Investigation on Mixed Complexes. VI[1]. *General Discussion on the Formation of Mixed Complexes*

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The main purpose of this series of investigations has been to ascertain the stability of mixed complexes, as compared with that of their parent complexes*. It seems to the present author that there have been few investigations of this problem. Bjerrum[2] has made a careful study of the factors which influence the ratios between the consecutive formation constants by sub-dividing these factors into the "statistical effect" and the "ligand effect". The former effect can be evaluated by calculation, and this principle can also be applied to the present investigation. The latter is further classified into the "electrostatic effect" and the "rest effect"; that is, if we regard metal-ligand bonds as purely ionic, the ligand effect should be an electrostatic one, while the rest effect may be mainly attributed to the covalency of the coordination bond. Bjerrum's considerations were ingenious and comprehensive. However, his efforts were mainly devoted to obtaining the values of consecutive formation constants of various complexes, and much importance was not paid to the stability of mixed complexes.

In this paper, factors which influence the relative stability of a mixed complex are pointed out and discussed on the basis of the experimental data previously obtained by various investigators.

Electrostatic Effect.—It is assumed here, for convenience, that a complex species consists of point charges representing a central metal ion and its ligands. For instance, in the following complexes it is assumed: that M, X and Y are point electrical charges, $+e$, $-e'$ and $-e''$,

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[1] Part V of this series: S. Kida, This Bulletin, 33, 2269 (1960).

* Throughout this series, $[MA_n]$ and $[MB_n]$ have been defined as denoting the parent complexes of the mixed complex, $[MA_iB_j]$, where A and B and M stand for the ligands, and the central metal ion, respectively, under the condition of $n=i+j$.

[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", Haase and Son, Copenhagen (1941).

Table I. CALCULATED FORMATION ENERGIES OF COMPLEXES OF VARIOUS TYPES, ON THE ASSUMPTION THAT THEY CONSIST OF POINT CHARGES

4-Coordinated planar type

$$E(\mathrm{MX_3Y})-\frac{1}{4}\{3E(\mathrm{MX_4})+E(\mathrm{MY_4})\}=(\mathrm{e}'-\mathrm{e}'')^2(2\sqrt{2}+1)/4r=0.957(\mathrm{e}'-\mathrm{e}'')^2/r$$

$$E(cis\text{-}\mathrm{MX_2Y_2})-\frac{1}{2}\{E(\mathrm{MX_4})+E(\mathrm{MY_4})\}=(\mathrm{e}'-\mathrm{e}'')^2(\sqrt{2}+1)/2r=1.207(\mathrm{e}'-\mathrm{e}'')^2/r$$

$$E(trans\text{-}\mathrm{MX_2Y_2})-\frac{1}{2}\{E(\mathrm{MX_4})+E(\mathrm{MY_4})\}=(\mathrm{e}'-\mathrm{e}'')^2\cdot\sqrt{2}/r=1.414(\mathrm{e}'-\mathrm{e}'')^2/r$$

4-Coordinated tetrahedral type

$$E(\mathrm{MX_3Y})-\frac{1}{4}\{3E(\mathrm{MX_4})+E(\mathrm{MY_4})\}=(\mathrm{e}'-\mathrm{e}'')^2\cdot 3\sqrt{6}/8r=0.917(\mathrm{e}'-\mathrm{e}'')^2/r$$

$$E(\mathrm{MX_2Y_2})-\frac{1}{2}\{E(\mathrm{MX_4})+E(\mathrm{MY_4})\}=(\mathrm{e}'-\mathrm{e}'')^2\cdot\sqrt{6}/2r=1.225(\mathrm{e}'-\mathrm{e}'')^2/r$$

6-Coordinated octahedral type

$$E(\mathrm{MX_5Y})-\frac{1}{6}\{5E(\mathrm{MX_6})+E(\mathrm{MY_6})\}=(\mathrm{e}'-\mathrm{e}'')^2(4\sqrt{2}+1)4r=1.664(\mathrm{e}'-\mathrm{e}'')^2/r$$

$$E(cis\text{-}\mathrm{MX_4Y_2})-\frac{1}{6}\{4E(\mathrm{MX_6})+2E(\mathrm{MY_6})\}=(\mathrm{e}'-\mathrm{e}'')^2(3\sqrt{2}+1)/2r=2.621(\mathrm{e}'-\mathrm{e}'')^2/r$$

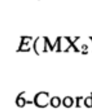
$$E(trans\text{-}\mathrm{MX_4Y_2})-\frac{1}{6}\{4E(\mathrm{MX_6})+2E(\mathrm{MY_6})\}=(\mathrm{e}'-\mathrm{e}'')^2\cdot 2\sqrt{2}/r=2.828(\mathrm{e}'-\mathrm{e}'')^2/r$$

$$E(cis\text{-}cis\text{-}\mathrm{MX_3Y_3})-\frac{1}{2}\{E(\mathrm{MX_6})+E(\mathrm{MY_6})\}=(\mathrm{e}'-\mathrm{e}'')^2(6\sqrt{2}+3)/4r=2.871(\mathrm{e}'-\mathrm{e}'')^2/r$$

$$E(cis\text{-}trans\text{-}\mathrm{MX_3Y_3})-\frac{1}{2}\{E(\mathrm{MX_6})+E(\mathrm{MY_6})\}=(\mathrm{e}'-\mathrm{e}'')^2(8\sqrt{2}+1)/4r=3.078(\mathrm{e}'-\mathrm{e}'')^2/r$$

$E(\mathrm{MX_6})$ or $E(\mathrm{MY_6})$ denotes the formation energy of the complex, $[\mathrm{MX_6}]$ or $[\mathrm{MY_6}]$, respectively.

respectively; that both the distances of M–X and M–Y are maintained constant at distance r; and that X and Y occupy corners of a regular square with M at its center.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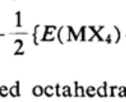
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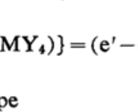
III

If we denote the formation energies of the complexes, I, II and III, by $E(\mathrm{MX_4})$, $E(\mathrm{MY_4})$ and $E(trans\text{-}\mathrm{MX_2Y_2})$, respectively, they can be represented as follows:

$$E(\mathrm{MX_4})=\frac{\mathrm{ee}'}{r}\times 4-\frac{(\mathrm{e}')^2}{\sqrt{2}r}\times 4-\frac{(\mathrm{e}')^2}{2r}\times 2$$

$$E(\mathrm{MY_4})=\frac{\mathrm{ee}''}{r}\times 4-\frac{(\mathrm{e}'')^2}{\sqrt{2}r}\times 4-\frac{(\mathrm{e}'')^2}{2r}\times 2$$

$$E(trans\text{-}\mathrm{MX_2Y_2})=\frac{\mathrm{ee}'}{r}\times 2+\frac{\mathrm{ee}''}{r}\times 2-\frac{\mathrm{e}'\mathrm{e}''}{\sqrt{2}r}\times 4-\frac{(\mathrm{e}')^2}{2r}-\frac{(\mathrm{e}'')^2}{2r}$$

Hence, we obtain:

$$E(trans\text{-}\mathrm{MX_2Y_2})-\frac{1}{2}\{E(\mathrm{MX_4})+E(\mathrm{MY_4})\}=\frac{\sqrt{2}}{r}(\mathrm{e}'-\mathrm{e}'')^2\geqq 0$$

From the equation we can conclude that the mixed complex has more formation energy than the average energies of the parent complexes. In other words, a mixed complex is easily formed from its respective parent complexes. Similar calculations can also be made for other types of complexes, as indicated in Table I.

Some investigators[2,3] have taken the electrostatic repulsion into consideration as a factor which greatly influences the stability of mixed complexes, but their considerations were limited to an electrostatic effect of ionic ligands, e. g., $\mathrm{Cl^-}$ or $\mathrm{C_2O_4{}^{2-}}$, the neutral ligand being neglected in most cases. It is now generally believed that in the so-called normal complexes, the electrostatic force plays an important role even in the case of a neutral ligand, since the ligand field theory has succeeded in explaining the absorption spectra and stabilities of these complexes, by regarding a neutral ligand as a point dipole[4]. In the present study, neutral ligands are also taken into account; in plactice, however, they are replaced by appropriate negative point charges.

Before this conclusion is applied to actual problems, it is necessary to discuss in more detail the meaning of the term " negative point

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[3] For instance, N. Bjerrum, *Z. Phys. Chem.*, **106**, 238 (1923); G. Schwarzenbach, *Helv. Chim. Acta*, **16**, 522 (1933).

[4] For instance, Y. Tanabe and S. Sugano, *J. Phys. Soc. (Japan)*, **9**, 753, 766 (1954).

charges" which were located around the central ion, in the above discussion.

The electric dipole moment is defined as the magnitude of the charge at one center of the molecule times the distance between centers. This distance, for practical purposes, may be considered equivalent to the internuclear distance for a diatomic molecule. In the case of metal complexes, one may consider that the centers of negative charges are closer to the metal ion than the nuclei of the donor atoms of the complex, for the following reasons: (1)

TABLE II. RELATIVE STABILITIES OF MIXED COMPLEXES OF VARIOUS TYPES

Type 1. $[MA_2] + [MB_2] \rightleftarrows 2[MAB]$

M	A	B	$\log K_m$	$\log K_{stat}$	$\log K_{stab}$	Reference
Cu(II)	(dig-H)$^-$	aca$^-$	−0.04	0.60	−0.64	a)
〃	en	〃	0.42	〃	−0.18	〃
〃	〃	$C_2O_4^{2-}$	1.10	〃	0.50	〃
〃	〃	$P_2O_7^{4-}$	1.70	〃	1.10	b)
Hg(II)	Cl$^-$	Br$^-$	2.0	〃	1.4	c)
〃	〃	I$^-$	1.75	〃	1.15	〃
〃	Br$^-$	〃	1.10	〃	0.50	〃

Type 2. $[MA_2] + [M(OH_2)_4] \rightleftarrows 2[MA(OH_2)_2]$

M	A	$\log K_m\left(=\log \frac{k_1}{k_2}\right)$	$\log K_{stat}$	$\log K_{stab}$	$\frac{1}{4}\log K$	Reference
Cu(II)	en	1.40	0.60	0.80	5.01	d)
Zn(II)	〃	0.77	〃	0.17	2.77	〃
Cd(II)	〃	0.92	〃	0.32	2.50	〃
Zn(II)	$C_2O_4^{2-}$	2.32	〃	1.72	2.59	〃
Co(II)	(salcylaldehyde)$^-$	1.04	〃	0.44	2.08	〃
Ni(II)	〃	1.2	〃	0.60	2.3	〃
Cu(II)	〃	1.5	〃	0.90	3.3	〃
Zn(II)	〃	0.9	〃	0.70	2.01	〃
Pb(II)	〃	3.4	〃	2.8	3.7	〃
Mg(II)	aca$^-$	1.46	〃	0.86	2.28	〃
Mn(II)	〃	1.06	〃	0.46	2.49	〃
Fe(II)	〃	0.98	〃	0.38	3.25	〃
Co(II)	〃	1.32	〃	0.72	3.18	〃
Ni(II)	〃	1.30	〃	0.70	3.03	〃
Cu(II)	〃	1.26	〃	0.64	4.55	〃

Type 3. $[MA_4] + [M(OH_2)_4] \rightleftarrows 2[MA_2(OH_2)_2]$

M	A	$\log K_m\left(=\log \frac{k_1k_2}{k_3k_4}\right)$	$\log K_{stat}$	$\log K_{stab}$	$\frac{1}{4}\log K$	Reference
Cu(II)	NH_3	2.63	1.56	1.07	3.17	e)
Zn(II)	〃	0.16	〃	1.40	2.37	〃
Cd(II)	〃	2.38	〃	0.82	1.78	〃
Cu(II)	Cl$^-$	2.8	〃	1.2	1.15	f)
Cd(II)	CN$^-$	2.36	〃	0.80	4.71	〃
〃	I$^-$	−0.68	〃	−2.34	1.62	〃
Sn(II)	Cl$^-$	2.98	〃	1.42	0.38	〃

Type 4. $[MA_3] + 2[M(OH_2)_6] \rightleftarrows 3[MA(OH_2)_4]$

M	A	$\log K_m\left(=\log \frac{k_1^2}{k_2k_3}\right)$	$\log K_{stat}$	$\log K_{stab}$	$\frac{1}{6}\log K$	Reference
Mn(II)	en	2.53	1.43	1.10	0.94	e)
Fe(II)	〃	3.32	〃	1.89	1.59	〃
Co(II)	〃	3.85	〃	2.42	2.30	〃
Ni(II)	〃	4.37	〃	2.94	3.10	〃
Fe(II)	dip	−5.0	〃	−6.43	2.93	d)
Mn(III)	$C_2O_4^{2-}$	10.52	〃	9.09	3.24	〃
Fe(III)	(salicylate)$^-$	17.7	〃	16.3	5.74	〃

(Table II Countinued)

Type 5. $[MA_6] + [M(OH_2)_6] \rightleftarrows 2[MA_3(OH_2)_3]$

M	A	$\log K_m\left(=\log \frac{k_1k_2k_3}{k_4k_5k_6}\right)$	$\log K_{stat}$	$\log K_{stab}$	$\frac{1}{6}\log K$	Reference
Co(II)	NH_3	4.77	2.60	1.87	0.85	e)
Ni(II)	〃	4.80	〃	2.20	1.46	〃
Al(III)	F^-	10.16	〃	7.56	3.31	f)
Cr(III)	NCS^-	7.8	〃	5.20	0.63	〃
Co(III)	NH_3	5.04	〃	2.44	5.87	e)

K_m: Disproportionation constant of a mixed complex.
K_{stab}: Stabilization constant of a mixed complex, defined as following; $\log K_{stab} = \log K_m - \log K_{stat}$ (according to Marcus c)) (see foot note p. 965[*1]).
K_{stat}: Statistical value of K_m, i.e., the calculated value of K_m on the assumption that formation of a mixed complex proceeds statistically (see also foot note p. 965[*1]).
$k_1, k_2, k_3 \cdots\cdots$: Consecutive formation constants of a complex in aqueous solution.
K: The gross formation constant (according to Bjerrum e)), $K = k_1 \cdot k_2 \cdot k_3 \cdots\cdots k_n$.
a) S. Kida, This Bulletin, **29**, 805 (1956).
b) R. De Witt and J. Watters, *J. Am. Chem. Soc.*, **76**, 3810 (1954).
c) Y. Marcus, *Acta Chem. Scand.*, **11**, 610 (1957).
d) A. E. Martelle and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc., New York (1952).
e) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", Haase and Son, Copenhagen (1957).
f) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).
dig-H = dimethyl glyoxime
en = ethylenediamine
aca = acetylacetone

the orbitals of a donor atom will suffer considerable deformation by the electric field of the central ion, which makes the center of negative charge (or "point negative charge") closer to the center of the complex; (2) when a metal complex is in solution, the outer part of the ligands is surrounded by molecules of the solvent, and its mutual electrostatic repulsion between ligands in a complex is reduced, since the dielectric constant of the solvent is generally large. Accordingly, the only important effect in the mutual electrostatic repulsion between ligands is that of the inner part of ligands, i.e., "point negative charge" which is situated close to the central ion.

Since the ionic radius of a certain metal ion is approximately constant regardless of its surroundings, the assumption that the distance between a negative point charge and the central ion is approximately constant regardless of the species of ligands can be applied to practical problems.

It is evident from Table I that the electrostatic ligand effect, as described above, always promotes the formation of a mixed complex. Table II shows that $\log K_{stab}$[*1] is generally positive, indicating that mixed complexes are more stable than statistically expected.

The Effect of ($\sigma-$) Covalent Bond[*2]. — Although the above discussion is based on the assumption that the bond between a metal ion and a ligand is purely ionic, it always contains some covalent character.

It has been shown by the above calculation, that although the mutual electrostatic repulsion between ligands in a complex reduces its stability, such an effect is smaller in a mixed complex than in parent ones, and consequently the formation of the mixed complex is favored. If pure covalent bonds are formed by coordination, the central metal ion accepts electrons from the ligands, and its electronegativity is decreased. In this case Pauling's electroneutrality principle should be satisfied. This principle may be expressed in the following way; if electrons of donor atoms are closely concentrated around the central atom, mutual repulsion of these electrons acts so as to keep

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[*1] For example, in case of an equilibrium of the form, $MX_4 + MF_4 \rightleftarrows 2MX_2Y_2$, by definition,

$$K_m = \frac{[MX_2Y_2]}{[MX_4][MY_4]}$$

If one assumes that there is no energy difference between the species on both sides of this equilibrium, one can calculate the value of K_m statistically. This calculated value is defined as K_{stat} in the present paper. Therefore, (K_m-K_{stat}) is useful as a measure of a stabilizing or unstabilizing effect in the formation of a mixed complex. In this paper, (K_m-K_{stat}) is designated as the stabilization constant of a mixed complex, and denoted by K_{stab}, i.e., it is the ratio of the observed equilibrium constants to the statistically calculated ones. Accordingly, if $\log K_{stab}$ has a positive value, the mixed complex is easily formed from its parent complexes, and vice versa in the case of the negative value.

[*2] In this section, the π-bond is not taken into consideration, and the "covalent" or the "covalency" is referred to the bond of σ-type only.

the ligands away from each other, just like the repulsion between the negative charges of ligands in the case of ionic complexes. Therefore, it seems to the present author that the electrostatic and the (σ-) covalent-bond effects work in the same direction.

From the above discussion, it is expected that the covalent bond effect is inclined to promote the formation of a mixed complex, quite analogously to the electrostatic effect, and accordingly, mixed-complex formation might also be favored in penetration complexes, such as those of cobalt(III) and chromium(III). The fact that this expectation is fulfilled is seen in Table II (though examples of this kind are rare). Furthermore, the stabilization constant of a mixed complex, K_{stab}*1, appears to have a tendency to become larger as the stabilities of the parent complex become larger. For instance, in the case of ethylenediamine complexes the increasing order of the value of the $\log K_{stab}$*1 of Mn(II), Fe(II), Co(II) and Ni(II) complexes is in accord with that of the stabilities of these complexes ($\log K$), as seen in Table II. Thus, since the $\log K_{stab}$'s*1 are neither random nor show an increase in value followed by a decrease, we may conclude from these results, that the covalent-bond effect has no tendency to depress the formation of a mixed complex.

Cases where Mixed Complexes are not Observed. — In the preceding papers1,5,6) some special cases were reported in which mixed complexes could not be detected. These are divided into two groups; 1) those similar to some nickel(II) complexes, and 2) those which may be exemplified with some platinum(II) complexes.

It is well known that nickel(II) forms two types of complexes; one having paramagnetic octahedral configuration, such as $[Ni(OH_2)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Ni\ en_3]^{2+}$ etc., and the other which has a diamagnetic square planar configuration, such as $[Ni(CN)_4]^{2-}$ and $[Ni(C_2O_2S_2)_2]^{2-}$*3 etc. It was verified, in the preceding paper5), that in both of the mixed solutions of $[Ni(OH_2)_6]^{2+}$ and $[Ni(C_2O_2S_2)_2]^{2-}$, and $[Ni\ en_3]^{2+}$ and $[Ni(CN)_4]^{2-}$, no mixed complexes were formed. It was also reported by Kato7) that an ammine-biuret nickel(II) complex could not be detected in solution, whereas an ammine-biuret copper(II) complex was easily formed in solution. This was attributed to the fact that the biuret nickel(II) complex has a planar configration, while the amine nickel(II) complex has an octahedral one. From these observations it appears that, in general, no mixed complex can be formed when the reacting species (parent complexes) are different in geometrical configuration.

It is to be noted that no mixed cyano platinum(II) complexes have been found; for instance, as was reported in the preceding papers1,6), each of the complex ions, e. g., $[Pt\ Cl_4]^{2-}$, $[Pt\ Br_4]^{2-}$ 6) and $[Pt\ en_2]^{2+}$, reacts with cyanide ions in solution forming the complex ion, $[Pt(CN)_4]^{2-}$, only, regardless of the fact that mixed cyano complexes of other metal ions, such as $[Pd(CN)_2\ en]$, $[Ni(CN)_2\cdot(C_2O_2S_2)]^{2-}$ and $[Cd(CN)_2\ en]$ are easily formed1,8). This example illustrates that mixed-complex formation does not always occur between complexes of the same configuration, since platinum(II) complexes are known to posses a diamagnetic square planar configuration.

TABLE III. FORCE CONSTANTS OF THE METAL-CARBON AND THE METAL-NITROGEN BONDS IN THE CYANO- AND THE AMMINE COMPLEXES1,2) (md./Å)

$[Pt(CN)_4]^{2-}$	3.43	$[Au(CN)_2]^-$	1.83
$[Pt(NH_3)_4]^{2+}$	2.80	$[Hg(CN)_2]^-$	2.61
$[Co(CN)_6]^{3-}$	2.33	$[Ag(CN)_2]^-$	1.83
$[Fe(CN)_6]^{4-}$	2.33	$[Hg\ NH_3]_2^{2+}$	1.70

1) S. Mizushima and T. Shimanouchi, "Infrared Spectra and Raman Effect", Kyoritsu Co., Tokyo (1958).

2) F. A. Cotton, "The Infrared Spectra of Transitional Metal Complexes", Ch. 5 in J. Lewis and D. G. Wilkins ed., "Modern Coordination Chemistry", Interscience Publ. Inc., New York (1960), p. 335.

In order to clarify the above fact, attention was first directed towards the platinum-cyanide bond, to which the strong covalency should be attributed on the basis of the infrared absorption studies as indicated in Table III. The behavior of the platinum(II) complexes mentioned above is paradioxical, if one considers only the σ-covalent-effect since σ-covalence of the coordination bond promotes the formation of a mixed complex, as discussed before. Therefore, there must be another factor which is greately responsible for this paradox......, the formation of π-bonds between platinum and carbon, a distinctive feature of the cyano complex.

The existence of π-bonding in cyano complexes has been discussed by many authors9). It is now believed that π-bonds plays an important role in regard to the remarkable stability of cyano complexes.

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5) S. Kida, This Bulletin, **32**, 982 (1959).
6) S. Kida, ibid., **33**, 587 (1960).
7) M. Kato, *Z. anorg. Chem.*, **300**, 84 (1959).
*3 $C_2O_2S_2$=dithiooxalate.

8) S. Kida, This Bulletin, **33**, 1204 (1960).
9) For instance, D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, **1954**, 332.

Assuming that the ligand which is capable of forming a π-bond with a central metal ion has a tendency to exclude the ligand which is not able to undergo π-bonding, one may expect that the ligand which has such a donor atom, containing an unsaturated π-oribital, could form a mixed cyano complex to a greater or less extent. A suitable example can be found in complexes of the type, $[Co(CN)_5X]^{n-}$ [10]; the pentacyano cobalt(III) complexes, $[Co(CN)_5 \cdot X]^{n-}$, can be synthesized, when $X=NO_2^-$, N_3^-, $S_2O_3^{2-}$, SCN^-, Cl^-, Br^- and I^-, while in the cases when $X=NH_3$ and F^-, which are considered to have no tendency to form π-bonds, the pentacyano complexes have not been synthesized. Furthermore, it is interesting to note that the stability of the pentacyano complex, $[Co(CN)_5X]^{n-}$, seems to increase in the order of $X=Cl^-$, Br^- and I^- [11], but on the other hand the reverse order is observed in the halogeno-pentammine cobalt(III) complexes[12].

Although the complex ion, $[Co(CN)_4 \text{ dip}]^-$, (dip=dipyridyl) can be prepared[13], the complex ion, $[Co(CN)_4 \text{ en}]^-$, is unknown. This fact may be due to the same reason as in the above case, since the dipyridyl molecule has an unsaturated π-orbital in its donor atom, whereas the ethylenediamine molecule has no such orbital. According to this assumption, it is expected that the ligand which has unsaturated π-orbitals in its donor atom, such as dipyridyl, forms the complex where $\log K_{stab}$*1 is negative, as seen in Table II; it is a remarkable exception to the general rule discussed above.

Now, we must consider the reason why the ligand which has the unsaturated π-orbital tends to exclude from the complex the ligand having no such orbital. As discussed before, electrons of donor atoms are concentrated on the central atom as the result of coordination, and thus, the repulsion of these electrons depresses the stability of the complex. This effect was considered analogous to the electrostatic one, and accordingly, it was expected to exert a similar influence on the formation of a mixed complex. On the other hand, the formation of π-bonds between the central metal ion and its donor atom allows electrons from the saturated d_π-orbitals of the central metal ion to be donated into unsaturated π-orbitals of ligand atom, lowering the electron concentration on the central metal atom. Thus, very strong coordination bonds can be formed in cyano complexes (especially in the case of platinum(II)), without decreasing the electronegativity of the central atom. Therefore the " σ-bond effect ", which is considered to promote mixed-complex formation, can be weakened by this " π-bond effect " to a greater or less degree.

Since the " σ-bond effect " discussed above is the only strong effect of many factors caused by σ-bond formation, when it is eliminated or weakened by π-bonding, some other effects, in turn, may possibly play an important role in determining the relative stability of mixed complexes, perhaps acting to depress mixed complex formation. For these new effects the present author has made some considerations; for instance, in the case of platinum(II) complexes dsp^2- and d^3p- hybridization of the orbitals can best be formed when all the ligands coordinated are the same species*4. This would make the mixed complex less stable than the parent ones.

In order to achieve a final conclusion, however, further studies are needed.

Summary

The stability of a mixed complex, $[MA_iB_j]$, was discussed and compared with the complexes, $[MA_n]$ and $[MB_n]$, (where A, B and M represent ligands and central ion, respectively, and $i+j=n$).

It was verified by calculation that the electrostatic effect exerts an influence so as to promote the formation of a mixed complex. The effect of σ-covalency of the coordination bond can be considered analogously to the electrostatic one, and is expected to have a similar influence upon mixed-complex formation. The above discussion is supported by experimental data, showing that the mixed complex is formed, in general, more often than can be expected statistically.

However, there are some exceptions to the above-mentioned rule, for instance, in the cases of cyano platinum(II) complexes or dipyridyl complexes. They are attributed to π-bonding between the ligands and the central ion. Discussion has been made concerning the reason why π-bonds depress the formation of mixed complexes.

The author wishes to express his sincere thanks to Professor R. Tsuchida of Osaka

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[10] J. Fujita, Reported at the Symposium on Coordination Compounds, Tokyo, November, 1958.

[11] J. Fujita, Private communication.

[12] S. Ahrland, *Acta Chem. Scand.*, **10**, 723 (1956).

[13] L. Cambi and E. Paglia, "Chemistry of Coordination Compounds", (A Symposium) Vol. 1, Pergamon Press (1958), p. 249.

*4 It was verified by Pauling that (L. Pauling, "Nature of the Chemical Bond", Cornell University Press, New York (1940).) dsp^2-hybridization brings about the larger overlapping of the σ-orbitals between the ligands and the central atom in planar complexes, such as those of platinum(II). Although not verified, the present author believes that it is very probable that in planar complexes π-bonding is most favorably achieved by d^3p-hybridization.

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