LBL-10467
Preprint c2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular
Research Division

Submitted to Accounts of Chemical Research

RECEIVED
LAWRENCE
BERKELEY LABORATORY

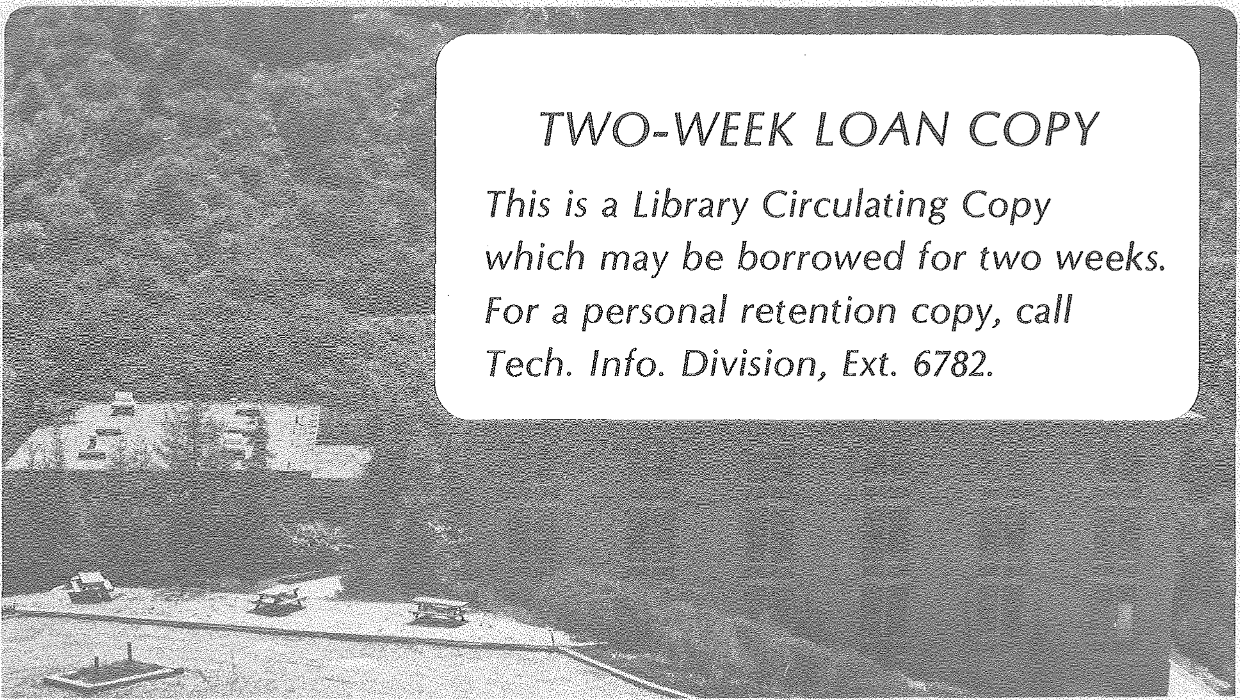
MAR 14 1980

LIBRARY AND
DOCUMENTS SECTION

STRUCTURAL CRITERIA FOR THE MODEL OF BONDING IN ORGANOACTINIDES AND -LANTHANIDES

Kenneth N. Raymond and Charles W. Eigenbrot, Jr.

January 1980



TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.

LBL-10467 c.2

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-10467

Structural Criteria for the Model of Bonding in Organoactinides and -lanthanides

By

Kenneth N. Raymond* and Charles W. Eigenbrot, Jr.
Contribution from the Department of Chemistry and Materials
and Molecular Research Division, Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720

Received:

---

*Author to whom correspondence should be addressed.

Introduction

Following the structure analysis of uranocene,[1] $U(C_8H_8)_2$, we found to our surprise that almost nothing was known about the structure and bonding of organoactinides and lanthanides — a situation we have endeavored to change during the intervening years. The reported synthesis of uranocene in 1968 by Mueller-Westerhoff and Streitwieser[2] sparked renewed interest in a field that had remained dormant since the synthesis of the cyclopentadienide compounds in the early 1950's. Two recent Accounts articles[3] have described some of the subsequent developments in this field. A question which frequently occurs in discussions of this chemistry is: "How covalent is the bonding in these compounds?" Within a careful and limited structural definition of covalent and ionic bonding, this question can be examined in some detail. This Account, while summarizing much of the structural information accumulated during the last ten years, will focus on the unifying structural trends in these compounds and the question of the mode of bonding. Complete reviews of the structural chemistry and further discussion of the structural aspects of the bonding can be found elsewhere.[4] Our discussion will consider scandium and yttrium as lanthanides, based on their general chemical similarity to the true lanthanides.

A Structural Definition of Covalent/Ionic Bonding

For the question of the presence or absence of any property to have meaning, the property itself must be well defined. While there are certainly many definitions of covalent/ionic bonding, and various physical techniques lend themselves to each definition, the following two criteria privide a phenomenological definition based only on structure:

1. *The geometries of ionic compounds tend to be irregular and depend on the steric bulk, number, and charge of the ligands. The coordination number observed is the result of a balance between ionic attractive forces and nonbonded repulsions. This is in marked contrast to the regular, directional bonds which typify covalent compounds.*
2. *Bond lengths for a series of structurally similar compounds will follow systematically from their "ion size" and coordination number — that is, ionic radii can be used to predict bond lengths. In contrast, the structure of predominantly covalent compounds show pronounced departures from such predictions.*

In simple ionic salts it is found that the difference between the cation-anion interatomic distances, R, is constant for a given ion. For example, R equals 2.81 and 2.98 Å for NaCl and NaBr, respectively, for a difference of .17 Å . Likewise for the analogous potassium salts the difference is .15 Å, and for the rubidium salts the difference is .15 Å.

Following Pauling's approach[5] one can write

$$R = r_+ + r_- \qquad (1)$$

where r_+ and r_- are radii of the cation and anion, respectively, and

$$\frac{r_+}{r_-} = \frac{Z_-^*}{Z_+^*} \qquad (2)$$

where Z_+^* and Z_-^* are the effective nuclear charges for the valence electrons of the cation and anion, respectively. This gives the so-called "univalent radii," and tacitly assumes a ±1 charge on each ion. The decrease in effective size that accompanies higher charge for a salt $M^{+i}X^{-j}_{i/j}$ is given by

$$R_{ij} = R_{11}\left(\frac{1}{ij}\right)^{1/n-1} \qquad (3)$$

where n is the Born exponent[5] (12 for most of the cations we will consider). In a similar fashion, the increase in effective ion size with coordination number is given by

$$\left(\frac{R_{II}}{R_I}\right) = \left(\frac{CN_{II}}{CN_I}\right)^{1/n-1} \qquad (4)$$

where R_{II} and R_I are the interionic distances for coordination II and I, respectively.

The most useful and complete tabulation of ionic radii today is that of Shannon[6] who has produced a self-consistent set of ionic radii from over 900 structure reports. These radii will be used throughout this Account, with corrections applied for changes in coordination number as described in Eq. (4), when appropriate.[7] The definition of coordination number that we will use is: the number of electron pairs involved in ligand-to-metal coordination.

Structural Types and Coordination Numbers of Organoactinides and -lanthanides

MCp_3X

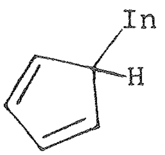
The structure of tris(benzylcyclopentadienyl)chlorouranium(IV)[8] provided the first accurate determination of a cyclopentadienyl actinide complex. The cyclopentadienyl (Cp) rings are pentahapto bound and the chloride anion is coordinated along the trigonal axis of the formally ten-coordinate complex. The geometry is that of a trigonally-compressed tetrahedron such that the Cl-U-(Cp centroid) bond angle is 100° (Figure 1). This geometry remains essentially invariant for a large number of lanthanide and actinide compounds of the general formula MCp_3X,[9] where X is a donor ligand, anion, or η^1 bridging cyclopentadienyl ring. The structure of one such adduct $(YbCp_3)_2$(pyrazine),[10] is also shown in Figure 1.

The strong Lewis acidity of the $LnCp_3$ complexes, the use of pyrazine as an effective electron transfer agent in transition metal chemistry, and our desire for an organolanthanide complex with a continuous π-bridging ligand system to compliment previous studies suggested to us the possibility of a pyrazine-bridged dimer. Such a complex would place the metal atoms far enough apart to eliminate through-space interactions so that any electron exchange would have to take place through the ligand π system.

The molecular unit of $(YbCp_3)$ pyrazine is a dimer located about a crystallographic inversion center. Two ytterbium atoms, each with three η^5-cyclopentadienide rings, are nearly linearly bridged by a pyrazine ring coordinated through its nitrogens. The magnetic susceptibility of the dinuclear complex exhibits simple Curie-Weiss behavior over the range 4 to 100 K, with $\mu_{eff} = 3.48\ \mu_B$. No other cyclopentadienyl lanthanide complex has had its moment measured below 77 K nor has the tempeature dependence of the susceptibility been closely examined before, but reports of the effective moment for several compounds at two or three temperatures have appeared: $LnCp_2Cl$[11] and $LnCpCl_2$[12] appear to follow the Curier-Weiss law down to 200 K, with $\mu_{eff} = 4.81$ and $4.33\ \mu_B$ and $\theta = 108$ and 8 K, respectively, for the ytterbium members of the series; a moment of $4.00\ \mu_B$ with $\theta = 21$ K has been reported for $YbCp_3$ down to 77 K.[13] The moments of several dicyclopentadienide lanthanide alkyls have been measured by Tsutsui _et al._[14] from 77 K to room temperature and the temperature dependence of these compounds was attributed to a "covalent interaction" involving the σ-bonded alkyl group. However, these moments appear to have been calculated from the Curie law [as $\mu = 2.83(\chi T)^{1/2}$] not from the slope, or Curie-Weiss law [as $\mu = 2.83\ (x(T + \theta))^{1/2}$].[15] Recalculation of the susceptibility from the reported moment using the Curie law shows that $1/\chi$ is approximately linear with temperature. The moments thus obtained from the slopes are then between 4.0 and 4.5 μ_B for the ytterbium complexes of Tsutsui — in agreement with the room-temperature values obtained for other compounds.

MCp_3

The structure of tris(cyclopentadienyl)indium(III)[16] (Figure 2) is composed of indium atoms which achieve a relatively regular four-coordinate tetrahedral environment of σ bonds by bonding to 2 η^1 Cp rings, with the third ring forming a η^1, η^1 bridge. The C-C bond lengths within the Cp rings show localized double bond character of the type



In short, $InCp_3$ provides a classic example of the structural effects of covalent bonding.

In stark contrast, the compounds $LnCp_3$ (Figure 3) show structures whose coordination numbers and geometries change markedly with the metal ion radius. The small (.87 Å) Sc^{3+} ion in $ScCp_3$[17] is eight-coordinate in a polymeric structure formed by 2 η^5 Cp rings and a third ring which forms an η^1, η^1 bridge. All of the Cp rings show undistorted pentagonal symmetry with no evidence of C-C double bond localization. The larger (1.13 Å) Sm^{3+} ion in $Sm(indenyl)_3$[18] is nine-coordinate with three η^5 rings providing all of the coordination. In tris(methylcyclopentadienyl)neodymium(III), $Nd(MeCp)_3$,[19] the metal ion (1.17 Å) is ten-coordinate through formation of a tetramer in which all three Cp rings form η^5 bonds to Nd and one of the rings also bridges to form an η^1 ring bridge to the adjacent metal ion. Thus there is a monotonic increase in coordination number with increasing ionic radius of the metal ion. It is clear from these examples that the principal determinant of coordination numbers and geometries is the metal size, indicating that an ionic mode of bonding best describes these MCp_3 compounds.

MCp_4

For the series MCp_4 (Figure 4) there is again a pronounced change in coordination number and structure as the metal ion size increases. In $TiCp_4$[20] the coordination number of the Ti^{4+} ion (.74 Å) is eight, from two η^5 rings and two η^1 rings.

For the larger Zr^{4+} ion (.91 Å) in $ZrCp_4$[21] there are three η^5 rings and one η^1 ring to give a total coordination number of ten. In UCp_4[22] all four Cp rings are η^5 bound in a tetrahedral array to give a total coordination number of twelve around the U^{4+} ion (1.17 Å). Thus, these MCp_4 compounds again demonstrate that metal ion size plays the dominant role in determining the coordination number and geometry, indicating an ionic mode of bonding.

The pmr spectra of tetra(allyl)uranium(IV) compounds have been interpreted as arising from all η^3 ligands[23] with the π-coordination giving a total coordination number of eight. The x-ray structure of tris(cyclopentadienyl)(2-methylallyl)-uranium(IV)[24] showed, in contrast, that the allyl group was η^1 bound, the σ structure of Figure 5. The monohapto coordination of the allyl group in UCp_3(2-methylallyl) might be considered surprising in comparison with the structure of UCp_4. In UCp_4, the four η^5 (π) Cp rings are at the apices of a tetrahedron coordinated with an average U-C bond length of 2.81(2) Å. Knowing that the π-bonded allyls are lower in energy in $U(allyl)_4$ and that all four rings in UCp_4 are π-bonded, one might expect that the trihapto (π) form in UCp_3(allyl) would be lower in energy than the monohapto (σ) form.

The opposing factors, steric repulsion and increase in coordinate bonds, which determine the structures of these complexes are depicted in Figure 5. The steric requirements for the π-bonded structures are similar, since the 2-methylallyl group and the Cp anion occupy approximately the same area on the surface of the coordination polyhedron in this compound. Thus the steric rearrangement energy required for the σ to π conversion must be nearly the same. Apparently this energy is greater than that released by one coordinate bond but less than two. Thus the ground state for the allyl complex is σ and for the Cp complex it is π.

The corresponding lanthanide allyl, $SmCp_2$(allyl), has been reported and preliminary indications, based on the absence of infrared absorptions in the 1610-1640 cm^{-1} region, are consistent with a π-bonded structure.[25] Since the π-bonded structure would be formally eight coordinate and the σ-bonded structure only seven coordinate, these observations are consistent with what we would predict: the π-structure as the ground state.

$M(COT)_2$

The compounds $Ti(C_8H_8)_2$ and $Ti_2(C_8H_8)_3$ exhibit similar structures,[26,27] involving one symmetrical η^8-coordinated COT ring and one nonplanar ring of lower hapticity per titanium. In the analogous zirconium complex,[28] the metal's larger size is manifested in an additional coordination site being occupied by a THF molecule in the otherwise similar structure.

Cyclooctatetraene complexes of larger metal ions such as cerium,[29] thorium,[1] and uranium[1] (see Figure 6) all exhibit two symmetrical η^8-coordinated COT rings. The thorium and uranium compounds exhibit almost exact D_{8h} molecular symmetry while the cerium compound is very close to D_{8d}. Structural parameters of these compounds are collected in Table I.

Two possible explanations suggest themselves for the failure of the early metals to accept a uranocene-type structure. One is to note that the lanthanide and actinide ions are substantially larger, thereby requiring more ligands to saturate their coordination sphere. Uranocene is formally ten-coordinate and coordination numbers of nine and ten are quite common for uranium complexes. The early metals cannot accommodate so large a coordination number and so one COT ring slips to the side – providing a total coordination number of seven or eight. This argument rests squarely on an ionic description of the bonding. Alternatively, one may note that two η^8-coordinated COT rings provide 20 π electrons to the metal center in violation of the effective atomic number rule. While actinide and lanthanide complexes do not in general follow this rule, Group IVB organometallic complexes usually have 16 or 18 valence electrons. Thus the second COT ring slips to one side to reduce the number of valence electrons. This argument views the bonding in the early metals as predominantly covalent while recognizing the lack of anything resembling the effective atomic number rule to apply in the case of the lanthanide or actinide analogues. This recognition is tantamount to viewing the bonding in the latter metals as largely ionic

The reaction of UCl_4 with excess $Na_2[(3)\text{-}1,2\text{-}C_2B_9H_{11}]$ yields the anion $U[(3)\text{-}1,2\text{-}C_2B_9H_{11}]_2Cl_2^{2-}$,[30] the only f-metal carborane complex to date. This complex ion is similar in structure to "bent" metallocenes of the type MCp_2X_2. Although lacking any crystallographically imposed symmetry, it has approximate C_{2v} symmetry when the dicarbollide ligands are considered as "baskets." The coordination geometry may be described as a distorted tetrahedron with η^5-coordinated dicarbollide ligands. A number of bis-dicarbollide d transition metal complexes are known which resemble ferrocene in structure.[31-33] The $U(\text{dicarbollide})_2Cl_2^{2-}$ ion has a formal coordination number of 8 with a geometry like that of $Zr(Cp)_2Cl_2$. It is interesting to note that while the dicarbollide ligand coordinates through a pentagonal face and is functionally isoelectronic with the Cp anion, it is substantially larger and carries a 2- charge. The steric factor helps explain why this metallocarborane is formed while a true UCp_2Cl_2 complex cannot be isolated.[34] Addition of COT^{2-} or Cp^- to the $U(\text{dicarbollide})_2Cl_2^{2-}$ complex ion produces uranocene — even with less than stoichiometric amounts of COT^{2-}. However, at least two equivalents of Cp^- are required to form a red compound that retains dicarbollide ion. These results indicate the ligating properties of the dicarbollide ion are intermediate between COT^{2-} and Cp^{-}, as one might expect based on its size and charge.

A ligand that is relatively new to organoactinide chemistry, pentamethylcyclopentadienide, shares this intermediacy with 1,2-dicarbollide. Both ligands are substantially larger and more electron rich than the unsubstituted cyclopentadienide. Thus, it has proven possible to synthesize true $M(C_5Me_5)_2Cl_2$ complexes.[35] The heightened utility of these new complexes provides opportunities not only of new, facile bis-Cp type derivative chemistry, but may also take advantage of the electronic effects of the pentamethyl-Cp ligand. Successive substitution of methyl groups for the hydrogens of a Cp ring produces a monotonic increase in its electron donating power or ligand field strength. An example of the possible electronic effects of such substitution is illustrated by manganocene. Electron diffraction studies[36] have shown that gaseous manganocene, $MnCp_2$, exists as the high-spin species and that dimethylmanganocene, $Mn(CH_3C_5H_4)_2$, exists as an equilibrium mixture of the high- and low-spin species. The fully methylated decamethylmanganocene is low spin at room temperature.[37]

The Covalent/Ionic Structural Criterion and 3d Metallocenes

Having seen the conclusions drawn by considering the general structural features (i.e. metal coordination number and ligand hapticity) of carbocyclic complexes of the actinides and lanthanides, we now turn to another structural criterion of the mode of bonding — the metal-to-carbon bond distance [R(M-C)]. Table II contains structural data collected from x-ray and gas phase electron diffraction studies of first row metallocenes. If these compounds involved ionic bonding, the metal-to-carbon distances could be predicted as the sum of the ionic radii of the metal ion and the Cp anion. Another way of saying this is that the difference between the metal-to-carbon distance and the ionic radius of the metal (the effective ionic radius of the Cp ligand) should be constant. In the d-transition metal metallocenes, one cannot assign an effective ionic radius to the Cp anion. If we plot R(M-C) vs the metal ion radius (Figure 7a) we see that this is not a smooth function.

The predominant covalency of these compounds can be illustrated in a graph of R(M-C) vs electron imbalance as defined by Haaland[36] (Figure 8). Haaland's definition is based on a molecular orbital treatment of the bonding in these compounds, considers the effects of electron occupancy of bonding and antibonding orbitals — and results in a linear correction of R(M-C) and predicted bond order.

Table III collects corresponding structural data for lanthanide and actinide Cp complexes. We can see that the effective ionic radius for the Cp lignad is essentially invariant in structures of 23 complexes, and is 1.64 ± .04 Å.

This consistency is illustrated in Figure 7b, where the plot of R(M-C) vs the metal ion radius is presented for the available lanthanide complexes. A linear least squares refinement of these data yields a line with slope equal to .98 and a correlation coefficient of .98 [Eq. (1) requires that the slope, $dR(M\text{-}C)/dr_+$, = 1]. A similar treatment of the MCp_2 data produces a slope equal to 1.18 and a correlation coefficient of 0.83 (Figure 7b). The relatively high correlation coefficient and near unit slope in the former case shows metal-to-carbon bond length varies in direct proportion to metal ion size, a clear indication of predominantly ionic bonding. Recently Day[34] has noted that the bond length criterion appears not to hold for the compound $U(MeCp)Cl_3THF_2$. However, this structure cannot strictly be compared to the series of compounds in question, since it departs so radically from their chemical formulation and structure types — three different kinds of ligands are present, none of which occupies a majority of the coordination sites. Even so, Table III reveals that the calculated radius of the methyl-Cp ligand in this compound is within two standard deviations of the average.

Bond Lengths in Metal COT Complexes

Of all the lanthanide and actinide organometallic complexes, there is probably the most evidence of covalency (from physical techniques such as nmr and XPS) in the COT complexes of the actinides.[4,61] For this reason, it is interesting to see how well the purely structural model described here applies to the systematics observed in the geometries of these complexes. Table IV collects data from x-ray structures of COT complexes of 12 d, f, and s block metals. Subtraction of the metal ionic radii from R(M-C) yields an effective ionic radius for $COT^{=}$, which will be constant if the ionic model is applicable. Indeed, the $COT^{=}$ ionic radius is essentially invariant, with the data averaging 1.56 ± .04 Å. The graph of metal ionic radius versus R(M-C) for these complexes appears in Figure 7b, and yields a slope of 1.01 and correlation coefficient of 0.97. These results are a good indication that, despite evidence indicating some covalency, there is no structural evidence for it.

The Bond Length Criterion and Silyl Amide Complexes

While bis(silylamido) complexes of the type $M[N(SiMe_3)_2]_3$ are not strictly organometallic, there has been a substantial amount of recent interest — in part due to their low formal coordination number and an interesting structural anomaly in the lanthanide compounds. In addition, many of these complexes have been subjected to x-ray structural determination which allows us to examine them with respect to the bond length criterion.

The fact that these compounds comprise a structurally related series is indisputable. Table V collects the pertinent data from the structures of twelve complexes from all over the periodic chart. All twelve crystallize in space group $P\bar{3}1c$ and share the following molecular details: the metal ion is coplanar with the NSi_2 plane of each of the three ligands and the silicon atoms of each of the ligands are tilted out of the MN_3 plane by about 50°. For all but the compounds of Sc, Nd, Eu, and Yb, the metal lies in the N_3 plane, whereas for the lanthanide compounds it is out of the N_3 plane by about 0.4 Å.

As before, subtraction of the appropriate values for the metal ion radius from R(M-N) should yield an effective ionic radius for the ligand if the bonding is predominantly ionic. This is the case: the effective ionic radius of the silylamide ligand is constant at 1.47 ± .03 Å. The least squares refinement of these twelve data yields a slope of 0.91 and a correlation coefficient of 0.96 (Figure 7a).

For the purpose of such calculations, the ligand is considered to donate one electron pair to the metal and the remaining pair is involved in bonding to the silicon atoms. These complexes are therefore formally three-coordinate. Suggestions[70] that the "short" M-N bond lengths in these compounds should be attributed to metal-to-ligand back bonding are clearly unwarranted. The previous analysis did not take into account the change in the effective size of the metal ions with coordination number, which in the case of three-coordinate silylamides is especially pronounced. We believe that the molecular details of these structures are satisfactorily explained by a purely ionic description of the M-N bond. In this light, the tilt of the silicon atoms out of the MN_3 plane is due to steric crowding, and the M-N bond lengths are determined simply by balancing the opposing factors of steric crowding and the attractive force between the metal and the ligands. The lanthanides' displacement out of the N_3 plane is best attributed to packing forces in the solid. This view is supported by the infrared spectra, where the characteristic pyramidal bands of the scandium compound in the solid state collapse to the characteristic planar band in the solution spectrum.[70]

Conclusion

We have developed a formalism, based only on structure, within which to address the question of the predominant mode of bonding in organometallic complexes of the lanthanide and actinide elements. The formalism considers the general structural features and the metal coordination number for a series of structurally related compounds. We have shown that the ionic model can explain these features as observed in organoactinides and -lanthanides well — while the same model does not work well in the d metal MCp_2 metallocenes, where covalent bonding often predominates. We have also shown that the ionic model can explain the observed structures of tris(silylamide) complexes of metals from all over the periodic table. While we caution that structural variations are not usually very sensitive to small changes in bonding and alternative definitions of "ionic" and "covalent" based on other physical methods may well lead to different conclusions within such formalisms, we conclude that within the limits of our structural criteria the bonding in organoactinides and -lanthanides is ionic.

Acknowledgment

This work was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng-48. We thank Professor R. A. Andersen for helpful comments and discussions.

References

1. A. Avdeef, K. N. Raymond, K. O. Hodgson and A. Zalkin, *Inorg. Chem.*, *11*, 1083 (1972).
2. a) A. Streitwieser and U. Mueller-Westerhoff, *J. Am. Chem. Soc.*, *90*, 7364 (1968). b) A. Streitwieser, U. Mueller-Westerhoff, G. Sonnichsen F. Mares, D. G. Morell, K. O. Hodgson and C. A. Harmon, *J. Am. Chem. Soc.*, *95*, 8644 (1973).
3. a) T. J. Marks, *Acc. Chem. Res.*, *9*, 223 (1976). b) M. Tsutsui, N. Ely and R. Dubois, *Acc. Chem. Res.*, *9*, 217 (1976).
4. E. C. Baker, G. W. Halstead and K. N. Raymond, *Struct. Bonding (Berlin)*, *25*, 23 (1976).
5. L. Pauling, "The Nature of the Chemical Bond," Third Ed., Cornell University Press, Ithaca, N.Y., 1960, pp 505-562.
6. R. D. Shannon, *Acta Crystallogr.*, *Sect. A*, *32*, 751 (1976).
7. For example, calculation of the ten-coordinate ionic radius for Zr^{4+} proceeds as follows: Judging the chloride to be a representative ionic compound we calculate

$$\frac{R_{10}}{R_8} = \left(\frac{10}{8}\right)^{1/n}$$

where

$$n = \frac{n_{Cl^-} + n_{Zr^{4+}}}{2}$$

and

$$R_8 = r_{Cl^-} + r_{Zr^{4+}} = (1.81 + .84)$$

The metal chlorides were used to calculate the known R_x's and calculations were based on the six-coordinate radius for the smaller metals and the eight-coordinate radius for the larger ones.

8. J. Leong, K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **12**, 1329 (1973).
9. Fischer and co-workers [R. D. Fischer, E. Klahne and J. Kopf, *Zeit. fur Natur.*, **33b**, 12, 1393 (1978)] have recently found that another ligand can add to form the complex $UCp_3(NCS)(NCCH_3)$ which has a trigonal bipyramidal arrangement with the Cp rings in the equatorial sites.
10. E. C. Baker and K. N. Raymond, *Inorg. Chem.*, **16**, 2710 (1977).
11. R. E. Maginn, S. Manastyrskyj and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 672 (1963).
12. S. Manastyrskyj, R. E. Maginn and M. Dubeck, *Inorg. Chem.*, **2**, 904 (1963).
13. J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).
14. N. M. Ely and M. Tsutsui, *Inorg. Chem.*, **14**, 2680 (1975).
15. It is not stated in Ref. 14 how μ_{eff} is calculated, but no θ value or slope is given and the reported room temperature moment agrees well with the room temperature moment via the Curie law. Experimental susceptibilities are not given at other temperatures.
16. F. W. B. Einstein, M. M. Gilbert and D. G. Tuck, *Inorg. Chem.*, **11**, 2832 (1972).

17. J. L. Atwood and K. D. Smith, J. Am. Chem. Soc., 95, 1488 (1973).

18. J. L. Atwood, J. H. Burns and P. G. Laubereau, J. Am. Chem. Soc., 95, 1830 (1973).

19. J. H. Burns, W. H. Baldwin and F. H. Fink, Inorg. Chem., 13, 1916 (1974).

20. J. L. Calderon, F. A. Cotton, B. G. DeBoer and J. Takats, J. Am. Chem. Soc., 93, 3592 (1971).

21. R. D. Rogers, R. V. Bynum and J. L. Atwood, J. Am. Chem. Soc., 100, 5238 (1978).

22. J. H. Burns, J. Organomet. Chem., 69, 225 (1974).

23. N. Paladino, G. Lugli, U. Pedretti, M. Brunelli and G. Giacemetti, Chem. Phys. Lett., 5, 15 (1970).

24. G. W. Halstead, E. C. Baker and K. N. Raymond, J. Am. Chem. Soc., 97, 3049 (1975).

25. M. Tsutsui and N. Ely, J. Am. Chem. Soc., 97, 3551 (1975).

26. H. Dietrich and M. Soltwisch, Angew. Chem. Intern. Ed. Engl., 8, 765 (1969).

27. H. Dierks and H. Dietrich, Acta Crystallogr., Sect. B, 24, 58 (1968).

28. D. J. Brauer and C. Kruger, J. Organometal. Chem., 42, 129 (1972).

29. K. O. Hodgson and K. N. Raymond, Inorg. Chem., 11, 3030 (1972).

30. F. R. Fronczek, G. W. Halstead and K. N. Raymond, J. Am. Chem. Soc., 99, 1769 (1977).

31. W. J. Evans, G. B. Dunks and M. F. Hawthorne, J. Am. Chem. Soc., 95, 4565 (1973) and references therein.

32. G. B. Dunks and M. F. Hawthorne, "Boron Hydride Chemistry," E. L. Muetterties, Ed., Academic Press, New York, N.Y., 1975.

33. M. F. Hawthorne, J. Organometal. Chem., 100, 97 (1975).

34. R. D. Ernst, W. J. Kennelly, C. S. Day, V. W. Day and T. J. Marks, J. Am. Chem. Soc., 101, 2656 (1979).

35. J. M. Manriquez, P. J. Fagan and T. J. Marks, J. Am. Chem. Soc., 100, 3939 (1978).

36. A. Almenningen, A. Haaland and S. Samdal, J. Organometal. Chem., 149, 219 (1978).

37. J. C. Smart and J. L. Robbins, J. Am. Chem. Soc., 100, 3936 (1978).

38. E. Gard, A. Haaland, D. P. Novak and R. Seip, J. Organometal. Chem., 88, 181 (1975).

39. A. Almenningen, A. Haaland and T. Motzfeldt, in "Selected Topics in Structure Chemistry," Universitetsforlaget, Oslo, 1967, p 105.

40. A. Haaland and J. E. Nilsson, Acta Chem. Scand., 22, 2653 (1968).

41. A. Almenningen, E. Gard, A. Haaland and J. Bunvoll, J. Organometal. Chem., 107, 273 (1976).

42. A. K. Hedberg, L. Hedberg and K. Hedberg, J. Chem. Phys., 63, 1262 (1975).

43. L. Hedberg and K. Hedberg, J. Chem. Phys., 53, 1228 (1970).

44. P. J. Wheatley, "Perspectives in Structural Chemistry," J. D. Dunitz and J. A. Ibers, Ed., John Wiley, N.Y. 1967.

45. W. Bunder and E. Weiss, Zeit. fur Nature, 33b, 1235 (1978).

46. J. D. Dunitz, L. E. Orgel and A. Rich, Acta Crystallogr., 9, 373 (1956).

47. W. Bunder and E. Weiss, J. Organometal. Chem., 92, 65 (1975).

48. J. W. Bats, J. J. DeBoer and D. Bright, Inorg. Chim. Acta, 5, 605 (1971).

49. J. H. Burns, W. H. Baldwin and P. G. Laubereau, Oak Ridge Chemistry Division Annual Prob. Report, ORNL-4891, 1973, p 42.

50. J. L. Atwood and K. D. Smith, J. Chem. Soc. Dalton Trans., 2487 (1973).

51. E. C. Baker, L. D. Brown and K. N. Raymond, Inorg. Chem., 14, 1376 (1975).

52. J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood and W. E. Hunter, J. Chem. Soc., Chem. Commun., 480 (1976).

53. R. D. Rogers, R. V. Bynum and J. L. Atwood, Abstracts of Papers Amer. Cryst. Assoc. Winter Meeting, 1979, L7.

54. A. Zalkin, private communication.

55. C. Wong, T. Yen and T. Lee, Acta Crystallogr., 18, 340 (1965).

56. R. R. Ryan, R. A. Penneman and B. Kanellakopulos, J. Am. Chem. Soc., 97, 4258 (1975).

57. J. H. Burns and P. G. Laubereau, Inorg. Chem., 10, 2789 (1971).

58. J. L. Atwood, C. F. Hains, M. Tsutsui and A. E. Gabela, J. Chem. Soc., Chem. Commun., 452 (1973).

59. a) G. Parego, M. Cesari, F. Farina and G. Lugli, Gazz. Chim. Ital., 105, 642 (1975). b) G. Parego, M. Cesari, F. Farina and G. Lugli, Acta Crystallogr., Section B, 32, 3034 (1976).

60. E. C. Baker, K. N. Raymond, T. J. Marks and W. A. Wachter, J. Am. Chem. Soc., 96, 7586 (1974).

61. J. P. Clark, J. C. Green, J. Chem. Soc. Dalton Trans., 505 (1977).

62. K. O. Hodgson and K. N. Raymond, Inorg. Chem., 12, 458 (1973).

63. K. O. Hodgson and K. N. Raymond, Inorg. Chem., 11, 171 (1972).

64. S. R. Ely, T. E. Hopkins, and C. W. DeKock, J. Am. Chem. Soc., 98, 1624 (1976). C. W. DeKock, S. R. Ely, T. E. Hopkins, and M. A. Brault, Inorg. Chem., 17, 625 (1978).

65. P. A. Kroon and R. B. Helmhodt, J. Organometal. Chem., 25, 451 (1970).

66. S. G. Goldberg, K. N. Raymond, C. A. Harmon, and D. H. Templeton, J. Am. Chem. Soc., 96, 1348 (1974).

67. J. H. Noordik, Th. E. M. van den Hark, J. J. Mooij, and A. A. K. Klaassen, Acta Cryst., B30, 833 (1974).

68. J. H. Noordik, H. M. L. Degens, and J. J. Mooij, Acta Cryst., B31, 2144 (1975).

69. G. M. Sheldrich and W. S. Sheldrich, J. Chem. Soc. (A), 2279 (1969).

70. P. G. Eller, D. C. Bradley, M. B. Hursthouse and D. W. Meek, Coord. Chem. Rev., 24, 1 (1977).

71. R. Allmann, W. Henke, P. Krommes and J. Lorberth, J. Organomet. Chem., 162, 283 (1978)

72. R. A. Andersen, D. H. Templeton and A. Zalkin, Inorg. Chem., 17, 2317 (1978).

Table I. Summary of crystal and molecular data for COT complexes

	$U(C_8H_8)_2$	$Th(C_8H_8)_2$	$[K(diglyme)][Ce(C_8H_8)_2$
Space group	$P2_1/n$	$P2_1/n$	Pnma
Density, g cm^{-3}	2.29	2.22	1.56
Molecules/unit cell	2	2	4
Site symmetry	C_i	C_i	C_s
Mean M-C bond length, Å	2.647(4)	2.701(4)	2.742(8)
Mean (center-of-ring)-M-C angle, deg.	43.40(7)	42.11(8)	40.8(5)
Mean C-C distance, Å	1.392(13)	1.386(9)	1.388(28)
Ring to ring distance, Å	3.847(10)	4.007(3)	4.151
Reference	1	1	29

Table IIa. Gas phase electron diffraction data

Compound	R(M-C)	Metal Ion Radius	Cp Radius	Ref.
VCp_2	2.280(5)	.79	1.49	38
$CrCp_2$	2.169(4)	.73	1.44	38
$MnCp_2$	2.383(3)	.83	1.55	39
$Mn(MeCp)_2$ (L.S.)	2.144(12)	.67	1.47	36
$Mn(MeCp)_2$ (H.S.)	2.433(8)	.83	1.60	36
$FeCp_2$	2.064(3)	.61	1.45	40
$CoCp_2$	2.119(3)	.65	1.47	41,42
$NiCp_2$	2.196(4)	.69	1.51	43

Table IIb. Single crystal x-ray data

Compound	R(M-C)	Metal Ion Radius	Effective Cp Radius	Ref.
VCp_2	2.24	.79	1.45	44
$CrCp_2$	2.14	.73	1.41	44
$MnCp_2$	2.41	.83	1.58	45
$FeCp_2$	2.045(4)	.61	1.44	46
$CoCp_2$	2.096(8)	.65	1.45	47
$NiCp_2$	2.15	.69	1.46	44
$[Fe(MeCp)_2]I_3^-$	2.05(2)	.55	1.50	48

Table III. Single crystal x-ray diffraction data

Compound	Observed R(M-C)	Metal Ion Radius	Cp Radius	Ref.
$ScCp_3$	2.49(2)	0.87	1.62	17
$Sm(ind)_3$	2.75(5)	1.13	1.62	18
$Nd(MeCp)_3$	2.79(5)	1.17	1.62	19
$PrCp_3CNC_6H_{11}$	2.77(2)	1.18	1.59	49
$(YbCp_3)_2(C_4H_4N_2)$	2.68(1)	1.04	1.64	10
$(ScCp_2Cl)_2$	2.46(2)	0.87	1.59	50
$[Yb(MeCp)_2Cl]_2$	2.585(8)	0.985	1.60	51
$(YbCp_2Me)_2$	2.613(13)	0.985	1.63	52
$GdCp_3(THF)$	2.72(6)	1.11	1.61	53
$Yb(Me_5C_5)_2(pyridine)_2$	2.741	1.14	1.60	54
UCp_3Cl	2.74	1.06	1.68	55
UCp_3F	2.74	1.06	1.68	56
$U(benzylCp)_3Cl$	2.733(1)	1.06	1.67	8
$U(indenyl)_3Cl$	2.78	1.06	1.72	57
$UCp_3(C_2H)$	2.73(5)	1.06	1.67	3b
$UCp_3(C_2C_6H_5)$	2.68	1.06	1.62	58
$UCp_3(p\text{-}xylyl)$	2.71(1)	1.06	1.65	59
$UCp_3(n\text{-}but)$	2.73(1)	1.06	1.67	59
$UCp_3(2\text{-}Me\text{-}allyl)$	2.74(1)	1.06	1.68	24
UCp_4	2.81(2)	1.17	1.64	22
$(ThCp_2C_5H_4)_2$	2.83	1.13	1.70	60
$UCp_3(NCS)(CH_3CN)$	2.763	1.08	1.68	9
$U(MeCp)Cl_3(THF)_2$	2.720	1.00	1.72	34

Table IV. Single crystal x-ray data for COT complexes

Compound[a]	R(M-C)	Metal Ion Radius	Eff. $COT^{=}$ Radius	Ref.
$U(COT)_2$	2.647	1.06	1.59	1
$U(Me_4COT)_2$	2.658	1.06	1.60	62
$Th(COT)_2$	2.701	1.13	1.57	1
$K(dg)[Ce(COT)_2]$	2.742	1.25	1.49	29
$[Ce(COT)Cl\cdot 2thf]_2$	2.710	1.20	1.51	63
$[Nd(COT)thf_2]$	2.68	1.18	1.50	64
$[Nd(COT)_2]$	2.79	1.18	1.61	
	2.68	1.16	1.52	
$Zr(COT)_2\cdot thf$	2.461	.89	1.57	28
$Ti(COT)Cp$	2.323	.76	1.56	65
$[K(dg)]_2(Me_4COT)$	3.003	1.46	1.54	66
$K_2(COT)(dg)$	2.98	1.38	1.60	67
	3.05	1.46	1.59	
$Rb_2(COT)(dg)$	3.10	1.52	1.58	68
	3.15	1.56	1.59	

---

[a] dg = diglyme.

Table V. Single crystal x-ray data for tris(hexamethyldisilylamido) compounds

Metal	R(M-N)	Metal Ion Radius	Effective Amide Radius	Ref.
Al	1.84(1)	.31	1.53	69
Ga	1.86(1)	.42	1.44	70
In	2.06(1)	.595	1.47	70
Tl	2.09	.695	1.40	71
Ti	1.929(4)	.46	1.47	70
V	1.910(4)	.44	1.47	70
Cr	1.903(6)	.41	1.49	70
Fe	1.917(4)	.44	1.48	70
Sc	2.047(6)	.53	1.52	70
Nd	2.29(2)	.82	1.47	72
Eu	2.259(9)	.78	1.48	70
Yb	2.158(13)	.71	1.45	70

Figure Captions

Figure 1. Perspective diagrams of U(BzCp)$_3$Cl (top, ref. 8) and Cp$_3$Yb(NC$_4$H$_4$N)YbCp$_3$ (bottom, ref. 10).

Figure 2. A perspective drawing of In(Cp)$_3$ (ref. 16).

Figure 3. Perspective drawings of ScCp$_3$ (top, ref. 17), Sm(indenyl)$_3$ (bottom left, ref. 18) and Nd(MeCp)$_3$ (bottom right, ref. 19).

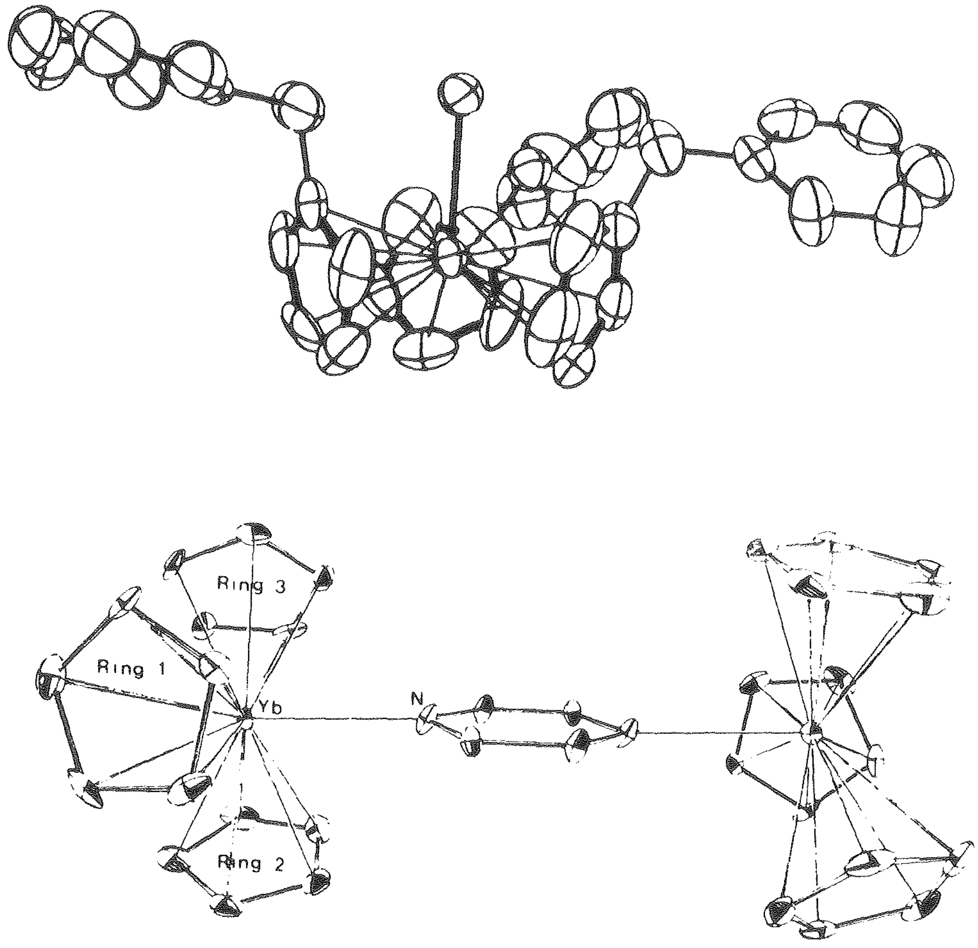
Figure 4. Structures of tetrakis(cyclopentadienide) complexes: TiCp$_4$ (left, ref. 20), ZrCp$_4$ (center, ref. 21) and UCp$_4$ (right, ref. 22).

Figure 5. The structure of U(Cp)$_3$(2-methylallyl) (top, ref. 24) and schematic representations of the σ-π interconversion process.

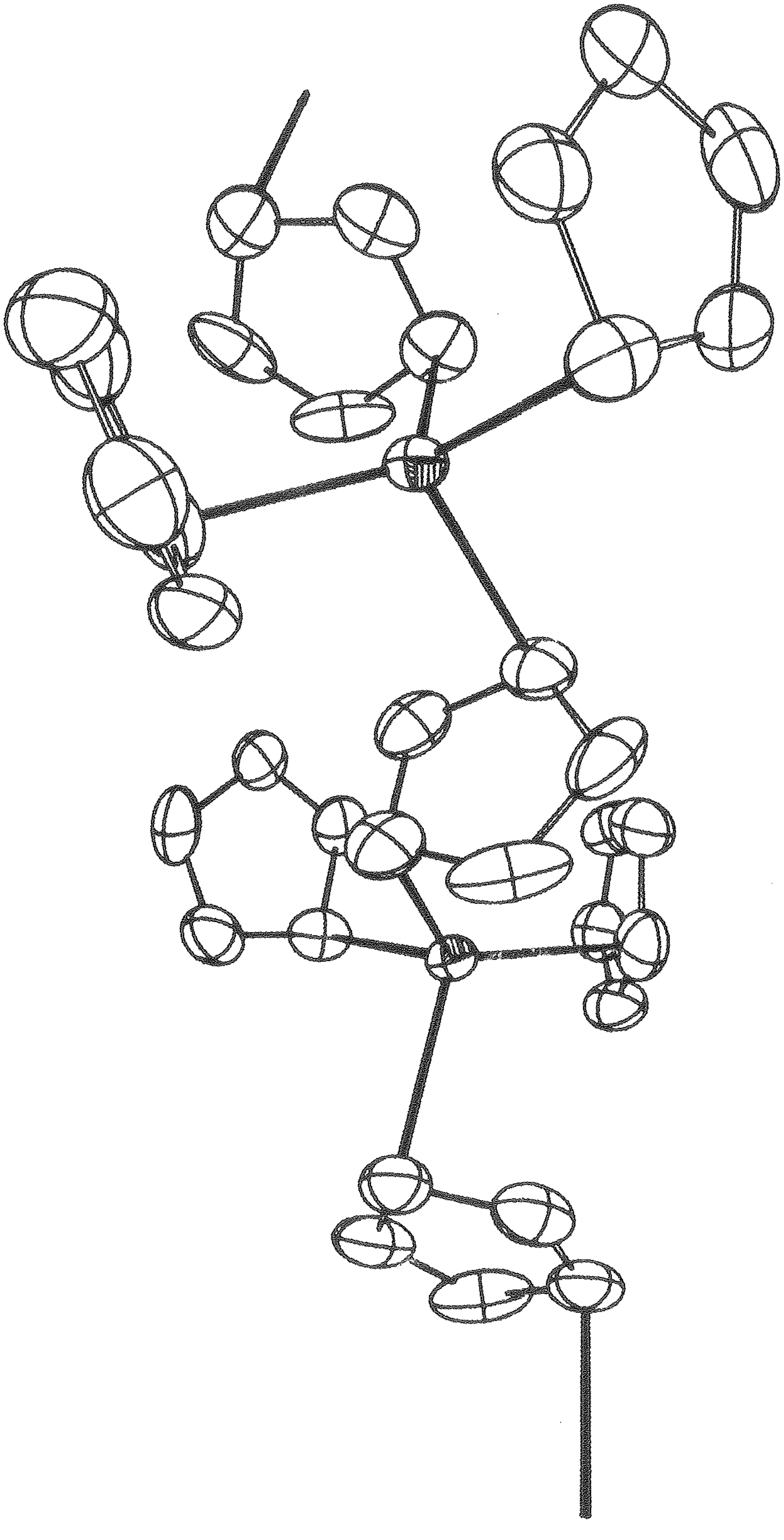
Figure 6. Perspective diagrams of U(COT)$_2$ (left, ref. 1), [K(diglyme)]$_2$(C$_8$H$_4$Me$_4$) (center, ref. 66), and [K9diglyme)][Ce(COT)$_2$] (left, ref. 29).

Figure 7. Plots of the average metal-ligand distances for three series of organometallic and silylamide structures.

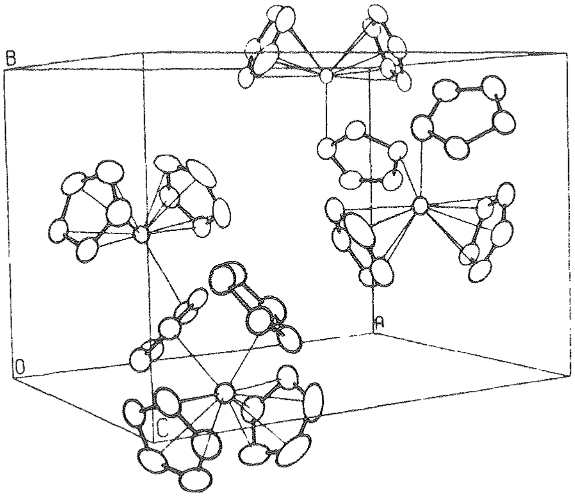
Figure 8. A plot of the average metal-carbon bond lengths for first row metallocenes (MCp_2) as a function of their "electron imbalance" (defined as the difference of bonding less antibonding electrons plus six – after Haaland, ref. 36).

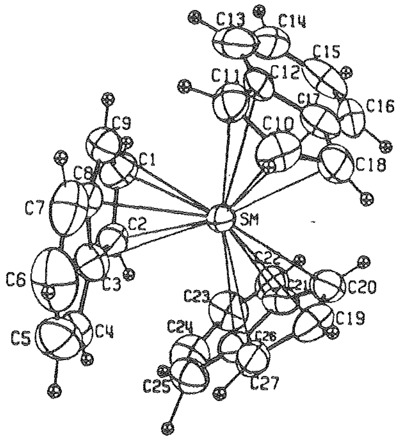

Ring 3
Ring 1
Yb
N
Ring 2

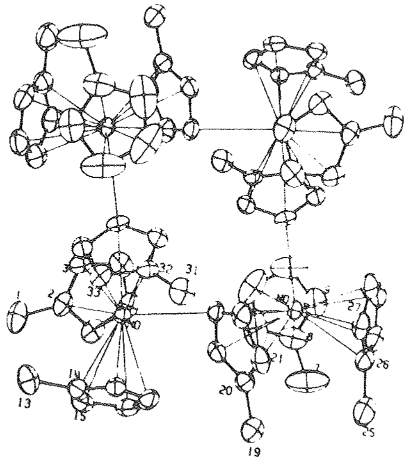
XBL 799-12047



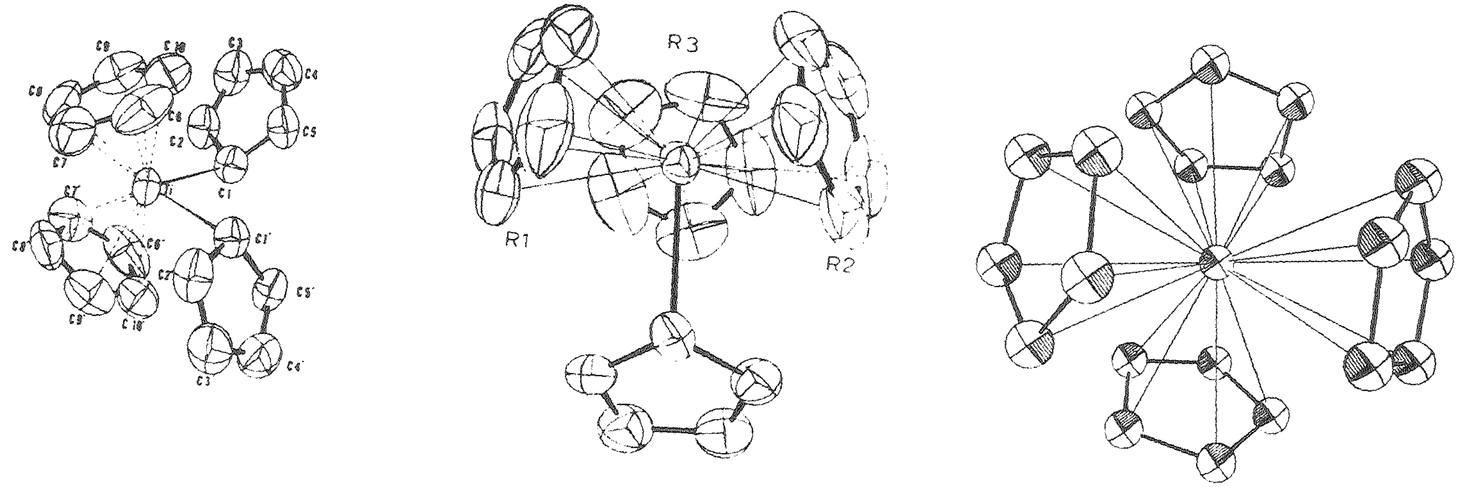
XBL 7911-12809



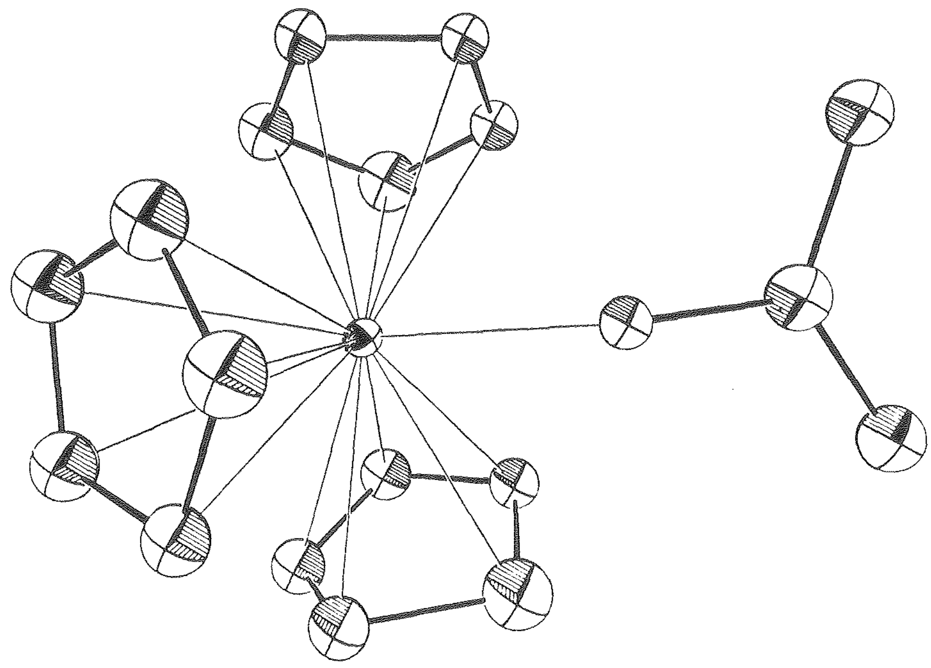

C13
C14
C15
C11
C12
C16
C17
C10
C9
C1
C18
C8
C7
C2
SM
C6
C3
C22
C20
C23
C21
C19
C5
C4
C24
C26
C25
C27

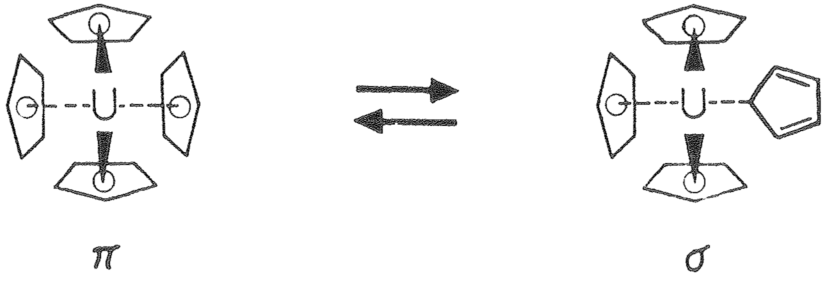

32
31
33
1
2
13
14
15
MO
27
21
20
26
19
25

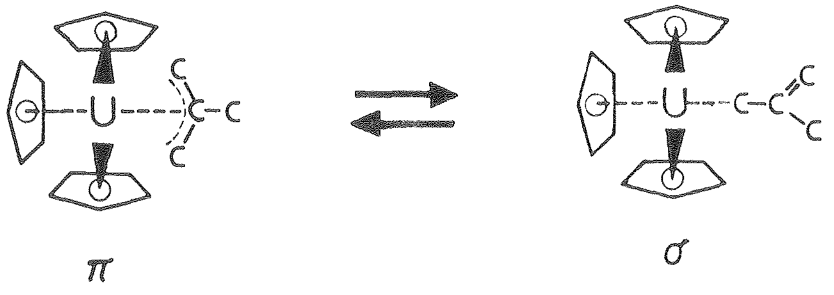
XBL 799-12048


C9
C10
C3
C4
C8
C6
C5
C2
C7
C1
C7'
C8'
C6'
C1'
C2'
C5'
C9'
C10'
C3'
C4'
R3
R1
R2

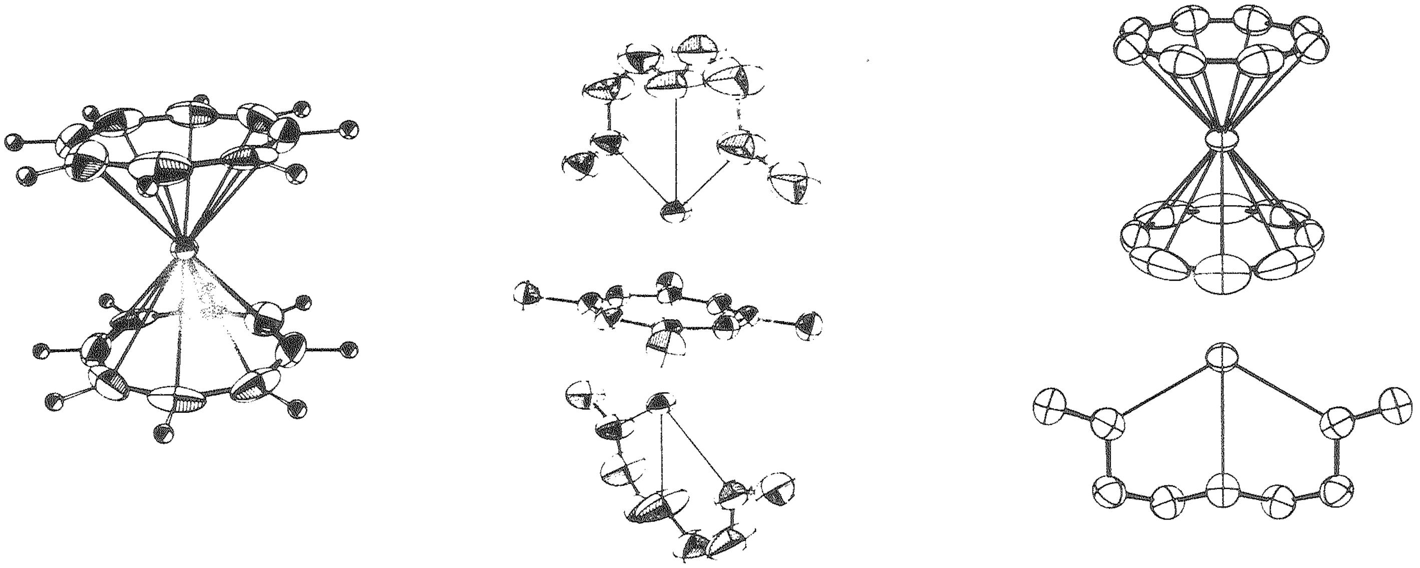
XBL 799-12049



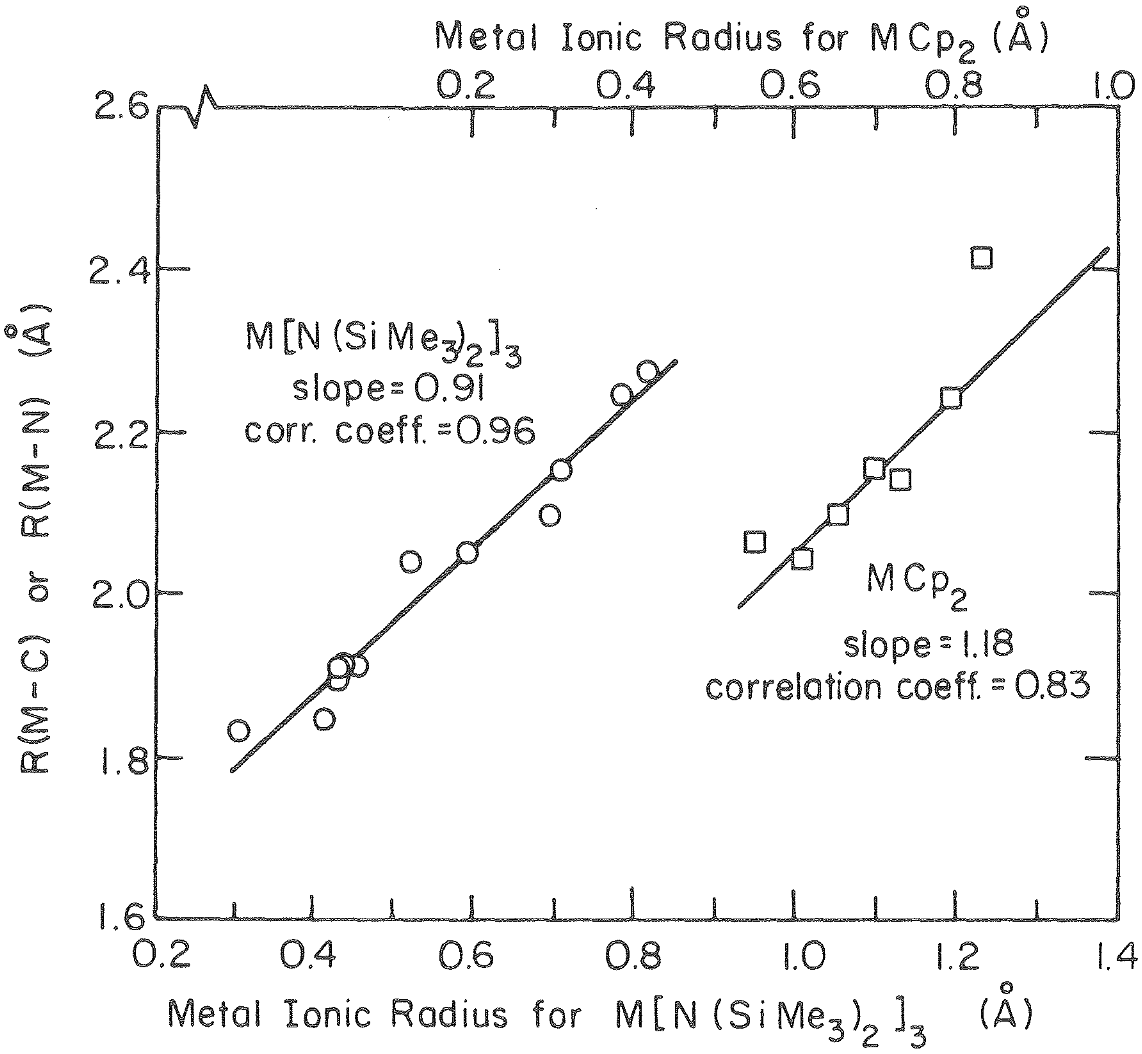



C
U
C
C
U
C
C
C
π
σ

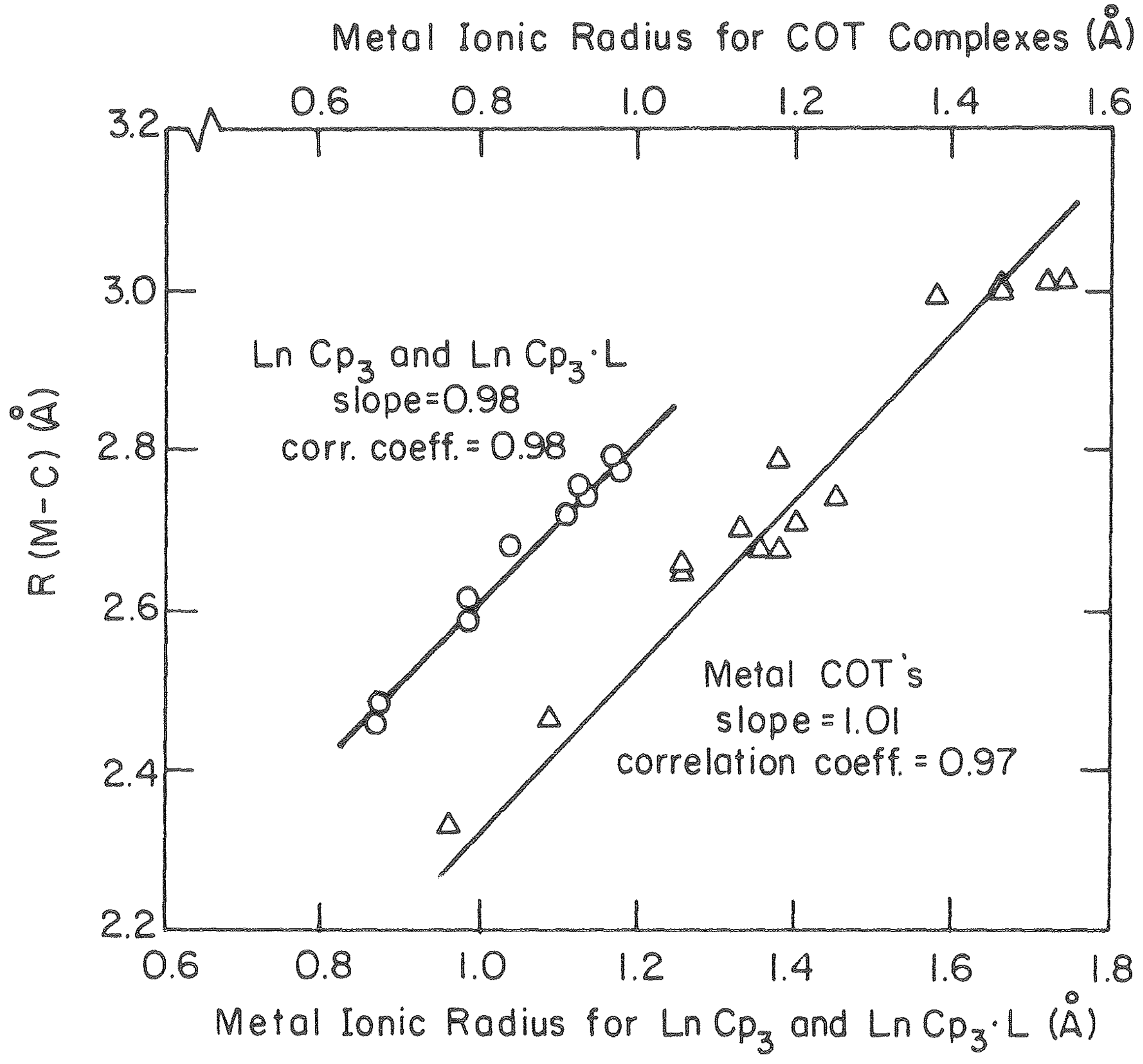
XBL 799-12046



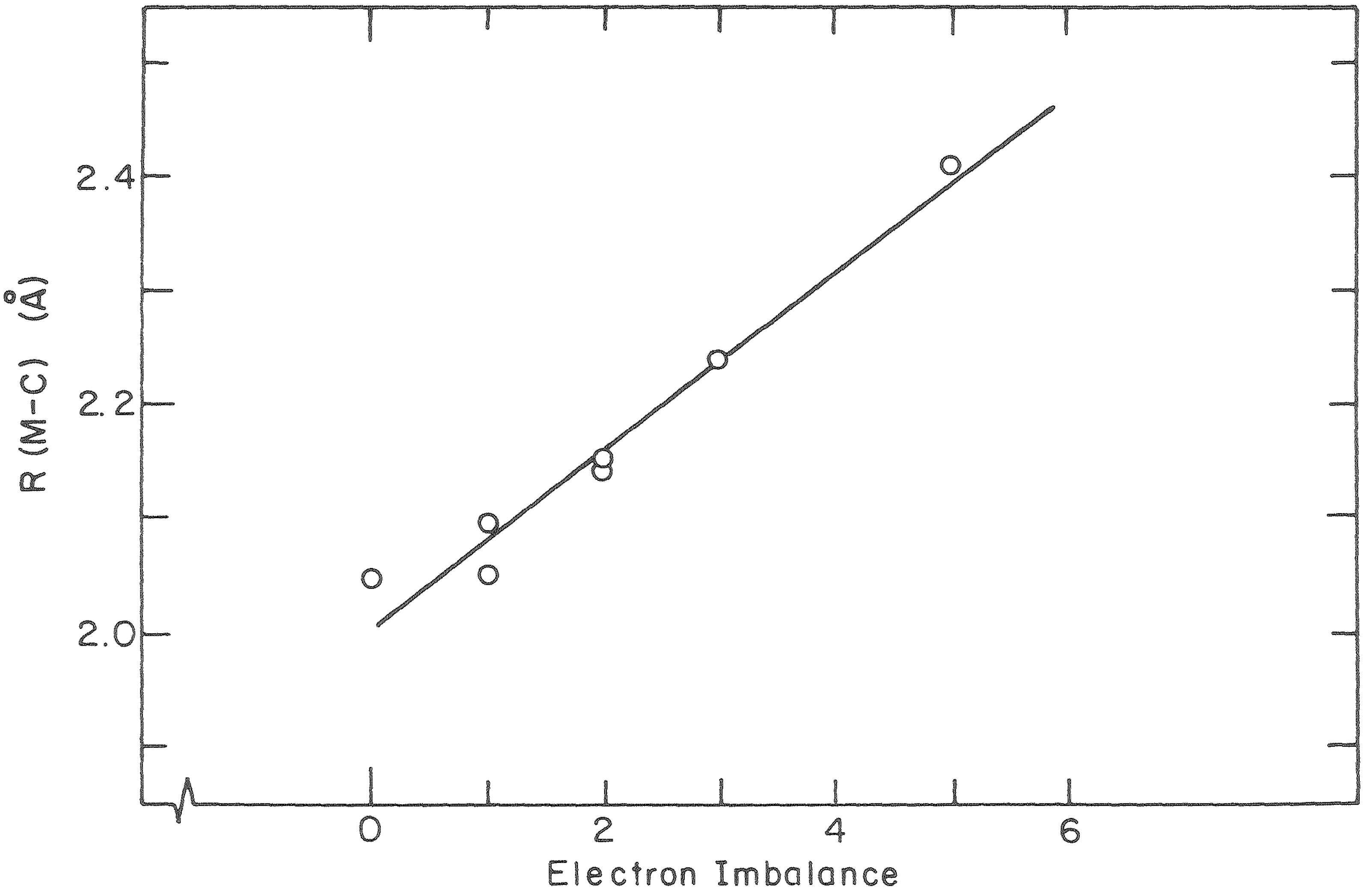
XBL 7911-12827



XBL 7911-7287



XBL 7911-7288



XBL 799-7063