suggests the desirability of further synthetic effort in this area.

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