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PRODUCTS OF THE REACTION OF AQUAPENTAAMMINECOBALT(III) IONS WITH ETHYLENEDIAMINE IN DIMETHYLSULFOXIDE[1)]

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From the products of the reaction of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with ethylenediamine (en) in dimethylsulfoxide, $[Co(NH_3)_5(enH)]Br_4$ and $[Co(NH_3)_{6-2n}(en)_n]X_3$ (n = 0, 1, 2, and 3) were isolated. Treatment of $[Co(NH_3)_5(enH)]Br_4$ with aqueous ammonia gave a novel complex, $[Co(NH_3)_5(en)]Br_3$ containing en as a monodentate ligand.

It has been shown that dimethylsulfoxide (DMSO) was a useful solvent for the syntheses of various cobalt(III) complexes, e.g. trans-$[Co(CN)_2(en)_2]X_3$,[2)] $[Co(NH_3)_4(en)](NO_3)_3$,[3)] $[Co(NH_3)_4(pn)](NO_3)_3$,[3)] $[Co(en)_2(H_2N(CH_2)_nNH_2)]X_3$ (n = 4, 10, 12, and 14),[4,5)] $[Co_2(en)_4(H_2N(CH_2)_nNH_2)_2]X_6$ (n = 4, 5, 6, 8, 10, and 12),[4,5)] and $[Co(H_2N(CH_2)_4NH_2)_3]Br_3$,[6)] where en and pn denote ethylenediamine and 1,2-diaminopropane respectively. Therefore, it seems worthwhile to elucidate the features of the reactions of cobalt(III) complexes in DMSO. In this letter, the products of the reaction of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with ethylenediamine in DMSO are examined and characterized.

<u>The product survey of the reaction of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with ethylenediamine</u> To a DMSO solution (80 ml) containing 8.3 g of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ (0.018 mol) was added 1.2 g of ethylenediamine (0.02 mol). The solution was stirred vigorously at 85°C for 10 min. The orange solution obtained was diluted with water to 1.5 l and then neutralized with conc. HCl. This was poured into an SP-Sephadex C-25 ion-exchange column (ϕ 5 x 40 cm). By elution with an 0.25 M NaBr solution, a single orange band was progressively separated into the three bands, reddish orange (trace amount, characterized as $[Co(H_2O)(NH_3)_5]^{3+}$), yellow, and yellowish orange. After the first and the second bands were eluted out with the 0.25 M NaBr solution, the last band was eluted out with an 0.7 M NaBr solution. The last yellowish orange eluate was concentrated by a rotary evaporator until yellowish orange crystals appeared. The product was recrystallized from water by the addition

of solid NaBr. Yield: 0.6 g. Anal. Calcd for $[Co(NH_3)_5(enH)]Br_4 = C_2H_{24}N_7Br_4Co$: C, 4.58; H, 4.61; N, 18.68%. Found: C, 4.37; H, 4.53; N, 18.78%. When the second yellow eluate was concentrated, crystals of $[Co(NH_3)_6]Br_3$ appeared and were filtered off. One-third of the filtrate was diluted with water and then poured into an SP-Sephadex C-25 column (ø 3.5 x 60 cm). The adsorbed species were eluted with an 0.08 M Na_3PO_4 solution. An orange band was separated into three bands with the progression of elution. These bands were labeled as F1, F2, and F3 in the order of elution. Each eluate was neutralized with conc. HCl and poured into a Sephadex column (ø 2.5 x 5 cm). The species F1 was eluted out with an 0.3 M HCl solution. Concentration of the eluate gave $[Co(en)_3]Cl_3 \cdot 3H_2O$. The species F2 and F3 were eluted out with 0.5 M KI solutions. Concentration of these eluates gave $[Co(NH_3)_2(en)_2]I_3$ and $[Co(NH_3)_4(en)]I_3$ respectively. The identification of these three species was made with their elemental analyses, infrared, visible and ultraviolet absorption spectra, and NMR spectra.

Preparation of $[Co(NH_3)_5(en)]Br_3$ Crystals of $[Co(NH_3)_5(enH)]Br_4$ (0.2 g) were dissolved into 4 ml of 1.5 M aqueous ammonia. Solid NaBr was added to the solution until a small amount of crystals appeared. Then, ethanol and ether were added to the solution. The crystals were filtered, washed with ethanol and then ether, and dried over NaOH. Anal. Calcd for $[Co(NH_3)_5(en)]Br_3 = C_2H_{23}N_7Br_3Co$: C, 5.41; H, 5.22; N, 22.09%. Found: C, 5.68; H, 5.34; N, 21.82%.

Visible absorption spectrum and acid dissociation constant of $[Co(NH_3)_5(enH)]^{4+}$ The complex $[Co(NH_3)_5(enH)]^{4+}$ gives two absorption bands at 480 nm (ε = 63) and 342 nm (ε = 51), indicating that the complex is of $[Co^{III}N_6]$ type (Fig. 1). In order to determine the equilibrium constant of the reaction

$$Co(NH_3)_5(enH)^{4+} \rightleftharpoons Co(NH_3)_5(en)^{3+} + H^+$$

pH titration was made with a standard NaOH solution at 25°C and an ionic strength of 0.1 (NaCl). The pK value obtained was 7.53, which is slightly larger than pK_1 value of enH_2^{2+} (7.1).[7) This is the same trend as those observed for $Co(NH_3)_5(HC_2O_4)^{2+}$,[8) $Co(NH_3)_5(HCO_3)^{2+}$,[8) and $CoCl(en)_2(enH)^{3+}$.[9)

Mechanism of the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with ethylenediamine in DMSO The products of the reaction in question were found to be $[Co(NH_3)_{6-2n}(en)_n]X_3$ (n = 0, 1, 2, and 3) and $[Co(NH_3)_5(enH)]Br_4$, indicating that the mechanism of the reaction is as follows:

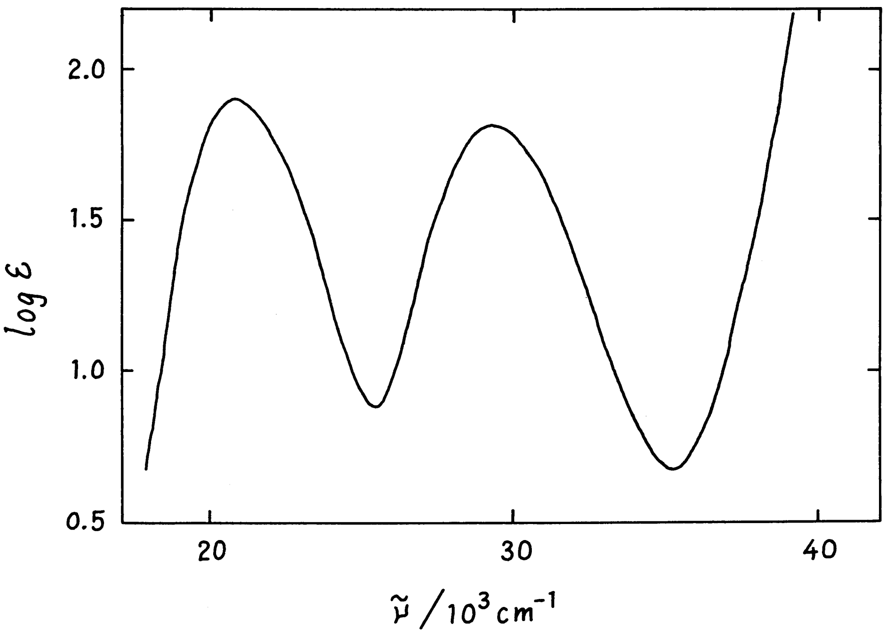

Fig. 1 Absorption spectrum of $[Co(NH_3)_5(enH)](ClO_4)_4$ in 0.02 M $HClO_4$.

$$[Co(NH_3)_5X]^{(3-m)+} + en \longrightarrow [Co(NH_3)_5(en)]^{3+} + X^{m-} \tag{1}$$

$$[Co(NH_3)_5(en)]^{3+} \longrightarrow [Co(NH_3)_4(en)]^{3+} + NH_3 \tag{2}$$

$$[Co(NH_3)_5X]^{(3-m)+} + NH_3 \longrightarrow [Co(NH_3)_6]^{3+} + X^{m-} \tag{3}$$

$$[Co(NH_3)_4(en)]^{3+} + en \longrightarrow [Co(NH_3)_2(en)_2]^{3+} + 2\ NH_3 \tag{4}$$

$$[Co(NH_3)_2(en)_2]^{3+} + en \longrightarrow [Co(en)_3]^{3+} + 2\ NH_3 \tag{5}$$

$$[Co(NH_3)_6]^{3+} + en \longrightarrow [Co(NH_3)_5(en)]^{3+} + NH_3 \tag{6}$$

The ligand X^{m-} given in reactions (1) and (3) may be DMSO.[10] The existence of reaction (6) was confirmed from the product survey of the reaction of $[Co(NH_3)_6](ClO_4)_3$ with ethylenediamine in DMSO.

It should be noted that the reaction of $[Co(H_2O)(NH_3)_5]^{3+}$ with ethylenediamine in DMSO gives $[Co(NH_3)_{6-2n}(en)_n]^{3+}$ very easily. In the standard method for the preparation of $[Co(NH_3)_6]^{3+}$,[11] activated charcoal is required as catalyst. The procedures which have been known for the preparation of $[Co(NH_3)_2(en)_2]^{3+}$ are laborious.[12] The procedures presented here provide a useful method for the preparation of various mixed ligand cobalt(III) complexes containing ammines and polyamines: For example, the reactions of $[Co(H_2O)(NH_3)_5](ClO_4)_3$ with 1,2-diaminopropane, 1,3-diaminopropane (tn), trans-1,2-diaminocyclohexane (cxyn), N-methylethylenediamine (N-meen), 1,4-diaminobutane (tmd), and 1,12-diaminododecane(don) in DMSO were found to give $[Co(NH_3)_{6-2n}(diamine)_n]^{3+}$, where n = 0, 1, 2, and 3 for pn, tn, cxyn, and N-meen and n = 0 and 1 for tmd and don.

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