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Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G2E1

Trigonal-Prismatic vs. Octahedral Coordination in a Series of Tris(benzene-1,2-dithiolato) Complexes. 1. Crystal and Molecular Structure of Tris(benzene-1,2-dithiolato)molybdenum(VI), $Mo(S_2C_6H_4)_3$[1]

MARTIN COWIE and MICHAEL J. BENNETT*

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The structure of $Mo(S_2C_6H_4)_3$ has been determined crystallographically and consists of four discrete molecules of the complex in the unit cell (space group *Pnam*, a = 16.093 (3) Å, b = 10.177 (1) Å, c = 11.906 (2) Å). Observed and calculated densities are 1.74 (2) and 1.75 g cm^{-3}, respectively. The molybdenum atoms occupy the 4(c) special positions and the molecules therefore have site symmetry m. On the basis of 1050 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ the structural data were refined by full-matrix, least-squares techniques to R = 0.035 and R_w = 0.034. The molybdenum atoms are each surrounded by six sulfur atoms in an almost perfect trigonal-prismatic coordination, with the two triangular faces of the prism being related by the crystallographic mirror plane. The dithiolene ligands span the three edges of the prism connecting the two triangular faces. The complex is distorted from ideal D_{3h} symmetry because of bending of the S_2C_6 ligand planes from the corresponding MoS_2 planes by 13.1, 21.1, and 30.0°. Some relevant average molecular parameters are Mo–S = 2.367 (6) Å, S–S(intraligand) = 3.110 (8) Å, S–S(interligand) = 3.091 (15) Å, and S–C = 1.727 (6) Å.

Introduction

The discovery of trigonal-prismatic (TP) coordination in a series of 1,2-dithiolene[2] complexes, $ReS_6C_6Ph_6$[3] (Ph = C_6H_5), $MoS_6C_6H_6$,[4] and $VS_6C_6Ph_6$,[5] heralded the first examples of nonoctahedral coordination being displayed by six-coordinate molecular complexes. Although TP coordination had been observed much earlier in MoS_2 and WS_2,[6] and later in NiAs,[7] these latter compounds were infinitely extended lattices and molecular packing was believed responsible for their unusual geometry.[8] It therefore was of interest to determine what factors were responsible for the preference of TP over octahedral coordination in these dithiolene complexes. In all three dithiolene prisms an amazing constancy in prism dimensions was observed with all having inter- and intraligand S–S distances of ca. 3.08 and 3.06 Å, respectively, and M–S (M = metal) distances of ca. 2.33 Å. The shortness of these "nonbonded" S–S contacts led to the conclusion that S–S bonding was involved in stabilizing the prism.[9,10] The similarity in the M–S distances, although the covalent and ionic radii of molybdenum and rhenium were 0.07 Å greater than those of vanadium, was thought to be a consequence of the S–S bonding.

In an attempt to explain the trigonal-prism stability Gray et al. proposed a molecular orbital scheme in which they attributed the prism stability to two features.[10] The first, overlap of the sulfur π_h orbitals (sulfur sp^2 hybrid orbitals at 120° to the M–S and S–C σ orbitals) with the metal d_{z^2} orbitals, gives rise to a stable $2a_1'$ orbital, which is always filled, and an empty antibonding $3a_1'$ orbital. The second interaction, between the ligand π_v orbitals (perpendicular to the ligand plane) and the metal $d_{x^2-y^2}$ and d_{xy} orbitals, gives rise to the stable 4e′ orbital, which is also occupied, and the empty 5e′ antibonding level. It was the occupancy of these stable orbitals to which Gray attributed the prism stability.

The subsequent structural determinations of $[Me_4N]_2[VS_6C_6(CN)_6]$[11] (Me = CH_3) and $[Ph_4As]_2[MoS_6C_6(CN)_6]$[12] showed non-trigonal-prismatic coordination and both in fact had geometries approximately midway between the TP and octahedral limits. In the molybdenum dianion the double occupancy of the $3a_1'$ molecular orbital, which is antibonding relative to prism stability, was believed to be an important factor in the distortion from TP coordination. In the vanadium dianionic complex the distortion was much more irregular and not readily predictable by Gray's scheme. However reversals in several of the molecular orbital levels have been considered[13,14] and these may account for the distortion. In addition, the anion in $[Ph_4As]_2[FeS_6C_6(CN)_6]$[18] was found to have an almost undistorted octahedral coordination. In this anion the destabilization of the prism can again be attributed to population of the antibonding $3a_1'$ level. The octahedral coordination is further stabilized relative to the TP because of additional occupancy of the 5e′ level which is also antibonding with respect to the prism.

The dianionic tris(dithiolenes) therefore lend support to Gray's hypothesis that the ligand π_h and metal d_{z^2} interaction is significant in stabilizing the prism. However no structural evidence was available testing the importance of the ligand π_v and metal d_{xy}, $d_{x^2-y^2}$ interaction. It seemed reasonable to expect that, in view of the proximity in energy of the 4e′ molecular orbital and the metal d orbitals, the 4e′ level would be sensitive to changes in d-orbital energies. Thus destabilizing the metal d orbitals might be expected to destabilize the resulting 4e′ level with a resulting decrease in prism stability. In this respect the series of compounds to be reported in this and the following two papers—$Mo(S_2C_6H_4)_3$, $[Ph_4As][Nb(S_2C_6H_4)_3]$, and $[Me_4N]_2[Zr(S_2C_6H_4)_3]$—is especially useful. The molybdenum and niobium complexes have electronic spectra[16,17] similar to those observed in previous TP complexes and this type of spectrum was believed characteristic of TP coordination. The spectrum of the zirconium complex,[17] however, is vastly different, implying a non-trigonal-prismatic coordination. Thus it was believed possible to test the importance of the 4e′ molecular orbital level in prism stability since in this isoelectronic series, from a molecular orbital viewpoint, only the metal d-orbital energies are changing, and this change in d-orbital energies seemed to be strongly influencing prism stability as witnessed by the differing electronic spectra. The determination of the structures of the three

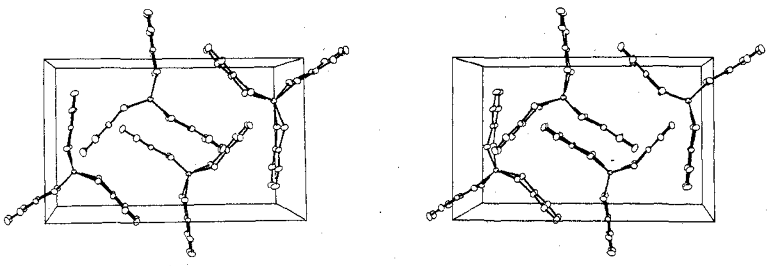

Figure 1. Stereodrawing of a unit cell of $Mo(S_2C_6H_4)_3$. The x axis is horizontal to the right, the y axis is vertical, from the bottom to the top of the page, and the z axis is almost perpendicular to the paper toward the reader. Vibrational ellipsoids are drawn at the 20% level.

isoelectronic 1,2-benzenedithiolene complexes mentioned above was therefore undertaken to gain further information on factors influencing trigonal-prism stability. In this paper we report the first complex in this series, $Mo(S_2C_6H_4)_3$.

Experimental Section

Dark green crystals of $Mo(S_2C_6H_4)_3$ suitable for x-ray diffraction study, prepared by the reaction of molybdenum pentachloride with benzenedithiol,[10] were kindly supplied by Professor J. Takats and Dr. J. L. Martin. Preliminary photography revealed *mmm* Laue symmetry, indicating an orthorhombic space group. The systematic absences as determined from Weissenberg ($0kl$, $1kl$; Cu Kα x radiation) and precession ($h0l$, $h1l$, $hk0$, $hk1$; Mo Kα x radiation) photographs are, for $0kl$, $k + l = 2n + 1$ and, for $h0l$, $h = 2n + 1$, consistent with the space groups *Pnam* and $Pna2_1$. Precise lattice parameters were obtained at 22 °C from a least-squares refinement of the setting angles of 12 reflections which were accurately centered on a Picker diffractometer using the Cu Kα_1 peak (λ 1.54051 Å) and a narrow source. The cell parameters and their standard deviations are $a = 16.093$ (3) Å, $b = 10.177$ (1) Å, and $c = 11.906$ (2) Å.

The observed density (1.74 (2) g cm^{-3}), obtained by flotation in aqueous zinc bromide solution, is in good agreement with the calculated value of 1.75 g cm^{-3}, obtained assuming four molecules of mol wt 516.6 per unit cell of volume 1952.8 Å^3. For space group $Pna2_1$ there are four general equivalent positions and no restrictions are possible. However for *Pnam* there are eight general equivalent positions so the molecules are restricted to lie either on the mirror planes or on inversion centers. The tris-chelate structure cannot have an inversion center; hence for space group *Pnam*, the molecule must possess symmetry *m*.

Intensity data were collected on the Picker automated four-circle diffractometer using Ni-filtered Cu Kα radiation and using a 2° takeoff angle. The crystal was aligned in a general orientation but with its a^* axis approximately coincident with the diffractometer ϕ axis. The crystal faces were identified and the perpendicular distances between parallel faces of the same form were measured as follows: {100}, 0.206 mm; {010}, 0.055 mm; {001}, 0.077 mm. A coupled 2θ–ω scan was used with a 2θ scan speed of 1°/min to collect all reflections with $2\theta \leq 125°$. The peak scan was approximately 2°, increasing as the α_1–α_2 resolution increased. Stationary-background counts of 40 s were collected on either side of the peak. The detector was a scintillation counter and was used in conjunction with a pulse height analyzer tuned to accept 95% of the Cu Kα peak. Three standard reflections were collected automatically every 100 reflections. In addition data collection was interrupted periodically to collect a further five standard reflections to investigate possible decomposition. No significant decomposition was observed over the duration of the data collection. Of the 1806 reflections collected, 1050 were significantly above background with $F_o^2 \geq 3\sigma(F_o^2)$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects. Terms used in the Zachariasen extinction correction were calculated at this stage.[18] Standard deviations, $\sigma(F)$, in the structure factors were computed[20] using a "p factor" of 0.03.

The linear absorption coefficient using Cu Kα radiation is 110.67 cm^{-1} giving rise to a range of transmission factors between 0.577 and 0.310.

Solution and Refinement of Structure

The structure was refined[21] by full-matrix, least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight w is $1/\sigma^2(F)$. The agreement indices R and R_w are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors by Cromer and Mann[22] were used for all atoms except hydrogen for which the values of Stewart et al.[23] were used. Anomalous dispersion terms of Cromer[24] for Mo and S were applied to the calculated structure factors.

The molybdenum and sulfur positions were obtained from a sharpened Patterson map. Two solutions are possible, corresponding to the Mo positions (0.09, 0.25, 0.25) or (0.16, 0.25, 0.25). This ambiguity arises because the accidentally "special" y coordinate results in a failure to differentiate Harker vectors of the form ($^1/_2 - 2x$, $^1/_2$, $^1/_2$) and ($2x$, $2y$, $^1/_2$). Although the space groups *Pnam* and $Pna2_1$ cannot be differentiated in the Patterson map, solely on the basis of Mo–Mo vectors, the Mo–S and S–S vectors indicated that the molecule had mirror symmetry, or at least approximate mirror symmetry, so the centrosymmetric space group *Pnam* was chosen and later verified by successful refinement of the model. The correct solution for the Mo and S positions, based on either of the two above possibilities for the Mo position, was obtained by refinement of both models. The model based on the Mo position (0.09, 0.25, 0.25) refined to $R = 0.349$ and $R_w = 0.435$ after one cycle whereas the alternate solution resulted in $R = 0.424$ and $R_w = 0.516$. In these refinements the thermal parameters were not refined. Refinement of the former model, varying the thermal parameters, yielded $R = 0.209$ and $R_w = 0.294$ thus confirming this as the probable solution.

A difference Fourier synthesis phased on the correct Mo and S positions clearly indicated all carbon positions. Inclusion of these in the least-squares refinement resulted in $R = 0.079$ and $R_w = 0.086$. The correction for absorption further reduced the agreement indices to $R = 0.065$ and $R_w = 0.075$. Refining the Mo and S atoms anisotropically then gave $R = 0.050$ and $R_w = 0.062$. At this stage a difference Fourier map showed clearly the positions of all hydrogen atoms. These were then included in all subsequent refinements, their idealized positions being calculated from the carbon positions, using a C–H distance of 0.98 Å, and their thermal parameters estimated as 15% greater than those of their attached carbon atoms. The hydrogen parameters were added as fixed contributions to the refinement yielding $R = 0.046$ and $R_w = 0.051$. Extinction corrections were applied at this time since a comparison of $|F_o|$ and $|F_c|$ for low-angle reflections suggested the problem may exist. Verification of the importance of the extinction correction is evident in the results of the refinements before and after the correction. Before correction all reflections with $(\sin\theta)/\lambda \leq 0.08$ were rejected from the refinement on the basis that $||F_o| - |F_c||/\sigma(F) > 5.0$, and in all cases $|F_o|$ was less than $|F_c|$ for these reflections. After the extinction correction, only one of these previously rejected reflections was still rejected. The final value of the extinction scale factor is 2.371×10^{-6}. The final model in which all atoms were refined anisotropically gave $R = 0.035$ and $R_w = 0.034$. In the final least-squares cycle 116 parameters were varied and the error in an observation of unit weight was 1.162 electrons.

The final values of $10|F_o|$ and $10|F_c|$, in electrons, are shown in Table I.[25] The final positional and isotropic thermal parameters[26] for all atoms are shown in Table II. Standard deviations are estimated from the inverse matrix obtained from the last refinement. The anisotropic thermal parameters[27] are shown in Table III.

Description of Structure

$Mo(S_2C_6H_4)_3$ crystallizes with four monomeric units in the cell as is shown in the stereoview of the packing in Figure 1. A three-dimensional view of the molecule, showing the numbering scheme, is represented in Figure 2. Hydrogen atoms, which are not shown, have the same number as their

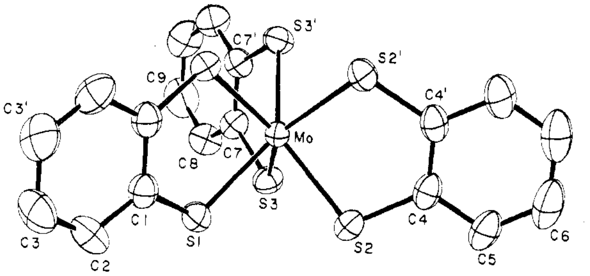

Figure 2. A molecule of $Mo(S_2C_6H_4)_3$ showing the numbering scheme. Hydrogen atoms are not shown. Vibrational ellipsoids are drawn at the 50% level.

Table II. Atom Coordinates and Isotropic Temperature Factors

Atom	x^a	y	z	B, Å^2
Mo	0.088 15 (5)	0.258 86 (7)	$^1/_4$	2.46^b
S(1)	0.007 7 (1)	0.137 1 (1)	0.3802 (1)	3.28^b
S(2)	0.063 2 (1)	0.428 6 (1)	0.3808 (1)	3.48^b
S(3)	0.193 9 (1)	0.204 7 (1)	0.3808 (1)	3.36^b
C(1)	−0.075 7 (4)	0.068 1 (5)	0.3096 (5)	3.19^b
C(2)	−0.139 0 (5)	0.001 6 (7)	0.3648 (7)	4.51^b
C(3)	−0.198 9 (4)	−0.063 8 (7)	0.3087 (7)	4.94^b
C(4)	0.078 7 (4)	0.574 1 (5)	0.3091 (5)	3.32^b
C(5)	0.087 2 (5)	0.693 6 (6)	0.3659 (6)	4.55^b
C(6)	0.095 9 (5)	0.808 0 (6)	0.3088 (7)	6.00^b
C(7)	0.255 7 (4)	0.095 1 (6)	0.3091 (5)	3.26^b
C(8)	0.307 3 (4)	0.006 7 (7)	0.3677 (7)	4.30^b
C(9)	0.356 5 (4)	−0.080 1 (7)	0.3096 (7)	5.30^b
H(2)	−0.138 9	0.001 6	0.4488	5.2
H(3)	−0.243 8	−0.112 1	0.3518	6.0
H(5)	0.087 3	0.693 7	0.4499	5.2
H(6)	0.102 3	0.892 1	0.3514	6.0
H(8)	0.307 4	0.006 6	0.4516	5.2
H(9)	0.392 5	−0.142 9	0.3523	6.0

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] These values are equivalent isotropic temperature factors[26] corresponding to the anisotropic thermal parameters shown in Table III.

attached carbon atom. Figure 3 shows the molecule viewed down its approximate threefold axis. In the packing diagram 20% probability ellipsoids of thermal motion are shown whereas Figures 2 and 3 show the 50% ellipsoids.

Intermolecular contacts are all normal, being comparable to the van der Waals contacts.

The sulfur atoms surround the molybdenum in an almost perfect trigonal-prismatic coordination with the dithiolene ligands radiating from the molybdenum atom in a "paddle-wheel" arrangement. The molecule deviates from approximate D_{3h} symmetry due to the bending of the $S_2C_6H_4$ planes from the MoS_2 planes by an average of 21.4°. In addition C_{3h} symmetry is not achieved due to the three differing $S_2C_6H_4$–MoS_2 dihedral angles (Figure 3). The molybdenum atom is located on the crystallographic mirror at $z = {}^1/_4$, with the two triangular faces of the prism being related by the mirror.

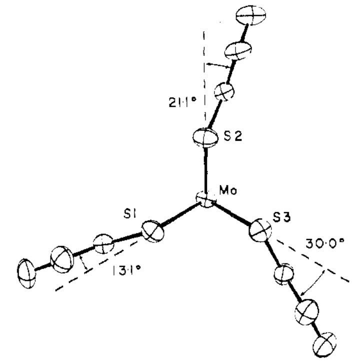

Figure 3. View of $Mo(S_2C_6H_4)_3$ projected down the approximate molecular threefold axis, showing the bend of the ligands. Vibrational ellipsoids are drawn at the 50% level.

Again, as was the case for the three previous trigonal-prismatic structures, $Re(S_2C_2Ph_2)_3$,[3] $Mo(S_2C_2H_2)_3$,[4] and $V(S_2C_2Ph_2)_3$,[5] the intra- and interligand sulfur–sulfur distances are approximately equal (3.110 (8) and 3.091 (15) Å, respectively, in the present study). For averaged quantities, the estimated standard deviation is the larger of an individual standard deviation or the standard deviation of a single observation as calculated from the mean. These agree favorably with those observed in other prisms and are especially close to those in $Mo(S_2C_2H_2)_3$ (3.10 and 3.11 Å).[28] It is interesting that the relative magnitudes of these intra- and interligand S–S distances are reversed compared to those in the other three dithiolene trigonal prisms, with the intraligand S–S distances being greater in the present study. This can be attributed to the constraint of the fixed ligand bite holding the intraligand sulfurs apart. That the ligand bite should be greater in the benzenedithiols than in the ethylenedithiols is apparent since the C–C distances in the former are longer, thereby ensuring a larger bite.

The mean Mo–S distance (2.367 (6) Å), although similar to the metal–sulfur distances in other trigonal prisms, is significantly longer than their average of approximately 2.33 Å. In fact they are more closely matched by the metal–sulfur distances in the non-trigonal-prismatic species $[VS_6C_6(CN)_6{}^{2-}]$,[11] $[MoS_6C_6(CN)_6{}^{2-}]$,[12,29] and $[WS_6C_6(CN)_6{}^{2-}]$[29] (2.36 (1), 2.374 (8), and 2.371 (10) Å, respectively). This difference is probably due to the difference in ligands, all previous examples being substituted ethylenedithiol ligands. For this reason a comparison of intramolecular distances and angles will prove more worthwhile within the series of compounds which are the topic of this and the following two papers, i.e., $Mo(S_2C_6H_4)_3$, $[Ph_4As][Nb(S_2C_6H_4)_3]$, and $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$. In addition the molybdenum–sulfur distances are again shorter than those observed in the

Table III. Anisotropic Temperature Factors (Å^2)

Atom	$U_{11}{}^a$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.0389 (4)	0.0259 (3)	0.0287 (3)	−0.0003 (4)	0.0	0.0
S(1)	0.0489 (10)	0.0400 (8)	0.0356 (8)	−0.0053 (8)	−0.0006 (9)	0.0033 (8)
S(2)	0.0547 (11)	0.0364 (8)	0.0409 (9)	0.0026 (8)	0.0030 (9)	−0.0070 (8)
S(3)	0.0455 (10)	0.0461 (9)	0.0358 (8)	0.0015 (8)	−0.0049 (8)	−0.0027 (7)
C(1)	0.039 (4)	0.034 (3)	0.048 (4)	0.002 (3)	0.000 (3)	−0.001 (3)
C(2)	0.051 (5)	0.064 (5)	0.056 (5)	−0.006 (4)	0.014 (4)	0.016 (4)
C(3)	0.039 (4)	0.074 (5)	0.075 (6)	−0.019 (4)	0.012 (4)	0.008 (4)
C(4)	0.034 (4)	0.033 (3)	0.059 (4)	0.004 (3)	−0.002 (3)	−0.007 (3)
C(5)	0.057 (5)	0.040 (3)	0.075 (5)	0.015 (4)	0.004 (5)	−0.013 (4)
C(6)	0.079 (6)	0.037 (4)	0.111 (7)	0.011 (4)	0.005 (5)	−0.010 (4)
C(7)	0.034 (4)	0.044 (4)	0.046 (4)	−0.000 (3)	−0.002 (3)	−0.004 (3)
C(8)	0.048 (5)	0.061 (4)	0.054 (5)	0.005 (4)	−0.001 (4)	0.004 (4)
C(9)	0.045 (5)	0.068 (5)	0.088 (7)	0.011 (4)	−0.009 (4)	0.014 (4)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$.[27]

Table IV. Selected Distances (Å) in $Mo(S_2C_6H_4)_3$

Atoms	Distances		Atoms	Distances
Mo–S(1)	2.370 (2)	2.367 (6)	C(1)–C(1)′	1.419 (11)
Mo–S(2)	2.360 (2)		C(1)–C(2)	1.388 (8)
Mo–S(3)	2.371 (2)		C(2)–C(3)	1.349 (10)
S(1)–S(1)′[a]	3.100 (3)	3.110 (8)	C(3)–C(3)′	1.394 (16)
S(2)–S(2)′	3.115 (3)		C(4)–C(4)′	1.408 (12)
S(3)–S(3)′	3.114 (3)		C(4)–C(5)	1.398 (8)
S(1)–S(2)	3.099 (2)	3.091 (15)	C(5)–C(6)	1.355 (8)
S(1)–S(3)	3.074 (2)		C(6)–C(6)′	1.400 (16)
S(2)–S(3)	3.101 (2)		C(7)–C(7)′	1.408 (12)
S(1)–C(1)	1.731 (6)	1.727 (6)	C(7)–C(8)	1.410 (8)
S(2)–C(4)	1.728 (6)		C(8)–C(9)	1.373 (10)
S(3)–C(7)	1.721 (6)		C(9)–C(9)′	1.418 (16)

[a] Primed atoms are related by a mirror at $z = 1/4$.

1,1-dithiolato complexes, $Fe[S_2CN(n\text{-}C_4H_9)_2]_3$,[30] $Ru[S_2CN(C_2H_5)_2]_3$,[31] $Cr[S_2P(CH_3)_2]_3$,[32] and $V[S_2P(OC_2H_5)_2]_3$[33] (2.418 (7), 2.382,[28] 2.436 (10), and 2.45 (2) Å, respectively) although the molybdenum covalent radius is greater than any of these metal radii. Thus a difference in the metal–sulfur bonding between the 1,1-dithiolato and 1,2-dithiolene complexes is obvious with the latter having a stronger M–S bond. This is in agreement with the proposed metal–sulfur multiple bonding in the tris(1,2-dithiolenes).[34]

The sulfur–carbon distances (mean 1.727 (6) Å) are similar to those in the other trigonal prisms and are once again consistent with a great deal of S=C double-bond character, as witnessed by their similarity with the double-bonded S=C distance of 1.720 (9) Å in thiourea[35] and its derivatives[36] (1.67 (2)–1.75 (1) Å). The mean carbon–carbon distance (1.393 (23) Å) is similar to that observed in benzene[37,28] (1.392 Å) and in several disubstituted benzene compounds.[38] However in the benzene dithiol ligands in this structure there is a significant range in C–C distances (see Table IV and Figure 4). In addition, these distances are consistent with a tendency toward the dithioketonic limit (Figure 5). However caution must be used since, due to increasing thermal motion of the carbon atoms as the distance from the central atom (Mo) increases, the bonds will appear shorter due to libration of the rings. Thus the shortening of C_B–C_C (Figure 4) could be attributed to thermal motion. However thermal motion of this type cannot cause bond lengthening, so the longer C_A–C'_A bond remains as evidence of the tendency of the ligand toward its oxidized formulation. At this point it is convenient to note that the thermal parameters in this and similar structures all show an anomalous feature. In molecules of this type it would appear reasonable to expect that the general trend of thermal amplitudes increases steadily progressing outward from the center of gravity of the molecule. This assumes that the thermal motion is dominated by rigid-body motion. However the sulfur atoms have larger thermal parameters than their attached carbon atoms. This observation, which appears throughout the tris(dithiolene) complexes, suggests either the unsuitability of the scattering factors used or large vibration of the core of the molecule. This feature precludes any attempt at correction of these bond lengths for thermal motion and hence severely restricts the discussion of the ligand geometry with respect to the pattern of carbon–carbon bond lengths.

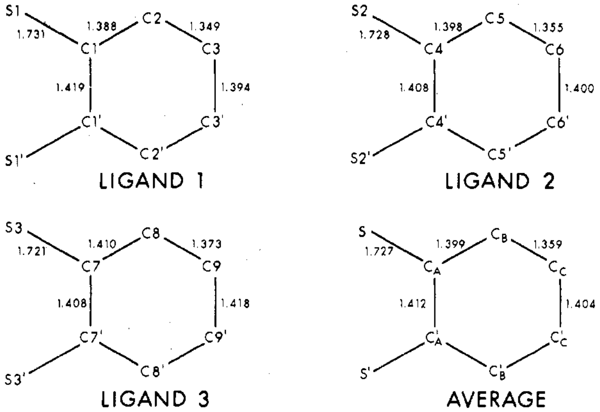

Figure 4. Dimensions within the dithiolene ligands.

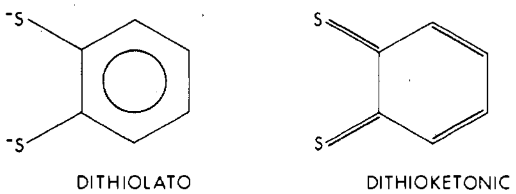

Figure 5. Dithiolato and dithioketonic limiting formulations for the benzene-1,2-dithiolato ligand.

The mean S–M–S angle involving trans sulfur atoms is 136 ± 1° in the known trigonal-prismatic structures[3-5,39] and, assuming the constraint of ligand bite, has been calculated[40] as approximately 172° in octahedral coordination. The mean value of 135.7 (11)° observed in $Mo(S_2C_6H_4)_3$ is clearly consistent with trigonal-prismatic coordination. The intra- and interligand S–Mo–S angles (82.1 (4) and 81.5 (6)°) are similar, as expected, and again agree with those found in other trigonal-prismatic structures. (See Table V.)

As mentioned, the molecule deviates from D_{3h} symmetry due to the bending of the ligand planes from the respective S–Mo–S planes, as shown in Figure 3, in which the molecule is viewed directly down the crystallographic c axis and approximate molecular threefold axis. Similar bending of the ligand planes was observed in $Mo(S_2C_2H_2)_3$[4] and also in $Mo(Se_2C_2(CF_3)_2)_3$,[39] where the ligand planes deviate from the MoS_2 and $MoSe_2$ planes by 18 and 18.6°, respectively. Although these deviations are uniform in these previous two examples, the molecules both having $3/m$ symmetry, they are

Table V. Selected Angles (deg) in $Mo(S_2C_6H_4)_3$

Atoms	Angles		Atoms	Angles
S(1)–Mo–S(1)′[a]	81.70 (8)	82.1 (4)	S(3)–C(7)–C(7)′	119.7 (2)
S(2)–Mo–S(2)′	82.57 (8)		C(2)–C(1)–C(1)′	118.2 (4)
S(3)–Mo–S(3)′	82.09 (8)		C(1)–C(2)–C(3)	122.1 (8)
S(1)–Mo–S(2)	81.85 (5)	81.5 (6)	C(2)–C(3)–C(3)′	119.7 (5)
S(1)–Mo–S(3)	80.85 (6)		C(5)–C(4)–C(4)′	118.9 (4)
S(2)–Mo–S(3)	81.89 (6)		C(4)–C(5)–C(6)	120.9 (7)
S(1)–Mo–S(2)′	136.17 (7)	135.7 (11)	C(5)–C(6)–C(6)′	120.1 (4)
S(1)–Mo–S(3)′	134.43 (6)		C(8)–C(7)–C(7)′	119.7 (4)
S(2)–Mo–S(3)′	136.51 (7)		C(7)–C(8)–C(9)	120.0 (7)
Mo–S(1)–C(1)	108.5 (2)		C(8)–C(9)–C(9)′	120.3 (5)
Mo–S(2)–C(4)	106.1 (2)		S(3)–S(1)–S(2)	60.30 (5)
Mo–S(3)–C(7)	103.9 (2)		S(1)–S(3)–S(2)	60.24 (5)
S(1)–C(1)–C(1)′	119.0 (2)		S(1)–S(2)–S(3)	59.46 (5)
S(2)–C(4)–C(4)′	119.6 (2)			

[a] Primed atoms are related by a mirror at $z = 1/4$.

Table VI

Deviations from Weighted Least-Squares Planes of Atoms to Determine the Planes (Å × 10^3)

	Plane							
Atom	1	2	3	4	5	6	7	8
Mo	0	0	0					
S(1)	0			0		5 (2)		
S(1)′	0				0	5 (2)		
S(2)		0		0			2 (2)	
S(2)′		0			0		2 (2)	
S(3)			0	0				0 (2)
S(3)′			0		0			0 (2)
C(1)						−74 (6)		
C(1)′						−74 (6)		
C(2)						−11 (7)		
C(2)′						−11 (7)		
C(3)						71 (8)		
C(3)′						71 (8)		
C(4)							−35 (6)	
C(4)′							−35 (6)	
C(5)							1 (7)	
C(5)′							1 (7)	
C(6)							28 (8)	
C(6)′							28 (8)	
C(7)								−8 (6)
C(7)′								−8 (6)
C(8)								6 (7)
C(8)′								6 (7)
C(9)								1 (7)
C(9)′								1 (7)

Planes[a] Determined

Plane	*A*	*B*	*C*	*D*
1	−0.6913	0.7225	0.0	−0.9227
2	−0.9740	−0.2266	0.0	1.9797
3	−0.3080	−0.9514	0.0	2.9444
4	−0.0016	−0.0019	1.0	4.5264
5	0.0016	−0.0019	1.0	1.4298
6	0.5094	−0.8605	0.0	−1.1429
7	−0.9899	0.1420	0.0	−0.3898
8	0.7424	0.6700	0.0	3.7136

[a] Plane equation: $AX + BY + CZ - D = 0$. X, Y, and Z are in angstroms and refer to the orthogonal coordinates along *a*, *b*, and *c**.

irregular for $Mo(S_2C_6H_4)_3$ with the ligand–MoS_2 dihedral angles being 13.1, 21.1, and 30.0° (mean 21.4°). Schrauzer[4,41] has attributed this as being due to intramolecular effects, saying that the sulfur may be in a state between sp^2 and sp^3 hybridization, with possible added stabilization from packing forces. In the present complex, molecular packing is probably a significant factor in bending the three ligands, as witnessed by the range in the dihedral angles shown above. However the intramolecular effects cited by Schrauzer cannot be overlooked in view of the similarity of these ligand-bend angles observed in all molybdenum dithiolene prisms. In this regard it is puzzling that the closely related $ReS_6C_6Ph_6$ and $VS_6C_6Ph_6$ have essentially planar ligand systems. The efficient packing in $Mo(S_2C_6H_4)_3$ can be seen in Figure 1 showing that the molecules fit together in a "gear-wheel" arrangement.

As shown in Table VII, a further indication of the regularity of the prism is given by the similarity of the angles between the three MoS_2 planes, all being close to the expected value of 120°. The two triangular faces of the prism are also almost exactly parallel.

The Mo–S–C angles (mean 106 (2)°) are comparable to the values of 109 (1) and 109.9 (6)° observed in $Re(S_2C_2Ph_2)_3$ and $V(S_2C_2Ph_2)_3$, however, they are smaller, again probably due to differences in the ligands. The S–C–C′ angles are in good agreement with the expected value of 120°. Similarly all C–C–C angles within the benzene rings are close to their expected value of 120°.

Table VII. Dihedral Angles between Selected Planes

Atoms in plane 1	Atoms in plane 2	Angle, deg
S(1), Mo, S(1)′	S(2), Mo, S(2)′	120.7
S(1), Mo, S(1)′	S(3), Mo, S(3)′	118.2
S(2), Mo, S(2)′	S(3), Mo, S(3)′	121.1
S(1), Mo, S(1)′	S(1), S(1)′, C(1), C(1)′, C(2), C(2)′, C(3), C(3)′	13.1
S(2), Mo, S(2)′	S(2), S(2)′, C(4), C(4)′, C(5), C(5)′, C(6), C(6)′	21.1
S(3), Mo, S(3)′	S(3), S(3)′, C(7), C(7)′, C(8), C(8)′, C(9), C(9)′	30.0

Although it was not unexpected that $Mo(S_2C_6H_4)_3$ had TP coordination, this molecular structure is important as a basis for comparison with the structures of the $[Nb(S_2C_6H_4)_3]^-$ and $[Zr(S_2C_6H_4)_3]^{2-}$ anions, since in $Mo(S_2C_6H_4)_3$ and $Mo(S_2C_2H_2)_3$ many of the differences in metric parameters can be attributed to the different ligands used. Therefore, in order to make quantitative comparisons in molecular parameters, it is preferable to use systems with identical ligands.

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Registry No. $Mo(S_2C_6H_4)_3$, 10507-76-3.

Supplementary Material Available: Table I, listing the observed and calculated structure amplitudes (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G2E1

Trigonal-Prismatic vs. Octahedral Coordination in a Series of Tris(benzene-1,2-dithiolato) Complexes. 2. Crystal and Molecular Structure of Tetraphenylarsonium Tris(benzene-1,2-dithiolato)niobate(V), $[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$[1]

MARTIN COWIE and MICHAEL J. BENNETT*

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The structure of $[(C_6H_5)_4As][Nb(S_2C_6H_4)_3]$ has been determined crystallographically and consists of four discrete anions and cations in the unit cell. The space group is $P2_1/n$ and the cell dimensions are $a = 22.983$ (7) Å, $b = 12.747$ (4) Å, $c = 13.150$ (3) Å, and $\beta = 92.09$ (2)°. Observed and calculated densities are 1.52 (2) and 1.54 g cm^{-3}, respectively. A total of 3604 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ were used in the full-matrix, least-squares refinement which converged at $R = 0.047$ and $R_w = 0.051$. In the $Nb(S_2C_6H_4)_3^-$ anion the niobium atom is surrounded by six sulfur atoms in a trigonal-prismatic coordination with the dithiolene ligands radiating from the metal in a "paddle-wheel" arrangement. The prism dimensions are the largest observed in any dithiolene trigonal prism with interligand S–S distances greater than those observed in the nonprismatic $Mo(S_2C_2(CN)_2)_3^{2-}$ and $W(S_2C_2(CN)_2)_3^{2-}$. The niobium prism also shows slight distortions from ideal trigonal-prismatic coordination with a significant range in Nb–S (2.428 (2)–2.458 (2) Å) and interligand S–S distances (3.178 (3)–3.294 (3) Å) and also in the range in interligand S–Nb–S angles (84.87 (7)–81.03 (7)°). The tetraphenylarsonium cation is tetrahedral with no unusual features. Some average molecular dimensions are Nb–S = 2.441 (11) Å, As–C = 1.888 (7) Å, S–C = 1.745 (9) Å, S–S(intraligand) = 3.150 (9) Å, and S–S(interligand) = 3.23 (5) Å.

Introduction

The series of transition metal–tris(dithiolene) complexes $Mo(S_2C_6H_4)_3$, $[Ph_4As][Nb(S_2C_6H_4)_3]$, and $[Me_4N]_2[Zr(S_2C_6H_4)_3]$ (Ph = C_6H_5, Me = CH_3) was studied in an attempt to determine the factors which stabilize trigonal-prismatic (TP) coordination in preference to octahedral coordination. In the first paper[2] of this series the structure of the molybdenum complex was described. The molybdenum atom was shown to be surrounded by six sulfur atoms in an almost perfect TP coordination.

Previous studies have shown that neutral tris(dithiolene) complexes of the early transition metals are TP[3–5] but that the dianionic tris(dithiolenes) are distorted toward octahedral coordination,[6–9] and in fact the $FeS_6C_6(CN)_6^{2-}$ dianion[9] has an almost perfect octahedral coordination. However at the time this work was undertaken no structural results had been reported on monoanionic tris(dithiolenes). The structure of a monoanionic tris(dithiolene) complex is therefore of significance since this intermediate species is a link between the TP and octahedral limits observed in the neutral and dianionic complexes.

On the basis of electronic spectral results,[10–12] it seemed as though both the molybdenum and niobium complexes were TP but that the zirconium complex was different, most probably being distorted toward the octahedral limit. Since the above complexes represent an isoelectronic series (neglecting the cations), it was believed that the destabilization of the d orbitals proceeding from Mo to Zr was destabilizing the molecular orbitals which were responsible for prism stability.[13] This in turn was leading eventually to destabilization of the TP coordination and a tendency toward octahedral coordination. It was therefore hoped that the changing d-orbital energies in this series would be mirrored by structural changes which could then be correlated to factors affecting prism stability. The structure of $[Ph_4As][Nb(S_2C_6H_4)_3]$ was therefore undertaken as an important member of the aforementioned series.

Experimental Section

Dark purple crystals of $[Ph_4As][Nb(S_2C_6H_4)_3]$ suitable for single-crystal x-ray diffraction study were prepared by the reaction of sodium cyclopentadienide with benzenedithiol and subsequent reaction with $Nb[N(CH_3)_2]_5$ and crystallization with tetraphenylarsonium chloride.[12] These were kindly supplied by Professor J. Takats and Dr. J. L. Martin. Preliminary photography indicated $2/m$ Laue symmetry consistent with a monoclinic space group. Systematic absences, as determined by Weissenberg (*h*0*l*, *h*1*l*; Cu Kα x radiation) and precession photographs (0*kl*, 1*kl*, *hk*0, hk1; Mo Kα x radiation), are, for 0*k*0, $k = 2n + 1$, and, for *h*0*l*, $h + l$ $2n + 1$, indicating the nonstandard space group $P2_1/n$, which was retained because of the convenient β angle. The cell parameters, obtained at 22 °C from a least-squares analysis of the setting angles of 12 reflections, which were centered accurately on the Cu Kα_1 peak (λ 1.540 51 Å) using a narrow source, are $a = 22.983$ (7) Å, $b = 12.747$ (4) Å, $c = 13.150$