Investigation on Mixed Complexes. II[1]. *Cyano Complexes of Copper and Nickel*

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(Received October 13, 1958)

A number of studies[2] have been made on the successive formation constants ($k_1, k_2, k_3, \ldots\ldots$) in a solution of metallic complexes, and it was found[3] that in any complex the ratio of the formation constants ($k_1 : k_2 : k_3 \ldots\ldots$) is not far different from the statistically expected one, except in some special cases. Furthermore, recent studies of Watters et al.[4], Marcus[5], Yamatera[6] and the present author[1] have shown that the mixed complexes are formed generally in the statistical way.

These facts seem to imply that in a metallic complex the strength of a coordination bond is not seriously influenced

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[1] Part I of this series: S. Kida, This Bulletin, **29**, 809 (1956).

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

[3] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[4] J. I. Watters, A. Aaron, and J. Mason, *J. Am. Chem. Soc.*, 75, 5212 (1953); R. DeWitt and J. Watters, ibid., **76**, 3810 (1954).

[5] Y. Marcus, *Acta Chem. Scand.*, **11**, 339, 599, 610, 811 (1957).

[6] H. Yamatera and K. Ohashi, Presented at the Symposium on the Co-ordination Compounds, Nagoya, Japan (1957).

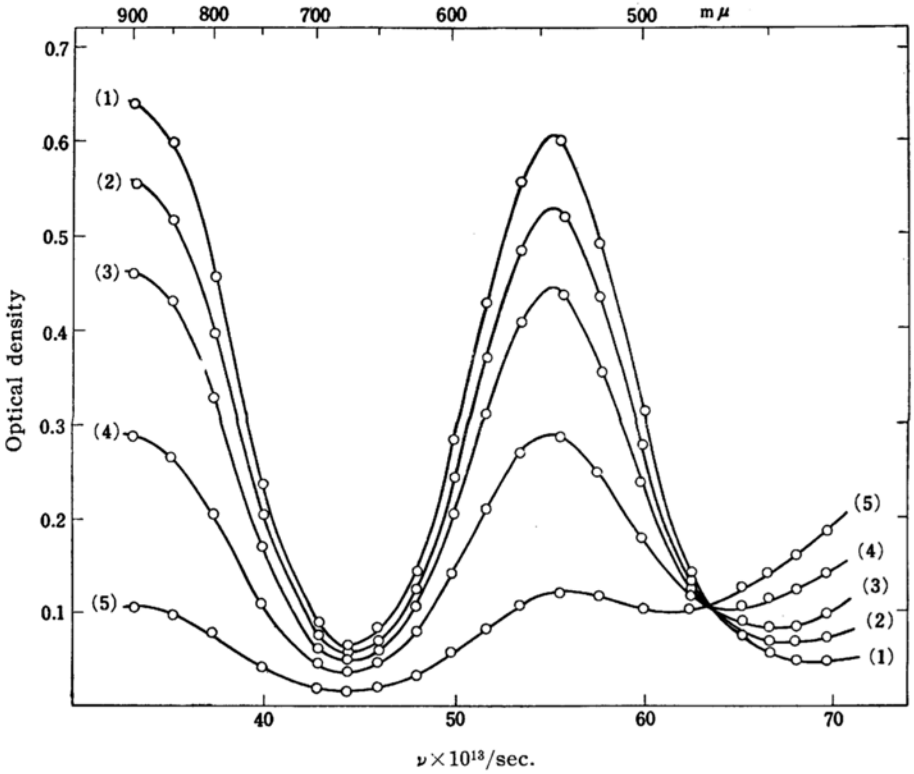

Fig. 1.

by the neighboring ligand; e. g., the strength of the Cu–N bonds are nearly constant in the two complexes, $[\mathrm{Cu\,en_2}]^{2+}$ and $[\mathrm{Cu\,en\,C_2O_4}]$.

However, it also should be noted that there are many cases in which the formations of the mixed complexes seem not to obey the above-mentioned statistical rule. For instance, the mixed cyano complexes known hitherto are few⁷⁾, and difficult to be prepared; this fact would be regarded as suggesting that at least in some cases mixed cyano complexes are not able to be formed or, if it is possibe, they have a strong tendency to be transformed into a complex having only the cyanide ions as ligands. Unfortunately, there is no satisfactory explanation for this phenomenon, since no systematic investigation has ever been made on the conditions leading to the formation of mixed cyano complexes.

This paper will give a report of the investigation which was made for the purpose of getting a clue to this problem.

Results and Discussion

$[\mathrm{Ni\,en_2}]^{2+}+\mathrm{CN}^-$.—It is well known that the tris-ethylenediamine nickel(II) ion has octahedral configuration, while the tetracyano nickelate(II) ion the planar one. However, it is quite uncertain whether mixed complexes, $[\mathrm{Ni\,en_2(CN)_2}]$ and $[\mathrm{Ni\,en(CN)_2}]$, which should be closely related to the above-mentioned, can be formed, or not. At first, an attempt, therefore, has been undertaken to clarify this question*.

A sodium cyanide solution was added to a solution of tris-ethylenediamine nickel(II) perchlorate in the ratio as indicated

TABLE I. THE COMPOSITION OF SOLUTIONS

Solution number	(1) cc.	(2) cc.	(3) cc.	(4) cc.	(5) cc.	(6) cc.
0.2 F $[\mathrm{Ni\,en_3}](\mathrm{ClO_4})_2$ and 0.1 M en	10	10	10	10	10	10
1.096 F NaCN	0	1	2	4	6	8
Water	10	9	8	6	4	2

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7) J. C. Bailar, "The Chemistry of the Coordination Compounds", p. 87; "General Survey", Reinhold Publ. Co., New York (1956).

* Ammine-cyano-nickel(II) compounds, such as $\mathrm{Ni(CN)_2NH_3}$, $\mathrm{Ni(CN)_2NH_3H_2O}$ and $\mathrm{Ni(CN)_2NH_3C_6H_6}$, have been known. [E. E. Aynsley and W. A. Campbell, *J. Chem. Soc.*, **1958**, 1723; K. A. Hofmann and F. Hochtler, *Ber.*, **36**, 1149 (1903)]. However, they are not touched on in this article, since they have complicated structures quite different from that of the mixed complexes in which we are interested here (J. H. Rayner and H. M. Powell, *J. Chem. Soc.*, **1952**, 319).

TABLE II

	(1)	(2)	(3)	(4)	(5)	(6)
([Ni]−1/4[CN])/[Ni]	1.00	0.863	0.726	0.452	0.178	0
D/D_1 for 900 mμ	1.00	0.867	0·719	0.450	0.163	0
for 580 mμ	1.00	0.859	0.714	0.459	0.162	0
for 560 mμ	1.00	0.862	0.718	0.453	0.160	0
1/4[CN]/[Ni]			0.274	0.548	0.822	1.00
D/D_6 for 310 mμ			0.275	0.550	0.841	1.00
for 330 mμ			0.280	0.556	0.816	1.00

Numbers in the first row denote solution numbers in Table I.

in Table I, and extinction measurements were carried out on each of the mixed solutions thus prepared. The results obtained are shown in Fig. 1.

The extinction curves in Fig. 1 tell us that only the tetracyano nickelate(II) and tris-ethylenediamine nickel(II) ions are present, no mixed cyano-amine complex being formed; if any of the mixed complexes were formed, the absorption curve would be more or less subject to deformation, or some new absorption maximum would appear correspondingly.

If we assume all of the added cyanide ion is consumed to form the tetracyano nickelate ion, the calculated values of ([Ni]−1/4[CN])/[Ni] and 1/4[CN]/[Ni] must accord with the experimentally obtainable values, D/D_1 and D/D_6, respectively, where [Ni] and [CN] denote the total concentration of all nickel species and the total concentration of cyanide ion in the solution and D_n is the optical density of the solution, n, shown in Table I and Fig. 1[**]. Actually, the satisfactory agreement between them can be found as is seen from Table II.

$[\mathrm{Cu\,en_2}]^{2+}+\mathrm{CN}^-$. — The experiment has been carried out to verify whether the mixed complex such as $[\mathrm{Cu\,en(CN)_2}]$ can be formed, or not, when a sodium cyanide solution is added to a solution of bis-ethylenediamine copper(II) perchlorate. Extinction mesurements were made on each of the mixed solutions shown in Table III. The results are shown in Fig. 2.

TABLE III. THE COMPOSITION OF SOLUTIONS

Solution number	(7) cc.	(8) cc.	(9) cc.	(10) cc.	(11) cc.	(12) cc.
0.02 F $[\mathrm{Cu\,en_2}](\mathrm{ClO_4})_2$ and 0.01 F NaOH	10	10	10	10	10	10
0.1096 F NaCN	0	1	2	4	6	8
Water	10	9	8	6	4	2

The extinction curves in Fig. 2 indicate that none of the mixed complexes such as $[\mathrm{Cu\,en(CN)_2}]$ is existent in the solutions, because the absorption band (due to $[\mathrm{Cu\,en_2}]^{2+}$) does not shift at all, being fixed at 500mμ, and yet none of the new absorption bands appears in the shorter wavelength region.

If we assume that four cyanide ions are consumed to convert a copper amine complex into a cyano complex, the calculated value, ([Cu]−1/4[CN])/[Cu], must accord with the experimentally obtainable value, D/D_7, as in the case of nickel. Actually the accordance can be found in Table IV, though it is not so satisfactory as in the case of nickel. Since cyanide complexes of divalent copper can not exist, the following reaction would have possibly occurred:

$$[\mathrm{Cu(en)_2}]^{2+}+4\mathrm{CN}^- \rightarrow$$
$$\overset{***}{[\mathrm{Cu(CN)_3}]^{2-}}+1/2(\mathrm{CN})_2+2\,\mathrm{en}$$

Stability constants of copper(I) cyanide complexes were determined by Penneman and Jones8).

$$k_1k_2=[\mathrm{Cu(CN)_2}^-]/[\mathrm{Cu}^+]\,[\mathrm{CN}^-]^2=1\times10^{24}$$
$$k_3=[\mathrm{Cu(CN)_3}^{2-}]/[\mathrm{Cu(CN)_2}^-]\,[\mathrm{CN}^-]$$
$$=3.8\times10^4$$
$$k_4=[\mathrm{Cu(CN)_4}^{3-}]/[\mathrm{Cu(CN)_3}^{2-}]\,[\mathrm{CN}^-]=50$$

From these data, it seems quite natural that tricyano copper(I) complex is mainly formed.

It must be noted that the possibility of

[**] If the reaction, $[\mathrm{Ni\,en_3}]^{2+}+4\,\mathrm{CN}^-\rightarrow[\mathrm{Ni(CN)_4}]^{2-}+3\,\mathrm{en}$, takes place quantitatively, optical densities of the mixed solutions can be given as follows:

$$D=\varepsilon_1([\mathrm{Ni}]-1/4\,[\mathrm{CN}])+\varepsilon_2(1/4[\mathrm{CN}]),$$

while, for the solutions (1) and (6), $D_1=\varepsilon_1[\mathrm{Ni}]$, and $D_6=\varepsilon_2[\mathrm{Ni}]$, where ε_1 and ε_2 are extinction coefficients of $[\mathrm{Ni\,en_3}]^{2+}$ and $[\mathrm{Ni\,(CN)_4}]^{2-}$, respectively. However, the ratios D/D_1 and D/D_6 may be reduced for some wavelength region: for the region of 900~560 mμ, $D/D_1=$ [(Ni]−1/4[CN])/[Ni] with $\varepsilon_2=0$, and for the region of 400~220 mμ, $D/D_6=1/4[\mathrm{CN}]/[\mathrm{Ni}]$ since ε_1 is quite small as compared with ε_2.

[***] For this complex the 4-coordinated configuration such as $[\mathrm{Cu(CN)_3OH_2}]^{2-}$ or $[\mathrm{Cu(CN)_3\,en}]^{2-}$, may be also considered. However, this is represented tentatively as $[\mathrm{Cu(CN)_3}]^{2-}$, and the discussion of this complex will be done in the next section.

8) R. A. Penneman and L. H. Jones, *J. Chem. Phys.*, **24**, 293 (1956).

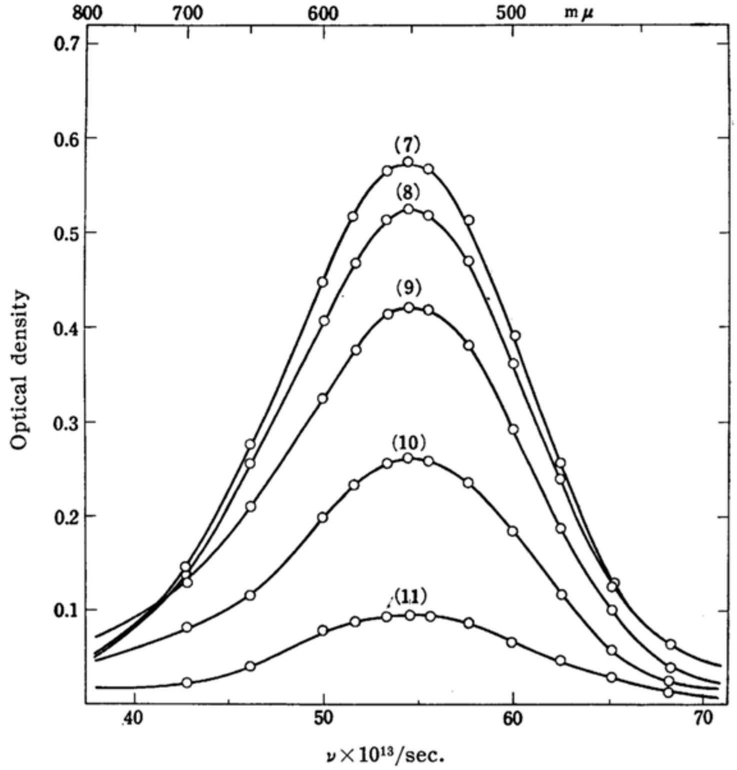

Fig. 2.

TABLE IV

	(7)	(8)	(9)	(10)	(11)	(12)
([Cu] − 1/4[CN])/[Cu]	1.00	0.863	0.726	0.452	0.178	0
D/D_7 for 600 mμ	1.00	0.916	0.728	0.450	0.176	0
for 550 mμ	1.00	0.918	0.734	0.458	0.166	0
for 520 mμ	1.00	0.913	0.738	0.456	0.165	0

Numbers in the first row denote solution numbers in Fig. 2.
[Cu] is the total concentration of all copper species in solution.

the existence of a complex of coordination number 5 such as $[\mathrm{Cu\,en_2\,CN}]^+$ can not be denied; the formation of this complex might be the cause of the unsatisfactory accordance of the calculated value with the experimental one unlike the case of nickel.

$[\mathrm{Cu(CN)_3}]^{2-}$ + en.—Absorption spectra of the tricyano copper(I) complex were measured both with and without excess of ethylenediamine, and it was found that both absorption curves completely coincide within the limit of the experimental error. This fact suggests that the tricyano copper(I) complex does not take an ethylenediamine molecule in the solution to form the mixed complex such as $[\mathrm{Cu(CN)_3\,en}]^{2-}$, and that the coordination number of the tricyano copper(I) complex may be 3 (perhaps sp^2 hybridization); if the coordintaion number were 4, the tricyanocopper(I) complex would have the configuration such as $[\mathrm{Cu(CN)_3\,OH_2}]^{2-}$, and it would become the mixed complex, $[\mathrm{Cu(CN)_3\,en}]^{2-}$, when the ethylenediamine is added to the solution.

$[\mathrm{Cu(CN)_2}]^-$ + en.—When ethylenediamine is added to a solution of the dicyano copper(I) complex, the solution becomes turbid and light blue, and then slowly changes into a transparent purple blue solution. The absorption spectrum of this solution completely coincides with that of the bis-ethylenediamine copper(II) complex in the visible region.

From the above results, we can easily understand the fact that neither dicyano nor tetracyano copper(I) complex is formed, but tricyano copper(I) complex, when the cyanide solution is added to the bis-ethylenediamine copper(II) complex solution.

Experimental

Extinction measurements were made by means of the Beckman D. U. spectrophotometer using 1 cm. quartz cells at room temperature.

In the case of $[\mathrm{Cu\,en_2}]^{2+}+\mathrm{CN}^-$, each of the solutions prepared as shown in Table III was heated just to boiling, and then cooled to the room temperature before extinction measurements were made; without this treatment, extinction data obtained are not reproducible.

$[\mathrm{Ni\,en_3}](\mathrm{ClO_4})_2$ and $[\mathrm{Cu\,en_2}](\mathrm{ClO_4})_2$.—The metal quantity of the former was analyzed with dimethylglyoxime, and that of the latter was determined by iodometry.

$[\mathrm{Cu(CN)_2}]^-$ and $[\mathrm{Cu(CN)_3}]^{2-}$ (in solution).—The copper(I) cyanide was dissolved in the potassium cyanide solution at the ratio of 1 : 1 and 1 : 2 to form these complexes, respectively.

Summary

1. Mixed amino-cyano nickel(II) complexes, such as $[\mathrm{Ni\,en_2(CN)_2}]$, $[\mathrm{Ni\,en\cdot(CN_4)_4}]^{2-}$ and $[\mathrm{Ni\,en(CN)_2}]$ in the solution containing the divalent nickel ion, ethylenediamine and cyanide ion, are not formed.

2. In the solution containing the divalent or the monovalent copper ion, ethylenediamine and the cyanide ion, no mixed amine-cyano copper(I) and copper(II) complexes are formed, except the copper(II) complex of coordination number 5.

3. Among cyano copper(I) complexes, tricyano copper(I) ion is the most stable, and its coordination number may be 3.

The author wishes to express his sincere thanks to Professor R. Tsuchida of Osaka University for his kind advice and encouragement during this work. The author's appreciation is also expressed to Dr. H. Yoneda for his helpful discussion.

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