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The Preparation and Properties of Metal Complexes in Non-aqueous Solution. II. Diiodotetrakisdimethylsulfoxidecobalt Iodide*[1]

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The object of this investigation was, in its early stage, to obtain diiodotetraamine-type cobalt(III) complexes. With this object in mind, the replacement of Cl^- in $[CoCl_2en_2]^+$, $[CoCl_2pn_2]^+$, *etc.* by I^- in the presence of a small amount of iodine was attempted, using dimethylsulfoxide (DMSO) as the solvent. The product thus obtained was, however, not the expected diiodotetraamine-type complex, but instead, $CoI_3 \cdot 4(DMSO)$ in all cases. This means that the substitution of I^- for Cl^- caused a purge of the coordinated amine ligands from the coordination sphere. Here it is surprising that even a tetradentate ligand, triethylenetetramine, is expelled by DMSO molecules. This suggests that DMSO has a strong coordinating ability with cobalt in the presence of I^-. Thus, the direct synthesis of $CoI_3 \cdot 4(DMSO)$ was also attempted from CoI_2, I_2, and DMSO in absolute ethanol, the same product was obtained. The present paper will describe the method of preparation and the properties of this complex.

Experimental

Preparation. *1) From trans*-$[CoCl_2en_2]NO_3$. One half gram of *trans*-$[CoCl_2en_2]NO_3$, 0.2 g of I_2, and 0.8 g of NaI were dissolved in 5 m*l* of warm DMSO. The mixture became a complete solution after one hour's gentle heating under constant stirring. This solution was added to 50 m*l* of ethanol and then placed in a refrigerator overnight. The precipitated sodium chloride was then filtered off, and the filtrate was stirred. A reddish-brown crystalline precipitate came out. The precipitate was filtered, washed with a small amount of ethanol and then with ether, and dried in a vacuum desiccator. Yield, 0.2 g.

Found: C, 12.49; H, 3.34; I. 50.57%. Calcd for $CoI_3 \cdot 4(C_2H_6SO)$: C, 12.77; H, 3.21; I, 50.61%.

From $[CoCl_2pn_2]NO_3$, $[CoCl_2tn_2]NO_3$, and $[CoCl_2 trien]NO_3$, the same product was obtained.

2) Direct Synthesis. One half gram of CoI_2 and 0.5 g of DMSO were dessolved in 10 m*l* of warm ethanol. The pink precipitate which appeared at first soon disappeared, and the solution became dark blue. Then, 0.15 g of I_2 in a small amount of ethanol was added slowly. Reddish-brown crystals came out. Crystals were filtered out, washed with ethanol and ether, and dried in a vacuum desicator. Yield, 2 g, In this preparation, the addition of iodine solution should be stopped before the blue color disappeared in

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[1] Presented at the 19th Symposium of Coordination Chemistry held at Tohoku University, Sendai, September 27, 1969.

the solution.

Physical Measurements. The IR spectra were recorded with a Hitachi EPI-S2 spectrophotometer equipped with NaCl optics. The KBr disk method was adopted for the complex, but for the ordinary and deuterated DMSO samples sandwiched with NaCl plates were used for the measurements.

The UV absorption spectra of the solutions were obtained with a Hitachi Spectrophotometer 124, using 1-cm quartz cells. The magnetic moment was determined by the Gouy method at 12°C.

Results and Discussion

IR Spectra. Figure 1 shows the IR spectrum of the new complex, $CoI_3 \cdot 4(DMSO)$, together with those of the know complex, $[Co(DMSO)_6]I_2$[1], and the free ligand, DMSO. These spectra consist of a relatively few bands, among which consist of a relatively few bands, among which the two appearing at about 950 cm^{-1} and at 1000–1100 cm^{-1} are significant in discussing the coordinated state of the lignad. There has been confusion concerning the assignment of these two bands.

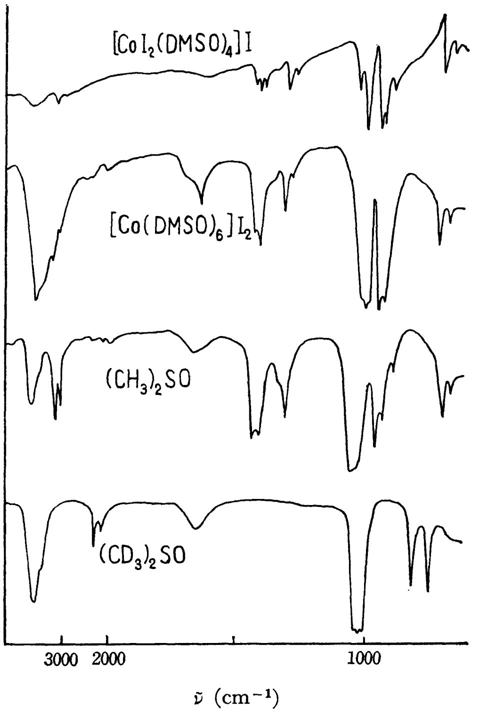

Fig. 1. IR absorption spectra of the free and coordinated states of dimethylsulfoxide.

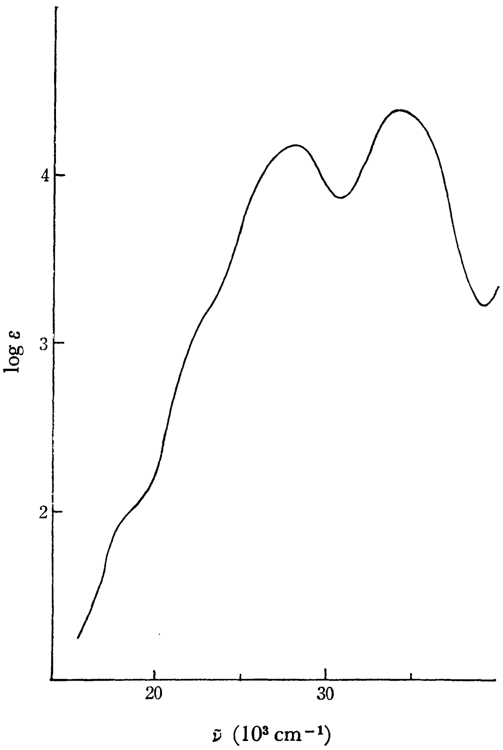

Fig. 2. Visible and UV absorption spectrum of $CoI_3 \cdot 4(DMSO)$ in 0.01 M NaI ethanol solution.

Cotton and his collaborator[1] studies the IR spectra of sulfoxide complexes and concluded that coordination occurred through oxygen in $[Co(DMSO)_6]I_2$, since the SO stretching frequencies of the complex were lower than those of the free ligand, which absorbed at 1100–1055 cm^{-1}. Their assignment seems unnatural, however, of the two bands, the one at the lower frequencies was taken as the SO stretching band in the case of the complex, while the one at the higher frequencies was taken as the SO stretching band in the case of the free ligand. Thus, Drago and Meek[2] rejected Cotton's assignment and asserted that the band at lower frequencies was due to the methyl rocking mode, and that at higher frequencies, to the SO stretching mode, both in the complex and in the free ligand. If this is valid, the SO stretching frequency is not very sensitive to the nature of the metal.

To confirm their assignments, the spectrum of deuterated DMSO was measured and compared with that of the ordinary DMSO. As may be been in Fig. 1, the band at lower frequencies completely disappears, while that at higher frequencies remains almost unchanged. This means that the lower one is due to the methyl rocking mode, which should be shifted further to lower frequencies upon the deuteration of the methyl group. Thus, the validity of Drago's assignment was confirmed. Since the SO stretching band of the free ligand is

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[1] F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem.*, **64**, 1534 (1960).

[2] R. S. Drago and D. W. Meek, *ibid.*, **65**, 1446 (1961).

shifted slightly to lower frequencies upon coordination to Co(II) (from 1100–1050 cm^{-1} to 1050–1000 cm^{-1}), coordination through oxygen was also confirmed. In the new complex, CoI_3,·4(DMSO), the frequency of each band is quite similar to that of $[Co(DMSO)_6]I_2$. Thus, the coordination through oxygen may be presumed. Although the new complex can be formulated as $[CoI_2(DMSO)_4]I$, in which the central cobalt ion is assumed to be tervalent, there is no indication in the IR spectra which positively supports the existence of the tervalent cobalt ion.

Visible and UV Absorption Spectra. Figure 2 show the visible and UV absorption spectra of CoI_3·4(DMSO) in an ethanol solution. The large absorption peaks at 28000 and 34200 cm^{-1} are assigned to charge-transfer band due to the coordinated I^-, because the spectrum of $[CoI(NH_3)_5]^{2+}$ has two bands at almost the same frequencies. The spectra have, in addition, two shoulders at about 17000 and 21200 cm^{-1} which are regarded as ligand-field bands.

Magnetic Moment. The magnetic moment of CoI_3·4(DMSO) was determined to be 4.45 B.M..

Structure of Complexes. From the abovementioned data, we can formulate the complex as $[CoI_2(DMSO)_4]I$. The electronic structure of the complex may be represented by a resonance hybrid of the following structures;

$$[Co^{3+}(I^-)_2(DMSO)_4]^+ \leftrightarrow [Co^{2+}(I^-)(I^0)(DMSO)_4]^+$$