to the plane of the cobalt ion and the secondary donor atoms as the plane of the complex. We distinguish among the methylenic protons by means of subscripts: α_5 protons belong to a methylene group (adjacent to an amine) in the five-membered chelate rings, and α_6 protons are the corresponding protons in six-membered chelate rings. Protons labeled β are the central protons of a six-membered chelate ring. We distinguish among the various cis isomers by underscoring the chelate ring displaced from the plane of the complex, e.g., [Co(2,2,2-tet)Cl₂]⁺ is the familiar uns-cis configuration of the β isomer of [Co(trien)Cl₂]⁺. The more familiar nomenclature is not readily applicable when there exists the possibility of more than one s-cis or uns-cis isomer which are independent of any other coordinated ligand.

(10) Fitzgerald, J. J. Ph.D. Thesis, Illinois Institute of Technology, 1972.
(11) Brubaker, G. R.; Schaefer, D. P. *Inorg. Chem.* **1970**, *9*, 2373.
(12) Hamilton, H. G.; Alexander, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 5065.
(13) DeHayes, L. J.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 2010.
(14) Brubaker, G. R.; Teller, R. G.; Brown, J. N. *Inorg. Chem.* **1976**, *15*, 1708.

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

Ligating Ability of the Coordinated Thiolato Sulfur Atom.[1] Interactions between Soft Metal Centers and the Thiolatocobalt(III) Complexes [(en)₂Co(SCH₂CH₂NH₂)]²⁺ and [(en)₂Co(SCH₂COO)]⁺

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

Recent interest in the efficacy of low-valent sulfur as an electron-transfer bridge[2-8] has led us to investigate the ligating ability of coordinated thiols—ligation of a coordinated thiol to a second metal center is the first step in the formation of an inner-sphere electron transfer precursor complex. Busch[9] and more recently Blinn[10] have qualitatively studied the ligating ability of *fac*-Co(SCH₂CH₂NH₂)₃ which functions as a tridentate ligand toward a variety of hard and soft metal centers. For a closer correspondence to the conditions and chemistry of extant redox studies[2-8] wherein only one thiolato sulfur atom bridges oxidant and reductant, we have investigated the ligating abilities of [(en)₂Co(SCH₂CH₂NH₂)]²⁺ and [(en)₂Co(SCH₂COO)]⁺ (hereafter referred to as Co(cys) and Co(tga), respectively). These complexes form strong adducts only with soft metal centers such as [Ag(aq)]⁺ and [CH₃Hg(aq)]⁺. The relevance of these specific studies has been extended by recent observations of Lane and co-workers[8,11] on reduction of Co(cys) and Co(tga) by the soft species Cu(I); while Cu(I) readily reduces Co(tga) via formation of a very stable precursor complex,[8] Co(cys) is not detectably reduced by Cu(I) but rather forms an unusual tetrameric complex (two cobalt(III) centers bridged by two Cu(I) centers) which provides a model for type 3 copper in multicopper oxidases.[11]

This study reports quantitative equilibrium constants for association of the title complexes with [Ag(aq)]⁺ and [CH₃Hg(aq)]⁺, as well as qualitative observations on association with other metal centers. The results of this study indicate that thiolato sulfur coordinated to cobalt(III) retains a high degree of Lewis basicity toward soft metals. Some unexpected behavior is noted in the Co(cys)/[CH₃Hg(aq)]⁺ equilibrium which may be indicative of the formation of a three-coordinate Hg(II) species—the existence of such species has recently been reviewed.[12] Also, a convenient, accurate spectrophotometric technique for the standardization of aqueous [CH₃Hg(aq)]⁺ solutions is presented.
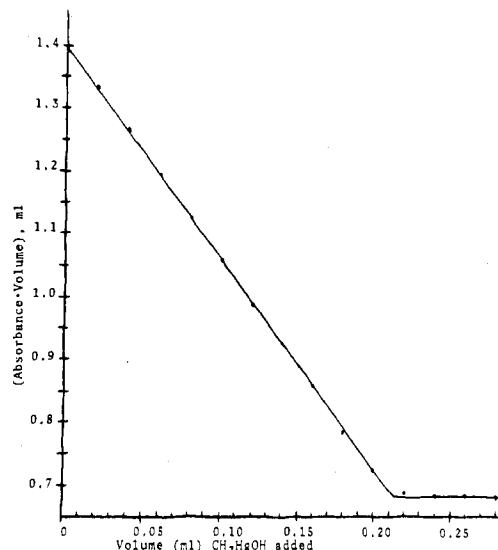

Figure 1. Spectrophotometric titration (λ 450 nm, l = 1.00 cm) of Co(tga) (initially 5.00×10^{-3} M) with CH₃HgOH in acid (pH ca. 0), a plot of absorbance × volume vs. volume (mL vs. mL).

Experimental Section

All common laboratory chemicals were of reagent grade. Water, HClO₄ and LiClO₄ were of previously specified purity.[2] Extensively recrystallized perchlorate salts of Co(cys) and Co(tga) were available from previous studies.[2,3,13,14] Silver perchlorate (G. F. Smith) solutions were standardized with sodium thiocyanate. Solutions of CH₃HgOH were prepared by the reaction of Ag₂O with CH₃HgCl in aqueous solution and then standardized by spectrophotometric titration (Figure 1) with a solution of Co(tga) (prepared from an accurately weighed sample of recrystallized [Co(tga)]ClO₄) at 450 nm where the molar extinction coefficients of Co(tga) and [Co(tga)HgCH₃]²⁺ are 93.6 ± 0.9 and 45.5 ± 0.7 M⁻¹ cm⁻¹, respectively (vide infra).

All solution studies were conducted in HClO₄/LiClO₄ media held at constant ionic strength at ambient temperature (22 ± 1 °C). Equilibrium constants governing association with silver(I) were determined by potentiometrically monitoring [Ag(aq)]⁺ as aliquots of aqueous AgClO₄ solution were added to solutions of the cobalt complex. All potentiometric measurements were conducted in Nalgene plasticware, with continual stirring, by using a Beckman Research pH/mV instrument equipped with an Orion solid-state Ag₂S working electrode and an Orion double junction (saturated NaCl and saturated NaClO₄ solutions in the inner and outer chambers, respectively) reference electrode with Ag/AgCl internal couple. This system exhibited Nernstian behavior throughout the concentration range of interest: calibration curves were determined each working day. Equilibrium constants governing association with methylmercury ion were determined by titrating with base an acidic solution containing both the cobalt(III) complex and [CH₃Hg(aq)]⁺ while simultaneously monitoring the optical density and pH of the solution. A typical titration curve is shown in Figure 2; at the beginning of the titration methylmercury is bound to the thiolatocobalt(III) complex, at the end of the titration it is bound to hydroxide, and in the intermediate region the methylmercury center is distributed according to the equilibrium

$$(\text{CoSR})\text{HgCH}_3{}^{n+} + \text{OH}^- = \text{CH}_3\text{HgOH} + \text{CoSR}^{(n-1)+} \quad (1)$$
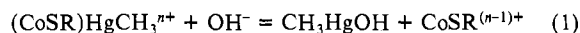
The steepness of the titration curve in the intermediate region permits determination of only two to four informative absorbance–pH data points per experiment. Spectrophotometric data were obtained by using a Cary 14 or Cary 118B spectrophotometer; pH data were obtained under a nitrogen atmosphere by using a Beckman pH/mV instrument equipped with a Sensorex thin probe combination electrode.

Solid samples of many adducts were prepared by mixing aqueous solutions of a thiolatocobalt(III) complex and a soft metal center in the presence of poorly coordinating anions. Table A[15] gives elemental analysis data for solid samples of the representative adducts [(Co(cys))₂Ag](ClO₄)₅, [(Co(cys))₂PtCl₂]Cl₄, [Co(tga)AgOH₂](NO₃)₂, and [Co(tga)AgOH₂](NO₃)(SiF₆)₁/₂.
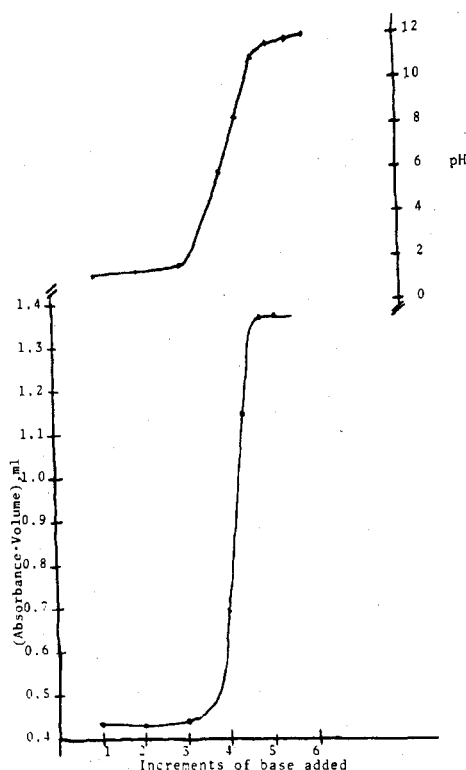
Figure 2. Typical titration of a Co(cys) + [CH₃Hg(aq)]⁺ solution with NaOH (λ 600 nm, l = 1.00 cm, [Co(cys)]$_{tot}$ ≃ [CH₃Hg]$_{tot}$ ≃ 0.01 M), plots of pH vs. increments of base added and absorbance × volume vs. increments of base added (data in Table G[15]).

Figure 3. Spectrophotometric titration (λ 425 nm, l = 1.00 cm) of Co(cys) (initially 6.00 × 10⁻³ M) with CH₃HgOH in acid (pH ca. 0), a plot of absorbance × volume vs. volume (mL vs. mL).
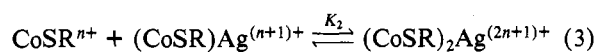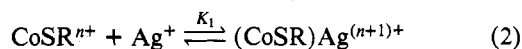
Table I. Selected Equilibrium Constants Governing Ag⁺ and CH₃Hg⁺ Adduct Formation with Sulfur-Containing Species in Aqueous Media[a]

adduct	K_f(consecutive), M⁻¹	μ, M	ref
Co(cys)Ag³⁺	(4.0 ± 0.2) × 10⁴	0.065[e]	b
(Co(cys))₂Ag⁵⁺	(3.1 ± 0.2) × 10³	0.065[e]	b
Co(tga)Ag²⁺	(4.8 ± 0.7) × 10⁴	0.058[e]	b
(Co(tga))₂Ag³⁺	(1.3 ± 0.2) × 10³	0.058[e]	b
(HOCH₂CH₂S)Ag	1.6 × 10¹³	0.1[f]	c
((HOCH₂CH₂)₂S)Ag⁺	3.4 × 10³	0.5[g]	d
((HOCH₂CH₂)₂S)₂Ag⁺	1.9 × 10²	0.5[g]	d
Co(cys)HgCH₃³⁺	(4.6 ± 0.1) × 10⁴	0.13[e]	b
(Co(cys))₂HgCH₃⁵⁺	(5.3 ± 0.5) × 10²	0.13[e]	b
Co(tga)HgCH₃²⁺	(3.3 ± 0.1) × 10⁵	0.11[e]	b
(HOCH₂CH₂S)HgCH₃	1.3 × 10¹⁶	0.1[f]	c
(HOCH₂CH₂S(HgCH₃))HgCH₃⁺	1.9 × 10⁶	0.1[f]	c

[a] Co(cys) ≡ [(en)₂Co(SCH₂CH₂NH₂)]²⁺; Co(tga) ≡ [(en)₂-Co(SCH₂COO)]⁺. [b] This work. [c] G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, 48, 28 (1965). [d] F. Marsicano and R. D. Hancock, *J. Coord. Chem.*, 6, 21 (1976). [e] LiClO₄, 22 °C. [f] KNO₃, 20 °C. [g] NaClO₄, 25 °C.

Results

Data defining the Co(cys)/Ag(I) and Co(tga)/Ag(I) equilibria are presented in Tables B[15] and C,[15] respectively. The experimentally accessible range of [Ag(aq)]⁺ was determined by instrument sensitivity at the lower limit and adduct precipitation at the upper limit. Assuming the successive equilibria for Co(cys) and Co(tga) (here each designated as CoSR)

$$\text{CoSR}^{n+} + \text{Ag}^+ \overset{K_1}{\rightleftharpoons} (\text{CoSR})\text{Ag}^{(n+1)+} \qquad (2)$$

$$\text{CoSR}^{n+} + (\text{CoSR})\text{Ag}^{(n+1)+} \overset{K_2}{\rightleftharpoons} (\text{CoSR})_2\text{Ag}^{(2n+1)+} \qquad (3)$$

we used an iterative nonlinear least-squares procedure[1,16] to calculate the values of K_1 and K_2 which best describe the

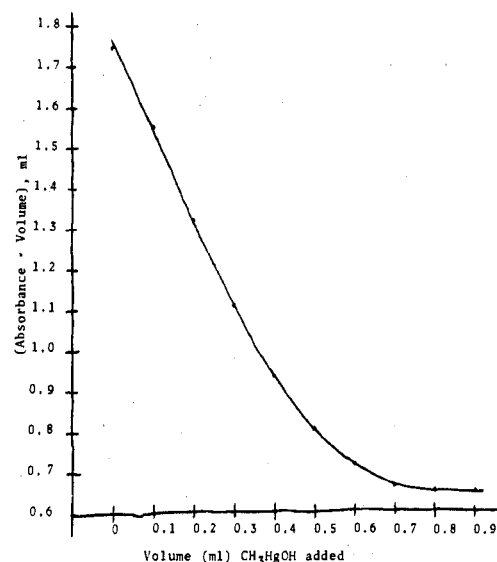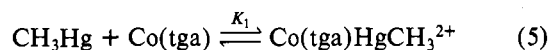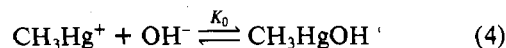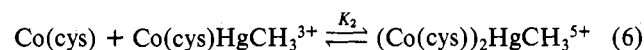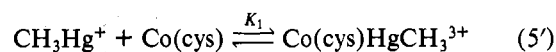observed data; these values are listed in Table I.

Data defining the Co(tga)/CH₃Hg equilibrium are presented in Table D.[15] These data are satisfactorily described by the equilibria

$$\text{CH}_3\text{Hg}^+ + \text{OH}^- \overset{K_0}{\rightleftharpoons} \text{CH}_3\text{HgOH} \qquad (4)$$

$$\text{CH}_3\text{Hg} + \text{Co(tga)} \overset{K_1}{\rightleftharpoons} \text{Co(tga)HgCH}_3^{2+} \qquad (5)$$

Taking K_0 to be 2.0 × 10⁹ M⁻¹,[17] our nonlinear least-squares analysis leads to the value of K_1 listed in Table I. However, the Co(cys)/CH₃Hg data require a third equation describing the formation of a 2:1 cobalt–mercury species as well as eq 4 and the analogue to eq 5. The difference between the Co(tga)/CH₃Hg and Co(cys)/CH₃Hg systems is manifested in the CH₃HgOH titration plots (Figures 1 and 3, respectively). The curvature in the Co(cys)–CH₃HgOH titration plot indicates a lower absorbance than would be observed if only the 1:1 [Co(cys)HgCH₃]³⁺ adduct were formed. The Co(cys)–CH₃HgOH titration data of Table E[15] were therefore fit to the following equilibria

$$\text{CH}_3\text{Hg}^+ + \text{Co(cys)} \overset{K_1}{\rightleftharpoons} \text{Co(cys)HgCH}_3^{3+} \qquad (5')$$

$$\text{Co(cys)} + \text{Co(cys)HgCH}_3^{3+} \overset{K_2}{\rightleftharpoons} (\text{Co(cys)})_2\text{HgCH}_3^{5+} \qquad (6)$$

by nonlinear least-squares techniques to yield the following parameter values: K_2 = (5.3 ± 0.5) × 10² M⁻¹, ϵ(425 nm) of [(Co(cys))₂HgCH₃]⁵⁺ is 65 ± 3 M⁻¹ cm⁻¹ at μ = 0.13 M. Using these derived parameter values, we analyzed the Co(cys)/CH₃Hg data of Table F[15] within eq 4, 5', and 6 to yield the value of K_1 listed in Table I.

A Job plot[18] for the adduct formed between Co(cys) and [PtCl₄]²⁻ (1.0 M HCl, [Co]$_{tot}$ + [Pt]$_{tot}$ = 2.0 × 10⁻⁴ M, λ 377 nm, l = 1.00 cm, absorbance readings taken 90 min after solution preparation) revealed that the adduct concentration is maximized at a Co/Pt ratio of 2.0.

Discussion

Elemental analyses of solid samples (Table A) confirm the existence of both 1:1 and 2:1 thiolato complex:soft metal adducts. The particular adduct which precipitates under specific solution conditions depends upon the interplay between several formation and solubility equilibria. A single-crystal X-ray diffraction study of the 2:1 adduct [(Co(cys))₂Ag]-

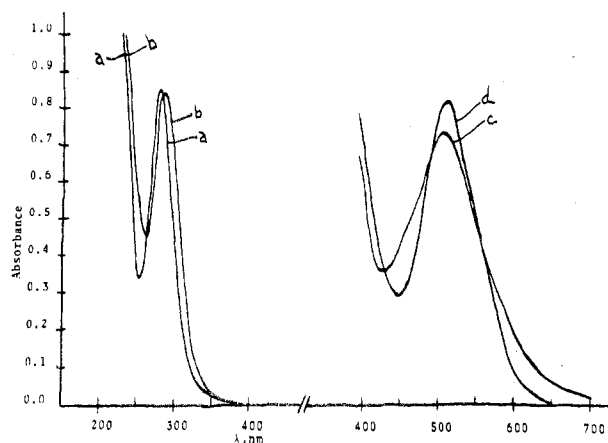**Figure 4.** Visible–UV spectra of Co(tga) and [Co(tga)Ag]$^{2+}$; l = 1.00 cm: (a) [Co(tga)]$_{tot}$ = 6.2 × 10^{-5} M, no Ag added; (b) [Co(tga)]$_{tot}$ = 6.2 × 10^{-5} M, [Ag]$_{tot}$ = 6.0 × 10^{-5} M; (c) [Co(tga)]$_{tot}$ = 4.1 × 10^{-3} M, no Ag added; (d) [Co(tga)]$_{tot}$ = 3.9 × 10^{-3} M, [Ag]$_{tot}$ = 3.8 × 10^{-3} M.

Table II. Visible–UV Spectrophotometric Parameters for Selected Thiolatobis(ethylenediamine)cobalt(III) Complexes and Adducts of These Complexes with Ag$^+$, CH$_3$Hg$^+$, and CH$_3^+$ ^{a}

complex	λ_{max} (ϵ)	λ_{max} (ϵ)
[(en)$_2$Co(SCH$_2$CH$_2$NH$_2$)]$^{2+}$	482 (142)	282 (13 800)
	600 (44) sh	
[(en)$_2$Co(S(R)CH$_2$CH$_2$NH$_2$)]$^{3+}$		
R = HgCH$_3$	500 (170)	275 (12 000)
R = Ag	495 (150)	285 (13 000)
R = CH$_3$ ^{b}	487 (177)	282 (8400)
[(en)$_2$Co(SCH$_2$COO)]$^+$	518 (152)	282 (11 700)
[(en)$_2$Co(S(R)CH$_2$COO)]$^{2+}$		
R = HgCH$_3$	515 (170)	280 sh
R = Ag	515 (180)	287 (11 000)
R = CH$_3$ ^{b}	499 (168)	280 (7300)

^{a} Wavelengths, λ, of maxima (max) and shoulders (sh) are in nm. Molar extinction coefficients, ϵ, given in parentheses, are in M^{-1} cm^{-1}. Spectra are recorded in dilute aqueous perchloric acid. ^{b} Data taken from ref 22.

(ClO$_4$)$_5$ confirms[1] that each silver atom is bound to the sulfur atoms of two Co(cys) moieties. The silver atom lies on a twofold axis with a Ag–S bond length of 2.40 (1) Å and a S–Ag–S angle of 164 (1)°. The sulfur atom is approximately tetrahedral with the four sites filled by cobalt, carbon, silver and an unshared pair of electrons. In general the primary coordination sphere of the cobalt(III) is unperturbed. Anion disorder has so far prevented refinement of this structure (isotropic thermal parameters) below R = 0.17.[1,19]

Adduct formation in solution is easily monitored by the spectral changes which accompany association of the coordinated thiol with a heavy-metal center (Figures 4 and 5, Table II). For example, brown solutions of Co(cys) turn red upon addition of [Ag(aq)]$^+$, [CH$_3$Hg(aq)]$^+$, or [Hg(aq)]$^{2+}$ (but not [Cd(aq)]$^{2+}$ or [Zn(aq)]$^{2+}$) due to the disappearance of the characteristic 600-nm shoulder in the Co(cys) spectrum (Figure 5). This 600-nm shoulder also disappears when the sulfur atom of Co(cys) is bonded to either one or two oxygen atoms (sulfenato[20] and sulfinato[21] complexes), an alkyl group (thioether[22] complex), or a sulfenyl group (disulfide[13,23] complex), implying that the 600-nm shoulder arises from a specific interaction between the thiolato ligand and the cobalt(III) center. Loss of the 600-nm shoulder therefore implies chemical modification of the Co(cys) thiolato functionality, and from the above we conclude that [Cd(aq)]$^{2+}$ and [Zn-(aq)]$^{2+}$ do not form detectable adducts with Co(cys). In general, spectrophotometric changes generated by adduct formation mimic those generated by alkylation of the coor-
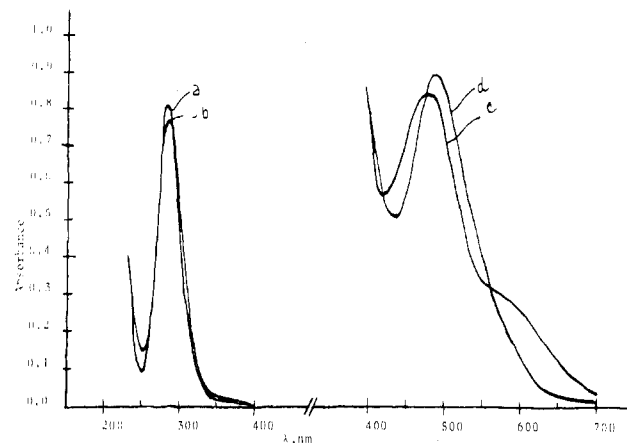

Figure 5. Visible–UV spectra of Co(cys) and [Co(cys)Ag]$^{3+}$; l = 1.00 cm: (a) [Co(cys)]$_{tot}$ = 6.0 × 10^{-5} M, no Ag added; (b) [Co(cys)]$_{tot}$ = 6.0 × 10^{-5} M, [Ag]$_{tot}$ = 6.0 × 10^{-5} M; (c) [Co(cys)]$_{tot}$ = 6.0 × 10^{-3} M, no Ag added; (d) [Co(cys)]$_{tot}$ = 5.6 × 10^{-3} M, [Ag]$_{tot}$ = 5.6 × 10^{-3} M.

dinated thiol ligand[22] (Table II). The presence of the diagnostic ligand-to-metal charge-transfer band at ca. 280 nm in the spectra of the adducts confirms that the adducts contain an intact sulfur–cobalt bond.[3]

The summary data of Table I show that the coordinated thiol ligands of the title complexes do not have nearly as large an affinity for Ag(I) as do free thiols but have about the same affinity as free thioethers. Likewise, the affinity of coordinated thiols for methylmercury is much less than that of free thiols but about the same as a thiol which is already coordinated to a mercury atom. These observations are in agreement with recent work showing coordinated thiols to have about the same nucleophilicity toward H$_2$O$_2$ as do free thioethers.[24,25] Thus it appears that it is the number of covalent bonding interactions involving sulfur, and not the formal charge of the sulfur compound or the chemical identity of the sulfur species, which primarily determines the Lewis basicity of the sulfur. While this generalization adequately describes the gross features of adduct formation with coordinated thiols, there are many subtleties observed in this, and other, work which are not yet readily explicable. For instance, the differences we observe (Table I) in heavy-metal affinities between Co(cys) and Co(tga) are not simply related to the formal charge of the complexes but are at least compatible with the different behavior of these complexes toward Cu(I) that has been observed by Lane and co-workers[8,11] (vide supra). Likewise, the high formation constant derived for the postulated three-coordinate mercury species [(Co(cys))$_2$HgCH$_3$]$^{5+}$ is unexpected, although other three-coordinate organomercury complexes are well documented.[12]

Registry No. Co(cys), 42901-32-6; Co(tya), 42901-31-5; Co-(cys)Ag^{3+}, 70224-71-4; (Co(cys))$_2$Ag^{5+}, 70235-80-2; Co(tga)Ag^{2+}, 42901-31-5; (Co(tga))$_2$Ag^{3+}, 70208-83-2; Co(cys)HgCH$_3^{3+}$, 70355-33-8; (Co(cys))$_2$HgCH$_3^{5+}$, 70355-34-9; Co(tga)HgCH$_3^{2+}$, 70355-32-7; [CH$_3$Hg(aq)]$^+$, 18042-02-9; [(Cocys)$_2$PtCl$_2$]Cl^4, 70343-03-2; [(Cocys)$_2$Ag](ClO$_4$)$_5$, 70198-15-1; [(Cotga)AgOH$_2$]-NO$_3$(SiF$_6$)$_{1/2}$, 70224-72-5; [(Cotga)AgOH$_2$](NO$_3$)$_2$, 70247-48-2.

Supplementary Material Available: Tables A–G giving elemental analysis data, Co(cys) and Co(tga) vs. [Ag(aq)]$^+$ titration data, Co(cys) and Co(tga) vs. [CH$_3$Hg(aq)]$^+$ titration data, Co(cys)–CH$_3$HgOH spectrophotometric titration data, and data used in the construction of Figure 2 (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Abstracted in part from the Ph.D. Thesis of M. J. Heeg, University of Cincinnati, 1978.
(2) G. J. Kennard and E. Deutsch, *Inorg. Chem.*, **17**, 2225 (1978).
(3) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **15**, 139 (1976).
(4) R. H. Lane, F. A. Sedor, M. J. Gilroy, P. F. Eisenhardt, J. P. Bennett, Jr., R. X. Ewall, and L. E. Bennette, *Inorg. Chem.*, **16**, 93 (1977).
(5) R. J. Balahura and N. A. Lewis, *Inorg. Chem.*, **16**, 2213 (1977).
(6) C. Shea and A. Haim, *J. Am. Chem. Soc.*, **93**, 3055 (1971).
(7) C. Shea and A. Haim, *Inorg. Chem.*, **12**, 3013 (1973).
(8) J. K. Farr and R. H. Lane, *J. Chem. Soc., Chem. Commun.*, 153 (1977).
(9) D. H. Busch and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962).
(10) R. E. DeSimone, T. Ontko, L. Wardman, and E. L. Blinn, *Inorg. Chem.*, **14**, 1313 (1975).
(11) R. H. Lane, N. S. Pantaleo, J. K. Farr, W. M. Coney, and M. G. Newton, *J. Am. Chem. Soc.*, **100**, 1610 (1978).
(12) D. L. Rabenstein, *Acc. Chem. Res.*, **11**, 100 (1978).
(13) M. Woods, J. Karbwang, J. C. Sullivan, and E. Deutsch, *Inorg. Chem.*, **15**, 1678 (1976).
(14) J. C. Sullivan, E. Deutsch, G. E. Adams, S. Gordon, W. A. Mulac, and K. H. Schmidt, *Inorg. Chem.*, **15**, 2864 (1976).
(15) Supplementary material.
(16) R. N. Moore and R. K. Ziegler, Report No. LA 2367, plus Addenda, Los Alamos Scientific Laboratory, Los Alamos, N.Mex., 1959.
(17) S. Libich and D. L. Rabenstein, *Anal. Chem.*, **45**, 118 (1973).
(18) L. I. Katzin and E. L. Gebert, *J. Am. Chem. Soc.*, **72**, 5455 (1950).
(19) $R = \sum ||F_o| - |F_c||/\sum |F_o|$.
(20) I. K. Adzamli, K. Libson, J. D. Lydon, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **18**, 303 (1979).
(21) B. A. Lange, K. Libson, E. Deutsch, and R. C. Elder, *Inorg. Chem.*, **15**, 2985 (1976).
(22) R. C. Elder, G. J. Kennard, M. D. Payne, and E. Deutsch, *Inorg. Chem.*, **17**, 1296 (1978).
(23) D. Nosco and E. Deutsch, work in progress.
(24) I. Kofi Adzamli, Ph.D. Thesis, University of Cincinnati, 1978.
(25) D. L. Herting, C. P. Sloan, A. W. Cabral, and J. H. Krueger, *Inorg. Chem.*, **17**, 1649 (1978).

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Cobalt(III) o-Semiquinone Complexes

Dennis G. Brown* and W. D. Hemphill

During the course of our work on the preparation of catecholato complexes of cobalt(III)[1] we became interested in the possibility of producing this type of system by oxidative addition of an o-quinone to a cobalt(I) species. We have, in fact, obtained a number of cobalt(III) compounds containing a coordinated catecholate dianion by this procedure.[2] However, in the synthesis of a number of cobalt(III) catecholates we obtain, as an additional product, a neutral compound now known to be a cobalt(III) complex of an o-semiquinone. It is the purpose of this report to describe the preparation and properties of three cobalt(III) complexes containing one tetradentate ligand and a coordinated 3,5-di-*tert*-butyl-o-benzosemiquinone anion. These free radical complexes are rather stable and show the unpaired electron to indeed be localized on the o-semiquinone ligand.

The occurrence of o-semiquinone complexes is by now well documented. Eaton demonstrated the occurrence of o-semiquinone coordination to a number of metal ions in solution.[3] Balch has also demonstrated o-semiquinone coordination in solution.[4] Several tris systems containing three o-semiquinones are also known.[5] Some of these were originally reported in the literature with a different formulation but have subsequently been characterized as tris(o-semiquinone) complexes. These systems are known especially with Fe(III) or Cr(III) in which substantial coupling between ligand and metal electrons occur, leading to unusual and interesting

magnetic behavior. This was in part responsible for some delay in recognizing these systems as true examples of o-semiquinone coordination. Recent work by Pierpont and Hendrickson has clearly characterized several tris iron(III) and chromium(III) o-semiquinone complexes.[6]

Von Zelewsky and Haas have reported in situ observation of a number of o-benzosemiquinone and chlorine-substituted o-benzosemiquinone complexes similar to those described here.[7] Their systems were prepared by addition of o-quinones to a cobalt(II) complex. We have earlier reported a very well-characterized 3,5-di-*tert*-butyl-o-semiquinone complex, [Co(trien)(DBsq)]²⁺, which was obtained by oxidation of the corresponding 3,5-di-*tert*-butylcatecholato complex.[8]

Results and Discussion

The reaction scheme shown in eq 1 represents a new method

$$(1)$$
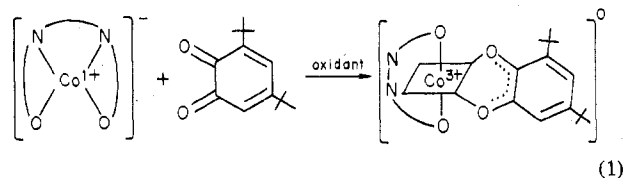
for obtaining cobalt(III) o-semiquinone complexes. The semiquinone complexes prepared, Co(BAE)(DBsq),[9] Co-(F₃BAE)(DBsq),[9] and Co(4,6-(OCH₃)₂salen)(DBsq),[9] are all soluble in nonaqueous solvents and form nonconducting solutions. The molecular weight of Co(BAE)(DBsq) has been measured and found to be 500 (theoretical 501.5) providing further evidence for the formulation shown in eq 1. The reaction scheme shown in eq 1 indicates that a one electron oxidation must take place during the course of the reaction to form the product. Since the reaction is carried out in the absence of O_2 the most likely oxidant is the o-quinone. Von Zelewsky and Haas have observed similar complexes in situ upon addition of o-quinones to a low-spin cobalt(II) complex,[7] thus the product in this reaction may arise from reaction between quinone and cobalt(II). It is also possible in our case that initial reaction between cobalt(I) and the o-quinone gives a cobalt(III) catecholato species which then undergoes a one-electron oxidation to the o-semiquinone complex.

In order for the o-semiquinone ligand to bind to the metal it must occupy cis coordination positions. As a result, the normally near-planar tetradentate ligand is forced to assume a nonplanar orientation. A number of cobalt(III) salen complexes have been reported which contain an additional bidentate ligand.[10] In these cases the configuration depicted in eq 1 has been found (this is the cis-β isomer with respect to the tetradentate ligand). Although definitive structural proof is not available in the complexes described here, the infrared spectra of these complexes have many similarities to the reported infrared spectra of Co(salen)L where L = a bidentate ligand (see Experimental Section).[10] Unfortunately the most interesting aspect of the infrared spectrum, the semiquinone C≏O stretch which occurs at 1440 cm⁻¹ in the [Co(trien)(DBsq)]²⁺ complex ion,[8] is not definitive in these complexes. This is because a rather strong and broad absorption band centered at 1440–1450 cm⁻¹ due to the tetradentate ligand overlaps the C≏O stretch. Nevertheless, the absence of a very strong C=O stretch at 1660 cm⁻¹ as well as the lack of a strong C–O stretch around 1250 cm⁻¹ indicate the absence of o-quinone or catecholate dianion coordination, thus indirectly indicating the presence of the o-semiquinone.

The magnetic moment measured for Co(BAE)(DBsq) is 1.79 μ_B, indicating one unpaired electron. Conclusive evidence for the localization of the unpaired electron on the o-semiquinone ligand comes from the ESR spectra. Figure 1 shows the ESR spectra of each of the three o-semiquinone complexes. Each spectrum shows an eight-line pattern due to coupling with