

In conclusion, these chemical studies have shown that the carbon-carbon triple bond is a sterically protected group, that the triple bond can be regarded as an electron-withdrawing apical substituent of the $-\text{CCO}_3-\text{(CO)}_9$ unit, and that the individual $-\text{CCO}_3(\text{CO})_9$ clusters have chemical properties similar to those of the parent clusters, $\text{YCCO}_3(\text{CO})_9$.

Acknowledgment.—We thank Dr. A. D. Campbell for supervising the microanalyses, the Director of the Computer Centre, University of British Columbia, for computing facilities for the final refinement, and the New Zealand Universities Grants Committee for grants for equipment and research fellowships (to R. J. D. and J. L. S.).

CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, DEPARTMENT OF CHEMISTRY, BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND 02912

Dithiolene Complex Adducts. The Crystal and Molecular Structure of Tetra-*n*-propylammonium Bis(maleonitriledithiolato)-1,10-phenanthrolinecobaltate, $[(n\text{-C}_3\text{H}_7)_4\text{N}][\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2(o\text{-phen})]^-$

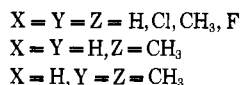
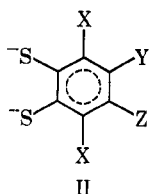
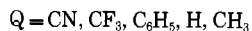
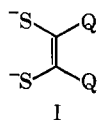
By GYANESHWARI P. KHARE AND RICHARD EISENBERG

Received July 17, 1969

The crystal and molecular structure of the tetra-*n*-propylammonium salt of the *o*-phenanthroline adduct $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2(o\text{-phen})^-$ 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 0.068 for 1490 nonzero reflections. The complex crystallizes in space group *Pbca* of the orthorhombic system in a unit cell of dimensions $a = 15.53$ (2) Å, $b = 27.01$ (3) Å, $c = 17.20$ (2) Å, and $V = 7219$ Å³. The experimental density is 1.29 (3) g/cm³; the calculated value is 1.30 g/cm³ for $Z = 8$. The coordination geometry about the cobalt ion is that of a tris-chelated octahedron with essentially C_2 molecular symmetry. The average Co-N distance is 2.01 (1) Å and the N-Co-N bond angle is 85.2 (5)°. The Co-S distances exhibit slight but significant differences depending on whether they are *trans* to an *o*-phenanthroline nitrogen atom in which case the average Co-S distance is 2.213 (5) Å or *trans* to another sulfur donor atom in which case the average distance is 2.247 (5) Å. The bond distances within the *o*-phenanthroline ligand range from 1.31 (2) to 1.48 (2) Å and follow approximately the individual bond orders predicted from simple valence bond considerations. All other bond distances, bond angles, and intermolecular contacts are normal.

Introduction

The cobalt and iron bis complexes of the 1,2-dithiolato ligand systems I and II are of particular interest



because of the structural differences which these systems can exhibit depending upon the overall oxidation state of the complex and the electron-withdrawing ability or π acidity of the particular ligand system.¹ Although I and II are represented in their classical dianion formulation, it is clear from the many studies which have been performed on them and their complexes that complexes of I and II exhibit extensive covalency and their ground states may be considered to be delocalized.¹⁰

To date, X-ray structural studies have shown that the complexes $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2^{2-}$ and $\text{Co}(\text{S}_2\text{C}_6\text{H}_8(\text{CH}_3)_2)^{2-}$ are truly monomeric in the solid, possessing essentially square-planar coordination geometries, whereas the related complexes $\text{Co}_2(\text{S}_2\text{C}_2(\text{CF}_3)_2)_4$,⁴ $\text{Co}_2(\text{S}_2\text{C}_6\text{Cl}_4)_4^{2-}$,⁵ and $\text{Fe}_2(\text{S}_2\text{C}_2(\text{CN})_2)_4^{2-}$ ⁶ exist in the solid state as five-coordinate dimers in which the metal atom from one planar unit is bound to a fifth sulfur atom of a second such unit in the apical position of a square pyramid. Chemical and polarographic studies⁷⁻¹¹ together with the X-ray structure determinations have established that the more highly oxidized neutral complexes and those monoanionic systems with good π -acceptor ligands tend to form stable five-coordinate dimers while the more reduced dianionic systems and those monoanions with poor π -acceptor ligands exhibit little or no tendency to form the dimer structure. The tendency to

(2) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500 (1964).

(3) R. Eisenberg, Z. Dori, H. B. Gray, and J. A. Ibers, *ibid.*, **7**, 741 (1968).

(4) J. H. Enemark and W. N. Lipscomb, *ibid.*, **4**, 1729 (1965).

(5) M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4253 (1968).

(6) W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967).

(7) A. Davison, D. V. Howe, and E. T. Shawl, *ibid.*, **6**, 458 (1967).

(8) A. L. Balch and R. H. Holm, *Chem. Commun.*, 552 (1966).

(9) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Amer. Chem. Soc.*, **88**, 4604 (1966).

(10) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *ibid.*, **88**, 4870 (1966).

(11) A. L. Balch, *Inorg. Chem.*, **6**, 2158 (1967).

(1) For a comprehensive review of metal-1,2-dithiolene complexes, see (a) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968); (b) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968); (c) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

ward dimerization thus appears to be related to the electron density around the metal atom in these complexes. Consistent with this notion are the greatly differing tendencies of these complexes to form adducts with mono- and bidentate Lewis bases such as pyridine, triphenylphosphine, triphenylarsine, diarsine, and *o*-phenanthroline.⁹⁻¹² Those complexes which show a strong tendency toward dimerization form stable adducts rapidly and essentially completely, while those complexes which are resistant to dimer formation form only relatively unstable adducts at best. We have therefore undertaken the structure determinations of several closely related adducts in order to establish whether or not the very significant differences in the relative adduct stabilities manifest themselves in significant structural differences.

In this paper and the one to follow, we present the structure determinations of the *o*-phenanthroline adducts of the two "isoelectronic" complexes $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2^-$ and $\text{Co}(\text{S}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)_2^-$. The dimeric nature of the former complex, which should be written as $\text{Co}_2(\text{S}_2\text{C}_2(\text{CN})_2)_4^{2-}$, has been established by conductivity and polarographic measurements,^{7,8} and its diamagnetism, which can be viewed as an indication of its dimeric structure, is observed in the solid state and in solutions of a variety of solvents such as cyclohexanone, acetone, and acetonitrile.^{13,14} In contrast, $\text{Co}(\text{S}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)_2^-$ is a stable spin-triplet monomer in both the solid and solution states.¹⁴ The *o*-phenanthroline adducts of the two complexes $\text{Co}_2(\text{S}_2\text{C}_2(\text{CN})_2)_4^{2-}$ and $\text{Co}(\text{S}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)_2^-$ were first reported by Langford, *et al.*¹² In their study, they determined the formation constant of the $\text{Co}(\text{S}_2\text{C}_6\text{H}_3(\text{CH}_3)_2)(o\text{-phen})^-$ adduct by direct observation of adduct dissociation but were unable to do so for the $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2(o\text{-phen})^-$ adduct because of its great stability relative to the original dimeric complex.

The results presented herein have appeared in preliminary form.¹⁵

Collection and Reduction of the X-Ray Data

The *o*-phenanthroline adduct of the dimeric complex $[(n\text{-C}_3\text{H}_7)_4\text{N}]_2[\text{Co}_2(\text{S}_2\text{C}_2(\text{CN})_2)_4]$ was prepared in a manner similar to that reported by Langford, *et al.*,¹² and beautiful green-black crystals of $[(n\text{-C}_3\text{H}_7)_4\text{N}][\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2(o\text{-phen})]$ suitable for single-crystal X-ray studies were grown from methanol-2-propanol solutions. The crystals were examined by optical goniometry and found to exhibit D_{2h} -mmm symmetry. Weissenberg and precession photographs, taken with $\text{Mo K}\alpha$ radiation, revealed that the complex crystallizes in an orthorhombic unit cell of refined (*vide infra*) dimensions $a = 15.53(2) \text{ \AA}$, $b = 27.01(3) \text{ \AA}$, $c = 17.20(2) \text{ \AA}$, and $V = 7219 \text{ \AA}^3$. An experimental density of $1.29(3) \text{ g/cm}^3$ determined using the flotation method with

carbon tetrachloride-benzene solutions is in good agreement with a calculated value of 1.30 g/cm^3 for eight molecules in the unit cell. The extinctions, $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd, which were determined on the basis of Weissenberg photographs of the $h0l$, $h1l$, and $h2l$ zones and precession photographs of the $0kl$, $1kl$, $hk0$, and hkl zones, are consistent with the centrosymmetric space group Pbca (D_{2h}^{15} , no. 61).¹⁶

A complete set of independent intensity data was collected from a single crystal at room temperature using a Picker four-circle automated diffractometer. A crystal of approximate dimensions $0.54 \times 0.44 \times 0.27 \text{ mm}$ parallel to the reciprocal lattice directions $[101]$, $[10\bar{1}]$, and $[010]$, respectively, was mounted in the c^* direction and aligned accurately on a Supper precession camera. After the crystal was transferred to the diffractometer, approximately 15 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 edges were then refined using the least-squares refinement procedure of Hamilton's MODEL diffractometer setting program.¹⁷ The mosaic spread of the crystal was estimated from open counter-narrow source ω scans through several strong reflections and it was found to have an average value of 0.4° .¹⁸ The data were collected by the θ - 2θ scan technique using Ni-filtered $\text{Cu K}\alpha$ radiation. The intensities were measured using a scintillation detector and pulse height analysis. Despite the increased effect of absorption, $\text{Cu K}\alpha$ radiation was employed to avoid the possibility of overlap in the counter aperture which could result from the large unit cell and the use of a shorter wavelength¹⁹ (other X-radiation sources of first-row transition metals such as Co ($\lambda_{\text{CoK}\alpha} 1.7902 \text{ \AA}$) and Fe ($\lambda_{\text{FeK}\alpha} 1.9373 \text{ \AA}$) were not available). The scan range was from 0.9 to 1.0° of the 2θ value of the reflection with a scan rate of $1^\circ/\text{min}$ and 10-sec background counts collected at both ends of the 2θ scan range. Intensity data were collected out to a 2θ value of 80° and a total of 2185 intensities in one octant of reciprocal space were measured. During the data collection, the intensities of four standard reflections in different regions of reciprocal space were monitored at least once every 200 reflections. None of these standards deviated from its mean value by more than 4%.

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. Standard deviations for the intensities were estimated

(16) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 150.

(17) 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.

(18) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

(19) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966).

(12) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 2958 (1964).

(13) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

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

(15) G. P. Khare, C. G. Pierpont, and R. Eisenberg, *Chem. Commun.*, 1692 (1968).

TABLE I
FINAL PARAMETERS FOR $[(n-C_3H_7)_4N][Co(S_2C_2(CN)_2)_2(o\text{-phen})]$. ATOMIC POSITIONAL AND THERMAL PARAMETERS ($\times 10^4$)

Atom ^a	x ^b	y	z	β_{11} ^d	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	2335 (1) ^c	675 (1)	1262 (1)	24 (2)	15 (1)	22 (1)	-1 (1)	-2 (1)	0 (1)
S ₁	2445 (3)	877 (1)	2507 (2)	35 (3)	15 (1)	19 (2)	-2 (1)	-3 (2)	0 (1)
S ₂	2544 (3)	1462 (2)	878 (2)	40 (3)	16 (1)	31 (2)	-1 (1)	-2 (2)	2 (1)
S ₃	2176 (3)	-117 (2)	1627 (2)	31 (3)	16 (1)	31 (2)	-1 (1)	-3 (2)	1 (1)
S ₄	3749 (2)	601 (2)	1186 (3)	25 (3)	16 (1)	36 (3)	-1 (1)	2 (2)	0 (2)
OPN ₁	1047 (7)	741 (4)	1293 (8)	22 (11)	16 (3)	16 (9)	-4 (4)	-5 (11)	2 (5)
OPN ₂	2164 (8)	493 (4)	140 (6)	26 (11)	16 (3)	9 (10)	-4 (5)	-16 (10)	-6 (4)
OPC ₁	490 (11)	817 (6)	1879 (8)	51 (11)	15 (4)	12 (8)	3 (5)	30 (8)	-1 (4)
OPC ₂	-410 (11)	860 (6)	1746 (12)	4 (11)	14 (4)	74 (14)	6 (5)	7 (10)	-1 (6)
OPC ₃	-738 (11)	828 (6)	992 (13)	33 (12)	14 (4)	32 (11)	2 (5)	-27 (10)	3 (5)
OPC ₄	-174 (11)	716 (6)	341 (13)	25 (12)	11 (3)	47 (11)	-2 (5)	18 (10)	-3 (5)
OPC ₅	727 (11)	685 (5)	545 (10)	35 (24)	6 (4)	33 (18)	-2 (6)	30 (17)	-2 (6)
OPC ₆	1329 (10)	553 (5)	-62 (9)	46 (22)	7 (3)	18 (16)	-2 (7)	-7 (17)	3 (6)
OPC ₇	1023 (10)	437 (5)	-850 (9)	16 (17)	11 (4)	29 (15)	-5 (6)	-7 (14)	1 (5)
OPC ₈	1590 (11)	271 (7)	-1414 (11)	26 (14)	21 (4)	39 (12)	0 (6)	11 (13)	2 (5)
OPC ₉	2446 (12)	228 (5)	-1185 (10)	78 (13)	12 (3)	31 (9)	-7 (6)	26 (12)	-1 (4)
OPC ₁₀	2721 (10)	351 (5)	-391 (10)	55 (12)	16 (3)	3 (7)	4 (5)	23 (9)	-7 (4)
OPC ₁₁	105 (11)	494 (6)	-1012 (10)	50 (17)	13 (4)	30 (14)	-5 (6)	-7 (12)	1 (5)
OPC ₁₂	-463 (10)	632 (6)	-470 (12)	56 (12)	15 (4)	32 (10)	-3 (5)	-18 (9)	-9 (5)
C ₁	2701 (10)	1486 (6)	2449 (15)	28 (11)	20 (4)	23 (10)	-1 (6)	-4 (11)	-9 (7)
C ₂	2778 (11)	1734 (7)	1753 (14)	35 (12)	7 (4)	52 (12)	-6 (6)	-12 (10)	-4 (6)
C ₃	3263 (12)	-303 (7)	1625 (9)	58 (13)	7 (4)	25 (9)	10 (6)	-7 (9)	3 (5)
C ₄	3901 (12)	4 (6)	1423 (9)	19 (10)	17 (4)	26 (9)	-3 (5)	6 (8)	7 (5)
CN ₁	2827 (11)	1728 (7)	3155 (15)	41 (12)	13 (5)	43 (14)	-3 (6)	3 (13)	-5 (6)
CN ₂	2908 (11)	1929 (6)	3739 (10)	71 (11)	21 (4)	47 (10)	-5 (5)	-3 (10)	-9 (5)
CN ₃	3031 (14)	2230 (10)	1717 (13)	49 (14)	25 (6)	47 (12)	2 (9)	-2 (11)	-4 (9)
CN ₄	3279 (13)	2646 (7)	1692 (12)	108 (15)	31 (5)	57 (10)	-18 (7)	-3 (9)	-8 (7)
CN ₅	3390 (10)	-794 (8)	1825 (10)	41 (14)	18 (6)	28 (12)	-2 (10)	-5 (10)	0 (7)
CN ₆	3519 (9)	-1206 (6)	2030 (8)	81 (12)	21 (5)	52 (11)	5 (7)	8 (9)	-1 (6)
CN ₇	4751 (16)	-179 (7)	1485 (11)	42 (21)	21 (6)	50 (15)	2 (11)	-5 (19)	3 (7)
CN ₈	5458 (10)	-304 (6)	1506 (10)	40 (9)	40 (5)	130 (13)	14 (5)	-11 (9)	10 (6)
Atom ^a	x ^b	y	z	B ^e					
CATN	172 (9)	2856 (5)	533 (8)	609 (39)					
CATC ₁	669 (10)	2640 (6)	1298 (10)	543 (46)					
CATC ₂	132 (12)	2199 (7)	1703 (11)	737 (54)					
CATC ₃	535 (10)	2070 (5)	2451 (11)	555 (46)					
CATC ₄	59 (11)	2447 (6)	-92 (11)	550 (44)					
CATC ₅	955 (12)	2268 (7)	-441 (12)	782 (60)					
CATC ₆	727 (13)	1832 (8)	-968 (12)	926 (67)					
CATC ₇	747 (10)	3299 (6)	318 (10)	476 (44)					
CATC ₈	428 (11)	3568 (7)	-410 (11)	694 (52)					
CATC ₉	1052 (11)	4010 (7)	-548 (10)	665 (53)					
CATC ₁₀	-772 (11)	3028 (7)	734 (11)	609 (51)					
CATC ₁₁	-795 (13)	3411 (7)	1409 (12)	833 (59)					
CATC ₁₂	-1783 (13)	3505 (7)	1553 (12)	963 (66)					

^a In our labeling scheme, C₁, C₂, C₃, and C₄ are the ethylenic carbon atoms of the dithiolene ligands bonded to S₁, S₂, S₃, and S₄, respectively. The atoms CN₁-CN₂, CN₃-CN₄, CN₅-CN₆, and CN₇-CN₈ are the CN groups bonded, respectively, to C₁, C₂, C₃, and C₄. The labeling scheme of the *o*-phenanthroline ligand is shown in Figure 2. The cation carbon atoms are labeled sequentially. ^b x, y, z are in fractional coordinates. ^c Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figure. ^d Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hkl\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. ^e Isotropic thermal parameters in $\text{\AA}^2 \times 10^3$.

according to counting statistics as outlined below, and it was found that 1527 of the 2153 intensities measured had values greater than their corresponding estimated standard deviations σ (*vide infra*). An absorption correction was then carried out for the observed structure amplitudes. With an absorption coefficient of 59.7 cm^{-1} , the resultant transmission coefficients are found to range from 0.13 to 0.25.

Solution and Refinement of the Structure

The positions of the Co atom and four S atoms were determined from a three-dimensional Patterson function. The positional parameters of these atoms, along with a variable isotropic thermal parameter assigned to

each of them, were refined through several cycles of least squares. The positions of all of the carbon and nitrogen atoms were then determined from a succession of difference Fourier maps based on phases obtained from the refined positions of the previously located atoms.

The complete trial structure (all atoms except hydrogens) was refined by a least-squares procedure. The function minimized was $\sum w(F_o - F_c)^2$ where the weights w were taken as $4F^2/\sigma^2(F^2)$ and the standard deviations σ were estimated according to the formula

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

TABLE II
 ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (\AA^2)

Atom ^a	Min	Intermed	Max
Co	0.167 (5)	0.185 (5)	0.235 (4)
S ₁	0.166 (9)	0.206 (8)	0.242 (7)
S ₂	0.209 (9)	0.221 (8)	0.250 (7)
S ₃	0.192 (9)	0.217 (9)	0.245 (8)
S ₄	0.174 (10)	0.232 (9)	0.246 (9)
OPN ₁	0.14 (6)	0.17 (4)	0.25 (3)
OPC ₂	0.02 (29)	0.24 (3)	0.33 (3)
OPC ₃	0.07 (9)	0.23 (3)	0.28 (3)
OPC ₄	0.14 (5)	0.20 (3)	0.29 (3)
OPC ₅	0.07 (17)	0.15 (4)	0.30 (4)
OPC ₆	0.13 (6)	0.18 (6)	0.25 (6)
OPC ₇	0.11 (8)	0.20 (4)	0.23 (4)
OPC ₈	0.16 (5)	0.25 (3)	0.28 (3)
OPC ₉	0.16 (4)	0.20 (3)	0.34 (3)
OPC ₁₁	0.20 (4)	0.21 (4)	0.27 (3)
OPC ₁₂	0.14 (5)	0.26 (3)	0.29 (3)
C ₁	0.15 (6)	0.19 (4)	0.29 (3)
C ₂	0.12 (6)	0.22 (3)	0.29 (3)
C ₃	0.13 (6)	0.20 (4)	0.28 (3)
C ₄	0.11 (5)	0.20 (4)	0.28 (3)
CN ₁	0.20 (5)	0.22 (4)	0.27 (4)
CN ₂	0.22 (3)	0.29 (2)	0.32 (2)
CN ₃	0.24 (3)	0.26 (4)	0.31 (4)
CN ₄	0.26 (3)	0.32 (3)	0.40 (3)
CN ₅	0.19 (5)	0.23 (4)	0.26 (4)
CN ₆	0.26 (3)	0.29 (3)	0.33 (2)
CN ₇	0.22 (6)	0.27 (4)	0.29 (4)
CN ₈	0.19 (3)	0.38 (2)	0.45 (2)

^a Thermal parameters of the atoms OPN₂, OPC₁, and OPC₁₀ did not refine as positive-definite.

in which CT is the total integrated count obtained in a scan of 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 are the Lorentz and polarization factors, and T is the transmission coefficient. The neutral Co, S, N, and C scattering factors were obtained from Ibers' tabulation²⁰ while anomalous parts of the Co and S scattering factors were obtained from Templeton's tabulation²¹ and included in the calculated structure factors.²² Only those reflections with F^2 greater than $\sigma(F^2)$ were included in the refinement and in the calculation of the discrepancy indices R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) and R' ($= (\sum w(F_o - F_c)^2 / \sum w F_o^2)^{1/2}$).

In the initial round of calculations, all atoms were assigned individual isotropic temperature factors. This refinement of 177 parameters including one variable scale factor converged rapidly to an R factor of 0.087 and a weighted R factor R' of 0.090. A difference Fourier based on this refinement provided evidence for anisotropic thermal motion of the heavy atoms.

After the elimination of several data errors due to either incorrect positioning or punching errors, a further refinement was carried out in which the Co and S atoms were given anisotropic thermal parameters and all other atoms were restricted to isotropic thermal models. Because of computer limitations, this partial anisotropic refinement was carried out in blocks. In

the initial cycle, the parameters of the eight nitrile group atoms of the two $S_2C_2(CN)_2^{2-}$ ligands were held fixed while all other positional, thermal, and scale parameters were refined. In the second cycle, the parameters of four cation carbon atoms were held fixed while all other positional, thermal, and scale parameters were refined. This refinement covered to a conventional R factor of 0.072 and a weighted R factor R' of 0.073 for 1490 reflections above σ . In the next four cycles of least-squares refinement, the carbon and nitrogen atoms of the anion were also assigned anisotropic thermal parameters while the cation carbon and nitrogen atoms remained restricted to isotropic thermal models. Since refinement of this model had to be carried out in blocks, parameters expected to have very low correlation coefficients were varied on different cycles. This final refinement converged to a conventional R factor of 0.069 and a weighted R factor R' of 0.068. In the final cycle, the largest parameter shifts, which were approximately seven-tenths of an estimated standard deviation, were observed for some of the anisotropic thermal parameters of the light atoms. None of the parameters of any atoms within the coordination sphere and chelate rings changed by more than one-fifth of an estimated standard deviation. In this refinement, however, the thermal parameters of three light atoms did not refine as positive-definite. A final difference Fourier map showed no peaks higher than $0.6 e^-/\text{\AA}^3$ or about 25% of the height of a carbon atom in this structure. Reasonable positions were found for many but not all of the *o*-phenanthroline and tetra-*n*-propylammonium hydrogen atoms but the contributions of these hydrogen atoms to $|F_o|$ were not included in any further calculation. The parameters obtained in this partial anisotropic refinement are taken as the final parameters for the structure and are given in Table

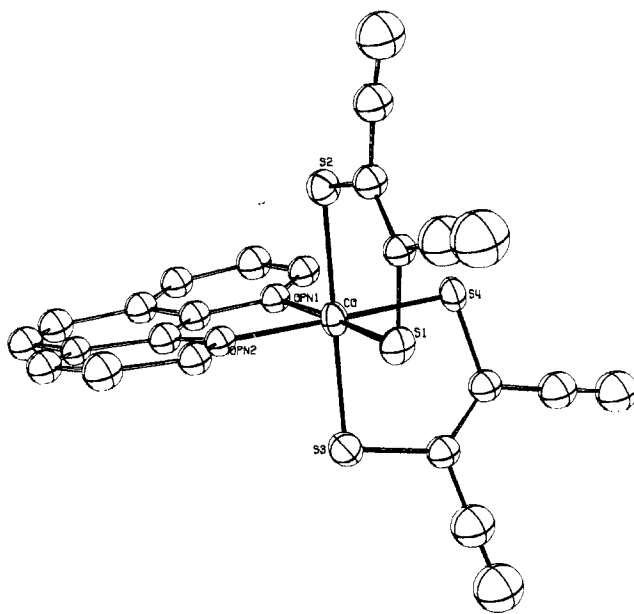


Figure 1.—A perspective drawing of the $Co(S_2C_2(CN)_2)_2(o\text{-phen})$ adduct.

(20) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(21) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, Table 3.3.2B.

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

TABLE III
OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS X 10) FOR [(n-C4H7)4N][Co(S2C2(CN)2)2(o-phen)]

Table with multiple columns of data for observed and calculated structure factor amplitudes. Columns are labeled with h, k, l and F values. The table is organized into several sections with headers like 'OBSERVED' and 'CALCULATED'.

I along with their standard deviations as obtained from the appropriate inverse matrix of the last least-squares cycle in which the parameter was refined. In Table II the root-mean-square amplitudes of vibration of the anion atoms are presented. The F0 and |F0| values (in electrons X 10) for the 1490 reflection included in the final refinement are tabulated in Table III. None of the |F0| values for reflections whose F2 values were less than sigma(F2) was found to be above 3 times the estimated standard deviation. With the weighting scheme em-

ployed, the estimate of the standard deviation of an observation of unit weight has the value 2.13.

Description of the Structure

The structure of the anionic adduct Co(S2C2(CN)2)2(o-phen)- is best described as a tris-chelated octahedron and, in most respects, appears to be typical of hexacoordinated Co(III). A perspective drawing of the adduct is presented in Figure 1 and all important intramolecular distances and angles are tabulated in Table IV.

TABLE IV
PRINCIPAL INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG)

		Anion	
Co-S ₁	2.217 (5)	S ₂ -Co-S ₁	92.3 (2)
Co-S ₂	2.250 (5)	S ₄ -Co-S ₃	92.2 (2)
Co-S ₃	2.244 (5)	OPN ₁ -Co-OPN ₂	85.2 (5)
Co-S ₄	2.210 (5)	S ₂ -Co-S ₃	177.8 (2)
Co-OPN ₁	2.009 (12)	OPN ₂ -Co-S ₁	176.8 (4)
Co-OPN ₂	2.009 (12)	OPN ₁ -Co-S ₄	178.1 (5)
S ₁ -S ₂	3.220 (6)	Co-S ₁ -C ₁	101.5 (9)
S ₃ -S ₄	3.211 (6)	S ₁ -C ₁ -C ₂	123 (2)
OPN ₁ -OPN ₂	2.72 (2)	S ₁ -C ₁ -CN ₁	116 (2)
S ₁ -C ₁	1.70 (2)	C ₂ -C ₁ -CN ₁	121 (2)
C ₁ -CN ₁	1.39 (2)	C ₁ -CN ₁ -CN ₂	178 (2)
CN ₁ -CN ₂	1.15 (2)	Co-S ₂ -C ₂	100.3 (8)
C ₁ -C ₂	1.38 (2)	S ₂ -C ₂ -C ₁	122 (2)
S ₂ -C ₂	1.71 (2)	S ₂ -C ₂ -CN ₃	116 (2)
C ₂ -CN ₃	1.40 (2)	C ₁ -C ₂ -CN ₃	122 (2)
CN ₃ -CN ₄	1.19 (2)	C ₂ -CN ₃ -CN ₄	177 (3)
S ₃ -C ₃	1.76 (2)	Co-S ₃ -C ₃	99.5 (7)
C ₃ -CN ₅	1.39 (2)	S ₃ -C ₃ -C ₄	122 (1)
CN ₅ -CN ₆	1.18 (2)	S ₃ -C ₃ -CN ₅	114 (2)
C ₃ -C ₄	1.34 (2)	C ₄ -C ₃ -CN ₅	124 (2)
S ₄ -C ₄	1.68 (2)	C ₃ -CN ₅ -CN ₆	177 (2)
C ₄ -CN ₇	1.41 (2)	Co-S ₄ -C ₄	102.2 (7)
CN ₇ -CN ₈	1.15 (2)	S ₄ -C ₄ -C ₃	124 (1)
OPN ₂ -OPC ₁₀	1.31 (2)	C ₃ -C ₄ -CN ₇	117 (2)
OPN ₂ -OPC ₈	1.35 (2)	C ₄ -CN ₇ -CN ₈	176 (2)
OPN ₁ -OPC ₅	1.39 (2)	Co-OPN ₁ -OPC ₁	132 (1)
OPN ₁ -OPC ₁	1.34 (2)	Co-OPN ₁ -OPC ₅	109 (1)
		OPC ₅ -OPN ₁ -OPC ₁	119 (1)
		Co-OPN ₂ -OPC ₁₀	131 (1)
		Co-OPN ₂ -OPC ₈	110 (1)
		OPC ₁₀ -OPN ₂ -OPC ₈	119 (1)
		OPC ₈ -OPC ₅ -OPN ₁	118 (2)
		OPC ₅ -OPC ₈ -OPN ₂	118 (2)
		Cation	
CATN-CATC ₁	1.63 (2)	CATC ₁ -CATN-CATC ₄	111 (1)
CATN-CATC ₄	1.55 (2)	CATC ₁ -CATN-CATC ₇	101 (1)
CATN-CATC ₇	1.54 (2)	CATC ₁ -CATN-CATC ₁₀	112 (1)
CATN-CATC ₁₀	1.58 (2)	CATC ₄ -CATN-CATC ₇	117 (1)
CATC ₁ -CATC ₂	1.61 (2)	CATC ₄ -CATN-CATC ₁₀	105 (1)
CATC ₂ -CATC ₃	1.47 (2)	CATC ₇ -CATN-CATC ₁₀	111 (1)
CATC ₄ -CATC ₅	1.59 (2)	CATN-CATC ₁ -CATC ₂	112 (1)
CATC ₅ -CATC ₆	1.53 (2)	CATC ₁ -CATC ₂ -CATC ₃	109 (2)
CATC ₇ -CATC ₈	1.53 (2)	CATN-CATC ₄ -CATC ₅	112 (1)
CATC ₈ -CATC ₉	1.56 (2)	CATC ₄ -CATC ₅ -CATC ₆	105 (2)
CATC ₁₀ -CATC ₁₁	1.55 (2)	CATN-CATC ₇ -CATC ₈	112 (1)
CATC ₁₁ -CATC ₁₂	1.58 (2)	CATC ₇ -CATC ₈ -CATC ₉	107 (2)
		CATN-CATC ₁₀ -CATC ₁₁	112 (1)
		CATC ₁₀ -CATC ₁₁ -CATC ₁₂	104 (2)

The average Co-N distance of 2.01 (1) Å is slightly, but not significantly, longer than the value of 1.96 (2) Å reported for Co(NH₃)₆³⁺²³ and other Co-N distances reported for a number of six-coordinate cobalt(III) complexes.²⁴⁻²⁷ The four independent Co-S distances average 2.23 (2) Å which is slightly less than the average Co-S distances of 2.258 (2) and 2.267 (3) Å reported in two independent studies of the tris-dithiocarbamate complex Co(S₂CN(C₂H₅)₂)₃.^{28,29} The shorter Co-S distance in the present study may be the result of the superior π-acceptor capability of the maleonitriledithiolate ligand relative to the dithiocarbamate ligand or it may result from the lack of steric strain in the five-membered chelate ring as opposed to the strained four-membered chelate ring formed by the dithiocarbamate

(23) M. T. Barnet, B. M. Craven, H. C. Freeman, N. E. King, and J. A. Ibers, *Chem. Commun.*, 307 (1966).

(24) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr., Sect. B*, **24**, 246 (1968).

(25) G. G. Messmer and E. L. Amma, *ibid.*, *Sect. B*, **24**, 417 (1968).

(26) F. A. Cotton and W. T. Edwards, *ibid.*, *Sect. B*, **24**, 474 (1968).

(27) B. F. Hoskins, F. D. Whillans, D. H. Dale, and D. C. Hodgkin, *Chem. Commun.*, 69 (1969).

(28) S. Melino, *Acta Crystallogr., Sect. B*, **24**, 1441 (1968).

(29) T. Brennan and I. Bernal, *J. Phys. Chem.*, **73**, 443 (1969); I. Bernal, private communication.

TABLE V
WEIGHTED LEAST-SQUARES PLANES AND THE DISTANCES OF THE ATOMS FROM THEIR RESPECTIVE PLANES^a
(ORTHORHOMBIC COORDINATES)

Atom	Distance, Å	Atom	Distance, Å
Metal-Chelate Ring 1: 15.27x - 4.79y - 0.77z - 3.14 = 0			
Co	0.005 (2)	C ₁	0.08 (2)
S ₁	-0.019 (4)	C ₂	0.14 (2)
S ₂	-0.023 (4)		
Metal-Chelate Ring 2: 1.29x + 7.30y + 16.50z - 2.88 = 0			
Co	-0.001 (2)	C ₃	0.00 (2)
S ₃	0.001 (4)	C ₄	-0.02 (2)
S ₄	0.003 (4)		
Metal-Chelate Ring 3: 1.68x + 26.11y - 3.99z - 1.65 = 0			
Co	0.003 (2)	OPC ₅	0.04 (1)
OPN ₁	-0.05 (1)	OPC ₆	0.04 (1)
OPN ₂	-0.05 (1)		
<i>o</i> -Phenanthroline Moiety: 2.23x + 26.14y - 3.57z - 1.67 = 0			
OPN ₁	0.03 (1)	OPC ₆	0.09 (1)
OPN ₂	0.05 (1)	OPC ₇	0.00 (1)
OPC ₁	-0.10 (1)	OPC ₈	-0.11 (2)
OPC ₂	-0.14 (2)	OPC ₉	-0.11 (1)
OPC ₃	-0.03 (2)	OPC ₁₀	-0.01 (1)
OPC ₄	0.04 (2)	OPC ₁₁	0.00 (1)
OPC ₅	0.08 (1)	OPC ₁₂	0.04 (2)
S ₂ C ₂ (CN) ₂ ²⁻ Ligand 1: 14.99x - 6.79y - 1.25z - 2.73 = 0			
S ₁	0.022 (4)	CN ₁	-0.06 (2)
S ₂	-0.023 (4)	CN ₂	-0.15 (2)
C ₁	0.00 (2)	CN ₃	0.08 (2)
C ₂	0.03 (2)	CN ₄	0.17 (2)
S ₂ C ₂ (CN) ₂ ²⁻ Ligand 2: 1.15x + 7.50y + 16.47z - 2.83 = 0			
S ₃	0.006 (4)	CN ₅	-0.04 (2)
S ₄	0.001 (4)	CN ₆	0.01 (1)
C ₃	-0.01 (2)	CN ₇	0.02 (2)
C ₄	-0.04 (2)	CN ₈	0.04 (2)

^a Best weighted least-squares planes calculated by the procedure of W. C. Hamilton, *Acta Crystallogr.*, **14**, 185 (1961), using the variance-covariance matrix.

ligand. The average Co-S distance of 2.23 (2) Å is, however, significantly longer than the 2.16-2.18 Å average values observed in the cobalt bis complexes of the 1,2-dithiolene ligand systems.²⁻⁵ The increase in the Co-S distance in the present structure relative to those observed in the cobalt bis-dithiolene complexes is taken to be a result of the increased coordination number and the reduced metal-sulfur π bonding in the six-coordinate adduct. In addition, we find significant differences between the Co-S bond lengths depending upon whether the sulfur atom is *trans* to another sulfur atom (2.247 (5) Å) or *trans* to an *o*-phenanthroline nitrogen donor atom (2.213 (5) Å). This difference in Co-S bond lengths is also observed in the structure of the Co(S₂C₆H₃(CH₃)₂)(*o*-phen)⁻ adduct,³⁰ thus indicating that in these adduct structures, the sulfur donor atoms exert a greater structural *trans* effect than the nitrogen donor atoms of the *o*-phenanthroline addendum.

Within the coordination sphere, the deviations of the bond angles from those found for perfect octahedral coordination are small. The average intrachelate ring S-Co-S bond angle is 92.2 (2)° compared with values of

(30) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **9**, 2218 (1970).

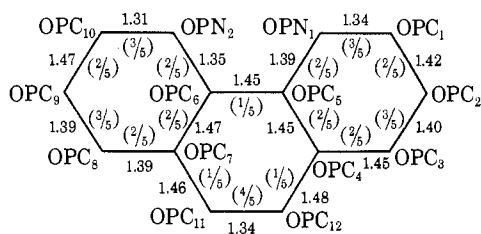


Figure 2.—The dimensions of *o*-phenanthroline ligand and the π bond orders for the corresponding bonds in the phenanthrene molecule as derived from valence bond considerations.

76.2 (2) and 76.2 (1)° observed in the strained chelate rings of $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2$.^{28,29} The small N–Co–N bond angle of 85.2° results from the fixed “bite” of the *o*-phenanthroline ligand (the intraligand N···N distance equals 2.72 (2) Å) and represents the most serious deviation from the octahedral geometry. The symmetry of the adduct is essentially C_2 .

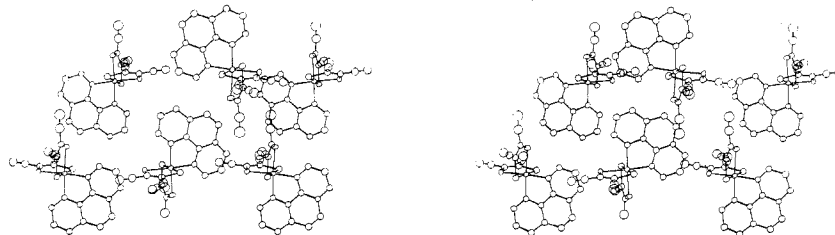


Figure 3.—These drawings present a view of the packing of $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2(o\text{-phen})^-$ anions down the *b* axis of the crystal. The drawings constitute a stereopair and may be viewed with a hand viewer.

The average S–C and C–C distances of 1.71 (1) and 1.36 (2) Å, respectively, in the $\text{S}_2\text{C}_2(\text{CN})_2^{2-}$ ligands agree reasonably well with the corresponding values reported for the previously determined bis complexes.^{2–5} One of the ligands does exhibit slight but significant deviations from planarity in the present structure but these deviations do not appear to be chemically significant and are probably the result of packing effects. In Table V, the equations of the least-squares planes through the metal–chelate rings and through the isolated ligands are presented together with the distances of the atoms from their respective planes.

The dimensions of the *o*-phenanthroline ligand show significant variations in the C–C and C–N bond distances which correlate approximately with bond orders calculated for the structurally similar phenanthrene molecule from valence-bond considerations.³¹ In Fig-

(31) L. Pauling, “The Nature of the Chemical Bond,” 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 201.

ure 2, the dimensions of the *o*-phenanthroline ligand and the calculated bond orders for the corresponding bonds in the phenanthrene molecule are shown. The estimated standard deviation for each of the *o*-phenanthroline distances is approximately 0.019 Å. In addition, slight deviations from planarity are found in the *o*-phenanthroline moiety and they are summarized in Table V along with the equation of the least-squares plane through the *o*-phenanthroline ligand.

The $(n\text{-C}_3\text{H}_7)_4\text{N}^+$ cation has its expected geometry. The coordination about the nitrogen atom is approximately tetrahedral with an average C–N bond distance of 1.57 (2) Å and an average C–C bond distance of 1.55 (4) Å. A similar, relatively long C–N single bond distance of 1.56 (3) Å has also been observed by Hamilton and Bernal in the tetra-*n*-butylammonium cation of the structure $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Fe}_2(\text{S}_2\text{C}_2(\text{CN})_2)_4]_6$.

All intermolecular contacts in the structure are nor-

mal. A stereoscopic drawing of the packing of the $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2(o\text{-phen})^-$ anions is presented in Figure 3. The anions are well separated with the closest Co–Co distance being over 9.3 Å.

A detailed comparison of the $\text{Co}(\text{S}_2\text{C}_2(\text{CN})_2)_2(o\text{-phen})^-$ structure with that of the related $\text{Co}(\text{S}_2\text{C}_6\text{H}_3(\text{CH}_3))_2(o\text{-phen})^-$ adduct is presented in the following paper along with a discussion relating the structural results to the stabilities of the two adducts relative to their respective bis complexes.

Acknowledgments.—We gratefully acknowledge the National Science Foundation (Grant GP-8079) and the Advanced Research Projects Agency for support of this research, and the Brown University Computer Center for the computing time needed for this determination. We also wish to thank Mr. Cortlandt Pierpont, Professor Gene B. Carpenter, and Dr. James A. Cunningham for their helpful remarks.