

sulfur to be protonated when it is coordinated to chromium, relative to when it is coordinated to cobalt. This would strongly favor the efficient acid-dependent aquation path for the chromium compound. The direction of this proposed variation in the Bronsted basicity of coordinated thiolato sulfur with the nature of the central metal ion is in accord with the observation that methyl iodide reacts more rapidly with the sulfur of $\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2$ than with the sulfur of $\text{Pd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2$ ⁵⁵ and with the observation that $\text{Cr}(\text{tga})$ and $\text{Cr}(\text{cys})$ salts are much more soluble than the corresponding cobalt compounds. These considerations, as well as

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relevant X-ray structural data, will be related to the rates of electron transfer through thiolato sulfur in a future communication.

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Registry No. $[\text{Cr}(\text{en})_2(\text{SCH}_2\text{COO})]\text{ClO}_4$, 41212-24-2; $[\text{Cr}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)_2]\text{ClO}_4$, 41777-29-1; $[\text{Cr}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)](\text{ClO}_4)_2$, 41777-30-4; $[\text{Cr}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]\text{I}_2$, 41777-31-5; $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{OOCCH}_2\text{SH})]^{2+}$, 41777-32-6; $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})(\text{NH}_2\text{CH}_2\text{CH}_2\text{SH})]^{3+}$, 41777-33-7.

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Crystal Structure Studies of Sulfur Trans Effects

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The single-crystal structures of mercaptoacetatobis(ethylenediamine)cobalt(III) chloride monohydrate, $[\text{Co}(\text{en})_2(\text{SCH}_2\text{COO})]\text{Cl}\cdot\text{H}_2\text{O}$, mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate, $[\text{Cr}(\text{en})_2(\text{SCH}_2\text{COO})]\text{ClO}_4$, and β -mercaptoethylaminebis(ethylenediamine)cobalt(III) dithiocyanate, $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)](\text{SCN})_2$, have been determined using the methods of X-ray crystallography. The unit cells and space groups are: $[\text{Co}(\text{en})_2(\text{SCH}_2\text{COO})]\text{Cl}\cdot\text{H}_2\text{O}$, monoclinic, $a = 12.071$ (8) Å, $b = 14.876$ (9) Å, $c = 7.539$ (5) Å, $\beta = 110.41$ (5)°, $P2_1/a$, $Z = 4$; $[\text{Cr}(\text{en})_2(\text{SCH}_2\text{COO})]\text{ClO}_4$, monoclinic, $a = 12.250$ (4) Å, $b = 10.155$ (3) Å, $c = 11.265$ (3) Å, $\beta = 95.21$ (4)°, $P2_1/n$, $Z = 4$; $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)](\text{SCN})_2$, orthorhombic, $a = 15.418$ (7) Å, $b = 11.563$ (6) Å, $c = 17.454$ (10) Å, $Pbca$, $Z = 8$. All intensity data were measured using a Syntex PI automated diffractometer. The structures have been refined by least-squares methods using anisotropic thermal parameters and including hydrogen atoms to final conventional R factors of 0.033, 0.037, and 0.032, respectively. All three complex cations are pseudo-octahedral six-coordinate species. Both mercaptoacetate and β -mercaptoethylamine anions chelate to form five-membered rings. The mercaptoacetate complexes both exhibit $\Delta\lambda\delta$ and $\Lambda\delta\delta\lambda$ configurations in their centric crystals. The β -mercaptoethylamine complex adopts the $\Delta\lambda\lambda\lambda$ and $\Lambda\delta\delta\delta$ configurations. All complexes appear weakly hydrogen bonded. In both cobalt complexes, the trans (to sulfur) Co-N distance is 0.04 Å longer than the average cis Co-N bond. The trans lengthening does not appear to occur in the chromium complex. The implications of the structural trans effect are discussed relative to the electron-transfer reactions of the three complexes with chromous ion.

Introduction

Sulfur-containing ligands have been the subject of intense study in recent years. New synthetic techniques have been discovered which allow the preparation of stable metal complexes^{2,3} whose free ligands are not stable. The peculiar effects of the sulfur-containing ligand on the geometric and electronic structures of dithiolate, dithiocarbamate, and β -dithioketone complexes^{2,4-6} are now well documented. The reactions of complexes of sulfur-containing ligands offer interesting contrasts. Thus, electron-transfer reactions of cobalt(III) complexes containing a thiolato ligand, β -mercaptoethylamine⁷ or mercaptoacetate,⁸ are extremely rapid; those of the analogous chromium(III) complexes⁷ are not. The aquation of these chromium complexes is found to proceed *via* chromium-sulfur and also chromium-nitrogen

bond fission at rates convenient for kinetic study,⁹ whereas the cobalt(III) analogs do not aquate.

To provide structural information on which to base an understanding of these reactions, we have determined the structures of a series of mixed ligand complexes of the type thiolato-X-bis(ethylenediamine)metal(III), $[\text{M}(\text{en})_2(\text{SRX})]^{n+}$, where the metal atom, M, is either cobalt or chromium and where thiolato-X is either β -mercaptoethylamine or mercaptoacetate. We wished to determine (a) if the complexes are all six coordinate with metal-bonded sulfur atoms, (b) the characteristic value of the metal-sulfur bond length, (c) whether some unusual structural detail such as a ground state trans effect, a peculiar conformation, or a set of unusual bond lengths (and presumably bond strengths) is present, and (d) whether the replacement of the carboxylate group of mercaptoacetate (tga) by methylenamine in β -mercaptoethylamine (cys) and the consequent change in charge of the complex cation led to significant changes in structure. We report here the single-crystal structural determinations of mercaptoacetatobis(ethylenediamine)cobalt(III) chloride monohydrate, mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate, and β -mercapto-

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ethylaminebis(ethylenediamine)cobalt(III) dithiocyanate.

Experimental Section

Collection and Reduction of Intensity Data. $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CO}_2)]\text{Cl}\cdot\text{H}_2\text{O}$. Dark red crystals of mercaptoacetatobis(ethylenediamine)cobalt(III) chloride monohydrate were obtained from E. A. Deutsch of the University of Chicago. A crystal was mounted along its a axis in a 0.2-mm glass capillary. Precession photographs of $h0l$, $hk0$, $h1l$, and $hk1$ zones (using Cu $K\alpha$ radiation) showed systematic absences of $h0l$ for h odd and $0k0$ for k odd. The monoclinic space group $P2_1/a$ (nonstandard setting¹⁰ of $P2_1/c$ no. 14, C_{2h}^5) with approximate cell constants, $a = 12.06$ (2), $b = 14.87$ (3), $c = 7.53$ (2) Å, and $\beta = 110.4$ (2)°, was indicated. As the photographs were taken, moisture appeared on the walls of the capillary and crystal efflorescence was assumed to be taking place.

A second crystal was obtained by recrystallization from an ethanol-water solution of the material supplied by Deutsch. This crystal of approximate dimensions $0.15 \times 0.15 \times 0.20$ mm, where the long dimension corresponded to the a direction, was mounted along a on a glass fiber. Although this mounting would not stop efflorescence, it would not collect water droplets in the X-ray beam as in the previous case. After the crystal was optically centered on the Syntex P1 diffractometer for intensity data collection, a full rotation photograph was taken and 15 rather intense reflections were chosen and centered using the manufacturer-supplied software.¹¹ The autoindexing program gave three axial choices, in agreement with those previously determined from precession photographs. Oscillation photographs ($\pm 14^\circ$) were taken about each of these axes to check crystal quality and to ensure that no common multiples had been introduced in the autoindexing process. Least-squares refinement using 2θ values found for the 15 precisely centered reflections gave the following lattice constants and errors: $a = 12.071$ (8), $b = 14.876$ (9), $c = 7.539$ (5) Å; $\beta = 110.41$ (5)°. Based on four formula units per unit cell, the calculated density is 1.70 g cm^{-3} and the measured density is 1.67 (5) g cm^{-3} (neutral buoyancy in $\text{CCl}_4\text{-CHBr}_3$). All data were measured at room temperature.

Intensity data were collected using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) with a graphite single crystal as monochromator. The sample crystal was positioned 45 mm from the collimator (diameter = 1 mm) and 90 mm from the counter (aperture diameter = 2 mm). The takeoff angle was 4° . A θ - 2θ scan mode was used with 2θ ranging from 1° below the calculated position for the $K\alpha_1$ reflection to 1° above the calculated position for the $K\alpha_2$ reflection. The scan rate was varied from 2 to 12° per minute, depending on the intensity of the reflection. Backgrounds were measured as stationary counts with the counter positioned at the lowest and highest 2θ values each for one-half the total scan time. Four reflections were used as standards and remeasured every 40 reflections to check on machine and crystal stability. A total of 2734 reflections were measured within a sphere $2\theta \leq 50^\circ$, of which 2234 were unique (hkl form).

The linear absorption coefficient, μ , of the compound for Mo $K\alpha$ radiation is 17.8 cm^{-1} . Minimum and maximum values of μR are 0.13 and 0.19, respectively. Since the maximum relative error in F_o due to absorption would be less than 5%, no correction was made.

The data were preprocessed by a program SYNTEX which has been inserted into our version of the program package XRAY67.¹² The integrated intensity (I) was calculated according to the expression¹³ $I = [\text{SC} - (B_1 + B_2)/B_R]T_R$ where SC are the scan counts, B_1 and B_2 are the background counts, B_R is the background time to scan time ratio, and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated

$$\sigma(I) = T_R[\text{SC} + (B_1 + B_2)/B_R^2 + (pI)^2]^{1/2}$$

where p in this case was set equal to 0.02.

The 96-step peak profiles¹⁴ were checked for uneven backgrounds and off-center peaks. If the backgrounds are uneven, automatic checks are made to see if (1) a neighboring reflection is intruding into one end of the scan (if so, the off-center one of the two is subtracted

out) or (2) the peak itself has considerable intensity at one end of the scan, which presumably occurs because the peak is too broad and/or too badly centered for the scan; if so, the intensity peak center (PC) in the 96-step scan is approximated¹⁵ using the expression

$$\text{PC} = \frac{\sum_{i=1}^n iC_i / \sum_{i=1}^n C_i}{n}$$

where C_i is the number of counts for the i th step. Those reflections whose centers are outside desired limits are rejected. (This crystal: one reflection, 1 2 -1 rejected.)

The standard reflections are used to automatically rescale the data in the following manner: the normalized integrated intensities of each of the standards in the group are summed; the ratio of any standard group sum to the first sum then gives a relative scale factor. Each reflection intensity is then multiplied by an interpolated scale factor depending on the time at which it was measured, giving a set of reflections with one relative scale factor. The rescale factors varied from 1.007 to 0.987. The changes in rescale factors were random but long term; no systematic cause was determined for this behavior. No individual standard varied by more than two esd's from its average value throughout the data collection. Thus, although some efflorescence of the crystal undoubtedly took place during the week-long intensity data collection period, it appears not to have significantly affected the measured intensities.

The set of unique, normalized, integrated intensities was processed to give values of $|F|$ and $|E|$. The polarization corrections are calculated on the basis that the beam is prepolarized to some extent by the monochromator crystal which is assumed to behave as 50% perfect and 50% perfectly mosaic. Of the 2234 unique reflections, 1656 were treated as observed, [$F_o^2 > 3\sigma(F_o^2)$].

$[\text{Cr}(\text{en})_2(\text{SCH}_2\text{CO}_2)]\text{ClO}_4$. Cherry red, well-developed crystals of mercaptoacetatobis(ethylenediamine)chromium(III) perchlorate were obtained from Deutsch. A relatively large, needle crystal ($0.15 \times 0.28 \times 1.48$ mm) was mounted on a glass fiber, along b , the long dimension, and precession photographs were taken of the $hk0$, $hk1$, $0kl$, $1kl$, and hkh zones using Cu $K\alpha$ radiation. The systematic absences noted were of $0k0$ for k odd and $h0l$ for $h + l$ odd. This corresponds to the nonstandard space group $P2_1/n$ which could be converted to $P2_1/c$ (no. 14, C_{2h}^5), the standard space group,¹⁰ by an appropriate choice of axes. However, the nonstandard monoclinic space group has a β angle much closer to 90° and so was used throughout the structure determination.

A second, smaller crystal ($0.13 \times 0.23 \times 0.45$ mm) was selected, mounted with its long dimension, b , coincident with the glass fiber axis, and positioned on the Syntex P1 diffractometer. The lattice constants obtained by least squares on 15 precisely centered reflections are $a = 12.250$ (4), $b = 10.155$ (3), $c = 11.265$ (3) Å; $\beta = 95.21$ (4)°. Based on four molecules in the unit cell the calculated density is 1.78 g cm^{-3} ; the measured density is 1.7 (1) g cm^{-3} (neutral buoyancy in $\text{CCl}_4\text{-CHBr}_3$).

Intensity data were recorded as described above using Mo $K\alpha$ radiation with the following differences; an unsymmetrical scan of 2θ of 0.7° below $K\alpha_1$ and 0.8° above $K\alpha_2$ positions was used for all reflections. A total of 1904 reflections, of which 1502 were unique, were measured for $2\theta \leq 43^\circ$. None of these reflections were rejected. A value of 0.02 was assigned to p in calculating $\sigma(F_o^2)$. Of the unique reflections, 1351 were treated as observed, [$F_o^2 > 3\sigma(F_o^2)$]. Four standards were measured for every 40 reflections, giving rescale factors (see above) which varied from 1.018 to 0.993 in an apparently random fashion. The linear absorption coefficient for this compound is 12.08 cm^{-1} . Maximum and minimum values of μR are 0.17 and 0.08, respectively. Since the maximum relative error expected in F_o due to absorption would be less than 4%, no correction was made.

$[\text{Co}(\text{en})_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})](\text{SCN})_2$. A large dark red crystal of mercaptoethylaminebis(ethylenediamine)cobalt(III) dithiocyanate, obtained from Deutsch, was mounted along its a axis on a glass fiber and precession photographs (using Cu $K\alpha$ radiation) of the $hk0$, $h0l$, $hk1$, and $h1l$ zones showed systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd. The orthorhombic space group $Pbca$ (no. 61, D_{2h}^{15}) was indicated.¹⁰

(14) The manufacturer-supplied software for data collection accumulates counts for each of 96 equal steps throughout the 2θ scan. These are then corrected for coincidence and a normalized intensity is calculated. This and other pertinent information is then written on magnetic tape for processing by our SYNTEX link of XRAY67.

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A second crystal was pneumatically ground into a sphere having a diameter of about 0.1 mm in order to reduce the anisotropy of the absorption of X-rays in the crystal. This sphere was mounted on a glass fiber and positioned on the Syntex P1 diffractometer. The orthorhombic lattice constants based on least-squares refinement of 2 θ values for 15 precisely centered reflections measured on this crystal are $a = 15.418$ (7), $b = 11.563$ (6), $c = 17.454$ (10) Å; $Z = 8$; $d_{\text{calcd}} = 1.55$ g cm $^{-3}$, $d_{\text{measd}} = 1.56$ (3) g cm $^{-3}$ (neutral buoyancy in CHCl $_3$ -CCl $_4$). These and subsequent intensity measurements were made using molybdenum radiation.

Intensity data were recorded as above with the following exceptions: the scan rate was varied from 0.5 to 24° per minute; five reflections were used as standards and remeasured every 40 reflections to check stability and form rescale factors which varied from 1.008 to 0.991 in an apparently random fashion during data collection; a total of 1708 reflections, of which 1493 were unique, were measured within a sphere of $2\theta < 41^\circ$. Four reflections (132, 222, 323, 324) were rejected (see above). Of the unique reflections, 1134 were treated as observed, [$F_o^2 > 3\sigma(F_o^2)$], where a value of $p = 0.02$ was used in the formula given above to calculate $\sigma(F_o^2)$. The linear absorption coefficient for this compound is 14.97 cm $^{-1}$. For a sphere of 0.1-mm diameter, the value of μR is 0.08. Since we estimate the maximum relative error in F_o due to absorption (due to a slightly nonspherical crystal) to be less than 1%, no correction was made.

Structure Solution and Refinement. [Co(en) $_2$ (tga)]Cl·H $_2$ O. A sharpened, origin-removed Patterson function¹² indicated the position of the cobalt atom. The corresponding Fourier map clearly showed the positions of all nonhydrogen atoms except the oxygen atom of the water molecule. The structure was refined using isotropic thermal parameters and unit weights to give $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o| = 0.134$. A difference map showed the position of the oxygen atom of the water molecule. Several cycles of least squares using anisotropic thermal parameters for all atoms gave $R = 4.7\%$. A difference Fourier showed 18 distinct peaks, each of which corresponded to one of the 18 peaks expected for the hydrogen atoms not of the water molecule. Hydrogen atoms were added at the positions found in the difference map and two cycles of refinement of all parameters including hydrogen atom positions and an overall hydrogen atom isotropic temperature factor led to an R value of 3.3%. The changes in all nonhydrogen-atom parameters were less than one-third of their esd's in the last cycle. Hydrogen atom 42 moved 1.2 esd in y , hydrogen atom 91 moved 1.0 esd in y , and hydrogen atom 92 moved 0.7 esd in y ; all other hydrogen atom shifts were less than 0.5 esd. A difference Fourier computed at this stage showed three peaks of about two-thirds the height of the average for a hydrogen atom in the previous map. None of these could be ascribed to the hydrogen atoms of the water molecule.

Examination of the R factors calculated for groups of reflections with increasing values of $\sin \theta / \lambda$ showed no systematic variation. Calculations using reflections grouped by F_o revealed that the 500 least intense observed reflections were probably given insufficient importance. The scattering curves were for Co $^{2+}$, Cl, S, O, N, C, and H.¹⁶ The use of unit weights, inclusion of hydrogen atom positional parameters as least-squares variables, and the use of less than the most modern scattering curves in all three of the structural determinations reported here may be reasonably criticized as less than ideal; therefore, several cycles of refinement were run using the Corfield weighting scheme¹³ where $p = 0.02$ and $w = F^2 / \sigma^2(F^2)$. The hydrogen atoms, located at their calculated positions based on expected geometry (C-H = 1.07 Å and N-H = 1.00 Å, with tetrahedral geometry) and given isotropic thermal parameters of 4.0 Å 2 , were included in the calculation but not allowed to vary in the least-squares refinement. The Cromer¹⁷ tabulation of scattering curves was used for Co, Cl, S, O, N, and C; that of Stewart¹⁸ was used for H. Anomalous dispersion corrections¹⁹ were incorporated as follows: Co, $\Delta f' = 0.4$, $\Delta f'' = 1.0$; Cl, $\Delta f' = 0.1$, $\Delta f'' = 0.2$; S, $\Delta f' = 0.1$, $\Delta f'' = 0.2$. This refinement, on F , converged with $R_1 = 0.036$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o^2)]^{1/2} = 0.034$ compared to the previous $R_1 = 0.033$. The

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Table I. [Co(en) $_2$ (tga)]Cl·H $_2$ O Fractional Atomic Positional Parameters^{a, b}

Atom	x	y	z
Co	0.20402 (5)	0.06658 (4)	0.77005 (8)
S	0.28554 (11)	-0.03677 (9)	0.99434 (18)
C(2)	0.1488 (5)	-0.0902 (4)	0.9847 (8)
C(1)	0.0405 (4)	-0.0508 (3)	0.8374 (6)
O(1)	0.0515 (3)	0.0193 (2)	0.7450 (4)
O(2)	-0.0565 (3)	-0.0868 (3)	0.8067 (5)
N(1)	0.3607 (4)	0.1083 (3)	0.7786 (6)
C(3)	0.4116 (5)	0.0381 (4)	0.6893 (8)
C(4)	0.3137 (5)	0.0067 (4)	0.5129 (8)
N(2)	0.2096 (4)	-0.0133 (3)	0.5670 (6)
N(3)	0.1231 (4)	0.1642 (3)	0.5876 (6)
C(5)	0.1340 (5)	0.2498 (3)	0.6952 (8)
C(6)	0.1144 (5)	0.2269 (3)	0.8765 (8)
N(4)	0.1945 (4)	0.1506 (3)	0.9652 (6)
Cl	0.3235 (1)	0.2598 (1)	0.4185 (2)
O(3)	-0.0164 (4)	0.3131 (3)	0.1873 (6)
H(11)	0.408 (6)	0.127 (4)	0.901 (9)
H(12)	0.354 (6)	0.163 (5)	0.720 (9)
H(21)	0.212 (6)	-0.062 (5)	0.619 (9)
H(22)	0.143 (6)	-0.007 (4)	0.467 (9)
H(31)	0.150 (6)	0.170 (4)	0.492 (9)
H(32)	0.048 (6)	0.148 (4)	0.536 (9)
H(41)	0.265 (6)	0.176 (4)	1.037 (9)
H(42)	0.162 (6)	0.117 (4)	1.046 (9)
H(51)	0.146 (5)	-0.091 (4)	1.109 (9)
H(52)	0.150 (5)	-0.151 (4)	0.946 (9)
H(61)	0.442 (5)	-0.016 (4)	0.777 (9)
H(62)	0.486 (6)	0.061 (4)	0.663 (9)
H(71)	0.332 (5)	-0.039 (4)	0.452 (9)
H(72)	0.289 (5)	0.060 (4)	0.408 (9)
H(81)	0.075 (5)	0.294 (4)	0.617 (9)
H(82)	0.221 (6)	0.269 (4)	0.719 (9)
H(91)	0.030 (6)	0.208 (4)	0.844 (9)
H(92)	0.122 (6)	0.279 (5)	0.959 (9)

^a The estimated errors in the last digit are given in parentheses. This form is used throughout the paper. ^b The numbering system for nonhydrogen atoms is indicated in Figure 1. The relation of the hydrogen atoms to these heavy atoms is given in Table XII.

standard deviation of an observation of unit weight was 1.10. The changes in the least-squares parameters do not appear significant; thus, with 48 nonhydrogen atom positional parameters, 15 changed by more than 1σ , four by more than 2σ , and one by more than 3σ (the z coordinate of the oxygen atom of the water molecule). Two of the corresponding bond lengths changed by more than 1σ : C(3)-C(4) 1.522 (5) here, 1.513 (7) previously; C(5)-C(3) 1.502 (5) here, 1.492 (7) previously. Thus, we have chosen to discuss the results obtained using unit weights in all three structural determinations described herein.

[Cr(en) $_2$ (tga)]ClO $_4$. A Patterson map was computed using the observed reflections and it indicated the presence of the four chromium atoms on the general position $(x, y, z; 1/2 + x, 1/2 - y, 1/2 + z; \bar{x}, \bar{y}, \bar{z}; 1/2 - x, 1/2 + y, 1/2 - z)$. An electron density map computed using signs derived from the heavy atom position showed many of the other atoms; a second map, using the added information for signs of F_o , clearly revealed the positions of all nonhydrogen atoms including the oxygen atoms of the perchlorate ion. Least-squares refinement using unit weights and isotropic temperature parameters yielded $R_1 = 0.11$. The perchlorate oxygen atom temperature parameters had risen to ~ 12 Å 2 , possibly indicating some disorder or large librational motion of the ion. Anisotropic temperature parameters were introduced for all atoms and refinement continued for several cycles varying all parameters until $R = 0.055$. At that point a difference Fourier synthesis clearly indicated positions for all of the hydrogen atoms in the structure. These atoms were added to the calculation and their positions refined as well as an overall hydrogen atom temperature parameter. Convergence was approached varying all parameters at $R = 0.037$. The overall hydrogen temperature parameter was 3.73 (2) Å 2 and had changed 1.1 σ in the last cycle of refinement. No other parameter changed by 0.5σ in the final cycle. The 226 parameters were varied in three blocks. The first block contained the scale factor and hydrogen atom overall temperature parameter. The second block contained the 54 hydrogen atomic positional parameters. The nonhydrogen atomic positional and anisotropic temperature parameters were varied as a third block. A difference Fourier map computed after the final

Table II. $[\text{Co}(\text{en})_2(\text{tga})]\text{Cl}\cdot\text{H}_2\text{O}$ Anisotropic^a Thermal Parameters ($\times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	232 (3)	226 (3)	221 (3)	-12 (2)	61 (2)	4 (2)
S	311 (6)	374 (7)	365 (6)	2 (5)	33 (5)	103 (5)
C(2)	479 (30)	385 (28)	454 (30)	-73 (23)	164 (25)	61 (24)
C(1)	370 (26)	393 (27)	252 (23)	-101 (21)	140 (19)	-74 (20)
O(1)	283 (16)	336 (17)	295 (16)	-14 (13)	78 (13)	41 (13)
O(2)	401 (20)	653 (25)	374 (19)	-226 (18)	127 (15)	-22 (18)
N(1)	281 (20)	383 (22)	337 (21)	-73 (17)	97 (17)	-13 (18)
C(3)	313 (26)	466 (31)	585 (33)	-9 (22)	231 (25)	-17 (26)
C(4)	431 (29)	480 (31)	455 (30)	1 (24)	224 (24)	-72 (25)
N(2)	307 (20)	328 (21)	310 (20)	31 (16)	98 (17)	-15 (17)
N(3)	353 (21)	288 (20)	295 (20)	30 (16)	101 (17)	19 (16)
C(5)	497 (30)	269 (24)	418 (28)	22 (22)	186 (24)	-10 (21)
C(6)	576 (33)	372 (25)	459 (30)	12 (23)	296 (26)	-56 (22)
N(4)	391 (22)	336 (21)	293 (20)	-75 (18)	118 (17)	34 (17)
Cl	539 (7)	367 (7)	495 (8)	-37 (6)	254 (6)	49 (6)
O(3)	803 (31)	781 (32)	537 (25)	221 (26)	246 (23)	219 (24)

^a The thermal parameters are of the form $\exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

cycle of refinement showed three peaks of the average height found previously for the hydrogen atoms. Two of these were in the vicinity of the perchlorate ion and may be ascribed to disorder of the oxygen atoms. The remaining peaks were less than 0.6 the height of the average hydrogen atom. Examination of the R factors computed for groups of reflections ordered in increasing value of $\sin \theta/\lambda$ showed no systematic trends. The scattering curves¹⁸ were for Cr^{2+} , Cl, S, O, N, C, and H. Corrections for anomalous dispersion were performed for chromium using¹⁹ $\Delta f' = 0.3$, $\Delta f'' = 0.8$.

$[\text{Co}(\text{en})_2(\text{cys})](\text{SCN})_2$. Patterson methods indicated the position of the cobalt atom. A Fourier map based on the cobalt position clearly revealed positions of six other atoms. Using information provided by the first electron density map, a second map was constructed which clearly showed positions of all nonhydrogen atoms excluding those of one thiocyanate group. A difference map indicated a disorder of one of the two thiocyanate groups and population parameters of 0.5 were assigned to atoms of both spatial configurations of the disordered moiety. Continued refinement of all nonhydrogen atoms using unit weights and anisotropic thermal parameters gave $R_1 = 4.9\%$. A difference Fourier indicated positions of all hydrogen atoms in the structure. These were added to the calculation and their positions as well as hydrogen atom isotropic temperature parameters were refined. Convergence was approached at $R = 0.032$ by varying all parameters. The overall scale factor oscillated in the last two cycles of refinement by 2.1σ . All other parameters changed by less than 1σ in the final cycle of refinement. Examination of R factors computed for groups of reflections ordered in increasing values of $\sin \theta/\lambda$ showed no systematic trends. The scattering curves¹⁸ were for Co^{3+} , S, N, C, and H. Corrections for anomalous dispersion¹⁹ were performed for cobalt using $\Delta f' = 0.4$, $\Delta f'' = 1.0$.

Results and Discussion

The final atomic positional parameters and their estimated standard deviations for $[\text{Co}(\text{en})_2(\text{tga})]\text{Cl}\cdot\text{H}_2\text{O}$ are listed in Table I. The anisotropic temperature factors for the nonhydrogen atoms are listed in Table II and the associated thermal vibrational ellipsoids may be seen in Figure 1, which has been drawn using ORTEPII.²⁰ Table A²¹ containing the observed and calculated structure factors for this structure is available. The root-mean-square amplitudes of vibration for the nonhydrogen atoms are listed in Table III.

For $[\text{Cr}(\text{en})_2(\text{tga})]\text{ClO}_4$ the final atomic positional parameters and their estimated standard deviations are given in Table IV. The associated anisotropic thermal parameters

Table III. $[\text{Co}(\text{en})_2(\text{tga})]\text{Cl}\cdot\text{H}_2\text{O}$ Root-Mean-Square Amplitudes of Vibration

Atom	Atom	Atom	Atom	Atom	Atom	Atom	Atom
Co	142	148	160	C(4)	176	213	233
S	156	185	231	N(2)	168	174	191
C(2)	173	216	235	N(3)	164	175	192
C(1)	147	169	221	C(5)	163	200	224
O(1)	164	169	195	C(6)	151	192	249
O(2)	163	194	282	N(4)	164	175	211
N(1)	156	185	205	Cl	175	215	240
C(3)	158	215	243	O(3)	202	260	320

Table IV. $[\text{Cr}(\text{en})_2(\text{tga})]\text{ClO}_4$ Fractional Atomic Positional Parameters^a

Atom	x	y	z
Cr	0.14981 (6)	0.15295 (7)	0.27537 (6)
S	0.20618 (11)	0.01640 (12)	0.43636 (11)
Cl	0.06747 (11)	0.38655 (14)	0.70944 (13)
N(1)	0.0240 (3)	0.0242 (4)	0.2124 (4)
N(2)	0.0231 (3)	0.2377 (4)	0.3631 (4)
N(3)	0.1157 (3)	0.2696 (4)	0.1212 (4)
N(4)	0.2626 (3)	0.0707 (4)	0.1700 (4)
O(1)	0.2592 (3)	0.2785 (3)	0.3464 (3)
O(2)	0.3880 (3)	0.3374 (4)	0.4879 (3)
O(3)	0.0178 (6)	0.2678 (6)	0.7092 (10)
O(4)	0.0067 (5)	0.4711 (9)	0.7746 (9)
O(5)	0.1727 (4)	0.3841 (8)	0.7605 (5)
O(6)	0.0539 (8)	0.4318 (11)	0.5977 (6)
C(1)	0.3189 (4)	0.2583 (5)	0.4460 (5)
C(2)	0.2991 (6)	0.1335 (6)	0.5133 (5)
C(3)	0.0686 (4)	0.0357 (6)	0.2902 (5)
C(4)	-0.0844 (4)	0.1796 (6)	0.3171 (5)
C(5)	0.1585 (5)	0.1994 (6)	0.0180 (4)
C(6)	0.2703 (4)	0.1471 (6)	0.0584 (5)
H(18)	-0.007 (4)	0.043 (6)	0.139 (5)
H(19)	0.046 (5)	-0.063 (6)	0.211 (5)
H(28)	0.041 (5)	0.223 (6)	0.441 (5)
H(29)	0.024 (5)	0.311 (6)	0.361 (5)
H(38)	0.150 (5)	0.341 (6)	0.136 (5)
H(39)	0.043 (5)	0.289 (6)	0.096 (5)
H(48)	0.245 (5)	-0.015 (6)	0.160 (5)
H(49)	0.318 (5)	0.065 (6)	0.210 (5)
H(21)	0.363 (5)	0.093 (6)	0.550 (5)
H(22)	0.285 (6)	0.149 (6)	0.596 (5)
H(31)	-0.136 (5)	-0.011 (6)	0.245 (5)
H(32)	-0.042 (5)	-0.014 (6)	0.372 (5)
H(41)	-0.143 (5)	-0.193 (6)	0.372 (5)
H(41)	-0.111 (5)	0.234 (6)	0.234 (5)
H(51)	0.155 (5)	0.254 (6)	-0.051 (5)
H(52)	0.106 (5)	0.129 (6)	-0.011 (5)
H(61)	0.321 (4)	0.226 (6)	0.082 (5)
H(62)	0.296 (4)	0.096 (6)	-0.006 (5)

^a The numbering system for nonhydrogen atoms is: O(3)-O(6) perchlorate oxygen atoms; all others shown in Figure 2. The relation of hydrogen atoms to these is: H(n8) and H(n9) bound to N(n), H(n1) and H(n2) bound to C(n).

for the nonhydrogen atoms are presented in Table V. The root-mean-square amplitudes of vibration for these atoms are listed in Table VI and the structure of this cation is illustrated in Figure 2. Table B containing the observed and calculated structure factors²¹ is available.

For $[\text{Co}(\text{en})_2(\text{cys})](\text{SCN})_2$ the final atomic positional parameters and their estimated standard deviations are listed in Table VII. The accompanying anisotropic thermal parameters are found in Table VIII and the corresponding root-mean-square displacements in Table IX. The structure of this cation is indicated in Figure 3. Table X presents the isotropic thermal parameters obtained in the last cycle of refinement. Table C, with the observed and calculated structure factors, is available.²¹

Coordination Geometry and Conformation. For both the cobalt and chromium complexes of mercaptoacetate, the geometrical structures and conformations are essentially

(20) C. K. Johnson, "A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustration," ORTEPII, Report ORNL-3794, 2nd revision, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1970. All structures have been plotted with 50% probability ellipsoids.

(21) See paragraph at end of paper regarding supplementary material.

Table V. $[\text{Cr}(\text{en})_2(\text{tga})]\text{ClO}_4$ Anisotropic^a Thermal Parameters ($\times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	210 (4)	200 (4)	246 (4)	-6 (3)	10 (3)	-5 (3)
S	373 (7)	251 (7)	328 (7)	-12 (6)	10 (6)	45 (6)
Cl	356 (8)	414 (9)	464 (9)	7 (7)	56 (6)	66 (7)
N(1)	291 (23)	365 (25)	344 (24)	-74 (20)	81 (19)	72 (20)
N(2)	349 (26)	333 (25)	433 (26)	53 (21)	27 (21)	-68 (21)
N(3)	307 (26)	392 (26)	385 (26)	-16 (20)	-20 (20)	85 (22)
N(4)	331 (24)	287 (24)	384 (25)	-7 (19)	81 (19)	7 (20)
O(1)	324 (19)	240 (18)	308 (20)	-25 (15)	-61 (17)	28 (16)
O(2)	402 (22)	433 (23)	453 (22)	-143 (20)	-76 (18)	-28 (19)
O(3)	1343 (62)	556 (40)	3843 (134)	-325 (41)	-443 (72)	444 (60)
O(4)	863 (46)	2085 (85)	2742 (102)	316 (52)	-69 (53)	-1557 (81)
O(5)	368 (30)	2485 (85)	1140 (46)	65 (41)	-136 (29)	134 (52)
O(6)	2548 (103)	3019 (127)	938 (53)	-779 (94)	-463 (59)	941 (71)
C(1)	329 (31)	284 (31)	372 (33)	5 (27)	32 (27)	-49 (26)
C(2)	874 (49)	477 (39)	508 (38)	-275 (36)	-343 (35)	156 (32)
C(3)	349 (32)	469 (36)	542 (37)	-85 (27)	150 (28)	-63 (29)
C(4)	264 (30)	505 (37)	556 (37)	5 (27)	108 (26)	-77 (30)
C(5)	497 (36)	578 (38)	279 (30)	-99 (31)	-7 (27)	65 (29)
C(6)	477 (35)	458 (35)	382 (32)	-22 (29)	165 (27)	33 (28)

^a The thermal parameters are of the form $\exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.

Table VI. $[\text{Cr}(\text{en})_2(\text{tga})]\text{ClO}_4$ Root-Mean-Square Amplitudes of Vibration ($\times 10^3$ Å)

Atom	Atom						
Cr	140	147	159	C(3)	155	209	273
S	154	183	191	C(4)	163	201	263
O(1)	147	160	205	C(5)	169	216	255
O(2)	154	218	246	C(6)	168	214	243
N(1)	135	171	236	Cl	172	200	235
N(2)	153	187	228	O(3)	205	358	645
N(3)	163	191	222	O(4)	258	312	640
N(4)	156	174	210	O(5)	181	347	500
C(1)	167	181	210	O(6)	235	444	640
C(2)	150	199	359				

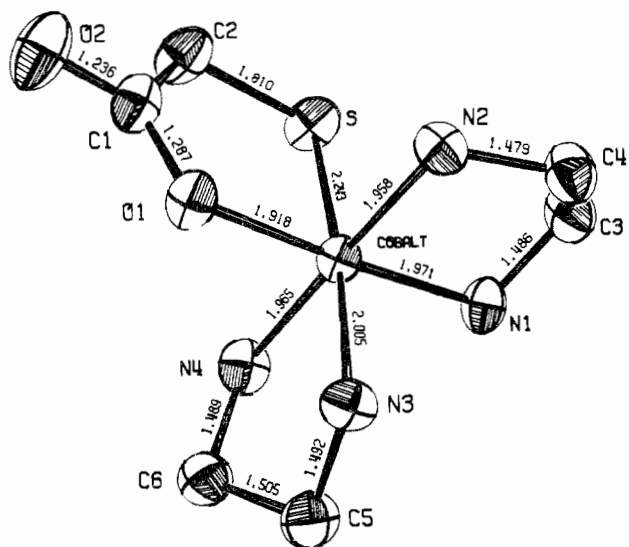


Figure 1. The structure of the complex cation mercaptoacetato-bis(ethylenediamine)cobalt(III), shown looking down the pseudo threefold axis. The thermal ellipsoids are drawn at 50% probability in all figures.

identical, as can be seen from Figures 1 and 2. The complex cation is six coordinate, binding two ethylenediamine groups and the mercaptoacetate dianion (tga), the latter through both sulfur and oxygen atoms to form a five-membered ring. Neither cation has any crystallographic symmetry and both are present in both right- and left-handed forms. The gauche conformation of the ethylenediamine chelates could lead to six different isomers, $\Delta\lambda\lambda$, $\Delta\lambda\delta$, or $\Delta\delta\delta$, and their accompanying enantiomers. The $\Delta\lambda\delta$ form is found in both the

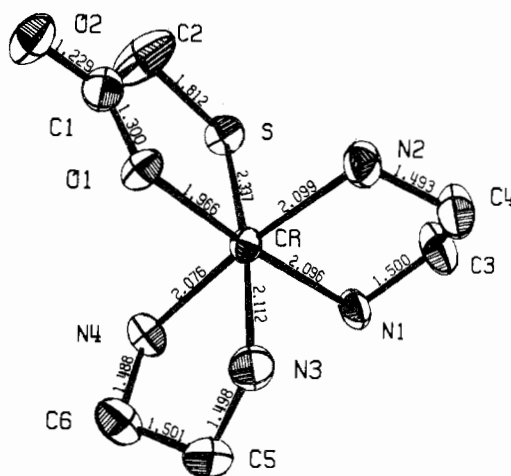


Figure 2. Perspective drawing of the cation mercaptoacetato-bis(ethylenediamine)chromium(III).

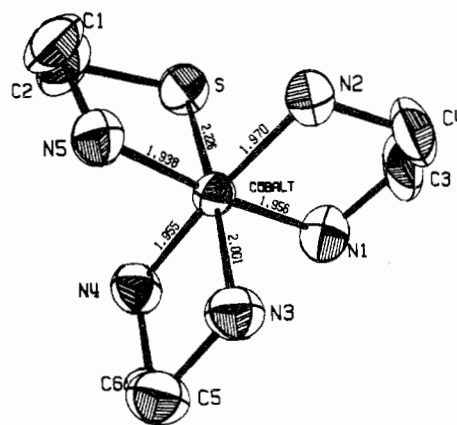


Figure 3. Perspective drawing of the cation β -mercaptoethylamine-bis(ethylenediamine)cobalt(III).

cobalt and chromium cations. The $\Delta\delta\delta$ form has been found for the structure of the oxolato-bis(ethylenediamine)chromium(III) ion by Lethbridge, Glasser, and Taylor.²² These authors state that the $\Delta\lambda\lambda$ form will be inherently the most stable but additional hydrogen bonds which can be formed to the $\Delta\delta\delta$ isomer overcome its inherent instability.

(22) J. W. Lethbridge, L. S. D. Glasser, and H. F. W. Taylor, *J. Chem. Soc. A*, 1862 (1970).

Table VII. [Co(en)₂(cys)](SCN)₂, Fractional Atomic Positional Parameters^{a,b}

Atom	x	y	z
Co	0.06279 (5)	0.20116 (7)	0.11813 (4)
S(1)	-0.01572 (12)	0.03976 (15)	0.12289 (10)
S(10)	0.3384 (1)	0.4782 (2)	0.3095 (1)
S(11) ^b	0.4482 (7)	0.1535 (9)	0.1049 (6)
S(12) ^b	0.3513 (7)	0.2719 (6)	0.1708 (5)
N(1)	0.1676 (4)	0.1080 (5)	0.1317 (3)
N(2)	0.0852 (3)	0.1833 (4)	0.0077 (3)
N(3)	0.1291 (3)	0.3496 (4)	0.1241 (3)
N(4)	0.0514 (3)	0.2191 (5)	0.2291 (3)
N(5)	-0.0425 (3)	0.2863 (4)	0.0957 (3)
N(10)	0.1567 (5)	0.0930 (6)	0.4498 (4)
N(11) ^b	0.3125 (12)	0.2960 (24)	0.1409 (21)
N(12) ^b	0.4392 (22)	0.1284 (26)	0.0667 (12)
C(1)	-0.1202 (4)	0.2134 (7)	0.0827 (5)
C(2)	-0.1179 (4)	0.1155 (8)	0.1362 (5)
C(3)	0.1921 (5)	0.0570 (7)	0.0580 (4)
C(4)	0.1740 (5)	0.1399 (7)	-0.0023 (4)
C(5)	0.1165 (5)	0.4009 (6)	0.2010 (4)
C(6)	0.1135 (4)	0.3070 (6)	0.2576 (4)
C(10)	0.1581 (4)	0.0467 (6)	0.3917 (5)
C(11) ^b	0.3687 (14)	0.2343 (28)	0.1268 (16)
C(12) ^b	0.4021 (17)	0.1864 (25)	0.1131 (19)
H(11)	-0.118 (4)	0.186 (5)	0.020 (4)
H(12)	-0.173 (4)	0.261 (6)	0.085 (3)
H(21)	-0.123 (5)	0.154 (7)	0.194 (4)
H(22)	-0.172 (4)	0.059 (6)	0.122 (4)
H(31)	0.251 (4)	0.042 (4)	0.049 (3)
H(32)	0.141 (5)	-0.018 (7)	0.061 (4)
H(41)	0.214 (5)	0.213 (7)	0.023 (4)
H(42)	0.177 (3)	0.112 (4)	-0.052 (3)
H(51)	0.061 (4)	0.444 (5)	0.196 (3)
H(52)	0.156 (4)	0.459 (5)	0.212 (3)
H(61)	0.169 (3)	0.262 (5)	0.263 (3)
H(62)	0.096 (3)	0.329 (4)	0.304 (3)
H(13)	0.154 (5)	0.054 (7)	0.167 (4)
H(14)	0.205 (5)	0.158 (6)	0.156 (4)
H(23)	0.076 (4)	0.252 (6)	-0.014 (4)
H(24)	0.046 (4)	0.123 (6)	-0.010 (4)
H(33)	0.185 (4)	0.339 (6)	0.112 (4)
H(34)	0.098 (4)	0.400 (5)	0.089 (3)
H(43)	-0.005 (4)	0.235 (6)	0.241 (4)
H(44)	0.060 (4)	0.147 (5)	0.248 (4)
H(53)	-0.053 (4)	0.336 (6)	0.131 (4)
H(54)	-0.034 (5)	0.336 (7)	0.049 (4)

^a The numbering system for nonhydrogen atoms is indicated in Figure 3. The relation of the hydrogen atoms to these is as follows: the first subscript of the hydrogen atom is the subscript of the heavy atom to which it is bonded; the second subscript of the hydrogen atom indicates the type of atom to which it is bonded, *i.e.*, 1 or 2 if bound to carbon, 3 or 4 if bound to nitrogen. The thiocyanate anions are S(10)C(10)N(10), S(11)C(11)N(11), and S(12)C(12)N(12). The latter two represent the disordered anion. ^b These atoms were assigned a population parameter of 0.5 to account for the disorder. All other atoms were given a value of unity.

Hawkins²³ calculates either the $\Delta\lambda\lambda$ or the $\Delta\lambda\delta$ form to be most stable, depending on the method of calculation, and claims all three forms to be within 0.5 kcal mol⁻¹ of each other in conformation energy.

The hydrogen bonding network found in [Co(en)₂(tga)]Cl·H₂O seems to be one of rather weak bonds. The chloride ion bonds to the water molecule [Cl⁻··O(3), 3.21 Å],²⁴ to two nitrogen atoms of one cation [Cl⁻··H(12)-N(1), Cl-H 2.6 Å, Cl-N 3.44 Å; Cl⁻··H(31)-N(3), Cl-H 2.7 Å, Cl-N 3.41 Å], and to another nitrogen atom on a second cation [Cl⁻··H(21)-N(2), Cl-H 2.7 Å, Cl-N 3.41 Å]. The water molecule is bound to two nitrogen atoms [O(3)··H(11)-N(1), O-H 2.2 Å, O-N 3.14 Å; O(3)··H(41)-N(4), O-H 2.5 Å, O-N

3.35 Å] as well as to the chloride ion. The carbonyl oxygen atom of the mercaptoacetic acid is apparently bound to a nitrogen atom of a second complex cation [O(2)··H(42)-N(4), O-H 2.0 Å, O-N 2.94 Å] and is close to two other nitrogen atoms [O(2)··H(31)-N(3), O-H 2.5 Å, O-N 3.03 Å; O(2)··H(22)-N(2), O-H 2.4 Å, O-N 3.15 Å]; however, the hydrogen atoms are rather far from the line joining the two heavier atoms in these two cases [\angle O(2)H(31)N(3) 120 (5)°, \angle O(2)H(22)N(2) 141 (6)°]. Finally, the carboxyl oxygen forms a single link [O(1)··H(22)-N(2), O-H 2.3 Å, O-N 3.21 Å].

The hydrogen bonding network found in [Cr(en)₂(tga)]·ClO₄ is quite different from that found above, although these hydrogen bonds also appear rather weak. Here, three of the perchlorate oxygen atoms are apparently bound to a total of four nitrogen atoms in different cations [O(6)··H(28)-N(2), O-H 2.8 Å, O-N 3.29 Å; O(4)··H(29)-N(2), O-H 2.7 Å, O-N 3.34 Å; O(4)··H(49)-N(4), O-H 2.4 Å, O-N 3.14 Å; O(3)··H(19)-N(1), O-H 2.4 Å, O-N 3.15 Å]. The carbonyl oxygen atom is bound to two nitrogen atoms on an adjacent cation [O(2)··H(39)-N(3), O-H 2.5 Å, O-N 3.23 Å; O(2)··H(18)-N(1), O-H 2.4 Å, O-N 3.22 Å]. The carboxyl oxygen is involved in the shortest hydrogen bond found in the crystal [O(1)··H(48)-N(4), O-H 2.1 Å, O-N 2.98 Å]. The repeated preference for the $\Delta\lambda\delta$ conformer in these two structures may well indicate some inherent stability of that form when only a few relatively weak hydrogen bonds are found. Thus, although the unit cells of the two compounds are different (Co: *a* = 12.07, *b* = 14.88, *c* = 7.54 Å, β = 110.41°; Cr: *a* = 12.25, *b* = 10.16, *c* = 11.27 Å, β = 95.21°), the counterions are different (Co, Cl⁻; Cr, ClO₄⁻), and the cobalt complex crystallizes as a monohydrate, whereas the chromium compound is anhydrous; the two complexes exhibit the same conformations. Since the inherent energy difference between these conformers is predicted to be only about 0.3 kcal mol⁻¹, it is difficult to ascertain whether the hydrogen bonds found here are determining which particular conformer occurs in the crystal. The calculated energies for the various conformations are expected²³ to be dependent on the metal-ligand bond lengths with larger differences in energy associated with the shorter bond lengths (Co-N 1.965, Cr-N 2.090). It could also be true that the van der Waals' repulsions in packing the two conformers (each in its own crystalline form) would differ by this large an energy. No calculation to date has treated such a contribution to the total energy.

For [Co(en)₂(cys)](SCN)₂, the coordination of the cobalt ion is sixfold, as expected, with both the sulfur and nitrogen atoms of the β -mercaptoethylamine ligand bound (Figure 3). The gauche conformation of each of the three ligands makes possible eight different isomers, $\Delta\lambda\lambda\lambda$, $\Delta\lambda\lambda\delta$, $\Delta\lambda\delta\delta$, and $\Delta\delta\delta\delta$, and their four enantiomers. This centric crystal contains both $\Delta\lambda\lambda\lambda$ and its enantiomer, $\Lambda\delta\delta\delta$. All possible isomers have been found for tris(ethylenediamine)cobalt(III) cations,²⁵ and relatively small energy differences are found between the various forms.²⁶ The $\Delta\lambda\lambda\lambda$ form found here is predicted to be the most stable for the isolated cation. The occurrence of the "unfavored" isomers has been postulated to result from an increase in the hydrogen bonding which becomes possible with change of conformation. In this structure, then, little strong hydrogen bonding is expected. That which is present links the amine nitrogen atoms to

(23) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley, New York, N. Y., 1971, pp 81-82.

(24) The results quoted for hydrogen bonds all include errors of less than 1 in the last digit given.

(25) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

(26) See ref 23, pp 75-82.

Table VIII. [Co(en)₂(cys)](SCN)₂ Anisotropic^a Thermal Parameters (×10³)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co	34 (1)	39 (1)	35 (1)	-3 (1)	-2 (1)	-1 (1)
S(1)	55 (1)	49 (1)	59 (1)	-14 (1)	9 (1)	-2 (1)
S(10)	77 (1)	66 (1)	54 (1)	10 (1)	-6 (1)	8 (1)
S(11) ^b	60 (5)	98 (5)	63 (5)	-12 (5)	-1 (5)	25 (4)
S(12) ^b	57 (5)	79 (3)	67 (4)	-1 (3)	-11 (4)	-1 (3)
N(1)	53 (4)	62 (4)	56 (4)	5 (3)	3 (3)	10 (3)
N(2)	47 (3)	45 (3)	48 (3)	2 (3)	7 (3)	-1 (3)
N(3)	56 (4)	54 (4)	47 (3)	-10 (3)	1 (3)	-2 (3)
N(4)	58 (3)	56 (4)	45 (3)	-5 (3)	7 (3)	-2 (3)
N(5)	48 (3)	51 (3)	63 (4)	5 (3)	-1 (3)	-8 (3)
N(10)	104 (6)	89 (6)	80 (5)	27 (5)	-15 (5)	-27 (5)
N(11) ^b	41 (13)	247 (28)	113 (18)	4 (15)	-16 (14)	-26 (19)
N(12) ^b	101 (19)	185 (23)	64 (15)	19 (17)	32 (15)	-4 (15)
C(1)	37 (4)	68 (6)	120 (7)	3 (4)	-23 (4)	-16 (5)
C(2)	37 (4)	91 (6)	106 (6)	-15 (4)	9 (4)	-1 (5)
C(3)	57 (5)	97 (6)	75 (6)	38 (5)	16 (4)	-18 (5)
C(4)	73 (5)	95 (6)	45 (5)	19 (5)	22 (4)	-12 (5)
C(5)	69 (5)	55 (5)	61 (5)	-9 (4)	-2 (4)	-11 (4)
C(6)	65 (5)	69 (5)	43 (4)	-6 (4)	-1 (4)	-19 (4)
C(11)	48 (4)	42 (4)	70 (5)	5 (3)	-11 (4)	8 (4)
C(11) ^b	5 (20)	149 (34)	35 (15)	-1 (16)	1 (13)	-5 (18)
C(12) ^{b,c}	5 (19)	115 (28)	104 (31)	13 (16)	21 (17)	12 (19)

^a The anisotropic thermal parameters are of the form $\exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. ^b These atoms were assigned a population parameter of 0.5. All other population parameters had a value of unity. ^c Thermal parameters for this atom refined nonpositive definite and were reset to these values.

Table IX. [Co(en)₂(cys)](SCN)₂ Root-Mean-Square Displacements (×10³ Å)

Atom	Atom						
Co	178	189	202	S(1)	191	234	269
N(1)	221	227	267	S(10)	216	260	274
N(2)	201	214	233	S(11) ^a	218	245	337
N(3)	210	218	256	S(12) ^a	223	271	280
N(4)	203	229	254	C(1)	176	252	361
N(5)	208	218	256	C(2)	180	306	329
N(10)	236	280	372	C(3)	156	290	347
N(11) ^a	194	334	502	C(4)	165	284	326
N(12) ^a	212	342	435	C(5)	211	257	272
C(6)	181	252	285	C(10)	185	223	274
C(11) ^a	72	185	387	C(12) ^{a,b}	4	312	356

^a These are the atoms of the disordered thiocyanate. ^b This atom reset positive definite.

Table X. [Co(en)₂(cys)](SCN)₂ Isotropic^a Thermal Parameters (×10)

	H(1j)	H(2j)	H(3j)	H(4j)	H(5j)	H(6j)
j = 1	74 (22)	54 (19)	21 (12)	75 (23)	32 (15)	24 (13)
j = 2	60 (20)	36 (16)	78 (22)	11 (13)	36 (16)	13 (12)
j = 3	55 (20)	44 (17)	61 (19)	45 (17)	36 (17)	
j = 4	61 (21)	56 (19)	41 (16)	43 (17)	64 (21)	

^a The isotropic thermal parameters are of the form $\exp(-B \sin^2 \theta/\lambda^2)$.

thiocyanate anions. The nitrogen-nitrogen distances less than 3.5 Å and the nitrogen-sulfur distances less than 3.9 Å have been inspected and the possible hydrogen bonds²⁷ are listed in Table XI.

Comparison of Structural Fragments. Although the hydrogen bonds are likely to be of some importance in determining the configuration found, it seems unlikely that they result in significant changes in the bond lengths found in the complex cations themselves. Thus, the bond lengths and angles of the ethylenediamine moiety are in close agreement with values found recently²⁸⁻³¹ in several rather pre-

cise structural determinations, where the average C-N distance of 1.48 Å has been obtained compared to 1.487 (8) Å for the average³² in [Co(en)₂(tga)]⁺, 1.495 (7) Å (av) in [Cr(en)₂(tga)]⁺, and 1.474 (10) Å (av) in [Co(en)₂(cys)]²⁺; and the average C-C distance of 1.51 has been obtained compared to 1.509 (9) Å (av) in [Co(en)₂(tga)]⁺, 1.508 (8) Å (av) in [Cr(en)₂(tga)]⁺, and 1.460 (10) Å (av) in [Co(en)₂(cys)]²⁺.

The structure of the coordinated mercaptoacetate dianion, tga, has been reported by Hansson³³ for Sb(tga)₂H in a somewhat less precise determination. The values found in the two determinations of tga reported here agree well as may be seen in Tables XII and XIII which report bond lengths and angles for [Co(en)₂(tga)]Cl·H₂O and Tables XIV and XV which list these values for [Cr(en)₂(tga)]ClO₄. The values found here in both cases are within the range of values previously found.

Tables XVI and XVII contain the bond lengths and angles found for [Co(en)₂(cys)](SCN)₂. The reported structures for the coordinated β-mercaptoethylamine anion agree relatively well with that found here. Thus, the S-C distance of 1.818 (8) Å found here compares to 1.823 (25) Å found³⁴ in [Mo(h⁵-C₅H₅)₂(cys)]⁺, 1.84 (1) Å in [Ni(Ni(cys)₂)₂]²⁺,³⁵ and 1.821 (15) Å in Ni(N(CH₃)₂CH₂CH₂S)₂.³⁶ The value of the C-C distance, 1.467 (12) Å, appears somewhat less than 1.511 (35), 1.51 (1), 1.510 (24) Å found in the three studies above, and the N-C distance of 1.483 (9) Å reported here is within the range 1.519 (29), 1.48 (1), 1.519 (17) Å previously reported.

The structure of the perchlorate anion found in [Cr(en)₂(tga)]ClO₄, and illustrated in Figure 4, shows some of the usual disorder and/or libration in the extreme values found

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Table XI. [Co(en)₂(cys)](SCN)₂ Possible Hydrogen Bonds^a (Å)

	X···X	H···X	Atoms	X···X	H···X
N(1)-H(13)···S(10)	3.45	2.6	N(1)-H(14)···S(12)	3.48	2.6
N(2)-H(23)···S(11)	3.45	2.7	N(2)-H(23)···N(10)	2.99	2.3
N(3)-H(34)···N(10)	3.14	2.6	N(4)-H(44)···S(10)	3.55	2.7
N(5)-H(53)···S(10)	3.32	2.6	N(5)-H(54)···S(11) ^b	3.57	2.7
N(5)-H(54)···N(12) ^b	3.01	2.1			

^a The errors estimated in the least-squares refinement are less than 1 in the last digit quoted. ^b N(5) forms a hydrogen bond to either S(11) or N(12) depending on the local positioning of the disordered thiocyanate group.

Table XII. [Co(en)₂(tga)]Cl·H₂O Bond Lengths (Å)

Co-S	2.243 (2)	Co-N(2)	1.958 (5)
Co-O(1)	1.918 (3)	Co-N(3)	2.005 (4)
Co-N(1)	1.971 (5)	Co-N(4)	1.965 (5)
O(1)-C(1)	1.287 (6)	O(2)-C(1)	1.236 (6)
C(1)-C(2)	1.507 (7)	C(2)-S	1.810 (6)
C(3)-C(4)	1.513 (7)	C(5)-C(6)	1.505 (9)
N(1)-C(3)	1.486 (8)	N(2)-C(4)	1.479 (8)
N(3)-C(5)	1.492 (7)	N(4)-C(6)	1.489 (7)
H(11)-N(1)	0.95 (6)	H(21)-N(2)	0.83 (7)
H(12)-N(1)	0.92 (7)	H(22)-N(2)	0.89 (6)
H(41)-N(4)	0.96 (7)	H(51)-C(2)	0.95 (8)
H(42)-N(4)	0.97 (8)	H(52)-C(2)	0.96 (7)
H(71)-C(4)	0.90 (7)	H(81)-C(5)	1.00 (6)
H(72)-C(4)	1.09 (6)	H(82)-C(5)	1.05 (7)
H(31)-N(3)	0.89 (8)	H(61)-C(3)	1.03 (6)
H(32)-N(3)	0.88 (6)	H(62)-C(3)	1.05 (7)
H(91)-C(6)	0.99 (7)	H(92)-C(6)	0.98 (7)

Table XIII. [Co(en)₂(tga)]Cl·H₂O Bond Angles (Degrees)

Metal Coordination Angles			
S-Co-O(1)	88.7 (1)	S-Co-N(1)	91.6 (1)
S-Co-N(3)	174.0 (3)	S-Co-N(4)	89.8 (1)
O(1)-Co-N(2)	89.7 (2)	O(1)-Co-N(3)	88.7 (2)
N(1)-Co-N(2)	85.6 (2)	N(1)-Co-N(3)	91.5 (2)
N(2)-Co-N(3)	92.6 (2)	N(2)-Co-N(4)	177.5 (1)
O(1)-Co-N(2)	90.1 (2)	O(1)-Co-N(4)	94.6 (2)
N(1)-Co-N(4)	94.6 (2)	N(3)-Co-N(4)	84.9 (2)
Ethylenediamine Angles			
N(1)-C(3)-C(4)	107.2 (4)	N(2)-C(4)-C(3)	107.4 (5)
N(4)-C(6)-C(5)	107.4 (4)	N(3)-C(5)-C(6)	106.7 (4)
C(3)-N(1)-Cr	107.9 (3)	C(4)-N(2)-Cr	110.9 (3)
C(5)-N(3)-Cr	108.5 (3)	C(6)-N(4)-Cr	110.3 (3)
Mercaptoacetate Angles			
O(1)-C(1)-C(2)	119.2 (4)	O(2)-C(1)-C(2)	119.5 (5)
C(1)-C(2)-S	113.8 (4)	O(1)-C(1)-O(2)	121.4 (4)
O(1)-C(1)-S	121.4 (3)	O(2)-C(1)-S	96.7 (2)

Table XIV. [Cr(en)₂(tga)]ClO₄ Bond Lengths (Å)

Cr-S	2.337 (2)	Cr-N(2)	2.099 (4)
Cr-O(1)	1.966 (3)	Cr-N(3)	2.112 (4)
Cr-N(1)	2.096 (4)	Cr-N(4)	2.076 (4)
N(1)-C(3)	1.500 (7)	N(2)-C(4)	1.493 (6)
N(3)-C(5)	1.498 (7)	N(4)-C(6)	1.488 (7)
C(3)-C(4)	1.508 (8)	C(5)-C(6)	1.501 (8)
O(1)-C(1)	1.300 (6)	O(2)-C(1)	1.229 (6)
C(1)-C(2)	1.507 (8)	C(2)-S	1.812 (6)
Cl-O(3)	1.350 (7)	Cl-O(4)	1.389 (9)
Cl-O(5)	1.363 (5)	Cl-O(6)	1.336 (8)
H(18)-N(1)	0.90 (5)	H(19)-N(1)	0.92 (6)
H(29)-N(2)	0.75 (6)	H(38)-N(3)	0.85 (6)
H(48)-N(4)	0.90 (6)	H(49)-N(4)	0.79 (6)
H(21)-C(2)	0.95 (6)	H(22)-C(2)	0.98 (6)
H(32)-C(3)	1.08 (6)	H(41)-C(4)	1.00 (6)
H(51)-C(5)	0.95 (6)	H(52)-C(5)	1.00 (6)
H(62)-C(6)	0.97 (6)	H(61)-C(6)	0.97 (6)
H-N(av)	0.87	H-C(av)	1.01

in refining the anisotropic thermal parameters. The bond lengths are given in Figure 4 and Table XIV, the angles in Table XV.

Of the two counterions in [Co(en)₂(cys)](SCN)₂, one

Table XV. [Cr(en)₂(tga)]ClO₄ Bond Angles (Degrees)

Metal Coordination Angles			
S-Cr-O(1)	85.8 (1)	S-Cr-N(1)	92.8 (1)
S-Cr-N(3)	173.3 (3)	S-Cr-N(4)	92.3 (1)
O(1)-Cr-N(2)	92.8 (1)	O(1)-Cr-N(3)	92.7 (1)
N(1)-Cr-N(2)	82.1 (2)	N(1)-Cr-N(3)	89.3 (2)
N(2)-Cr-N(3)	93.3 (2)	N(2)-Cr-N(4)	173.1 (2)
Ethylenediamine Angles			
N(1)-C(3)-C(4)	108.1 (4)	N(2)-C(4)-C(3)	109.1 (4)
N(4)-C(6)-C(5)	108.3 (4)	N(3)-C(5)-C(6)	107.9 (4)
C(3)-N(1)-Cr	109.0 (3)	C(4)-N(2)-Cr	110.0 (3)
C(5)-N(3)-Cr	108.3 (3)	C(6)-N(4)-Cr	111.7 (3)
Mercaptoacetate Angles			
S-C(2)-C(1)	115.7 (4)	O(1)-C(1)-C(2)	117.6 (4)
O(2)-C(1)-C(2)	122.8 (4)	O(1)-C(1)-O(2)	119.6 (5)
Perchlorate Angles			
O(3)-Cl-O(4)	106.9 (5)	O(3)-Cl-O(5)	113.2 (5)
O(4)-Cl-O(5)	108.7 (4)	O(3)-Cl-O(6)	106.7 (6)
O(4)-Cl-O(6)	105.0 (6)	O(5)-Cl-O(6)	115.8 (5)

Table XVI. [Co(en)₂(cys)](SCN)₂ Bond Lengths (Å)

Co-S(1)	2.226 (2)	Co-N(3)	2.001 (5)
Co-N(1)	1.956 (5)	Co-N(4)	1.955 (5)
Co-N(2)	1.970 (5)	Co-N(5)	1.938 (5)
S(1)-C(2)	1.818 (8)	N(1)-C(3)	1.465 (9)
C(1)-C(2)	1.467 (12)	N(2)-C(4)	1.469 (9)
C(3)-C(4)	1.450 (11)	N(3)-C(5)	1.481 (9)
C(5)-C(6)	1.469 (10)	N(4)-C(1)	1.482 (9)
C-C(av)	1.462	N(5)-C(1)	1.483 (9)
S(10)-C(10)	1.641 (8)	N-C(av)	1.476
S(11)-C(11)	1.587 (28)	C(10)-N(10)	1.147 (11)
S(12)-C(12)	1.614 (31)	C(11)-N(11)	1.150 (35)
H(11)-C(1)	1.13 (7)	C(12)-N(12)	1.197 (41)
H(12)-C(1)	0.99 (6)	H(13)-N(1)	0.90 (8)
H(21)-C(2)	1.10 (8)	H(14)-N(1)	0.92 (7)
H(22)-C(2)	1.08 (7)	H(23)-N(2)	0.97 (7)
H(31)-C(3)	0.94 (6)	H(24)-N(2)	0.97 (7)
H(32)-C(3)	1.17 (8)	H(33)-N(3)	0.90 (7)
H(41)-C(4)	1.14 (8)	H(34)-N(3)	0.97 (6)
H(42)-C(4)	0.93 (5)	H(43)-N(4)	0.92 (7)
H(51)-C(5)	0.99 (6)	H(44)-N(4)	0.91 (6)
H(52)-C(5)	0.93 (6)	H(53)-N(5)	0.85 (7)
H(61)-C(6)	1.00 (5)	H(54)-N(5)	1.01 (7)
H(62)-C(6)	0.89 (5)	H-N(av)	0.93
H-C(av)	1.02		

[S(10)C(10)N(10)]⁻ has reasonable thermal parameters and bond lengths [S-C, 1.641 (8) Å; C-N, 1.147 (11) Å] and bond angle 178.7 (6)°; the second thiocyanate anion is disordered. Attempts to refine the anion as ordered led to a bent (~155°) three-atom array with unreasonable bond lengths and thermal parameters. The success of the refine-

Table XVII. [Co(en)₂(cys)](SCN)₂ Bond Angles (Degrees)

Metal Coordination Angles					
S(1)-Co-N(2)	92.5 (2)	N(1)-Co-N(2)	85.2 (2)	N(3)-Co-N(5)	90.2 (2)
S(1)-Co-N(3)	174.5 (2)	N(1)-Co-N(3)	92.5 (2)	N(4)-Co-N(5)	94.1 (2)
S(1)-Co-N(4)	90.2 (2)	N(1)-Co-N(4)	90.7 (2)	N(2)-Co-N(3)	92.9 (2)
S(1)-Co-N(5)	88.8 (2)	N(1)-Co-N(5)	174.7 (2)	N(2)-Co-N(4)	175.1 (2)
S(1)-Co-N(1)	89.0 (2)	N(3)-Co-N(4)	84.5 (2)	N(2)-Co-N(5)	90.1 (2)
Ethylenediamine Angles					
N(3)-C(5)-C(6)	108.5 (5)	C(6)-N(4)-Co	110.3 (4)	C(4)-N(2)-Co	108.3 (4)
C(5)-C(6)-N(4)	107.6 (5)	N(2)-C(4)-C(3)	108.7 (6)	C(3)-N(1)-Co	109.2 (4)
C(5)-N(3)-Co	108.9 (4)	C(4)-C(3)-N(1)	108.7 (6)		
Mercaptoethylamine Angles					
S(1)-C(2)-C(1)	108.1 (5)	C(2)-S(1)-Co	94.2 (3)		
C(2)-C(1)-N(5)	108.8 (6)	C(1)-N(5)-Co	114.8 (4)		
Thiocyanate Angles					
S(10)-C(10)-N(10)	178.7 (6)	S(11)-C(11)-N(11)	177 (3)	S(12)-C(12)-N(12)	176 (3)

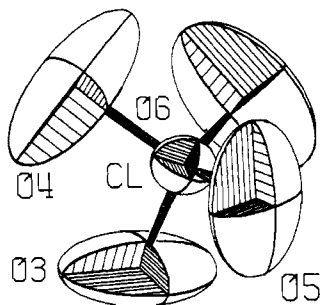


Figure 4. Perspective drawing of the perchlorate anion. The disk shapes of the 50% probability ellipsoids presumably indicate librational motion and/or disorder.

ment with two half-weight anions (no. 11 and no. 12, where the second is nearly the first turned head to tail) may be seen in the relatively good agreement of the final bond lengths (Table XVI) and angles (Table XVII) with those of the ordered anion and in the relatively low (3.2%) final value of the *R* factor. The partial failure of this treatment is evident in the unrealistic vibrational amplitudes (Table IX) found for the disordered anion atoms, especially the carbon atoms, C(11) and C(12).

Sulfur Structural Trans Effect. A comparison of metal-nitrogen atom bond distances is presented in Table XVIII. In both of the cobalt complexes there is a significant lengthening of the trans cobalt-nitrogen bond length by 0.04 Å (5 and 4σ). Thus, in cobalt(III) complexes, the sulfur atom, whether present as mercaptoacetate or β-mercaptoethylamine, shows the same structural trans effect. While the change of 0.04 Å is certainly less than that observed for nitrosyl [0.239 (7) Å],³⁷ hydride ion [0.165 (15) Å],³⁸ and alkyl ligands [0.184 (8) Å],³⁹ where the last two have been observed for rhodium(III) complexes, it appears that a thiolato ligand exerts a significant trans structural effect whereas the nitro, chloro, thiosulfate, and thiocyanato anions⁴⁰ do not.

As can be seen from Table XVIII, the sulfur atom does not appear to exert a significant trans effect in the chromium-tga complex. The difference between cis and trans bond lengths (0.022 Å) is less than twice the error (0.014 Å); however, it is not possible to say unequivocally that no lengthening of the trans chromium-nitrogen bond is taking place.

This difference in structural trans effect between cobalt

Table XVIII. Metal-Nitrogen Bond Distances (Å)

	Co-tga	Co-cys	Co-tga
Cis ^a	1.971 (5)	1.956 (5)	2.099 (4)
	1.958 (5)	1.955 (4)	2.096 (4)
	1.965 (5)	1.970 (5)	2.076 (4)
Cis (av) ^b	1.965 (7)	1.960 (9)	2.090 (13)
Trans	2.005 (4)	2.001 (5)	2.112 (4)
Δ ^c	0.040 (8)	0.041 (10)	0.022 (14)

^a Nitrogen atoms cis or trans relative to sulfur atom. ^b The error in the average value has been computed according to the formula $\sigma_{\bar{d}} = [\sum_{i=1}^n (d_i - \bar{d})^2 / (n - 1)]^{1/2}$. ^c The error in the difference has been computed using the formula $\sigma_{\Delta} = [\sigma^2_{\text{cis}} + \sigma^2_{\text{trans}}]^{1/2}$.

and chromium complexes may explain, in part, the difference in relative rates of electron-transfer reactions of these complexes with chromous ion. Orgel has postulated⁴¹ that for a bridged inner-sphere electron-transfer reaction a weak field ligand trans to the bridging group should stabilize the metal orbital which must accept the transferred electron and thus lower the activation energy and increase the reaction rate relative to that for a complex with a strong field ligand in the trans position. The lengthened trans cobalt-nitrogen bond presumably indicates a relative stabilization of the *d_{z²}* acceptor orbital in the ground state and also that further stretching of this bond in the activated complex would occur more easily than in the [Cr(en)₂(tga)]⁺ ion. This leads to the expectation of a relatively more rapid electron-transfer reaction for the cobalt compound⁸ than the chromium moiety,⁷ as has been observed.

A general comparison of the cobalt and chromium metal-ligand bond distances shows some interesting if not unexpected differences. Thus, the metal-nitrogen distance for chromium is 0.125 (9) Å longer than for cobalt. The difference between that found^{42,43} for [Cr(en)₃]³⁺ and for²⁸⁻³⁰ [Co(en)₃]³⁺ is 0.109 (4) Å. The difference between the metal-sulfur distances of 0.094 (3) Å is somewhat smaller than the value of 0.117 (8) Å for the cobalt(III)- and chromium(III)-tris(ethyl xanthate)^{44,45} complexes. The difference between the metal-oxygen distances on going from chromium to cobalt is much smaller (0.048 Å); however, the chromium-oxygen distance of 1.966 (3) Å agrees well with that determined for the tris(glycinato)chromium(III) complex⁴⁶ of 1.965 (2) Å and the cobalt-oxygen distance of

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1.918 (3) Å found in $[\text{Co}(\text{en})_2(\text{tga})]^+$ is within the range of those previously determined for cobalt-proline^{47,48} complexes of 1.924 (7) and 1.88 (14) Å, although perhaps longer than that for a cobalt-glutamate⁴⁹ complex of 1.87 (1) Å. It thus becomes clear that it is not possible to assign a constant radius to "octahedral" cobalt(III) or to chromium(III). However, the internal comparison of cis and trans metal-nitrogen bond lengths avoids these difficulties and shows, at least for the cobalt compound, a significant structural trans effect.

Finally, the cobalt-sulfur bond distance, 2.225 (2) Å, for the cobalt-cysteine dication is somewhat shorter than that found for the cobalt-tga monocation, 2.243 (2) Å. The complex cation which bears a net charge of 2+ might be expected to bind its ligands more tightly than the cation with

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a net charge of 1+. This shortening might also result from reduction of interligand repulsion on replacement of mercaptoacetate by the more flexible β -mercaptoethylamine ligand.

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Registry No. $[\text{Co}(\text{en})_2(\text{tga})]\text{Cl}\cdot\text{H}_2\text{O}$, 41212-23-1; $[\text{Cr}(\text{en})_2(\text{tga})]\text{ClO}_4$, 41212-24-2; $[\text{Co}(\text{en})_2(\text{cys})](\text{SCN})_2$, 41212-25-3.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2690.

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Enthalpies of Mixing of the Binary Liquid Mixtures of Copper(I) Chloride and Copper(I) Bromide with the Corresponding Cesium Salts

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The enthalpies of mixing of liquid copper(I) chloride and copper(I) bromide with the corresponding cesium salts have been measured at 810° (both salts) and 663° (CuCl only). The molar enthalpies of mixing at 810° can be represented by the following semiempirical relations: for CuCl-CsCl, $\Delta H^M = -N_{\text{CsCl}}N_{\text{CuCl}}(7423 + 5053N_{\text{CuCl}})$ cal/mol; for CuBr-CsBr, $\Delta H^M = -N_{\text{CsBr}}N_{\text{CuBr}}(6248 + 4348N_{\text{CuBr}})$ cal/mol. N is the mole fraction of the indicated salt. There is no significant change of the mixing enthalpy for CuCl-CsCl with temperature. The new experimental results show clear analogies with the corresponding data for the lithium halide-cesium halide mixtures and are interpreted in terms of the ionic conformal solution theory of Reiss, Katz, and Kleppa.

Introduction

The enthalpies of mixing of the mixed cation-common anion alkali halide mixtures are reasonably well accounted for by the ionic conformal solution theory of Reiss, Katz, and Kleppa (RKK),¹ particularly as further developed by Blander² and by Davis and Rice.³ A discussion of these systems was recently given by Melnichak and Kleppa.⁴

On the other hand, the behavior of the mixtures of the silver, thallium(I), and copper(I) halides with the corresponding alkali halides is less well understood. In these salts one has the highly polarizable cations Ag^+ , Tl^+ , and Cu^+ , which differ in important respects from the less polarizable alkali metal cations. Presumably there are also covalent bonding contributions which are of different magnitude in the different salts and which may contribute significantly to the mixing enthalpies.⁵

Among these systems those which contain silver and thallium salts have been studied in some detail both by the emf method⁶⁻⁹ and by calorimetry.^{10,11} Less is known about the corresponding mixtures of the copper(I) halides, for which only emf and phase diagram information has been reported.^{12,13} The present investigation was initiated in order to obtain reliable calorimetric data for the liquid copper halide-alkali halide systems. It covers the mixtures of copper(I) chloride and bromide with the corresponding cesium salts. Work on mixtures with the other alkali halides is in progress.

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