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Some Additional Corrections to the  
Modern Theory and Nomenclature of Complex Compounds

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The forces which occur in a coordination sphere may be almost purely ionic or almost purely atomic, or of intermediate character, depending on the structure of the atoms contained in the sphere. However, since the character of the chemical bonds involves differences in the formation and stability conditions of coordinate spheres as a whole, formal concepts concerning the magnitude of the maximum coordination number are no longer adequate for the theory of complex compounds.

In our previous paper, (1) we indicated a number of criteria which must be considered in judging the stability of a chemical compound; we particularly recommended comparison of electronic and nuclear structures for compounds having atomic bonds.

We will now give somewhat more detailed consideration to the applicability of these concepts in the case of the formation of complex compounds.

1. The Formation of Complex Halides

We wish to emphasize again that the concepts developed below naturally cannot be extended to the case of the ideal ionic bond; however, such extension is quite unnecessary. If we assume that an ideal ionic bond exists in the compound  $AX_3$ , the theory of Kossel, Magnus et al. says that we may expect the formation of ions of the types  $[AX_6]^{2-}$ , or  $[AX_4]^{2-}$ , regardless of the structure of the central atoms.

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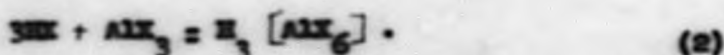
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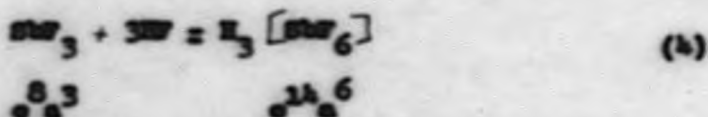
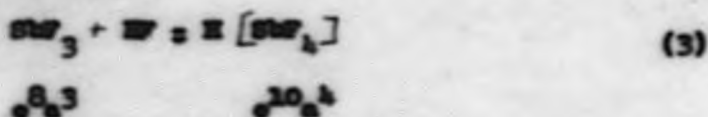
However, if the bond is intermediate in character, as is usually the case, and especially if it is closer to the atomic type, one must compare electron and nuclear configurations. One immediately finds that  $AlX_3$  ( $e^6 a^3$ ) and  $SnX_3$  ( $e^8 a^3$ ) have different electron configurations, even though their nuclear configurations are the same<sup>1a</sup>; in the case of  $AlX_3$ , in which the central atom acquires stable electronic and nuclear configurations, the formation of complex compounds will take place in agreement with Werner's theory; e.g.  $e^8 a^4$  and even  $e^{12} a^6$ ;



and



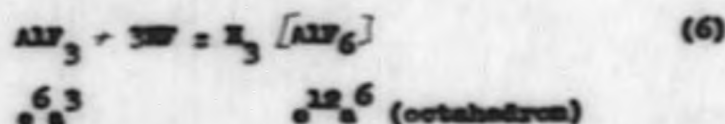
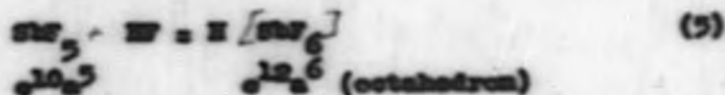
However, in  $SnX_3$  ( $e^8 a^3$ ), in contrast to  $SnX_3$  ( $e^{10} a^5$ ) and  $AlX_3$  ( $e^6 a^3$ ), the configuration is quite stable. The contrast is again evident in the formation of complex ions.  $SnX_3$ , in contrast to  $SnX_3$  and  $AlX_3$ , requires a configuration which is not much more stable than the original; this can be seen from the following equations




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1a. Where X, for instance, represents Br or even Cl.

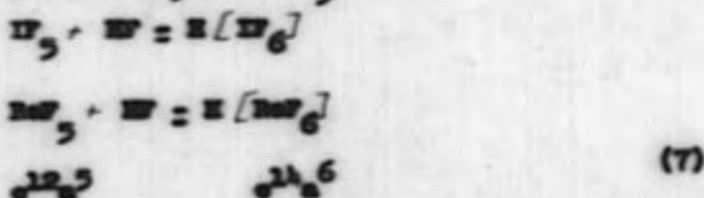
in contrast to



The tendency toward formation of the complex ion  $(\text{SnX}_6)^{4-}$  must thus be diminished.

As we have just seen,  $\text{SnF}_3$  must acquire a very stable configuration in going over to  $\text{SnF}_6^-$ ; it is easy to see that the situation is not as favorable for all compounds of the type  $\text{AX}_3$ . If atoms A still retains 6 electrons, for instance, they will act as 1 electron, since they affect the stability of the molecules and may destroy its symmetry.

For example, let us consider  $\text{IF}_3$  and  $\text{ReF}_3$ :



In case (7), unlike (5), the complex compounds must be less stable. (In this connection, we must make the very likely assumption that atomic bonds may occur within a coordination sphere. Incidentally, W. Klemm's (2) assumption that ionic bonding exists in  $\text{IF}_7$ , but not in  $\text{IF}_3$ , seems unjustified).

These concepts are confirmed by experimental evidence. In our previous paper, we pointed that the  $[\text{ReCl}]_6^-$  ion is unstable; this has since been confirmed by Geilmann and Wriggs (3); instead of this ion, the  $(\text{ReCl}_6)^-$  ion is

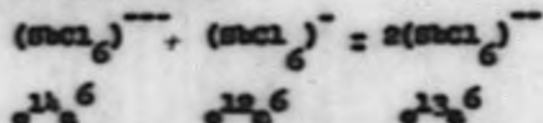
formed, its greater charge stabilizing the crystalline lattice.

In all the voluminous literature on  $IF_5$  (Ruff and Brude (4) et al. (5)), we have not yet been able to find any reference of the  $IF_6^-$  ion. An investigation of the possibility of forming such compounds would be very desirable. In general, the presence of 1 electron in the central atom can give rise to paradoxical phenomena, such as the occurrence of compounds with an anomalous primary valence or an anomalous coordination number.

An interesting and instructive example which has received too little attention is the formation of complex compounds of, for instance, tetravalent antimony (Weinland and Schmid (6)) or, more exactly, of the  $(SbCl_6)^{--}$  ion.

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The reaction is as follows:



The possibility of obtaining substantial equilibrium concentrations of the comparatively unstable  $(SbCl_6)^{--}$  ion (1 i electron) is due principally to the instability of the  $(SbCl_6)^{--}$  ion (2 i electrons).

If we consider this fact, as well as the presence of 1 i electron in the  $(SbCl_6)^{-}$  ion ( $\sigma^{13}_a^6$ ), there is a finite possibility that the  $(AX_6)^{-}$  ion will occur in place of the  $(AX_6)^{--}$  ion, and that the  $(AX_5)^{--}$  ion ( $\sigma^{12}_a^5$ ) will occur instead of the  $(AX_6)^{--}$  ion ( $\sigma^{14}_a^6$ ).

The above considerations are also entirely applicable to compounds of the type  $AX_4$ .

For elements in the earlier periods,  $AX_4$  ( $\sigma^8_a^4$ ) compounds in general do not tend toward complex formation; for elements in the later periods, there is



increased probability of forming the coordination sphere  $[AX_6]^{m-}$  ( $e^{12}a^6$ ); on the other hand, the  $[AX_4]$  ( $e^{10}a^4$ ) compounds acquire the rather unfavorable configuration  $e^{14}a^6$  on going over to the  $[AX_6]^{m-}$  form, with which the  $[AX_5]^{m-}$  ( $e^{12}a^5$ ) form can, in principle, begin to compete. Thus in the case of  $TaX_4$ , for instance, we can expect the formation of the comparatively stable compound  $HfX_5$ , as well as  $H_2Ta_6$ ; we can similarly expect to find  $HfX_5$  formed from  $VX_4$  and  $HfX_5$  from  $MoX_4$ .

The above examples show that in individual cases (in connection with the unfavorable structure and the resulting reduced stability of the complex ion with a coordination number of 6) a coordination number of 5 can occur and has been observed.

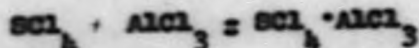
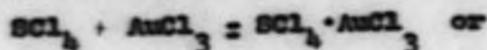
It should be mentioned that the compounds  $K_2 [SbF_5]$  and  $Ca_2 [SbF_5]$  have been described in the literature (7). Petersen (8) was acquainted with the compound  $(NH_4)_3VF_5$ , as well as with  $(NH_4)_3VF_6$ . The compound  $HfF_5$  is described in one of the old papers (9).

We must here point out a very important fact in connection with the value of the coordination number in such compounds, especially in the case of the fluorides, in which the forces occurring within the coordination sphere are very similar to ionic bonds.

In such cases, the coordination number which apparently corresponds to the formula of the compound often does not occur in the crystalline lattice; the action of electrostatic forces often results in the formation of the most stable (for instance, octahedral) configuration, as was shown by Hassel and Mark (9a) in the case of  $(NH_4)_3ErF_7$ . It is interesting to compare C. Brosset's recent X-ray data (10) on the structures of  $Ti [AlF_4]$  and  $Ti_2 [AlF_5]$  with previous X-ray data obtained by other authors investigating  $AlF_3$  and  $N_3AlF_3$ .

In all of these cases, the central Al atom (ion) is always surrounded by an octahedron of  $F^-$  ions (even in the case of  $Tl [AlF_6]$ ). All of the 6  $F^-$  ions in the case of  $AlF_3$ , 4 of the 6  $F^-$  ions in the case of  $Tl [AlF_6]$ , 2 of the 6 in the case of  $Tl_2 [AlF_5]$  and none of the 6 in the case of  $H_3 (AlF_6)$  belong to a second coordination sphere.

It is thus possible that many compounds, for instance of types  $MAX_3$  or  $M_2AX_3$ , and especially the fluorides, have a coordination number in the crystalline lattice which does not correspond to the formula of the compound. In addition, the abovementioned effect of 1 electron can play a more decisive role only in the case of bonds (between the central and peripheral atoms) which are almost purely ionic in character. It is therefore very probable that the abovementioned mechanism plays a part in the formation of complex compounds between  $SCl_4$ ,  $PtCl_4$  and  $PbBr_2$  on the one hand and  $AuCl_3$ ,  $PtCl_3$  and  $AlCl_3$  on the other hand (10a).<sup>5</sup> These association compounds often have a coordination number of 5; for instance (11),

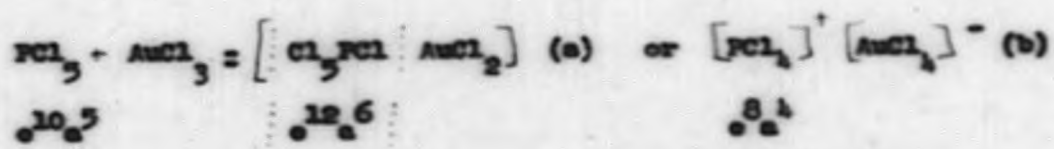


Werner, questioning the applicability of a coordination number of 5, wrote a formula of the type of  $[Cl_3S][ClAuCl_3]$  (i.e., with two nuclei) for these compounds, rather than represent them as  $[Cl_3S(AuCl_3)]$ .

It is possible that in this case we are dealing with an interaction which is more profound than a pure polarization effect. The unfavorable structures of these compounds can give rise to interactions of types (a) and (b):

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\* i.e., compounds which readily form halide acids.



where the P atom is surrounded by the group  $\overset{12}{\underset{6}{\text{a}}}$  in case (a), and by the group  $\overset{8}{\underset{4}{\text{a}}}$  in case (b).

In the second case, which corresponds to Werner's formula, the reaction product consists of ions, both ions having favorable nuclear and electron configurations compared to the initial components.

Mention should be made here of recent paper by Fischer and J. U. Bernmann (11a), who showed that  $\text{AlCl}_3$  reacts with  $\text{PCl}_5$  form  $\text{PAlCl}_8$ , which is a very stable compound. These authors described these compounds as having the structure  $\left[ \text{PCl}_4 \right]^+ \left[ \text{AlCl}_4 \right]^-$  (i.e. the "b" form).

Regardless of whether  $\text{PAlCl}_8$  has structure (a) or (b), the formation of such compounds agrees with such a reaction mechanism.

W. Biltz (12) has recently shown that  $\text{HBeI}_5$  is formed when  $\text{KBeI}_6$  is treated with acid. A determination of the structure of this compound would be very desirable.

## 2. On the Possibility of Extending these Conclusions to other Groups of Compounds (Hydrides, Cyanides, etc.)

Chemistry has suffered from the fact that the authors have heedlessly applied the same structural formulas to halides and cyanides, and to halides and hydrides, simply following the substitution rule.

In this connection, I particularly wish to emphasize that although several general principles, including some developed by me, apply to many such groups of compounds, each individual group has its own peculiarities; for instance, the effect of 1 electron and stability of molecules, which I pointed out in a previous paper



(13), decreases as we go from the hydrides to the chlorides.

According to K. Fajans, F. Haber and P. Debye, it is usually assumed that when the fluorine in  $AX_n$  is replaced by Cl, Cr, or I, the polarizability of the peripheral atom increases, and the electron cloud is drawn more and more toward the central atom. This phenomenon in chemistry was treated on the basis of purely electrostatic concepts; in the limiting case, such a polarization of the electron shell would lead to the attraction of an electrode to the central atom, resulting in a diminution of its charge:  $CuI_2 \rightarrow CuI + \frac{1}{2}I_2$ .

Aside from this phenomenon, there are several known cases of the formation of compounds which had previously been described by Sidgwick's rule (see previous article (14)). Unfortunately, the mechanism of the completion of the noble gas electron configuration of the central atom has not, until now, been compared sufficiently with other cases of the formation of atomic bonds, and, in particular, the theoretical limits of this phenomenon have not been indicated. The character of these bonds was actually the subject of problematical discussions, a typical example of which is the following quotation from Ephraim (15):

"There is little connection, if any, between the existence of the metal carbonyls and the unsaturated nature of CO. These compounds are more to be regarded as covalent compounds of CO, from which the latter can be split off again unchanged".

According to Pauling (16), the bonds in fluorides and oxides are actually ionic, whereas in cyanides, chlorides, bromides and iodides, etc., electron pair (i.e. covalent) bonding is more common. The complexity of the phenomena does not justify so neat a division of the compounds into two groups. Many compounds are known both within various classes of the same group (for instance, chlorides and



cyanides) and within a single class, (e.g., fluorides) in which the nature of the bonds must differ radically. For instance, we may compare  $UF_4$ ,  $U_2F_8$ ,  $UF_6$  and  $OsF_6$ . Also, the fact that  $NH_4 [FeF_6]$  has considerable magnetic susceptibility and  $K_3Fe(CN)_6$  does not give sufficient evidence to class the first compound as having ionic bonding and the second compound as having atomic bonding; a more careful consideration of the properties of these compounds is necessary.

The complex cyanides of the transition elements, which have electrons in various quantum states, are quite different from other complex cyanides and halides. To quote W. Klemm (17):

"As for the cyanides and ... for carbonyls such as  $Fe(CO)_5$  - there is no necessity for assuming mysterious "secondary valences" between the iron and the CO groups. It is quite sufficient to conceive of these bonds as atomic bonds created by having one electron of the CO group go over to the iron and then form an atomic bond with the remaining free electron of the CO group."

It is difficult to understand why one electron of the "CO group" should go over to the iron atom in order to interact with the other electron of "CO group" to form an atomic bond.

The separate consideration of individual cases in the formation of atomic bonds cannot orient the investigator among the bewildering complexities of the phenomena, and can no longer satisfy him. We will make an attempt to supply this blank. As I showed some time ago (18), the existence of electrons with different quantum numbers in the central atom involves a lack of equivalence in the bonds and a lowered stability of the system; this condition is particularly evident in the hydrides and metallo-organic compounds. Such a central atom must be

anxious to eliminate this "energetic unbalance", and can accomplish this in two ways. Firstly, it can donate electrons from a higher level to some atom or group of atoms, i.e., form an ionic bond with this atom or group, while the bonds with other groups remain atomic in nature. Secondly, it can acquire a large number of electrons from other atoms in order to fill up its external d, s and p electron shells and form the shells of the corresponding noble gas.

$[\text{CrR}_2] \text{OH}$ , which I have discussed previously (18), is an example of the first case. This oxyhydrate is a strong base, in contrast to  $\text{Sn}_3\text{OH}$ , as a result of the presence of the  $4s$  electron in Cr, in addition to the  $3d^5$  electrons. When the chromium gives the  $4s$  electron over to the OH group and splits off the  $\text{OH}^-$  ion, the chromium holds on to the  $4R$  groups through the atomic bonds. This difference in the nature of the bonds created by a single atom within one and the same compound is due principally to the structure of the central atom.

Well-known examples of the second case are the formation of nickel carbonyl  $[\text{Ni}(\text{CO})_4]$  or chromium carbonyl  $\text{Cr}(\text{CO})_6$ , the central atom accepting 8 electrons from the 4 CO groups in the first case and 12 electrons from the 6 CO groups in the second.

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It is interesting to note in which cases the various atoms follow one path or the other, to see whether there is any intermediate type of process, and to see the reasons for exceptions to the rule of effective atomic numbers or the substitution rule such as those mentioned in my previous paper.

### 3. The Formation of Donor and Acceptor Bonds.

The concept of electrovalent and covalent bonds arose some 20 years ago; the corresponding current terms are ionic and atomic bonds. Each year sees the appearance of new gradations in bond character. According to Kossel, atoms seldom

show pure ionic or atomic bonding, but usually form bonds of mixed character. Chemists pay particular attention to the creation of a bond-forming electron pair (Sidgwick); either partner A and partner B each contribute an electron, or both electrons come from one partner (the donor) and are shared by it and a second partner (the acceptor).

It has been known since the electrostatic theories of chemical bonding were developed that as a result of the extremely small electron affinities of the atoms of the long periods, very few elements are capable of forming anions (S, Se, etc.).

When a polyvalent central atom forms bonds, they are usually atomic in character, the central atom participating in the formation of each bond to the extent of either one electron ( $SF_6$ ,  $CF_4$  etc.) or two electrons ( $SO_3$ ); in the second case, it is often the donor.

Let us designate an atomic bond as a donor or acceptor bond, according to whether the central atom acts as donor or acceptor; let us call the bonds "mutual" if each atom contributes one electron to the bond. The expression "mutual bond" is identical with a "covalent bond" in the sense of Sidgwick's theory, but not in the sense of Lewis' theory. Let us point out the following important property of this type of bonding: central atoms which have comparatively high electron affinities and thus figure as anions (O, S, Cl) in ionic compounds, form either mutual bonds ( $CCl_4$ ,  $SF_6$ ) or donor bonds ( $ClO_4^-$ ,  $SO_4^{2-}$ ,  $SO_3$ ) in atomic compounds.



On the other hand, many elements whose d-shells are almost complete (Cr-Fe-Ni, Mo-Ru-Pd, W-Os-Pt) always figure as cations in the formation of ionic bonds (donate electrons). These atoms show an outstanding ability to attract considerable numbers of electrons (up to 12) from peripheral groups into their own electron shells, and by forming acceptor bonds to complete the electron shell of the noble gas at the end of the corresponding period.

It is important to note that in most cases, the peripheral partners of the central atom are usually not atoms, but molecules or complex ions such as the  $\text{CN}^-$  ion, NO or CO; when the central atom has taken on a large number of such groups, it often can hold onto several additional simple atoms or ions.

The rule of effective atomic numbers determines the possibility of formation of compounds by means of this type of bond (I have called these bonds acceptor bonds); this rule states that the stability of the compound is at a maximum if  $\Delta = 0$ , where  $\Delta$  is the difference between the atomic number of the following noble gas and the effective number of valence electrons of the elements.

~~IV. Discussion of the Rule of Effective Atomic Numbers. Statement of New Rules for Forming Compounds with Acceptor Bonds by Transition Elements.~~

In my previous paper, I spoke of the wide application of the rule of effective atomic numbers (1) in chemistry, and mentioned a number of exceptions which indicated the inadequacy of this rule.

Starting with the basic theoretical assumptions mentioned in that paper, I can immediately point out serious errors which chemists have made in the matter

of stability of compounds such as carbonyls, complex cyanides, etc., even though accepting the formulation of compounds having transition elements as central atoms which I made for the purpose of calculating an acceptor bond.

The first serious error was omitting the stability condition resulting from the nuclear configuration ( $a^N$ ), and substituting instead the stability conditions resulting from the electron configuration  $e^N$ .

The second error, which was no less serious, was neglecting the initial ionic state of the central atom, - i.e., underestimating the transition from one type of bond to the other. The stronger the field of the central ion before the formation of the acceptor atomic bond, the easier it is to draw an electron from the peripheral anions into the shell of the central ion, and the easier it is to form these bonds and attain the condition  $\Delta = 0$ ; the degree of complex formation must be then greater, and the probability of dissociation of the coordination spheres, resulting in the formation of considerable concentration of the "initial" central ion, that much smaller. However, our discussion cannot be limited to the abovementioned inadequacies in the theories. The following factor cannot be ignored in any detailed discussion of the subject:

All compounds of the bond type discussed must be divided into three structural groups; as we will see below, two of these groups: (a) the cyanides, etc., and their derivatives, and (b) the carbonyls and their derivatives, must differ from each other considerably. This also offers a criterion for assigning substances to one group or the other: (a) in the crystal lattices of the complex cyanides and other similar compounds, where the coordination sphere has a negative charge, i.e., is an anion and is thus surrounded by peripheral cations ( $K^+$ , etc.),

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the presence of the latter ions decreases the degree of complex formation, since they cause a certain depolarization of the peripheral ions (e.g.  $\text{CN}^-$  ions), bound to the central atom and thus also cause the electron cloud to be drawn from the central atom toward the cations which are outside of the complex anion, weakening the acceptor bonds. On the other hand, the increase in the charge of the central ion must be more favorable for the stability of the compound in the case of cyanides than in the case of carbonyls (see subsequent contributions). (b) In the carbonyls and their derivatives, in which the coordination sphere is not an ion, and therefore is not surrounded by ions of opposite charge, no such depolarization occurs, and this must increase the stability of the compound. (c) Furthermore, one must expect that the coordination spheres which represent complex cations and which are surrounded by peripheral anions are subjected to a much weaker external depolarization effect, and in this respect must therefore be closer to the "b" group.

If we examine the matter of the "a" and "b" groups a little more closely, we can arrive at several important supplemental conclusions concerning the stability of these compounds; this will form the principal subject of my next paper. We will restrict ourselves here to the single conclusion needed for discussing the large body of factual material; namely, that one can assume that the comparatively unstable configurations of type a<sup>3</sup> will be considerably better expressed in the general stability of compounds in group "a" than in the stability of those in group "b".

This being the case, we will now formulate the following three laws, which will govern the operation of this process and indicate the stability of the compounds formed.

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In all cases in which atoms of the intermediate (and subsequent) elements of long periods, in an effort to attain the configuration of the noble gas which closes that period, take on molecules, radicals and groups of atoms (CO, NO,  $\text{CN}^-$ , etc.) which can form an acceptor bond with these central atoms by donating the necessary electrons, the stability of the resulting compounds is determined by the following factors:

1) The number of electrons gained by the central atom and thus the number ( $\Delta$ ) of electrons still needed to equal the number in the shell of noble gas; the closer  $\Delta$  is to zero, the more likely the compound is to be stable. Naturally, the  $\Delta$  can only equal zero or a negative number. Compounds for which  $\Delta > 0$  must be unstable (this rule corresponds to the old rule of effective atomic numbers).

2) The stability of these compounds is also determined by the number of groups surrounding the central atom. According to the considerations outlined in our previous paper (19), the combinations  $\text{AX}_6$  ( $n^6$ ) and  $\text{AX}_8$  ( $n^8$ ) must be the most stable. The combination  $\text{AX}_7$  ( $n^7$ ) must always be unstable. The combination  $\text{AX}_5$  ( $n^5$ ) must reduce the stability of the configuration considerably. The configuration  $\text{AX}_3$  ( $n^3$ ) must be practically unstable in the case of the carbonyls and their derivatives, since when  $\Delta = 0$ , this configuration could only occur in elements with full d-shells (for instance in zinc:  $\text{Zn}(\text{CO})_3$ ), where the tendency toward the formation of this type of bond is greatly reduced.

3) The stability of these compounds is also determined by the initial ionic state of the central atom, i.e. by the initial valence (charge) of the central ion. The greater positive charge of the latter must, since it aids penetration of the electrons of the peripheral ions into the shell of the central

atoms, reinforces the stability of the compound, all other things being equal, assuming that the creation of a higher valence state in the central ion is not practically impossible in simple compounds. For instance, the compounds of  $\text{Co}^{3+}$  (all other things being equal) must be more stable than those of  $\text{Co}^{2+}$  (the charge of the central atom is greater); at the same time, any conceivable compounds of  $\text{Co}^{4+}$  must be unstable, since it is practically impossible to form the  $\text{Co}^{4+}$  ion because of the enormous ionization potential  $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ , which comes to some 55 E. This is easily demonstrated by reference to the data compiled by J. Sherman (19).

When the valence of the central ion is low ( $Z = 1$ ), the addition of all electrons up to  $\Delta = 0$  must be quite difficult in the case of compounds of group "a", and, as has been shown in one of my papers, must often be impossible.

In general, the complex compound must be very stable when all three factors reinforce each other. When this is not the case, the compound is less stable, and when  $\alpha^2$  is unfavorable or  $Z$  is small, the compound may be unstable even if  $\Delta = 0$ .

Two extremely important factors must be emphasized in this connection. (1) When a given atom possesses configurations of the coordination sphere which are more stable (according to the above criteria) than the configuration in question, the latter configuration is unlikely to be formed. When no more stable form is possible, however, the atom may be forced to form the comparatively unstable form (see our next paper, e.g. the complex cyanides of chromium) if this will cause a decrease in free energy. In this respect, the complex cyanides, for instance, are in a more favorable position with the regard to possibility of formation and stability than are the carbonyls, (assuming that the central atoms in the former case are in the ionic state; see my next papers) since in this case, the central atoms can draw solvent molecules as well as  $\text{CN}^-$  ions into the coordination sphere. (2) When loosely held components ( $\text{H}_2\text{O}$ , etc.) are carefully removed from the

coordination sphere of the crystalline complex compounds, one can expect to obtain complex compounds with anomalous coordination numbers. For instance, one can predict, (and this can also be verified experimentally) that if the water is very carefully removed from aquopentacyano derivatives, the latter will go over to pentacyano derivatives, whereas under other conditions it would only be possible to obtain hexacyano derivatives.

A few words concerning notation: for the sake of convenience, I will write  $\Delta^0$  instead of  $\Delta = 0$ , and  $\Delta^n$  instead of  $\Delta = n$ .  $\Delta^{-2}$  stands for  $\Delta = -2$ . The ionic state of the atom will be signalized by  $s^n$ , which stands for  $s = n$ . Thus  $s^3$  means that the initial valence of the initial ion was  $s = 3$ .

5. Supplemental Rule for Formation of Abovedescribed Compounds.

As a supplement to the above rules, which follow directly from my theoretical principles, I should also like to mention the following special rule regarding the influence of the  $s^3$  configuration on the stability of the abovementioned type of compounds with acceptor bonds.

Starting with the abovementioned divisions into groups "a" and "b", and the conclusion that the configuration  $s^3$  must exert a stronger influence on the stability on the complex cyanides than on that of the carbonyls, one may promulgate the rule given below; I must regard this rule as only 'quite probable' until it is tested by application to a large mass of experimental material.

Complex cyanides with the nuclear configurations  $s^3$  about the central atom must be comparatively unstable even at  $\Delta^0$ . (See previous page concerning possible exceptions). Carbonyls with the nuclear configuration  $s^3$  must be less stable at  $\Delta^0$  than carbonyls with the configurations  $s^6$  and  $s^4$ , and must be unstable when  $\Delta \neq 0$ .

In subsequent papers, I will subject both my fundamental and supplemental



rules to careful testing.

6. The Chemical Formulas and Nomenclature of Compounds of this Type.

In complex compounds of this type (e.g.  $K_4 [Fe(CN)_6]$ ), the central atom has taken a considerable number of doublets. Its original valence is thus changed, contrary to the theory of Werner and Kossel.

Thus the iron atom in  $K_4 [Fe(CN)_6]$  cannot be regarded as divalent, despite Werner's commonly accepted potassium hexacyanoferrate terminology; it is also incorrect to write  $K_4 [Fe^{II}(CN)_6]$  or  $K_4 [FeII(CN)_6]$  (after Stock), as is usually done. In order to represent the original valence of the central atom (19), I propose that the Roman numerals be replaced by asterisks; i.e., not  $K_4 [Fe^{II}(CN)_6]$ , but  $K_4 [Fe^{**}(CN)_6]$ , thus signifying that the central atom in this compound is not divalent, and that only a genetic characteristic of the material is being indicated; such atoms will be called pseudo-divalent rather than divalent.

This broadens the problem of nomenclature of complex compounds, since both the Werner and the modern nomenclatures assign a valence to the central atom which does not correspond to reality.

I believe that there are two possible solutions.

a) Use the Werner nomenclature exclusively for a designating pseudo-valence and the Stock nomenclature for designating the valence of the central atom; for instance  $K_4 Fe(CN)_6$  - potassium hexacyanoferrate,  $[Fe(H_2O)_6] Cl_2$  - hexaquoferrum II chloride. Despite its simplicity, however, this solution has serious defects. Often, for instance, it will be difficult to decide which valence the central atom is exhibiting; many misunderstandings are possible on this basis, especially since it cannot be expected that every worker in the field will apply the Werner nomenclature only in the way which we have proposed.

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b) I therefore deem it advisable to suggest a nomenclature of complex compounds on the basis of the following principles. On the one hand, this nomenclature will permit an exact description of the composition of the compounds; on the other hand, the author will be relieved of the necessity of changing the nomenclature every few years as a result of changes in the theoretical and experimental status of the question of the valency of the central atom in the given compound.

1. The qualitative and quantitative status of the cation will be expressed in terms of one word.

2. The qualitative and quantitative status of the anion will be expressed in terms of one word.

3. The cation will be indicated before the anion, as is done by Werner.

4. When there are not atoms (or groups) outside of the coordination sphere, the name consists of one word.

5. The name of the ion consists of (a) numerical prefixes (di, tri, tetra, penta, etc.), which show how many of the given atoms (or groups) are inside or outside of the coordination sphere, and (b) the name of these atoms (or groups), each following its respective number.

The designation "mono"<sup>(1)</sup> is not used (the absence of a numerical prefix before the name of the atom (or group) indicates that only one of the latter is present in the compound.

The group designations of the Werner theory are retained.

The elements are named according to the international nomenclature, as in the Werner theory.

6. In a complex ion, the peripheral groups are named first; the central atom (ion) is named last.

7. The suffix "ate" for the names of ions is retained. In the following table, W. stands for Werner.

I thus name

$K_4 [Fe(CN)_6]$  tetrakalium hexacyanoferrate (instead of kalium hexacyanoferrate, as given by W).

$K_3 [Fe(CN)_6]$  trikalium hexacyanoferrate (instead of kalium hexacyanoferrate, as given by W).

$Ag_2^2 [Co(CN)_5 H_2 O]$  diargentum aquopentacyanocobaltate (instead of argentum aquopentacyanocobaltate as given by W.).

$[Cr(NH_3)_6] Cl_2$  hexamminchromium dichloride (instead of hexamine chromochloride as given by W).

$[Cr(NH_3)_5] Cl$  chloropentamminchromium chloride (instead of pentamine chloro-chromo-chloride as given by W).

$[Cr(NH_3)_4 Cl_2]$  Dichlor-tetramminchromium, which almost coincides with Werner's dichlorotetramminchromium (in general, we see no essential objection to using

P. 903 the conjunctive "o").

$[Cr(NH_3)_4] Cl_2$  tetramminchromium-dichloride (instead of tetramine chromochloride as given by W).

#### SUMMARY

1. Several general conclusions are drawn concerning the influence of electronic structure on the magnitude of the coordination number in the halides.

2. The character of the atomic bond in complex compounds is discussed.

It is found advisable to differentiate between "donor" and "acceptor" bonding in the coordination sphere, depending on the nature of the participation of the central atom in the formation of the bond.



3. The Sidgwick (effective atomic number) rule is found to be obviously incapable of accounting for the formation and stability of complex compounds having acceptor bonding and central atoms with electrons in various quantum states. Instead, I have started out with concepts previously developed by me, and formulated a 3-in-1 rule for the formation and stability of this type of compound. Supplemental rules and remarks are also included.

In forthcoming papers, these rules will be applied to the practical question of evaluating the stability of the various groups of complex compounds.

4. Essential corrections are made in the Werner and modern concepts of the valency of the central atom in the compounds covered by these rules, and corrections to the chemical formulas to these compounds are proposed.

5. A new nomenclature of these compounds is proposed, based on my discussion of the Werner and modern nomenclatures of complex compounds, which do not correspond to the effective valence of the central atom.

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