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## New Route to the Preparation of $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$

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A binuclear complex, $\mu$-carbonato-bis(pentaamminecobalt(III)) sulfate tetrahydrate, has been reported by Kremer and Mac-Coll[1] and Kranig.[2] They have obtained this salt by mixing $CoSO_4$, $(NH_4)_2CO_3$, and $NH_4OH$ at low temperatures and bubbling air through the mixture for a period of 24 h.

It has been shown[3,4] that in the reaction of aquopentaamminecobalt(III) ion with carbon dioxide, hydroxopentaamminecobalt(III) species, which is in equilibrium with the aquopentaamminecobalt(III) ion in aqueous solution, plays an important role in the rate-determining step. In the process of carbon dioxide uptake, formation of $[(NH_3)_5CoCO_3H]^{2+}$ has been proposed as a possible intermediate step. Now, in the same way that a proton is split from this intermediate to form the $[(NH_3)_5CoCO_3]^+$ ion, we could also imagine the splitting of a water molecule between the above-mentioned intermediate and the $[(NH_3)_5CoOH]^{2+}$ ion, to form a binuclear complex

$$[(NH_3)_5CoCO_3H]^{2+} + [HOCo(NH_3)_5]^{2+} \rightarrow [(NH_3)_5CoCO_3Co(NH_3)_5]^{4+} + H_2O$$

In order to examine the possibility of the occurrence of this reaction, $[Co(NH_3)_5H_2O]I_3$, prepared according to the method described by Schlessinger,[5] was employed as a starting material in the reaction

$$2[Co(NH_3)_5H_2O]I_3 + 3Ag_2CO_3 + 2(NH_4)_2SO_4 \xrightarrow[H_2O]{CO_2} 6AgI\downarrow + 2(NH_4)_2CO_3 + [(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$$

Reaction of $[Co(NH_3)_5H_2O]I_3$ (32.7 mmol), $(NH_4)_2SO_4$ (65.7 mmol), and $Ag_2CO_3$ (48.9 mmol) in 200 ml of water at 0 °C, with constant stirring and bubbling of $CO_2$ gas for a period of 2 h, produced an oily liquid, which was then crystallized into deep red crystals, by addition of absolute alcohol. An acidified solution of this product showed no reaction with $K_2S_2O_8$, therefore excluding $[Co(NH_3)_5H_2O]ISO_4$ as a possible reaction product. Yield of the binuclear complex was 49%, based on the amount of $[Co(NH_3)_5H_2O]I_3$ used. Anal. Calcd: $NH_3$, 27.75; Co, 19.19; $SO_4$, 31.38. Found: $NH_3$, 27.50; Co, 19.10; $SO_4$, 31.40. A sample of this complex salt (0.5 g) was heated at 600 °C to a constant weight (0.2501 g). The loss of weight according to the reaction

$$[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O \rightarrow 2CoSO_4 + 10NH_3 + CO_2 + {}^1/_2O_2 + 4H_2O$$

corresponded to 49.98% volatiles ($NH_3$, $CO_2$, $H_2O$, and $O_2$) in the compound (calcd 49.34%). In addition, the deep violet residue ($CoSO_4$) was analyzed for its sulfate content (exptl 61.57%; calcd 61.93%).

Potentiometric titration of a $1.63 \times 10^{-3}$ M solution of the complex, which showed an initial pH of 7.2, gave a mole ratio of $H^+$:Co equal to 0.93 which is consistent with the reaction

$$[(NH_3)_5CoCO_3Co(NH_3)_5]^{4+} + 2H^+ \xrightarrow{H_2O} 2[(NH_3)_5CoH_2O]^{3+} + CO_2$$

The electronic spectrum of the complex showed a d–d transition at 505 m$\mu$ (log $\epsilon$ = 2.14) and a shoulder growing at 350 m$\mu$ on a uv band consistent with the data expected of a $N_5Co$–O–CO–O chromophore.[6] The near-uv band showed a maximum at 255 m$\mu$.

Adding $H_2SO_4$ to the complex for a complete conversion to the $[(NH_3)_5CoH_2O]^{3+}$ ion shifted the bands to 490 m$\mu$ (log $\epsilon$ = 1.69) and 340 m$\mu$, respectively, which are values reported for the aquopentaamminecobalt(III) complex ion.[7]

The DTA curve of the complex was obtained by a Netzch 404 instrument. It showed, against Kaolin as reference, three endothermic peaks at 170, 310, and 490 °C corresponding to the loss of water of crystallization, ammonia, and carbon dioxide, respectively.

These experimental data conclusively prove the formation of a binuclear complex. Furthermore, this reaction is found to be a more convenient synthetic procedure for the formation of the binuclear complex and probably would be suitable for the preparation of similar complexes of Rh and Ir.

**Registry No.** $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2$, 49731-04-6; $[Co(NH_3)_5H_2O]I_3$, 15612-06-3.

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## Correlation of Electron Paramagnetic Resonance Line Intensities with Magnetic Moments for Some Spin-Crossover Systems

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In 1973 we reported observation of separate paramagnetic resonance (EPR) lines due to the $S = {}^1/_2$ and $S = {}^5/_2$ states in the spin-crossover system of tris(dicyclohexyldithiocarbamato)iron(III) (CHDF) at room temperature and 127 K.[1] Identification of these lines was based primarily on the temperature dependence of the line intensities. In particular we identified a broad asymmetric line at $g_{\text{eff}} \simeq 4.3$ that decreased in intensity at low temperature as due to the $S = {}^5/_2$ state; this is consistent with the observation that shortening the metal–ligand bond[2] and decreasing the thermal energy available favors the low-spin case. Also, theory predicts a broad line in the region of $g_{\text{eff}} \simeq 4.3$ for reasonable values of the fine-structure parameters in the $S = {}^5/_2$ system.[3]

Recently Hall and Hendrickson[4] have reported EPR spectra of similar compounds at much lower temperatures than were

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