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Complexes Derived from Strong Field Ligands. XV. The Formation of Trinuclear Complexes by Coördination of Tris-(β-mercaptoethylamine)-cobalt(III) to Metal Ions

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Tris-(β-mercaptoethylamine)-cobalt(III), CoL_3, is diamagnetic and apparently exists in only a single isomeric form. That form is probably the facial or 1–2–3 geometric isomer. CoL_3 forms highly crystalline compounds of the general formula $[M(CoL_3)_2]X_n$. The centrally located metal atom M is bound by three mercaptide bridges to each CoL_3 unit. These examples establish the existence of triple bridges in mercaptide systems. For M = Ni(II), $\mu_{eff} = 3.2$ B.M.

During the course of earlier studies on the complexes of transition metal ions with β-mercaptoethylamines, di- and trinuclear complexes have been isolated and characterized.[1,2] In the larger number of cases, these unusual materials have been derived from planar complexes of the stoichiometry ML_2 (where L represents $NH_2CH_2CH_2S^-$ and M is Ni or Pd) by utilizing those substances as coördinating agents and causing them to react with metal ions to form products of the composition $[M'(ML_2)_2]^{2+}$. It has been shown that the metal ions in the side and central positions may be permuted at will by the application of this principle.[2] Further, the generality of the reaction provides strong inferential evidence favoring a *cis* orientation of the mercapto groups in planar mononuclear derivatives of mercaptoamines. This result is in keeping with the orientation of the π-orbitals on the central atom. The d_{xz} and d_{yz} orbitals may each interact with the π-orbital of an individual sulfur atom in the *cis* structure, while a competitive situation exists in π-bonding in the *trans* planar case.

The unsymmetrical nature of β-mercaptoethylamine also leads to the possibility of geometrical isomerism in the octahedral case (facial, 1–2–3, and peripheral, 1–2–6). The most readily available example for the search for this type of isomerism should be provided by tris-(β-mercaptoethylamine)-cobalt(III), CoL_3. This light blue substance has been prepared by several investigators.[3,4] The material exhibits only a very slight solubility in water and the usual organic solvents. It has been prepared by direct oxidation of cobalt(II) in the presence of the ligand[3] and by the displacement of ammonia from $Co(NH_3)_6^{3+}$.[4] A third synthesis is reported here, in which the β-mercaptoethylamine displaces $EDTA^{4-}$ from the hexadentate complex $Co(EDTA)^-$.

$$Co(EDTA)^- + NH_2CH_2CH_2SH \longrightarrow Co(NH_2CH_2CH_2S)_3 + H_3EDTA^-$$

The very slight solubility of the product results in gelatinous precipitates by the direct oxidation. The relatively slow displacement reactions permit crystallization of the product as it forms, thereby leading to a relatively tractable solid of larger crystal size. Magnetic measurements ($\chi_M = -55.4 \times 10^{-6}$ c.g.s. unit, $T = 300°$) establish the expected spin paired state of the cobalt atom in $Co(NH_2CH_2CH_2S)_3$.

The availability of three distinct synthetic routes for the preparation of the cobalt(III) complex provides an opportunity to look for geometric isomers although more general separation techniques are not available because of the limited solubility of the substance. The oxidative procedure and the reaction with $Co(EDTA)^-$ might be expected to give quite different results in this regard. The former should yield an equilibrium mixture of isomers while the latter should be highly stereospecific, with a good probability of producing only a single isomer.[5,6] Despite this situation, the only detectable difference in samples

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(1) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962).

(2) D. C. Jicha and D. H. Busch, *ibid.*, **1**, 878 (1962).

(3) E. Felder, E. Paolio, and U. Tiepolo, *Farmaco* (Pavia), *Ed. Sci.*, **10**, 836 (1955).

(4) R. G. Neville and G. Gorin, *J. Am. Chem. Soc.*, **78**, 4891, 4893 (1956).

(5) D. H. Busch, D. W. Cooke, K. Swaminathan, and Y. A. Im, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, ed., The MacMillian Co., New York, N. Y., 1961, p. 139.

(6) D. H. Busch, K. Swaminathan, and D. W. Cooke, *Inorg. Chem.*, **1**, 260 (1962).

obtained by different procedures is in the state of subdivision of the solid.

By analogy with the nickel(II) and palladium(II) complexes of the form ML_2, a *cis* or *facial* configuration may be favored for the cobalt(III) complex, CoL_3. The *facial* arrangement of the sulfur atoms of three ligand molecules would favor the formation of π-bonds with the t_{2g} electrons of the central atom. The d_{xy}, d_{xz}, and d_{yz} orbitals are of proper symmetry to form three equivalent mutually orthogonal π-bonds to groups located in the 1, 2, and 3 positions in the octahedral structure. In consequence, the *facial* configuration is most rationally assumed for the cobalt(III) complex. This conclusion receives strong support in the experiments reported below.

The tendency of the coördinated sulfur atoms in $Co(NH_2CH_2CH_2S)_3$ to form bridges to other metal ions has been investigated and two unusual trinuclear compounds have been prepared in high yield and purity by taking advantage of this proclivity. The insoluble complex CoL_3 dissolves in solutions of Co(II) or Ni(II) ions and also in solutions of $Co(NH_3)_5Br^{2+}$. In all cases, deep red-brown solutions are obtained. The addition of potassium bromide to solutions prepared by the dissolution of CoL_3 in aqueous cobalt(II) chloride results in the crystallization of dark red-brown crystals of the composition $[Co^{III}\{Co^{III}(L)_3\}_2]Br_3$. Magnetic measurements ($\chi_M = -115 \times 10^{-6}$ c.g.s. unit, $T = 303°$) confirm the oxidation state of three for all three cobalt atoms. It is apparent that air oxidation of cobalt(II) to cobalt(III) occurs rapidly and extensively in this system. The displacement reaction

$$Co(NH_3)_5Br^{2+} + 2CoL_3 \longrightarrow [Co(CoL_3)_2]^{3+} + Br^- + 5NH_3$$

proceeds smoothly, yielding an identical product for which $\chi_M = -119 \times 10^{-6}$ c.g.s. unit, $T = 303°$.

An interesting interrelation exists between the structures of CoL_3 and the trinuclear species $[Co(CoL_3)_2]^{3+}$. In the event that the structure of CoL_3 involves mutual *cis* orientation of all three sulfur atoms, as suggested above, each mole of this complex may form three sulfur bridges to the unique (third) cobalt atom. Thus the sulfur atoms from two moles of CoL_3 can occupy all six coördination positions about the third cobalt atom, as shown in Fig. 1. It follows that the anhydrous salt $[Co(CoL_3)_2]Br_3$ should dissolve without reaction to produce a solution containing a tri-univalent electrolyte. The molar conductance of 362 ohm^{-1} is consistent with this view. Although it must be admitted that the coördination of bromides might occur in the solid state and that the rate of aquation might be extremely fast, thereby producing a tri-univalent electrolyte by coördination of solvent molecules in solution, the result is consistent with the proposal that only sulfur atoms are bound to the centermost cobalt. The argument remains equivocal at this point.

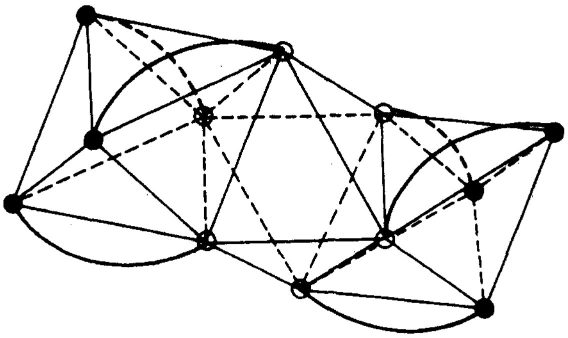

Fig. 1.—The proposed structure for $[M\{Co^{III}(L)_3\}_2]X_n$ ($L = H_2NCH_2CH_2S^-$): ○ = sulfur; ● = nitrogen.

The product formed by the dissolution of the cobalt complex CoL_3 in media containing the nickel(II) ion offers a parallel but more convincing behavior. It is immediately suggested that the

$$2Co(NH_2CH_2CH_2S)_3 + Ni^{2+} \longrightarrow [Ni\{Co(NH_2CH_2CH_2S)_3\}_2]^{2+}$$

nickel–dicobalt complex should behave as a di-univalent electrolyte. The molar conductance of 231 ohm^{-1} is completely consistent with this requirement of the hypothesis. Further, if the proposed structure is correct, the nickel(II) atom in $[Ni(CoL_3)_2]Br_2$ is located in an octahedral site, with perhaps only a weak trigonal component associated with the threefold axis passing through the centers of the three metal ions. In consequence, the precepts of modern ligand field theory suggest that the nickel(II) atom may well exhibit a normal spin-free ground state.[7] This expectation is fully supported by the observed magnetic moment of 3.23 B.M. for the bromide salt. The fact must be emphasized that this result is not explainable in terms of the weakened donor ability of a sulfur atom which might occur as a result of prior coördination to another metal atom. For example, in the compounds $[Ni(NiL_2)_2]X_2$, $[Ni(PdL_2)_2]X_2$, and $[Pd(NiL_2)_2]X_2$, the nickel(II)

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(7) C. H. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81** 538 (1959).

atom is best able to form a square planar array of donor atoms and the expected diamagnetism is observed.[1,2] It is, of course, not unusual to observe spin-free nickel(II) in complexes with strong donors,[8] although the inorganic chemist is just beginning to realize that the stereochemical limitations and efficacies of various ligands may play as significant a role in establishing the multiplicity of the ground state as does the ligand field strength.

The existence and properties of trinuclear materials of the composition $[M(CoL_3)_2]X_n$ is best explained on the basis of the structure given in Fig. 1. These substances serve to further generalize the great bridge forming tendency of the coördinated mercaptide group, revealing that triple, as well as double, bridges may be formed. It is likely that single mercaptide bridges are actually the least abundant. Continuing investigations in these Laboratories suggest that forced *trans* planar structures, such as that of $Ni(R_2NCH_2CH_2S)_2$,[9] are not conducive to bridge formation. It is expected that the several investigations on the complexes of mercaptoamines presently in progress in these Laboratories will further delineate the factors determining the tendency of the mercaptide function to coördinate to one and two metal ions. It is not unlikely that this function might bind three metal ions together under particularly favorable conditions.

Experimental

The determinations of conductances and magnetic moments were conducted as reported previously.[1,2] Infrared spectra were routinely utilized for control purposes. Analyses were performed by Galbraith Microanalytical Laboratories.

Tris-(β-mercaptoethylamine)-cobalt(III) $[Co(NH_2CH_2CH_2S)_3]$.—Five g. of potassium ethylenediaminetetracetatocobaltate(III) dihydrate (0.0109 mole) was dissolved in 75 ml. of water. To this solution were added 3.79 g. of β-mercaptoethylamine hydrochloride (0.0334 mole) and 2.62 g. of sodium hydroxide (0.0654 mole) in 75 ml. of water. The resulting solution was stirred and heated gently during the displacement reaction which ensued. After several minutes a heavy blue flocculent solid started to precipitate from solution. Stirring was continued for an additional period of approximately 0.5 hr., and the solid was collected by filtration. Because of its flocculent nature the solid produced a thick matte on the filter funnel making it extremely difficult to wash the substance free of solution. Therefore, the partially dry solid was transferred to a flask and washed by decantation with 100-ml. portions of water until the wash water was nearly colorless. The solid was filtered again and washed twice with 25-ml. portions of water and twice with 25-ml. portions of absolute ethanol; yield, 2.1 g. A small amount of the complex crystallized from the filtrate on standing for several hours (0.18 g.); total yield, 2.28 g. (91.6%). *Anal.* Calcd. for $[Co(NH_2CH_2CH_2S)_3]$: C, 25.08; H, 6.32; N, 14.62; S, 33.47. Found: C, 25.03; H, 6.02; N, 14.63; S, 33.13.

Hexakis-(β-mercaptoethylamine)-tricobalt(III) Bromide, $[Co\{Co(NH_2CH_2CH_2S)_3\}_2]Br_3$. Method 1.—Bromopentamminecobalt(III) bromide, $[Co(NH_3)_5Br]Br_2$, (3.96 g., 0.010 mole) was added to a suspension of 4.74 g. of tris-(β-mercaptoethylamine)-cobalt(III) in 400 ml. of water. The resulting suspension was heated and stirred for approximately 1 hr., during which time much of the solid dissolved forming a deep red-brown solution. The solubilization was accompanied by the evolution of ammonia gas. A small amount of undissolved $[Co(NH_2CH_2CH_2S)_3]$ was removed by filtration and washed free of the solution with a small quantity of water. The solution was filtered again at room temperature and concentrated *in vacuo* to approximately 250 ml. The filtrate was warmed and a warm saturated solution of potassium bromide (3.5 g.) was added slowly. The solution was allowed to stand in the cold for a few hours. The dark crystals (red-brown when viewed under a microscope) were filtered, washed twice with cold absolute ethanol, and dried *in vacuo* over P_4O_{10} with continuous pumping; yield, 2.91 g. Concentration of the highly colored filtrate to one-third its volume produced 3.54 g. of crystalline product upon cooling for several hours; total yield, 6.45 g. (73.8%). *Anal.* Calcd. for $[Co\{Co(NH_2CH_2CH_2S)_3\}_2]Br_3$: C, 16.50; H, 4.16; N, 9.62; S, 22.03; Br, 27.45. Found: C, 16.77; H, 4.39; N, 9.78; S, 21.53; Br, 27.39.

Hexakis-(β-mercaptoethylamine)-tricobalt(III) Bromide. Method 2.—The substitution of cobalt(II) chloride 6-hydrate in place of the bromopentamminecobalt(III) bromide resulted in the formation of a deep red solution from which $[Co\{Co(NH_2CH_2CH_2S)_3\}_2]Br_3$ was isolated by the addition of a saturated solution of potassium bromide in water; yield, 65.9%. *Anal.* Calcd. for $[Co\{Co(NH_2CH_2CH_2S)_3\}_2]Br_3$: C, 16.50; H, 4.16; N, 9.62; S, 22.03; Br, 27.45. Found: C, 16.61; H, 4.58; N, 9.73; S, 22.47; Br, 27.38.

The corresponding chloride salt is much more soluble in water and in absolute ethanol and could not be isolated in an acceptable state of purity.

Hexakis-(β-mercaptoethylamine)-dicobalt(III)-nickel(II) Bromide, $[Ni\{Co(NH_2CH_2CH_2S)_3\}_2]Br_2$.—This compound was prepared by Method 2 employed for the corresponding cobalt(III) adduct of $[Co(NH_2CH_2CH_2S)_3]$ and isolated in the form of the bromide salt by the addition of a saturated solution of potassium bromide to a warm solution of the chloride salt. The bromide of nickel(II) is slightly less soluble than the cobalt(III) adduct and larger crystals are formed if the solution is kept warm during the addition of potassium bromide; yield, 80.6%. *Anal.* Calcd. for $[Ni\{Co(NH_2CH_2CH_2S)_3\}_2]Br_2$: C, 18.16; H, 4.58; N, 10.60; S, 24.25; Br, 20.15. Found: C, 18.34; H, 4.72; N, 10.34; S, 23.97; Br, 19.86.

Aqueous solutions of the cobalt(III) and nickel(II) adducts of $[Co(NH_2CH_2CH_2S)_3]$ undergo no apparent decomposition upon standing for a few days; however, the

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(8) P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960).

(9) C. Root and D. H. Busch, unpublished results.

addition of aqueous ammonia promotes the separation of [Co($NH_2CH_2CH_2S)_3$] from solution.

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The Influence of Metal Chelation on the Structure of Chelidamic Acid

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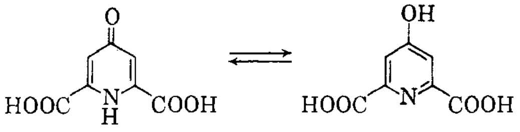
The acid dissociation constants of 2,6-dicarboxy-4-hydroxypyridine (chelidamic acid) have been determined potentiometrically in water at 25°. Metal chelation was found to have an acid-strengthening effect on the 4-hydroxy group in chelidamic acid. The extent of this effect varied with the metal ion that was chelated. The pK_a of the hydroxy group in the metal chelate was found to increase in the order: Cu(II) < Co(II) < Zn(II) < Ni(II) < Mn(II).

The interest in the behavior of metal chelates has been centered largely around the effects that the ligand molecule, or various modifications of it, has on the chemistry of the metal ion. On the other hand the effect of metal ion chelation on the properties of the organic moiety should be of great interest, especially to biochemists.

It is well known that 2-hydroxypyridine and 4-hydroxypyridine in solution exist largely in their tautomeric forms as 2-pyridone and 4-pyridone, respectively, due to keto–enol tautomerism. In the present study, chelidamic acid, a substituted 4-pyridone with chelate-forming groups, was selected to determine whether chelation had any effect on this keto–enol tautomerism.



Keto form Enol form

Experimental

Purification of Chelidamic Acid and 2,6-Pyridinedicarboxylic Acid.—Chelidamic acid, obtained from K and K Laboratories, Inc., New York, N. Y., was purified by the following procedure: the crude acid was dissolved in 1 *M* NH_3 and warmed with animal charcoal, the solution was filtered, and the filtrate was neutralized with dilute HNO_3 to precipitate a pale yellow solid. This solid was redissolved in warm dilute HNO_3 and the solution was cooled and diluted, to yield a white precipitate. This precipitate was washed repeatedly with ice-cold water and finally recrystallized from ethanol. The compound obtained was colorless, m.p. 250°; lit.[1] m.p. 248°. The equivalent weight of the compound was determined by a potentiometric titration (calcd., 91.56; found, 92.20).

2,6-Pyridinedicarboxylic acid was obtained from K and K Laboratories, Inc., New York, N. Y. The compound, after recrystallizing several times from hot water and finally from ethanol, was colorless and melted with decomposition at 252° (lit.[2] 255°). The equivalent weight of the compound was determined by a potentiometric titration (calcd., 83.56; found, 83.80).

Acid Dissociation Constants.—The acid dissociation constants of chelidamic acid were determined potentiometrically as follows: a weighed quantity of the acid was dissolved in 100 ml. of water and titrated in a water-jacketed vessel at 25 ± 0.1° in an atmosphere of nitrogen with a solution of carbonate-free NaOH. A Beckman Model G pH meter, equipped with a glass–saturated calomel electrode pair and calibrated with buffer solutions at pH 4.00 and 7.00, was used for all pH measurements.

The acid dissociation constants of chelidamic acid also were determined spectrophotometrically by measuring the absorbances of a series of solutions of varying pH containing 4×10^{-5} *M* chelidamic acid. The ionic strength of each solution was maintained at 0.1 by the addition of $NaClO_4$.

The pH values of solutions in the extreme ranges (<2 or >11) were adjusted with perchloric acid or carbonate-free sodium hydroxide. In the intermediate ranges of pH, buffer solutions were used. The buffer components were CH_3CO_2H, Na[O_2CCH_3], $NaBO_2$, K_2HPO_4, KH_2PO_4, and NH_3.

The ultraviolet spectra of all solutions were obtained with a Beckman Model DB or Cary Model 11 recording

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[1] E. Riegel and M. C. Reinhard, *J. Am. Chem. Soc.*, **48**, 1334 (1926).

[2] M. Henze, *Ber.*, **67**, 751 (1934).