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Trigonal-Prismatic vs. Octahedral Coordination in a Series of Tris(benzene-1,2-dithiolato) Complexes. 3. Crystal and Molecular Structure of Bis(tetramethylammonium) Tris(benzene-1,2-dithiolato)zirconate(IV), $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$[1]

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The structure of $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$ has been determined crystallographically from 1126 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The compound crystallizes in the space group $P2_12_12$ with cell dimensions $a = 9.931$ (2) Å, $b = 14.368$ (2) Å, and $c = 11.098$ (2) Å. The Zr atoms of the anion occupy the 2(a) special positions and the four cations occupy the general equivalent positions in the cell. Observed and calculated densities are 1.38 (2) and 1.381 g cm^{-3}, respectively. Refinement of the structure by full-matrix, least-squares techniques in which 160 parameters were varied resulted in $R = 0.029$ and $R_w = 0.035$. The sulfur atoms surround the zirconium atom in a distorted octahedral coordination, intermediate between the trigonal-prismatic and octahedral limits. $Zr(S_2C_6H_4)_3^{2-}$ lies closer to the octahedral limit than either $V(S_2C_2(CN)_2)_3^{2-}$, $Mo(S_2C_2(CN)_2)_3^{2-}$, or $W(S_2C_2(CN)_2)_3^{2-}$ but is still significantly distorted toward trigonal-prismatic coordination. The tetramethylammonium cation contains no unusual features with the four carbon atoms describing a tetrahedral coordination about the nitrogen atom. Some important average molecular parameters are Zr–S = 2.543 (10) Å, S–C = 1.765 (7) Å, S–S (intraligand) = 3.265 (14) Å, N–C = 1.47 (5) Å, S–Zr–S(trans) = 164 (6)°, and trigonal twist angle = 37°. There is a wide range in interligand S–S distances from 3.424 (3) to 3.665 (2) Å.

Introduction

Previously we described the structures of $Mo(S_2C_6H_4)_3$ and $[Ph_4As][Nb(S_2C_6H_4)_3]$ (Ph = C_6H_5).[2-4] In both complexes six sulfur atoms surround the metals in trigonal prismatic (TP) coordination. The niobium prism was found to have a significantly larger TP frame than any other previously studied TP dithiolene[5] complex and in addition was found to be slightly distorted from TP geometry compared to the Mo analogue. It was shown, by comparison of $Nb(S_2C_6H_4)_3^-$ to other tris(dithiolene) complexes, that interligand S–S bonding is not important in stabilizing the prismatic geometry since the interligand S–S distances in the Nb complex are longer than those in the nonprismatic $Mo(S_2C_2(CN)_2)_3^{2-}$ and $W(S_2C_2(CN)_2)_3^{2-}$ complexes.[6,7] Rather it is believed that a significant stabilizing feature in the TP geometry is the ability to utilize metal d orbitals, not involved in σ bonding, for strong π interactions with ligand orbitals, most notably the metal d_{xy}, $d_{x^2-y^2}$ and ligand π_v and the metal d_{z^2} and ligand π_h interactions.[8] The title complex was therefore studied as the last member in this isoelectronic series in a further attempt to determine the factors which stabilize TP coordination rather than the more usual octahedral coordination.

Experimental Section

Bright red crystals of $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$, suitable for single-crystal x-ray diffraction studies, were kindly supplied by Professor J. Takats and Dr. J. L. Martin. These crystals were prepared[9] by the reaction of sodium cyclopentadienide and benzenedithiol, the subsequent reaction with $Zr[N(C_2H_5)_2]_4$, and crystallization with tetramethylammonium chloride. Preliminary photography showed *mmm* Laue symmetry indicating an orthorhombic space group. Systematic absences determined by Weissenberg (0*kl*, 1*kl*; Cu Kα x radiation) and precession photography (*h*0*l*, *h*1*l*, *hk*0, *hk*1; Mo Kα x radiation) are, for *h*00, $h = 2n + 1$ and, for 0*k*0,

$k = 2n + 1$, consistent with the space group $P2_12_12$. Precise lattice parameters were obtained at 22 °C from a least-squares analysis performed on the setting angles of 12 high-angle reflections, accurately centered on a Picker automatic four-circle diffractometer, using Cu $K\alpha_1$ x radiation (λ 1.540 56 Å). The resulting cell parameters and estimated standard deviations are $a = 9.931$ (2) Å, $b = 14.368$ (2) Å, and $c = 11.098$ (2) Å. The observed density [1.38 (2) g cm^{-3}], obtained by flotation in a mixture of chloro- and bromobenzenes, is consistent with the theoretical value of 1.381 g cm^{-3}, calculated assuming two formula units with fw 660.2 occupy the unit cell of volume 1587.9 Å^3. Since the space group $P2_12_12$ has four general equivalent positions, the $Zr(S_2C_6H_4)_3^{2-}$ dianion is therefore restricted to having twofold symmetry and must sit on the crystallographic twofold axis. The two tetramethylammonium cations can either be related by the twofold axis or sit on the twofold axis.

Intensity data were collected on the Picker automatic diffractometer using Ni-filtered Cu $K\alpha$ x radiation and using a 2° takeoff angle. The crystal was mounted in a general orientation but with the a^* axis approximately coincident with the ϕ axis of the diffractometer. A coupled 2θ–ω scan technique, with a scan speed of 1° min^{-1}, was employed for data collection with all unique reflections with $2\theta \leq 125°$ being collected. The 2θ scan range for each reflection was $2° + \Delta 2\theta$ where $\Delta 2\theta$ is a correction for the dispersion of the $K\alpha_1$–$K\alpha_2$ doublet. Stationary-background counts on each side of the peak were recorded for 40 s. A scintillation counter was used in conjunction with a pulse height analyzer, tuned to accept 95% of the Cu $K\alpha$ peak. Three standard reflections were collected automatically every 100 reflections. In addition, five further reflections were collected manually to assess decomposition. No significant decomposition was observed so no correction was necessary.

Of the 1403 unique reflections collected, 1126 were significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The significant data were then reduced to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects. Standard deviations in the structure factors were calculated as previously described[10] using 0.03 for p.

The crystal faces were identified and their perpendicular distances to an arbitrarily chosen origin measured as follows: (010), 3.27 × 10^{-3} cm; $(0\bar{1}0)$, 10.84 × 10^{-3} cm; $(\bar{1}00)$, 20.64 × 10^{-3} cm; (001), 3.09 × 10^{-3} cm; (110), 0; $(1\bar{1}0)$, 0; $(1,0,\overline{12})$, 0. The face $(1,0,\overline{12})$ is acknowledged as a very unusual choice, but its position is most consistent with the indices chosen, since it is opposite to the (001) face but inclined to it by about 5°. The absorption coefficient for Cu $K\alpha$ x radiation is 66.63 cm^{-1}, leading to a range in transmission factors from 0.756 to 0.423.

In the original data collection several irregularities were observed. These occurred as "pulses" in the counter and their exact cause was unknown but was probably due to some electronic device connected to the diffractometer power line. The reflections where this was actually observed were rejected. However it was believed (on the basis that several $|F_o|$ values were extremely high compared to the corresponding $|F_c|$) that these pulses had occurred throughout the data collection. For this reason the hkl data were recollected along with the $h\bar{k}\bar{l}$ data so all three data sets could be compared and faulty reflections could be excluded. The second set of hkl data was later merged with the $h\bar{k}\bar{l}$ data. The initial hkl data set was not used beyond the preliminary refinements. The same data collection techniques were used for the second hkl data set and the $h\bar{k}\bar{l}$ data as were used for the original hkl data. Terms used in the Zachariasen extinction correction[11] were calculated at this time.

Solution and Refinement of Structure

The structure was refined[12] 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 $w = 1/\sigma^2(F_o)$. The agreement indices are defined as

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$$

$$R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^{\,2}]^{1/2}$$

Nonhydrogen scattering factors were those compiled by Cromer and Mann[13] whereas the hydrogen scattering factors were those of Stewart et al.[14] Anomalous dispersion corrections by Cromer[15] for Zr and S were applied to the calculated structure factors.

The zirconium and sulfur positions were obtained from the Zr–Zr, Zr–S, and S–S vectors in a sharpened Patterson synthesis. From the placement of these vectors it was immediately obvious that the zirconium coordination was close to octahedral and was definitely not trigonal prismatic. A least-squares refinement with the zirconium and three independent sulfur atoms refined isotropically gave $R = 0.297$ and $R_w = 0.384$. A difference Fourier synthesis phased on the Zr and three S atoms clearly located all other nonhydrogen atoms and several least-squares cycles resulted in the agreement indices $R = 0.088$ and $R_w = 0.106$. Refining the Zr, S, and the tetramethylammonium N and C atoms anisotropically gave $R = 0.069$ and $R_w = 0.088$. Applying the absorption correction to the observed data further reduced the agreement indices to $R = 0.050$ and $R_w = 0.063$. In order to test whether the proper enantiomer had been chosen, a change of "hand" of the model was performed and this refined to $R = 0.057$ and $R_w = 0.073$. This clearly showed that the former model was more suitable, based on a Hamilton's "R factor test"[16] at better than the 0.005 significance level, and this model was used in all subsequent refinements. Refining the carbon atoms of the dithiolene ligands anisotropically gave $R = 0.042$ and $R_w = 0.061$.

A difference Fourier map was calculated at this time and it showed the location of all dithiolene hydrogen atoms. These hydrogen atoms were included in all subsequent refinements as fixed contributions, their positions being idealized from the carbon atom positions and the idealized phenyl group geometry using a C–H distance of 0.98 Å and their thermal parameters being 10–15% greater than those of their attached carbon atoms. Refinement of this model yielded $R = 0.039$ and $R_w = 0.059$.

Applying an extinction correction had no observable effect on the agreement indices leaving them at $R = 0.039$ and $R_w = 0.059$. However merging the hkl and $h\bar{k}\bar{l}$ data and subsequent refinement yielded $R = 0.034$ and $R_w = 0.053$. In a final difference Fourier map the tetramethylammonium hydrogen atoms still could not be located so they were included in a final refinement as a fixed contribution as free rotating rigid groups.[17] The ideal tetrahedral coordination of the carbon atoms was assumed and the centers of gravity and angles defining the orientation of the "hydrogen triangles" were calculated using the assumed geometry, a C–H distance of 1.0 Å, and the direction cosines of the nitrogen–carbon bonds. This resulted in the final agreement indices of $R = 0.029$ and $R_w = 0.035$. In addition this significantly improved the agreement between $|F_o|$ and $|F_c|$ for many low-angle reflections for which $|F_o| \gg |F_c|$. The very poor agreement of these low-angle reflections had originally motivated us to collect the second data set since we believed these "bad" reflections were due to power line pulses (which incidentally were observed periodically). However it was discovered that the poor agreement was due to an inadequate description of the methyl hydrogen atoms. Some discrepancies still exist in the data and this is still no doubt the reason. Ideally one would like to refine the hydrogen hindered-rotor groups but this is impractical considering their high thermal motion.

In the final least-squares refinement, 160 parameters were varied and the error in an observation of unit weight was 1.292 electrons, based on 1126 observations.

The observed and calculated structure amplitudes, $10|F_o|$ and $10|F_c|$, are given in Table I.[19] The final fractional coordinates and isotropic B's of all atoms and the rigid-body parameters are shown in Table II. Standard deviations were obtained from the inverse matrix of the final least-squares analysis. Table III lists the anisotropic thermal parameters (U_{ij}'s). See Tables IV–VII for selected distances and angles, weighted least-squares planes, and dihedral angles between the planes.

Description of Structure

The structure consists of four monomeric cations and two dianions in the unit cell. All interionic contacts are normal, being comparable to the van der Waals separations of the atoms involved. The four $(CH_3)_4N^+$ cations occupy the general equivalent positions in the unit cell and the two $Zr(S_2C_6H_4)_3^{2-}$ anions sit on the crystallographic twofold axis with the zirconium atoms occupying the 2(a) special positions. The twofold axis bisects ligand 1 [S(1), S(1)′, C(1), C(1)′, C(2), C(2)′, C(3), and C(3)′]. Figure 1 shows the anion and cations together. Figure 2 shows a perspective view of the $Zr(S_2C_6H_4)_3^{2-}$ anion seen down the approximate molecular threefold axis and showing the location of the crystallographic twofold axis. The numbering scheme is indicated in both drawings. Thermal ellipsoids are shown at the 50% probability

Table II. Atomic Coordinates and Isotropic Temperature Factors

Atom	x^a	y	z	B, Å^2
Zr	0.0	0.0	−0.189 83 (6)	3.01^b
S(1)	−0.1645 (2)	−0.0080 (2)	−0.013 2 (1)	4.56^b
S(2)	0.0535 (2)	0.1716 (1)	−0.214 2 (2)	4.15^b
S(3)	−0.1851 (2)	0.0474 (1)	−0.335 0 (1)	4.33^b
C(1)	−0.0697 (7)	−0.0046 (7)	0.120 7 (5)	4.55^b
C(2)	−0.1364 (10)	−0.0100 (8)	0.232 6 (6)	7.08^b
C(3)	−0.0686 (11)	−0.0036 (10)	0.339 1 (5)	8.76^b
C(4)	−0.0580 (7)	0.2186 (4)	−0.322 0 (5)	3.71^b
C(5)	−0.0480 (8)	0.3120 (5)	−0.352 7 (6)	5.13^b
C(6)	−0.1351 (10)	0.3523 (6)	−0.435 5 (7)	6.07^b
C(7)	−0.2330 (10)	0.2999 (8)	−0.486 9 (8)	6.57^b
C(8)	−0.2475 (8)	0.2068 (6)	−0.457 0 (6)	5.08^b
C(9)	−0.1597 (7)	0.1658 (5)	−0.373 7 (5)	3.93^b
N	−0.4980 (8)	−0.2008 (3)	−0.138 4 (5)	4.45^b
C(10)	−0.3933 (9)	−0.2662 (8)	−0.119 8 (14)	10.92^b
C(11)	−0.5023 (15)	−0.1388 (7)	−0.026 4 (8)	10.01^b
C(12)	−0.4761 (11)	−0.1372 (7)	−0.239 3 (8)	9.07^b
C(13)	−0.6332 (9)	−0.2452 (6)	−0.140 8 (10)	7.08^b
Rigid Bodies				
H(2)	−0.2398	−0.0170	0.230 8	7.90
H(3)	−0.1198	−0.0085	0.417 7	9.60
[$D^c = 4.610°$; $E^c = 1.571°$; $F^c = 1.571°$]				
H(5)	0.0269	0.3512	−0.314 3	6.20
H(6)	−0.1241	0.4203	−0.456 6	7.00
H(7)	−0.2981	0.3283	−0.546 9	7.90
H(8)	−0.3209	0.1671	−0.494 9	6.30
[$D = 3.391°$; $E = 2.447°$; $F = 3.747°$]				
Hindered Rotors				
H(9)	−0.3503	−0.2810	−0.198 5	11.00
H(10)	−0.3250	−0.2381	−0.063 6	
H(11)	−0.4316	−0.3238	−0.082 7	
[barrier^d = 0.02; radius = 0.946 Å; $D = 0.721°$; $E = 1.373°$; $F = 0.0°$]				
H(12)	−0.5980	−0.1260	−0.006 0	11.00
H(13)	−0.4537	−0.0797	−0.044 6	
H(14)	−0.4571	−0.1722	−0.041 6	
[barrier = 0.02; radius = 0.946°; $D = 0.625°$; $E = 3.106°$; $F = 0.0°$]				
H(15)	−0.3775	−0.1230	−0.244 7	9.5
H(16)	−0.5275	−0.0785	−0.223 8	
H(17)	−0.5078	−0.1674	−0.314 4	
[barrier = 0.02; radius = 0.946 Å; $D = 0.676°$; $E = 6.091°$; $F = 0.0°$]				
H(18)	−0.6652	−0.2550	−0.056 8	8.0
H(19)	−0.6972	−0.2034	−0.185 3	
H(20)	−0.6265	−0.3065	−0.183 8	
[barrier = 0.02; radius = 0.946 Å; $D = 0.444°$; $E = 4.689°$; $F = 0.0°$]				

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] Equivalent isotropic temperature factors[21] corresponding to the anisotropic thermal parameters shown in Table III. [c] D, E, and F are the angles by which the coordinates of the rigid body are rotated with respect to a set of axes X, Y, and Z. The origin of these axes is placed at the center of the ring with the X axis parallel to a^*, the Z axis parallel to c, and the Y axis parallel to the line defined by the intersection of the plane containing a^* and b^* with the plane containing b and c. [d] Barrier (B_d) is the relative barrier to rotation of the hindered-rotor group: $B_d = V_0/2kt$, where V_0 is the potential barrier to rotation (kcal mol^{-1}). The low value of B_d (0.02) gives the groups essentially free rotation.

level except for carbon atoms which are shown arbitrarily small for clarity of the drawing. Hydrogen atoms, which are not shown in the drawings are numbered from H(2) to H(8) on the phenyl rings, having the same number as their attached carbon atom, and from H(9) to H(20), being bonded, in groups of three, sequentially to methyl carbon atoms C(10)–C(13).

In the dianion, the six sulfur atoms are approximately equidistant from the zirconium atom and form a coordination polyhedron which is intermediate between an octahedron and a trigonal prism. Since the $ZrS_2C_6H_4$ fragments are approximately planar, the symmetry of $Zr(S_2C_6H_4)_3^{2-}$ approximates D_3. The dithiolene ligands radiate from the zirconium atom in a "propeller-like" arrangement as opposed to the "paddle-wheel" arrangement in the trigonal prisms. The two triangular faces, defined by S(1)′, S(2), S(3)′ and by S(1), S(2)′, S(3), are almost parallel, the angle between them being only 4.1°.

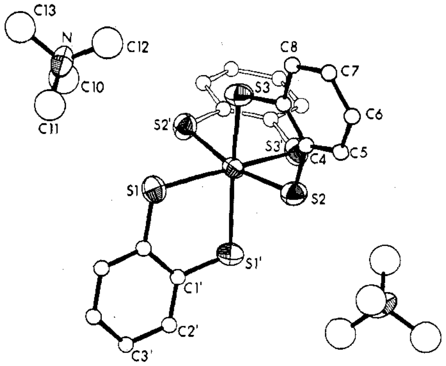

Figure 1. Perspective view of $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$ showing the numbering scheme. Thermal ellipsoids are shown at the 50% probability level, except carbon atoms which are shown arbitrarily small for clarity of the drawing.

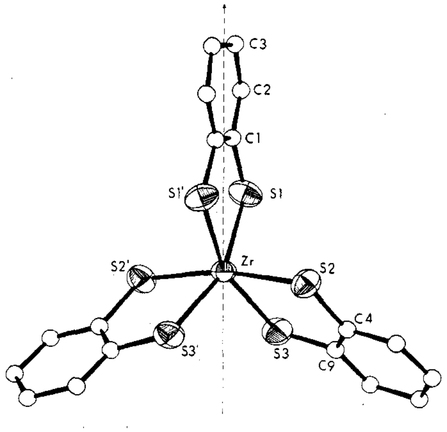

Figure 2. Representation of the $Zr(S_2C_6H_4)_3^{2-}$ anion viewed down the approximate molecular threefold axis and showing the crystallographic twofold axis. Thermal ellipsoids are shown at the 50% probability level except carbon atoms which are shown arbitrarily small.

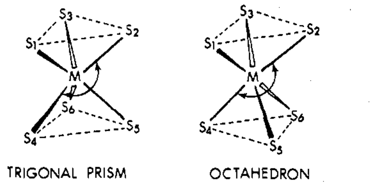

Figure 3. Trans S–M–S angles in the trigonal prism and octahedron.

In describing the degree of distortion of the metal coordination from either of the trigonal-prismatic or octahedral limits, two parameters are especially useful: the S–M–S angles (M = metal) involving sulfur atoms which are almost trans to each other and the projection angle between the two triangular faces of the prism (trigonal twist angle). In a regular trigonal prism the S–M–S angle between pseudo-"trans" sulfur atoms is approximately 136°. In an octahedron this angle is 180°. These two extremes are shown in Figure 3, the S(2)–M–S(4) angle being the angle of interest. However, for an intraligand S–Zr–S angle of ca. 80°, considering only the geometric constraints of the ligand, a trans S–Zr–S angle of 170° is obtained as the corrected octahedral limit.[30] The

Table III. Anisotropic Thermal Parameters (Å^2)

Atom	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.0369 (4)	0.0467 (4)	0.0309 (3)	0.0033 (5)	0.0	0.0
S(1)	0.0519 (10)	0.0724 (12)	0.0491 (8)	−0.0014 (13)	0.0142 (8)	−0.0058 (13)
S(2)	0.0503 (10)	0.0535 (9)	0.0536 (10)	−0.0022 (8)	−0.0099 (8)	0.0043 (8)
S(3)	0.0479 (10)	0.0663 (10)	0.0502 (10)	0.0035 (9)	−0.0149 (9)	−0.0029 (8)
C(1)	0.093 (5)	0.042 (3)	0.038 (3)	−0.021 (6)	0.013 (3)	−0.003 (5)
C(2)	0.134 (8)	0.080 (6)	0.055 (4)	−0.051 (6)	0.042 (5)	−0.029 (5)
C(3)	0.200 (12)	0.096 (5)	0.036 (3)	−0.065 (11)	0.021 (4)	−0.015 (7)
C(4)	0.049 (4)	0.055 (4)	0.038 (3)	0.009 (3)	0.004 (3)	0.005 (3)
C(5)	0.074 (6)	0.061 (4)	0.060 (4)	0.011 (4)	0.012 (4)	0.009 (4)
C(6)	0.080 (6)	0.080 (6)	0.071 (5)	0.033 (5)	0.011 (5)	0.024 (5)
C(7)	0.081 (7)	0.116 (7)	0.052 (5)	0.044 (6)	−0.004 (5)	0.026 (6)
C(8)	0.058 (5)	0.088 (6)	0.047 (4)	0.022 (4)	−0.012 (4)	0.014 (5)
C(9)	0.049 (4)	0.070 (4)	0.030 (3)	0.018 (4)	0.005 (3)	0.002 (3)
N	0.042 (3)	0.054 (3)	0.073 (3)	−0.005 (4)	−0.000 (5)	0.017 (3)
C(10)	0.048 (6)	0.110 (8)	0.257 (16)	0.028 (5)	0.031 (8)	0.081 (10)
C(11)	0.153 (10)	0.113 (7)	0.114 (7)	−0.049 (9)	−0.003 (11)	−0.018 (6)
C(12)	0.083 (8)	0.137 (8)	0.124 (7)	−0.012 (6)	0.006 (6)	0.075 (7)
C(13)	0.063 (6)	0.095 (7)	0.111 (8)	−0.018 (5)	−0.009 (6)	0.032 (6)

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

Table IV. Selected Distances (Å) in $[Me_4N]_2[Zr(S_2C_6H_4)_3]$

Atoms[a]	Distance	Atoms	Distance
Zr-S(1)	2.555 (2)	C(2)-C(3)	1.364 (11)
Zr-S(2)	2.537 (2)	C(3)-C(3)′	1.366 (22)
Zr-S(3)	2.538 (2)	C(4)-C(5)	1.388 (9)
S(1)-S(1)′[a]	3.275 (3)	C(5)-C(6)	1.389 (10)
S(2)-S(3)	3.255 (2)	C(6)-C(7)	1.355 (13)
S(1)-S(2)′	3.424 (3)	C(7)-C(8)	1.386 (11)
S(2)-S(3)′	3.662 (2)	C(8)-C(9)	1.400 (9)
S(1)-S(3)	3.665 (2)	C(9)-C(4)	1.388 (9)
S(1)-C(1)	1.759 (6)	N-C(10)	1.416 (10)
S(2)-C(4)	1.764 (6)	N-C(11)	1.530 (10)
S(3)-C(9)	1.772 (7)	N-C(12)	1.462 (9)
C(1)-C(1)′	1.391 (14)	N-C(13)	1.487 (10)
C(1)-C(2)	1.410 (8)		

[a] Primed atoms are related to unprimed atoms of the same number by the twofold axis.

Table V. Selected Angles (deg) in $[MeN]_2[Zr(S_2C_6H_4)_3]$

Atoms	Angle	Atoms	Angle
S(1)-Zr-S(1)′	79.74 (8)	C(2)-C(3)-C(3)′	119.9 (6)
S(2)-Zr-S(3)	79.80 (6)	C(9)-C(4)-C(5)	118.6 (6)
S(1)-Zr-S(3)	92.06 (6)	C(4)-C(5)-C(6)	121.4 (7)
S(1)-Zr-S(2)′	84.51 (7)	C(5)-C(6)-C(7)	119.6 (8)
S(3)-Zr-S(2)′	92.40 (6)	C(6)-C(7)-C(8)	120.7 (8)
S(3)-Zr-S(3)′	101.19 (8)	C(7)-C(8)-C(9)	119.9 (8)
S(1)-Zr-S(2)	105.03 (7)	C(8)-C(9)-C(4)	119.8 (6)
S(2)-Zr-S(2)′	167.76 (8)	S(2)′-S(1)-S(3)	62.10 (5)
S(1)-Zr-S(3)′	159.80 (7)	S(2)′-S(3)-S(1)	55.71 (5)
Zr-S(1)-C(1)	107.7 (2)	S(1)′-S(2)-S(3)′	62.19 (5)
Zr-S(2)-C(4)	108.2 (2)	C(10)-N-C(11)	106.8 (10)
Zr-S(3)-C(9)	108.0 (2)	C(10)-N-C(12)	114.7 (8)
S(1)-C(1)-C(1)′	122.4 (2)	C(10)-N-C(13)	112.4 (6)
S(2)-C(4)-C(9)	121.9 (5)	C(11)-N-C(12)	105.1 (6)
S(3)-C(9)-C(4)	121.8 (5)	C(11)-N-C(13)	103.8 (8)
C(1)′-C(1)-C(2)	118.2 (5)	C(12)-N-C(13)	112.9 (7)
C(1)-C(2)-C(3)	121.8 (9)		

values observed for the $Zr(S_2C_6H_4)_3^{2-}$ dianion [167.76 (8) and 159.80 (7)°] are thus closer to the octahedral limit and on this basis the zirconium coordination can be described as distorted octahedral. The nonequivalence of these two independent values indicates that the distortion is not regular and that one ligand (containing S(1) and S(1)′) is rotated more toward the trigonal-prismatic structure than the other two ligands.

The other indication of the degree of distortion from the prismatic or octahedral limits is the trigonal twist or projection angle shown in Figure 4. In the trigonal prism where the two triangular faces are eclipsed, this angle equals 0°, whereas in the ideal octahedron this angle is 60°. Again however, because

Table VI. Deviations (Å × 10^3) from Weighted Least-Squares Planes of Atoms Used to Determine Planes[a]

	Plane				
Atom	1	2	3	4	5
Zr	0	0			
S(1)		0	0		3 (3)
S(1)′		0			−3 (3)
S(2)	0			0 (3)	
S(2)′			0		
S(3)	0		0	2 (3)	
S(3)′					
C(1)					−16 (10)
C(1)′					16 (10)
C(2)					−46 (13)
C(2)′					46 (13)
C(3)					44 (15)
C(3)′					−44 (15)
C(4)				−32 (10)	
C(4)′					
C(5)				−15 (11)	
C(5)′					
C(6)				14 (12)	
C(6)′					
C(7)				−13 (14)	
C(7)′					
C(8)				−16 (15)	
C(8)′					
C(9)				44 (15)	
C(9)′					

Plane[b]	A	B	C	D
1	0.5985	−0.2147	−0.7718	−1.6254
2	−0.0622	0.9978	0.0	0.0
3	0.9176	0.3961	−0.0337	−1.5424
4	0.6201	−0.2685	−0.7372	−1.4221
5	−0.0717	0.9974	0.0	0.0

[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^{*}. [b] The equivalent planes related to those listed by the crystallographic twofold axis have the equations $AX + BY - CZ + D = 0$.

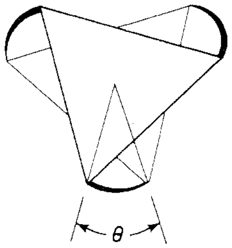

Figure 4. Trigonal twist angle projected perpendicular to the molecular threefold axis.

Table VII. Dihedral Angles between Selected Planes

Atoms in plane 1	Atoms in plane 2	Angle, deg
Zr, S(2), S(3)	Zr, S(2)′, S(3)′	101.1
Zr, S(2), S(3)	Zr, S(1), S(1)′	104.7
Zr, S(2), S(3)	S(2), S(3), C(4), C(5), C(6), C(7), C(8), C(9)	3.9
Zr, S(1), S(1)′	S(1), S(1)′, C(1), C(1)′, C(2), C(2)′, C(3), C(3)′	0.5
S(2), S(3), C(4), C(5), C(6), C(7), C(8), C(9)	S(2)′, C(3)′, C(4)′, C(5)′, C(6)′, C(7)′, C(8)′, C(9)′	95.0
S(2), S(3), C(4), C(5), C(6), C(7), C(8), C(9)	S(1), S(1)′, C(1), C(1)′, C(2), C(2)′, C(3), C(3)′	108.2
S(1), S(2)′, S(3)	S(1)′, S(2), S(3)′	4.1

of the constraint of ligand bite in these bidentate ligands, the octahedral limit is not attained. Rather, this angle will be limited by the ratio of intraligand S–S distances to the M–S distances. For the $Zr(S_2C_6H_4)_3^{2-}$ dianion, this ratio (1.284) yields[31] (on the basis of minimizing interligand repulsions) a twist angle of approximately 48° for the corrected octahedral limit. An average twist angle in this structure is calculated at 37° using equilateral triangles that correspond to a best fit with the observed individual atom coordinates. Thus the twist angle differs from the corrected octahedral limit by only 11°. By comparison, in the structure[32] of $Al(O_2C_7H_5)_3$, the observed trigonal twist angle (48.1°) is essentially that calculated using the constraints of ligand bite and this appears typical of structures where the only factor favoring the prism is minimization of the interligand repulsions. Thus the deviation of 11° from the corrected octahedral limit is significant and indicates a genuine tendency toward trigonal-prismatic coordination in this structure. It is also desirable to list the individual twist angles within each ligand as a measure of the deviation of each ligand from the TP and octahedral limits. This has been calculated by the means suggested by Dymock and Palenik[33] and gives twist angles of 34.3 and 41.0° for the two independent ligands. The smaller value is for the ligand involving S(1) and S(1)′ and confirms the slight preference of this ligand for the TP coordination, as was shown by the trans S–Zr–S angles. However the variation in individual twist angles is not great so the average twist angle is a meaningful measurement of the degree of distortion from the TP and octahedral extremes.

The Zr–S distances (average 2.543 (10) Å) are longer than those observed in the molybdenum– and niobium–tris(benzenedithiol) complexes (see Table VIII) and thus complete a trend through this series with the metal–sulfur distances increasing approximately as predicted by their ionic radii.[34] As with the niobium complex, the metal–sulfur distances again contain irregularities of statistical significance. The Zr–S distance within the ligand bisected by the twofold axis (2.555 (2) Å) is longer than the other two independent Zr–S distances (2.537 (2) and 2.538 (2) Å). This is the opposite to what is expected since the longer Zr–S distance corresponds to the ligand which is closer to the TP limit. On the basis of the proposed π interactions[2–4,8] which stabilize the TP geometry, one would expect the Zr–S(1) distance to be shorter than Zr–S(2) and Zr–S(3). However the chemical significance of the tendency of ligand 1 toward the TP limit should not be overemphasized since variations of the magnitude observed in the two independent twist angles are possibly a consequence of packing forces.

The intraligand S–Zr–S angles (average 79.77 (8)°) are slightly less than those observed in $Mo(S_2C_6H_4)_3$ and $Nb(S_2C_6H_4)_3^-$ (82.1 (4) and 80.35 (15)°, respectively) and complete a trend through the series. This trend is due to the relatively fixed ligand bite which does not increase as rapidly as the metal–sulfur distances.

The S–C distances seem to be an excellent indication of the tendency of the ligand toward either the oxidized or reduced formulations. In $Zr(S_2C_6H_4)_3^{2-}$ the average S–C distance (1.765 (7) Å) is very close to that predicted for a single-bonded sulfur–carbon distance (1.77 Å).[35,36] Thus the ligand geometry approximates that corresponding to the dithiolato formulation and the formal oxidation state of IV appears to be a reasonable description for the zirconium atom in this structure. This structure is important in demonstrating that the ligand can attain the dithiolato limit. The carbon–carbon distances within the ligands are close to those observed in benzene and derivatives.[37,38] However, as in the molybdenum and niobium complexes, shortening of the C_C–C_D bond is observed (see Figure 5), probably due to thermal motion of the rings. In addition, in ligand 1, which is bisected by the crystallographic twofold axis, the bond lengths vary significantly throughout the ring. One worrying feature of this ring is the presence of anomalously high thermal parameters (U_{11}'s) of the carbon atoms. This seems to indicate either a disorder or a systematic error is present. The disorder could correspond to the nonequivalence of Zr–S(1) and Zr–S(1)′ distances for a particular model. However, this problem is unlikely to affect the general conclusions of this study. The C–C bond lengths within the rings are therefore unreliable and no chemical significance should be placed on their differences.

The interligand S–S distances are, as expected, much longer than the intraligand distances, this being due merely to the distortion toward the octahedron which maximizes the interligand separations. In addition the intraligand S–S distances in $Zr(S_2C_6H_4)_3^{2-}$ are longer than those in $Mo(S_2C_6H_4)_3$ and $Nb(S_2C_6H_4)_3^-$ and are due to increasing S–C distances through the series. The S–C–C and C–C–C angles within the ligands are all close to the expected value of 120°.

Table VIII. Selected Distances (Å) for Tris(1,2-dithiolene) Complexes

Compd	M–S	S–S (intra)	S–S (inter)	S–C	Ref
$Re(S_2C_2Ph_2)_3$	2.32 (1)[a]	3.032 (10)	3.050 (8)	1.69 (5)	22, 23
$Mo(S_2C_2H_2)_3$	2.33 (1)	3.10	3.11	1.70 (3)	24
$V(S_2C_2Ph_2)_3$	2.337 (6)	3.061 (12)	3.07 (13)	1.69 (1)	25
$V[S_2C_2(CN)_2]_3^{2-}$	2.36 (1)	3.14 (4)	3.20 (23)	1.72 (3)	26
$Mo[S_2C_2(CN)_2]_3^{2-}$	2.374 (8)	3.113[b]	3.188	1.74 (2)	6, 7
$W[S_2C_2(CN)_2]_3^{2-}$	2.371 (10)	3.112	3.193	1.73 (2)	7
$Fe[S_2C_2(CN)_2]_3^{2-}$	2.261 (2)	3.147 (2)	3.19	1.731 (4)	27
$In[S_2C_2(CN)_2]_3^{3-}$	2.604 (14)	3.40 (4)	3.89 (4)	1.72 (3)	28
$Mo(S_2C_6H_4)_3$	2.367 (6)	3.110 (8)	3.091 (15)	1.727 (6)	2, 3
$Nb(S_2C_6H_4)_3^-$	2.441 (11)	3.150 (9)	3.23 (5)	1.745 (9)	2, 4
$Zr(S_2C_6H_4)_3^{2-}$	2.543 (10)	3.265 (14)	3.58 (14)	1.765 (7)	This work
$Ta(S_2C_6H_4)_3^-$	2.430 (28)	3.149 (27)	*c*	1.746 (15)	29

[a] 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. [b] Where standard deviations are not shown, they were not given in the original paper. [c] Due to the irregular distortion and the large range in values, the average value is not meaningful.

Table IX. Selected Angles (deg) for Tris(1,2-dithiolene) Complexes

Compd[d]	S-M-S (intra)	S-M-S (trans)	Projection angle[c]	Dihedral MS_2-ligand angle	Coordination
$Re(S_2C_2Ph_2)_3$	81.4 (5)	~136	<1		Trigonal prism
$Mo(S_2C_2H_2)_3$	82.5	~136	0	18	Trigonal prism
$V(S_2C_2Ph_2)_3$	81.7 (2)	~136	8.5[a]		Trigonal prism
$V[S_2C_2(CN)_2]_3^{2-}$		158.6	Twisted[b]		Distorted octahedron
$Mo[S_2C_2(CN)_2]_3^{2-}$	82.3 (6)	156	28	~2	Distorted octahedron
$W[S_2C_2(CN)_2]_3^{2-}$	82.1 (2)	156	28	~2	Distorted octahedron
$Fe[S_2C_2(CN)_2]_3^{2-}$	88.0 (1)		~60		Octahedron
$In[S_2C_2(CN)_2]_3^{3-}$	81.5 (14)	169.3 (18)			Distorted octahedron
$Mo(S_2C_6H_4)_3$	82.1 (4)	135.7 (11)	0	13.1, 21.1, 30.0	Trigonal prism
$Nb(S_2C_6H_4)_3^-$	80.35 (15)	135.1 (14)	0.7	22.4	Trigonal prism
$Zr(S_2C_6H_4)_3^{2-}$	79.77 (8)	164 (6)	37.0	3.9, 0.5	Distorted octahedron
$Ta(S_2C_6H_4)_3^-$	80.8 (7)	155 (6)	54, 16, 16	10.0, 17.6, 30.0	Distorted octahedron

[a] Calculated in ref 50 from atomic coordinates given in the original paper. [b] No coordinates or twist angle given. [c] Trigonal twist angle projected perpendicular to molecular threefold axis. [d] References shown in Table VIII.

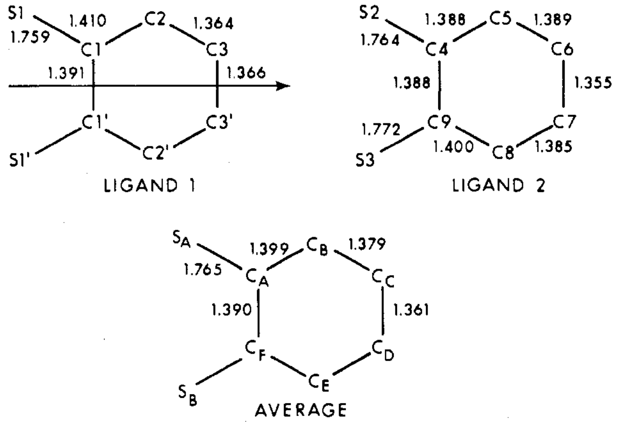

Figure 5. Dimensions within the dithiolene ligands.

An interesting feature observed in $Mo(S_2C_6H_4)_3$ and isoelectronic $Nb(S_2C_6H_4)_3^-$ is the large bend of the MS_2 planes from the ligand S_2C_6 planes (21.4 and 22.4°, respectively). This has also been observed in $Mo(S_2C_2H_2)_3$[24] and $Mo[Se_2C_2(CF_3)_2]_3$[39] but was not observed in $Re(S_2C_2Ph_2)_3$[22,23] or $V(S_2C_2Ph_2)_3$.[25] In $Zr(S_2C_6H_4)_3^{2-}$ these planes are approximately coplanar, the dihedral angles between the ZrS_2 and S_2C_6 planes being 3.9 and 0.5°. This is in agreement with the explanation previously proposed[4] that the d_{xy}, $d_{x^2-y^2}$ and π_v interaction which stabilizes the TP geometry also favors bending of the ligand plane to maximize this π overlap. Therefore in the distorted octahedral coordination where this prism-stabilizing influence is not present the ligands are essentially coplanar with the ZrS_2 planes.

Comparison of the angular parameters in Table IX allows the complexes to be placed in order of increasing tendency toward the trigonal-prismatic structure. Consideration must be given to the general criticism of x-ray crystallographic studies that one cannot guarantee that the observed geometry corresponds to the ground state. Thus the differences between $V(S_2C_2(CN)_2)_3^{2-}$ and $Mo(S_2C_2(CN)_2)_3^{2-}$ (or $W(S_2C_2(CN)_2)_3^{2-}$) may not be significant. In this regard it is significant that the structure of $[Ph_4As]_2[V(S_2C_2(CN)_2)_3]$ is reported to be isomorphous with its Mo and W analogues[7,40] and the high degree of distortion of the $V(S_2C_2(CN)_2)_3^{2-}$ anion in the $[Me_4N^+]_2$ salt may be due to packing effects because of the smaller size of the cation. The order for the dianionic species is then

$$\begin{aligned}&\text{corrected octahedral limit} \simeq Fe(S_2C_2(CN)_2)_3^{2-} < Zr(S_2C_6H_4)_3^{2-}\\ &\quad < V(S_2C_2(CN)_2)_3^{2-}, Mo(S_2C_2(CN)_2)_3^{2-}, W(S_2C_2(CN)_2)_3^{2-}\\ &\quad << \text{trigonal-prismatic limit}\end{aligned}$$

The corresponding order for the isoelectronic series, as described in this and the preceding two papers,[3,4] is

$$\begin{aligned}&\text{corrected octahedral limit} < Zr(S_2C_6H_4)_3^{2-} << Nb(S_2C_6H_4)_3^-\\ &\quad \leqslant Mo(S_2C_6H_4)_3 \text{ trigonal-prismatic limit}\end{aligned}$$

The order for all tris(dithiolene) complexes reported is

$$\begin{aligned}&\text{corrected octahedral limit} \simeq Fe(S_2C_2(CN)_2)_3^{2-} \simeq In(S_2C_2(CN)_2)_3^{3-}\\ &\quad < Zr(S_2C_6H_4)_3^{2-} < V(S_2C_2(CN)_2)_3^{2-}, Mo(S_2C_2(CN)_2)_3^{2-},\\ &\quad W(S_2C_2(CN)_2)_3^{2-} < Ta(S_2C_6H_4)_3^- << V(S_2C_2Ph_2)_3\\ &\quad \leqslant Re(S_2C_2Ph_2)_3, Mo(S_2C_2H_2)_3, Nb(S_2C_6H_4)_3^-, Mo(S_2C_6H_4)_3\\ &\quad = \text{trigonal-prismatic limit}\end{aligned}$$

A general rationalization for these trends is presented later.

The tetramethylammonium cations are shown in Figure 1. As expected the cations have close to tetrahedral geometry, with the small distortions being due possibly to packing effects. The average N–C distance (1.47 (5) Å) agrees quite well with that predicted (1.47 Å) assuming single-bonded covalent radii.[35,36] This value is also in good agreement with previous structural determinations in which the tetramethylammonium cation was involved.[41,42] The range in N–C distances (1.416 (10)–1.530 (10) Å) may also represent a slight disorder problem as well as packing distortions.

Although this complex is of considerable interest in relation to other tris(dithiolenes), it is also interesting in its own right. The number of structurally characterized six-coordinate zirconium complexes is small[43] and indeed this complex is believed to be the first example of a six-coordinate zirconium–sulfur complex. The Zr–S distances (average 2.543 (10) Å) agree well with the sums of the ionic radii[44] (2.56 Å) for Zr(IV) and S^{2-}.

Discussion

The isoelectronic series of tris(1,2-dithiolato) complexes described in this and the two preceding papers[3,4] shows

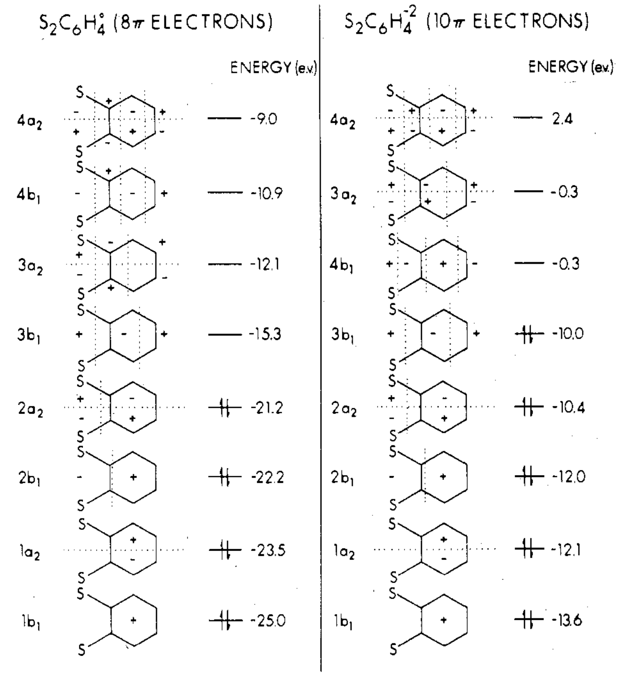

Figure 6. Representations of the π molecular orbitals of the benzene-1,2-dithiolato ligand in the reduced ($S_2C_6H_4^{2-}$) and oxidized ($S_2C_6H_4^0$) forms.

dramatic changes in the coordination polyhedra. These changes, from an almost perfect trigonal prism in the neutral molybdenum complex, to a very slightly distorted trigonal prism in the niobium complex anion, to a distorted octahedron in the zirconium complex dianion, are accompanied by smooth increases in metal–sulfur, sulfur–carbon, and interligand sulfur–sulfur distances (see Table VIII). These changes correspond to the increasing importance of the dithiolato over the dithioketonic formulation for the ligand.

Two molecular orbital schemes have been presented in an attempt to explain the stability of the trigonal prism in certain tris(1,2-dithiolato) complexes, one by Schrauzer and Mayweg[45] and the other by Gray et al.[8] Since the Schrauzer scheme has been challenged[25b,40,46] on the basis of electron spin resonance studies and has been shown to be inconsistent with the electronic spectra[8,9] in the series of compounds $Mo(S_2C_6H_4)_3$, $[Ph_4As][Nb(S_2C_6H_4)_3]$, and $[Me_4N]_2[Zr(S_2C_6H_4)_3]$ whereas Gray's scheme is consistent with these spectra, Gray's calculations are preferred and are used in all subsequent discussions.

It must first be pointed out that although the ethylenedithiolato ligand was used in Gray's calculations and the benzenedithiolato ligand is being compared in the above series, the same arguments apply. In the ethylenedithiolato ligand the highest occupied ligand π orbital is the $3\pi_v$ whereas the equivalent orbital in the benzenedithiolato ligand is the $5\pi_v$. However these orbitals have the same symmetry (b_1) with respect to overlap with the metal d orbitals and it has been shown by Birss and Das Gupta[47] that their energies are very similar (−10.2 and −10.0 eV, respectively, with a probable error of 0.3 eV). In order to maintain consistency with the nomenclature of Gray's scheme[8], the label $3\pi_v$ will be used in further discussions, although for the benzenedithiolato ligand the $5\pi_v$ is intended. The representations of the π orbitals and energy levels of the benzene-1,2-dithiolato ligand in the reduced ($S_2C_6H_4^{2-}$) and the oxidized ($S_2C_6H_4^0$) forms are shown in Figure 6.

Gray has therefore postulated that the preference of the tris(dithiolene) complexes for TP coordination is due to the ability to utilize the d orbitals, not involved in σ bonding, in a stabilizing π interaction with the ligands. Two such interactions are possible: (1) overlap of the metal d_{z^2} and ligand π_h orbitals (sp^2-hybridized lone pair on sulfur) producing the stable $2a_1'$ and antibonding $3a_1'$ levels; (2) overlap of the metal d_{xy}, $d_{x^2-y^2}$ and ligand π_v orbitals (p orbitals perpendicular to the ligand plane) producing the stable 4e′ and antibonding 5e′. The series $Mo(S_2C_6H_4)_3$, $Nb(S_2C_6H_4)_3^-$, and $Zr(S_2C_6H_4)_3^{2-}$ permits examination of this latter postulate, since in this isoelectronic series no change in the geometry of the coordination polyhedra can be attributed to the occupation of the antibonding $3a_1'$ orbital, as has been postulated[6,7] for the destabilization of the prisms in $Mo(S_2C_2(CN)_2)_3^{2-}$ and $W(S_2C_2(CN)_2)_3^{2-}$.

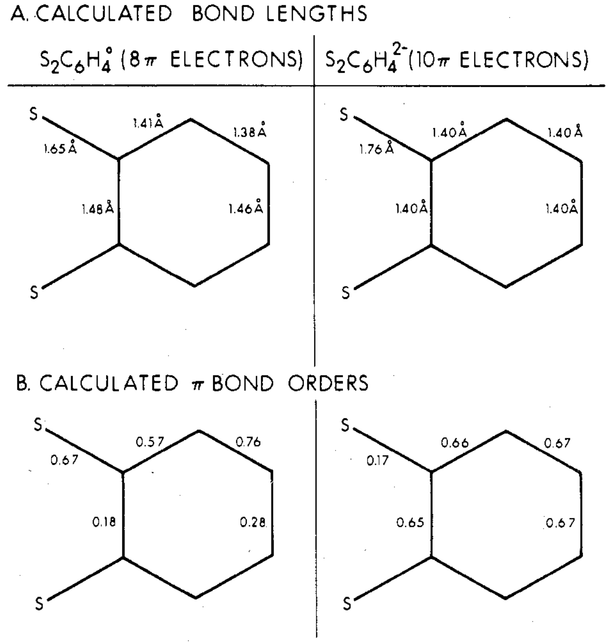

Figure 7. Calculated bond lengths and π-bond orders for $S_2C_6H_4^0$ and $S_2C_6H_4^{2-}$.

The 4e′ level should be extremely sensitive to the metal d-orbital energies due to the near-equivalence in energy of the d orbitals and the 4e′ level.[8] The $2a_1'$ level will also be affected but not as much, due to the greater energy separation of it with the metal d orbitals. As the d-orbital energies increase, the 4e′ level should be destabilized and should become more ligand ($3\pi_v$) in character. This increase in the ligand character of the 4e′ level should be paralleled by a structural change, corresponding to an increase in the contribution of the reduced-form structure. The ligand undergoes extensive geometric changes upon the reduction

$$S_2C_6H_4^0 \text{ (8 } \pi \text{ electrons)} + 2e^- \rightarrow S_2C_6H_4^{2-} \text{ (10 } \pi \text{ electrons)}$$

as is shown in Figure 7, the results of which were derived from Birss' calculations. In principle, both sulfur–carbon and carbon–carbon distances could be used in assessing the relative importance of the reduced and oxidized structures in a particular case. In practice, the high uncertainty in the carbon–carbon bond lengths (due to naturally higher standard deviations and large effects due to thermal motion) makes them unsuitable for a semiquantitative discussion and the more reliable sulfur–carbon distances provide the only useful guide. Sulfur–carbon bond lengths for the tris(benzene-1,2-dithiolato) complexes, described in this and previous papers,[2-4] and the theoretical geometries of the oxidized and reduced formulations can be ordered as follows: $S_2C_6H_4^0$ (1.648 Å) < $Mo(S_2C_6H_4)_3$ (1.727 (6) Å), < $Nb(S_2C_6H_4)_3^-$ (1.745 (9) Å) < $Zr(S_2C_6H_4)_3^{2-}$ (1.765 (7) Å) $\simeq$ $S_2C_6H_4^{2-}$ (1.763 Å). This series indicates that the ligand tends toward the reduced

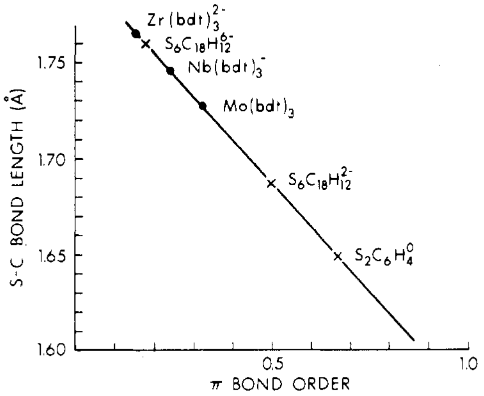

Figure 8. Plot of S-C bond length vs. S–C π-bond order for the benzenedithiolato (bdt) ligand.

geometry as the energy of the d orbital increases.

In assessing the ligand and metal orbital character of the 4e′ level, it should be noted that appropriate extremes do not correspond to $[S_2C_6H_4]_3{}^0$ and $[S_2C_6H_4]_3{}^{6-}$, written hereafter as $S_6C_{18}H_{12}{}^0$ and $S_6C_{18}H_{12}{}^{6-}$, since the ligand $3\pi_v$ orbitals give rise to the $2a_2'$ level as well as the 4e′ level.[8] This $2a_2'$ level is nonbonding, entirely located on the ligand, and is always occupied by two electrons. Hence the discussion of the 4e′ level must utilize limiting geometries defined by $[S_6C_{18}H_{12}]^{2-}$ and $[S_6C_{18}H_{12}]^{6-}$, that is, allowing for the $2a_2'$ occupancy.

Figure 8 shows the plot of S–C bond length vs. S–C π-bond order for the benzenedithiol ligand, as calculated by Birss and Das Gupta.[48] The limiting extremes $S_2C_6H_4$ and $S_2C_6H_4{}^{2-}$ are shown on this plot. For the ligand system $S_6C_{18}H_{12}{}^{2-}$ the S–C π-bond order is calculated as 0.50 and the corresponding S–C bond length is 1.69 Å. If the 4e′ level were completely ligand in character, the ligand $3\pi_v$ orbitals would contain six electrons and would be described as $S_6C_{18}H_{12}{}^{6-}$. The S–C π-bond order and S–C bond length for this extreme are 0.17 and 1.76 Å, respectively. The two limits, $S_6C_{18}H_{12}{}^{2-}$ and $S_6C_{18}H_{12}{}^{6-}$, then correspond to the extremes that the 4e′ orbital is completely metal and completely ligand in character, respectively.

In $Mo(S_2C_6H_4)_3$ the average S–C bond length (1.727 (6) Å) corresponds to a π-bond order of 0.32 and thus lies approximately midway between the $S_6C_{18}H_{12}{}^{6-}$ and $S_6C_{18}H_{12}{}^{2-}$ extremes. The 4e′ level therefore has approximately equal contributions from the metal and ligand orbitals. In $Nb(S_2C_6H_4)_3{}^-$ the S–C bond length of 1.745 (9) Å and π-bond order of 0.24 corresponds to three-fourths of the electron density of 4e′ being on the ligand and only one quarter of the electron density being on the metal. The S–C bond length of 1.765 (7) Å in $Zr(S_2C_6H_4)_3{}^{2-}$ indicates that the ligand has reached the limiting reduced formulation. It is to be noted, however, that there is a tendency in the zirconium coordination toward the trigonal prism, indicating possibly that the 4e′ level still has a small amount of metal contribution. It is also possible that the tendency toward the prism is favored by the overlap of the ligand π_h and metal d_{z^2} orbitals, which may still be operative. In addition several authors[49,50] have explained trigonal-prism stability based solely on σ-bonding arguments. It is possible therefore that the slight tendency toward the TP geometry in the zirconium complex is favored by σ bonding.

The series of complexes $Mo(S_2C_6H_4)_3$, $Nb(S_2C_6H_4)_3{}^-$, and $Zr(S_2C_6H_4)_2{}^{2-}$ therefore shows the importance of the interaction of the metal $d_{x^2-y^2}$ and d_{xy} with the ligand π_v orbitals in stabilizing the trigonal prism. In addition the prism stability in this series is maximized in $Mo(S_2C_6H_4)_3$, where the 4e′ orbital contains approximately equal contributions from metal and ligand and thus the electrons are completely delocalized over the metal–ligand framework. In the 1,1-dithiolato complexes the ligands do not have orbitals of the proper symmetry and energy to overlap with the $d_{x^2-y^2}$ and d_{xy} orbitals of the metal.[48] Therefore this delocalization is not possible and all tris(1,1-dithiolato) complexes have distorted octahedral coordinations.

Interligand sulfur–sulfur bonding has also been presented as a reason for prism stability,[7,8,39,45] and the trends observed in the benzenedithiol series can also be explained by assuming that a breakdown in S–S bonding occurs, progressing from the molybdenum complex to the zirconium complex. As the d energies increase, so also do the metal radii. Therefore, as the metal radii increase from Mo to Nb to Zr, the interligand S–S distances increase and the slight distortion observed in $Nb(S_2C_6H_4)_3{}^-$ can be explained as a partial breakdown in this S–S bonding. At $Zr(S_2C_6H_4)_3{}^{2-}$ presumably the sulfur atoms have been forced far enough apart to result in a distorted octahedral coordination, due to an almost complete breakdown in S–S bonding. A significant argument, however, against sulfur–sulfur bonding as a major stabilizing force in the prism can be seen in a comparison of $Mo(S_2C_2(CN)_2)_3{}^{2-}$ and $W(S_2C_2(CN)_2)_3{}^{2-}$ with $Nb(S_2C_6H_4)_3{}^-$. In the niobium complex the interligand sulfur–sulfur distances are greater than those in the molybdenum or the tungsten dianions (see Table VIII), yet the niobium complex is trigonal prismatic whereas the dianions are distorted octahedrons. The major argument for sulfur–sulfur bonding has been the short sulfur–sulfur contacts observed in the prisms, as compared with the predicted van der Waals contacts (3.70 Å). However the close contacts probably arise as a consequence of other factors which stabilize the prism and are probably not themselves the reason for this geometry. It is believed that the forces between the sulfur atoms are repulsive in nature rather than attractive, as proposed.[7,8,45] This can offer a possible explanation for the geometry observed[25] in $V(S_2C_2Ph_2)_3$, which is distorted slightly from the prism by a trigonal twist of 8.5°. If, as suspected, the prism dimensions in the rhenium and molybdenum complexes[23,24] have reached their minimum, due to increasing S–S repulsions, then in the vanadium complex the smaller size of the metal could result in poor overlap of the metal and ligand orbitals (possibly ligand π_h with metal d_{z^2}). It is then possible that in order to attain the maximum stability, the prism distorts slightly by the observed trigonal twist. In this respect a complete structural determination of $Cr(S_2C_2Ph_2)_3$ is desirable, since x-ray power photographs indicated[22-24] it was isomorphous with $V(S_2C_2Ph_2)_3$. However, since the chromium radius is smaller than that of vanadium,[34] if the above arguments apply, the coordination of the chromium complex should be more distorted from the prism than the vanadium complex.

It is now possible, we believe, to account for the distortions from TP coordination which have been observed in some of the anionic tris(dithiolenes). In the anions $Mo(S_2C_2(CN)_2)_3{}^{2-}$, $W(S_2C_2(CN)_2)_3{}^{2-}$, $Fe(S_2C_2(CN)_2)_3{}^{2-}$, and $In(S_2C_2(CN)_2)_3{}^{3-}$, the destabilization of the prism can be attributed to population of molecular orbitals (3a′ and 5e′) which are antibonding with respect to trigonal-prism stability. The Mo and W complexes presumably have some prism-stabilizing interactions remaining and therefore are intermediate between the corrected octahedral and TP limits. The stabilizing factor still present is possibly the result of metal d_{xy}, $d_{x^2-y^2}$ and ligand π_v overlap since the d_{z^2}–π_h overlap is no longer significant due to population of the antibonding $3a_1'$ level. In the Fe and In complexes the 5e′ antibonding level also becomes populated and this further destabilizes the prism by reducing the remaining d_{xy}, $d_{x^2-y^2}$ and π_v interaction. This results in coordinations in the Fe and In complexes which are close to the octahedral limits as governed by their respective M–S to interligand S–S distance ratios.

The distortion observed in $V(S_2C_2(CN)_2)_3^{2-}$ is rather surprising when it is considered that it has an electron configuration similar to that of the TP molecule $Re(S_2C_2Ph_2)_3$, with only one electron in the antibonding $3a_1'$ level. This distortion is even more surprising since in the neutral TP molecule $V(S_2C_2Ph_2)_3$ this $3a_1'$ orbital is still singly occupied due to reversals of the $2a_2'$ and $3a_1'$ levels.[40] Thus the neutral and dianionic vanadium complexes have electron configurations $...[3a_1']^1[2a_2']^0$ and $...[2a_2']^2[3a_1']^1$, respectively. So it seems that destabilization of the prism in the vanadium complex is not due to occupation of the antibonding $3a_1'$ level but rather to the double occupancy of the nonbonding $2a_2'$ level. It was observed[25] that even in the neutral vanadium complex the prism is distorted significantly. We believe this is due to poor π interactions between the V atom and the ligands due to the small size of the metal. Occupancy of the $2a_2'$ level results in a tendency of the ligand toward the dithiolato limit and therefore an increase in S–C bond lengths. The prism dimensions therefore increase, with a corresponding weakening of metal–ligand π overlap, especially d_{z^2}–π_h. Since the metal–ligand overlap in the V complex was not as strong as observed in other prisms, this further prism expansion is believed to be enough to destabilize the prism and favor octahedral coordination.

In both the $Ta(S_2C_6H_4)_3^-$ and $Zr(S_2C_6H_4)_3^{2-}$ anions the destabilization of the trigonal prism, relative to that of $Nb(S_2C_6H_4)_3^-$ and $Mo(S_2C_6H_4)_3$, results from increasing metal d-orbital energies, which causes a corresponding destabilization of the 4e′ molecular orbital. Zirconium, with the least stable d orbitals of this series has a coordination which is most distorted toward the octahedral limit. Tantalum, with d orbitals only slightly less stable than those of niobium,[49] seems to be barely destabilized from trigonal-prismatic coordination, having two ligands which are close to the TP limit.

In conclusion, the series of complexes $Mo(S_2C_6H_4)_3$, $[Ph_4As][Nb(S_2C_6H_4)_3]$, and $[Me_4N]_2[Zr(S_2C_6H_4)_3]$ and, more recently,[29] $[Ph_4As][Ta(S_2C_6H_4)_3]$ has shown the importance of the metal d_{xy}, $d_{x^2-y^2}$ and ligand π_v overlap in determining trigonal-prism stability. The metal d_{z^2} and ligand π_h overlap has also been shown by other workers[6,7,8,24] to be a significant factor in stabilizing the prism. Contrary to popular belief, sulfur–sulfur bonding is not believed to be a significant factor in determining trigonal-prism stability in tris(dithiolenes). Rather the trigonal-prismatic coordination is favored over the octahedral coordination because of the above stabilizing π interactions which are possible in the trigonal prism but not in the octahedron.

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Registry No. $[(CH_3)_4N]_2[Zr(S_2C_6H_4)_3]$, 58919-13-4.

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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(1) This and the preceding two papers[3,4] are based in part on a dissertation submitted by M. Cowie to the Graduate school of the University of Alberta in partial fulfillment of the requirement for the Ph.D. degree, June 1974.

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(19) Supplementary material.

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(21) The equivalent isotropic *B*'s are calculated from the expression $B = {}^4/_3 \sum_{i,j=1}^{3} B_{ij} a_i a_j$, where a_i and a_j are the translation vectors of the direct lattice.

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