tigation, and only those points for which $Z \leq 1.4$ were used. This resulted in a much better fit for models A and B; σ_Z improved so much for model B that it now gave the better fit. In further calculations, addition of the (9, 8) species to model A, giving model C, caused no change to the fit, while adding it to model B (giving model D) actually resulted in a small increase in the value of σ_Z. Thus, having taken into account models previously selected to give either very good or best fits between experimental and calculated Z values for measurements in 1 M NaCl medium, results of this investigation show that the smallest σ_Z value is obtained for model B.

Subsequently various other combinations of possible species were considered in an attempt to find a model that would give an even better fit than model B. A marked improvement in σ_Z could, however, only be obtained by adding the dimeric species (3, 2) to either model A or B; of these two models, E and F, the latter fits best.

Since dimeric species in the cationic state have been shown to exist in strong acid medium,[11] the possibility that lower protonated dimers such as a neutral (4, 2) species and a singly charged anion (3, 2) will occur at higher pH seems reasonable. From a statistical point of view the (3, 2) species is acceptable since the value of the stability constant, $\beta_{3,2}$, is greater than 3 times its standard deviation which corresponds, technically at least, to a confidence level of better than 99%.[7]

Obviously this result can not be regarded as sufficient evidence for the existence of a (3, 2) species, but it does show that the possible presence of this dimer should be taken into account in future investigations of molybdenum(VI) equilibria, especially at relatively low concentrations. Although model F has given the best fit, it should be pointed out that the rather small difference between the σ_Z values for models E and F does not justify a final choice between the (11, 7) and (12, 8) species, i.e., between the ions $H_3Mo_7O_{24}^{3-}$ and $Mo_8O_{26}^{4-}$. However, results of X-ray scattering and Raman measurements carried out on a series of 2.0 M lithium molybdate solutions in the range $Z \leq 1.5$, which have just been reported (at the time of writing), are found to be best interpreted in terms of the formation of the $Mo_8O_{24}^{6-}$ ion;[12] the existence of the $Mo_7O_{24}^{6-}$ ion in solution has been reconfirmed as well.

Since the equilibrium constants of a number of species likely to occur in acidified molybdenum(VI) solution have been verified, their values can now be applied with greater confidence to interpret or evaluate data obtained by other experimental techniques. For instance, values for equilibrium constants are essential for the determination of enthalpy and entropy quantities of individual species from calorimetric data for this system of overlapping equilibria. Such thermodynamic data together with structural information of characterized species should provide a much better understanding of the true nature of the system. As yet, no satisfactory explanation can be given as to why only certain species predominate under a given set of conditions. In fact, the question as to what accounts for the critical stability of a particular polynuclear configuration has yet to be answered for the whole field of isopoly and heteropoly complexes and not merely for molybdenum(VI) isopolyions.

Registry No. $HMoO_4^-$, 14259-84-8; $Mo(OH)_6$, 13597-71-2; $HMo_2O_7^-$, 72004-03-6; $Mo_7O_{24}^{6-}$, 12274-10-1; $HMo_7O_{24}^{5-}$, 12371-76-5; $H_2Mo_7O_{24}^{4-}$, 12371-78-7; $H_3Mo_7O_{24}^{3-}$, 52015-50-6; $Mo_8O_{26}^{4-}$, 12346-58-6; $HMo_8O_{28}^{7-}$, 53237-16-4.

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Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Ligating Ability of the Coordinated Thiolato Sulfur Atom. 2.[1] The Crystal Structure of {[(en)₂Co(SCH₂COO)]₂Ag}(ClO₄)₃, a Model for an Inner-Sphere Electron-Transfer Precursor Complex

Mary Jane Heeg, R. C. Elder,* and Edward Deutsch

Recently we have examined the interactions of (thiolato)-cobalt(III) complexes with the soft metals Ag(I) and CH_3Hg^{II} and reported equilibrium association constants[1] for these metals with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$ (hereafter referred to as Co(cys) and Co(tga), respectively). Supportive of that study, we now present the

Co(cys)   Co(tga)
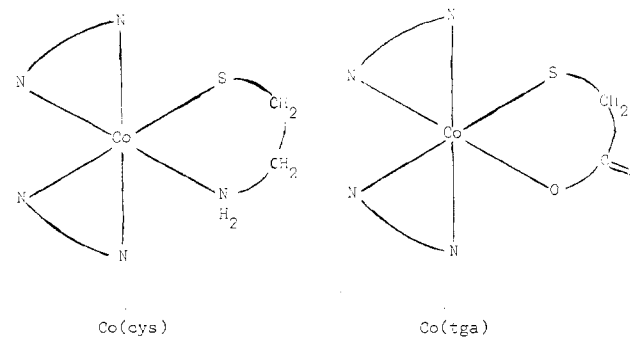
single-crystal X-ray structure determination of the 2:1 adduct {[Co(tga)]₂Ag}(ClO₄)₃ which clearly indicates sulfur to be the bridging atom between cobalt(III) and silver(I). Changes in the cobalt coordination sphere accompanying the binding of the coordinated thiolato sulfur atom to silver are important with respect to the changes one might expect when a potentially reducing metal (e.g., Cu(I), Cr(II), Co(I)) approaches a (thiolato)cobalt(III) compound to form the precursor complex in prelude to inner-sphere electron transfer.[2]

Experimental Section

{[Co(tga)]₂Ag}(ClO₄)₃ was prepared by the addition of AgClO₄ to an acidic solution of [Co(tga)]ClO₄[3] in approximate stoichiometric ratios. Typically, 10 mL (0.018 M) of [Co(tga)]ClO₄ was mixed with 3 mL (1.0 M) of HClO₄ and 1 mL (0.09 M) of AgClO₄. The solution was allowed to stand at room temperature for a few days until large red crystals formed. The rate of crystal formation is very dependent on HClO₄ concentration.

Precession photographs of the title complex indicated a monoclinic unit cell with systematic absences consistent with the space groups[4] $C2/c$ and Cc ($h + k =$ odd for hkl and $l =$ odd for $h0l$). A crystal of approximate dimensions $0.23 \times 0.21 \times 0.11$ mm was mounted on a Syntex P1̄ diffractometer (Mo Kα, graphite monochromator), and unit cell parameters were confirmed by precisely centering on 19 pairs of reflections at $\pm(18° \leq 2\theta \leq 25°)$: $a = 16.267$ (5) Å, $b = 8.9885$ (7) Å, $c = 22.145$ (4) Å, $\beta = 99.82$ (2)°, $V = 3190.4$ Å³, $Z = 4$, $\rho_{calcd} = 1.967$ g cm⁻³. Equipment and methods of data collection have previously been described.[5] Within the sphere $2.5 \leq 2\theta \leq 60°$, 5639 reflections were scanned, resulting in 3350 unique, observed ($I > 2\sigma(I)$) reflections. Four standard reflections were measured between every 36 test reflections to provide a drift correction that exhibited long-term, random variation and ranged from 0.94 to 1.02. Gaussian absorption

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Table I. Fractional Atomic Positional Parameters[a]

atom	x	y	z
Ag[b]	0.0	0.22650 (5)	0.25
Co	0.16910 (3)	0.39531 (6)	0.38437 (2)
S	0.12367 (7)	0.20200 (11)	0.32336 (4)
Cl(1)[b]	0.0	−0.23649 (18)	0.25
Cl(2)	0.16194 (7)	0.38377 (12)	0.12698 (5)
N(1)	0.1967 (2)	0.5080 (3)	0.3148 (1)
N(2)	0.2840 (2)	0.3223 (4)	0.3947 (1)
N(3)	0.0568 (2)	0.4781 (3)	0.3791 (1)
N(4)	0.2040 (2)	0.5578 (3)	0.4431 (1)
C(12)	0.2771 (3)	0.4539 (6)	0.2999 (2)
C(21)	0.3320 (3)	0.4152 (7)	0.3579 (2)
C(34)	0.0562 (3)	0.5833 (5)	0.4323 (2)
C(43)	0.1355 (3)	0.6676 (5)	0.4409 (2)
C(1)	0.0937 (3)	0.0844 (4)	0.3820 (2)
C(2)	0.1280 (2)	0.1412 (4)	0.4462 (1)
O(1)	0.1519 (1)	0.2769 (2)	0.4525 (1)
O(2)	0.1325 (2)	0.0552 (3)	0.4900 (1)
O(11)[b,c]	0.0	−0.4026 (10)	0.25
O(12)	0.0057 (5)	−0.2129 (8)	0.3141 (4)
O(13)	0.0886 (6)	−0.2170 (9)	0.2710 (4)
O(14)	0.0313 (8)	−0.0999 (14)	0.2310 (6)
O(15)	0.0464 (9)	−0.3484 (17)	0.2325 (6)
O(21)	0.1812 (6)	0.4882 (6)	0.0849 (2)
O(22)	0.1401 (3)	0.4676 (8)	0.1715 (2)
O(23)	0.2342 (3)	0.3067 (5)	0.1442 (3)
O(24)	0.0951 (3)	0.2964 (4)	0.0964 (2)

[a] The numbering system for the cation is shown in Figure 1.
O(2x) are bound to Cl(2). O(1x) and the symmetry-related set
are close to Cl(1). [b] These atoms lie on a twofold axis; therefore,
no errors appear on the x and z coordinates. [c] The population
parameters for the oxygen atoms of the disordered perchlorate are
as follows: O(11), 0.34; O(12), 0.60; O(13), 0.53; O(14), 0.30;
O(15), 0.23.

corrections[6] were applied (μ = 21.09 cm^{-1}) and checked against a
series of ψ scans. Transmission coefficients varied from 0.60 to 0.80.
Other details of the data collection are as follows: scan rate 1–6°/min;
scan range from 0.7° in 2θ below calculated Kα_1 peak to 0.8° above
Kα_2 peak; *hkl* varied from 0,0,$\overline{35}$ to 20,12,35.

The centric space group *C2/c* was assumed and gave satisfactory
refinement[7] throughout. Inspection of a Patterson synthesis yielded
the positions of the heavier atoms (Ag, Co, S, 2 Cl) which were refined
with isotropic temperature factors[8] to yield a conventional *R* factor[9]
of 30%. The silver atom lies on the twofold axis at 0, y, $^1/_4$ and 0,
$\bar{y}$, $^3/_4$. All other nonhydrogen atoms were located from a series of
Fourier maps and their positions were refined by least-squares
techniques. The hydrogen atoms were placed in calculated positions
(N–H = 0.85 Å, C–H = 0.95 Å (tetrahedral geometry)) and given
the following isotropic temperature factors: *B*(methylene hydrogen
atoms) = 6.0 Å^2; *B*(amine hydrogen atoms) = 4.0 Å^2. No hydrogen
parameters were refined.

Both independent perchlorate anions exhibit some degree of disorder.
The perchlorate anion containing Cl(1) is required by symmetry to
lie on a twofold axis and displays such severe disorder that a tetrahedral
description is inadequate. The region around Cl(1) in a difference
map showed nine distinct peaks consisting of 4 pairs of symmetry-
related positions and one peak lying on the rotation axis. These are
assigned as partial oxygen atoms (O(11)–O(15)) with population
parameters assigned in the same ratios as peak heights. The population
parameters were held invariant while the model was refined to con-
vergence with the usual[5] weighting scheme. Final *R* factors[9] are R_1
= 0.048 and R_2 = 0.051. The highest peak on a final difference map
is 0.7 e Å^{-3}. Neutral atom scattering factors[10] were used with those
for Ag, Co, S, and Cl corrected for anomalous dispersions.[11] The

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R. *J. Am. Chem. Soc.* **1974**, *96*, 2955.
(7) All computations were performed by using a local version of XRAY67:
Stewart, J. M., University of Maryland, crystallographic computer
system.
(8) Isotropic thermal parameters were of the form exp(−*B*(sin^2 θ)/λ^2).
(9) $R_1 = \sum ||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum_w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.
(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.
(11) "International Tables for X-ray Crystallography"; Kynoch Press:
Birmingham, England, 1974; Vol. IV, p 149.

Table II. Bond Lengths (Å)

Cation			
Ag–S	2.370 (1)	N(1)–C(12)	1.485 (7)
Co–S	2.247 (1)	N(2)–C(21)	1.479 (7)
Co–N(1)	1.958 (3)	N(3)–C(34)	1.510 (6)
Co–N(2)	1.956 (4)	N(4)–C(43)	1.483 (6)
Co–N(3)	1.957 (3)	C(12)–C(21)	1.475 (7)
Co–N(4)	1.974 (3)	C(34)–C(43)	1.479 (7)
Co–O(1)	1.906 (3)	C(1)–C(2)	1.525 (6)
S–C(1)	1.805 (5)	C(2)–O(2)	1.232 (5)
O(01)–C(2)	1.280 (5)		

Anions			
Cl(1)–O(11)	1.493 (9)	Cl(2)–O(21)	1.396 (7)
Cl(1)–O(12)	1.423 (9)	Cl(2)–O(22)	1.337 (7)
Cl(1)–O(13)	1.447 (10)	Cl(2)–O(23)	1.362 (5)
Cl(1)–O(14)	1.419 (14)	Cl(2)–O(24)	1.415 (5)
Cl(1)–O(15)	1.354 (16)		

Table III. Bond Angles (Deg)

S–Ag–S[a]	169.34 (9)	Ag–S–Co	119.59 (5)
S–Co–N(1)	91.3 (1)	Ag–S–C(1)	104.2 (1)
S–Co–N(2)	91.2 (1)	Co–S–C(1)	96.9 (1)
S–Co–N(3)	92.9 (1)	Co–N(1)–C(12)	109.5 (2)
S–Co–N(4)	175.2 (2)	Co–N(2)–C(21)	109.2 (2)
S–Co–O(1)	88.11 (8)	Co–N(3)–C(34)	108.8 (2)
N(1)–Co–N(2)	85.6 (1)	Co–N(4)–C(43)	109.9 (2)
N(1)–Co–N(3)	95.3 (1)	N(1)–C(12)–C(21)	107.9 (4)
N(1)–Co–N(4)	93.2 (1)	N(2)–C(21)–C(12)	108.3 (4)
N(1)–Co–O(1)	174.7 (1)	N(3)–C(34)–C(43)	107.4 (4)
N(2)–Co–N(3)	175.7 (1)	N(4)–C(43)–C(34)	107.2 (3)
N(2)–Co–N(4)	90.5 (1)	S–C(1)–C(2)	111.9 (3)
N(2)–Co–O(1)	89.1 (1)	O(1)–C(2)–O(2)	122.4 (3)
N(3)–Co–N(4)	85.2 (1)	O(1)–C(2)–C(1)	118.4 (3)
N(3)–Co–O(1)	89.8 (1)	O(2)–C(2)–C(1)	119.1 (3)
N(4)–Co–O(1)	87.4 (1)	Co–O(1)–C(2)	121.9 (2)
O(21)–Cl(2)–O(22)	103.4 (4)	O(22)–Cl(2)–O(23)	113.8 (4)
O(21)–Cl(2)–O(23)	104.3 (4)	O(22)–Cl(2)–O(24)	112.7 (3)
O(21)–Cl(2)–O(24)	107.2 (3)	O(23)–Cl(2)–O(24)	114.0 (3)

[a] Transformed to $-x$, y, $^1/_2 - z$.

value of p^5 was 0.03. Tables I–III contain the positional parameters,
bond lengths, and bond angles, respectively, for the nonhydrogen atoms.
Listings of observed and calculated structure factors, hydrogen
positional parameters, and nonhydrogen thermal parameters and
vibrational ellipsoids are available.[12]

Results and Discussion

Silver(I) is known to have a high affinity for thiols[13] and,
to a lesser extent, coordinated thiols.[1] This structure deter-
mination confirms that sulfur, not the carboxylate oxygen, is
bound to silver in [Co(tga)]$_2$Ag^{3+}. A nearly linearly coor-
dinated silver atom (S–Ag–S = 169°) links two Co(tga)
complexes through sulfur as shown in Figure 1. The octa-
hedral coordination of the parent Co(tga) moiety is only
slightly disturbed by small changes in bond lengths and angles.
As is usual in perchlorate salts[5,14] of these types of complexes,
hydrogen bonds are weak and few in number. N(2) hydrogen
bonds to the carbonyl oxygen, O(2′) of a second complex
related by the inversion center at $^1/_4$, $^1/_4$, $^1/_2$ (N(2)···O(2′)
= 2.89 Å). N(1) forms a hydrogen bond to an oxygen of the
ordered perchlorate (N(1)···O(23) = 2.99 Å). The observed
conformations of the ethylenediamine ligands about cobalt are
$\Lambda(\delta\lambda)$ and $\Delta(\lambda\delta)$. Since the silver atom lies on a twofold axis
which relates the two Co(tga) moieties, each [Co(tga)]$_2$Ag^{3+}
adduct is chiral; however, the crystal contains pairs of enan-
tiomers related by centers of inversion.

The silver–sulfur bond, 2.370 (1) Å, is rather short. How-
ever, Ag–S bonds have been found[15–25] to span the range from

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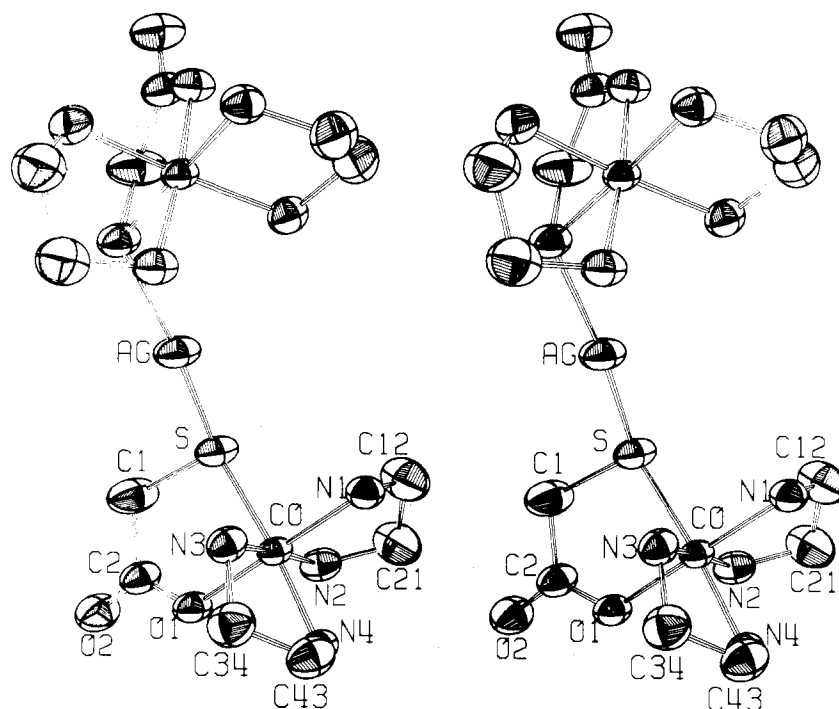(14) Lange, B. A.; Libson, K. L.; Deutsch, E.; Elder, R. C. *Inorg. Chem.*
1976, *15*, 2985.

Figure 1. Stereoview of the dimeric cation $[Co(tga)]_2Ag^{3+}$. The twofold axis passes through the silver atom and relates one Co(tga) moiety to the other.

2.36 to greater than 3.0 Å, depending on the coordination numbers of both silver and sulfur. In the solid state, silver exhibits coordination numbers varying from 2 to 5, with higher coordination numbers (4, 5) associated with bond lengths from 2.5 to 3.0 Å. Three-coordination yields bonds averaging 2.55 Å, whereas for two-coordination, the average is 2.41 Å. The most relevant comparison is to $\{[Pt(SCH_2CH_2P(C_2H_5)_2)_2]\text{-}Ag\}NO_3$[25] where a thiolato sulfur atom bridges a two-coordinate Ag(I) and a four-coordinate Pt(II), with an Ag–S bond distance of 2.400 (7) Å. The angle at silver in this adduct is 171° which is typical[15,18] and agrees with the value of 169° found in this study.

The coordination geometry about cobalt in the title compound is quite similar to the parent complex, Co(tga), and to the benzyl thioether derivative,[26] $[(en)_2Co(S(CH_2C_5H_6)\text{-}CH_2COO)]^{2+}$ = Co(Bztga). The structural trans effect,[27] STE, found here, 0.017 (3) Å, is decreased from the value of 0.043 (6) Å for Co(tga) to essentially the same value, 0.014 (11) Å, observed for Co(Bztga). However, the Co–S bond length for the title complex, 2.247 (1) Å, is in much better agreement with that for Co(tga), 2.243 (2) Å, than for Co-

(Bztga), 2.274 (1) Å, illustrating the poor correlation of Co–S bond length with STE.

We have shown previously[28] that the rates of reactions involving cleavage of the trans Co–N bond are highly correlated with the length of the trans Co–N bond (i.e., the STE), a longer bond being a weaker bond which is more readily stretched and ultimately broken. The rates of inner-sphere electron transfer to cobalt(III) through the coordinated sulfur atom are also expected to be dependent on the energy necessary to stretch the trans Co–N bond; but, in addition, these rates will also be dependent on the energy necessary to stretch the Co–S bond and on several other factors.[30] Formation of $[Co(tga)]_2Ag^{3+}$ from Co(tga) leads to a decrease in the trans Co–N bond length while the Co–S bond length remains about the same. Thus $[Co(tga)]_2Ag^{3+}$ does *not* reflect the bond length changes thought to be necessary in order to attain the transition state for inner-sphere electron transfer. If the structural changes in Co(tga) upon adduct formation with Ag(I) accurately model those which accompany formation of a precursor complex, we must conclude that the structural changes in the ground-state precursor complex are relatively unimportant factors in determining the overall energetics of inner-sphere electron transfer and that the remarkable ability of thiolato sulfur to bridge electron transfer from chromium(II) to cobalt(III)[3,29] must arise from other causes.

Supplementary Material Available: Tables containing lists of structure factors, anisotropic thermal parameters, vibrational ellipsoids, and hydrogen atomic positions (18 pages). Ordering information is given on any current masthead page.

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(27) The STE is defined as [Co–N(trans)] – [av Co–N(cis)], where Co–N-(cis) includes those bonds cis to sulfur and trans to nitrogen. The error is computed as $\sigma(STE) = [(\sigma(trans))^2 + (\sigma(cis))^2]^{1/2}$ and $\sigma(cis) = [(d_i - \bar{d})^2/(n(n-1))]^{1/2}$.

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