Contribution from the Department of Chemistry, State University of
New York at Stony Brook, Stony Brook, New York 11790

Crystal and Molecular Structures of Bis(tetraphenylarsonium) Tris(1,2-dicyanoethylenedithiolato)molybdenate(IV), $[(C_6H_5)_4As]_2[Mo(mnt)_3]$, and Its Tungsten Analog $[(C_6H_5)_4As]_2[W(mnt)_3]$

GARY F. BROWN and EDWARD I. STIEFEL*[1]

Received January 3, 1973

The structures of bis(tetraphenylarsonium) tris(1,2-dicyanoethylenedithiolato)molybdenate(IV), $[(C_6H_5)_4As]_2[Mo(S_2C_2(CN)_2)_3]$, and its tungsten analog, $[(C_6H_5)_4As]_2[W(S_2C_2(CN)_2)_3]$, have been determined from X-ray data collected by diffractometer methods. The Mo and W complexes each crystallize in the orthorhombic space group *Pbcn* (No. 60) with four molecules per unit cell of dimensions $a = 20.02$ (2), $b = 15.22$ (1), $c = 18.66$ (2) Å and $a = 20.15$ (2), $b = 15.24$ (2), $c = 18.66$ (3) Å, respectively. The observed and calculated densities are 1.47 (1) and 1.479 g cm^{-3} for the Mo and 1.57 (1) and 1.583 g cm^{-3} for the W complex. Full-matrix least-squares refinement of 173 parameters (not including hydrogens) gives a conventional R factor (on F) of 0.067 (for 1643 nonzero reflections) in the Mo complex. For the tungsten compound, $R = 0.055$ for 105 atomic thermal and group parameters (1465 independent reflections). Despite their spectral differences, these compounds are isomorphous and nearly isostructural. The coordination geometry of the MS_6 framework is close to D_3 symmetry and consists of two parallel S_3 triangles twisted 28° from the trigonal prism. The triangles are at a distance such that the trigonal compression is midway between values for the octahedron and the known trigonal prisms. These complexes are thus among the few examples which by all criteria find themselves close to midway between the octahedron and the trigonal prism. The metal–sulfur bonds average 2.38 Å in both cases and the dimensions of the ligands reveal their closeness to "dithiolate" character. Ligand repulsions, inter-donor-atom bonding, and molecular orbital arguments are discussed in attempting to understand the "in-between" geometry.

Introduction

Since their first preparation by King[2] the tris(1,2-dithiolene)[3-10] complexes have been extensively studied. Much initial impetus for this work came from the discovery of the facile one-electron redox reactions which these complexes undergo.[6,7] Further stimulation was provided by the observation that the neutral tris complexes possessed the theretofore unobserved trigonal-prismatic coordination. Since the initial discovery of trigonal-prismatic coordination for $Re[S_2C_2(C_6H_5)_2]_3$[8] and its extension to other tris(dithiolate) complexes,[9,10] a variety of complexes have been found to adopt trigonal-prismatic coordination. In each of these examples,[11-13] however, the trigonal-prismatic coordination is favored by some overwhelming structural constraint in the ligand system. The tris(dithiolate) [and tris(diselenate)][14] complexes are the only cases where trigonal-prismatic coordination is not overwhelmingly enforced by constraints of the ligand system. As evidence for this we simply recall that in the reduced forms (charges of −2, −3) there is evidence for near-octahedral structures[15,16] or for structures distorted to positions between the octahedron and the trigonal prism.[17]

In the last few years other structures have also been claimed to lie between the two limiting six-coordinate geometries. These "in-between" complexes have been mostly in the class of tris(1,1-dithiolates) of transition metals.[18-20] For these complexes, twist angles[21] between 30 and 56° have been reported which have led some authors[19,20] to claim that these complexes were approaching trigonal-prismatic coordination. Our preliminary structural results[22] on $[(C_6H_5)_4As]_2[Mo(mnt)_3]$ showed a twist angle of 28° again indicating an "in-between" structure. However, detailed consideration of the shapes of six-coordinate polyhedra led us[21] to conclude that an additional criterion, one describing the extent of trigonal compression, is required to fully describe the shape of the coordination geometry. This consideration led us to conclude that $[(C_6H_5)_4As]_2[Mo(mnt)_3]$ was by all criteria indeed midway between an octahedron and a trigonal prism. The tris(1,1-dithiolates), on the other hand, formed highly compressed structures whose minimal distortions from an octahedron could be viewed as a consequence solely of the short bite of these ligands. These considerations have been detailed previously[21] and have received support in the recent work of Kepert.[23]

In this paper we present a full exposition of the structure of $[(C_6H_5)_4As]_2[Mo(mnt)_3]$ using improved data (now from a diffractometer). In addition, the structure of the complex $[(C_6H_5)_4As]_2[W(mnt)_3]$ is reported. This latter structure solution was undertaken since the W complex showed vastly different spectroscopic properties from the Mo complex while neutral, isostructural[10] Mo- and W-tris(dithiolene) complexes display remarkable spectral similarities.[9] Despite the spectroscopic differences, the W complex has proved effectively isostructural to its Mo analog. Finally, the dia-

---

(1) Recipient of Camille and Henry Dreyfus Foundation Teacher-Scholar Grant.

(2) R. B. King, *Inorg. Chem.*, 2, 641 (1963).

(3) J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 145 (1968).

(4) R. Eisenberg, *Progr. Inorg. Chem.*, 12, 295 (1970).

(5) E. Hoyer, W. Dietzsch, and W. Schroth, *Z. Chem.*, 11, 41 (1971).

(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 86, 2799 (1964).

(7) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Amer. Chem. Soc.*, 86, 4198 (1964).

(8) R. Eisenberg and J. A. Ibers, *J. Amer. Chem. Soc.*, 87, 3776 (1965); *Inorg. Chem.*, 5, 411 (1966).

(9) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 88, 1956 (1966).

(10) R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 6, 1844 (1967).

(11) J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, 91, 2395 (1969).

(12) W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, 9, 1825 (1970).

(13) E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, 11, 2652 (1972).

(14) C. G. Pierpont and R. Eisenberg, *J. Chem. Soc. A*, 2285 (1971).

(15) A. Segueira and I. Bernal, Abstracts, American Crystallographic Association Meeting, Minneapolis, Minn., summer 1967, p 75.

(16) E. I. Stiefel, L. E. Bennett, Z. Dori, T. H. Crawford, C. Simo, and H. B. Gray, *Inorg. Chem.*, 9, 281 (1970).

(17) E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, 89, 3353 (1967).

(18) D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, 11, 823 (1972).

(19) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 511 (1968).

(20) D. L. Johnston, W. L. Rohrbaugh, and W. D. Horrocks, *Inorg. Chem.*, 10, 1474 (1971).

(21) E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 11, 434 (1972).

(22) G. F. Brown and E. I. Stiefel, *Chem. Commun.*, 729 (1970).

(23) D. L. Kepert, *Inorg. Chem.*, 11, 1561 (1972).

magnetic Mo complex has recently been used as a host for single-crystal electron paramagnetic resonance studies of the isomorphous V complex.^{24} Here, we report the crystal as well as molecular structures of both complexes.

Experimental Section

$[(C_6H_5)_4As]_2[W(mnt)_3]$. Collection and Reduction of Intensity Data. Dark purple crystals, prepared as previously described,^{16} were recrystallized and grown by evaporation from ethanol–methylene chloride solution. Examination of zero and upper level precession photographs revealed Laue symmetry *mmm* and the systematic absence of reflections $h + k = 2n + 1$ for $hk0$; $k = 2n + 1$ for $0kl$; and $l = 2n + 1$ for $h0l$. The symmetry information is uniquely consistent with the orthorhombic space group *Pbcn*. The calculated and observed densities [measured by flotation (in CCl_4-C_6H_6) of 1.583 and 1.57 (1) g cm^{-3}] are consistent with four molecules in the unit cell. Least-squares refinement^{25} of 20 strong reflections ($2\theta \geqslant 20°$) measured on the diffractometer gave cell constants as $a = 20.15$ (2), $b = 15.24$ (2), and $c = 18.66$ (3) Å with a cell volume = 5730 Å^3. The calculated linear absorption coefficient is 37.52 cm^{-1}. Corrections for absorption were not made due to the relatively small size and uniform (*vide infra*) dimensions of the crystal.

Intensity data were collected, using Nb-filtered Mo Kα radiation, at room temperature with a General Electric quarter-circle diffractometer (XRD-490) on line with an IBM 1800 computer. A small uniform crystal (0.20 × 0.20 × 0.30 mm) was mounted along the b^* axis on an eucentric goniometer head. Initial alignment was performed with an optical goniometer and precession camera and was completed by the optimization of 2θ, χ, ϕ, and in values for 15 high-intensity reflections according to the procedure described by Furnas.^{26}

A total of 1465 reflections with $I_{\text{obsd}} > 3\sigma(I)$ were measured using a moving-crystal, moving-counter technique. The scanning of each reflection was done in 26 intervals ($\Delta 2\theta = 0.08°$) with a counting time of 8 sec per step. Two standard reflections, 004 and 600, were checked every 20 measurements and the variation was less than 3%. The raw data were integrated and corrected for background and LP effects resulting in a set of F_o^2. A Wilson plot showed an overall temperature factor of 5.301 and a scale factor of 0.0481.

Solution and Refinement of the Structure. Prior to the X-ray investigation of $[(C_6H_5)_4As]_2[W(mnt)_3]$, the structure of the molybdenum analog, $[(C_6H_5)_4As]_2[Mo(mnt)_3]$, had been solved using film data.^{22} The anion is crystallographically required to have C_2 symmetry. The results on the two complexes indicated them to be isomorphous and possibly isostructural. Upon substituting the final coordinates of the Mo, As, and S atoms for the analogous atomic positions in the present tungsten complex, the agreement factor (R)^{27} was 0.266, after one least-squares cycle.^{28} Insertion of the carbon and nitrogen coordinates, for both cation and anion, from the Mo structure yielded $R = 0.152$ using isotropic thermal parameters. At this point the temperature factors for the carbon atoms in one of the phenyl rings increased to values above 20. Since this ring had the poorest, least-squares plane in the original (film data) Mo structure, this was not surprising or disturbing. After removing these carbons, a difference Fourier map revealed six peaks ranging in electron density from 1.8 to 2.4 e/Å^3 for this phenyl group and direct substitution of the peak coordinates gave a nonweighted R of 0.092. Since the "new" phenyl ring was not grossly displaced from its original position, it appeared that the Mo and W complexes were, indeed, isostructural.

Upon determining the position for each carbon atom of the four independent phenyl rings in the tetraphenylarsonium cation, initial and approximate group parameters (x_c, y_c, z_c ϕ, θ, ρ) were calculated. After several cycles of least-squares group refinement, using a procedure described by Ibers,^{29} the value of R was 0.092. Final stages of refinement included anisotropic thermal parameters for W, As, and S atoms, addition of anomalous dispersion effects (W, As, S),^{30} and the use of a weighting routine.^{31} The last cycle of least-squares refinement, where the change in each variable was less than $^1/_{12}$ the estimated standard deviation, resulted in a R of 0.055 and a R_w of 0.067 for 153 parameters.^{31} The highest peak on the final difference Fourier was 0.496 e/Å^3, less than 30% the height of the last carbon atom peak. Table I shows the final atomic and thermal parameters of 14 nongroup (excluding phenyl ring carbon and hydrogen) atoms and the final group positional and thermal parameters. Table II gives the final derived positional parameters for the group carbon atoms.

$[(C_6H_5)_4As]_2[Mo(mnt)_3]$. Collection and Reduction of Intensity Data. Suitable dark green crystals of the molybdenum complex, prepared as previously described,^{16} were grown from a concentrated acetone–2-propanol solution. A small uniform crystal (0.40 × 0.35 × 0.35 mm) was examined optically and mounted perpendicular to a large face, which later proved to be 010. Zero and upper level precession photographs showed (as previously described for the W complex) the orthorhombic space group *Pbcn* (No. 60). The cell constants, measured from diffractometer data (*vide infra*), are $a = 20.02$ (2), $b = 15.22$ (1), $c = 18.66$ (2) Å. The flotation measured density (C_6H_6-CCl_4) of 1.47 (1) g cm^{-3} agrees with a calculated density of 1.479 g cm^{-3}, assuming four molecules in a unit cell with a volume of 5686 Å^3. The calculated linear absorption coefficient is 16.71 cm^{-1}. Corrections for absorption were not deemed necessary.

Intensity data for the molybdenum complex were originally collected on film^{22} and the structure was solved using Patterson and difference Fourier methods. The results were satisfactory for heavy atom positions and bond distances (Mo, As, S). However, the final refinement of the carbon and nitrogen positions of the anion and one of the phenyl rings left something to be desired. Therefore, a new set of intensity data was collected from a single crystal (0.30 × 0.30 × 0.40 mm) at room temperature with a diffractometer (as described above for the W complex). Manual alignment of the crystal, mounted along b^*, utilized 25 reflections. A set of refined cell constants was determined by three least-squares cycles of 18 high-intensity reflections ($2\theta \geqslant 20°$).

Solution and Refinement of the Structure. Direct substitution of the previously determined W, As, and S coordinates for the Mo, As, and S atomic positions refined to an isotropic $R = 0.286$. Further substitution of the rest of the asymmetric unit of the tungsten complex resulted in an unweighted $R = 0.110$. The inclusion of anisotropic motion for the Mo, As, and S atoms, plus anomalous dispersion effects, gave $R = 0.064$. The above results lend further evidence to the isostructural nature of these two complexes.

Three more cycles of least-squares refinement for 173 positional and thermal parameters (without rigid group refinement and not including hydrogens) gave $R = 0.067$ and $R' = 0.052$. The changes in all variables was significantly less ($^1/_6$) than the estimated standard deviation of those parameters. The highest peak on the final Fourier map was 0.617 e Å^3, which is less than one-third the density of the last carbon atom found. A list of final atomic and thermal parameters is given in Table III.^{32}

Description of the Structures

$[(C_6H_5)_4As]_2[Mo(mnt)_3]$. The crystal structure is fully

---

(24) W. L. Kwik and E. I. Stiefel, *Inorg. Chem.*, in press.

(25) Computations were performed on an IBM-360-67 at the Computing Center of S.U.N.Y.-Stony Brook. The following programs were used for operations indicated: refinement of cell dimensions, Prewitt's PODEX; on-line (IBM 1800) collection of diffractometer data, Okaya's LIMPT, CCXDP, and PRIMB; processing raw data into F_o^2, G. Brown's XRD18; Wilson plot program, XDATA; Patterson function and difference Fourier maps, Zalkin's FORDAP; least squares and group refinement, Brown University version of Busy and Levy's ORFLS (BUGLES); calculation of approximate group orientation angles, Watkin's RBANG; bond distances, angles, least-squares planes, and estimated standard deviation, Brown University version of ORFFE (BUFFE) and J. Wood MOLECULAR GEOMETRY; calculation of twist angle (ϕ), A. Rosen's ROTATE; stereoview and unit cell diagram, Johnson's ORTEP.

(26) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Schenectady, N. Y., 1957, Chapter 10, p 138.

(27) Conventional residual $R = |F_o| - |F_c|/|F_o|$ and weighted residual $R' = w(|F_o| - |F_c|)^2/w|Fd^2$ where w = weight and F_o and F_c are the observed and calculated structure factors.

(28) In all cases form factors were obtained from Iber's tabulation, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1968, Table 3.3.1A.

(29) J. A. Ibers in "International Union of Crystallography-International Congress," Abstracts of the Communications, A239, Moscow, 1966, and references cited therein.

(30) D. H. Templeton, "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1968, Table 3.3.1A.

(31) A weighting scheme suggested by Cruickshank was employed where $w = (a + |F_ol + b|F_ol^2)^{-1}$ with $a = 34 = 2/F_{\text{min}}$ and $b = 2/266 = 2/F_{\text{max}}$. See J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press, Oxford, 1955, p 114.

(32) A listing of the structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2140.

Table I. Final Parameters for $[(C_6H_5)_4As]_2[W(mnt)_3]$

Atomic Positional and Isotropic Thermal Parameters

Atom	*x*	*y*	*z*	*B*, Å^2
W	0.0	0.17625 (6)	0.2500	
As	0.36748 (8)	0.16886 (9)	0.40450 (9)	
S_1	0.0491 (4)	0.2084 (3)	0.3631 (2)	
S_2	0.0479 (2)	0.0593 (3)	0.1848 (2)	
S_3	0.0893 (2)	0.2633 (3)	0.2082 (2)	
N_1	0.1807 (9)	0.3234 (9)	0.4595 (9)	8.5 (4)
N_2	0.0612 (10)	−0.1783 (13)	0.1586 (11)	11.1 (5)
N_3	0.2321 (9)	0.3994 (12)	0.2601 (8)	9.0 (4)
C_1	0.1157 (7)	0.2774 (9)	0.3485 (9)	4.3 (4)
C_2	0.0207 (7)	−0.0377 (10)	0.2220 (7)	4.5 (4)
C_3	0.1325 (8)	0.3009 (9)	0.2832 (9)	4.3 (3)
C_4	0.1504 (9)	0.3046 (10)	0.4095 (11)	5.8 (4)
C_5	0.0420 (10)	−0.1157 (15)	0.1914 (11)	8.8 (5)
C_6	0.1870 (10)	0.3567 (12)	0.2723 (10)	6.8 (5)

Anisotropic Thermal Parameters

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0.00263 (4)	0.00391 (6)	0.00331 (5)	0.0	−0.00071 (3)	0.0
As	0.00280 (6)	0.00426 (4)	0.00557 (8)	0.00007 (6)	−0.00038 (6)	0.00026 (6)
S_1	0.0033 (1)	0.0056 (2)	0.0033 (2)	−0.0007 (2)	−0.0004 (1)	−0.0001 (2)
S_2	0.0035 (2)	0.0053 (2)	0.0043 (2)	0.0005 (2)	−0.0004 (1)	−0.0003 (2)
S_3	0.0035 (2)	0.0048 (2)	0.0043 (2)	−0.0004 (2)	−0.0002 (1)	0.0003 (2)

Group Positional and Thermal Parameters

Group[a]	x_c[b]	y_c	z_c	ϕ	θ	ρ	*B*, Å^2
R_1	0.5014 (4)	0.0446 (5)	0.3946 (4)	2.473 (8)	2.500 (7)	0.045 (8)	6.0 (2)
R_2	0.3962 (3)	0.3783 (5)	0.4292 (4)	1.180 (12)	2.103 (6)	−2.879 (12)	5.5 (2)
R_3	0.2688 (4)	0.0929 (5)	0.5300 (4)	0.121 (8)	−2.73 (2)	−0.828 (7)	6.8 (2)
R_4	0.2860 (4)	0.1450 (4)	0.2535 (4)	1.864 (7)	−2.6 (7)	1.621 (7)	5.80 (2)

[a] R_1, R_2, R_3, and R_4 are the four phenyl rings attached to the arsonic atom. [b] x_c, y_c, and z_c are the fractional coordinates of the ring centers. Angles ϕ, θ, and ρ (in radians) are the group orientation angles.

Table II. Derived Parameters for the Group Phenyl Carbon Atoms for $[(C_6H_5)_4As]_2[W(mnt)_3]$

Group atom	*x*	*y*	*z*
R_1C_1	0.4460 (5)	0.0992 (8)	0.3973 (6)
R_1C_2	0.4440 (4)	0.0222 (8)	0.3573 (6)
R_1C_3	0.4993 (6)	−0.0324 (5)	0.3546 (6)
R_1C_4	0.5567 (5)	−0.0001 (8)	0.3919 (6)
R_1C_5	0.5587 (4)	0.0671 (8)	0.4319 (6)
R_1C_6	0.5034 (6)	0.1217 (6)	0.4346 (6)
R_2C_1	0.3851 (12)	0.2890 (5)	0.4194 (6)
R_2C_2	0.3626 (7)	0.3490 (8)	0.3687 (6)
R_2C_3	0.3738 (8)	0.4383 (6)	0.3785 (6)
R_2C_4	0.4074 (12)	0.4677 (5)	0.4390 (6)
R_2C_5	0.4299 (7)	0.4077 (8)	0.4898 (6)
R_2C_6	0.4187 (8)	0.3184 (6)	0.4780 (6)
R_3C_1	0.3128 (6)	0.1266 (8)	0.4795 (5)
R_3C_2	0.2842 (7)	0.1819 (5)	0.5302 (7)
R_3C_3	0.2402 (5)	0.1482 (8)	0.5807 (5)
R_3C_4	0.2248 (6)	0.0592 (8)	0.5805 (5)
R_3C_5	0.2534 (7)	0.0039 (5)	0.5299 (7)
R_3C_6	0.2974 (5)	0.0376 (7)	0.4794 (6)
R_4C_1	0.3202 (6)	0.1539 (9)	0.3179 (5)
R_4C_2	0.2537 (6)	0.1297 (6)	0.3183 (5)
R_4C_3	0.2194 (4)	0.1208 (8)	0.2539 (7)
R_4C_4	0.2517 (6)	0.1361 (9)	0.1892 (5)
R_4C_5	0.3182 (6)	0.1603 (6)	0.1888 (5)
R_4C_6	0.3525 (4)	0.1692 (8)	0.2531 (7)

[a] Orthorhombic coordinates.

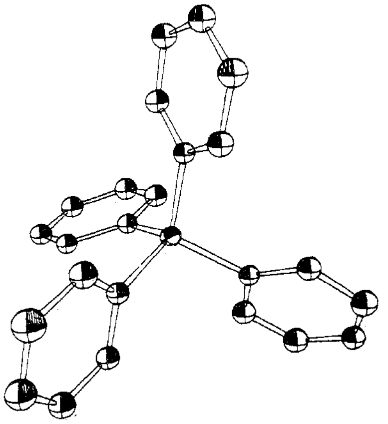

Figure 1. A view of the tetraphenylarsonium cation.

defined by the parameters given in Table III, the cell constants, and the symmetry operations of space group *Pbcn*. The unit cell consists of four anions and eight cations corresponding to $Mo(mnt)_3{}^{2-}$ and $(C_6H_5)_4As^+$, respectively. The closest Mo-Mo approach is greater than 10 Å. The closest interanionic contact is larger than 4.5 Å, while the closest cation-anion approach (not including cation hydrogens) is between a cyano nitrogen and a phenyl carbon at a distance of 3.27 Å. These and other cation-anion separations appear to be quite normal and we now present a discussion of each independent ion.

In the cation, the arsenic atom is surrounded tetrahedrally (see Figure 1) by the carbons of four phenyl groups with the average As-C (bonded) distance being 1.89 Å. This is in excellent agreement with other recent determinations of this cation.[15,33] The phenyl rings are planar and the average C-C (bonded) distance is 1.40 Å, ranging from 1.36 (2) to 1.44 (2) Å. Selected bond distances, angles, and equations of least-squares planes are presented in Tables IV and V.

A perspective drawing of the inner network of the anion is shown in Figure 2. The cyanide groups have been omitted from the figure in order to emphasize the coordination and the tris chelate geometry. Important distances and angles are tabulated in Figure 3 and Table VI. Crystallographic

(33) F. A. Cotton and J. J. Lippard, *Inorg. Chem.*, 5, 416 (1966).

Table III. Final Parameters for $[(C_6H_5)_4As]_2[Mo(mnt)_3]$

Atomic Positional and Isotropic Thermal Parameters

Atom	x	y	z	B, Å^2
Mo	0.0[b]	0.1761 (1)[a]	0.2500[b]	
As	0.36731 (6)	0.16889 (9)	0.40425 (7)	
S_1	0.0485 (2)	0.2073 (2)	0.3638 (2)	
S_2	0.0480 (2)	0.0585 (2)	0.1845 (2)	
S_3	0.0894 (2)	0.2640 (2)	0.2083 (2)	
N_1	0.1795 (6)	0.3253 (9)	0.4602 (7)	8.0 (3)
N_2	0.0585 (8)	−0.1786 (12)	0.1596 (9)	11.2 (4)
N_3	0.2330 (7)	0.4005 (8)	0.2617 (7)	8.5 (3)
C_1	0.1154 (6)	0.2776 (8)	0.3485 (7)	4.4 (3)
C_2	0.0192 (6)	−0.0386 (8)	0.2207 (6)	5.4 (3)
C_3	0.1329 (6)	0.3014 (7)	0.2833 (6)	4.6 (3)
C_4	0.1532 (6)	0.3043 (8)	0.4092 (9)	6.0 (3)
C_5	0.0408 (7)	−0.1195 (13)	0.1889 (10)	8.9 (5)
C_6	0.1873 (7)	0.3559 (9)	0.2700 (7)	5.8 (3)
R_1C_1	0.4457 (6)	0.0987 (7)	0.3957 (6)	4.4 (3)
R_1C_2	0.4414 (7)	0.0215 (9)	0.3577 (8)	6.2 (3)
R_1C_3	0.4975 (8)	−0.0328 (9)	0.3518 (8)	7.1 (3)
R_1C_4	0.5549 (7)	−0.0117 (9)	0.3897 (8)	6.0 (3)
R_1C_5	0.5589 (7)	0.0643 (10)	0.4313 (8)	6.9 (4)
R_1C_6	0.5028 (8)	0.1228 (8)	0.4360 (7)	5.6 (3)
R_2C_1	0.3857 (5)	0.2891 (7)	0.4170 (6)	4.2 (3)
R_2C_2	0.3625 (6)	0.3468 (8)	0.3662 (6)	5.3 (3)
R_2C_3	0.3739 (7)	0.4368 (9)	0.3772 (7)	5.9 (3)
R_2C_4	0.4088 (7)	0.4661 (9)	0.4390 (8)	6.1 (3)
R_2C_5	0.4314 (7)	0.4079 (10)	0.4900 (8)	7.0 (4)
R_2C_6	0.4178 (6)	0.3187 (9)	0.4813 (7)	5.6 (3)
R_3C_1	0.3126 (6)	0.1277 (8)	0.4782 (7)	4.5 (3)
R_3C_2	0.2860 (7)	0.1814 (10)	0.5289 (8)	6.4 (3)
R_3C_3	0.2396 (8)	0.1494 (11)	0.5826 (9)	8.8 (4)
R_3C_4	0.2248 (8)	0.0586 (10)	0.5808 (9)	7.8 (4)
R_3C_5	0.2536 (7)	0.0055 (10)	0.5297 (8)	6.4 (3)
R_3C_6	0.2972 (6)	0.0367 (8)	0.4782 (7)	5.2 (3)
R_4C_1	0.3210 (6)	0.1541 (8)	0.3167 (7)	4.6 (3)
R_4C_2	0.2531 (6)	0.1308 (8)	0.3200 (7)	4.8 (3)
R_4C_3	0.2186 (6)	0.1196 (8)	0.2539 (8)	5.8 (3)
R_4C_4	0.2512 (8)	0.1364 (9)	0.1908 (8)	6.4 (4)
R_4C_5	0.3171 (8)	0.1593 (10)	0.1873 (8)	6.6 (3)
R_4C_6	0.3533 (6)	0.1698 (9)	0.2533 (8)	6.2 (3)

Anisotropic Thermal Parameters[c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.00284 (5)	0.00405 (7)	0.00387 (6)	0.0[d]	−0.00068 (5)	0.0[d]
As	0.00277 (4)	0.00421 (6)	0.00382 (5)	0.00007 (5)	−0.00042 (4)	0.00022 (6)
S_1	0.00331 (1)	0.0058 (2)	0.00038 (1)	−0.0003 (1)	−0.0004 (1)	0.0001 (1)
S_2	0.0036 (1)	0.0054 (2)	0.0045 (1)	0.0008 (1)	−0.0008 (1)	−0.0004 (1)
S_3	0.0032 (1)	0.0054 (2)	0.0044 (1)	−0.0005 (1)	−0.0003 (1)	0.0004 (1)

[a] The numbers in parentheses in this and succeeding tables represent the estimated standard deviations of the last significant figure. [b] Special position parameters fixed by symmetry. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [d] The symmetry of the special position of Mo restrains the thermal parameter $\beta_{12} = \beta_{23} = 0$.

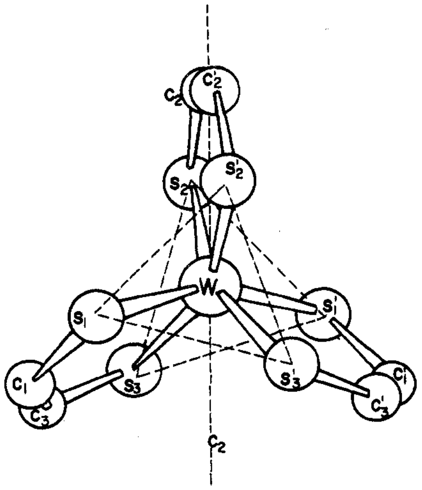

Figure 2. A perspective drawing of the inner network of the anion (W or Mo) showing the atom numbering used.

symmetry requires Mo to lie on a twofold axis which bisects one of the mnt ligands and relates the other two. A stereoview of the anion is shown in Figure 4. Six sulfur donor atoms are located around the metal at an average distance of 2.373 Å forming an MoS_6 polyhedron which is not shaped like either the trigonal prism or the octahedron. Although the molecule possesses only the crystallographically required C_2 symmetry, it is convenient to introduce idealized D_3 symmetry for the purpose of discussion.[34] In this context the structure consists of two approximately parallel, roughly equilateral S_3 triangles (dihedral angle = 178.6°) with an average side (interligand S· · ·S) of 3.188 Å, separated by a distance of 2.99 Å. As shown in Figure 2, the S_3 triangles are twisted with respect to each other by an average of 28°.[22] This twist angle (ϕ) would ideally be 0° in the trigonal prism

---

(34) The individual angles in the S_3 triangle are S_1-S_2-S_3 = 61.3°, S_2-S_3-S_1 = 59.3°, and S_3-S_1-S_2 = 59.3°. Although these differences are distinctly outside of experimental error we feel that they are sufficiently small to warrant idealization to D_3.

Table IV. Bond Distances and Angles for $(C_6H_5)_4As^+$ in $[(C_6H_5)_4As]_2[Mo(mnt)_3]$

Atoms	Dist, Å	Atoms	Angles, deg
$As-R_1C_1$	1.91 (1)	$R_1C_1-As-R_2C_1$	113.2 (5)
$As-R_2C_1$	1.88 (1)	$R_1C_1-As-R_4C_1$	105.4 (5)
$As-R_3C_1$	1.89 (1)	$R_2C_1-As-R_3C_1$	110.3 (5)
$As-R_4C_1$	1.87 (1)	$R_3C_1-As-R_4C_1$	108.1 (5)
		$R_1C_1-As-R_3C_1$	110.8 (5)
$R_1C_1-R_1C_2$	1.38 (2)	$R_4C_1-As-R_2C_1$	108.7 (5)
$R_1C_2-R_1C_3$	1.40 (2)		
$R_1C_3-R_1C_4$	1.39 (2)	$R_1C_1-R_1C_2-R_1C_3$	120 (1)
$R_1C_4-R_1C_5$	1.39 (2)	$R_1C_2-R_1C_3-R_1C_4$	119 (1)
$R_1C_5-R_1C_6$	1.44 (2)	$R_1C_3-R_1C_4-R_1C_5$	120 (1)
$R_1C_6-R_1C_1$	1.42 (2)	$R_1C_4-R_1C_5-R_1C_6$	120 (1)
		$R_1C_5-R_1C_6-R_1C_1$	116 (1)
$R_2C_1-R_2C_2$	1.37 (1)	$R_1C_6-R_1C_1-R_1C_2$	123 (1)
$R_2C_2-R_2C_3$	1.40 (2)		
$R_2C_3-R_2C_4$	1.42 (2)	$R_2C_1-R_2C_2-R_2C_3$	118 (1)
$R_2C_4-R_2C_5$	1.38 (2)	$R_2C_2-R_2C_3-R_2C_4$	120 (1)
$R_2C_5-R_2C_6$	1.39 (2)	$R_2C_3-R_2C_4-R_2C_5$	121 (1)
$R_2C_6-R_2C_1$	1.43 (2)	$R_2C_4-R_2C_5-R_2C_5$	119 (1)
		$R_2C_5-R_2C_6-R_2C_1$	119 (1)
$R_3C_1-R_3C_2$	1.36 (2)	$R_2C_6-R_2C_1-R_2C_2$	122 (1)
$R_3C_2-R_3C_3$	1.42 (2)		
$R_3C_3-R_3C_4$	1.41 (2)	$R_3C_1-R_3C_2-R_3C_3$	122 (1)
$R_3C_4-R_3C_5$	1.38 (2)	$R_3C_2-R_3C_3-R_3C_4$	117 (1)
$R_3C_5-R_3C_6$	1.38 (2)	$R_3C_3-R_3C_4-R_3C_5$	120 (1)
$R_3C_6-R_3C_1$	1.42 (2)	$R_3C_4-R_3C_5-R_3C_6$	123 (1)
		$R_3C_5-R_3C_6-R_3C_1$	118 (1)
$R_4C_1-R_4C_2$	1.41 (2)	$R_3C_6-R_3C_1-R_3C_2$	120 (1)
$R_4C_2-R_4C_3$	1.42 (2)		
$R_4C_3-R_4C_4$	1.37 (2)	$R_4C_1-R_4C_2-R_4C_3$	117 (1)
$R_4C_4-R_4C_5$	1.37 (2)	$R_4C_2-R_4C_3-R_4C_4$	119 (1)
$R_4C_5-R_4C_6$	1.44 (2)	$R_4C_3-R_4C_4-R_4C_5$	123 (1)
$R_4C_6-R_4C_1$	1.37 (2)	$R_4C_4-R_4C_5-R_4C_6$	118 (1)
		$R_4C_5-R_4C_6-R_4C_1$	119 (1)
		$R_4C_6-R_4C_1-R_4C_2$	123 (1)

Table V. Equations of Least-Square Planes[a] for Phenyl Rings and the Distance of the Atoms from Their Respective Planes for $[(C_6H_5)_4As]_2[Mo(mnt)_3]$

Atom	Dist, Å	Atom	Dist, Å
Ring 1: $-0.337x - 0.502y + 0.796z = 2.136$[b]			
R_1C_1	−0.021	R_1C_4	−0.004
R_1C_2	0.031	R_1C_5	0.005
R_1C_3	−0.019	R_1C_6	0.008
Ring 2: $-0.874x + 0.080y + 0.479z = -2.647$			
R_2C_1	−0.018	R_2C_4	−0.004
R_2C_2	0.004	R_2C_5	−0.020
R_2C_3	0.012	R_2C_6	0.031
Ring 3: $0.771x - 0.180y + 0.611z = 9.934$			
R_3C_1	0.009	R_3C_4	−0.004
R_3C_2	0.012	R_3C_5	0.003
R_3C_3	−0.004	R_3C_6	0.003
Ring 4: $-0.266x + 0.963y + 0.038z = 0.787$			
R_4C_1	−0.009	R_4C_4	0.013
R_4C_2	0.013	R_4C_5	−0.005
R_4C_3	−0.015	R_4C_6	0.004

[a] Calculated with program MOLECULAR GEOMETRY. [b] Orthorhombic coordinates.

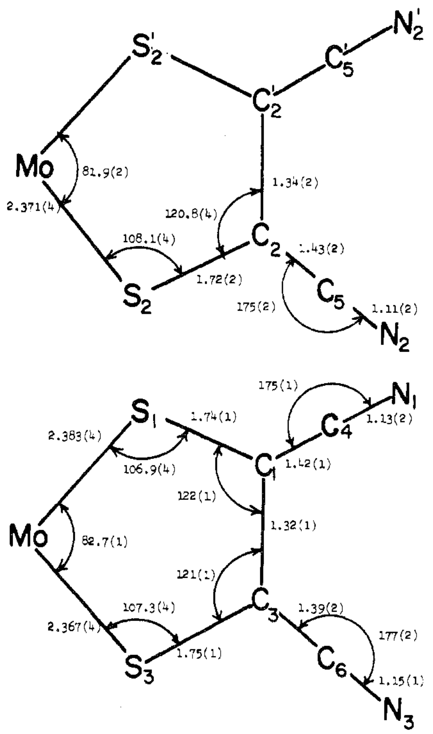

Figure 3. Distances and angles in the chelate rings for the $Mo(mnt)_3{}^{2-}$ structure.

and 60° in the perfect octahedron. An additional measure of the shape of the coordination polyhedron is the compression ratio s/h, where s is a side of the S_3 triangle and h is the perpendicular distance between triangles. Here, $s/h = 1.07$, a value between the prismatic (1.00) and octahedral (1.22) ratios. The twist angle and the compression ratio are related by the bite angle which in this case is 82°.

A further useful criterion in the discussion of coordination geometry is the average L-M-L angle (trans) involving pairs of donor atoms which are farthest apart. This angle averages 136 ± 1° in the known trigonal prisms and 180° in the perfect octahedron. The average trans angle for $Mo(mnt)_3{}^{2-}$ is 156°, again in between the limiting geometries. This number is marginally closer to the trigonal-prismatic geometry. However, achieving a perfect octahedron is not possible assuming the observed M-S distance and bite. Thus, the bite angle is 82° and the closest the trans angle could approach to the ideal octahedral value is 172°. [The complement of the chelate (bite) angle must equal the supplement of the trans angle.] Using this corrected value for the octahedral complex, the structure shows itself to be near midway between the limits.

Other possible criteria for describing the $Mo(mnt)_3{}^{2-}$ anion arise from consideration of dihedral angles between various planes in the MoS_6 polyhedron and the ligands. For example, the dihedral angles as defined by two intersecting S-Mo-S planes should be 120° in the trigonal prism and 90° (not considering the chelate constraint) in the perfect octahedron. Here we find the two independent angles are 109 (S_1-Mo-S_3 *vs.* $S_1{}'$-Mo-$S_3{}'$) and 114° (S_1-Mo-S_3 *vs.* S_2-Mo-$S_2{}'$). Additionally, the dihedral angles between the S_3 planes and the S-Mo-S plane of one chelate ring should have very different values in the two limiting cases. This angle should be 90° in the prism and is calculated as 59° in the octahedron. The angles found in $Mo(mnt)_3{}^{2-}$ are 79 (S_2-S_3-$S_1{}'$ *vs.* S_2-Mo-$S_2{}'$), 72 (S_2-S_3-$S_1{}'$ *vs.* S_1-Mo-S_3), and 71° (S_2-S_3-$S_1{}'$ *vs.* $S_1{}'$-Mo-$S_3{}'$). Once again a structure midway between the octahedron and the trigonal prism is apparent.

The mnt ligand atoms are nearly planar as shown by the least-squares planes in Table VI. Also, the Mo atom lies virtually on the plane formed by each ligand (see Table VI). The average dihedral angles of ~2° between S-Mo-S planes and the rest of the ligand reveal no significant distortions from planarity. The net closeness of the ligands to the "dithiolate" form is shown by the average S-C and C-C (non-cyano carbon) bond distances of 1.74 and 1.33 Å, respectively.

$[(C_6H_5)_4As]_2[W(mnt)_3]$. The crystal and molecular structure of $[(C_6H_5)_4As]_2[W(mnt)_3]$ is extremely similar to that of $[(C_6H_5)_4As]_2[Mo(mnt)_3]$. The tungsten atom is

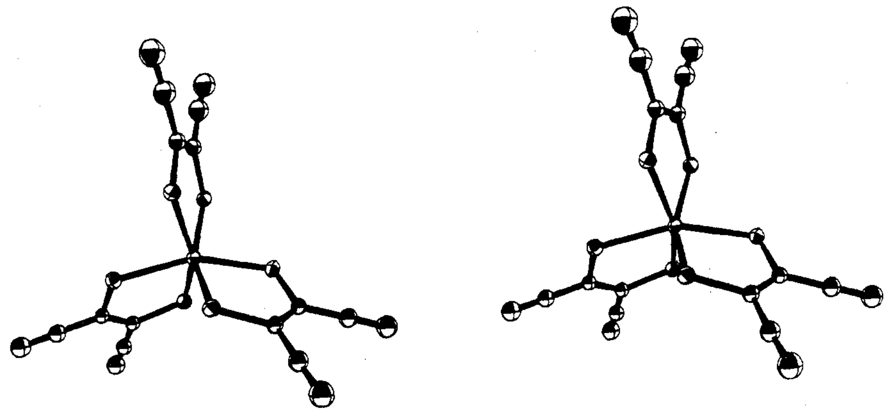

Figure 4. A stereoview of the anion $Mo(mnt)_3{}^{2-}$.

Table VI. Planes through the $Mo(mnt)_3{}^{2-}$ Anion[a]

Atom	Dist, Å	Atom	Dist, Å
Ligand Related by the Twofold Axis plus the Metal $-0.587x + 0.806y + 0.0762z = 2.512$			
N_1	0.016	S_3	−0.032
C_4	−0.004	C_3	0.021
C_1	0.027	C_6	0.056
S	−0.027	N_3	0.029
Mo	0.001		
Ligand on the Twofold Axis plus the Metal $0.790x - 0.000y + 0.613z = 2.861$			
N_2	−0.109	S_2	0.009
C_5	−0.054	Mo	0.000
C_2	−0.032		

[a] Orthorhombic coordinates.

surrounded by six sulfur-donor atoms at an average distance of 2.371 Å forming a WS_6 polyhedron which is, by all the criteria mentioned in the Mo discussion, in between the octahedral and trigonal-prismatic geometries. Looking down the pseudo threefold axis we find two approximately parallel S_3 triangles (dihedral angle = 178.7°), with an average side of 3.193 Å. These S_3 triangles are separated by 2.97 Å and twisted 28° (ϕ) with respect to the trigonal prism.[35] The mnt ligands are planar and have "dithiolate" dimensions. The four phenyl rings stem in a tetrahedral fashion from the arsenic atom. For the purpose of description and discussion the reader is referred to Figure 5 and Tables VII and VIII which contain selected distances, angles, least-squares planes, and dihedral angles for $[(C_6H_5)_4As]_2[W(mnt)_3]$. A comparison of the MS_6 (M = Mo, W) polyhedra shows the WS_6 to be slightly compressed and twisted (toward the octahedron) with respect to the MoS_6 framework. This comparison is, however, probably meaningless, since the structural differences are, for the most part, less than the estimated standard deviations.

Crystal Packing. These two diamagnetic complexes serve as ideal hosts for electron paramagnetic resonance studies[24] of the isomorphous V complex (and possibly others as well). The packing of *only the* anions is shown in the stereoview of the unit cell in Figure 6. The twofold axes are along the *b* direction of the unit cell. The pseudo-threefold axis for each molecule lies in the *ac* plane and the four axes constitute two parallel pairs related by a glide plane. Thus, in the eyes of an experiment (such as a single-crystal epr study) which can identify the threefold axis, the molecules in the unit cell are inequivalent except in specific orientations of the crystal.[24]

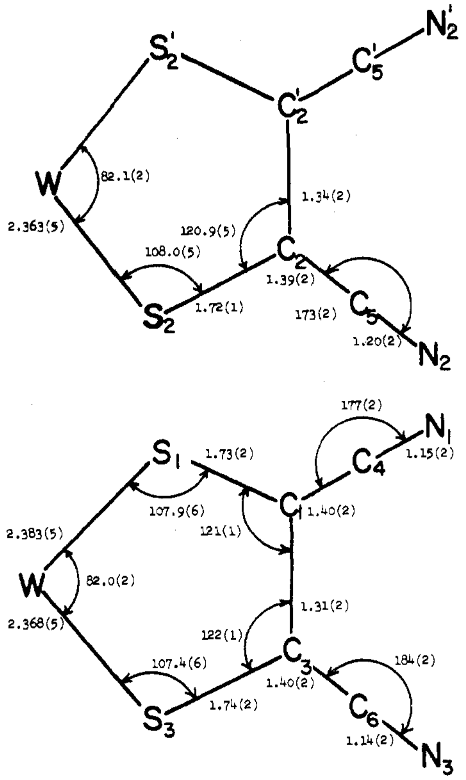

Figure 5. Distances and angles in the chelate rings for the $W(mnt)_3{}^{2-}$ structure.

Discussion

The structures reported in this paper establish the coordination geometry for reduced tris(dithiolate) complexes of the second and third transition row elements. Previous studies[15-17] had established that dianionic and trianionic tris(dithiolate) complexes of first-row transition metals possessed either octahedral or "in-between" structures. Thus, the structural shift from the trigonal prism toward the octahedron as electrons are added to a complex seems to be general for all three transition rows. The simplest interpretation of this trend recalls that the octahedron is that coordination geometry which minimizes interligand repulsions. As electrons are added to the system, that geometry which minimizes repulsion becomes favored. An alternate, but not exclusive (of the previous) explanation involves inter-donor-atom bonding forces. Thus, the original suggestion[9] of weak intersulfur atom bonding forces as stabilizing factors for the trigonal prism and square plane has received considerable support of late. Eisenberg's determination[14] of the structure

---

[35] The compression ratio $(s/h)^{22}$ equals 1.08, quite close to the value of 1.09 for the Mo complex.

Table VII. Selected Distances, Angles, and Dihedral Angles in $[(C_6H_5)_4As]_2[W(mnt)_3]$

For $(C_6H_5)_4As^+$

Atoms	Dist, Å	Atoms	Angle, deg
$As-R_1C_1$	1.91 (1)	$R_1C_1-As-R_2C_1$	113 (1)
$As-R_2C_1$	1.88 (1)	$R_1C_1-As-R_4C_1$	107 (1)
$As-R_3C_1$	1.89 (1)	$R_2C_1-As-R_3C_1$	109 (1)
$As-R_4C_1$	1.89 (1)	$R_3C_1-As-R_4C_1$	107 (1)
		$R_1C_1-As-R_3C_1$	110 (1)
		$R_4C_1-As-R_2C_1$	110 (1)

For $W(mnt)_3{}^{2-}$

Dihedral planes	Dihedral angle, deg	Atoms		Angle, deg
$(S_1-W-S_3)-(S_1'-W-S_3')$	109.8 (1)	S_2-W-S_3'		154.5 (2)
$(S_1-W-S_3)-(S_2-W-S_2')$	113.5 (1)		("trans")	
$(S_2-W-S_2')-(S_2-S_3-S_1')$	76.9 (1)	S_1-W-S_1'		156.2 (2)
$(S_1-W-S_3)-(S_2-S_3-S_1')$	71.5 (1)	$S_1'-S_2-S_3$		60.3 (1)
$(S_2-W-S_2')-(S_2-S_2C-S_2')$	0.1 (5)	$S_3-S_1'-S_2$	("S_3")	61.7 (1)
$(S_1-W-S_3)-(S_1-S_3C-S_3)$	3.1 (5)	$S_2-S_3-S_1'$		58.0 (1)
$(S_1-W-C_3)-(S_1-S_1C-S_3)$	2.8 (5)			
$(S_1'-S_2-S_3)-(S_1-S_2'-S_3')$	178.6 (2)			
$(S_1'-S_2-S_3)-(S_1-S_2'-S_3')$	1.4 (2)			

Table VIII. Equations for Selected Best Least-Squares Planes for $W(mnt)_3{}^{2-}$ and the Distances of the Atoms from Their Respective Planes

Atom	Dist, Å	Atom	Dist, Å
Plane through the mnt Ligand and Metal Related by the Twofold Axis $-0.583x + 0.810y + 0.073z = 2.511$			
N_1	−0.024	S_3	−0.032
C_4	0.033	C_3	0.026
C_1	0.022	C_6	0.059
S_1	−0.027	N_3	0.039
W	0.000		
Plane through the mnt Ligand and Metal Located on the Twofold Axis $0.785x + 0.000y + 0.619z = 2.887$			
N_2	−0.087	S_2	0.005
C_5	−0.012	W	0.000
C_2	0.004		

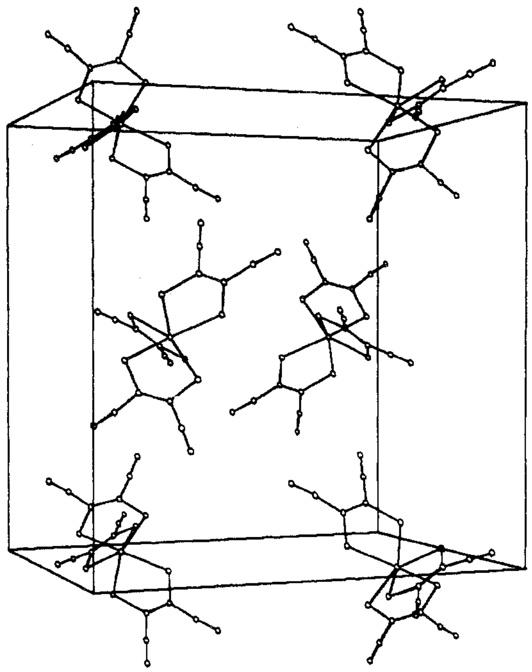

Figure 6. The arrangement of the $Mo(mnt)_3{}^{2-}$ anions in the unit cell. (The *c* axis is horizontal, *a* is vertical, while *b* is going into the paper. The molecular C_2 is parallel to *b*.)

of $Mo[Se_2C_2(CF_3)_2]_3$ showed surprisingly short interligand Se-Se distances while structural work on polysulfur cations[36] reveals the likelihood of weak bonding forces at large S-S (2.6-3.2 Å) distances in these *oxidized* species. Thus, it is in the oxidized tris(dithiolene) species that the S-S interactions are most important and since interligand S-S contacts are closer in the eclipsed trigonal prism than in the staggered octahedron, the trigonal prism is favored for the oxidized complexes. A final explanation for the trend can be offered in terms of the molecular orbital scheme previously devised to explain the bonding in neutral prismatic tris(dithiolene) complexes.[9] In that scheme the lowest empty molecular orbital in the neutral Mo and W complexes is of a_1' symmetry. This orbital is an antibonding combination of metal d_{z^2} and ligand in-plane π orbitals.[37] The bonding interaction corresponding to this orbital has been postulated as a possible stabilizing factor for the trigonal prism. Thus, the d_{z^2}-in-plane π overlap is virtually completely destroyed by twisting from the trigonal prism. Upon reducing the neutral Mo and W complexes by two electrons, both electrons enter this a_1' antibonding orbital. Since this counteracts the M-S bonding features of this interaction, the complex is now able to twist toward the octahedron. (It should be noted that the a_1 symmetry interaction contains a totally symmetric linear combination of sulfur in-plane π orbitals and thus represents at least formally a sulfur-sulfur bonding interaction. Upon twisting from the trigonal prism to the octahedron S-S overlap is also reduced and this diminishes the S-S bonding.)

At this point one might rightly question why the reduced complexes do not twist all the way to the octahedron. Here the constraint of the relatively rigid ligand system must be considered. Thus, as discussed in detail elsewhere,[21] the reduced complex ions $Mo(mnt)_3{}^{2-}$ and $W(mnt)_3{}^{2-}$ could not twist further toward the octahedron (assuming constant M-L distance and bite) without also producing a further trigonal compression. It would seem that such a compression is not disallowed by the geometric constraints of the problem. Rather, an explanation must be sought in the detailed description of the bonding in these complexes. One could speculate that some of the factors stabilizing the trigonal prism are still at work and that the resultant geometry is a compromise chosen by nature when the factors favoring the octahedron or the trigonal prism are closely balanced. (For example, residual S-S bonding of a_1 symmetry may be partially preserved in the in between structure.) We note that the situation found here is vastly different from that found in tris complexes of 1,1-dithiolate and other short bite ligands. In these cases complexes with twist angles between the octahedron and the trigonal prism are found but these complexes are also highly compressed with respect to the octahedron. By several criteria, the distortions from the octahedron in these cases can be viewed as a direct consequence of the short and rigid bite of the ligand. As the above discussion has indicated, and as Kepert[23] has also shown, the same cannot be said of the nontrigonal prismatic tris(dithiolene) complexes.

Another structural question can be raised with respect to these complexes. Will it be possible to isolate a given tris(dithiolene) complex in both trigonal-prismatic and nontrigonal-prismatic form? It seems reasonable that the struc-

---

[36] R. J. Gillespie and J. Passmore, *Accounts Chem. Res.*, 4, 413 (1971).

[37] The in-plane π orbitals are sulfur orbitals which lie in the plane of the ligand as defined by SCCS.

ture found in the present case is the most stable form of the complex. However, it remains possible that a trigonal prism may be at a local minimum in the potential energy surface which describes the intramolecular isomerization processes in these complexes. If this is the case and the barrier between the trigonal prism and the octahedron is sufficiently high, then it should be possible to isolate these two geometric isomers for a given complex. It should then also be possible to resolve the nonprismatic complex into *d* and *l* forms. In the crystal structure reported here there are of course two *d* and two *l* isomers in each unit cell. If, on the other hand, as seems more likely (from admittedly negative evidence), there is but one distinct energy minimum for any given complex, then only one geometry will be found for each complex. The nonprismatic structures will have two equivalent minima representing *d* and *l* forms. Whether any of the complexes in question is resolvable is a question which awaits an experimental answer.

The structures of $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$ complexes as determined here are quite similar to the averaged structure of $V(mnt)_3^{2-}$ as determined in its bis$[N(CH_3)_4^+]$ salt.[17] The latter structure is, however, highly distorted, but we note that $[(C_6H_5)_4As]_2[V(mnt)_3]$ crystals are isomorphous[16,24] to its Mo and W analogs. It seems reasonable that despite earlier contentions to the opposite[17] the high degree of distortion of the $V(mnt)_3^{2-}$ anion in the bis$[N(CH_3)_4^+]$ salt may be due to the small size and more stringent packing requirements of the cation. It is significant, however, that the averaged (to D_3) structure has dimensions (twist angle and compression ratio)[21] quite similar to those reported here. Thus, we conclude that the structures of $M(mnt)_3^{2-}$ complexes (M = V, Cr, Mo, W, and Re) are all quite similar.

Despite the identity of the structures there are some distinct differences in magnetic and spectral properties to be discussed. Thus, $Cr(mnt)_3^{2-}$ shows a magnetic moment corresponding to two unpaired electrons, while the $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$ species are diamagnetic. Considering the ligands as dianionic dithiolates (as seems reasonable from the observed dimensions in these complexes) these are M(IV), d^2 systems. The diamagnetism of the Mo and W species was initially taken to indicate a trigonal-prismatic structure for these complexes.[38] It is apparent that all the diamagnetism reveals is that the complex cannot be very close to octahedral where near degeneracy of a_1 and e levels (derived from t_{2g}) could lead to two unpaired electrons. The experimental results can be accommodated in two ways within D_3 symmetry. Thus, for the Cr complex either the e level is lowest or the a is lowest but the e level is sufficiently close to allow the high-spin state. For the Mo and W complexes the results can be explained (within the ligand field argument being considered) by having the a_1 orbital lowest and sufficiently below e to be doubly occupied. The extent to which the structure must deviate from an octahedron to achieve this (t_{2g}) splitting is not at all clear. Thus, diamagnetism cannot in any way be used as a structural diagnostic in these or similar systems.

We now turn to the electronic spectra of the Mo and W species. We note first that the spectrum in each case does not change on going from the solid state to solution. We therefore infer that the solution structures are similar to those determined here in the solid state. However, the spectra of the Mo and W complexes differ grossly from one another. The W complex is red and has five peaks below 30,000 cm^{-1} with the lowest at 17,540 cm^{-1}. The Mo complex is green and shows four peaks below 30,000 cm^{-1} with the lowest at 14,980 cm^{-1}. This result is in sharp contrast to the neutral isostructural tris(dithiolene) species which display gross spectral similarities. It remains possible, however, that the electrons undergoing transition are more closely involved with metal orbitals in the dianionic than in the neutral complexes. This would lead to the absorption band positions being a much stronger function of metal for the dianions. In any event, it is reasonable that while spectral similarities are best interpreted in terms of structural similarities, spectral differences of the types observed here do not necessarily imply structural differences.

Registry No. $[(C_6H_5)_4As]_2\{Mo[S_2C_2(CN)_2]_3\}$, 25595-41-9; $[(C_6H_5)_4As]_2\{W[S_2C_2(CN)_2]_3\}$, 25595-42-0.

Acknowledgment. We are grateful to Professor Richard Eisenberg of Brown University for providing crystallographic programs and a preprint of ref 14. We thank Dr. Y. Okaya for assistance with the diffractometer data collection. This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Foundation of the State University of New York, NSF Institutional Grant No. 31-8302A, and the Stony Brook Computer Center.

---

[38] A. Callaghan, A. J. Layton, and R. S. Nyholm, *Chem. Commun.*, 399 (1969).