Investigation on Mixed Complexes. V. A Conductometric Study of Cyano-ethylenediamine Complexes

By Sigeo KIDA

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In the preceding papers of this series[1-3], the present author has dealt with the formation of mixed cyano complexes in solution. It was indicated spectrophotometrically that the octahedral nickel(II) complex ion, such as the hexaquo nickel(II) ion or the bis-(ethylenediamine)-nickel(II) ion, does not react with planar nickel(II) complexes, for example tetracyano niccolate(II) or bis-(dithio-oxalato)-niccolate(II) ion, to form a mixed complex. However, nickel(II) complexes have a tendency to react with each other, when they are of similar configuration, to produce mixed complexes as shown in the following expression:

$$[Ni(C_2S_2O_2)]^{2-} + [Ni(CN)_4]^{2-} \rightleftarrows 2[Ni(C_2S_2O_2)(CN)_2]^{2-}$$

where $C_2S_2O_2$ indicates dithio-oxalate. However, in the case of platinum(II) complex ions such as tetrachloro platinate(II), tetrabromo platinate(II) and tetracyano platinate(II) ions, all of which are of similar configuration, no tendency of forming any mixed cyano-halogeno complex has been observed in solution.

In order to ascertain the exact conditions under which a cyano mixed complex is formed, one needs to carry out further experiments, but unfortunately it is not always easy to find substances which are suitable for the examination by spectrophotometric methods as previously reported. In the present investigation therefore, the conductometric method has been applied to the complexes of platinum(II), palladium(II), zinc(II) and cadmium(II), which are all colorless and hence can not be studied by the spectrophotometric method[4].

1) Part IV of this series: S. Kida, This Bulletin, 33, 1204 (1960).
2) S. Kida, ibid., 33, 587 (1960).
3) S. Kida, ibid., 32, 981 (1959).

Results and Discussion

It is known that the conductivity of a solution has no linear relationship to the concentration of the dissolved salt in the range of 10^{-2} F, used in the present study. A linear relationship, however, is required by the method of continuous variation[5]. However, the data reported in the present work show that, so far as only the detection of a mixed complex formation is desired, the conductometric continuous variation method can be applied satisfactory for this purpose.

Eight solutions were prepared for the respective metals by mixing a solution of the ethylenediamine complex with the potassium cyanide solution in the ratios as shown in Table I. The conductivity was measured at 25°C.

TABLE I. COMPOSITION OF MIXED SOLUTIONS USED IN THE CONDUCTOMETRIC MEASUREMENTS

0.01 F $[M\,en_n]X_2$	20	10	10	10	10	10	5	5	ml.
0.02 F KCN	10	7.5	10	12.5	15	20	12.5	15	
[CN]/[M]	1	1.5	2	2.5	3	4	5	6	

X=Cl, NO_3, $1/2(SO_4)$

4) The absorption of these complexes in the ultraviolet region are irregular and complicated, probably owing to the presence of association bands resulting from the complex and simple ions in the solution.
5) R. C. Brasted and W. E. Cooley, "Physical Methods in Coordination Chemistry", Ch. 18 in J. C. Bailar and D. H. Busch, ed., "The Chemistry of the Coordination Compounds", Reinhold Pub. Co., New York, (1956), pp. 569-572 and references therein.

The reaction proceeds to decrease the total ionic charge in the solution as follows:

$$[M\,en_n]^{2+} + 4CN^- \rightarrow [M(CN)_4]^{2-} + n\,en \qquad (1)$$

or

$$[M\,en_n]^{2+} + 2CN^- \rightarrow [M\,en(CN)_2] + (n-1)en \qquad (2)$$

(M=Ni, Pd, Pt, Zn and Cd; n=2 for Pd and Pt; n=3 for Ni, Zn and Cd).

Therefore, if a reaction of type 1 took place in solution the curves in Figs. 1 and 2 should have minimum points at [M]/[CN]=1:4, while that of type 2 should give a minimum point at [M]/[CN]=1:2. In fact, as can be seen in Figs. 1 and 2, minimum points are found at [M]/[CN]=1:4 on curves A and E, and at [M]/[CN]=1:2 on curves B, C and D. This shows that, in the former cases, mixed complexes, such as $[Ni\,en(CN)_2]$ and $[Pt\,en(CN)_2]$, are not formed, but the following reactions take place:

$$[Ni\,en_3]^{2+} + 4CN^- \rightarrow [Ni(CN)_4]^{2-} + 3\,en$$

and

$$[Pt\,en_2]^{2+} + 4CN^- \rightarrow [Pt(CN)_4]^{2-} + 2\,en$$

while in the latter cases the mixed complexes

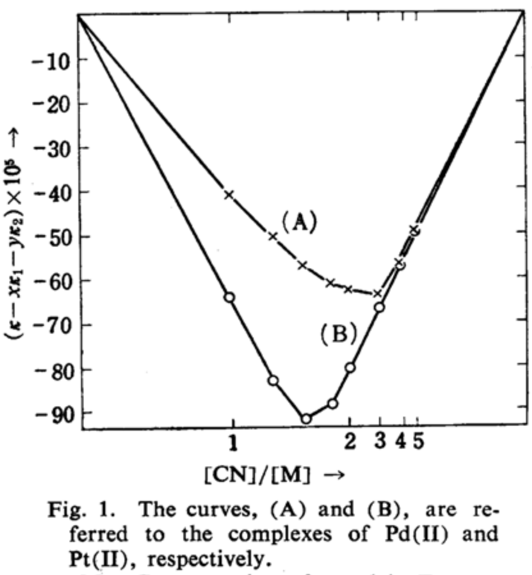

Fig. 1. The curves, (A) and (B), are referred to the complexes of Pd(II) and Pt(II), respectively.
[M]=Concentration of metal in F.
[CN]=Concentration of cyanide ion in F.
κ=Specific conductivity of a mixed solution ($\Omega^{-1}\times cm^{-1}$).
κ_1=Specific conductivity of a 0.01 F $[M\,en_n]X_2$ solution ($\Omega^{-1}\times cm^{-1}$).
κ_2=Specific conductivity of a 0.02 F KCN solution ($\Omega^{-1}\times cm^{-1}$).
x=Volume of the complex solution/Volume of the mixed solution.
y=Volume of the cyanide solution/Volume of the mixed solution.

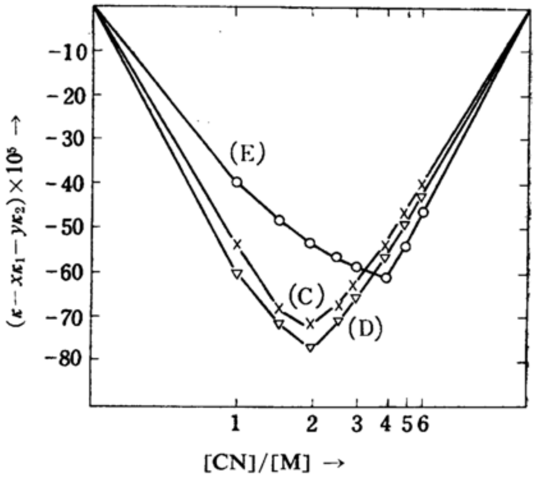

Fig. 2. Curves, (C), (D) and (E), are referred to the complexes of Zn(II), Cd(II) and Ni(II), respectively.

of zinc(II), cadmium(II) and palladium(II) were formed in the solutions through the following reactions:

$$[Zn\,en_3]^{2+} + 2CN^- \rightarrow [Zn\,en(CN)_2] + 2\,en^{6)}$$
$$[Cd\,en_3]^{2+} + 2CN^- \rightarrow [Cd\,en(CN)_2] + 2\,en^{6)}$$
$$[Pd\,en_2]^{2+} + 2CN^- \rightarrow [Pd\,en(CN)_2] + en$$

The result obtained for the nickel complex is in accord with that in the spectrophotometric investigation[3], showing that this conductometric method can be used for the purpose above mentioned. In the cases of zinc, cadmium and palladium complexes, minimum points are found only at [M]/[CN]=1:2 and not at [M]/[CN]=1:4. Neverthless, it should be noted that the formation of tetracyano complexes can not be neglected, since the reaction, $[M\,en(CN)_2] + 2CN^- \rightarrow [M(CN)_4]^{2-} + en$, does not give rise to any decrease in ionic charge in the solution, and accordingly the formation of dicyano complex succeeded by that of tetracyano complex does not always give a minimum point at [M]/[CN]=1:4.

It should also be noted that the curve of the platinum complex is in sharp contrast to that of palladium as a result of their different behavior; the formation of mixed cyano complexes was verified in all the cases of the other metallic ions, but no mixed cyano complex of platinum(II) has ever been observed.

6) It is known that $[Zn\,en_3]^{2+}$ and $[Cd\,en_3]^{2+}$ have octahedral configuration, while $[Zn(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ are tetrahedral in configuration. However, J. Bjerrum (*Chem. Revs.*, **46**, 381 (1950)) has pointed out that tetrammine or bis-ethylenediamine zinc(II) and cadmium(II) complexes tend to be four-co-ordinated and have a tetrahedral configuration as in $[Zn\,en_2]^{2+}$ and $[Cd\,en_2]^{2+}$, but do not tend to have an octahedral one as in $[Zn\,en_2(OH_2)_2]^{2+}$ or $[Cd\,en_2(OH_2)_2]^{2+}$. Therefore, the mixed complexes present in the solution may possibly have tetrahedral configurations of the formulae, $[Cd\cdot en(CN)_2]$ and $[Zn\,en(CN)_2]$.

The cause of this fact will be the subject of the next investigation.

Experimental

Conductometric Measurement.—The conductivities of the solutions were measured at 25°±0.1°C with Kohlrausch's bridge. The cell constant was determined by using a standard potassium chloride solution of 0.01 F. In the cases of platinum(II) and palladium(II) complexes, the substitution reaction of the cyanide ion for the ethylenediamine molecule was slow, and accordingly the mixed solution was allowed to stand in a thermostat until the conductivity came to show a constant value in each case.

Materials. — $[Pt\,en_2]Cl_2$[7], $[Ni\,en_3](NO_3)_2$[8], $[Zn\,en_3]SO_4$[9] and $[Cd\,en_3]Cl_2$[10] were prepared according to the methods described in the references. $[Pd\,en_2]Cl_2$[11] was prepared in a way similar to that for $[Pt\,en_2]Cl_2$. The purity was checked by determining the chloride with silver nitrate.

7) F. Basolo, J. C. Bailar and B. R. Tarr, *J. Am. Chem. Soc.*, **72**, 2433 (1950).
8) A. Werner, *Z. anorg. Chem.*, **21**, 212 (1899).
9) A. Grünberg, ibid., **157**, 201 (1926).
10) A. Werner, ibid., **21**, 226 (1899).
11) H. D. K. Drew, F. W. Pinkard, G. H. Prester and W. Wardlaw, *J. Chem. Soc.*, **1932**, 1906.

Summary

The conductometric method was applied to the determination of the formation of mixed complexes in solution, using the method of continuous variation. It was shown that

1) $[Ni\,en_3]^{2+}$ reacts with CN^- and forms $[Ni(CN)_4]^{2-}$ only, leading to the same conclusion as in the spectrophotometric investigation carried out previously.

2) $[Pt\,en_2]^{2+}$ forms only a tetracyano complex, but no mixed dicyano complex.

3) $[Pd\,en_2]^{2+}$, $[Zn\,en_3]^{2+}$ and $[Cd\,en_3]^{2+}$ form dicyano-ethylenediamine complexes in solution.

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Department of Chemistry
Wakayama University
Masagocho, Wakayama