

The Reactivity of the Coordinated Mercapto Group With Various Metal Ions

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Received December 29, 1976

The reactions of tris(2-mercaptoethylamine)cobalt(III), CoL_3 , with cadmium(II), copper(II) and zinc(II) has resulted in the isolation of $[\text{Cd}(\text{CoL}_3)_2]\text{-CdBr}_4$, $[\text{Zn}(\text{CoL}_3)_2]\text{ZnBr}_4$ and $[\text{Cu}(\text{CoL}_3)_2]\text{Br}\cdot 2\text{CuBr}$. These complexes have been characterized by chemical analyses, electronic and infrared spectra and conductivity measurements. The metal ions, Cd, Zn, Cu are believed to be coordinated by one CoL_3 ligand and a bridging bromide. The reactions of tris(2-mercaptoethylamine)cobalt(III) with potential reducing metal ions such as Fe^{+2} or VO^{+2} and oxidizing metal ions such as $\text{Cr}(\text{H}_2\text{O})_6^{+3}$, UO_2^{+4} , and Ce^{+4} has resulted in the isolation of salts of $\text{Co}(\text{CoL}_3)_2^{+3}$. Possible mechanisms which will result in the formation of the $\text{Co}(\text{CoL}_3)_2^{+3}$ cation are discussed.

Introduction

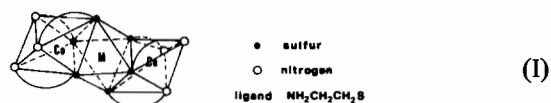
The coordinated mercapto group can function as an effective nucleophile. It can be alkylated or benzylated [1-3] and can also function as a ligand to certain metal ions [4-9]. The fact that the complex $\text{Ni}[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S}_2)_2]\text{Cl}_2$ ($[\text{Ni}(\text{NiL}_2)_2]\text{Cl}_2$) is diamagnetic and all three nickel(II) ions are in a square planar environment [10], suggests that the coordinated mercapto group in the bidentate chelating agent $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2$ (NiL_2) is a strong field ligand. Another example which illustrates that the coordinated mercapto group can function as a strong field ligand is that the tridentate chelating agent, $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_3$ (CoL_3) can force iron(III) into a low spin state [8].

There has been little research into whether the coordinated mercapto group is selective in its chemical reactivity to various electrophiles. Such research is important because the mercapto group often is coordinated to metal ions in many biological molecules [11, 12] and information about the relative reactivity of the coordinated mercapto group might give insight into the specific reactivity of active sites in some metalloproteins. At present it is known that the coordinated mercapto groups on NiL_2 have a greater affinity for the softer cadmium(II) than for the harder but crystal field stabilized nickel(II)

ion [7]. We have also observed that NiL_2 and CoL_3 do not function as chelating agents for all metal ions. The reactions of certain metal ions (M^{+n}) with NiL_2 resulted in the formation of the cation $\text{Ni}(\text{NiL}_2)_2^{+2}$ rather than the heterometallic complexes of the type $\text{M}(\text{NiL}_2)_2^{+n}$. Similarly the reactions of CoL_3 with certain metal ions resulted in the isolation of salts containing the cation $\text{Co}(\text{CoL}_3)_2^{+3}$ rather than the heterometallic cation $\text{M}(\text{CoL}_3)_2^{+n}$. In this paper we will attempt to correlate the nature of the products of the reactions of CoL_3 with various metal ions as a function of the specific metal ion.

Results and Discussion

It has been reported that CoL_3 will function as a tridentate ligand to Ru^{+3} , Co^{+3} , Ni^{+2} and Fe^{+3} [6, 8, 9]. All these metal ions are commonly found in a six coordination geometry and therefore it is reasonable to assume that these metal ions in the complex $\text{M}(\text{CoL}_3)_2^{+2,+3}$ are coordinated to six sulfur atoms (I). However,



zinc(II), cadmium(II) and copper(I) are all d^{10} systems and these metal ions are most commonly found in a tetrahedral geometry. We have isolated the products from the reaction of CoL_3 with Zn^{+2} , Cd^{+2} and Cu^{+2} (a reduction occurred) and the stoichiometries of these products $\text{Cd}(\text{CoL}_3)_2\text{CdBr}_4$, $\text{Zn}(\text{CoL}_3)_2\text{ZnBr}_4\cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{CoL}_3)_2\text{Br}\cdot 2\text{CuBr}\cdot \text{H}_2\text{O}$ are similar to the products isolated in previous studies. An attempt was made to prepare $\text{Hg}(\text{CoL}_3)_2\text{-HgBr}_4$ but only an impure product was isolated. Although it is tempting to assume that the $\text{Cu}(\text{I})$, $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ are in a six coordinate environment bonded to six coordinated sulfur groups, it is also possible that these complexes are in tetrahedral (II) or five coordinate environments (III). The molar con-

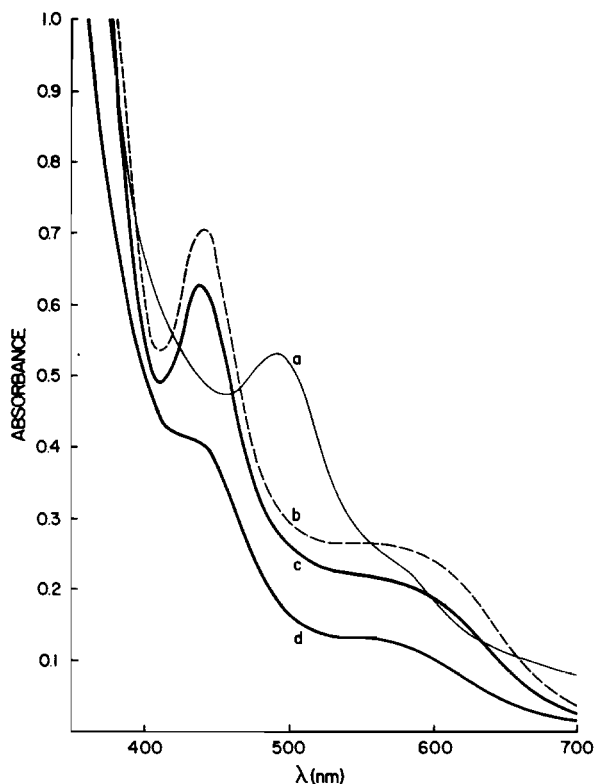
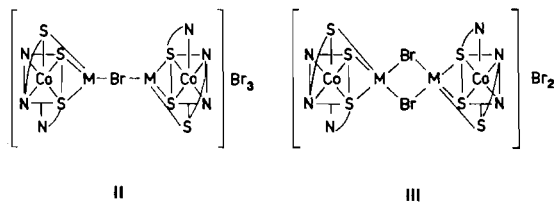


Figure 1. Electronic spectra of $M(\text{CoL}_3)_2^{n+}$ complexes. a) $\text{Fe}(\text{CoL}_3)_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, b) $\text{Co}(\text{CoL}_3)_2\text{Br}_3$, c) $\text{Cd}(\text{CoL}_3)_2\text{CdBr}_4$, d) $\text{Zn}(\text{CoL}_3)_2\text{ZnBr}_4 \cdot 2\text{H}_2\text{O}$. The concentration of all complexes was $1 \times 10^{-4} M$.

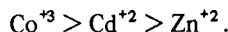
ductivity of the $\text{Zn}(\text{CoL}_3)_2\text{ZnBr}_4 \cdot 2\text{H}_2\text{O}$ ($8.81 \times 10^{-4} M$ in water) is 400 ohm^{-1} while the conductivity for the $\text{Cd}(\text{CoL}_3)_2\text{CdBr}_4$



($1.06 \times 10^{-3} M$ in water) is 490 ohm^{-1} . Such conductivities suggest that at least four ions are in solution [13]. Structure II is most consistent with this data. A crystal structure will be required to resolve the final structure of these complexes.

The infrared spectra of all these complexes are similar. The electronic spectra of $\text{Co}(\text{CoL}_3)_2\text{Br}_3$, $\text{Zn}(\text{CoL}_3)_2\text{ZnBr}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cd}(\text{CoL}_3)_2\text{CdBr}_4$ all have peaks at $560 \text{ m}\mu$ and $440 \text{ m}\mu$ (Fig. 1) (the only exception is $\text{Fe}(\text{CoL}_3)_2\text{Cl}_3$. The iron(III) has a t_{2g}^5 electronic configuration [8]. The similarity of these electronic spectra suggest that the central metal ions in all the above complexes are not involved in the electronic transitions responsible for the $560 \text{ m}\mu$

and $440 \text{ m}\mu$ bands. These transitions must involve the terminal CoL_3 groups. It is also likely that the electron transitions at $560 \text{ m}\mu$ and $440 \text{ m}\mu$ involve a charge transfer from cobalt(III) to sulfur. The extinction coefficients are too high to be only a d-d type transition and the nonbonding electron pairs on the sulfurs are too diffuse to be effectively delocalized into the cobalt(III). The extinction coefficients (Fig. 1) at 560 nm and 440 nm vary with the central metal ion. The ability of the coordinated sulfur to accept electrons from the terminal cobalt(III) ions must be influenced by the nature of the central metal ion. The order of intensities of the bands as a function of the central metal ion is:



It is known that the softer Cd^{+2} interacts more strongly with the relatively soft sulfur atoms than the harder zinc(II) [14]. There were no bands observed in the visible region of electronic spectra of $\text{Cu}(\text{CoL}_3)_2\text{Br} \cdot 2\text{CuBr} \cdot \text{H}_2\text{O}$. The extent of interaction of the monovalent copper with the coordinated sulfurs should be less than the divalent zinc. Finally, we would expect the low spin d^6 trivalent cobalt(III) to have the strongest interaction with the coordinated mercapto groups. One of the factors which determine the value of the extinction coefficients for a compound is the difference in the dipole moment of the excited state and the ground state for the molecule. It is expected that the extent of charge transfer from the cobalt(III) to the sulfurs should influence this dipole moment difference. We would also expect the wavelength maximum to vary as the degree of charge transfer from the cobalt(III) to sulfur varies. However the band maxima observed are broad and therefore small differences in energies are not observable.

Although the $\text{Cu}(\text{CoL}_3)_2\text{Br} \cdot 2\text{CuBr} \cdot \text{H}_2\text{O}$ was prepared from divalent copper, this complex is diamagnetic. Therefore all the copper ions are likely to be in the univalent state. This insoluble complex might be formulated as a double salt, $[\text{Cu}(\text{CoL}_3)_2]\text{Br} \cdot 2\text{CuBr} \cdot \text{H}_2\text{O}$ or as a neutral complex formulated as $(\text{CuL}_3)\text{CuBr}_2\text{CuBr}(\text{OH}_2)\text{Cu}(\text{CoL}_3)$. Some double salts can function as a solid state electron conductor, however, this compound proved to be a nonconductor.

In contrast to the above reactions where CoL_3 functions as a chelating agent to various metal ions, there are several examples of reactions of metal ions (other than Co(III) with CoL_3) in which a rearrangement type product is isolated, $\text{Co}(\text{CoL}_3)_2\text{X}_3$. On the basis of thermodynamic stability the most stable trinuclear cation employing CoL_3 as a ligand is $\text{Co}(\text{CoL}_3)_3^{+3}$. All the heterometallic complexes of the type $M(\text{CoL}_3)_2^{n+}$, where $M = \text{Fe}^{+3}, \text{Ru}^{+3}, \text{Ni}^{+2}, \text{Zn}^{+2}, \text{Cd}^{+2}$, if left in aqueous solution for a long enough period of time will eventually result in the

formation of salts of $\text{Co}(\text{CoL}_3)_2^{+3}$. We have even been able to isolate $[\text{Co}(\text{CoL}_3)_2](\text{B}(\text{C}_6\text{H}_5)_4)_3$ by refluxing CoL_3 in water for several days and then adding $\text{NaB}(\text{C}_6\text{H}_5)_4$. The stability of $\text{Co}(\text{CoL}_3)_2^{+3}$ cation is due to the fact that each cobalt ion contains six electrons in the t_{2g} orbital and therefore each cobalt(III) ion has the maximum ligand field stabilization in an octahedral field. The inevitable isolation of the salts of $\text{Co}(\text{CoL}_3)_2^{+3}$ upon the reactions of CoL_3 with all the metal ions listed above is a good example of thermodynamic control of products. On the other hand the isolation of the heterometallic complexes of $\text{M}(\text{CoL}_3)_2^{+n}$ are examples of kinetic control of a reaction.

We have observed that certain metal ions will speed up the formation of the thermodynamically stable product, the salts of $\text{Co}(\text{CoL}_3)_2^{+3}$. The reactions of FeCl_2 , and VOSO_4 with CoL_3 in water resulted in the isolation of $\text{Co}(\text{CoL}_3)_2\text{Cl}_3$ and $[\text{Co}(\text{CoL}_3)_2]_2(\text{SO}_4)_3$ respectively. These reactions were complete within one to three hours. However, refluxing CoL_3 in water for 3 hours did not result in any significant formation of salts of $\text{Co}(\text{CoL}_3)_2^{+3}$.

A possible mechanism for the formation of the $\text{Co}(\text{CoL}_3)_2^{+3}$ cation might involve M^{+2} coordinating to one, two or possibly all three sulfurs on the CoL_3 . Upon coordination of M^{+2} to CoL_3 , an electron from M^{+2} transfers to the cobalt(III) by means of a bridging sulfur. There is precedence for such an inner-sphere electron transfer mechanism [15, 16]. However it is also possible for an electron transfer from M^{+2} to cobalt(III) by means of a direct metal-metal bond. Both $\text{Fe}(\text{CoL}_3)_2^{+3}$ and $\text{Ru}(\text{CoL}_3)_2^{+3}$ contain one unpaired electron [9]. Based on an EPR study of these complexes, the unpaired electron can delocalize from the Fe^{+3} or Ru^{+3} to both terminal cobalts. This delocalization occurs in part by a direct iron-cobalt or ruthenium-cobalt bond [9]. By employing a better reducing agent than Fe^{+3} or Ru^{+3} such as Fe^{+2} , or VO^{+2} , which could coordinate to the face of CoL_3 , a more complete transfer of an electron from M^{+2} to the cobalt(III) is expected. Such an irreversible transfer of an electron to the cobalt(III) would be more likely if M^{+2} is coordinated to all three sulfurs instead of one sulfur. By M^{+2} coordinating to the face of CoL_3 , a shorter $\text{M}-\text{Co}(\text{III})$ distance will result and the electron transfer process should occur with less energy. Whether the electron transfer occurs through the sulfurs into the cobalt(III) or directly into the cobalt(III), the resulting cobalt(II) complex should be relatively labile thereby producing free cobalt(II) in solution. The cobalt(II) in the presence of CoL_3 and a potential oxidizing agent should result in the highly stable low spin diamagnetic $\text{Co}(\text{CoL}_3)_2^{+3}$ salts.

The reaction of Cr^{+2} with CoL_3 resulted in the isolation of a mixture of complexes containing both chromium and mercaptoethylamine. We have not been able to separate this mixture. Asher and Deutsch

observed that the product of the reaction of N,S-(2-mercaptoethylamine)bis(ethylenediamine)cobalt(III) ($\text{Coen}_2\text{L}^{+2}$) with chromium(II) is pentaquo(2-mercaptoethylammonium-S)chromium(III) ($\text{Cr}(\text{H}_2\text{O})_5\text{LH}^{+3}$) [16]. Based on the isolated product it appears that an electron transfer reaction occurred from $\text{Cr}(\text{II})$ to the $\text{Co}(\text{III})$ via the bridging mercapto group. After the electron transfer, the Co to S bond is broken and the 2-mercaptoethylamine remained coordinated to the chromium(III). Although we do not know the exact nature of the products we isolated in the reaction of CoL_3 and Cr^{+2} , it is reasonable to assume that a similar mechanism is involved in this reaction as was observed by Deutsch and Archer.

We also observed that the reaction of CoL_3 with Fe^{+3} in the presence of an iodide ion (versus chloride ion) resulted in the isolation of the compound $\text{Co}(\text{CoL}_3)_2\text{I}_3$. Iodide is a better reducing anion than chloride. Since the iodide is not likely to bond to the coordinated mercapto group, it is more likely that a direct electron transfer occurs from the iodide to the cobalt(III).

There is some synthetic data which cannot be explained by the above inner-sphere electron transfer mechanism. The reaction of $\text{Cr}(\text{H}_2\text{O})_6^{+3}$, Ce^{+4} , and UO_2^{+2} with CoL_3 resulted in the isolation of the chloride or bromide salts of $\text{Co}(\text{CoL}_3)_2^{+3}$. All these metal ions are more likely to function as oxidizing agents rather than reducing agents. These reactions must go by a different mechanism than the one just discussed. Nevertheless there is no doubt that an electron transfer process is involved. The reaction of copper(II) (a potential oxidizing agent, like Ce^{+4} , UO_2^{+2} , $\text{Cr}(\text{H}_2\text{O})_6^{+3}$) with CoL_3 resulted in the isolation of $\text{CoL}_3-\text{Cu}(\text{I})$ complex. However, the same reaction of $\text{Cu}(\text{II})$ with CoL_3 at higher temperatures resulted in the isolation of the bromide salt of $\text{Co}(\text{CoL}_3)_2^{+3}$. The only likely source of electrons for the reduction of copper(II) is the electrons on the coordinated sulfur. The oxidation of the mercaptide group will most likely result in labilizing the cobalt to sulfur bond. Presently we are studying in detail the reactions of CoL_3 with various types of oxidizing agents.

Experimental

Materials

The CoL_3 , $\text{Co}(\text{CoL}_3)_2\text{Br}_3$ [6], were prepared by methods found in the literature. All other inorganic and organic chemicals were of reagent grade.

Physical Measurements

Infrared spectra were obtained on a Perkin-Elmer 337 in Nujol mull, electronic spectra were taken on a Beckman DK-2A and a Beckman Acta recording

spectrophotometer. The conductivity of each aqueous solution was measured using an Industrial Instruments conductivity bridge at a frequency of 1000 Hz. The conductivity of the solid was obtained by preparing a pellet under a pressure of 3.17×10^7 kg/m². The pellet was placed in a dead weight gauge between platinum electrodes and the conductivity was measured with the Industrial Instrument conductivity bridge. Nitrogen analyses were carried out using a Coleman 29 Nitrogen analyzer and carbon and hydrogen analysis were performed by Galbraith Analytical Laboratories.

Preparation of Metal Complexes

$[Co(NH_2CH_2CH_2S)_3]_2Cd \cdot CdBr_4$

To a suspension of 2.35 g of tris(2-mercaptoethylamine)cobalt(III) (8.2×10^{-3} mol) and 200 ml of water was added 40 ml of an aqueous solution of 4.9×10^{-3} mol of $(NH_4)_2CdCl_4$ (prepared from 0.9 g of $CdCl_2$ and excess NH_4Cl). This mixture immediately turned deep red-brown. The solution was heated and stirred for approximately one hour, after which it was filtered to remove any unreacted tris(2-mercaptoethylamine)cobalt(III). The solution was allowed to stand until it reached room temperature and was filtered again. The filtrate was concentrated *in vacuo* to 180 ml and a saturated aqueous solution containing 3.0 g of potassium bromide was added to the filtrate. The solution was placed in a refrigerator for 48 hours and resulting black crystals were filtered and washed twice with absolute ethanol and dried *in vacuo* over P_2O_5 . *Anal.* Calcd. for $Cd[Co(NH_2CH_2CH_2S)_3]_2Br_4$: C, 12.85; H, 3.22; N, 7.5; Found: C, 12.70; H, 3.23; N, 7.3.

$[Zn[Co(NH_2CH_2CH_2S)_3]_2]ZnBr_4 \cdot 2H_2O$

The same procedure was employed as above except $ZnCl_2$ was the source of zinc. *Anal.* Calcd. for $Zn[Co(NH_2CH_2CH_2S)_3]_2ZnBr_4 \cdot 2H_2O$: C, 13.62; H, 3.78; N, 7.96. Found: C, 13.64; H, 4.23; N, 7.79.

$Cu(CoL_3)_2Br \cdot 2CuBrH_2O$

To a solution of $CuCl_2 \cdot 2H_2O$ (.57 g, 0.003 mol) in 75 ml of water, a slurry of CoL_3 (1.58 g, 0.0055 mol) in 75 ml of water was added. The mixture was stirred at room temperature for one hour, in which time a dark brown solution formed. This solution was filtered, then concentrated *in vacuo* to about 40 ml. A saturated solution of KBr (1.001 mol) was then added and the reaction solution left to stand at 10 °C overnight. A fine black powder was collected by filtration and washed with cold absolute ethanol. *Anal.* Calcd. for $(CoL_3)_2Cu_3Br_3H_2O$: C, 14.09; H, 3.75; N, 8.22; Co, 11.52; Cu, 18.64. Found: C, 14.09; H, 4.05; N, 8.21; Co, 10.92; Cu, 18.27.

Reactions of Tris(2-mercaptoethylamine)cobalt(III) with Iron(II), Cerium(IV), UO_2^{+2} , $Cr(H_2O)_6^{+3}$ and VO^{+2} Ions

Tris(2-mercaptoethylamine)cobalt(III) (0.0035 mol) was added to the metal chloride salt (0.0018 mol) in 100 ml of H_2O . The solution became brown on mixing the mixture. The slurry was heated and stirred for one and half hours to three hours and then the unreacted CoL_3 was filtered out of solution. The solution was concentrated using a rotating evaporator to about 50 ml. A saturated aqueous solution of $NaBr$ or $NaB(C_6H_5)_4$ was added to the solution. Cooling followed by filtering a black powdery product resulted in the isolation of $Co(CoL_3)_2Br_3$ or $[Co(CoL_3)_2] \cdot (B(C_6H_5)_4)_3$. These products were washed with cold absolute ethanol and dried under vacuum.

An alternative method was used to isolate the chloride salts of the cation $[Co(CoL_3)_2]^{+3}$. Upon filtering out the unreactive CoL_3 , 300 ml of acetone was added to the solution. A precipitate resulted after storage at 0 °C for ten hours. The precipitate was washed with absolute ethanol and then acetone.

A similar procedure was employed using $VOSO_4 \cdot 2H_2O$ except that after the unreacted CoL_3 was filtered out of solution, the filtrate was reduced to 50 ml on a steam bath and 90 mls of isopropyl alcohol was then added. The electronic spectrum of $Co_6L_{12}(SO_4)_3$ corresponds to $Co_3L_6Br_3$. Also no vanadium-oxygen stretches were observed in the infrared spectrum. *Anal.* Calcd. for $Co_6(NH_2CH_2CH_2S)_{12}(SO_4)_3 \cdot 2H_2O$: C, 17.1; H, 5.66; N, 11.31. Found: C, 17.02; H, 5.35; N, 11.31.

Qualitative analyses for the heterometal in the precipitate were negative in all the above cases and the electronic and infrared spectra and nitrogen analyses correspond to that of $Co(CoL_3)_2X_3$, where $X = Cl, Br$ or $B(C_6H_5)_4$. The X-ray powdery pattern of the $Co(CoL_3)_2Br_3$ isolated from the above reactions corresponded to that of $Co(CoL_3)_2Br_3$ prepared from the reaction of CoL_3 with Co^{+2} in air.

Acknowledgments

Support of this research by the Bowling Green State University Faculty Research Committee and the Research Corporation's Frederick Gardner Cottrell Grant-in-aid is gratefully acknowledged. Special thanks to G. Freeh for doing several of the preliminary experiments for this research. P. Butler acknowledges the NSF-URP for a summer grant.

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