Investigation on Mixed Complexes. IV. The Formation of a Mixed Complex by Reaction of Tetracyanoniccolate(II) with Bis-(dithiooxalato)-niccolate(II)

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In the preceding paper of this series[1], it was demonstrated that the chlorocyano- and bromocyano- platinum(II) complex could not be formed in solution. However, one can not say that the formation of any mixed cyano complexes must be ruled out. Since it is commonly known that bis-(dithiooxalato)-niccolate(II) and tetracyanoniccolate(II) ions have the planar configuration, one should expect that a reaction between these reactants in solution might produce a complex containing both cyano and dithiooxalato as ligand. The purpose of the present paper is to present spectrophotometric evidence for the formation of a mixed cyano complex of the type, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, in solution.

Equivalent quantities of potassium bis-(dithiooxalato)-niccolate(II) and potassium tetracyanoniccolate(II) were mixed in solution. At first, the dark red color of the bis-(dithiooxalato)-niccolate(II) ion was predominant in the solution, then the color slowly changed to orange, the reaction being complete in two hours at room temperature (15°C). This change was followed spectrophotometrically, and the results are shown in Fig. 1. The intensity of the absorption band at 501 mμ of the bis-(dithiooxalato)-niccolate(II) ion decreases remarkably with time, while a new band appears at 380 mμ, the intensity of which increases in nearly reciprocal proporation to that of the band at 541 mμ. This implies that a reaction such as,

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

might be taking place in solution. The reasons are: 1) the blue shift of the band from 501 mμ to 380 mμ is indicative of the replacement of the dithiooxalate ion by cyanide ions, since the former is placed behind the latter in the spectrochemical series[2], and 2) the frequency of the new band is nearly equal to the mean of frequencies of the bands of the parent complexes, $[Ni(C_2S_2O_2)_2]^{2-}$ and $[Ni(CN)_4]^{2-}$, as shown in Table I. This is the relationship which can always be seen between the mixed complex and its parent complexes[3,4].

Previously[5], polarographic measurements were carried out on a mixed solution of potassium bis-(dithiooxalato)-niccolate(II) by Maki, Kida and Tsuchida, and it was reported that a new compound, perhaps the mixed complex, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, must be formed in the solution. Thus, the present result is not in consistent with the previous one.

Similar spectrophotometric observations were made also on the bis-dithiooxalato- and the tetracyano- platinum(II) and palladium(II) complexes. Unfortunately, no indication of the expected reactions, such as

$$[Pt(C_2S_2O_2)_2]^{2-} + [Pt(CN)_4]^{2-} \rightleftharpoons 2[Pt(C_2S_2O_2)(CN)_2]^{2-} \quad \text{and}$$

$$[Pd(C_2S_2O_2)_2]^{2-} + [Pd(CN)_4]^{2-} \rightleftharpoons 2[Pd(C_2S_2O_2)(CN)_2]^{2-},$$

could be detected. At present, however, it is quite uncertain whether this is due to the total inertness of these parent complexes or to the extreme instability of the ligand-mixed complexes.

Therefore, another attempt was made as follows: in order to obtain some information on the possible reaction between the bis-(dithiooxalato)-platinate(II) ion and the cyanide ion, a potassium cyanide solution and a potassium

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[1] Part III of this series; S. Kida, This Bulletin, 33, 587 (1960).

[2] Y. Shimura and R. Tsuchida, This Bulletin, 29, 311 (1956); R. Tsuchida, ibid., 13, 388 (1938).

[3] S. Kida, ibid., 29, 805 (1956).

[4] Y. Shimura and R. Tsuchida, ibid., 28, 572 (1955).

[5] N. Maki, S. Kida and R. Tsuchida, ibid., 32, 573 (1959).

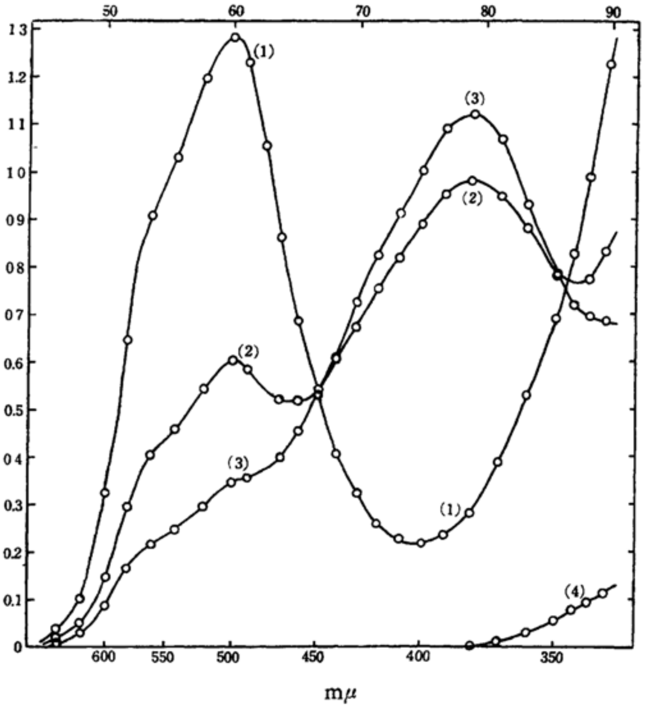

Fig. 1.

(1) $1/3\times10^{-3}$ F $K_2[Ni(C_2S_2O_2)_2]$ solution
(2) $1/3\times10^{-3}$ F $K_2[Ni(C_2S_2O_2)_2]$ and $1/3\times10^{-3}$ F $K_2[Ni(CN)_4]$ solution, (1/2 hr. after mixing)
(3) The same as solution (2), (2 hr. after mixing)
(4) $1/3\times10^{-3}$ F $K_2[Ni(CN)_4]$ solution

TABLE I. FREQUENCIES OF ABSORPTION BANDS OF THE COMPLEXES

$K_2[Ni(C_2S_2O_2)_2]$	$K_2[Ni(CN)_4]$	New band	$(\nu_1+\nu_2)/2$
59.7 (501 mμ)	96.9 (310 mμ)	78.9 (380 mμ)	78.3

$\nu\times10^{13}$: the frequency of the absorption maximum (sec^{-1})

bis-(dithiooxalato)-platinate(II) solution were mixed in the ratio 2:1. The intensity of the absorption band due to the bis-(dithiooxalato)-platinate(II) ion at 430 mμ was appreciably reduced, while in a shorter wavelength region, the absorption showed a uniform increase in intensity. No distinct new band was formed, as shown in Fig. 2.

This uniform increase in absorption intensity in the shorter wavelength region may be regarded as being due to the decomposition of the bis-(dithiooxalato)-platinate(II) ion, since it can be demonstrated spectrophotometrically that, in an alkaline solution, this ion is subject to a slow decomposition which results in increased absorption at the shorter wavelength[6]. Accordingly, a mixed complex, such as $[Pt(C_2S_2O_2)(CN)_2]^{2-}$, is unlikely to be present in the solution, though it is better not to draw a decisive conclusion until more experimental data are obtained. On the other hand, there is no doubt that some quantity of the tetracyanoplatinate(II) ion has been produced in this solution, because the characteristic band, of this ion, at 279 mμ, is evidently found in the absorption curve 6 in Fig. 2.

Experimental

Solutions of the following concentrations were mixed, $(2/3)\times10^{-3}$ F potassium bis-(dithiooxalato)-niccolate(II) and $(2/3)\times10^{-3}$ F potassium tetracyano-niccolate(II), and the mixed solution was placed in the dark at room temperature (15°C). The reaction was almost complete in two hours. It was ascertained by extinction measurements that the decomposition of bis-(dithiooxalato)-niccolate(II) ion was small during the experiment.

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[6] This was verified by extinction measurements on a weakly alkaline solution of this complex.

The bis-(dithiooxalato)-palladate (II) ion so rapidly decomposed in an alkaline solution that extinction measurements of this complex could not be carried out in a solution containing potassium cyanide.

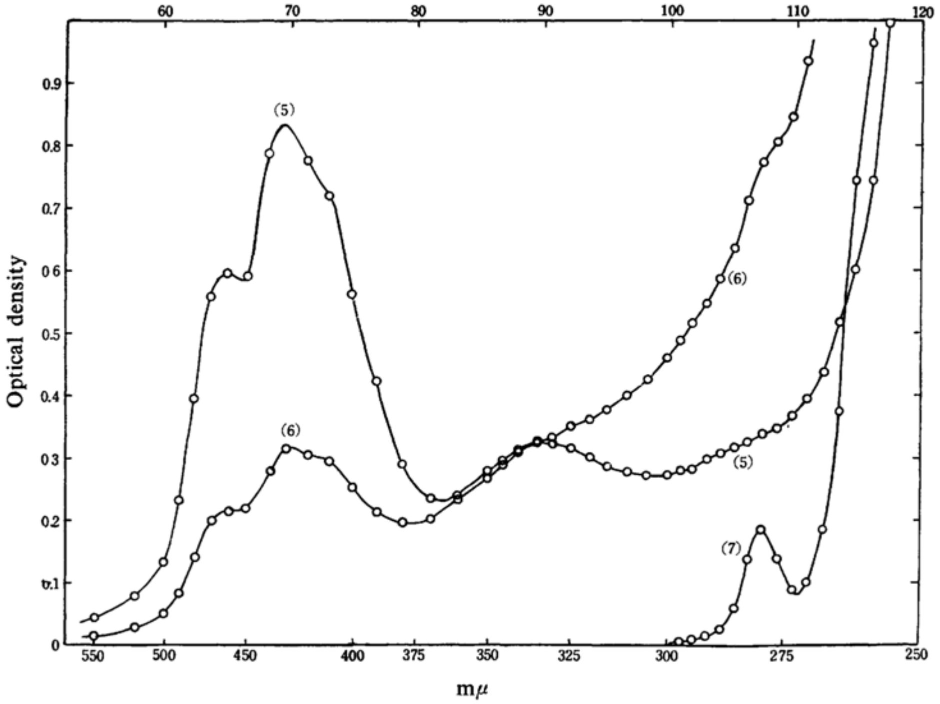

Fig. 2.

(5) 10^{-4} F $K_2[Pt(C_2S_2O_2)_2]$ solution
(6) 10^{-4} F $K_2[Pt(C_2S_2O_2)_2]$ and 2×10^{-4} KCN solution, (2 days after mixising)
(7) 10^{-4} F $K_2[Pt(CN)_4]$

Solutions of potassium cyanide (0.1 F) and of potassium bis-(dithiooxalato)-platinate(II) (0.2 F) were mixed and placed in the dark at room temperature (15°C). For extinction measurements, 5 ml. of the solution was diluted to 500 ml. The extinction measurements were carried out with a Beckman model DU spectrophotometer.

The complexes, $K_2[Ni(C_2S_2O_2)_2]$7), $K_2Pd(C_2S_2O_2)_2]$7), $K_2[Pt(C_2S_2O_2)_2]$7), $K_2[Ni(CN)_4]\cdot H_2O$8), $K_2[Pd(CN)_4]\cdot 3H_2O$8), and $K_2[Pt(CN)_4]\cdot 3H_2O$9), were prepared according to the literature cited.

Summary

It has been concluded, by the spectrophotometric method, that 1) potassium bis-(dithiooxalato)-niccolate(II) and potassium tetracyanoniccolate(II) react in solution to form a mixed complex, $[Ni(C_2S_2O_2)(CN)_2]^{2-}$, 2) in the case of palladium(II) and platinum(II), bis-(dithiooxalato)- and tetracyano- complexes do not react in solution, unlike the case of nickel(II), and 3) the dithiooxalate ion in the complex, $[Pt(C_2S_2O_2)_2]^{2-}$, is replaced by the cyanide ion in solution, the tetracyanoplatinate(II) ion being formed, but the formation of the mixed complex, such as $[Pt(C_2S_2O_2)(CN)_2]^{2-}$, is not certain.

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8) W. C. Fernelius, "Inorganic Syntheses", vol. II. McGraw-Hill Book Co. Inc., 1946, pp. 243, 227.

9) G. Brauer, "Handbuch der präparativen anorganishe Chemie", F. Enke Verlag, Stuttgart, 1954, p. 1179.