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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]

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Received December 1, 1975 AIC50859J

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, $c = 13.150$

(3) Å, and $\beta = 92.09$ (2)°. The observed density, obtained by flotation in aqueous zinc bromide solution, is 1.52 (2) g cm^{-3} and is in reasonable agreement with the theoretical value of 1.54 g cm^{-3} calculated assuming four formula units with mol wt 896.9 per unit cell of volume 3867.1 Å^3.

Intensity data were collected on the Picker automatic diffractometer, using Ni-filtered Cu Kα x radiation and using a 2° takeoff angle. The crystal was aligned in a general orientation but with its b^* axis approximately coincident with the ϕ axis of the instrument. Crystal faces were identified and perpendicular distances between faces of the same form were measured as follows: $\{100\}$, 0.206 mm; $\{\bar{2}10\}$, 0.206 mm; $\{\bar{2}\bar{1}0\}$, 0.206 mm; $\{\bar{1}01\}$, 0.155 mm; $\{101\}$, 0.175 mm.

In the data collection a coupled 2θ–ω scan was used with a 2θ scan speed of 1°/min to collect all reflections with $2\theta \leq 115°$. The peak scan was 2° (2 min) for low-angle reflections but increased with increasing 2θ due to compensation for α_1–α_2 separation. Background counts were measured for 20 s at the limits of the 2θ scan. The scattered x rays were detected by a scintillation counter 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. Another five standard reflections were collected manually every 10 h to detect more precisely decomposition and crystal centering errors. No significant decomposition was observed.

Of the 5862 unique reflections collected, 3604 were considered as significantly above background using the criterion $I/\sigma(I) \geq 3.0$. The data were reduced to structure factor amplitudes by correction for Lorentz, polarization, and absorption effects. For Cu Kα x radiation, the linear absorption coefficient is 68.42 cm^{-1} which yielded a range of transmission factors of 0.436–0.313. Standard deviations were estimated using a "p factor" of 0.03 as outlined previously.[14] Terms used in the Zachariasen extinction correction were calculated at this stage.[15]

Solution and Refinement of Structure

The structure was refined by full-matrix, least-squares techniques,[16] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and $w = 1/\sigma^2(F)$. The agreement indices R and R_w are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. Nonhydrogen atom scattering factors used were those of Cromer and Mann.[17] Values by Stewart et al.[18] were used for hydrogen. Anomalous dispersion corrections by Cromer[19] for Nb, As, and S were applied to the calculated structure factors.

The niobium and arsenic positions were obtained from the Nb–Nb, As–As, and Nb–As vectors in the sharpened Patterson map. One cycle of least-squares refinement with these atoms gave $R = 0.421$ and $R_w = 0.507$. A difference Fourier synthesis phased on this information yielded the six sulfur positions and refinement of the positions and isotropic thermal parameters for these eight atoms gave $R = 0.270$ and $R_w = 0.359$. A second difference Fourier clearly located all of the carbon atom positions. Refinement of this model with niobium, arsenic, and sulfur atoms refined isotropically, by treating the phenyl groups as rigid bodies with C–C distances of 1.395 Å, and by having individual isotropic temperature factors for each carbon atom yielded $R = 0.076$ and $R_w = 0.087$. Correction for absorption effects and secondary extinction further reduced the agreement indices to $R = 0.064$ and $R_w = 0.072$. Anisotropic refinement of the Nb, S, and As atoms gave $R = 0.056$ and $R_w = 0.065$. All hydrogen atoms were located in a difference Fourier map calculated at this time and were included in all subsequent calculations as fixed contributions, their positions being idealized from the known carbon positions assuming a C–H distance of 0.98 Å. The hydrogen atoms were assigned thermal parameters approximately 10–15% higher than those of their attached carbon atoms. Dithiolene carbon atoms were treated in all subsequent refinements as individual atoms. A least-squares calculation refining these dithiolene carbon atoms isotropically gave $R = 0.049$ and $R_w = 0.051$. The final model in which the dithiolene carbon atoms were refined anisotropically yielded the agreement indices $R = 0.047$ and $R_w = 0.048$.

In the final least-squares refinement 284 parameters were varied and the error in an observation of unit weight was 1.641 electrons. The final value of the refined extinction parameter, C, was 8.74×10^{-7}.

The observed and calculated structure amplitudes, $10|F_o|$ and $10|F_c|$, are shown in Table I.[20] The final fractional coordinates and isotropic B's of all atoms 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).[21] See Tables IV and V for selected distances and angles and Table VI for weighted least-squares planes.

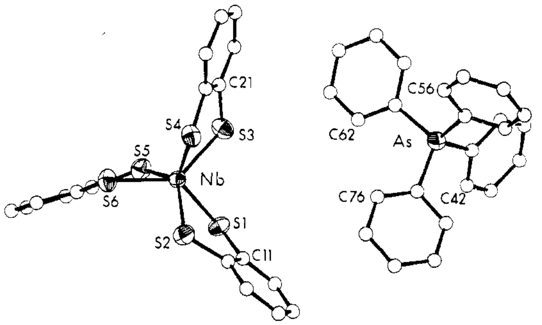

Figure 1. View of the $Nb(S_2C_6H_4)_3^-$ anion and $(C_6H_5)_4As^+$ cation together, projected down the crystallographic b axis. Vibrational ellipsoids are shown at the 50% level except for carbon atoms which are given arbitrarily lower thermal parameters for clarity of the drawing. The numbering scheme is shown.

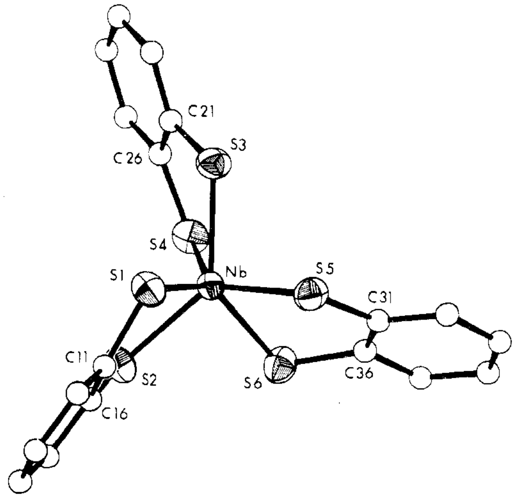

Figure 2. View of the $Nb(S_2C_6H_4)_3^-$ anion showing the numbering scheme. Vibrational ellipsoids are shown at the 50% level, except the carbon atoms which are given arbitrarily lower thermal parameters for clarity.

Description of Structure

The structure of $[Ph_4As][Nb(S_2C_6H_4)_3]$ consists of four monomeric anions and cations packed in the unit cell. A view of the anion and cation together, projected down the crystallographic b axis, is shown in Figure 1. Figure 2 shows the $Nb(S_2C_6H_4)_3^-$ anion alone. The numbering scheme is shown in both drawings. The carbon atoms of the phenyl rings are numbered consecutively progressing around the ring with the tens digit representing the ring number and the units digit representing the atom sequence. In the tetraphenylarsonium cation the first carbon of each ring (C(41), C(51), C(61), and C(71)) is bonded to the arsenic atom. Hydrogen atoms have the same number as their attached carbon atom. In both representations the carbon atoms are given artificially low thermal parameters for clarity of the drawing. The other atoms are represented by their 50% probability ellipsoids of thermal motion.

There are no unusually close contacts between ions, the closest contacts being comparable to the van der Waals separations of the atoms involved.

As is shown in Figures 1 and 2, the niobium atom is surrounded by six sulfur atoms in a trigonal-prismatic (TP) coordination with the dithiolene ligands radiating from the metal in a "paddle-wheel" arrangement, as has been observed

Table II. Atom Coordinates and Isotropic Temperature Factors

Atom	x^a	y	z	B, Å^2
Nb	0.581 36 (2)	0.214 18 (5)	0.195 28 (4)	2.47^b
As	0.209 39 (3)	0.157 80 (7)	0.267 35 (6)	3.31^b
S(1)	0.521 86 (8)	0.113 0 (1)	0.074 6 (1)	3.26^b
S(2)	0.572 10 (8)	0.341 3 (2)	0.056 7 (1)	3.60^b
S(3)	0.516 30 (8)	0.132 9 (2)	0.316 9 (1)	3.75^b
S(4)	0.561 93 (8)	0.365 9 (1)	0.301 0 (1)	3.54^b
S(5)	0.633 90 (8)	0.050 3 (1)	0.224 2 (1)	3.54^b
S(6)	0.681 63 (7)	0.279 8 (2)	0.198 9 (1)	3.51^b
C(11)	0.487 6 (3)	0.202 7 (6)	−0.006 7 (5)	2.82^b
C(12)	0.441 2 (3)	0.174 1 (6)	−0.073 1 (5)	3.43^b
C(13)	0.416 4 (3)	0.242 0 (7)	−0.141 1 (6)	4.21^b
C(14)	0.436 4 (3)	0.345 5 (7)	−0.144 5 (6)	4.09^b
C(15)	0.482 4 (3)	0.376 5 (6)	−0.082 0 (6)	3.69^b
C(16)	0.509 1 (3)	0.307 4 (6)	−0.013 2 (5)	3.06^b
C(21)	0.521 0 (3)	0.212 0 (7)	0.425 4 (5)	3.81^b
C(22)	0.498 9 (4)	0.177 0 (7)	0.518 2 (7)	4.93^b
C(23)	0.497 1 (4)	0.245 8 (9)	0.600 5 (7)	6.19^b
C(24)	0.516 5 (4)	0.345 2 (9)	0.592 1 (7)	6.09^b
C(25)	0.539 5 (3)	0.381 8 (7)	0.503 9 (7)	4.70^b
C(26)	0.540 5 (3)	0.314 3 (6)	0.418 0 (6)	3.41^b
C(36)	0.725 6 (3)	0.171 6 (6)	0.173 3 (5)	3.19^b
C(35)	0.783 7 (3)	0.187 5 (6)	0.150 5 (6)	3.86^b
C(34)	0.819 8 (3)	0.103 2 (8)	0.132 8 (6)	4.97^b
C(33)	0.798 3 (4)	0.002 4 (7)	0.141 5 (6)	5.04^b
C(32)	0.741 8 (4)	−0.013 7 (6)	0.164 8 (6)	4.66^b
C(31)	0.704 0 (3)	0.071 7 (6)	0.183 5 (5)	3.17^b
Rigid Bodies				
(a) Phenyl Carbon Atoms				
C(41)	0.158 9 (2)	0.043 5 (3)	0.239 7 (4)	3.4 (2)
C(42)	0.165 6 (3)	−0.018 4 (4)	0.153 3 (3)	4.1 (2)
C(43)	0.131 9 (3)	−0.108 7 (4)	0.138 7 (4)	4.5 (2)
C(44)	0.091 5 (2)	−0.137 1 (3)	0.210 5 (4)	4.7 (2)
C(45)	0.084 7 (3)	−0.075 2 (4)	0.296 8 (3)	4.9 (2)
C(46)	0.118 4 (3)	0.015 1 (4)	0.311 4 (4)	4.3 (2)
[$D^c = 3.710$ (3)°; $E^c = 0.982$ (4)°; $F^c = 4.924$ (4)°]				
C(51)	0.168 8 (2)	0.269 7 (3)	0.325 9 (4)	3.4 (2)
C(52)	0.111 8 (2)	0.291 4 (4)	0.291 6 (4)	4.4 (2)
C(53)	0.084 5 (1)	0.383 3 (4)	0.322 6 (3)	4.9 (2)
C(54)	0.114 0 (2)	0.453 3 (3)	0.387 7 (4)	4.9 (2)
C(55)	0.171 0 (2)	0.431 5 (4)	0.422 0 (4)	4.7 (2)
C(56)	0.198 4 (1)	0.339 7 (4)	0.391 0 (3)	4.0 (2)
[$D = 5.779$ (3)°; $E = 2.731$ (4)°; $F = 4.418$ (3)°]				
C(61)	0.267 9 (4)	0.109 8 (4)	0.360 0 (10)	3.6 (2)
C(62)	0.321 1 (5)	0.072 5 (4)	0.326 5 (5)	5.1 (2)
C(63)	0.361 3 (3)	0.027 9 (4)	0.396 1 (7)	5.7 (2)
C(64)	0.348 2 (4)	0.020 7 (4)	0.499 0 (10)	5.1 (2)
C(65)	0.295 0 (5)	0.058 0 (4)	0.531 8 (5)	4.9 (2)
C(66)	0.254 8 (3)	0.102 6 (4)	0.462 2 (7)	4.3 (2)
[$D = 2.023$ (3)°; $E = 1.217$ (8)°; $F = 5.084$ (8)°]				
C(71)	0.237 0 (5)	0.209 8 (4)	0.142 9 (8)	3.3 (1)
C(72)	0.196 3 (5)	0.221 2 (4)	0.062 2 (4)	4.4 (2)
C(73)	0.212 6 (7)	0.268 0 (5)	−0.028 5 (7)	5.5 (2)
C(74)	0.269 6 (5)	0.303 4 (4)	−0.038 4 (8)	5.4 (2)
C(75)	0.310 3 (5)	0.292 0 (4)	0.042 3 (4)	6.3 (2)
C(76)	0.294 0 (7)	0.245 2 (5)	0.133 0 (7)	5.2 (2)
[$D = 1.109$ (4)°; $E = 2.521$ (8)°; $F = 4.425$ (8)°]				
(b) Phenyl Hydrogen Atoms				
H(12)	0.799 0	0.261 9	0.144 6	4.5
H(13)	0.861 3	0.115 2	0.115 1	5.0
H(14)	0.824 3	−0.059 8	0.128 1	5.0
H(15)	0.725 0	−0.088 0	0.170 5	4.5
[$D = 3.159°$; $E = 0.277°$; $F = 5.085°$]				
H(22)	0.484 0	0.102 9	0.522 9	5.4
H(23)	0.480 9	0.218 4	0.666 3	6.0
H(24)	0.515 8	0.394 8	0.653 0	6.0
H(25)	0.553 7	0.455 7	0.496 2	5.4
[$D = 3.448°$; $E = 1.285°$; $F = 1.748°$]				
H(32)	0.426 7	0.098 2	−0.068 5	4.1
H(33)	0.382 6	0.219 9	−0.186 9	4.7
H(34)	0.418 2	0.396 3	−0.194 9	4.7
H(35)	0.497 8	0.450 9	−0.084 6	4.1
[$D = 0.281°$; $E = 2.406°$; $F = 4.929°$]				
H(42)	0.194 5	0.001 6	0.102 0	4.6
H(43)	0.136 9	−0.153 5	0.077 3	5.1
H(44)	0.067 4	−0.202 0	0.200 4	5.0
H(45)	0.055 6	−0.095 3	0.348 2	5.5
H(46)	0.113 2	0.059 7	0.373 0	5.1
[$D = 3.707°$; $E = 0.981°$; $F = 5.973°$]				
H(52)	0.090 5	0.241 4	0.245 2	5.0
H(53)	0.043 6	0.398 9	0.298 3	5.9
H(54)	0.094 4	0.519 1	0.410 0	5.5
H(55)	0.192 2	0.481 6	0.468 5	5.1
H(56)	0.239 1	0.324 1	0.415 4	4.7
[$D = 5.779°$; $E = 2.732°$; $F = 5.465°$]				
H(62)	0.330 5	0.077 3	0.252 9	5.1
H(63)	0.399 4	0.001 3	0.372 5	6.1
H(64)	0.377 0	−0.010 7	0.548 6	5.8
H(65)	0.285 6	0.053 1	0.605 2	5.3
H(66)	0.216 6	0.129 0	0.485 6	4.7
[$D = 2.020°$; $E = 1.219°$; $F = 6.134°$]				
H(72)	0.155 5	0.195 7	0.069 1	5.1
H(73)	0.183 6	0.275 6	−0.086 4	5.6
H(74)	0.281 4	0.336 4	−0.103 4	6.2
H(75)	0.351 1	0.317 3	0.035 2	6.8
H(76)	0.323 0	0.237 4	0.190 9	5.6
[$D = 1.111°$; $E = 2.515°$; $F = 5.467°$]				

[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[22] 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, 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.

in all previous dithiolene prisms.[2-5] The two triangular faces of the prism are bound by S(1), S(3), S(5) and by S(2), S(4), S(6). These two faces are almost exactly parallel, being tilted by only 0.6° to each other (see Table VII). In addition these two triangular faces are close to being eclipsed, the average twist angle between the two faces being only 0.7°.

The prism is expanded significantly from all previous determinations.[2-5] The mean Nb–S distance (2.441 (11) Å) is significantly longer than the Mo–S distance (2.367 (6) Å) in $Mo(S_2C_6H_4)_3$[2] and thus is the longest metal–sulfur distance yet observed in any TP molecule (compare 2.32 (1), 2.33 (1), and 2.337 (6) Å in $Re(S_2C_2Ph_2)_3$, $Mo(S_2C_2H_2)_3$, and $V(S_2C_2Ph_2)_3$, respectively. [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.] This increase in metal–sulfur distance (0.074 Å) proceeding from $Mo(S_2C_6H_4)_3$ to $Nb(S_2C_6H_4)_3^-$ is approximately in agreement with that predicted considering the greater ionic radius of Nb(V) compared to that of Mo(VI). The larger Nb–S distances also result in larger S–S distances. Due to the relatively inflexible ligand bite this manifests itself in interligand S–S distances (3.23 (5) Å) which are longer than the intraligand distances (3.150 (9) Å). These S–S distances (both inter- and intraligand) are the largest yet observed in a TP molecule, with the examples, cited above, having intraligand S–S distances of 3.032 (10), 3.10, and 3.061 (12) Å and interligand S–S distances of 3.050 (8), 3.11, and 3.07 (13) Å, respectively. It

Table III. Anisotropic Thermal Parameters (Å^2)

Atom	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb	0.0324 (3)	0.0310 (4)	0.0302 (3)	−0.0003 (3)	0.0007 (2)	−0.0025 (3)
As	0.0385 (5)	0.0502 (6)	0.0370 (5)	−0.0037 (4)	0.0025 (4)	−0.0057 (5)
S(1)	0.0510 (12)	0.0340 (11)	0.0383 (11)	−0.0004 (9)	−0.0071 (9)	−0.0022 (9)
S(2)	0.0515 (12)	0.0430 (12)	0.0420 (11)	−0.0098 (11)	−0.0024 (9)	0.0051 (10)
S(3)	0.0547 (12)	0.0407 (13)	0.0475 (12)	−0.0054 (10)	0.0120 (10)	−0.0034 (10)
S(4)	0.0413 (11)	0.0397 (12)	0.0535 (12)	−0.0008 (9)	0.0059 (9)	−0.0093 (10)
S(5)	0.0457 (12)	0.0388 (12)	0.0496 (13)	0.0048 (9)	−0.0042 (10)	0.0083 (10)
S(6)	0.0385 (10)	0.0394 (12)	0.0556 (12)	−0.0022 (10)	0.0009 (9)	−0.0093 (11)
C(11)	0.036 (4)	0.036 (5)	0.036 (4)	−0.005 (4)	0.000 (3)	−0.001 (4)
C(12)	0.045 (5)	0.048 (5)	0.037 (4)	−0.007 (4)	−0.006 (4)	0.000 (4)
C(13)	0.049 (5)	0.069 (7)	0.041 (5)	0.004 (5)	−0.004 (4)	0.004 (5)
C(14)	0.054 (5)	0.062 (6)	0.039 (5)	0.011 (5)	−0.007 (4)	0.008 (5)
C(15)	0.053 (5)	0.041 (5)	0.046 (5)	0.006 (4)	0.002 (4)	0.006 (4)
C(16)	0.036 (4)	0.049 (5)	0.031 (4)	0.006 (4)	0.005 (3)	−0.005 (4)
C(21)	0.040 (4)	0.066 (6)	0.039 (5)	0.006 (5)	0.007 (4)	−0.008 (5)
C(22)	0.063 (6)	0.067 (7)	0.058 (6)	0.008 (5)	0.011 (5)	0.010 (5)
C(23)	0.079 (7)	0.111 (9)	0.045 (6)	0.022 (7)	0.011 (5)	0.005 (6)
C(24)	0.081 (7)	0.109 (9)	0.041 (6)	0.032 (7)	−0.006 (5)	−0.021 (6)
C(25)	0.045 (5)	0.076 (7)	0.057 (6)	0.014 (5)	−0.011 (4)	−0.025 (5)
C(26)	0.040 (4)	0.044 (5)	0.046 (5)	0.006 (4)	0.000 (4)	−0.007 (4)
C(31)	0.038 (4)	0.048 (5)	0.034 (4)	0.010 (4)	−0.002 (4)	0.001 (4)
C(32)	0.061 (6)	0.053 (6)	0.063 (6)	0.010 (5)	−0.004 (5)	0.011 (5)
C(33)	0.061 (6)	0.067 (7)	0.064 (6)	0.029 (5)	0.010 (5)	0.012 (5)
C(34)	0.043 (5)	0.086 (7)	0.061 (6)	0.020 (5)	0.005 (4)	0.019 (6)
C(35)	0.040 (5)	0.066 (6)	0.040 (5)	0.003 (4)	−0.004 (4)	0.007 (4)
C(36)	0.045 (5)	0.042 (5)	0.034 (4)	0.007 (4)	−0.002 (4)	0.002 (4)

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

Table IV. Selected Distances (Å) in $[Ph_4As][Nb(S_2C_6H_4)_3]$

Atoms	Distance	Atoms	Distance
Nb-S(1)	2.428 (2)	S(4)-C(26)	1.760 (8)
Nb-S(2)	2.442 (2)	S(5)-C(31)	1.739 (7)
Nb-S(3)	2.458 (2)	S(6)-C(36)	1.750 (7)
Nb-S(4)	2.433 (2)	C(11)-C(12)	1.402 (9)
Nb-S(5)	2.436 (2)	C(12)-C(13)	1.356 (10)
Nb-S(6)	2.451 (2)	C(13)-C(14)	1.398 (10)
As-C(41)	1.891 (4)	C(14)-C(15)	1.374 (10)
As-C(51)	1.883 (4)	C(15)-C(16)	1.392 (9)
As-C(61)	1.880 (4)	C(16)-C(11)	1.424 (9)
As-C(71)	1.896 (4)	C(21)-C(22)	1.410 (10)
S(1)-S(2)	3.143 (3)	C(22)-C(23)	1.396 (12)
S(3)-S(4)	3.160 (3)	C(23)-C(24)	1.349 (13)
S(5)-S(6)	3.147 (3)	C(24)-C(25)	1.374 (12)
S(1)-S(3)	3.204 (3)	C(25)-C(26)	1.422 (10)
S(1)-S(5)	3.282 (3)	C(26)-C(21)	1.385 (10)
S(3)-S(5)	3.184 (3)	C(31)-C(32)	1.419 (10)
S(2)-S(4)	3.245 (3)	C(32)-C(33)	1.363 (11)
S(2)-S(6)	3.178 (3)	C(33)-C(34)	1.383 (12)
S(4)-S(6)	3.294 (3)	C(34)-C(35)	1.382 (11)
S(1)-C(11)	1.736 (7)	C(35)-C(36)	1.395 (9)
S(2)-C(16)	1.740 (7)	C(36)-C(31)	1.375 (10)
S(3)-C(21)	1.747 (7)		

Table V. Selected Angles (deg) in $[Ph_4As][Nb(S_2C_6H_4)_3]$

Atoms	Angle	Atoms	Angle
S(1)-Nb-S(2)	80.40 (7)	C(41)-As-C(71)	109.0 (2)
S(3)-Nb-S(4)	80.47 (7)	C(51)-As-C(61)	109.6 (2)
S(5)-Nb-S(6)	80.18 (7)	C(51)-As-C(71)	105.9 (2)
S(1)-Nb-S(5)	84.87 (7)	C(61)-As-C(71)	114.6 (2)
S(1)-Nb-S(3)	81.94 (7)	C(11)-C(12)-C(13)	122.4 (7)
S(3)-Nb-S(5)	81.18 (7)	C(12)-C(13)-C(14)	119.5 (7)
S(2)-Nb-S(4)	83.46 (7)	C(13)-C(14)-C(15)	120.0 (7)
S(2)-Nb-S(6)	81.03 (7)	C(14)-C(15)-C(16)	121.2 (7)
S(4)-Nb-S(6)	84.81 (7)	C(15)-C(16)-C(11)	120.0 (7)
S(1)-Nb-S(4)	133.25 (7)	C(16)-C(11)-C(12)	117.8 (6)
S(1)-Nb-S(6)	134.51 (7)	C(21)-C(22)-C(23)	119.6 (8)
S(3)-Nb-S(2)	136.61 (7)	C(22)-C(23)-C(24)	120.5 (9)
S(3)-Nb-S(6)	136.50 (7)	C(23)-C(24)-C(25)	121.8 (10)
S(5)-Nb-S(2)	135.63 (7)	C(24)-C(25)-C(26)	119.9 (9)
S(5)-Nb-S(4)	133.86 (7)	C(25)-C(26)-C(21)	120.0 (8)
Nb-S(1)-C(11)	106.5 (2)	C(26)-C(21)-C(22)	119.1 (8)
Nb-S(2)-C(16)	106.1 (3)	C(31)-C(32)-C(33)	121.1 (8)
Nb-S(3)-C(21)	105.5 (3)	C(32)-C(33)-C(34)	120.3 (8)
Nb-S(4)-C(26)	105.4 (3)	C(33)-C(34)-C(35)	119.5 (8)
Nb-S(5)-C(31)	106.1 (3)	C(34)-C(35)-C(36)	120.4 (8)
Nb-S(6)-C(36)	106.0 (3)	C(35)-C(36)-C(31)	120.5 (7)
S(1)-C(11)-C(16)	120.2 (6)	C(36)-C(31)-C(32)	118.0 (7)
S(2)-C(16)-C(11)	119.0 (5)	S(3)-S(1)-S(5)	58.80 (6)
S(3)-C(21)-C(26)	119.7 (6)	S(5)-S(3)-S(1)	61.83 (6)
S(4)-C(26)-C(21)	121.1 (6)	S(3)-S(5)-S(1)	59.37 (6)
S(5)-C(31)-C(36)	121.1 (6)	S(6)-S(2)-S(4)	61.69 (6)
S(6)-C(36)-C(31)	119.9 (6)	S(2)-S(4)-S(6)	58.16 (6)
C(41)-As-C(51)	110.6 (2)	S(2)-S(6)-S(4)	60.15 (6)
C(41)-As-C(61)	107.1 (2)		

is interesting that in all previous dithiolene prisms there had been an amazing constancy in prism dimensions (M–S and S–S distances), especially when it is considered that the metal radii varied by about 0.07 Å (consider, for example, $ReS_6C_6Ph_6$[3] and $VS_6C_6Ph_6$[5]). $Nb(S_2C_6H_4)_3^-$ is therefore the first example where this is no longer true, having a significantly larger framework than all of the previous dithiolene prisms. The prism in $Mo(Se_2C_2(CF_3)_2)_3$[23] is of course larger than the niobium prism (Mo–Se = 2.492 (2) Å; interligand Se–Se = 3.222 (3) Å; intraligand Se–Se = 3.317 (5) Å), but this is due to the larger Se radius compared to that of S.

Although distinctively TP, the niobium prism has several subtle distortions from the ideal geometry. The increasing Nb–S distances cause an increase in the interligand S–S distances, whereas the fixed geometry of the ligand maintains a relatively short bite distance. Therefore the edges of the prism are no longer square but rather are rectangular. In addition there is a significant range in Nb–S distances from 2.428 (2) to 2.458 (2) Å and an even more pronounced range in interligand S–S distances from 3.178 (3) to 3.294 (3) Å, all resulting in small but distinct distortions from TP geometry.

The sulfur–carbon distances (1.745 (9) Å), although similar to those of the other tris(dithiolenes), are longer than any observed previously and more significantly are longer than those in $Mo(S_2C_6H_4)_3$ (1.727 (6) Å)[2] where the same ligand is involved. Thus the sulfur–carbon bonds have less double-bond character in the niobium complex and the ligands are therefore more dithiolate and less dithioketonic in character than for $Mo(S_2C_6H_4)_3$. The mean carbon–carbon distance within the ligands is again consistent with those observed in benzene[24] and in several disubstituted benzene derivatives.[25] Again, as was the case for $Mo(S_2C_6H_4)_3$, there is a wide range

Table VI

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

	Plane							
Atom	1	2	3	4	5	6	7	8
Nb	0	0	0	-714^a	-710^a	687^a		
S(1)	0			−1 (2)			0	
S(2)	0			9 (2)				0
S(3)		0			4 (2)		0	
S(4)		0			4 (2)			0
S(5)			0			−6 (2)	0	
S(6)			0			1 (2)		0
C(11)				−48 (7)				
C(12)				41 (7)				
C(13)				78 (8)				
C(14)				10 (8)				
C(15)				−71 (8)				
C(16)				−86 (7)				
C(21)					−90 (7)			
C(22)					−12 (9)			
C(23)					−67 (9)			
C(24)					60 (9)			
C(25)					−23 (8)			
C(26)					−67 (7)			
C(31)						36 (7)		
C(32)						−42 (8)		
C(33)						−52 (9)		
C(34)						−4 (9)		
C(35)						57 (8)		
C(36)						55 (7)		

Coefficients of the Plane Equation $AX + BY + CZ = D^b$

Plane	*A*	*B*	*C*	*D*
1	−0.8413	0.3686	0.3953	−9.1444
2	0.7683	−0.2315	0.5967	11.0967
3	−0.0706	0.1393	0.9877	1.9792
4	−0.6239	0.3044	0.7198	−6.3172
5	0.9191	−0.3096	0.2438	11.2653
6	0.2788	0.0011	0.9063	6.8577
7	−0.3396	−0.9393	0.0484	−5.3688
8	−0.3423	−0.9380	0.0545	−8.5348

[a] These atoms were not included in the plane calculations. [b] *X*, *Y*, and *Z* are in angstroms and refer to the orthogonal coordinates along *a*, *b*, and *c**.

Table VII. Dihedral Angles between Selected Planes

Atoms in plane 1	Atoms in plane 2	Angle, deg
Nb, S(1), S(2)	Nb, S(3), S(4)	119.7
Nb, S(1), S(2)	Nb, S(5), S(6)	120.1
Nb, S(3), S(4)	Nb, S(5), S(6)	120.2
Nb, S(1), S(2)	S(1), S(2), C(11), C(12), C(13), C(14), C(15), C(16)	22.8
Nb, S(3), S(4)	S(3), S(4), C(21), C(22), C(23) C(24), C(25), C(26)	22.6
Nb, S(5), S(6)	S(5), S(6), C(31), C(32), C(33), C(34), C(35), C(36)	21.8
S(1), S(3), S(5)	S(2), S(4), S(6)	0.6

in C–C distances (Figure 3). From the diagram showing the average C–C bond lengths one sees that the C(2)–C(3), C(3)–C(4), and C(4)–C(5) distances are significantly shorter than the other three. This may be interpreted as indicating some contribution from the dithioketonic formulation. But this simple interpretation should not be made in the absence of a full analysis of the thermal parameters and an assessment of their effect on the observed uncorrected bond distances.

The intra- and interligand S–Nb–S angles average 80.35 (15) and 82.9 (17)°, respectively, and are therefore a further indication of the slight distortion from trigonal-prismatic coordination. Possibly a more significant indication of the distortion, however, is the range in the interligand S–Nb–S angles, from 84.87 (7) to 81.03 (7)°. The S–Nb–S angles, involving sulfur atoms approximately trans to each other, average 135.1 (14)°, which is again similar to the value of 136 (1)° found in the other prisms. The angles between the NbS_2 planes, as shown in Table VII, are all close to the expected 120°. The Nb–S–C angles average 105.9 (4)° all in close agreement with each other. The S_A–C(1)–C(6) and S_B–C(6)–C(1) angles (Figure 3) are all close to the expected value of 120°. This good internal agreement of the Nb–S–C and also the S–C–C angles adds further proof that the deviations in the interligand S–Nb–S angles are indeed significant.

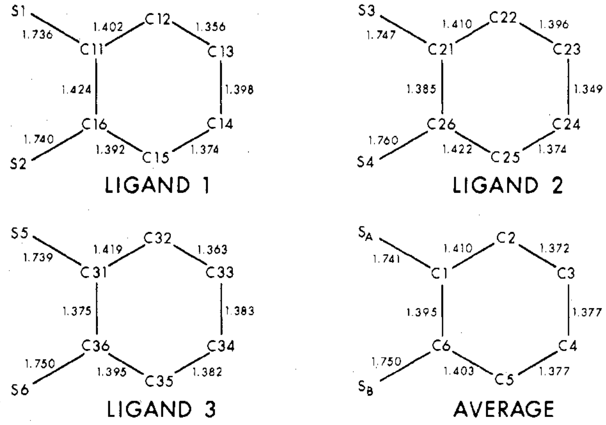

Figure 3. Dimensions within the three dithiolene ligands and average ligand dimensions.

As was observed in $Mo(S_2C_6H_4)_3$,[2] $Mo(S_2C_2H_2)_3$,[4] and $Mo[Se_2C_2(CF_3)_2]_3$,[23] the ligand planes again deviate considerably from the corresponding MS_2 planes. These deviations are more regular in $Nb(S_2C_6H_4)_3^-$ than in $Mo(S_2C_6H_4)_3$ (see Table VII). Their mean values, 22.4 and 21.4°, respectively, are however in good agreement and both are larger than the values of 18 and 18.6° observed in $Mo(S_2C_2H_2)_3$ and $Mo[Se_2C_2(CF_3)_2]_3$, respectively. The irregular dihedral angles in $Mo(S_2C_6H_4)_3$ are probably a consequence of packing forces. It seems that in the present complex the flexibility, afforded by the rotational freedom of the phenyl groups of the tetraphenylarsonium cation, allows effective packing without major deformation of the ligand planes. It is probable then that the structure observed in the crystal closely approximates the structure in solution.

It is interesting that this folding of the ligand planes from the MS_2 planes has been observed in the trigonal-prismatic molybdenum dithiolenes and also in the molybdenum–diselenato complex and now has been observed in $Nb(S_2C_6H_4)_3^-$ which is isoelectronic with the molybdenum analogue. In contrast, the ligand planes were found to be coplanar with the MS_2 planes in both $Re(S_2C_2Ph_2)_3$[3] and $V(S_2C_2Ph_2)_3$.[5] This folding of the ligand planes with respect to the MS_2 planes about their S–S axes is not restricted to these trigonal-prismatic complexes, as Köpf, Kutoglu, and Debaerdemaeker have observed it in bis(cyclopentadienyl)dithiolenemetal complexes.[26-30] These authors have rationalized the bending as due to interaction of the π orbitals perpendicular to the ligand plane and metal orbitals as derived from the Ballhausen–Dahl bonding scheme.[31] Although recent work[32-36] contradicts this bonding scheme and favors instead the Alcock model,[37] similar conclusions about the ligand bending have been reached by Lauher and Hoffmann[38] based on the Alcock model. By folding of the ligand a greater π overlap is possible than in the case where the MS_2 plane is coplanar with the dithiolene ligand plane. It is noteworthy that this orbital overlap which is postulated as causing folding is very similar to the ligand π_v and metal d_{xy}, $d_{x^2-y^2}$ overlap which has been postulated as a stabilizing factor in the trigonal prism.[2,10] In addition in tris(methyl vinyl ketone)tungsten,[39] the tungsten atom was found to be surrounded by six carbon atoms in a TP coordination. Here again the ligands are folded relative to the metal–ligand planes, this time about the C=C axes. The authors attribute the prism stability in this molecule as due to π interaction of the metal d orbitals with the olefinic double bond which is in addition to the metal–carbon σ bonds. This additional stabilizing π overlap can only occur in the TP geometry and here only if the ligand planes bend with respect to the WC_2 planes.

It seems likely therefore that the ligand folding in the TP dithiolenes has a similar origin to these above examples. Possibly in the situation where the MS_2 and dithiolene planes are coplanar the overlap between the metal d_{xy}, $d_{x^2-y^2}$ and ligand π_v orbitals is less than that attainable if the ligands fold relative to the MS_2 planes. Thus by folding about their S–S axes the ligands achieve a more stabilizing π interaction with the metal orbitals. This still does not, however, explain the coplanarity of the ligand–MS_2 planes in $ReS_6C_6Ph_6$ and $VS_6C_6Ph_6$. Previously it had been assumed that these two complexes were the norm and that the prisms in which the ligand planes were folded were unusual. It is possible, however, that the opposite is true and that the Re and V complexes cannot achieve the more stabilizing bent ligand configurations because of steric interactions between the bulky phenyl groups. In this regard it is noteworthy that ligand folding in the dithiolene prisms has been observed with the $S_2C_2H_2$, $S_2C_6H_4$, and $Se_2C_2(CF_3)_2$ ligands whereas the coplanar ligand has been observed in TP geometry only with $S_2C_2Ph_2$.

This argument is in total agreement with the belief that the metal d_{xy}, $d_{x^2-y^2}$ and ligand π_v overlap is significant in stabilizing the prism.[10,12] This overlap cannot be achieved in the octahedral configuration, and in all dithiolenes which tend toward octahedral coordination the MS_2 and ligand planes are approximately coplanar. An apparent exception to this is the $Ta(S_2C_6H_4)_3^-$ anion,[40] in which two ligands are folded (17.6 and 30.0°) and the third is coplanar. However viewing the overall geometry of the anion reveals that this is not totally unexpected since in its coordination, approximately intermediate between TP and octahedral, two ligands assume configurations closer to the TP limit whereas the third is close to the octahedral limit. It is this third ligand which is coplanar and the former two which are folded. Thus, a closer look at the $Ta(S_2C_6H_4)_3^-$ geometry reveals that in fact it is not an exception but rather it agrees with the above argument.

The tetraphenylarsonium cation is shown in Figure 1. The geometry of the cation is quite normal with no unusual features. The arsenic atom is surrounded in almost perfect tetrahedral coordination with the C–As–C angles being close to the predicted 109.5°, and all deviations from this value are easily explained by intermolecular interactions. The arsenic–carbon bonds are similar and the mean (1.888 (7) Å) approximates the value predicted from the sums of the covalent radii (1.94 Å), assuming an arsenic–carbon single bond involving sp^2-hybridized carbon atoms. These observed bond lengths agree favorably with other determinations[8,41,42] where the tetraphenylarsonium cation was involved.

Discussion

The constancy in prism dimensions previously observed and the short S–S distances were believed to be a consequence of S–S bonding which stabilized the prism.[10,43] However, as mentioned, in the $Nb(S_2C_6H_4)_3^-$ anion the prism dimensions are greatly enlarged and yet the TP geometry persists. It could be argued, based on the above assumption, that although the S–S interactions have weakened due to expansion of the sulfur cage, enough S–S overlap still exists to retain the prism stability. This is not, however, believed to be the case. It is felt that interligand S–S bonding is not a significant factor in determining prism stability. Rather it is believed that the stability of the trigonal prism is due to the ability of the metal d orbitals, which do not participate in σ bonding, to overlap with the ligand π orbitals as postulated by Gray et al.[10]

In this respect a comparison of $Mo(S_2C_2(CN)_2)_3^{2-}$ and $Nb(S_2C_6H_4)_3^-$ proves enlightening. The molybdenum complex has a distorted octahedral coordination whereas the niobium complex is TP. On the basis of S–S bonding arguments this result is indeed difficult to rationalize since the interligand S–S distances in the niobium anion (range 3.178 (3)–3.294 (3) Å) are longer than those in the molybdenum dianion (range 3.123 (7)–3.279 (8) Å) thereby ensuring a weaker interaction between these sulfur atoms in $Nb(S_2C_6H_4)_3^-$. We interpret this as implying that S–S bonding is *not* important in stabilizing the prism as has previously been thought; otherwise one would expect $Nb(S_2C_6H_4)_3^-$ to have distorted octahedral coordination. A similar conclusion is reached by comparison of $Nb(S_2C_6H_4)_3^-$ with $W(S_2C_2(CN)_2)_3^{2-}$ since the latter is almost isostructural with its molybdenum analogue.

Furthermore the recent structural determination of $[Ph_4As][Ta(S_2C_6H_4)_3]$[40] has shown that the Ta coordination is highly distorted from TP toward the octahedral limit. This is especially significant when one considers that the only difference between it and the Nb analogue is in the central metal and therefore in the metal d-orbital energies. Moreover, metal size is not a significant factor in destablizing the prism in this complex since the Ta–S distances (range 2.396 (2)–2.467 (3) Å) are less than the Nb–S distances (range 2.428 (2)–2.458 (2) Å) in the TP species $Nb(S_2C_6H_4)_3^-$. Thus destabilization of the prism cannot be attributed to weakening of any S–S bonding which might result from expansion of the sulfur cage by a larger metal. Rather it seems that the metal d orbitals are the significant factor in the differences in coordination geometry observed in $Ta(S_2C_6H_4)_3^-$ and $Nb(S_2C_6H_4)_3^-$. The less stable Ta 5d orbitals[44] destabilize the 4e′ molecular orbital relative to the niobium complex and thus cause destabilization of the prism. It seems also that our previous hypothesis,[13] that matching metal d- and ligand π-orbital energies are an important consideration in retaining TP coordination, is true. Assuming the importance of the 4e′ orbital in determining prism stability, then destabilization of the metal d orbitals should have the same relative effect as stabilizing the ligand orbitals.

Thus the $Nb(S_2C_6H_4)_3^-$ anion is, as hoped, a valuable link between the trigonal-prismatic and the octahedral coordinations. Although trigonal prismatic, this anion is beginning to show slight distortions and therefore is believed to be near to the limit of prism stability.

Acknowledgment. We thank the National Research Council of Canada and the University of Alberta for financial support of this research. We are indebted to Dr. J. L. Martin and Professor J. Takats for supplying the crystals and for many helpful discussions and to Dr. J. T. Purdham for assistance in preparing the manuscript. M.C. thanks the National Research Council of Canada for a graduate scholarship.

Registry No. $[Ph_4As][Nb(S_2C_6H_4)_3]$, 50589-75-8.

Supplementary Material Available: Table I, listing the observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

References and Notes

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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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Received December 1, 1975 AIC50860I

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 (*0kl*, *1kl*; Cu Kα x radiation) and precession photography (*h0l*, *h1l*, *hk0*, *hk1*; Mo Kα x radiation) are, for *h00*, $h = 2n + 1$ and, for *0k0*,