product is thermally unstable and isomerizes under the reaction conditions to produce what may well be the more stable *cis* product. A second route to the observed product involves collapse of the original *trans*-octahedral structure to a trigonal-bipyramidal intermediate. This intermediate is considered to have the fluoro ligand in an apical position and one of the ethylenediamine ligands in the trigonal plane. The remaining apical and trigonal positions are occupied by the second ethylenediamine molecule.

After the collapse of the octahedron the entering anion attacks in the trigonal plane of the intermediate to produce a *cis* product. At the present time it is not possible to prove or disprove either of the proposed routes to the final product. However, we are currently investigating various synthetic approaches to complexes of the type *trans*-$[Cr(en)_2FX]^{n+}$ which should shed some light on the nature of the intermediates involved in the synthesis of the *cis* complexes.

Acknowledgment.—The authors wish to thank Professor Cläus Schaffer and his coworker, Jørgen Glerup, of the University of Copenhagen, for supplying us with a sample of *trans*-difluorobis(ethylenediamine)chromium(III) iodide which aided us in the identification of one of our products.

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The Crystal and Molecular Structure of the High-Spin Square-Planar Complex Triphenylmethylarsonium Bis(toluene-3,4-dithiolato)cobaltate–0.5-Ethanol

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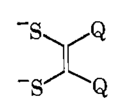
The crystal and molecular structure of the high-spin complex triphenylmethylarsonium bis(toluene-3,4-dithiolato)cobaltate–0.5-ethanol, $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods. The structure has been refined by least-squares procedures to a conventional R factor of 0.063 for 1108 nonzero reflections. The complex crystallizes in space group $P\bar{1}$ of the triclinic system with two molecules in a unit cell of dimensions $a = 18.61 \pm 0.01$, $b = 10.848 \pm 0.006$, $c = 10.206 \pm 0.005$ Å, $\alpha = 112.45 \pm 0.02°$, $\beta = 71.55 \pm 0.02°$, $\gamma = 115.90 \pm 0.02°$, and $V = 1685.4$ Å^3. An observed density of 1.359 ± 0.010 g/cm^3 is in excellent agreement with the calculated value of 1.355 g/cm^3 for $Z = 2$. The $Co(tdt)_2^-$ anions are crystallographically required to have centers of symmetry since the two cobalts per unit cell occupy the (0, 0, 0) and ($^1/_2$, 0, $^1/_2$) special positions of the space group. The S_4 coordination about the cobalts is very nearly square planar with average intra- and interligand S–S distances of 3.098 and 3.028 Å, respectively, and estimated standard deviations for these values of 0.007 Å. The planar $Co(tdt)_2^-$ anions have an ordered *trans* configuration of the tdt ligand methyl groups and thus possess C_{2h} symmetry. The $(C_6H_5)_3(CH_3)As^+$ cation has its expected tetrahedral geometry about arsenic. Ethanol solvent molecules were trapped during crystallization of the complex, presumably because of the asymmetric nature of the cation. These solvent molecules are disordered about the (0, $^1/_2$, 0) center of symmetry with only one molecule per unit cell. Thus, the crystal structure of the complex consists of the packing of essentially planar anions, bulky cations, and trapped solvent molecules. The anions are well separated and exhibit none of the magnetic interactions which characterize the structures of the other related mononegative bis complexes. A ground-state electronic structural assignment for the spin-triplet $Co(tdt)_2^-$ complex is proposed on the basis of molecular orbitals calculated for a closely related nickel complex using the observed structural parameters.

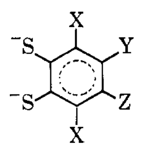
Introduction

The bidentate sulfur-donor ligand systems of types I and II have been found to be excellent stabilizers of the square-planar geometry for a wide variety of metals and ground-state configurations.[2] Although we show I and II in their classical dianion formulation, it is clear from electronic and molecular structural studies that these ligand systems coordinate to form unsaturated five-membered metal–chelate rings in which π bonding plays an important stabilizing role. Complexes of the four ligand systems maleonitriledithiolate (mnt, I with Q = CN), *cis*-stilbenedithiolate ($S_2C_2(C_6H_5)_2$), *cis*-1,2-bis(trifluoromethyl)ethylenedithiolate ($S_2C_2(CF_3)_2$), and toluene-3,4-dithiolate (tdt, II with X = Y = H, Z = CH_3) have received particular attention in these studies.



Q = CH, CF_3, C_6H_5, CH_3, H

I



X = Y = Z = H, CH_3, Cl
X = Y = H, Z = CH_3
X = H, Y = Z = CH_3

II

The considerable interest and activity which de-

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(2) Four of the more recent papers dealing with the synthesis, characterization, and electronic structural properties of the bis square-planar complexes and their oxidation–reduction reactions are: (a) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965); (b) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *ibid.*, **88**, 43 (1966); (c) M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *ibid.*, **88**, 4870 (1966); (d) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967). References to earlier studies in this field are given therein.

veloped in the bis complexes of the bidentate sulfur-donor ligand systems have prompted several detailed structural investigations on them.[3-8] Most of the structure determinations have been performed on members of the bis(maleonitriledithiolate) series including the dianion of Ni,[3] the dianion of Co,[4] the monoanion of Cu,[5] and the monoanion of Ni.[7] The coordination geometry surrounding the metals in these complexes is essentially square-planar and the point group symmetry of all of the anions is very nearly D_{2h}. Despite the differences that are found to exist in the packing of the molecules, the mnt series appears quite remarkable since no significant variations are observed in the geometry and dimensions of the anions in all four structures. The molecular structure of the neutral complex $Ni(S_2C_2(C_6H_5)_2)$ has also been reported[8] and its coordination geometry is essentially identical with that found for the bis(mnt) anions. Recent studies, however, have demonstrated that certain members of the bis complexes of Co and Fe exist as five-coordinate dimers in which the metal is surrounded by a square pyramid of sulfur atoms.[6,9] In this paper and one to follow,[10] we present the structure determinations of the two closely related monoanionic complexes bis(toluene-3,4-dithiolato)cobaltate[11] and bis(3,4,5,6-tetrachlorobenzene-1,2-dithiolato)cobaltate.[2c] These detailed structural studies play an important role in evaluating descriptions of the electronic structures of these bis complexes and in elucidating the factors which influence their tendency toward dimerization.

The monoanion $Co(tdt)_2^-$ is probably the most extraordinary of the bis complexes of the bidentate sulfur-donor ligand systems. The complex was first synthesized in 1963[11] and found to have a stable spin-triplet ground state in solid salts and in solutions utilizing a wide variety of solvents. Therefore, the complex $Co(tdt)_2^-$ is the first apparent example of a square-planar transition metal complex possessing a high-spin ground-state configuration. A detailed single-crystal X-ray investigation was therefore undertaken in order to confirm the apparent square-planar coordination for the $Co(tdt)_2^-$ anion and to establish structural parameters for electronic structural studies of this unusual system. In addition, we believed it important to establish the packing of the $Co(tdt)_2^-$ anions in the crystal since structural studies of the related complexes $[(C_6H_5)_3(CH_3)P][Ni(mnt)_2]$[7] and $[(n\text{-}C_4H_9)_4N][Cu(mnt)_2]$[5] revealed the planar anionic units to lie in relatively close proximity to one another. Spin–spin interactions which may thus occur in the crystalline state have been proposed as an important factor in the magnetic properties of the paramagnetic $Ni(mnt)_2^-$ complex.[12]

The structure determination of the $(C_6H_5)_3(CH_3)As^+$ salt of the $Co(tdt)_2^-$ complex anion proved considerably more difficult than was originally anticipated. Although a set of integrated precession intensity data was initially collected in 1964, the problem defied solution for reasons which became apparent when it was reinvestigated and solved in 1966. The space group and unit cell determinations along with certain preliminary considerations are taken from the work at Brookhaven National Laboratory. A refinement of the cell constants, the collection of a new set of intensity data, and the solution of the structure were carried out at Columbia University.

Unit Cell and Space Group Determination

A generous supply of dark blue crystals of $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]$ were kindly given to us by Dr. Raymond Williams.[2b] The crystals were examined optically and by Weissenberg and precession photography and found to belong to the triclinic system. A convenient primitive cell was chosen with the dimensions a = 18.60, b = 11.01, c = 10.32 Å, α = 114.2°, β = 71.0°, γ = 116.7°, and V = 1695 Å^3. A Delaunay reduction performed on this cell failed to reveal the presence of any symmetry. The reduced cell parameters which were not used in any subsequent calculations are a = 18.09, b = 16.82, c = 10.32 Å, α = 95.3°, β = 103.6°, and γ = 141.4°. No piezoelectric effect was looked for in the unit cell determination. An experimental density of 1.36 ± 0.03 g/cm^3 determined by pycnometry was in reasonable agreement with a value of 1.35 g/cm^3 calculated for two $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]$ molecules using the preliminary cell constants given above. On the basis of these results, we assumed the centrosymmetric space group $P\bar{1}$ for the complex. This assumption implies that no symmetry conditions need be imposed on the molecule and all of its atoms may occupy general positions of the space group. Although this was found not to be the case, the satisfactory agreement ultimately obtained between observed and calculated structure factors strongly suggests that $P\bar{1}$ is the correct choice.

Collection and Reduction of the Intensity Data

A complete set of intensity data was collected from a single crystal at room temperature using a Picker diffractometer fitted with a General Electric quarter-circle cradle. The crystal was mounted in the $\overline{a^*}$ direction on a eucentric goniometer head and aligned accurately on a Supper precession camera. After transferring the crystal to the goniostat, the direction of $\overline{a^*}$ was adjusted to coincide with the polar axis of the diffractometer by centering the $\bar{h}00$ reflections in a diffracting position at χ = 90° for all values of the polar or spindle angle ϕ. Approximately 40 reflections

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[3] R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).

[4] J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1500 (1964).

[5] J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1507 (1964).

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

[7] C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966).

[8] D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966).

[9] (a) A. L. Balch and R. H. Holm, *ibid.*, 552 (1966); (b) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *J. Am. Chem. Soc.*, **88**, 4604 (1966); (c) W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967).

[10] M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, *J. Am. Chem. Soc.*, in press.

[11] H. B. Gray and E. Billig, *ibid.*, **85**, 2019 (1963).

[12] J. F. Weiher, L. R. Melby, and R. E. Benson, *ibid.*, **86**, 4329 (1964).

of both general and special classes were then 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. After this had been accomplished, the orientation and unit cell parameters were refined by a least-squares procedure using W. C. Hamilton's mode 1 diffractometer setting program.[13] The refinement yielded the following values of the cell constants and their estimated standard deviations: $a = 18.61 \pm 0.01$, $b = 10.848 \pm 0.006$, $c = 10.206 \pm 0.005$ Å, $\alpha = 112.45 \pm 0.02°$, $\beta = 71.55 \pm 0.02°$, $\gamma = 115.90 \pm 0.02°$, and $V = 1685.4$ Å^3. The mosaic spread of the crystal was then determined from open source–narrow counter ω scans[14] and found to be relatively isotropic with an average value of 0.30°.

The intensities of 1142 independent reflections with an angular range $\theta_{Cu} \leqslant 35°$ were measured by the stationary crystal–stationary counter technique using nickel-filtered Cu Kα radiation. Only a small number of reflections beyond $\theta = 35°$ appeared to have significant intensity. Since these reflections are composed primarily of contributions from the heavy atoms, their intensities were not determined. The peak heights of the measured reflections were counted for 20-sec durations while the background was measured in 10-sec counts both above and below the 2θ value for each reflection. The data were collected in two arbitrary segments, each being assigned its own scale factor. In processing the data, we considered a reflection to be unobserved if the peak count did not exceed the combined background counts for the reflection. The usual Lorentz-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. An absorption correction was then carried out for the observed structure amplitudes using the GONO9 diffractometer absorption program. The six crystal faces were first identified by optical goniometry and their dimensions carefully measured. With an absorption coefficient of 73.4 cm^{-1} and approximate crystal dimensions of 0.36 × 0.19 × 0.08 mm, the resultant transmission coefficients were found to range from 0.23 to 0.58. The F_o values were then brought to an approximate absolute scale through a modification of Wilson's method.

Solution and Refinement of the Structure

Because of the assumption of space group $P\bar{1}$ with two molecules in the unit cell and the rather asymmetric nature of the $(C_6H_5)_3(CH_3)As^+$ cation, it was presumed that all atoms of the molecule occupy the 2(i) general positions of the space group $\pm[x, y, z]$.[15] This presumption requires that the two $Co(tdt)_2^-$ anions are symmetry related through a center of inversion. If, in addition, the complex anions are very nearly square planar, one would expect to see a high-density Patterson peak corresponding to the intermolecular Co–Co vector which is also reinforced by intermolecular S–S vectors and C–C vectors. In addition, the presence of As in the unit cell yields doubly degenerate sets of As–Co and As–S vectors together with one nondegenerate As–As vector.

Numerous models based on a computed three-dimensional Patterson function were formulated in accordance with the assumption of general positions, but none of these models was successfully refined. After a careful reexamination of the Patterson map a completely consistent set of vectors was derived in which the two cobalts per unit cell were located at the centers of symmetry (0, 0, 0) and ($^1/_2$, 0, $^1/_2$) while the two arsenics remained in general positions of the space group. The positions of the four independent sulfur atoms were then quickly determined from the Patterson function. The positional parameters of the S and As atoms along with variable isotropic temperature factors assigned to each of them and the two Co's were refined through several cycles of least squares. From a subsequent difference Fourier based on phases obtained from these heavy atoms, 11 of the 12 anion benzene ring carbons and all 19 of the cation carbons were located in very reasonable positions. No attempt was made at this stage of refinement to find the methyl groups of the tdt ligands because of expected disorder in their positions.

The trial structure was refined using the JGLS least-squares group refinement procedure in which the phenyl rings were constrained to their well-known geometry (D_{6h} symmetry, C–C = 1.392 Å, C–H = 1.08 Å). The function minimized was $\Sigma w(F_o - F_c)^2$ where the weights w of the reflections were set equal to the squares of the reciprocals of the corresponding standard deviations σ. The function $(TLp)^{-1}[CT + CB + (0.03(CT - CB))^2]^{1/2}/2F_o$ was used to estimate the value of σ for each reflection where CT is the total count, CB is the total background count, Lp is the Lorentz-polarization factor, and T is the transmission coefficient for the particular reflection.[16] The neutral Co, As, S, and C scattering factors were taken from Ibers' tabulation[17] while the anomalous parts of the Co, As, and S scattering factors were obtained from Templeton's tabulation[18] and included in the calculated structure factors.[19]

In the refinement, each phenyl ring was assigned a single variable isotropic thermal parameter and six variable positional parameters which include the three

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(13) In addition to the mode 1 setting program, the main programs for the IBM 7094 used in this work were Hamilton's GONO9 diffractometer absorption program, the Busing–Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the ORFFE function and error program, and the JGLS group refinement least-squares program written by J. A. I. Various other programs from the Brookhaven Crystallographic Library were also used in the investigation. Most of the computation was performed on Columbia's 7094.

(14) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10, p 138.

(15) "International Tables for X-Ray Crystallography," The Kynoch Press, Vol. I, Birmingham, England, 1965, p 75.

(16) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(17) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1965, Table 3.3.1A.

(18) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1965, Table 3.3.2B.

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

fractional coordinates of the ring center and three rotation angles describing the ring orientation. The initial refinement of the cation phenyl rings together with the 19 nongroup atoms, each of which had a variable isotropic temperature factor, converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.148 and a weighted R factor R' ($R' = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$) of 0.168 for the 93 positional, scale, and thermal parameters. A difference Fourier based on this refinement showed in the asymmetric unit six peaks with electron density greater than 1.2 e/Å^3 or approximately 50% of the height of a carbon atom in this structure. One of these peaks was easily identified as the missing carbon atom in the benzene ring of one of the anions while two others were identified as the ordered methyl groups of the tdt ligands. The three remaining peaks which were located more than 3.5 Å from either the cations or anions were assigned as the atoms of a trapped molecule of ethanol from which the crystals had been grown. These six atoms were included in the next round of isotropic refinements but no attempt was made to distinguish which of the solvent atoms was oxygen. This refinement of 117 positional, scale, and thermal parameters converged to conventional and weighted R factors of 0.093 and 0.120 for 1113 nonzero reflections.

A difference Fourier based on this refinement revealed electron density as high as 0.7 e/Å near the arsenic atoms and as high as 0.6 e/Å^3 in regions near the anions, thus providing evidence for some anisotropic vibration of the heavy atoms. The isotropic refinement also led to temperature factors for the solvent molecule ranging from 12 to 20 Å^2. This was the first indication that the solvent molecule sites in the unit cell may not be fully occupied. A subsequent redetermination of the density and an elemental analysis later confirmed this notion.[20]

After the elimination of several indexing and punching errors, a further refinement was carried out in which the Co, As, and S atoms were allowed to vibrate anisotropically, while all other atoms were restricted to isotropic vibration. In addition, fixed contributions from the phenyl ring hydrogens were added to the calculated structure factors. This final refinement of 150 positional, thermal, and group parameters converged to the final conventional and weighted R factors of 0.063 and 0.077, respectively. With the weighting scheme employed, the estimate of the standard deviation of an observation of unit weight has the value 2.77. The final agreement between F_o and $|F_c|$ for reflections of high intensity appears good, thus indicating the reasonableness of the 0.03 factor used in the estimation of $\sigma(F^2)$. A difference Fourier based on this refinement showed no peaks higher than 0.45 e/Å^3 or about 20% of the height of a carbon atom, and reasonable positions were found for 12 of the remaining 18 hydrogen atoms in the asymmetric unit. The contributions of these additional hydrogens to $|F_c|$ were not included in any additional calculations.

The parameters obtained in this final round of calculations are taken as the final parameters for the structure and are given in Table I. Standard deviations, as obtained from the inverse matrix, are also given. Table II lists the fractional coordinates of the cation phenyl ring carbon atoms which can be derived from the group parameters in Table I.

The F_o and $|F_c|$ values (in electrons × 10) for the 1108 observed reflections included in the final refinement are tabulated in Table III. The $|F_c|$ values for the unobserved reflections are omitted from this table.

The anisotropic thermal parameters can be interpreted in terms of the real amplitudes of vibration, since they are essentially uncorrelated with the scale factors. It should also be noted that in the partial anisotropic refinement, 35 carbon atoms including the phenyl ring carbons and the solvent atoms were restricted to isotropic vibration. In Table IV, the principal values of the root-mean-square amplitudes of vibration are listed. The orientations of the thermal ellipsoids, which may be derived from the parameters in Table I, are shown in Figure 1.

In order to check the correctness and accuracy of the initial set of integrated precession data, a final structure factor calculation was performed using the parameters of Table I. Only the scale factors for the different levels and zones were adjusted. This calculation yielded an agreement factor of $R = 0.143$ between the 998 structure amplitudes from the precession data and the final calculated structure factors. The precession data, which were collected using Mo Kα radiation, were uncorrected for absorption. Thus, the precession data which were of good quality could have led to essentially the same structure.

Description of the Structure

The location of the Co atoms at centers of symmetry removes the constraint that all of the anions in the crystal must be parallel but necessitates the immediate coordination geometry around the cobalts to be planar. The CoS_4 geometry is, in fact, very nearly square

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[20] In order to establish clearly whether or not an ethanol molecule was present in the asymmetric unit, the density was carefully redetermined by pycnometric methods and yielded an experimental value of 1.359 ± 0.010 g/cm^3. Densities were then calculated for several molecular formulas with the use of the refined cell constants. These calculated values are: (a) $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]$, $\rho_c = 1.312$ g/cm^3; (b) $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot C_2H_5OH$, $\rho_c = 1.399$ g/cm^3; (c) $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$, $\rho_c = 1.355$ g/cm^3. Clearly, the values for (a) and (b) are in significant disagreement with the experimental density and strongly indicate the improbability of either molecular formula. On the other hand, the calculated density for the hemiethanolate (c) is in excellent agreement with the experimental value of 1.359 g/cm^3. Crystals from the sample used in the X-ray investigation were then submitted for elemental analysis, including a direct oxygen determination, to Midwest Microlab., Inc. *Anal.* Calcd for $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]$: C, 57.56; H, 4.36; O, 0.00; S, 18.60. Calcd for $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot C_2H_5OH$: C, 57.22; H, 4.90; O, 2.18; S, 17.44. Calcd for $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$: C, 57.38; H, 4.64; O, 1.13; S, 18.00. Found: C, 57.65; H, 4.66; O, 1.23; S, 17.75. The analytical data thus appear to favor the hemiethanolate formula, and the direct determination of 1.23% oxygen provides positive evidence that trapped ethanol molecules are present in the crystal. The density and analytical results strongly support conclusions based on an examination of the final distances of the complex which indicates that only one ethanol molecule can be present in each unit cell. This examination and conclusions based on it are discussed in the text. The very satisfactory agreement which was ultimately obtained in the refinement is taken as further confirmation of the correctness of the hemiethanolate assignment.

TABLE I

FINAL PARAMETERS FOR $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$

Atomic Positional and Isotopic Thermal Parameters

Atom	x	y	z	B, Å^2
Co(1)	0.0000	0.0000	0.0000	...
Co(2)	0.5000	0.0000	0.5000	...
As	0.2686 (1)[a]	−0.0431 (2)	0.0115 (2)	...
S(1)	0.1201 (2)	0.1576 (5)	−0.0402 (4)	...
S(2)	−0.0243 (2)	0.1310 (6)	0.2182 (4)	...
S(3)	0.5178 (3)	0.2228 (6)	0.5592 (5)	...
S(4)	0.3727 (3)	−0.0607 (6)	0.4953 (5)	...
C(1)	0.1299 (9)	0.295 (2)	0.125 (2)	4.2 (4)
C(2)	0.0667 (9)	0.282 (2)	0.239 (2)	3.9 (4)
C(3)	0.074 (1)	0.388 (2)	0.374 (2)	5.9 (5)
C(4)	0.148 (1)	0.505 (2)	0.386 (2)	4.6 (4)
C(5)	0.2110 (9)	0.521 (2)	0.274 (2)	4.7 (4)
C(6)	0.203 (1)	0.415 (2)	0.136 (2)	5.7 (5)
C(7)	0.423 (1)	0.229 (3)	0.572 (2)	6.6 (5)
C(8)	0.356 (1)	0.104 (2)	0.546 (2)	5.9 (5)
C(9)	0.277 (1)	0.099 (3)	0.552 (2)	7.5 (5)
C(10)	0.275 (1)	0.238 (3)	0.585 (2)	8.4 (6)
C(11)	0.338 (2)	0.364 (3)	0.612 (2)	9.3 (6)
C(12)	0.412 (1)	0.359 (3)	0.600 (2)	8.7 (6)
CH_3(1)	0.158 (1)	0.618 (2)	0.537 (2)	7.3 (5)
CH_3(2)	0.193 (1)	0.247 (3)	0.597 (2)	11.7 (7)
$AsCH_3$	0.2248 (9)	−0.109 (2)	−0.164 (2)	4.9 (4)
X(1)[b]	0.006 (2)	0.395 (4)	0.025 (3)	11.9 (8)
X(2)	0.045 (4)	0.485 (7)	−0.049 (6)	25 (2)
X(3)	0.113 (3)	0.549 (5)	−0.111 (5)	19 (1)

Anisotropic Thermal Parameters

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0.0043 (2)	0.0127 (8)	0.0113 (6)	0.0034 (3)	−0.0022 (2)	0.0001 (5)
Co(2)	0.0055 (2)	0.0170 (8)	0.0090 (5)	0.0012 (3)	−0.0021 (3)	0.0026 (6)
As	0.00379 (9)	0.0120 (4)	0.0078 (3)	0.0026 (1)	−0.0014 (1)	0.0012 (3)
S(1)	0.0048 (2)	0.0129 (9)	0.0113 (7)	0.0028 (4)	−0.0013 (3)	0.0009 (7)
S(2)	0.0046 (2)	0.0138 (8)	0.0107 (6)	0.0023 (4)	−0.0016 (3)	0.0015 (6)
S(3)	0.0072 (3)	0.0160 (1)	0.0170 (8)	0.0017 (4)	−0.0036 (4)	0.0024 (7)
S(4)	0.0054 (3)	0.023 (1)	0.0136 (8)	0.0006 (4)	−0.0020 (3)	0.0041 (8)

Group Positional and Thermal Parameters

Group	x_c[d]	y_c	z_c	ϕ	θ	ρ	B, Å^2
Ring 1	0.1127 (5)	−0.135 (1)	0.2624 (8)	3.391 (8)	0.005 (7)	2.584 (6)	5.9 (2)
Ring 2	0.3589 (4)	0.3064 (9)	0.0973 (8)	2.57 (2)	1.246 (7)	1.61 (2)	4.7 (2)
Ring 3	0.4060 (5)	−0.1754 (8)	−0.0329 (8)	2.32 (7)	1.477 (6)	6.31 (7)	4.9 (2)

[a] The numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [b] X(1), X(2), and X(3) refer to the atoms of the trapped ethanol molecule which is discussed in the text. The positional and thermal parameters given above are taken from the final round of calculations in which the multiplicity factors of these atoms were held fixed at 1.0 and all three atoms were assigned carbon atom scattering factors. An additional calculation in which X(1), X(2), and X(3) were assigned fixed multiplicity factors of 0.5 and X(1) was assumed to be the ethanol oxygen yielded the following parameters for the three atoms.

Atom	x	y	z	B, Å^2
X(1) (oxygen)	0.007 (2)	0.400 (3)	0.023 (3)	7.9 (7)
X(2)	0.046 (3)	0.499 (6)	−0.050 (5)	9 (1)
X(3)	0.113 (2)	0.547 (4)	−0.109 (4)	7 (1)

[c] The form of the anisotropic thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [d] x_c, y_c, and z_c are the fractional coordinates of the ring centers. The angles ϕ, θ, and ρ (in radians) are the ring orientation angles which bring about alignment (except for translation) of an internal coordinate system within the ring with a fixed external coordinate system which have been defined in previous papers. See, for example, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965), or S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

planar with average intra- and interligand S–S distances of 3.098 and 3.028 Å, respectively, and estimated standard deviations for these values of 0.007 Å. Principal intramolecular distances and angles for the complex are tabulated in Table V. In addition, the two $Co(tdt)_2^-$ anions are shown with their dimensions in Figure 1. The average Co–S and S–C bond lengths of 2.166 and 1.78 Å agree reasonably well with the corresponding distances which have been found in the related bis(mnt) structures (2.161 and 1.72 Å in $Co(mnt)_2^{2-}$,[4] 2.146 and 1.71 Å in $Ni(mnt)_2^-$,[7] 2.166 and 1.76 Å in $Ni(mnt)_2^{2-}$,[3] and 2.170 and 1.72 Å in $Cu(mnt)_2^-$ [5]).

Both anions are essentially planar and possess C_{2h} symmetry although only C_i symmetry is required. The Co atoms necessarily sit on the best weighted least-squares planes through the entire anion units. In Table VI, the equations of the best least-squares

TABLE II

DERIVED PARAMETERS FOR GROUP CARBON ATOMS

Group atom[a]	*x*	*y*	*z*
R(1)C(1)	0.1823 (6)[b]	−0.092 (1)	0.162 (1)
R(1)C(2)	0.1655 (7)	−0.210 (1)	0.207 (1)
R(1)C(3)	0.0960 (8)	−0.252 (1)	0.307 (1)
R(1)C(4)	0.0431 (6)	−0.178 (1)	0.363 (1)
R(1)C(5)	0.0599 (7)	−0.060 (1)	0.318 (1)
R(1)C(6)	0.1294 (8)	−0.018 (1)	0.217 (1)
R(2)C(1)	0.3188 (6)	0.159 (1)	0.063 (1)
R(2)C(2)	0.3262 (6)	0.238 (1)	0.205 (1)
R(2)C(3)	0.3663 (6)	0.386 (1)	0.239 (1)
R(2)C(4)	0.3989 (6)	0.454 (1)	0.132 (1)
R(2)C(5)	0.3915 (7)	0.375 (1)	−0.011 (1)
R(2)C(6)	0.3514 (7)	0.227 (1)	−0.045 (1)
R(3)C(1)	0.3469 (6)	−0.121 (1)	−0.014 (1)
R(3)C(2)	0.3714 (7)	−0.113 (1)	0.105 (1)
R(3)C(3)	0.4305 (7)	−0.167 (1)	0.087 (1)
R(3)C(4)	0.4651 (6)	−0.229 (1)	−0.051 (1)
R(3)C(5)	0.4406 (7)	−0.238 (1)	−0.171 (1)
R(3)C(6)	0.3815 (7)	−0.184 (1)	−0.152 (1)

[a] C(1) is attached to As. The other C atoms are numbered in succession so that C(4) is *para* to C(1). [b] The errors are derived from estimated errors in the group parameters and are meant to be used in error analyses on inter-ring distances. As always, intra-ring distances are fixed by the group refinement procedure.

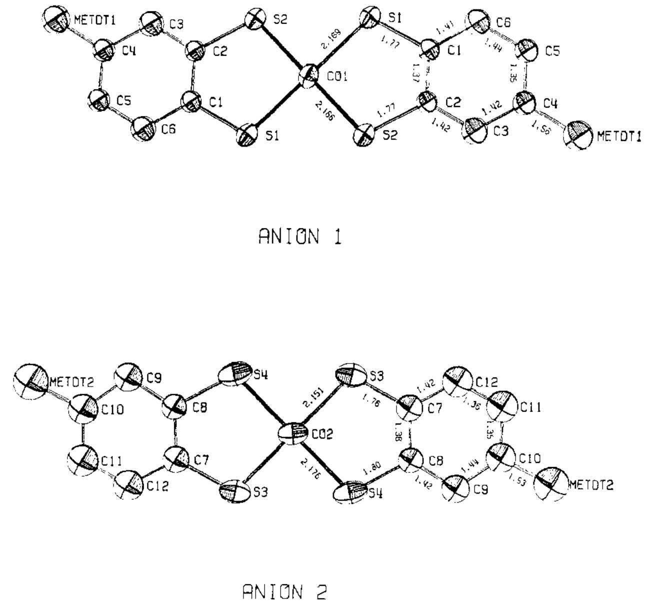

Figure 1.—The $Co(tdt)_2^-$ anions showing their bond distances and ellipsoids of thermal motion. The ellipsoids have been scaled to 30% probability distributions.

planes through the ligands[21] and the distances of the atoms from their respective planes are given. Only three possibly significant deviations from planarity are noted in the anions.

One of the most interesting and surprising features of the anion geometry is the complete ordering of the tdt methyl groups which necessarily yields a *trans* configuration for the complex. It is possible that the *trans* isomer preferentially crystallizes out from a solution containing equal amounts of both geometric configurations.

The $(C_6H_5)_3(CH_3)As^+$ cation had its expected tetrahedral geometry about the arsenic. The independent cation distances and angles are listed in Table V. It appears that, because of the asymmetric nature of the $(C_6H_5)_3(CH_3)As^+$ ion, enough volume remains unoccupied in the unit cell for an ethanol solvent molecule to be trapped during crystallization. The ethanol atoms are represented in Table I as X(1), X(2), and X(3) with X(1) probably being the oxygen. As was previously mentioned, the high-temperature factors for these atoms were taken as an indication that the ethanol molecule sites are not fully occupied. An examination of the final distances calculated for the complex reveals that the ethanol molecules can occupy only half of the solvent molecule sites and that they are probably disordered about the (0, $^1/_2$, 0) center of symmetry. Thus, the molecular formula of the complex is $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$.[20] An additional cycle of refinement was carried out in which X(1), X(2), and X(3) were assigned fixed multiplicity factors of 0.5. X(1) was also assumed to be the ethanol oxygen. In this final calculation, no anion or cation parameter changed by more than one standard deviation and the conventional and weighted *R* factors remained at their previous values of 0.063 and 0.077. The final parameters obtained for the ethanol molecule from this refinement are given in footnote *b* of Table I and the dimensions of the ethanol molecule are given in Table V. However, because of the observed disorder no true significance should be attached to these dimensions.

The crystal structure of the complex consists of the packing of essentially planar anions, bulky cations, and trapped solvent molecules. The anions are very well separated with the nearest Co–Co distance being the lattice repeat value of 10.21 Å. The calculated dihedral angle between the two $Co(tdt)_2^-$ anions in the unit cell is 60.5°. A stereoview of the packing of the complex is presented in Figure 2. All intermolecular contacts in the crystal appear normal with the closest approaches to the two Co's being made by phenyl hydrogens at distances of 3.34 and 3.28 Å, respectively. The nearest approach of the ethanol molecule to the planar anions occurs between X(1) and C(1) at approximately 3.5 Å. An examination of the thermal parameters in Table I also indicates that in the crystal, anion 2 is vibrating more freely than anion 1.

Discussion

The $Co(tdt)_2^-$ anions in $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$ are completely separated whereas in the $[(C_6H_5)_3(CH_3)P][Ni(mnt)_2]$[7] and $[(n\text{-}C_4H_9)_4N][Cu(mnt)_2]$[5] complexes the monoanionic planar units are separated by less that 4.5 Å.[22] On the basis of the reasonably close proximity of the anions in the $[(C_6H_5)_3(CH_3)P][Ni(mnt)_2]$ structure, the low magnetic moment determined for that complex in the solid ($\mu_{eff} \sim$ 1.0 BM) was explained by a spin-quenching mechanism in which magnetic interactions were pro-

[21] W. C. Hamilton, *Acta Cryst.*, **14**, 185 (1961).

[22] In the $[(C_6H_5)_3(CH_3)P][Ni(mnt)_2]$ crystal, the observed Ni···Ni distances are 4.40 and 4.45 Å. The observed Cu···Cu distances in $[(n\text{-}C_4H_9)_4N][Cu(mnt)_2]$ are 4.03 and 4.43 Å.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10) FOR $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$

K	L	OBS	CAL
*******H= 0******			
0	0	[illegible]	0
0	1	749	663
0	2	1550	1555
0	3	10	54
0	4	423	427
0	5	667	621
0	6	456	493
1	2	219	234
1	3	789	806
1	4	1134	1096
1	5	539	534
1	6	523	520
2	4	730	771
2	5	231	218
2	6	447	462
-1	0	1453	1604
-1	1	576	494
-1	2	1901	2057
-1	3	735	853
-1	4	1065	1038
-1	5	37	25
-1	6	649	682
-1	7	121	143
-1	-1	489	433
-2	0	235	260
-2	2	694	695
-2	3	361	310
-2	4	611	551
-2	5	278	210
-2	6	814	759
-2	7	70	26
-2	-1	581	631
-2	-2	718	697
-2	-3	679	783
-3	0	160	172
-3	1	51	61
-3	2	296	235
-3	3	736	367
-3	4	336	306
-3	5	105	83
-3	6	448	422
-3	-1	307	767
-3	-2	720	707
-3	-3	155	205
-3	-4	649	655
-4	0	765	303
-4	1	247	238
-4	2	147	173
-4	3	51	140
-4	4	276	274
-4	5	141	132
-4	6	186	204
-4	-1	41	40
-4	-2	471	479
-4	-3	123	85
-4	-4	246	247
-5	0	465	429
-5	1	57	63
-5	2	692	682
-5	3	313	278
-5	4	362	354
-5	5	63	47
-5	6	126	141
-5	-1	217	221
-5	-2	254	248
-5	-3	69	93
-6	0	50	51
-6	1	51	9
-6	2	107	117
-6	3	173	170
-6	4	217	219
-6	5	109	108
-6	-1	364	380
-6	-2	189	156
-7	1	117	119
-7	2	114	164
-7	3	84	63
*******H= 1******			
0	4	242	206
0	5	470	487
0	6	112	66
1	6	140	124
-1	2	787	920
-1	3	870	830
-1	4	767	771
-1	5	709	668
-1	6	618	598
-1	7	163	186
-7	0	73	70
-7	1	41	38
-7	2	88	60
-7	3	230	284
-7	4	11	8
*******H= 2******			
0	7	221	247
-1	5	397	360
-1	6	354	355
-1	7	333	307
-6	6	471	487
-7	0	381	414
-7	1	299	297
-7	2	185	278
-7	3	173	174
-7	4	521	579
-7	5	263	260
*******H= 3******			
-6	6	84	70
-7	0	274	293
-7	1	799	797
-7	2	130	145
-7	3	372	419
-7	4	292	279
-7	5	420	413
*******H= 4******			
-6	6	51	46
-7	0	80	95
-7	1	217	236
-7	2	197	213
-7	3	195	205
-7	4	58	47
-7	5	104	120
*******H= 5******			
-6	6	367	145
-7	2	270	283
-7	3	123	161
-7	4	63	54
-7	5	84	108
*******H= 6******			
-7	5	207	216
*******H= -1******			
0	1	1144	1274
0	2	469	516
0	3	284	343
0	4	205	176
0	5	319	326
0	6	38	14
0	-1	319	285
0	-2	1430	1373
0	-3	1258	1207
1	1	173	166
1	2	192	143
1	3	462	419
1	4	354	347
1	5	343	345
1	6	61	54
1	-1	745	690
2	1	195	213
2	2	21	24
2	3	776	764
2	4	144	144
2	5	120	171
2	6	159	134
3	3	105	113
3	4	427	410
3	5	59	73
-1	0	419	455
-1	1	758	730
-1	2	1160	1038
-1	3	641	606
-1	4	177	172
-1	5	676	688
-1	6	198	162
-1	-1	827	746
-1	-2	650	685
-1	-3	118	69
-1	-4	371	367
-1	-5	109	113
-2	0	1167	1172
-2	1	1017	1049
-2	2	155	108
-2	3	250	267
-2	4	325	301
-2	5	872	819
-2	6	180	167
-2	7	376	355
-2	-1	611	536
-2	-2	27	45
-2	-3	330	289
-2	-4	47	77
-2	-5	259	279
-2	-6	88	48
-3	0	563	505
-3	1	836	836
-3	2	814	835
-3	3	242	225
-3	4	209	181
-3	5	256	298
-3	6	417	446
-3	-1	346	356
-3	-2	54	71
-3	-3	252	290
-3	-4	32	40
-3	-5	158	134
-4	0	303	286
-4	1	945	956
-4	3	644	650
-4	4	291	277
-4	5	342	340
-4	6	452	447
-4	-1	477	420
-4	-2	267	266
-4	-3	591	568
-4	-4	161	163
-5	0	246	225
-5	1	334	316
-5	3	788	775
-5	4	374	349
-5	5	447	416
-5	0	349	348
-5	-1	599	616
-5	-2	520	511
-5	-3	416	430
-6	0	501	484
-6	1	151	172
-6	2	197	188
-6	3	548	557
-6	4	381	359
-6	5	352	388
-6	-1	476	470
*******H= -2******			
0	0	323	447
0	1	38	47
0	2	599	598
0	3	356	372
0	4	221	192
0	5	529	498
0	6	226	222
0	-1	1018	1025
0	-2	521	515
0	-3	217	215
0	-4	299	269
0	-5	79	64
0	-6	120	107
1	0	179	177
1	1	411	417
1	2	184	200
1	3	404	427
1	4	217	219
1	5	493	518
1	6	375	392
1	-1	129	185
1	-3	415	516
1	-4	205	196
2	0	96	220
2	1	194	210
2	3	49	34
2	4	267	272
2	5	290	305
2	-1	277	386
2	-2	1147	1180
3	0	178	180
3	1	111	104
3	2	675	648
3	3	102	100
3	4	401	375
3	5	341	350
4	2	547	569
4	3	499	528
4	4	188	195
-1	0	46	50
-1	1	965	988
-1	2	507	443
-1	3	842	849
-1	4	244	207
-1	5	728	251
-1	6	138	131
-1	-1	1300	1265
-1	-2	1028	1054
-1	-3	96	84
-1	-4	183	162
-1	-5	147	154
-1	-6	257	263
-2	0	1048	1008
-2	1	568	572
-2	2	733	718
-2	3	648	610
-2	4	539	508
-2	5	45	59
-2	6	120	118
-2	-1	396	418
-2	-2	642	618
-2	-3	190	183
-2	-4	170	160
-2	-5	374	391
-2	-6	230	237
-3	0	80	81
-3	1	42	22
-3	2	197	209
-3	3	31	5
-3	4	131	94
-3	5	90	88
-3	6	85	66
-3	-1	503	507
-3	-2	334	318
-3	-3	421	413
-3	-4	213	179
-3	-5	450	459
-4	0	67	44
-4	1	141	159
-4	2	395	438
-4	3	48	17
-4	4	57	66
-4	5	147	142
-4	6	138	137
-4	-1	413	403
-4	-2	84	84
-4	-3	247	233
-4	-4	201	218
-5	0	281	282
-5	1	27	46
-5	2	397	400
-5	3	200	227
-5	4	125	104
-5	5	106	122
-5	-1	123	74
-5	-2	83	76
-6	0	166	191
-6	1	30	4
-6	2	14	98
-6	3	45	39
-6	4	134	132
-6	-1	293	266
*******H= -3******			
0	0	463	495
0	1	930	834
0	2	292	272
0	3	490	433
0	4	235	233
0	5	66	76
0	6	137	140
0	-1	500	465
0	-2	718	724
0	-3	805	749
0	-4	796	669
0	-5	734	706
0	-6	475	491
0	-7	271	275
1	0	491	512
1	1	277	237
1	2	321	294
1	3	707	685
1	4	479	447
1	6	192	197
1	-1	899	924
1	-2	787	774
1	-3	378	395
1	-4	349	282
1	-5	841	659
1	-6	617	595
1	-7	434	444
2	0	61	43
2	1	482	463
2	2	714	685
2	3	512	529
2	4	306	306
2	5	150	153
2	-1	1254	1247
2	-2	1086	1171
2	-3	777	767
2	-4	505	451
2	-5	662	705
3	0	659	647
3	1	919	916
3	2	411	432
3	3	891	856
3	5	632	584
3	-1	421	387
3	-2	844	762
3	-3	1210	1169
4	0	161	173
4	1	1133	1158
4	2	262	242
4	3	555	554
4	-1	667	709
-1	0	662	684
-1	1	283	259
-1	2	35	14
-1	3	253	283
-1	4	267	253
-1	5	109	98
-1	6	39	25
-1	-1	625	594
-1	-2	123	81
-1	-3	223	227
-1	-4	396	352
-1	-5	101	88
-1	-6	145	185
-2	0	724	743
-2	1	112	120
-2	2	578	580
-2	3	98	75
-2	4	185	191
-2	5	55	49
-2	6	98	67
-2	-1	449	394
-2	-2	44	64
-2	-3	37	52
-2	-4	248	233
-2	-5	69	73
-3	0	195	216
-3	1	70	53
-3	2	385	394
-3	3	288	291
-3	4	156	216
-3	5	30	41
-3	6	115	80
-3	-1	263	242
-3	-2	243	236
-3	-3	412	410
-3	-4	184	147
-3	-5	62	75
-4	0	631	615
-4	1	76	104
-4	2	111	127
-4	3	72	73
-4	4	165	125
-4	5	296	300
-4	-1	140	150
-4	-2	68	46
-4	-4	51	69
-5	0	206	190
-5	1	67	101
-5	2	460	501
-5	3	98	57
-6	0	181	153
-6	1	209	192
-6	2	275	255
-6	3	168	178
*******H= -4******			
0	1	173	150
0	2	98	109
0	3	385	360
0	4	668	644
0	5	361	371
0	6	254	310
0	-1	68	72
0	-2	787	764
0	-3	449	448
0	-4	445	352
0	-5	507	523
0	-6	173	163
1	0	1179	1284
1	1	449	438
1	2	204	207
1	3	276	278
1	4	287	283
1	5	245	253
1	-1	515	504
1	-2	714	676
1	-3	108	82
1	-4	422	442
1	-5	751	741
1	-6	532	547
1	-7	221	234
2	0	568	513
2	1	422	413
2	2	191	198
2	3	429	434
2	4	360	356
2	5	27	44
2	-1	1985	2120
2	-2	1083	1144
2	-3	46	88
2	-4	197	220
2	-5	118	128
2	-6	502	474
2	-7	183	172
3	0	93	110
3	1	402	413
3	2	804	758
3	3	293	315
3	4	356	326
3	5	101	140
3	-1	75	126
3	-2	1063	500
3	-3	690	681
3	-4	329	325
3	-5	279	271
3	-6	201	188
4	0	342	346
4	1	18	30
4	2	934	869
4	3	49	74
4	4	336	338
4	-1	154	169
4	-2	324	365
4	-3	221	208
4	-4	80	40
5	0	213	189
5	-1	506	485
-1	0	317	332
-1	1	297	303
-1	2	679	643
-1	3	634	596
-1	4	719	709
-1	5	423	440
-1	6	484	497
-1	-1	35	37
-1	-2	49	91
-1	-3	684	685
-1	-4	130	138
-1	-5	476	455
-1	-6	110	176
-2	0	481	469
-2	1	646	653
-2	2	583	564
-2	3	709	671
-2	4	653	644
-2	5	486	503
-2	6	458	448
-2	-1	537	591
-2	-2	133	84
-2	-3	760	761
-2	-4	626	609
-2	-5	203	178
-3	0	769	720
-3	1	1200	1261
-3	2	685	665
-3	3	472	482
-3	4	181	168
-3	5	367	357
-3	-1	562	552
-3	-2	684	681
-3	-3	392	377
-3	-4	701	727
-4	0	684	701
-4	1	422	437
-4	2	821	826
-4	3	292	297
-4	4	181	183
-4	-1	124	123
-4	-2	817	820
-4	-3	548	529
-5	0	260	271
-5	1	45	34
-5	2	464	463
-5	3	95	100
*******H= -5******			
0	1	71	63
0	2	733	706
0	3	79	52
0	4	192	167
0	5	169	174
0	-1	484	438
0	-2	108	118
0	-3	827	752
0	-4	672	648
0	-5	181	167
1	0	987	1017
1	1	813	765
1	2	491	485
1	3	149	145
1	4	41	39
1	5	119	135
1	-1	437	407
1	-2	403	413
1	-3	732	725
1	-4	885	790
1	-5	109	104
1	-6	232	224
1	-7	84	80
2	0	287	209
2	1	281	327
2	2	39	39
2	3	217	216
2	4	119	94
2	5	347	370
2	-1	68	56
2	-2	525	507
2	-3	208	182
2	-4	325	325
2	-5	134	132
2	-6	36	16
2	-7	124	111
3	0	174	182
3	1	196	154
3	2	192	163
3	3	69	41
3	4	273	240
3	-1	46	46
3	-2	1190	1104
3	-3	55	44
3	-4	164	169
3	-5	137	141
3	-6	64	83
3	-7	60	63
4	0	488	445
4	1	49	59
4	2	165	164
4	4	227	253
4	-1	247	241
4	-2	311	285
4	-3	239	263
4	-4	111	83
4	-5	261	266
4	-6	107	113
4	-7	192	175
5	0	249	219
5	1	120	132
5	-1	186	196
-1	0	210	206
-1	1	241	265
-1	2	340	219
-1	3	189	173
-1	4	46	42
-1	5	270	302
-1	-1	272	257
-1	-2	152	113
-1	-3	247	228
-1	-4	340	330
-1	-5	74	59
-1	-6	166	159
-2	0	626	612
-2	1	411	450
-2	2	154	144
-2	3	251	222
-2	4	86	74
-2	5	248	274
-2	-1	171	164
-2	-2	64	23
-2	-3	280	329
-2	-4	88	59
-2	-5	99	67
-3	0	104	94
-3	1	512	509
-3	2	291	288
-3	3	361	382
-3	4	108	110
-3	5	323	334
-3	-1	164	168
-3	-3	621	642
-3	-4	177	189
-4	0	312	307
-4	1	288	289
-4	2	80	86
-4	3	273	249
-4	4	47	16
-4	-1	374	371
-4	-2	44	85
-4	-3	641	615
-5	0	57	43
-5	1	423	418
-5	2	99	85
-5	3	613	625
*******H= -6******			
0	0	311	315
0	1	323	232
0	2	42	59
0	3	384	354
0	4	327	326
0	5	109	98
0	-1	378	347
0	-2	186	154
0	-3	545	543
0	-4	46	45
0	-6	104	45
1	0	97	107
1	1	560	602
1	2	242	234
1	3	41	34
1	4	64	36
1	5	232	237
1	-1	107	93
1	-2	337	360
1	-3	479	530
1	-4	159	220
1	-5	129	115
1	-6	151	134
1	-7	85	34
2	2	67	39
2	3	31	11
2	4	294	265
2	5	318	299
2	-1	554	538
2	-2	83	86
2	-3	72	16
2	-4	297	280
2	-5	20	24
2	-6	614	591
2	-7	107	109
3	0	374	315
3	1	144	144
3	2	92	92
3	3	142	124
3	4	296	284
3	-1	243	206
3	-2	335	386
3	-3	233	251
3	-4	227	197
3	-5	256	241
3	-6	366	394
3	-7	373	383
4	0	138	109
4	1	170	177
4	2	349	380
4	3	56	80
4	4	65	71
4	-1	195	171
4	-2	186	185
4	-3	936	899
4	-4	385	399
4	-5	478	451
4	-6	147	149
4	-7	179	187
5	0	710	724
5	1	560	544
5	-1	378	374
-1	0	289	282
-1	1	312	322
-1	2	255	247
-1	3	274	265
-1	4	242	236
-1	5	152	164
-1	-1	155	92
-1	-2	50	39
-1	-3	617	629
-1	-4	267	283
-1	-5	234	193
-2	0	514	542
-2	1	68	65
-2	2	83	87
-2	4	101	92
-2	5	185	180
-2	-1	394	392
-2	-2	121	47
-2	-3	345	317
-2	-4	64	61
-2	-5	186	208
-3	0	38	74
-3	1	303	276
-3	2	53	39
-3	3	457	489
-3	4	167	171
-3	-1	469	458
-3	-2	131	107
-3	-3	287	287
-3	-4	233	234
-4	0	61	44
-4	2	111	125
-4	3	444	457
-4	-1	439	436
-4	-2	130	137
-5	1	426	423
*******H= -7******			
0	1	793	789
0	2	190	205
0	4	63	79
0	-1	862	822
0	-2	341	357
0	-3	419	363
0	-4	228	203
0	-5	632	651
0	-6	161	136
1	0	70	90
1	1	736	757
1	2	47	22
1	3	616	619
1	4	264	253
1	-1	716	759
1	-2	164	144
1	-3	638	640
1	-4	165	167
1	-5	519	515
1	-6	90	111
2	0	185	161
2	1	320	338
2	2	505	522
2	3	544	542
2	4	355	360
2	-1	899	879
2	-2	463	431
2	-3	631	635
2	-4	36	9
2	-5	667	624
2	-6	206	285
2	-7	425	449
3	0	267	250
3	1	437	440
3	2	596	600
3	3	317	307
3	4	127	126
3	-1	722	702
3	-2	717	680
3	-3	563	590
3	-4	320	318
3	-5	530	533
3	-6	311	311
3	-7	609	628
4	0	610	597
4	1	452	462
4	2	252	234
4	3	189	191
4	-1	525	496
4	-2	781	726
4	-3	868	846
4	-4	643	606
4	-5	447	433
4	-6	307	299
4	-7	443	416
5	0	564	565
5	1	673	631
5	-1	549	574
-1	0	473	474
-1	1	683	697
-1	2	50	49
-1	3	570	561
-1	4	205	184
-1	-1	713	678
-1	-2	88	119
-1	-3	433	431
-1	-4	371	360
-1	-5	691	751
-2	0	181	167
-2	1	388	395
-2	2	193	184
-2	3	116	203
-2	4	26	42
-2	-1	361	373
-2	-2	89	94
-2	-3	633	658
-2	-4	175	158
-3	0	81	73
-3	1	239	219
-3	2	227	238
-3	3	60	69
-3	-1	431	396
-3	-2	101	126
-3	-3	501	526
-4	0	253	246
-4	1	215	221
-4	2	234	241
-4	-1	123	94
*******H= -8******			
0	0	810	795
0	1	122	121
0	2	924	918
0	3	226	248
0	4	729	720
0	-1	409	419
0	-2	659	645
0	-3	126	117
0	-4	361	367
0	-5	224	221
0	-6	223	198
1	0	603	651
1	1	96	81
1	2	771	712
1	3	203	209
1	4	538	506
1	-1	141	146
1	-2	804	793
1	-3	202	190
1	-4	192	225
1	-5	339	354
1	-6	185	194
2	0	327	360
2	1	164	151
2	2	293	295
2	3	191	171
2	4	240	224
2	-1	311	339
2	-2	530	487
2	-3	598	581
2	-4	319	309
2	-5	345	356
2	-6	245	240
2	-7	189	215
3	0	39	46
3	2	152	145
3	3	50	14
3	-1	333	353
3	-2	203	167
3	-3	204	195
3	-4	214	191
3	-5	334	316
3	-6	279	263
3	-7	133	140
4	0	27	43
4	1	117	114
4	2	160	163
4	3	200	193
4	-1	348	358
4	-2	97	103
4	-3	24	28
4	-4	153	146
4	-5	278	283
4	-6	146	138
4	-7	67	95
5	0	247	244
5	1	79	85
5	-1	331	325
-1	0	733	719
-1	1	277	272
-1	2	389	404
-1	4	548	543
-1	-1	263	250
-1	-2	358	404
-1	-3	121	94
-1	-4	537	524
-1	-5	309	349
-2	0	678	664
-2	1	386	395
-2	2	165	161
-2	3	37	65
-2	-1	214	214
-2	-2	431	444
-2	-3	182	191
-2	-4	724	744
-3	0	485	476
-3	1	187	188
-3	2	320	347
-3	-1	82	58
-3	-2	352	361
*******H= -9******			
0	1	154	178
0	2	469	475
0	3	161	173
0	-1	582	556
0	-2	57	69
0	-3	85	75
0	-4	103	92
0	-5	78	57
1	0	547	572
1	1	135	124
1	2	265	266
1	3	127	126
1	-1	516	508
1	-2	275	268
1	-3	151	140
1	-4	569	564
1	-5	66	54
1	-6	99	115
2	0	632	644
2	1	322	321
2	2	124	83
2	3	68	49
2	-1	101	88
2	-2	667	617
2	-3	99	101
2	-4	951	893
2	-5	170	153
2	-6	576	592
3	0	563	573
3	1	202	197
3	2	185	193
3	3	189	171
3	-1	694	656
3	-2	730	704
3	-3	114	104
3	-4	431	420
3	-5	125	111
3	-6	531	518
4	0	195	227
4	1	40	58
4	2	457	452
4	-1	257	250
4	-2	316	270
4	-3	190	190
4	-4	49	18
4	-5	139	124
4	-6	267	263
4	-7	199	186
5	0	207	220
5	1	131	101
5	-1	107	103
-1	0	65	72
-1	1	77	43
-1	2	170	161
-1	-2	145	151
-1	-3	111	123
-2	0	88	79
-2	1	52	90
-2	2	724	755
-2	-1	203	211
-2	-2	320	325
-3	0	97	105
-3	1	142	147
-3	-1	93	97
*******H=-10******			
0	1	259	250
0	2	56	58
0	3	138	98
0	-1	172	189
0	-2	119	123
0	-3	81	65
0	-4	59	45
0	-5	65	92
1	0	232	236
1	1	104	122
1	2	212	190
1	3	43	54
1	-2	728	694
1	-3	29	11
1	-4	205	239
1	-5	30	9
2	0	431	410
2	1	254	263
2	2	267	279
2	-1	400	423
2	-2	506	499
2	-3	182	171
2	-4	516	509
2	-5	101	108
2	-6	370	378
3	0	186	183
3	1	74	69
3	2	507	490
3	-1	228	234
3	-2	463	467
3	-3	474	477
3	-4	389	384
3	-5	48	56
3	-6	314	317
4	0	319	315
4	1	209	197
4	2	404	406
4	-1	393	407
4	-2	117	89
4	-3	255	258
4	-4	398	390
4	-5	148	113
4	-6	163	190
5	0	437	534
5	1	189	191
-1	0	287	267
-1	1	333	347
-1	2	262	296
-1	-1	141	113
-1	-2	166	169
-1	-3	76	117
-2	0	163	147
-2	1	74	30
-2	-1	146	146
-2	-2	119	121
*******H=-11******			
0	1	167	187
0	2	177	185
0	-1	432	441
0	-2	458	475
0	-3	221	207
0	-4	425	449
1	0	275	278
1	1	435	426
1	2	409	414
1	-1	665	656
1	-2	608	585
1	-3	417	435
1	-4	300	293
1	-5	331	336
2	0	206	200
2	1	560	575
2	2	538	555
2	-1	313	308
2	-2	296	306
2	-3	801	754
2	-4	318	292
2	-5	290	262
3	0	441	446
3	1	516	521
3	2	558	540
3	-1	390	403
3	-2	214	227
3	-3	474	454
3	-4	439	422
3	-5	314	295
3	-6	75	59
4	0	92	119
4	1	466	481
4	-1	119	138
4	-2	130	125
4	-3	423	429
4	-4	130	130
4	-5	180	188
4	-6	95	87
5	0	41	39
5	1	355	350
5	-1	150	164
-1	0	356	374
-1	1	67	78
-1	-1	271	251
-1	-2	390	470
*******H=-12******			
0	-1	161	147
0	-2	52	35
0	-3	149	131
1	0	52	68
1	1	51	28
1	-1	88	110
1	-2	110	120
1	-3	46	8
1	-4	46	54
2	0	83	57
2	-1	58	54
2	-2	218	211
2	-3	117	110
2	-4	43	46
2	-5	204	202
3	-1	187	210
3	-2	117	123
3	-3	36	13
3	-4	54	53
3	-5	324	314
4	0	31	41
4	-1	33	35
4	-2	101	127
4	-3	168	179
4	-4	310	307
4	-5	311	208
5	0	65	68
5	-1	323	324
*******H=-13******			
1	-1	51	21
1	-2	145	164
2	0	120	111
2	-1	40	23
2	-2	31	7
2	-3	112	100
3	0	33	74
3	-1	53	27
3	-2	169	144
3	-3	244	247
4	-1	125	171
4	-2	64	51
4	-3	58	45
4	-4	104	111
5	-1	38	47

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å)

Atom	Minimum	Intermediate	Maximum
Co(1)	0.202 (6)	0.228 (6)	0.273 (6)
Co(2)	0.193 (6)	0.253 (5)	0.331 (7)
As	0.180 (3)	0.226 (3)	0.242 (3)
S(1)	0.209 (7)	0.255 (6)	0.274 (9)
S(2)	0.209 (7)	0.249 (6)	0.277 (9)
S(3)	0.242 (7)	0.294 (7)	0.346 (8)
S(4)	0.240 (7)	0.257 (7)	0.381 (10)

posed between the closely spaced planar units.[12] On the other hand, magnetic susceptibility measurements on $Co(tdt)_2^-$ show the complex to be a full-spin triplet in the solid ($\mu_{eff} = 3.18$ BM) with no indication of any pairwise magnetic interactions.[2b] The separation of the $Co(tdt)_2^-$ anions in the crystal is entirely consistent with these observations.

The assignment of the unusual high-spin ground-state configuration of $Co(tdt)_2^-$ represents an important step in elucidating the electronic structures of the ML_2^{n-} complexes containing the unsaturated bidentate sulfur ligand systems. A molecular orbital calculation of the SCCC type has recently been performed by Hawkes on the complex $Ni(bdt)_2^-$ (bdt = benzene-1,2-dithiolate) assuming D_{2h} symmetry and using the structural parameters from $Co(tdt)_2^-$.[23] This calculation, which assumes no hybridization of the sulfur 3s and 3p orbitals, yields an energy level ordering which differs significantly from that obtained in an earlier calculation by Shupack, *et al.*, on the related $Ni(mnt)_2^-$ system.[24] In the earlier calculation, sulfur hybrid orbitals were employed for the in-plane σ and π bonding. The energy level ordering proposed by Hawkes[23] gives good agreement with *both* optical and esr data for the NiL_2^{n-} ($n = 0, 1, 2$) complexes whereas the earlier calculation exhibits inconsistencies with the esr data for the monoanionic systems.[25]

The ordering of the energy levels of interest obtained by Hawkes is $4a_g \sim 5a_g$ $(x^2 - y^2, z^2) < L\ (\pi) < 3b_{3g}\ (yz) < 4b_{2g}(xy) < 3b_{1g}\ (xy)$ as opposed to the ordering of $3a_g\ (z^2) < 3b_{3g}\ (yz) < L\ (\pi) < 4b_{2g}\ (xz) < 4a_g\ (x^2 - y^2) < 3b_{1g}\ (xy)$ put forth by Shupack, *et al.* Because of the consistency of the former with experimental data and the greater inherent accuracy of the more recent calculation in which no hybridization was assumed, we use the ordering proposed by Hawkes in

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[23] M. J. Hawkes, Ph.D. Thesis, Columbia University, 1967.

[24] S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964).

[25] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid.*, **86**, 4580 (1964).

TABLE V

PRINCIPAL INTRAMOLECULAR DISTANCES AND ANGLES

Distances, Å		Angles, deg	
		Anion	
Co(1)–S(1)	2.169 (4)	S(1)–Co(1)–S(2)	91.7 (2)
Co(1)–S(2)	2.166 (4)	S(3)–Co(2)–S(4)	90.9 (2)
Co(2)–S(3)	2.151 (6)	Co(1)–S(1)–C(1)	104.7 (5)
Co(2)–S(4)	2.177 (5)	Co(1)–S(2)–C(2)	104.4 (5)
S(1)–S(2)	3.112 (6)	Co(2)–S(3)–C(7)	106.0 (8)
S(1)–S(2)′	3.019 (6)	Co(2)–S(3)–C(8)	106.1 (6)
S(3)–S(4)	3.084 (9)	S(1)–C(1)–C(2)	119 (1)
S(3)–S(4)′	3.037 (9)	S(1)–C(1)–C(6)	119 (1)
S(1)–C(1)	1.77 (2)	S(2)–C(2)–C(1)	120 (1)
S(2)–C(2)	1.77 (2)	S(2)–C(2)–C(3)	120 (1)
S(3)–C(7)	1.77 (2)	S(3)–C(7)–C(8)	120 (1)
S(4)–C(8)	1.80 (2)	S(3)–C(7)–C(12)	122 (2)
C(1)–C(2)	1.37 (2)	S(4)–C(8)–C(7)	117 (2)
C(2)–C(3)	1.42 (2)	S(4)–C(8)–C(9)	119 (2)
C(3)–C(4)	1.42 (2)	C(2)–C(3)–C(4)	118 (1)
C(4)–C(5)	1.35 (2)	C(3)–C(4)–C(5)	122 (2)
C(5)–C(6)	1.44 (2)	C(4)–C(5)–C(6)	119 (1)
C(6)–C(1)	1.41 (2)	C(5)–C(6)–C(1)	118 (1)
C(4)–CH_3(1)	1.56 (2)	C(3)–3(4)–CH_3(1)	118 (1)
C(7)–C(8)	1.38 (2)	C(5)–C(4)–CH_3(1)	120 (1)
C(8)–C(9)	1.42 (2)	C(8)–C(9)–C(10)	113 (2)
C(9)–C(10)	1.44 (3)	C(9)–C(10)–C(11)	126 (3)
C(10)–C(11)	1.35 (3)	C(10)–C(11)–C(12)	118 (3)
C(11)–C(12)	1.36 (3)	C(11)–C(12)–C(7)	122 (2)
C(12)–C(7)	1.42 (3)	C(9)–C(10)–CH_3(2)	117 (2)
C(10)–CH_3(2)	1.53 (3)	C(11)–C(10)–CH_3(2)	117 (3)
		Cation	
As–AsCH_3	1.96 (2)	AsCH_3–As–R(1)C(1)	109
As–R(1)C(1)	1.88 (2)	AsCH_3–As–R(2)C(1)	109
As–R(2)C(1)	1.89 (2)	AsCH_3–As–R(3)C(1)	112
As–R(3)C(1)	1.89 (2)	R(1)C(1)–As–R(2)C(1)	108
		R(1)C(1)–As–R(3)C(1)	111
		R(2)C(1)–As–R(3)C(1)	108
		Ethanol Molecule[a]	
X(1)–X(2)	1.35 (5)	X(1)–X(2)–X(3)	135 (6)
X(2)–X(3)	1.18 (5)		

[a] Because of the observed disorder, no true significance should be attached to these values. Estimated standard deviations appear overly optimistic for these dimensions.

TABLE VI

BEST WEIGHTED LEAST-SQUARES PLANES THROUGH THE tdt LIGANDS AND DISTANCES OF THE ATOMS FROM THEIR RESPECTIVE PLANES[a]

Atom	Distance, Å	Atom	Distance, Å
Anion 1:	$13.852x - 9.416y + 6.728z = -0.100$ (Triclinic Coordinates)		
S(1)	0.008 (5)	C(4)	0.00 (2)
S(2)	−0.002 (5)	C(5)	−0.02 (2)
C(1)	−0.04 (2)	C(6)	−0.08 (2)
C(2)	−0.02 (2)	M(1)	0.10 (2)
C(3)	−0.01 (2)		
Anion 2:	$-0.952x + 2.669y - 9.826z = -5.391$ (Triclinic Coordinates)		
S(3)	−0.005 (5)	C(10)	0.02 (2)
S(4)	0.004 (4)	C(11)	0.03 (2)
C(7)	−0.03 (2)	C(12)	0.06 (2)
C(8)	−0.05 (2)	M(2)	0.01 (3)
C(9)	−0.04 (2)		

[a] Weights were based on the variance–covariance matrix as obtained from the final cycle of least-squares refinement.

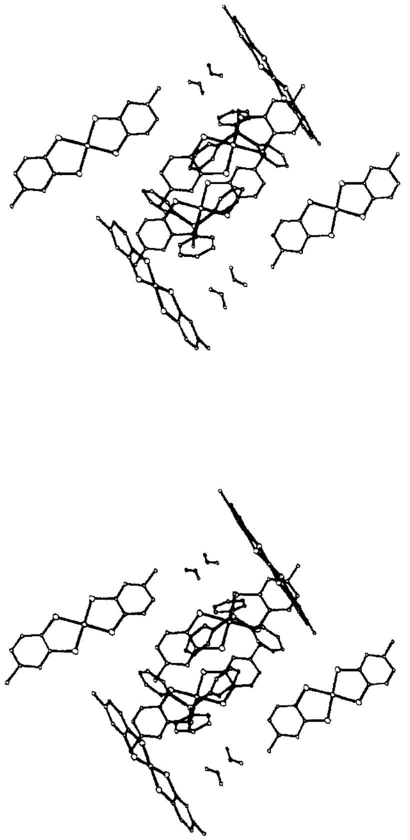

Figure 2.—These drawings present a view of the packing of $[(C_6H_5)_3(CH_3)As][Co(tdt)_2]\cdot 0.5C_2H_5OH$ in the crystal. The ethanol molecules are shown in both possible orientations. The drawings constitute a stereopair and may be viewed with a hand viewer.

suggesting a ground-state configuration for the $Co(tdt)_2^-$ complex. The separation of the $3b_{3g}$ (yz) and $4b_{2g}$ (xz) orbitals is apparently too small to yield a low-spin $(3b_{3g})^2 = {}^1A_g$ ground-state configuration, and the $3b_{3g}$ (yz) and $4b_{2g}$ (xz) levels are calculated to lie very close to one another. Thus, the predicted ground state is the spin-triplet configuration $(3b_{3g})^1(4b_{2g})^1 = {}^3B_{1g}$ and the two unpaired electrons are located in out-of-plane π orbitals which are delocalized over the entire complex. A full discussion of the electronic structures of the $ML_2{}^{n-}$ complexes including details of the calculation, population analyses, and experimental data will be presented in a forthcoming paper.[26]

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[26] M. J. Baker-Hawkes and H. B. Gray, to be published.