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Dithiolene Complex Adducts. The Crystal and Molecular Structure of Tetra-*n*-butylammonium Bis(toluene-3,4-dithiolato)-1,10-phenanthrolinecobaltate, $[(n\text{-}C_4H_9)_4N][Co(S_2C_6H_3(CH_3))_2(o\text{-phen})]$

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The crystal and molecular structure of the tetra-*n*-butylammonium salt of the *o*-phenanthroline adduct $Co(S_2C_6H_3(CH_3))_2(o\text{-phen})^-$ has been determined from three-dimensional single-crystal X-ray diffraction data collected by counter techniques. The structure has been refined by least-squares methods to a conventional R factor of 0.091 for 1425 statistically reliable reflections. The complex crystallizes in space group $P2_1/c$ of the monoclinic system in a unit cell of dimensions $a = 9.73$ (2) Å, $b = 20.90$ (3) Å, $c = 22.37$ (3) Å, $\beta = 112.0$ (1)°, and $V = 4216$ Å^3. The experimental density is 1.26 (3) g/cm^3; the calculated value is 1.24 g/cm^3 for $Z = 4$. The coordination geometry about the cobalt ion is that of a tris-chelated octahedron of dimensions which are in close agreement with those found for the related adduct $Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$. The average Co–N distance is 2.04 (2) Å and the N–Co–N bond angle is 80.3 (9)°. As in $Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$, the Co–S distances exhibit slight but significant differences depending upon whether they are *trans* to another sulfur donor atom (average Co–S distance of 2.253 (7) Å) or *trans* to an *o*-phenanthroline nitrogen donor (2.215 (7) Å). The structure shows disorder in the position of the toluene-3,4-dithiolate methyl groups and the terminal atoms of three of the *n*-butyl chains of the cation. All other bond distances, bond angles, and intermolecular contacts are normal. The bonding in the two adducts $Co(S_2C_6H_3(CH_3))_2(o\text{-phen})^-$ and $Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$ thus appears to be similar and it is concluded that the difference in the equilibrium $Co\text{–}S_4^- + o\text{-phen} \rightleftarrows Co(o\text{-phen})\text{–}S_4^-$ for the two dithiolene complexes is *primarily* due to differences in the relative stabilities of the original bis complexes.

Introduction

In the preceding paper,[2] the molecular structure determination of the *o*-phenanthroline adduct of the anionic complex $Co(S_2C_2(CN)_2)_2^-$ was described. In this paper, we present the crystal and molecular structure of the tetra-*n*-butylammonium salt of the *o*-phenanthroline adduct of the related complex $Co(S_2C_6H_3(CH_3))_2^-$. This pair of structure determinations was undertaken because of the greatly differing chemical and magnetic properties of the two complexes $Co(S_2C_2(CN)_2)_2^-$ and $Co(S_2C_6H_3(CH_3))_2^-$. The former complex, which should be written correctly as $Co_2(S_2C_2(CN)_2)_4^{2-}$, exists in the solid state and in a variety of solutions as a diamagnetic five-coordinate dimer[3] which cleaves in the presence of coordinating solvents and Lewis bases to form relatively stable five- and six-coordinate adducts.[4,5] On the other hand, the complex $Co(S_2C_6H_3(CH_3))_2^-$ exists as a truly monomeric square-planar complex with an unusual spin triplet ground state[6] and forms only relatively unstable six-coordinate adducts with bidentate ligands such as *o*-phenanthroline and diarsine.[4] The very significant difference in the equilibrium $Co\text{–}S_4^- + o\text{-phen} \rightleftarrows Co(o\text{-phen})\text{–}S_4^-$ for the two systems and, also, the difference in the ease with which the adducts dissociate suggested that the adducts might exhibit significant structural differences. A detailed comparison of the two adduct structures and a discussion relating the structural results to the properties of the adducts are also presented in this paper.

Collection and Reduction of the X-Ray Data

The *o*-phenanthroline adduct of the complex $[(n\text{-}C_4H_9)_4N][Co(S_2C_6H_3(CH_3))_2]$ was prepared in a manner similar to that of Langford, *et al.*[4] Recrystallization was performed from an acetone–2-propanol solution containing excess *o*-phenanthroline, and green-black crystals of $[(n\text{-}C_4H_9)_4N][Co(S_2C_6H_3(CH_3))_2(o\text{-phen})]$ suitable for a single-crystal X-ray study were thus obtained. It was necessary to have an excess of *o*-phenanthroline in the solution in order to crystallize the adduct since otherwise only crystals of the planar complex $[(n\text{-}C_4H_9)_4N][Co(S_2C_6H_3(CH_2))_2]$ were obtained. It was also necessary to use the larger cation $(n\text{-}C_4H_9)_4N^+$, as opposed to $(C_2H_5)_4N^+$ or $(n\text{-}C_3H_7)_4N^+$, in order to obtain crystals suitable for single-crystal X-ray analysis.

A crystal of approximate dimensions 0.33 × 0.17 × 0.14 mm parallel to a, b, c, respectively, was mounted along the a axis and optically aligned. Weissenberg and precession photographs taken with Mo Kα radiation indicated that the complex crystallizes in a monoclinic unit cell of refined (*vide infra*) dimensions $a = 9.73$ (2) Å, $b = 20.90$ (3) Å, $c = 22.37$ (3) Å, $\beta = 112.0$ (1)°, and $V = 4216$ Å^3. An experimental density of 1.26 (3) g/cm^3 was determined using the flotation method with benzene–carbon tetrachloride solutions, which is in good agreement with a calculated value of 1.24 g/cm^3 for four molecules per unit cell. The extinctions of $h0l$ for l odd and $0k0$ for k odd observed from Weissenberg photographs of the $0kl$, $1kl$, and $2kl$ zones and precession photographs of the $hk0$, $hk1$, $h0l$, and $h1l$ zones uniquely determine the space group to be $P2_1/c\text{-}C_{2h}^5$ (no. 14).[7]

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[1] National Institutes of Health Predoctoral Fellow, 1969–1970.

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[5] A. L. Balch, *Inorg. Chem.*, **6**, 2158 (1967).

[6] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 43 (1966).

[7] "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 99.

Intensity data were collected at room temperature using a Picker four-circle automated diffractometer. Twelve reflections of both general and special classes were centered in the counter aperture by varying 2θ, χ, and ϕ in conjunction with the left–right and top–bottom balancing features of the variable receiving aperture. The orientation angles and unit cell parameters were then refined using the least-squares refinement procedure of Hamilton's MODEL diffractometer setting program.[8] The mosaic spread of the crystal was determined using the open-counter, narrow-source ω-scan technique[9] and found to have an average value of 0.3°. An independent set of intensity data was collected by the θ–2θ scan technique using Ni-filtered Cu Kα radiation. The intensities were measured using a scintillation detector in conjunction with pulse height analysis. The scan range was from -0.75 to $+0.75°$ of the 2θ value of the reflection with a scan rate of 1°/min and 10-sec background counts collected at both ends of the 2θ scan range. Data were collected for values of 2θ ranging from 5 to 80° and a total of 2711 independent reflections were measured. During data collection, the intensities of four standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 4.5% during the time required to collect the data.

After the data had been corrected for background, the usual Lorentz and polarization factors were applied to the observed intensities to yield a set of $|F_o|^2$ values, where $|F_o|$ is the observed structure factor amplitude. Of the 2711 independent reflections measured, only 1453 had values above σ (*vide infra*) while 543 reflections had negative net intensities. An absorption correction was then applied to the observed structure amplitudes. With an absorption coefficient of 51.1 cm^{-1}, the resultant transmission coefficients are found to range between 0.50 and 0.58.

Solution and Refinement of the Structure

From a sharpened, origin-removed three-dimensional Patterson function, the positions of the cobalt and four sulfur atoms were determined. An isotropic thermal parameter was then assigned to each of the five atoms and two cycles of least-squares refinement were performed in which the individual positional and isotropic thermal parameters were refined. The positions of 39 of the 45 carbon and nitrogen atoms were determined from a number of difference Fourier maps based on phases obtained from the refined positions of the previously located atoms.

This trial structure containing 1 cobalt, 4 sulfur, 3 nitrogen, and 36 carbon atoms was refined by a least-squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$ where the weights w were taken as $4F^2/\sigma^2(F^2)$ and the standard deviations σ were estimated according to the formula

$$\sigma(F^2) = \frac{1}{TLp}[CT + (t_c/2t_b)^2(B_1 + B_2) + (0.03I)^2]^{1/2}$$

in which CT is the total integrated count obtained in time t_c, B_1 and B_2 are the two background counts, each obtained in time t_b, I is the net integrated count, Lp represents the Lorentz and polarization factors, and T is the transmission coefficient. The neutral Co, S, N, and C scattering factors were obtained from Ibers' tabulation[10] while the anomalous parts of the Co and S scattering factors were obtained from Templeton's tabulation[11] and included in the calculated structure factors.[12] Only those reflections with F^2 greater than $\sigma(F^2)$ were included in the refinements and in the calculation of the discrepancy indices R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $(= (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2})$.

In the initial round of calculations, each of the 45 atoms was assigned an individual isotropic thermal parameter. This refinement converged to an R factor of 0.152 and a weighted R factor R' of 0.145. A difference Fourier map based on this refinement revealed considerable electron density at both possible positions of the methyl carbon atoms of the two toluenedithiolate ligands. In addition, the region of the difference map around the cation indicated a *trans–gauche* disorder in the terminal carbon atom positions of two of the *n*-butyl chains and revealed only a large area of positive electron density for the δ- and γ-carbon atoms of a third *n*-butyl chain. The difference map also provided evidence for anisotropic thermal motion of the heavy atoms.

In the next round of calculations, anisotropic thermal parameters were assigned to the cobalt and four sulfur atoms while all other atoms were restricted to the isotropic thermal model. In addition, the methyl carbon atoms of the toluene rings were represented by half-atoms at the two possible positions of each ring, and the terminal carbon atoms of the two *n*-butyl chains, in which *trans–gauche* disorder was noted, were represented by half-atoms at the *trans* and *gauche* positions. The two end carbon atoms of the third chain ($CAT\mathrm{C}_{15}$ and $CAT\mathrm{C}_{16}$), which appeared to exhibit complete disorder, were represented by two carbon atoms placed in positions approximating a *trans* ordering of that butyl chain. The least-squares refinement of this trial structure was carried out in blocks because of computer limitations. Parameters expected to have low correlation coefficients were not necessarily varied on the same cycle. For example, in one cycle, the positional and thermal parameters of all atoms in the anion, including the anisotropic thermal parameters of the heavy atoms, were refined while in a different cycle, the positional and thermal parameters of all atoms in the cation and all atoms in the anion except

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[8] In addition to the MODEL setting program, the main programs for the IBM 360-50 used in this work were local versions of W. C. Hamilton's GONO9 absorption program, the Busing–Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the Busing–Martin–Levy ORFFE function and error program, and C. K. Johnson's ORTEP plotting program. Various other local programs were also used in the investigation.

[9] T. C. Furnas, "Single Crystal Orienter Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

[10] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3. 1A.

[11] D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3. 2B.

[12] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

TABLE I
FINAL PARAMETERS FOR
$[(n\text{-}C_4H_9)_4N][Co(S_2C_6H_3(CH_3))_2(o\text{-phen})]$
Atomic Positional and Isotropic Thermal Parameters

Atom	x[a]	y	z	B, Å^2
Co	−0.2025 (4)[c]	0.1810 (2)	0.0360 (2)	[b]
S$_1$	−0.0348 (7)	0.1416 (3)	0.1282 (3)	[b]
S$_3$	−0.2364 (7)	0.2649 (3)	0.0903 (3)	[b]
S$_2$	−0.3821 (8)	0.1282 (4)	0.0516 (3)	[b]
S$_4$	−0.3692 (7)	0.2212 (4)	−0.0563 (3)	[b]
C$_1$	−0.434 (3)	0.291 (1)	−0.034 (1)	5.7 (7)
C$_2$	−0.545 (3)	0.330 (1)	−0.080 (1)	7.0 (7)
C$_3$	−0.597 (3)	0.386 (1)	−0.059 (2)	7.9 (8)
C$_4$	−0.544 (3)	0.403 (1)	0.006 (2)	9.1 (8)
C$_5$	−0.426 (3)	0.367 (1)	0.055 (1)	7.6 (8)
C$_6$	−0.377 (3)	0.312 (1)	0.033 (1)	6.0 (7)
C$_7$	−0.291 (3)	0.080 (1)	0.117 (1)	7.5 (8)
C$_8$	−0.371 (3)	0.031 (1)	0.138 (1)	7.3 (8)
C$_9$	−0.295 (4)	−0.006 (1)	0.191 (2)	8.9 (8)
C$_{10}$	−0.149 (3)	0.000 (1)	0.229 (1)	7.2 (7)
C$_{11}$	−0.063 (3)	0.045 (1)	0.208 (1)	6.1 (7)
C$_{12}$	−0.144 (3)	0.086 (1)	0.154 (1)	5.6 (6)
*Me*C$_1$	−0.704 (5)	0.429 (2)	−0.110 (2)	6 (2)[d]
*Me*C$_1'$	−0.641 (6)	0.451 (3)	0.025 (3)	12 (2)
*Me*C$_2$	−0.050 (5)	−0.040 (2)	0.291 (2)	5 (1)[d]
*Me*C$_2'$	−0.406 (7)	−0.054 (3)	0.193 (3)	15 (3)
*OP*N$_1$	−0.165 (2)	0.110 (1)	−0.019 (1)	6.0 (6)
*OP*N$_2$	−0.023 (2)	0.218 (1)	0.023 (1)	5.4 (5)
*OP*C$_1$	−0.243 (3)	0.055 (2)	−0.037 (1)	7.9 (8)
*OP*C$_2$	−0.194 (3)	0.006 (1)	−0.071 (1)	8.1 (8)
*OP*C$_3$	−0.066 (3)	0.017 (1)	−0.083 (1)	6.1 (7)
*OP*C$_4$	0.006 (3)	0.075 (1)	−0.067 (1)	5.9 (7)
*OP*C$_5$	−0.036 (3)	0.121 (1)	−0.030 (1)	5.7 (7)
*OP*C$_6$	0.035 (3)	0.177 (1)	−0.010 (1)	5.8 (7)
*OP*C$_7$	0.173 (3)	0.190 (2)	−0.018 (1)	7.2 (8)
*OP*C$_8$	0.237 (3)	0.248 (2)	0.005 (1)	8.4 (8)
*OP*C$_9$	0.183 (3)	0.292 (1)	0.038 (1)	8.8 (9)
*OP*C$_{10}$	0.041 (3)	0.277 (1)	0.046 (1)	6.8 (7)
*OP*C$_{11}$	0.147 (3)	0.088 (1)	−0.072 (1)	7.4 (8)
*OP*C$_{12}$	0.226 (3)	0.144 (1)	−0.051 (1)	6.5 (7)
*CAT*N	−0.193 (2)	0.219 (1)	0.296 (1)	7.6 (6)
*CAT*C$_1$	−0.325 (3)	0.185 (1)	0.241 (1)	8.6 (8)
*CAT*C$_2$	−0.452 (3)	0.174 (1)	0.263 (1)	11.3 (9)
*CAT*C$_3$	−0.580 (3)	0.124 (1)	0.216 (1)	9.1 (9)
*CAT*C$_4$	−0.632 (3)	0.172 (1)	0.159 (1)	11.8 (9)
*CAT*C$_5$	−0.066 (3)	0.218 (1)	0.268 (1)	5.3 (7)
*CAT*C$_6$	0.075 (3)	0.254 (1)	0.311 (1)	8.6 (8)
*CAT*C$_7$	0.178 (3)	0.255 (1)	0.274 (1)	11 (1)
*CAT*C$_8$	0.153 (4)	0.301 (2)	0.228 (2)	3 (2)[d]
*CAT*C$_8'$	0.270 (6)	0.309 (3)	0.288 (3)	11 (2)
*CAT*C$_9$	−0.231 (3)	0.284 (1)	0.308 (1)	8.3 (8)
*CAT*C$_{10}$	−0.286 (3)	0.327 (2)	0.249 (1)	10.4 (9)
*CAT*C$_{11}$	−0.293 (4)	0.398 (2)	0.267 (2)	16 (1)
*CAT*C$_{12}$	−0.323 (6)	0.449 (3)	0.219 (3)	9 (2)[d]
*CAT*C$_{12}'$	−0.432 (8)	0.428 (4)	0.224 (3)	15 (3)
*CAT*C$_{13}$	−0.140 (3)	0.185 (2)	0.362 (1)	9.3 (8)
*CAT*C$_{14}$	−0.116 (3)	0.116 (2)	0.358 (1)	11 (1)
*CAT*C$_{15}$	−0.073 (5)	0.072 (2)	0.418 (2)	23 (2)
*CAT*C$_{16}$	−0.183 (5)	0.077 (2)	0.436 (2)	22 (2)

Anisotropic Thermal Parameters[e]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.0153 (8)	0.0049 (2)	0.0025 (1)	0.0014 (3)	0.0018 (3)	−0.0006 (1)
S$_1$	0.0166 (14)	0.0044 (3)	0.0028 (2)	−0.0003 (5)	0.0016 (5)	−0.0008 (2)
S$_3$	0.0295 (16)	0.0049 (3)	0.0024 (2)	0.0030 (6)	0.0019 (5)	−0.0005 (2)
S$_2$	0.0188 (15)	0.0062 (4)	0.0044 (3)	−0.0001 (7)	0.0037 (5)	−0.0009 (3)
S$_4$	0.0213 (16)	0.0062 (4)	0.0026 (2)	0.0019 (6)	0.0017 (5)	−0.0006 (2)

[a] x, y, z are in fractional coordinates. [b] Atoms refined anisotropically. [c] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figure. [d] Fractional occupancy factors were set at 0.5 for each of the disordered atoms and were held fixed throughout the refinement. This assumption does not appear to be strictly correct for the toluene-3,4-dithiolate methyl groups as well as for *CAT*C$_8$. [e] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

for those of the o-phenanthroline moiety were refined. In all, a total of four cycles of least-squares refinement were performed. In the next to last cycle, only the positional and thermal parameters of the carbon and nitrogen atoms were varied whereas in the final cycle of refinement, the positional and anisotropic thermal parameters of the heavy atoms were refined along with the positional parameters of the light atoms. This refinement converged to a conventional R factor of 0.091 and a weighted R factor R' of 0.084 for 1425 reflections above $\sigma(F^2)$. A final difference Fourier map showed no peaks higher than ~0.40 e$^-$/Å^3 whereas the average electron density of a carbon atom in this structure was approximately 3.0 e$^-$/Å^3. Although reasonable positions were found for many of the hydrogen atoms associated with the toluene and o-phenanthroline groups, the contributions of these hydrogen atoms to $|F_c|$ were not included in any further calculations. Because of the already low ratio of observations to parameters (~6:1) and the relative cleanness of the difference map, no further refinements were performed. The parameters obtained in this partial anisotropic refinement are therefore taken as the final parameters for the structure and are given in Table I along with their standard deviations as obtained from the inverse matrix of either the last or the next to last cycle of least squares, whichever is appropriate. In Table II, the root-mean-square amplitudes of vibration of the Co and S atoms are presented. The F_o and $|F_c|$ values (in

TABLE II
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Co	0.227 (6)	0.244 (7)	0.343 (6)
S$_1$	0.226 (11)	0.276 (11)	0.328 (11)
S$_3$	0.223 (11)	0.293 (12)	0.400 (10)
S$_2$	0.273 (12)	0.297 (11)	0.383 (11)
S$_4$	0.231 (11)	0.293 (11)	0.390 (10)

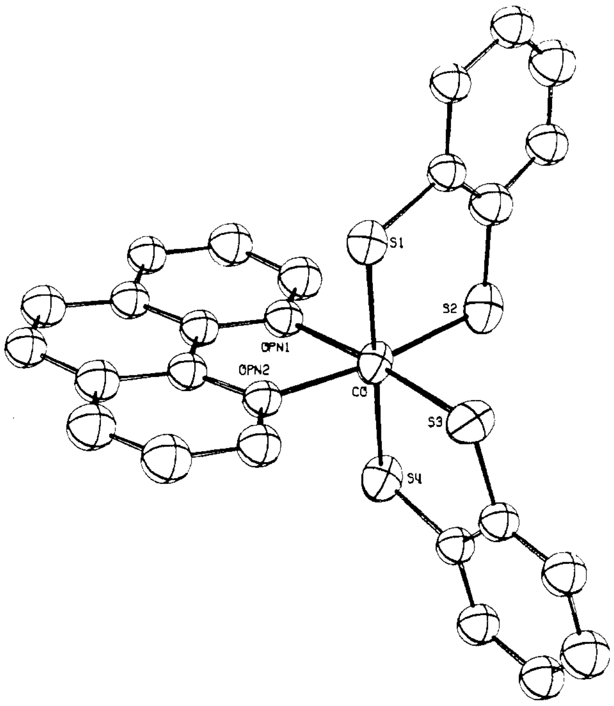
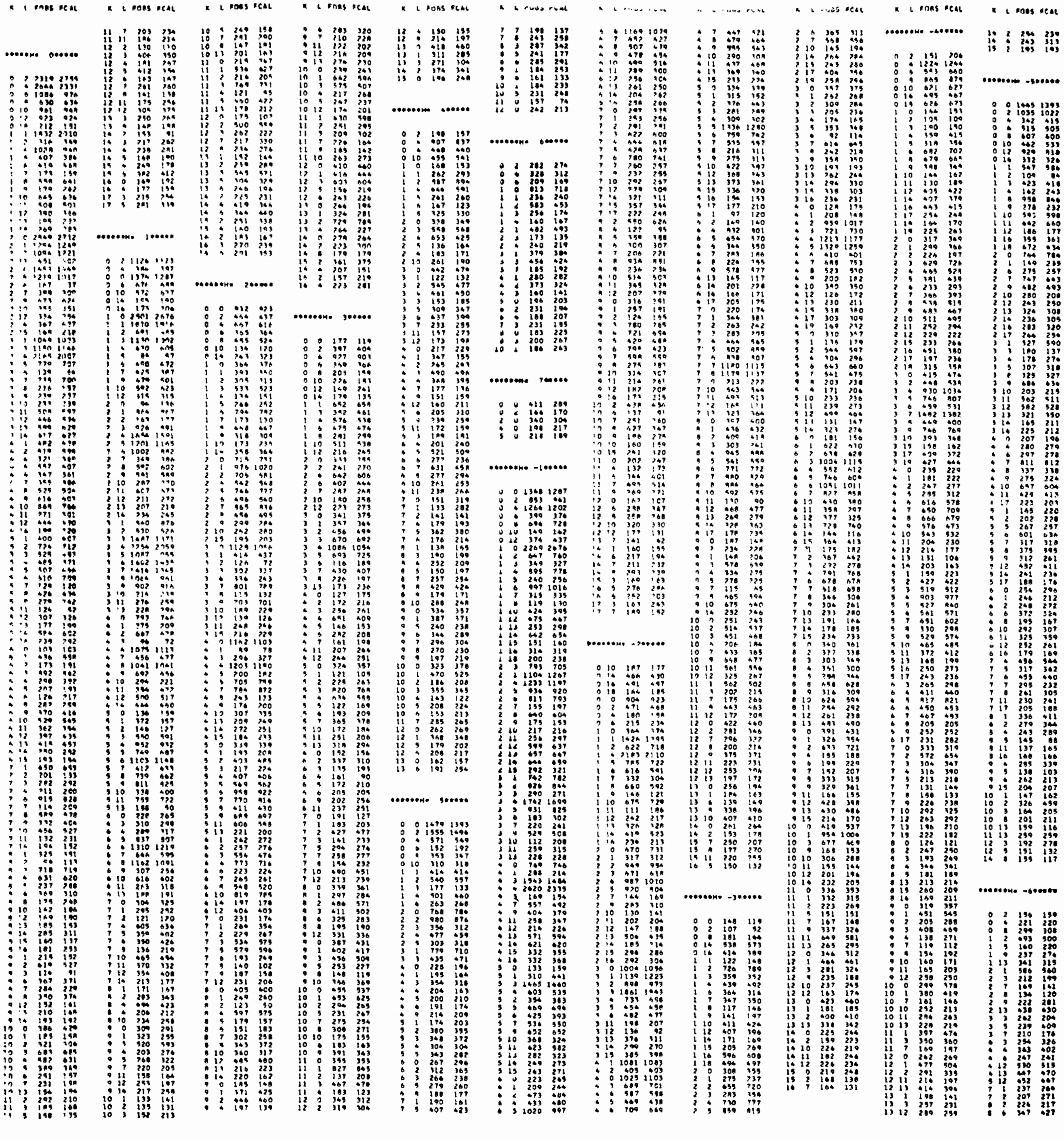


Figure 1.—A perspective drawing of the $Co(S_2C_6H_3(CH_3))_2(o\text{-phen})^-$ adduct. The thermal ellipsoids have been scaled to approximately 30% probability distributions. The methyl groups of the toluene-3,4-dithiolate ligands are not shown because of disorder.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10) FOR $[(n\text{-}C_4H_9)_4N][Co(S_2C_6H_3(CH_3))_2(o\text{-phen})]$



electrons × 10) for the 1425 reflections included in the final refinement are tabulated in Table III. None of the $|F_c|$ values for reflections whose F^2 value was less than $\sigma(F^2)$ was found to be greater than twice the estimated standard deviation. With the weighting scheme employed, the estimate of the standard deviation of an observation of unit weight has the value 2.23.

Description of the Structure

The anionic adduct $Co(S_2C_6H_3(CH_3))_2(o\text{-phen})^-$ possesses a tris-chelated octahedral structure which is strikingly similar in dimensions to that of the related complex $Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$.[2] A perspective drawing of the molecular geometry is shown in Figure 1 and all important intramolecular distances and angles are tabulated in Table IV. As in the case of the $Co(S_2C_2(CN)_2)_2(o\text{-phen})$ adduct, the Co–S distances exhibit significant differences depending on whether the sulfur donor atom is *trans* to another sulfur atom, in which case the average Co–S distance is 2.253 (7) Å, or *trans* to one of the *o*-phenanthroline nitrogen donor atoms, in which case the average Co–S distance is 2.215 (7) Å. The average Co–S value is 2.23 Å with an estimated standard deviation of 0.02 Å. This average value is longer than the 2.166 (4) Å average value observed for the Co–S distances in the parent complex anion $Co(S_2C_6H_3(CH_3))_2^-$.[13]

TABLE IV

PRINCIPAL INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG)

		Anion	
Co–S$_1$	2.254 (8)	S$_1$–Co–S$_2$	91.0 (3)
Co–S$_2$	2.203 (8)	S$_1$–Co–S$_3$	89.6 (3)
Co–S$_3$	2.227 (7)	S$_2$–Co–S$_3$	91.1 (3)
Co–S$_4$	2.252 (7)	S$_3$–Co–S$_4$	91.0 (3)
Co–*OP*N$_1$	2.05 (2)	S$_2$–Co–S$_4$	89.6 (3)
Co–*OP*N$_2$	2.03 (2)	*OP*N$_1$–Co–*OP*N$_2$	80.3 (9)
S$_1$–S$_2$	3.14 (1)	S$_4$–Co–*OP*N$_1$	87.4 (6)
S$_1$–S$_3$	3.17 (1)	S$_4$–Co–*OP*N$_2$	95.1 (5)
S$_2$–S$_3$	3.16 (1)	S$_2$–Co–*OP*N$_1$	93.4 (7)
S$_2$–S$_4$	3.18 (1)	S$_3$–Co–*OP*N$_2$	95.5 (7)
S$_3$–S$_4$	3.16 (1)	S$_1$–Co–*OP*N$_1$	92.9 (5)
S$_1$–*OP*N$_1$	2.97 (2)	S$_1$–Co–*OP*N$_2$	84.5 (5)
S$_1$–*OP*N$_2$	3.17 (2)	Co–S$_1$–C$_1$	105 (1)
S$_2$–*OP*N$_1$	3.09 (2)	Co–S$_2$–C$_6$	106 (1)
S$_3$–*OP*N$_2$	3.16 (2)	Co–S$_3$–C$_7$	104 (1)
S$_4$–*OP*N$_1$	3.12 (2)	Co–S$_4$–C$_{12}$	103 (1)
S$_4$–*OP*N$_2$	2.89 (2)	Co–*OP*N$_1$–*OP*C$_5$	111 (2)
*OP*N$_1$–*OP*N$_2$	2.63 (3)	Co–*OP*N$_2$–*OP*C$_6$	113 (2)
S$_1$–C$_1$	1.74 (2)	*OP*N$_1$–*OP*C$_5$–*OP*C$_6$	118 (3)
S$_2$–C$_6$	1.77 (2)	*OP*N$_2$–*OP*C$_6$–*OP*C$_5$	117 (3)
S$_3$–C$_7$	1.72 (3)	*OP*C$_1$–*OP*N$_1$–*OP*C$_5$	122 (2)
S$_4$–C$_{12}$	1.81 (2)	*OP*C$_6$–*OP*N$_2$–*OP*C$_{10}$	122 (2)
C$_1$–C$_2$	1.43 (3)	C$_1$–C$_2$–C$_3$	120 (3)
C$_2$–C$_3$	1.41 (3)	C$_2$–C$_3$–C$_4$	121 (3)
C$_3$–C$_4$	1.40 (3)	C$_3$–C$_4$–C$_5$	122 (3)
C$_4$–C$_5$	1.46 (3)	C$_3$–C$_5$–C$_6$	116 (3)
C$_5$–C$_6$	1.40 (3)	C$_5$–C$_6$–C$_1$	123 (3)
C$_6$–C$_1$	1.46 (3)	C$_6$–C$_1$–C$_2$	118 (3)
C$_7$–C$_8$	1.47 (3)	C$_7$–C$_8$–C$_9$	119 (3)
C$_8$–C$_9$	1.38 (3)	C$_8$–C$_9$–C$_{10}$	126 (3)
C$_9$–C$_{10}$	1.36 (3)	C$_9$–C$_{10}$–C$_{11}$	116 (3)
C$_{10}$–C$_{11}$	1.45 (3)	C$_{10}$–C$_{11}$–C$_{12}$	117 (2)
C$_{11}$–C$_{12}$	1.45 (3)	C$_{11}$–C$_{12}$–C$_7$	125 (3)
C$_{12}$–C$_7$	1.36 (3)	C$_{12}$–C$_7$–C$_8$	115 (3)
C$_3$–*Me*C$_1$	1.51 (4)		
C$_4$–*Me*C$_1'$	1.55 (6)		
C$_9$–*Me*C$_2$	1.59 (4)		
C$_{10}$–*Me*C$_2'$	1.50 (6)		
*OP*N$_1$–*OP*C$_1$	1.34 (3)		
*OP*N$_1$–*OP*C$_5$	1.39 (2)		
*OP*C$_1$–*OP*C$_2$	1.46 (3)		
*OP*C$_2$–*OP*C$_3$	1.40 (3)		
*OP*C$_3$–*OP*C$_4$	1.38 (3)		
*OP*C$_4$–*OP*C$_5$	1.43 (3)		
*OP*C$_4$–*OP*C$_{11}$	1.44 (3)		
*OP*C$_5$–*OP*C$_6$	1.36 (3)		
*OP*N$_2$–*OP*C$_6$	1.36 (3)		
*OP*N$_2$–*OP*C$_{10}$	1.39 (2)		
*OP*C$_6$–*OP*C$_7$	1.45 (3)		
*OP*C$_7$–*OP*C$_8$	1.37 (3)		
*OP*C$_7$–*OP*C$_{12}$	1.41 (3)		
*OP*C$_8$–*OP*C$_9$	1.39 (3)		
*OP*C$_9$–*OP*C$_{10}$	1.49 (3)		
*OP*C$_{11}$–*OP*C$_{12}$	1.39 (3)		
		Cation	
*CAT*N–*CAT*C$_1$	1.57 (3)	*CAT*C$_1$–*CAT*N–*CAT*C$_5$	103 (2)
*CAT*N–*CAT*C$_5$	1.58 (2)	*CAT*C$_1$–*CAT*N–*CAT*C$_9$	112 (2)
*CAT*N–*CAT*C$_9$	1.48 (3)	*CAT*C$_1$–*CAT*N–*CAT*C$_{13}$	115 (2)
*CAT*N–*CAT*C$_{13}$	1.54 (3)	*CAT*C$_5$–*CAT*N–*CAT*C$_9$	112 (2)
*CAT*C$_1$–*CAT*C$_2$	1.52 (3)	*CAT*C$_5$–*CAT*N–*CAT*C$_{13}$	111 (2)
*CAT*C$_2$–*CAT*C$_3$	1.68 (3)	*CAT*C$_9$–*CAT*N–*CAT*C$_{13}$	105 (2)
*CAT*C$_3$–*CAT*C$_4$	1.54 (3)	*CAT*N–*CAT*C$_1$–*CAT*C$_2$	109 (2)
*CAT*C$_5$–*CAT*C$_6$	1.55 (2)	*CAT*C$_1$–*CAT*C$_2$–*CAT*C$_3$	112 (2)
*CAT*C$_6$–*CAT*C$_7$	1.53 (3)	*CAT*C$_2$–*CAT*C$_3$–*CAT*C$_4$	93 (2)
*CAT*C$_7$–*CAT*C$_8$	1.35 (4)	*CAT*N–*CAT*C$_5$–*CAT*C$_6$	113 (1)
*CAT*C$_7$–*CAT*C$_8'$	1.40 (5)	*CAT*C$_5$–*CAT*C$_6$–*CAT*C$_7$	106 (2)
*CAT*C$_9$–*CAT*C$_{10}$	1.52 (3)	*CAT*C$_6$–*CAT*C$_7$–*CAT*C$_8$	117 (3)
*CAT*C$_{10}$–*CAT*C$_{11}$	1.54 (4)	*CAT*C$_6$–*CAT*C$_7$–*CAT*C$_8'$	113 (3)
*CAT*C$_{11}$–*CAT*C$_{12}$	1.46 (5)	*CAT*N–*CAT*C$_9$–*CAT*C$_{10}$	114 (2)
*CAT*C$_{11}$ *CAT*C$_{12}'$	1.47 (7)	*CAT*C$_9$–*CAT*C$_{10}$–*CAT*C$_{11}$	112 (3)
*CAT*C$_{13}$–*CAT*C$_{14}$	1.47 (3)	*CAT*C$_{10}$–*CAT*C$_{11}$–*CAT*C$_{12}$	123 (4)
*CAT*C$_{14}$–*CAT*C$_{15}$	1.57 (5)	*CAT*C$_{10}$–*CAT*C$_{11}$–*CAT*C$_{12}'$	112 (4)
*CAT*C$_{15}$–*CAT*C$_{16}$	1.27 (5)	*CAT*N–*CAT*C$_{13}$–*CAT*C$_{14}$	113 (3)
		*CAT*C$_{13}$–*CAT*C$_{14}$–*CAT*C$_{15}$	121 (3)
		*CAT*C$_{14}$–*CAT*C$_{15}$–*CAT*C$_{16}$	104 (4)

The Co–N distance of 2.04 (2) Å is slightly but not significantly longer than the corresponding distance of 2.01 (1) Å in $Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$ despite the great difference in the complex + addendum ⇄ adduct equilibrium for the two systems. We observe, however, that the Co–N distance of 2.04 (2) Å in the present case is *possibly* significantly longer than the Co–N distance in other Co(III) complexes (for example, 1.94 (2) Å in $[Co(NH_3)_6]I_3$,[14] 1.94 (2) Å in *trans*-$Co(en)_2(NCS)(SO_3)$,[15] and 1.97 (1) Å in $[Co(en)_2(CH_3NHCH_2COO)]I_2$[16]). It should be noted that all of these Co–N distances involve saturated amine ligands. One other relevant distance is the Co–py distance of 2.04 (1) Å in the cobaloxime complex $Co(C_4H_7O_2N_2)_2(C_3H_5O_2)(py)$[17] which agrees with the value found in the present structure. The bond angles within the coordination sphere (Table IV) show only minor deviations from those expected for octahedral coordination with the exception of the N–Co–N bond angle of 80.3 (9)° which results from the fixed N · · · N "bite" of 2.63 (3) Å of the *o*-phenanthroline ligand.

The average S–C distance of 1.76 (2) Å in the toluenedithiolate ligands is in close agreement with the values of 1.77 (2) and 1.76 (2) Å reported for the bis(substituted benzenedithiolate) complexes $[(C_6H_5)_4(CH_3)As][Co(S_2C_6H_3(CH_3))_2]\cdot 0.5C_2H_5OH$[13] and $[(n\text{-}C_4H_9)_4N]_2[Co_2(S_2C_6Cl_4)_4]$,[18] respectively. These values, in turn, are slightly, but consistently, longer than the corresponding values of 1.72 (2), 1.72 (1), 1.69 (1), and 1.70 (1) Å reported for the cobalt–ethenedithiolate complexes $[(n\text{-}C_3H_7)_4N][Co(S_2C_2(CN)_2)_2(o\text{-phen})]$,[2] $[(n\text{-}C_4H_9)_4N]_2[Co(S_2C_2(CN)_2)_2]$,[19] $Co_2(S_2C_2(CF_3)_2)_4$,[20] and $(\pi\text{-}C_5H_5)Co(S_2C_2(CN)_2)$,[21] respectively.

The toluene-3,4-dithiolate ligands are planar within experimental error. The least-squares planes[22] through the ligands and the deviations of the atoms from their respective planes are given in Table V. The *o*-phenanthroline moiety shows only possibly significant deviations from planarity and the least-squares plane through it is also given in Table V. The C–C bond distances in the *o*-phenanthroline ligand average 1.41 (3) Å, which is in agreement with the value found for $Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$, but the distances in the present structure do not appear to correlate as closely with the predicted bond orders as in the previous structure, presumably because of the greater uncertainty in the light-atom positions in the present case.

The $(n\text{-}C_4H_9)_4N^+$ cation in this structure has the expected tetrahedral geometry although it does exhibit *trans–gauche* disorder in two of the *n*-butyl chains. Disorder of this type has also been observed in a number

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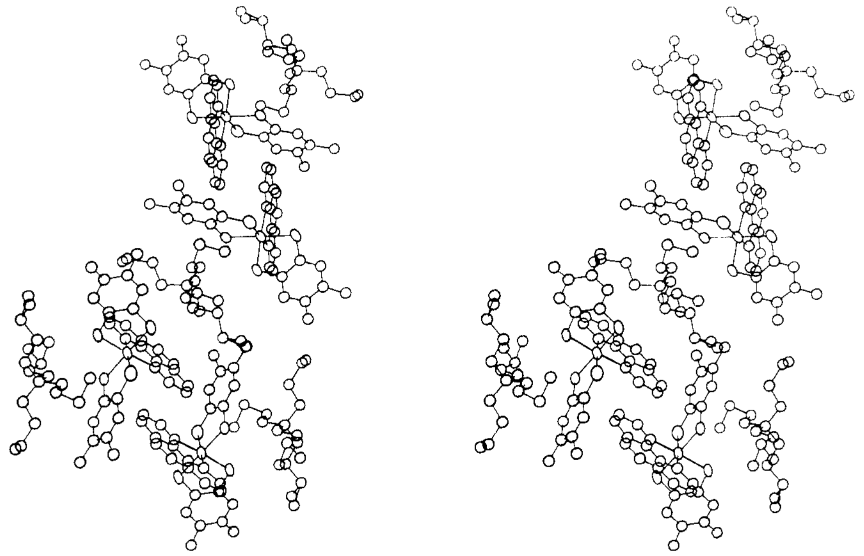

Figure 2.—A stereoscopic view of the packing of the anions as viewed down the *a* axis of the crystal. The *b* axis is approximately 25° in the counterclockwise direction from the vertical. The drawings constitute a stereopair and can be viewed with a hand viewer. The disordered atoms are shown in both possible orientations.

TABLE V

WEIGHTED LEAST-SQUARES PLANES[a] AND THE DISTANCES OF THE ATOMS FROM THEIR RESPECTIVE PLANES (MONOCLINIC COORDINATES)

Atom	Distance, Å	Atom	Distance, Å
Chelate Ring 1: $-3.73x + 15.95y + 14.01z - 4.16$			
Co	-0.012 (4)	C_1	-0.10 (2)
S_1	0.027 (6)	C_6	-0.17 (2)
S_2	0.038 (7)		
Chelate Ring 2: $8.28x + 10.41y - 10.59z = -0.169$			
Co	-0.005 (4)	C_7	-0.03 (2)
S_3	0.013 (7)	C_{12}	-0.06 (2)
S_4	0.012 (7)		
Chelate Ring 3: $2.84x - 9.35y + 15.08z = -1.73$			
Co	0.002 (4)	OPC_5	0.05 (2)
OPN_1	-0.05 (2)	OPC_6	0.02 (2)
OPN_2	-0.03 (2)		
Toluene Dithiolate 1: $-4.11x + 14.23y + 15.96z = 4.21$			
S_1	-0.008 (6)	C_4	0.05 (2)
S_2	0.007 (7)	C_5	0.01 (2)
C_1	-0.02 (2)	C_6	0.05 (2)
C_2	-0.06 (2)	Me_1	0.07
C_3	-0.04 (3)	Me_1'	-0.23
Toluene Dithiolate 2: $8.06x + 11.14y - 10.54z = 0.089$			
S_3	0.005 (7)	C_{10}	-0.04 (3)
S_4	-0.007 (7)	C_{11}	-0.02 (2)
C_7	0.02 (2)	C_{12}	-0.00 (2)
C_8	0.04 (2)	MeC_2	0.17
C_9	0.02 (2)	MeC_2'	-0.50
o-Phenanthroline Moiety: $2.20x - 9.09y + 16.17z = -1.66$			
OPN_1	-0.00 (2)	OPC_6	-0.03 (2)
OPN_2	-0.00 (2)	OPC_7	0.02 (2)
OPC_1	0.03 (2)	OPC_8	0.01 (2)
OPC_2	0.04 (2)	OPC_9	0.03 (2)
OPC_3	0.02 (2)	OPC_{10}	-0.02 (2)
OPC_4	-0.09 (2)	OPC_{11}	0.01 (2)
OPC_5	0.00 (2)	OPC_{12}	0.03 (2)

[a] See ref 22.

of previous studies.[23,24] In addition, the relatively large thermal parameters for the carbon atoms in the cation are taken to be indicative of the relatively great amount of motional freedom which the chains of the $(n\text{-}C_4H_9)_4N^+$ cation possess in this structure. The dimensions of the cation are tabulated in Table IV.

All intermolecular contacts are normal and are therefore not tabulated. The anions are well separated and a stereoscopic drawing of the packing as viewed down the *a* axis is shown in Figure 2.

Discussion

In Table VI, the dimensions of a number of 1,2-dithiolene complexes of cobalt are summarized. Two of these complexes are six-coordinate adducts, two are five-coordinate dimers, and two are essentially square-planar monomers. The most significant differences in the dimensions of the CoS_2C_2 chelate rings in these structures may be found in the cobalt–sulfur bond lengths which are approximately 0.06 Å longer in the six-coordinate adducts than in the various bis complexes. The increased Co–S bond lengths are directly attributable to decreased metal–sulfur π bonding in the octahedral systems. There are no other significant changes found in the chelate ring dimensions in going from the four- or five-coordinate bis complexes to the six-coordinate Lewis base adducts.

In view of the greatly differing chemical, magnetic, and structural properties of $Co(S_2C_6H_3(CH_3))_2^-$ and $Co_2(S_2C_2(CN)_2)_4^{2-}$, the striking similarity found in the structures and dimensions of the *o*-phenanthroline adducts of these two complexes was somewhat unexpected. From the present structural results, we conclude that the bonding in the two adduct systems is very similar and that the ligand field stabilization energies for the two six-coordinate complexes are close in value. Hence, the difference in the complex + *o*-phen $\rightleftharpoons$ adduct equilibrium for the two dithiolene systems is primarily determined by a difference in the relative stabilities of the planar complex $Co(S_2C_6H_3$-

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TABLE VI

A COMPARISON OF THE DIMENSIONS OF SOME COBALT–DITHIOLENE COMPLEXES

	$Co(S_2C_6H_3(CH_3))_2(o\text{-phen})^-$ [a]	$Co(S_2C_2(CN)_2)_2(o\text{-phen})^-$ [b]	$Co(S_2C_6H_3(CH_3))_2^-$ [c]	$Co(S_2C_2(CN)_2)_2^{2-}$ [d]	$Co_2(S_2C_2(CF_3)_2)_4^0$ [e]	$Co_2(S_2C_6Cl_4)_4^{2-}$ [f]
			Bond Distances, Å			
Co–S	2.253 (7), 2.215 (7)	2.247 (5), 2.213 (5)	2.166 (4)	2.161 (3)	2.161 (4)	2.185 (7)
Co–S′ (dimer bridge)	...	...	...	...	2.382 (4)	2.404 (7)
Co–N (adduct)	2.04 (2)	2.01 (1)	...	...	...	...
S–C	1.76 (2)	1.72 (2)	1.77 (2)	1.723 (7)	1.694 (4)	1.76 (2)
C–C	1.41 (3)	1.36 (2)	1.38 (2)	1.34 (1)	1.39 (2)	1.41 (3)
			Bond Angles, Deg			
S–Co–S (intra)	91.0 (3)	92.3 (2)	91.3 (2)	91.4 (1)	89.8 (2)	90.1 (2)
Co–S–C	104 (1)	101 (1)	105.3 (5)	103.8 (3)	105.5 (2)	104.8 (7)

[a] This work. [b] Reference 2. [c] Reference 9. [d] Reference 11. [e] Reference 12. [f] Reference 10.

$(CH_3))_2^-$ and the dimeric system $Co_2(S_2C_2(CN)_2)_4^{2-}$. This conclusion is reinforced by the observation that the Co–S dimer linkages in the structurally known dimeric systems (Table VI) are considerably longer than the Co–S distances in the basal planes of these complexes. The important differences in the properties of the two bis-dithiolene complexes $Co(S_2C_6H_3(CH_3))_2^-$ and $Co_2(S_2C_2(CN)_2)_4^{2-}$ relate directly to the π-acceptor properties of their respective dithiolene ligands. The π acidity of the ligand system, in turn, influences the electron density in the vicinity of the Co atom in these complexes. For those systems in which sufficient electron density is withdrawn from the Co atom to favor the formation of a five-coordinate dimer structure, the aforementioned equilibrium lies strongly in favor of the Lewis base adduct whereas for those complexes in which there is little or no tendency for axial ligation and dimer formation, the equilibrium lies in favor of the original bis planar complex. The significantly reduced importance of differences in ligand π acidity in six-coordinate complexes is demonstrated by the nearly identical structures we find for the two *o*-phenanthroline adducts of the cobalt–bis(dithiolene) complexes.

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The Structural Chemistry of Prussian Blue Analogs. A Single-Crystal Study of Manganese(II) Hexacyanocobaltate(III), $Mn_3[Co(CN)_6]_2 \cdot xH_2O$

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The crystal structure of hydrated manganese(II) hexacyanocobaltate(III), $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ (x = 12–14), has been determined from three-dimensional X-ray data using integrated precession photographs. The cubic face-centered cell with a = 10.421 (5) Å of space group O_h^5-Fm3m contains $1^1/_3$ formula units. The measured and calculated (for x = 13) densities are 1.65 and 1.62 g/cm³. The final R factor is 10.5%. Co–C–N–Mn bridges connect octahedral CoC_6 and $MnN_4(H_2O)_2$ groups to a three-dimensional framework with 4 Mn at 4a (0, 0, 0) and $2^2/_3$ Co randomly distributed on 4b ($^1/_2$, $^1/_2$, $^1/_2$); 16 C and 16 N are at 24e (x, 0, 0) and 8 water molecules belonging to the coordination octahedron of Mn are situated close to the empty nitrogen positions. Additional water molecules are distributed around 8c ($^1/_4$, $^1/_4$, $^1/_4$). The Co–C, C–N, Mn–N, and Mn–O distances are 1.865 (2), 1.136 (3), 2.209 (2), and 2.391 (6) Å. The shortest O···H–O distances of 2.67–2.90 Å are in agreement with hydrogen-bond lengths obtained from infrared spectra.

Introduction

Although the polynuclear transition metal cyanides of the Prussian Blue type have been known for a long time, the complete solution of their crystal structure has not yet been achieved. Due to their extremely low solubility these compounds have been prepared only as colloidal precipitates.[1] The products resulting when aqueous solutions of a metal salt and of a hexacyanometalate are mixed contain variable amounts of water and often also of potassium. Most of the polynuclear

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