

Synthesis, Spectroscopy and Electrochemistry of some Polynuclear Complexes of Aminoethanethiol*

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Abstract

Polynuclear S-bridged complexes of the general formula $\{[Co_2L_6]M\}^{n+}$ with $M = Co(III), Cd(II), Pb(II), Ni(II), Zn(II)$ and $Hg(II)$ were prepared from $[Co(2\text{-aminoethanethiolate})_3]$ and the appropriate metal salt. Proton and ^{13}C NMR spectra are consistent with structures previously proposed for these species with ^{13}C chemical shifts dependent on the bridging metal ion. Electrochemical studies are consistent with a model in which an S-bonded ML_6 moiety (*i.e.*, the bridging metal ion and the six aminoethanethiolate ligands) acts as a 'dodecadentate' ligand bonded to two Co^{3+} ions. Reduction of the terminal cobalt ions in these trinuclear complexes is observed in the range -0.75 to -1 V vs. SCE on mercury, gold or glassy carbon working electrodes. For complexes with relatively labile bridging ions, the electrode reaction is irreversible, presumably due to rapid decomposition of the labile cobalt(II) product. For the tricobalt(III) derivative, however, the electrode reaction is reversible consistent with other recent observations on cage or otherwise stereorestrictive ligand systems [1].

Introduction

Cysteamine, or 2-aminoethanethiol, may be considered to be a decarboxylated and/or demethylated derivative of either cysteine or penicillamine. For this reason, and the known capacity of divalent sulfur containing compounds to protect against both ionizing radiation [2] and alkylating [3] agents, transition metal complexes of cysteamine were of considerable interest for many years.

Several complexes of cysteamine with transition metals are known [4–10]. Among these are the complexes with the stoichiometry ML_2, ML_3, M_3L_4 and M_3L_6 ($L = \text{cysteamine}$). Perhaps the more extensively studied of these complexes are those formed

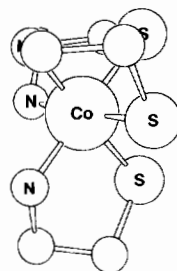


Fig. 1. Tris-(2-aminoethanethiolato)cobalt(III).

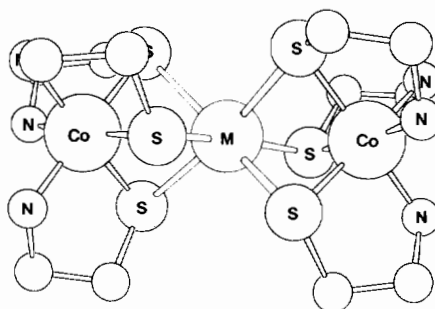


Fig. 2. A Hexakis-(μ -(2-aminoethanethiolato-N,N:S))bis-(cobalt(III))metalla cation.

in the reaction of tris-(2-aminoethanethiolato)-cobalt(III) (Fig. 1) with a several metal ions to form complexes of the type $[M(Co(\text{aminoethanethiolate})_3)_2]^{n+}$ (Fig. 2) where M is cobalt(III) [6, 7], ruthenium(III) [8], iron(III) [9], nickel(II) [6] or zinc(II) [10].

These complexes have been studied using a variety of techniques, including, ESR [8], electronic spectroscopy [6–10] and circular dichroism [10]. Circular dichroism spectra of the cobalt(III) and zinc(II) complexes were used in an effort to separate the contributions of the terminal cobalt(III) ions to the electronic and CD spectra from that of the bridging metal ion [10]. In that study, it was assumed that the zinc(II) ion is 'transparent' (*i.e.* that the d^{10} electronic configuration does not contribute to the electronic spectrum of the polynuclear complex).

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In the present study, we have prepared new complexes with the bridging metal ions cadmium(II), mercury(II) and lead(II) and we have reinvestigated several known polynuclear complexes in order to evaluate the effects of bridging metal ions. These complexes were characterized vibrational, electronic and circular dichroism spectra, proton and carbon-13 NMR, and electrochemical methods.

Experimental Methods

Physical Methods

Elemental Analysis

Elemental analysis (C, H, N) was performed by Micro-Tech Inc., Skokie, Ill. or by Alfred Bernhardt Mikroanalytisches Lab., Elbach, Germany.

Electronic Spectroscopy

Electronic spectra were measured in aqueous solution using a Cary model 14 spectrophotometer. Circular dichroism spectra were measured using a Cary model 60 spectropolarimeter with a Cary model 6002 circular dichroism attachment.

Vibrational Spectroscopy

Infrared spectra were measured as nujol mulls between KBr disks using either a Pye-Unicam Model SP 3-300 spectrophotometer or a Nicolet model 5-MX fourier transform infrared spectrometer.

Proton NMR

Proton NMR spectra were collected at 80 MHz using a Varian CFT-20 NMR spectrometer. Samples were dissolved in a minimum amount of either D₂O or DMSO (d₆). Either tetramethylsilane or 1,4-dioxane were used as internal references. All chemical shifts are reported relative to TMS.

Carbon-13 NMR

Carbon-13 NMR spectra were collected at 20 MHz using a Varian CFT-20 NMR spectrometer in the deuterium locked, proton noise decoupled mode. Spectra were collected using a 21 μ S (equivalent to a 90° pulse) pulse and a 1.0 s acquisition time. Samples were dissolved in a minimum amount of either D₂O or DMSO (d₆). Either tetramethylsilane or 1,4-dioxane (67.5 ppm) were used as internal references. All chemical shifts are reported relative to TMS.

Electrochemical Methods

Cyclic voltammograms and differential pulsed polarograms were measured using a Princeton Applied Research model 174A polarographic analyzer equipped with a Princeton Applied Research model 175 function generator. Under slow scanning conditions, the results were plotted using a Hewlett-Packard

X-Y recorder. Faster scans were recorded using a Nicolet model 2009 digital oscilloscope with a model 206 plug in amplifier.

The potentials were measured in 5×10^{-4} M aqueous solution using either 0.1 M KNO₃ or 0.1 M KCl as a supporting electrolyte. Potentials were measured relative to a PAR SCE reference electrode using a platinum wire counter electrode and either a gold wire, hanging mercury drop, carbon paste or glassy carbon working electrode.

Syntheses

Tris(2-aminoethanethiolato)cobalt(III)(Co(L)₃) was prepared by the method of Gorin *et al.* [11].

Hexakis(μ -(2-aminoethanethiolato-N,S:S))triacobalt(III) bromide and hexakis(μ -(2-aminoethanethiolato-N,S:S))bis(cobalt(III))nickel(II) bromide were prepared by the method of Busch and Jicha [6].

Hexakis(μ -(2-aminoethanethiolato-N,S:S))bis(cobalt(III))zinc(II) tetrakis(μ -(2-aminoethanethiolato-N,S:S))-trizinc(II) perchlorate was prepared by the method of Brubaker and Douglas [10].

Hexakis(μ -(2-aminoethanethiolato-N,S:S))bis(cobalt(III))iron(III) chloride was prepared by the method of Blinn *et al.* [9].

Hexakis(μ -(2-aminoethanethiolato))bis(cobalt(III))ruthenium(III) iodide was prepared by the method of DeSimone *et al.* [8].

Hexakis(μ -(2-aminoethanethiolato-N,S:S))bis(cobalt(III))cadmium(II) perchlorate ([Co(L)₃]₂-Cd](ClO₄)₂) was prepared by the addition of 12 grams (0.04 mol) of cadmium(II) nitrate to a slurry of 3 grams (0.01 mol) of tris-(2-aminoethanethiolato)cobalt(III) and 20 grams of sodium perchlorate in 200 ml water. The mixture was allowed to react for 1 hour at room temperature and the solid removed by filtration. The solid was recrystallized from a 0.5 M sodium perchlorate solution.

Hexakis(μ -(2-aminoethanethiolato-N,S:S))bis(cobalt(III))trimercury(II) perchlorate ([Co(L)₃]₂-Hg₃](ClO₄)₆) was prepared by the addition of 15 grams (0.04 mol) of mercuric nitrate to a slurry of 3 grams (0.01 mol) of tris-(2-aminoethanethiolato)cobalt(III) and 20 grams of sodium perchlorate in 200 ml water. The mixture was allowed to react for 1 hour at room temperature and the solid removed by filtration. The solid was recrystallized from a 0.5 M sodium perchlorate solution. ([Co(L)₃]₂Hg₃)-(NO₃)₆) was prepared by the same method as the perchlorate salt substituting potassium nitrate for sodium perchlorate. *Anal. Calcd.* for [Hg₃Co₂(H₂NCH₂CH₂S)₆](NO₃)₆: C, 9.20%; H, 2.43%; N, 10.73%. *Found:* C, 9.20%; H, 2.58%; N, 10.80%.

Hexakis(μ -(2-aminoethanethiolato-N,S:S))bis(cobalt(III)) lead(II) perchlorate, ([Co(L)₃]₂Pb)-(ClO₄)₂) was prepared by the addition of 15 grams (0.05 mol) of lead(II) nitrate to a slurry of 3 grams (0.01 mol) of tris-(2-aminoethanethiolato)cobalt(III)

TABLE I. Properties of Some Polynuclear 2-Aminoethanethiol Complexes.

Complex	r_M^a	IP_M^b	X_M^c	E_c^d	ν_1^e	ν_2^f	$^{13}C_1^g$	$^{13}C_2^h$
CoL ₃				-0.974	580	440		
Zn(CoL ₃) ₂ ²⁺	0.88	39.72	1.65		567	430	31.31	47.06
Cd(CoL ₃) ₂ ²⁺	1.09	37.47	1.69	-0.821	565	420	32.33	46.48
Hg ₃ (CoL ₃) ₂ ⁶⁺	1.16	34.2	2.00		540	403	36.45	49.00
Pb(CoL ₃) ₂ ²⁺	1.33	31.94	1.87	-0.953	549	428	32.37	47.04
Fe(CoL ₃) ₂ ³⁺	0.69	54.8	1.64	-0.787	595	445	31.57	46.22
Co(CoL ₃) ₂ ³⁺	0.69	51.3	1.70	-0.761	550	437	32.31	46.21
Ni(CoL ₃) ₂ ²⁺	0.83	35.17	1.75	-0.781	560	440	32.23	46.18
Ru(CoL ₃) ₂ ³⁺	0.82	>28.47	1.42	-0.823	590	438	31.83	46.38

^aIonic radius. ^bThird ionization potential. ^cAllred-Rochow electronegativity. ^dCathodic peak potential vs. SCE. ^eWavelength of the ¹A_{1g} → ¹T_{2g} transition. ^fWavelength of the ¹A_{1g} → ¹T_{2g} transition. ^g¹³C NMR chemical shift of the carbon atoms bonded to the thiol. ^h¹³C NMR chemical shift of the carbon atoms bonded to the amine.

and 20 grams of sodium perchlorate in 200 ml water. The mixture was allowed to react for 1 hour at room temperature and the solid removed by filtration. The solid was recrystallized from a 0.5 M sodium perchlorate solution. Hexakis-(μ -(2-aminoethanethiolato-N,S:S)bis(cobalt(III))lead(II) nitrate ([Co(L)₃)₂Pb](NO₃)₂) was prepared by the same method as the perchlorate salt, substituting potassium nitrate for sodium perchlorate.

Optically pure tris-(2-aminoethanethiolato)cobalt(III) was prepared by the addition of aqueous base to a sample of Hexakis-(μ -(2-aminoethanethiolato-N,S:N)bis(cobalt(III)))zinc(II) tetrakis-(μ -(2-aminoethanethiolato-N,S:S)trizinc(II)) perchlorate resolved by the method of Brubaker and Douglas [10]. All other resolved complexes were prepared small scale (1/10 scale) versions of the methods described above using optically pure tris-(2-aminoethanethiolato)cobalt(III).

Results

Syntheses and Structures

Mononuclear complexes typically are synthesized from an appropriate metal salt and the free ligand in an alcohol. Solubility of the mononuclear species is limited (with the exception of some N-substituted derivatives [12]), so that products of acceptable purity are readily obtained by thorough washing of the first formed complex [6].

Polynuclear complexes are readily prepared in a heterogeneous reaction between a suspension of the mononuclear cysteamine complex in a solution of an excess of the appropriate metal salt in water or an alcohol. Charged polynuclear species are

sufficiently soluble to facilitate study in aqueous, alcohol, DMF or DMSO solutions.

Synthetic procedures and most studies in solution compete with the formation of the hexakis-(μ -(2-aminoethanethiolato-N,S:S))tricobalt(III) cation. In most solvents, the relatively more labile complexes with post transition metal bridges, nickel(II), iron(II) or iron(III) dissociate the labile metal and excess ligand to produce a product which is spectroscopically identical with the hexakis-(μ -(2-aminoethanethiolato-N,S:S))tricobalt(III) cation. Qualitatively, this process is independent of dissolved oxygen, proceeding at about the same rate in oxygen free electrolysis cells as in air equilibrated spectrophotometer cells. The hexakis-(μ -(2-aminoethanethiolato-N,S:S))tricobalt(III) cation is detectable in a millimolar aqueous solution of bridged heterometallic complex in about one hour.

Spectroscopy and Electrochemistry

The ¹³C NMR spectra of these complexes (Table I) are characterized by excellent signal to noise ratios and narrow lines. The spectra do not suffer significantly from coupling with either nitrogen or the metal ions which often makes the proton NMR spectra of cobalt(III) amine complexes difficult to interpret [13]. For each complex, the ¹³C spectrum appears at a two singlets between 46.18 and 49.00 ppm from TMS, assigned to the carbon atoms bonded to the amine nitrogens, and between 31.57 and 36.45 assigned to the carbon atoms bonded to the thiol sulfur atoms. The chemical shifts are dependent on the bridging ion, but we have found no strong correlation with any other fundamental, observable or derived property of the bridging ions.

The ¹H NMR spectra for some cysteamine complexes are also given in Table I. In contrast with the

^{13}C spectra, the ^1H spectra are broad and complex, indicative of complex coupling patterns [14].

Vibrational spectra, measured in the solid state, show small bridging ion dependent shifts in the 1620–1540 cm^{-1} , 1325–1230 cm^{-1} , 1160–1020 cm^{-1} and 1000–800 cm^{-1} regions. In the vibrational spectra of the lead(II) and mercury(II) bridged complexes, the bands at about 1600 cm^{-1} show a splitting of some 5 cm^{-1} ; the bands at about 1040 and 980 cm^{-1} are split by *ca.* 10 cm^{-1} . We have found no obvious correlation between the vibrational frequencies and any other fundamental or derived property of the ions in any complex.

The electronic spectra (Table I), measured in approximately millimolar aqueous solutions, are in excellent agreement with those reported earlier [6–9]. Complexes with transition metal bridges exhibit spectra which are composites of the bridge and terminal ion spectra. The electronic spectra of complexes with post-transition metal ion bridges show a measurable variation in the wavelength of the low energy electronic transition.

Circular dichroism spectra are consistent with those reported earlier [10] (Table I). The features of these spectra are consistent with a charge-transfer perturbed ligand field model in trigonal symmetry. There is a measurable variation in the wavelength of the low energy Cotton effect for complexes with post-transition metal ion bridges.

Electrochemical data (Table I) were obtained using several working electrodes; the measured potentials in a given medium and against the same reference were independent of the working electrode material. Cyclic voltammograms on non-metallic electrodes are typically broad, reflecting the relatively slow heterogeneous electron transfer rate typical of these materials. Operation of the PAR 174A/175 instruments in a 'cyclic differential pulsed' mode, though scan rate limited by the model 174A clock, gave well resolved peaks with interpretable diffusion currents and cathodic–anodic peak separations.

In general, polynuclear complexes with transition metal ion bridges displayed quasi-reversible to reversible cyclic voltammograms. Polynuclear complexes with post-transition metal ions displayed quasi-reversible to irreversible behavior. Voltammograms for the mercury(II) bridged complex were too broad to be interpreted regardless of the working electrode material or conditions of measurement; these are the only complexes in this group which were insufficiently stable to allow electrochemical measurements under these conditions. Surprisingly, comparable experiments on metallic and non-metallic working electrodes revealed little tendency toward unusual electrode behaviour (*i.e.*, adsorption) among these thiol complexes.

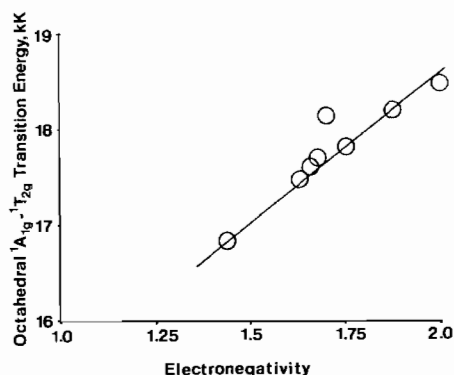


Fig. 3. Plot of the lowest energy electronic transition as a function of the Allred electronegativity of the bridging ion.

Discussion

Several of the subject complexes have been known for many years [6–10]. At the origin of this study, we expected the properties of the terminal cobalt(III) ions to be relatively independent of the bridging ion. It was our expectation that the tricobalt(III) complex could be reduced by one electron to produce an 'intervalence compound', and that the heterometallic complexes would offer variable barriers to intervalence electron or energy transfer.

As expected, electronic structures conform to simple crystal field symmetry considerations with dominant charge transfer effects. For polynuclear complexes with the 'transparent' post-transition metal bridging ions (Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+}) the octahedral $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ transition (the average of the ^1E and $^1\text{A}_2$ in D_3 symmetry) varies inversely with the Allred electronegativity [15] of the bridging ion (Fig. 3). We interpret this observation in terms of a decrease in the interelectron repulsion terms in the ground state of the terminal cobalt(III) ions. In a crystal field model, this corresponds to a decrease in the energy of the fully occupied t_{2g} levels [10]; in a MO model; it corresponds to a lowering of the M–S π bonding energy by delocalization into the bridging metal ion. In these models, the first excited state (which is a σ antibonding level) is relatively unperturbed by the bridging metal ion, so the increased energy difference derives largely from ground state stabilization. Though we do not find this correlation with a derived quantity particularly satisfying, we have not found any strong correlation among other fundamental or observed properties of the bridge ions and polynuclear complexes.

Literature data for M–S bond lengths in six coordinate structures indicates that while the terminal (or bridged) cobalt(III)–S bond distance should be about 226 pm [16], the Hg(II)–S distance is 272 pm, Cd(II)–S is 252 pm, and Pb(II)–S distance is 297

pm [17]. Comparable data is not available for six coordinate Zn(II) or Ni(II), but for the three cited examples the difference in ionic sizes is expected to impose a substantial bond strain across the shared trigonal face.*

At the estimated metal–metal distance, we also expect to find substantial orbital overlap between the bridged and terminal metal ions. There is no evidence in our measurements for any direct metal–metal interaction, and the barrier to intervalence electron transfer between the equivalent terminal cobalt ions is so great that, in all of our measurements, these ions are physically and chemically independent.

Electrochemical data obtained from fresh solutions (*vide supra*) of the soluble polynuclear complexes (0.1 M KNO₃, glassy carbon, carbon paste, HMDE or gold working electrodes) at variable potential sweep rates (10 mV–10 V sec⁻¹) is indicative of a one electron reduction. The first reduction (*ca.* –0.75 to –1 V *vs.* SCE) is interpreted as a terminal Co(III)–Co(II) step.

There is no evidence of unusual adsorption effects between these thiol complexes and the metallic electrodes; the smooth curves are consistent with a single electroactive component in solution. The cyclic voltammograms are broad, consistent with slow heterogeneous electron transfer rates, particularly on the non-metallic working electrodes. The formal potentials for these processes, however, are quite independent of the electrode materials, supporting electrolytes and scan rates.

For relatively labile bridging metal ions (Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Fe³⁺, Ni²⁺), this process is electrochemically irreversible ($p_c - p_a > 80$ mV though $i_c < i_a$ for Ru³⁺ and Ni²⁺). For the substitution inert Co(III) bridged Co(III) complex, reduction of the terminal Co(III) moieties is reversible. This suggests that, upon reduction of the terminal ion, the complex rapidly dissociates except in the case of the substitution inert bridging ions. Electrochemically reversible cobalt(III)/(II) couples, though relatively rare, are found in complexes with cryptand ligands [19], some macrocyclic ligands [20], with the unusual tridentate ligand tribenzo[b,f,j]-1,5,9-triazacyclododecine [(TRI) [21], and in some complexes with 1,4,7-triazacyclononane [22]. In the absence of evidence of unusual interactions between

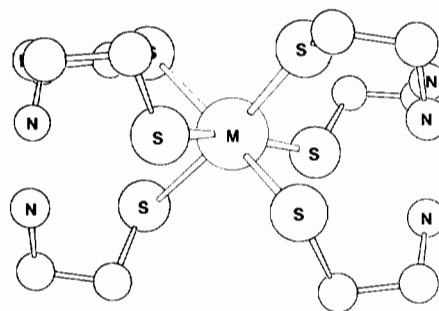


Fig. 4. The proposed hexakis-(2-aminoethanethiolato)metalla anion – a ‘dodecadentate’ ligand.

the metal ions, we ascribe the electrochemical reversibility of the cobalt(III)/(II) couple in these complexes to stabilization of the lower oxidation state through the π acid character of the divalent sulfur ions.

In these cases, the behavior is interpretable in terms of an EDTA-like ‘dodecadentate’ ligand in which the six sulfur donors are bonded (more or less permanently in the case of inert ions) to one ion, and three primary amine donors ‘dangle’ from each end (Fig. 4). One or two metal ions may be chelated by this ‘ligand’ in an N₃S₃ environment in which the sulfur atoms bridge between the metal ions (Fig. 2). Our proposed ‘dodecadentate ligand’ has only been isolated as a cobalt(III) chelate. Numerous attempts over several years to prepare tris-(cysteamine) complexes with other metal ions have failed in our laboratory.

Conclusions

The observed dependence of the electronic structure of [Co(2-aminoethanethiolate)₃] on the electro-negativity of the bridging ion (in the absence of ligand field effects) suggests that there is no simple way to partition electronic spectra between bridging and terminal transition metal ions in polynuclear 2-aminoethanethiol complexes.

The electrode reactions of sulfur bridged heterometallic cysteamine complexes are characterized by quasi-reversible to irreversible behavior, beginning with reduction of a terminal tris-(2-aminoethanethiolato)cobalt(III) group. Reduction of the terminal Co(III) moieties of the substitution inert Co(III) bridged complex is reversible. This suggests that these polynuclear complexes dissociate upon reduction of the terminal ion except in the case of substitution inert bridges. In these cases, the behavior is interpretable in terms of a hexakis-(2-aminoethanethiolato)metallo anion serving as a ‘dodecadentate’ ligand in which the six sulfur donors are bonded to a metal ion, and three primary amine donors ‘dangle’ from each end. This ligand is capable

*This strain may be more apparent than real. Experience with strain energy calculations [18a] indicates that angle deformation, such as that envisioned across a shared octahedral face, contributes little to the total intramolecular strain energy of most transition metal complexes. Angle deformation force constants are typically only about 10% of bond stretching force constants, and neither are particularly large for the heavier metals [18b].

of binding one or two additional metal ions in an N_3S_3 environment comprised of shared sulfur atoms and primary amine donors.

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