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Contribution from the Chemistry Department,
Tehran University, Tehran, Iran

New Route to the Preparation of $[(\text{NH}_3)_5\text{CoCO}_3\text{Co}(\text{NH}_3)_5](\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

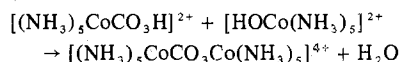
Mansour Abedini

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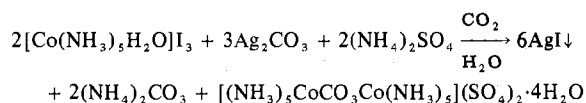
AIC60300Z

A binuclear complex, μ -carbonato-bis(pentaamminecobalt(III)) sulfate tetrahydrate, has been reported by Kremer and Mac-Coll¹ and Kranig.² They have obtained this salt by mixing CoSO_4 , $(\text{NH}_4)_2\text{CO}_3$, and NH_4OH at low temperatures and bubbling air through the mixture for a period of 24 h.

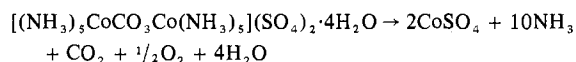
It has been shown^{3,4} that in the reaction of aquopentaamminecobalt(III) ion with carbon dioxide, hydroxopentaamminecobalt(III) species, which is in equilibrium with the aquopentaamminecobalt(III) ion in aqueous solution, plays an important role in the rate-determining step. In the process of carbon dioxide uptake, formation of $[(\text{NH}_3)_5\text{CoCO}_3\text{H}]^{2+}$ has been proposed as a possible intermediate step. Now, in the same way that a proton is split from this intermediate to form the $[(\text{NH}_3)_5\text{CoCO}_3]^{2+}$ ion, we could also imagine the splitting of a water molecule between the above-mentioned intermediate and the $[(\text{NH}_3)_5\text{CoOH}]^{2+}$ ion, to form a binuclear complex



In order to examine the possibility of the occurrence of this reaction, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$, prepared according to the method described by Schlessinger,⁵ was employed as a starting material in the reaction

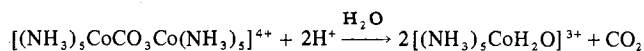


Reaction of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$ (32.7 mmol), $(\text{NH}_4)_2\text{SO}_4$ (65.7 mmol), and Ag_2CO_3 (48.9 mmol) in 200 ml of water at 0 °C, with constant stirring and bubbling of CO_2 gas for a period of 2 h, produced an oily liquid, which was then crystallized into deep red crystals, by addition of absolute alcohol. An acidified solution of this product showed no reaction with $\text{K}_2\text{S}_2\text{O}_8$, therefore excluding $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{ISO}_4$ as a possible reaction product. Yield of the binuclear complex was 49%, based on the amount of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$ 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



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



The electronic spectrum of the complex showed a d-d transition at 505 m μ ($\log \epsilon = 2.14$) and a shoulder growing at 350 m μ on a uv band consistent with the data expected of a $\text{N}_5\text{Co}-\text{O}-\text{CO}-\text{O}$ chromophore.⁶ The near-uv band showed a maximum at 255 m μ .

Adding H_2SO_4 to the complex for a complete conversion to the $[(\text{NH}_3)_5\text{CoH}_2\text{O}]^{3+}$ ion shifted the bands to 490 m μ ($\log \epsilon = 1.69$) and 340 m μ , respectively, which are values reported for the aquopentaamminecobalt(III) complex ion.⁷

The DTA curve of the complex was obtained by a Netzsch 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. $[(\text{NH}_3)_5\text{CoCO}_3\text{Co}(\text{NH}_3)_5](\text{SO}_4)_2$, 49731-04-6; $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{I}_3$, 15612-06-3.

References and Notes

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Contribution from the Physics and Chemistry Departments,
Kent State University, Kent, Ohio 44242

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

Cathy Flick, Edward Gelerinter,* Julia B. Zimmerman, and Norman V. Duffy

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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(dicyclohexyldithiocarbamate)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 $g_{\text{eff}} \approx 4.3$ 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 bond² and decreasing the thermal energy available favors the low-spin case. Also, theory predicts a broad line in the region of $g_{\text{eff}} \approx 4.3$ for reasonable values of the fine-structure parameters in the $S = 5/2$ system.³

Recently Hall and Hendrickson⁴ have reported EPR spectra of similar compounds at much lower temperatures than were

* To whom correspondence should be addressed at Physics Department, Kent State University.