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# Crystal and Molecular Structure of Tetraphenylarsonium Tris(benzenedithiolato)tantalate(V)

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The crystal and molecular structure of tetraphenylarsonium tris(benzenedithiolato)tantalate(V), $[(C_6H_5)_4As][Ta(S_2C_6H_4)_3]$, has been determined from three-dimensional X-ray diffraction methods using data collected with an automated diffractometer. The compound crystallizes in the triclinic space group $P1$ (No. 1) with one molecule per unit cell of dimensions $a = 9.442$ (1), $b = 9.752$ (1), $c = 11.872$ (2) Å and $\alpha = 77.37$ (1), $\beta = 71.20$ (1), $\gamma = 74.23$ (1)°. The observed and calculated densities are 1.67 (2) and 1.66 g cm$^{-3}$, respectively. A total of 3700 reflections with $2\theta < 50°$ were collected; of these, 3532 with $I_{obsd} > 3\sigma(I)$ were used in the structure derivation giving final conventional values of $R = 0.027$ and $R_w = 0.031$ (the number of parameters refined in the last full-matrix least-squares cycle was 280). The coordination geometry of the Ta is severely distorted from the trigonal-prismatic geometry observed in the corresponding Nb structure, in accord with our expectations based on spectral differences. The average Ta–S bond length, 2.43 (1) Å, is very similar to the one found in Nb. The distortion is quite unique with two of the chelate rings being close to the prismatic limit while the third one is twisted about the twofold axis of the prism to the octahedral extreme; the individual twist angles are 16, 16, and 54°. As a result, the two triangular faces are no longer parallel but inclined by 12°. The relevance of the observed distortion to the factors affecting the trigonal-prismatic geometry is discussed.

## Introduction

The prediction of coordination geometry for six-coordinate complexes up until 1965 was a relatively simple task. The maxim "six-coordination equals octahedral geometry" had yet to be challenged, and consequently the compounds were believed to have this geometry or something close to it. It was therefore of significance when the structural report on $Re[S_2C_2(C_6H_5)_2]_3$ established trigonal-prismatic coordination for this complex.[1] Since this first report, other complexes[2–9] have been shown to adapt this geometry; however, except for complexes containing unsaturated 1,2-dithiols or 1,2-diselenols, ligand constraint is the presumed overwhelming factor in stabilizing the prismatic geometry. The factors responsible for the observed geometries in transition metal dithiolenes are not as well understood, albeit both Gray[10] and Schrauzer[11] have pointed out the possible importance of interligand S–S bonding and the delocalized bonding set up by overlap of ligand π orbitals with metal d orbitals of proper symmetry. Systematic studies to test these previous postulates and to establish a hierarchy of importance have been scattered and quite limited. The observation of trigonal-prismatic geometry in the neutral complexes $V[S_2C_2(C_6H_5)_2]_3$, $Mo(S_2C_2H_2)_3$, and $Re[S_2C_2(C_6H_5)_2]_3$ and the corresponding similarity in interligand S–S distances were taken as evidence of the significance of sulfur–sulfur interaction;[12] however, the delocalized bonding also contributed heavily toward the stabilization of the prism. A more enlightening study was the recent report of Bennett et al.[13] on the isoelectronic series of compounds $Mo(S_2C_6H_4)_3$, $Nb(S_2C_6H_4)_3^-$, and $Zr(S_2C_6H_4)_3^{2-}$. The molybdenum complex is trigonal prismatic, the niobium complex is a slightly distorted trigonal prism, and the zirconium complex is approaching octahedral geometry. It was pointed out that the proper matching of metal d-orbital energies with the energy of the appropriate ligand orbitals is likely to be an important factor in the unusual bonding of this type of complex. However, other factors such as central metal ion size and the overall charge of the complex may contribute to structural changes in this series.

Based upon spectroscopic evidence, we observed[15] that the series of complexes $M(S_2C_6H_4)_3^-$ (M = Nb, Ta, Sb) should show a distortion from trigonal-prismatic geometry in the order given. Because the central metal ion size and overall charge of the complex remain essentially constant for the series, this observation has an important bearing on the point raised by Bennett et al. and on the question of prism stabilization by 1,2-dithiols. Furthermore, the reliability of predictions based upon spectroscopic evidence has recently been called into question by the study[14] of the closely related $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$, where mnt = maleonitriledithiolate. Despite the spectral differences of the two compounds, they were found to be essentially isostructural. Thus, we have an additional incentive to examine the structure of at least the Ta complex. Here we report the results of such a study.

## Experimental Section

**$[(C_6H_5)_4As]Ta(S_2C_6H_4)_3$ Data Collection.** Dark brown crystals were prepared as previously described.[15] Weissenberg photographs using Cu Kα radiation and precession photographs using Mo Kα radiation indicated $\bar{1}$ Laue symmetry with no systematic absences. Least-squares refinement of 24 reflections with $35° < 2\theta < 50°$ (Mo K$\alpha_1$, λ 0.70926 Å), automatically centered on a Picker automatic four-circle diffractometer, yielded the cell dimensions and errors $a = 9.442$ (1) Å, $b = 9.752$ (1) Å, $c = 11.872$ (2) Å, $\alpha = 77.37$ (1)°, $\beta = 71.20$ (1)°, $\gamma = 74.23$ (1)°, and $V = 985.40$ Å$^3$. The calculated density based on a formula weight of 984.98 amu was 1.66 g/cm$^3$ compared to 1.67 (2) g/cm$^3$ by flotation in a mixture of $CCl_4$ and $CBr_4$. Thus due to the lack of a center of symmetry in the tetraphenylarsonium group, it seemed that the space group must be $P1$. A cell reduction by known method[16] was attempted but the cell chosen was found to be a reduced cell.

The crystal fragment used resembled a distorted square pyramid with an overall height of 0.284 mm; the crystal faces were approximated by $\{011\}$, $\{100\}$, $\{\bar{1}0\bar{3}\}$, $\{1\bar{2}2\}$, and $\{\bar{5}\bar{2}\bar{2}\}$. Intensity data were collected using Mo Kα radiation ($\bar{\lambda}$ 0.71069 Å)[17] and a coupled $2\theta$–$\omega$ scan technique with a $2\theta$ scan rate of 0.5° min$^{-1}$ and a 2° scan width which was corrected for $\alpha_1\alpha_2$ dispersion. Stationary-background counts were made for 40 sec at each end of the scan range. A set of three standard reflections was collected every 50 reflections and an additional set of 10 standard reflections was collected every 12 hr, but no evidence of decomposition was observed.

Of a total of 3700 reflections with $2\theta < 50°$ collected, 3532 or 95% with $I_{obsd} > 3\sigma(I)$ were considered observed. Standard deviations were calculated using a "$p$ factor"[18] of 0.03. Two reflections at low angles, 001 and 00$\bar{1}$ were rejected due to unusual background counts.

**Solution and Refinement of the Structure.** From a Patterson map,[19] two possible As positions consistent with the Ta at (0, 0, 0) were readily apparent, one at (0.426, 0.393, 0.443) and the other related by a center of symmetry. Not knowing which enantiomer was correct, the former position was arbitrarily chosen as a starting point, and the scale factor was subsequently refined[20–22] leading to $R_1 = 0.291$ and $R_2 = 0.309$. A difference Fourier at this point revealed 12 possible positions for the sulfur atoms, two pairs of which were barely resolved. The above positions were separated into two groups of six positions by arbitrarily choosing one as a starting point and eliminating the position generated

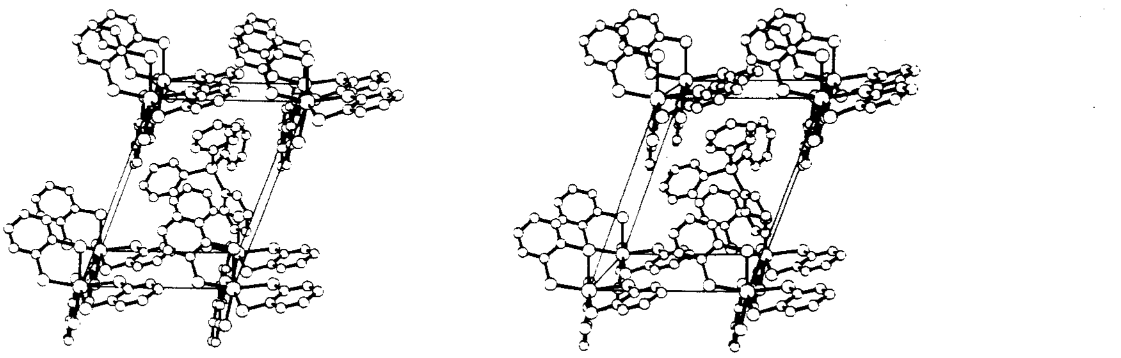

**Figure 1.** The content of one unit cell viewed with the *a* axis horizontal and *c* axis vertical.

**Table I.** Atom Coordinates and Isotropic Temperature Factors for $Ta(S_2C_6H_4)_3^-$

| Atom | *x* | *y* | *z* | $B$,[a] Å$^2$ |
|---|---|---|---|---|
| Ta | 0.0 (0) | 0.0 (0) | 0.0 (0) | 3.84 |
| As | −0.43558 (8) | −0.39454 (9) | −0.44126 (6) | 3.97 |
| S(1) | −0.0537 (3) | 0.2569 (2) | −0.0151 (2) | 4.90 |
| S(2) | 0.0991 (3) | −0.2403 (3) | −0.0645 (3) | 6.78 |
| S(3) | 0.2436 (2) | −0.0559 (3) | 0.0412 (2) | 5.07 |
| S(4) | −0.2486 (3) | −0.0614 (3) | 0.0465 (2) | 5.60 |
| S(5) | −0.0983 (2) | 0.0322 (3) | 0.2104 (2) | 4.92 |
| S(6) | 0.0508 (3) | 0.0645 (3) | −0.2184 (2) | 5.33 |
| C(1) | −0.0208 (9) | 0.336 (1) | −0.1675 (8) | 5.29 |
| C(2) | −0.035 (1) | 0.485 (1) | −0.198 (1) | 6.64 |
| C(3) | −0.007 (1) | 0.546 (1) | −0.316 (1) | 7.64 |
| C(4) | 0.033 (1) | 0.461 (2) | −0.405 (1) | 7.77 |
| C(5) | 0.050 (1) | 0.316 (1) | −0.3751 (8) | 6.13 |
| C(6) | 0.0233 (9) | 0.251 (1) | −0.2555 (7) | 4.83 |
| C(7) | 0.316 (1) | −0.239 (1) | 0.0434 (7) | 5.28 |
| C(8) | 0.444 (1) | −0.305 (1) | 0.0859 (9) | 6.82 |
| C(9) | 0.505 (2) | −0.446 (2) | 0.089 (1) | 9.16 |
| C(10) | 0.435 (2) | −0.530 (1) | 0.050 (1) | 9.17 |
| C(11) | 0.315 (2) | −0.471 (1) | 0.005 (1) | 8.16 |
| C(12) | 0.250 (1) | −0.320 (1) | −0.0014 (7) | 5.28 |
| C(13) | −0.2982 (9) | 0.080 (1) | 0.2351 (7) | 4.77 |
| C(14) | −0.389 (1) | 0.154 (1) | 0.3279 (9) | 6.87 |
| C(15) | −0.548 (1) | 0.186 (2) | 0.352 (1) | 8.17 |
| C(16) | −0.609 (1) | 0.135 (1) | 0.282 (1) | 7.57 |
| C(17) | −0.523 (1) | 0.067 (1) | 0.191 (1) | 6.49 |
| C(18) | −0.3631 (9) | 0.036 (1) | 0.1641 (7) | 4.79 |

[a] These are "equivalent" isotropic thermal parameters calculated from the anisotropic thermal parameters by SFLS5.

**Table II.** Atom Coordinates and Isotropic Temperature Factors for Rigid Bodies (Phenyl Carbons)

| Atom | *x* | *y* | *z* | $B$, Å$^2$ |
|---|---|---|---|---|
| C(19) | −0.3777 (9) | −0.2608 (7) | −0.3805 (6) | 3.98 |
| C(20) | −0.4075 (8) | −0.2649 (7) | −0.2568 (7) | 5.59 |
| C(21) | −0.357 (1) | −0.1701 (7) | −0.2138 (4) | 7.18 |
| C(22) | −0.2760 (9) | −0.0713 (7) | −0.2945 (6) | 6.75 |
| C(23) | −0.2462 (8) | −0.0672 (7) | −0.4182 (7) | 6.77 |
| C(24) | −0.297 (1) | −0.1620 (7) | −0.4612 (4) | 5.94 |
| | $D = 3.657$ (4), $E = 1.422$ (5), $F = 0.968$ (4) | | | |
| C(25) | −0.275 (1) | −0.4670 (8) | −0.5735 (4) | 4.11 |
| C(26) | −0.197 (1) | −0.6105 (7) | −0.5598 (7) | 5.03 |
| C(27) | −0.0783 (8) | −0.6654 (6) | −0.6557 (6) | 6.49 |
| C(28) | −0.039 (1) | −0.5766 (8) | −0.7652 (4) | 6.97 |
| C(29) | −0.117 (1) | −0.4331 (7) | −0.7789 (7) | 8.40 |
| C(30) | −0.2356 (8) | −0.3782 (2) | −0.6831 (6) | 7.49 |
| | $D = 5.849$ (5), $E = 0.812$ (5), $F = 2.910$ (4) | | | |
| C(31) | −0.4734 (7) | −0.5529 (5) | −0.3207 (5) | 3.47 |
| C(32) | −0.3667 (7) | −0.6157 (6) | −0.2554 (4) | 3.67 |
| C(33) | −0.3855 (8) | −0.7389 (5) | −0.1711 (4) | 4.68 |
| C(34) | −0.5111 (7) | −0.7992 (5) | −0.1521 (5) | 5.04 |
| C(35) | −0.6178 (7) | −0.7364 (6) | −0.2174 (4) | 5.40 |
| C(36) | −0.5990 (8) | −0.6132 (5) | −0.3017 (4) | 4.70 |
| | $D = 0.488$ (3), $E = 2.493$ (4), $F = 1.369$ (3) | | | |
| C(37) | −0.609 (1) | −0.305 (8) | −0.4961 (5) | 4.11 |
| C(38) | −0.711 (1) | −0.1865 (8) | −0.4460 (7) | 5.19 |
| C(39) | −0.8384 (8) | −0.1175 (6) | −0.4884 (7) | 7.04 |
| C(40) | −0.863 (1) | −0.1672 (8) | −0.5809 (5) | 6.57 |
| C(41) | −0.760 (1) | −0.2859 (8) | −0.6310 (7) | 6.20 |
| C(42) | −0.6331 (8) | −0.3548 (6) | −0.5886 (7) | 5.17 |
| | $D = 2.301$ (4), $E = 2.202$ (6), $F = 2.688$ (6) | | | |

from this by the false center of symmetry. In this way, two sets of six chemically reasonable sulfur positions were generated. One set seemed to be more intense than the other and this was chosen for further refinement. One cycle of full-matrix least-squares refinement of the positional and isotropic thermal parameters for the tantalum, arsenic, and six sulfur atoms gave $R_1 = 0.175$ and $R_2 = 0.222$. However, one sulfur atom thermal parameter was anomalously large and was subsequently lowered for an additional cycle of refinement. This sulfur atom again exhibited a high thermal parameter and so was removed before calculating another difference Fourier at which time $R_1 = 0.154$ and $R_2 = 0.199$. This Fourier map revealed the correct position for the remaining sulfur as well as the positions of the 18 benzenedithiolate carbon atoms. An additional cycle of refinement including the new atoms gave $R_1 = 0.121$ and $R_2 = 0.152$. Another difference Fourier was needed to locate the tetraphenylarsonium carbon atoms. Including the tetraphenylarsonium phenyl rings as rigid bodies with C–C bond lengths fixed at 1.397 Å and adding anomalous dispersion corrections[25] yielded $R_1 = 0.071$ and $R_2 = 0.082$ after two cycles of refinement. Due to the highly irregular shape of the crystal fragment and the fact that $\mu = 39.68$ cm$^{-1}$, an absorption correction was made on the basis of an experimental $\phi$ scan. Transmission factors varied from 0.837 to 0.736. An additional cycle of refinement gave $R_1 = 0.068$ and $R_2 = 0.081$. Changing the enantiomeric form followed by two cycles of refinement yielded $R_1 = 0.061$ and $R_2 = 0.073$ which is a significant improvement at the 0.005 confidence level by a Hamilton $R$ factor test.[26] Adding all of the hydrogen atoms as rigid bodies with temperature factors 10–15% higher than the carbons to which they are attached and with fixed C–H bond lengths of 0.98 Å gave $R_1 = 0.059$ and $R_2 = 0.072$ after another cycle of refinement. Finally, using anisotropic temperature factors for Ta, As, 6 S, and 18 benzenedithiolate carbon atoms converged in two cycles of full-matrix least-squares refinement to the final values $R_1 = 0.027$ and $R_2 = 0.031$. The number of parameters being refined in the last two cycles was 280 and the shifts in all positional parameters were less than half the estimated standard deviation. The final standard deviation of an observation of unit weight was 1.466. A final difference Fourier revealed no peaks greater than 0.55 e/Å$^3$. A table of observed and calculated structure factors is available.[27]

## Description of the Structure

The final positional and thermal parameters together with their estimated standard deviations are shown in Tables I–III. The closest cation anion contact is 2.72 Å between a tetraphenylarsonium hydrogen and benzenedithiolato carbon atom. All nonhydrogen contacts exceed 3.30 Å.

The unit cell, Figure 1, was arbitrarily chosen with a Ta at each corner since the space group is $P\bar{1}$.

In the tetraphenylarsonium ion, shown in the center of Figure 1, the phenyl rings, including the hydrogens, were treated as rigid bodies. The resulting geometry is in good agreement with other determinations[14,28,29] of this cation with average As–C bond distance, Table IV, being 1.889 (7) Å while

**Table III.** Anisotropic Thermal Parameters (Å$^2$)[a]

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ta | 0.0483 (2) | 0.0434 (2) | 0.0468 (2) | −0.01332 (12) | −0.02001 (12) | −0.00016 (11) |
| As | 0.0429 (4) | 0.0541 (5) | 0.0418 (4) | −0.0107 (4) | −0.0101 (4) | 0.0007 (4) |
| S(1) | 0.0663 (13) | 0.0482 (12) | 0.0628 (13) | −0.0125 (10) | −0.0304 (11) | −0.0032 (10) |
| S(2) | 0.0848 (18) | 0.0614 (16) | 0.0958 (20) | −0.0237 (14) | −0.0113 (15) | −0.0295 (15) |
| S(3) | 0.0509 (12) | 0.0596 (14) | 0.0705 (13) | −0.0097 (10) | −0.0249 (10) | −0.0037 (10) |
| S(4) | 0.0611 (13) | 0.0784 (16) | 0.0651 (13) | −0.0272 (12) | −0.0224 (10) | −0.0108 (12) |
| S(5) | 0.0562 (12) | 0.0694 (16) | 0.0512 (11) | −0.0068 (11) | −0.02734 (9) | −0.0059 (11) |
| S(6) | 0.0717 (14) | 0.0692 (16) | 0.0497 (11) | −0.0236 (13) | −0.0179 (10) | −0.0019 (11) |
| C(1) | 0.052 (5) | 0.060 (6) | 0.077 (6) | −0.021 (4) | −0.035 (4) | 0.017 (5) |
| C(2) | 0.073 (6) | 0.054 (6) | 0.111 (8) | −0.022 (5) | −0.047 (6) | 0.022 (5) |
| C(3) | 0.059 (6) | 0.067 (7) | 0.142 (10) | −0.027 (5) | −0.044 (7) | 0.040 (7) |
| C(4) | 0.065 (6) | 0.108 (10) | 0.103 (8) | −0.042 (7) | −0.041 (6) | 0.049 (8) |
| C(5) | 0.047 (5) | 0.100 (8) | 0.071 (6) | −0.030 (5) | −0.022 (4) | 0.015 (5) |
| C(6) | 0.044 (4) | 0.076 (6) | 0.055 (5) | −0.027 (4) | −0.018 (4) | 0.007 (4) |
| C(7) | 0.067 (6) | 0.066 (6) | 0.042 (4) | −0.000 (5) | −0.001 (4) | 0.008 (4) |
| C(8) | 0.080 (7) | 0.085 (8) | 0.059 (6) | 0.023 (6) | −0.006 (5) | 0.000 (5) |
| C(9) | 0.125 (11) | 0.104 (11) | 0.076 (8) | 0.039 (9) | −0.022 (7) | −0.012 (8) |
| C(10) | 0.153 (13) | 0.065 (8) | 0.068 (7) | 0.042 (9) | 0.012 (7) | 0.013 (6) |
| C(11) | 0.139 (11) | 0.053 (7) | 0.072 (7) | −0.014 (7) | 0.031 (7) | −0.006 (5) |
| C(12) | 0.076 (6) | 0.047 (5) | 0.047 (5) | 0.002 (5) | 0.010 (4) | 0.009 (4) |
| C(13) | 0.056 (5) | 0.062 (5) | 0.049 (4) | −0.010 (4) | −0.017 (4) | 0.007 (4) |
| C(14) | 0.065 (6) | 0.112 (9) | 0.064 (6) | −0.011 (6) | −0.000 (5) | −0.034 (6) |
| C(15) | 0.073 (7) | 0.101 (10) | 0.106 (9) | −0.002 (7) | 0.000 (6) | −0.029 (8) |
| C(16) | 0.049 (6) | 0.098 (9) | 0.115 (9) | −0.015 (6) | −0.014 (6) | 0.002 (7) |
| C(17) | 0.054 (5) | 0.085 (8) | 0.091 (7) | −0.019 (5) | −0.021 (5) | −0.001 (6) |
| C(18) | 0.054 (5) | 0.067 (6) | 0.049 (4) | −0.021 (4) | −0.021 (4) | 0.016 (4) |

[a] The $U$'s are the mean-square amplitudes of vibration in angstroms from the general temperature factor expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

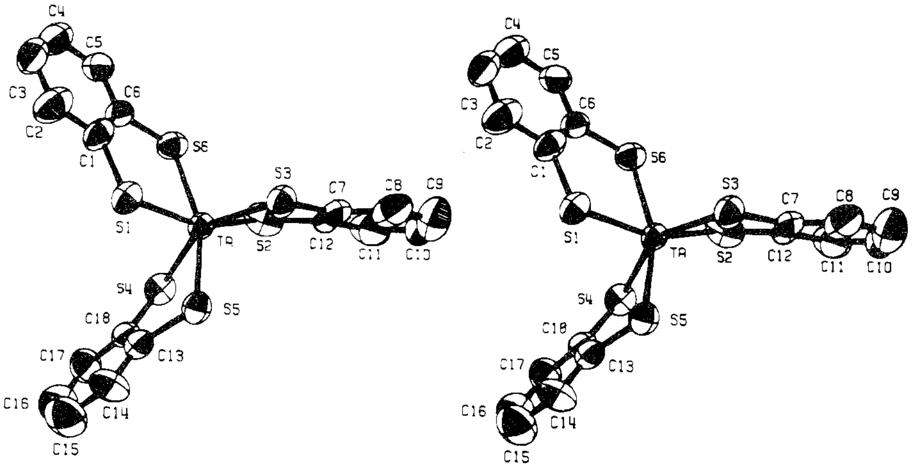

**Figure 2.** A stereoview of the anion Ta$(S_2C_6H_4)_3^-$. The numbering scheme is identical with the one used in the tables. The ellipsoids represent 50% probability.

the C–As–C angles average 109.5 (7)°.

**Table IV.** Intraionic Distances

| Atoms | Distance, Å | Atoms | Distance, Å |
|---|---|---|---|
| Ta–$S_{av}$ | 2.430 (12) | S(1)–S(3) | 3.646 (3) |
| C–$S_{av}$ | 1.746 (8) | S(4)–S(6) | 3.722 (3) |
| S–S(intra) | 3.149 (16) | S(1)–S(5) | 3.059 (3) |
| As–$C_{av}$ | 1.889 (7) | S(2)–S(6) | 3.132 (4) |
|  |  | S(3)–S(5) | 3.204 (3) |
| As–C(19) | 1.890 (5) | S(2)–S(4) | 3.265 (4) |
| As–C(25) | 1.904 (5) | S(1)–S(6) | 3.123 (4) |
| As–C(31) | 1.888 (4) | S(2)–S(3) | 3.177 (4) |
| As–C(37) | 1.874 (4) | S(4)–S(5) | 3.146 (3) |

A stereoview of the Ta$(S_2C_6H_4)_3^-$ anion is shown alone in Figure 2. The important bond distances and angles consistent with the numbering scheme of Figure 2 are to be found in Figure 3 and Table V. It is evident that the anion is distorted from the trigonal-prismatic geometry found in the closely related Nb complex.[13] The average ligand twist angle is ~29°. However, the mode of distortion, unique among dithiolene complexes studied thus far, makes such a statement meaningless since it tacitly implies a symmetric trigonal distortion of the two triangular faces which is far from being true in the present compound. A clearer picture of the distortion is obtained by the individual chelate twist[30] or tilt[31] angles (defined in Figure 4) which are $\phi_{1,6} \simeq 54°$, $\phi_{2,3} \simeq 16°$, $\phi_{4,5} \simeq 16°$ and $\chi_{1,6} \simeq 37°$, $\chi_{2,3} \simeq 10°$, $\chi_{4,5} \simeq 10°$ (the subscripts refer to the sulfur atoms forming the chelate rings), respectively. It seems that part of the anion retains nearly the trigonal-prismatic configuration, $\phi = 0°$, while the remaining chelate is close to the octahedral limit, $\phi = 60°$. In this regard, it is interesting to note that the "expected octahedral limit" based upon bite size and M–S bond lengths[32] is 49°, and hence the most severely distorted chelate in our case has even passed this limit. Of course the above angle is for molecules which suffer symmetrical distortions, in particular keeping parallel triangular $S_3$ planes. This is not the case here, and the angle between the two planes is 11.8°, allowing for the observed twist angle. The fact that part of the molecule retains a configuration close to that found in the trigonal prism is further evidenced by the angles S(2)–Ta–S(5) of 122.28 (10)° and S(3)–Ta–S(4) of 147.19 (8)°, which are close to 136° found in trigonal-prismatic complexes. In addition, the dihedral

**Table V.** Intraionic Angles

| Atoms | Angle, deg | Pair | Atoms | Angle, deg |
|---|---|---|---|---|
| S(1)-Ta-S(5) | 78.73 (9) | a | S(1)-C(1)-C(6) | 119.9 (7) |
| S(2)-Ta-S(6) | 79.15 (10) | a | S(6)-C(6)-C(1) | 120.3 (6) |
| S(1)-Ta-S(6) | 80.29 (9) | | S(2)-C(12)-C(7) | 121.5 (7) |
| S(4)-Ta-S(5) | 80.52 (7) | b | S(3)-C(7)-C(12) | 120.1 (10) |
| S(2)-Ta-S(3) | 81.52 (9) | b | S(4)-C(18)-C(13) | 121.0 (6) |
| S(2)-Ta-S(4) | 83.42 (9) | c | S(5)-C(13)-C(18) | 120.4 (7) |
| S(3)-Ta-S(5) | 83.20 (7) | c | | |
| S(1)-Ta-S(3) | 99.02 (8) | d | C(6)-C(1)-C(2) | 120.3 (9) |
| S(4)-Ta-S(6) | 99.15 (8) | d | C(1)-C(2)-C(3) | 119.6 (12) |
| S(1)-Ta-S(4) | 105.42 (8) | e | C(2)-C(3)-C(4) | 120.4 (10) |
| S(3)-Ta-S(6) | 106.36 (8) | e | C(3)-C(4)-C(5) | 119.7 (10) |
| S(2)-Ta-S(5) | 122.28 (10) | | C(4)-C(5)-C(6) | 121.4 (12) |
| S(3)-Ta-S(4) | 147.19 (8) | | C(5)-C(6)-C(1) | 118.5 (9) |
| S(5)-Ta-S(6) | 158.09 (8) | f | C(12)-C(7)-C(8) | 120.0 (10) |
| S(1)-Ta-S(2) | 158.69 (8) | f | C(7)-C(8)-C(9) | 122.4 (14) |
| S(1)-S(3)-S(5) | 52.57 (7) | g | C(8)-C(9)-C(10) | 118.0 (13) |
| S(2)-S(4)-S(6) | 52.77 (8) | g | C(9)-C(10)-C(11) | 122.1 (12) |
| S(3)-S(1)-S(5) | 56.27 (7) | i | C(10)-C(11)-C(12) | 120.9 (4) |
| S(4)-S(6)-S(2) | 56.11 (8) | i | C(11)-C(12)-C(7) | 116.5 (11) |
| S(3)-S(5)-S(1) | 71.16 (8) | j | C(18)-C(13)-C(14) | 120.1 (8) |
| S(6)-S(2)-S(4) | 71.12 (9) | j | C(13)-C(14)-C(15) | 120.8 (11) |
| | | | C(14)-C(15)-C(16) | 117.2 (11) |
| Ta-S(1)-C(1) | 110.1 (4) | | C(15)-C(16)-C(17) | 122.4 (10) |
| Ta-S(6)-C(6) | 109.4 (3) | | C(16)-C(17)-C(18) | 120.8 (10) |
| Ta-S(2)-C(12) | 104.9 (4) | | C(17)-C(18)-C(13) | 118.4 (9) |
| Ta-S(5)-C(13) | 103.9 (3) | | | |
| Ta-S(3)-C(7) | 108.0 (4) | | C(37)-As-C(31) | 111.2 (2) |
| Ta-S(4)-C(18) | 103.4 (3) | | C(37)-As-C(19) | 110.1 (3) |
| | | | C(37)-As-C(25) | 107.7 (3) |
| | | | C(31)-As-C(19) | 109.6 (2) |
| | | | C(31)-As-C(25) | 107.4 (2) |
| | | | C(19)-As-C(25) | 110.8 (3) |

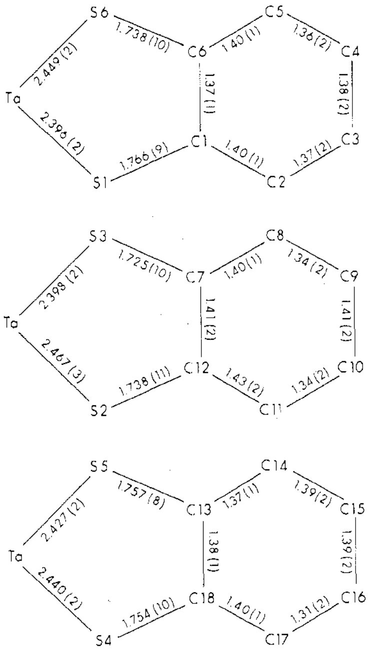

Figure 3. Bond distances with their estimated esd's in the chelate rings for $Ta(S_2C_6H_4)_3^-$.

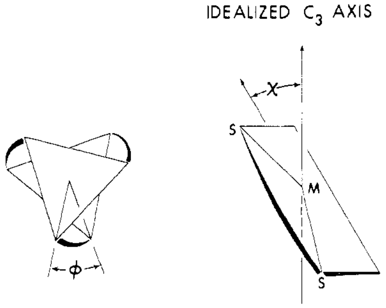

Figure 4. Pictorial representation of the ligand twist (φ) and tilt (χ) angles. For sake of clarity, only one of the chelate rings is shown in our illustration of χ.

**Table VI.** Dihedral Angles

| Atoms in Plane 1 | Atoms in Plane 2 | Angle, deg |
|---|---|---|
| Ta, S(1), S(6) | Ta, S(2), S(3) | 107.6 |
| Ta, S(1), S(6) | Ta, S(4), S(5) | 106.4 |
| Ta, S(2), S(3) | Ta, S(4), S(5) | 116.5 |
| Ta, S(1), S(6) | S(1), S(6), C(1), C(2), C(3), C(4), C(5), C(6) | 0.0 |
| Ta, S(2), S(3) | S(2), S(3), C(7), C(8), C(9), S(10), S(11), S(12) | 17.6 |
| Ta, S(4), S(5) | S(4), S(5), C(13), C(14), C(15), C(16), C(17), C(18) | 30.0 |
| S(1), S(3), S(5) | S(2), S(4), S(6) | 11.8 |

**Table VII.** Summary of Distances (Å) for Related Tris(benzenedithiolato) Complexes

| | M-S | S-S(intra) | S-S(inter) | C-S |
|---|---|---|---|---|
| $Mo(bdt)_3$ | 3.367 (3) | 3.110 (5) | 3.091 (9) | 1.727 (3) |
| $Nb(bdt)_3^-$ | 2.441 (5) | 3.150 (5) | 3.23 (2) | 1.745 (4) |
| $Ta(bdt)_3^-$ | 2.430 (12) | 3.149 (16) | | 1.746 (8) |
| $Zr(bdt)_3^{2-}$ | 2.543 (6) | 3.265 (10) | 3.58 (8) | 1.765 (4) |

angle, Table VI, formed by the planes defined by Ta, S(2), S(3) and Ta, S(4), S(5) is 116.5°, again close to the expected 120° for a trigonal prism.

In contrast to the data above, the S-Ta-S angles for sulfur atoms which are approximately trans to each other, Table V, average 154.7° which is intermediate between the octahedral 171° (this is the limiting trans angle for the average chelate bite angle of ca. 81° observed in this structure) and trigonal-prismatic values.

For purposes of comparison a summary of some pertinent average distances for this molecule and related tris(benzenedithiolato) complexes is presented in Table VII. Two previously identified trends are important for the present results. As can be seen in the table, for the series of complexes $Mo(S_2C_6H_4)_3$, $Nb(S_2C_6H_4)_3^-$, and $Zr(S_2C_6H_4)_3^{2-}$, there is monotonic increase in all the quoted distances. This trend and especially the increased value of the C-S bond length can be taken as evidence for the increased importance of the dithiolate formulation of the ligand system as we go from molybdenum to niobium to zirconium. Furthermore, concurrent with this change in ligand character, the coordination geometry of the complexes changes from trigonal prismatic ($Mo(S_2C_6H_4)_3$) to nearly octahedral ($Zr(S_2C_6H_4)_3^{2-}$). Based on these observations, it would be expected that the unique, highly twisted chelate group in the present complex should exhibit longer C-S and Ta-S bond lengths than the ligand systems representing the relatively undistorted part of the molecule. As can be seen in Figure 3, the variations in the C-S bond lengths, from 1.725 (10) to 1.766 (9) Å, are, at best, significant. However, the Ta-S bond distances do cover a considerable range, from 2.396 (2) to 2.467 (3) Å. Unfortunately, it is also evident that the variations in these bond lengths are not consistent with the above expectations. The only possible pattern that can be recognized for the Ta-S distances is one which is characterized by three short and three long bond lengths belonging to opposite triangles of sulfur atoms formed by the three chelating ligands [i.e., S(1)S(3)S(5) with $Ta-S_{av}$ = 2.407 (11) Å and S(2)-S(4)S(6) with $Ta-S_{av}$ = 2.452 (8) Å]. Whether this distortion is chemically significant is not known at the present time. It must be pointed out, however, that even within the same triad the Ta-S bond lengths vary significantly. Furthermore, the tantalum structure is plagued by high thermal motion indicating that without realistic corrections for thermal motion, the significance of the above variations is highly suspect. Nevertheless, even in the absence of a clear understanding of the observed variations of the bond lengths in the tantalum structure, a comparison of the average distances between tantalum and niobium is instructive.[33] As can be observed in Table VII, the average M–S, S–C, and intraligand S---S distances are essentially the same in the two complexes. This indicates that the origin of the distortion seen in the tantalum complex cannot be traced to a specific change in bond length on going from niobium to tantalum. On the other hand, the similarities also underline the fact that subtle, small effects are apparently sufficient in these complexes to result in gross structural changes. It must also be remembered that some of the averages computed for the tantalum complex are based on significantly different distances and that we are quoting the averages only as a possible point of comparison with the analogous niobium structure. In this regard, as a result of the observed distortion, the interligand S---S contacts, Table IV, range from 3.059 (3) to 3.722 (3) Å; the average here clearly has little meaning. It is interesting to note, however, that the shortest contact, 3.059 (3) Å, is in fact shorter than the interligand S---S distance in the trigonal-prismatic $Mo(S_2C_6H_4)_3$; the distances involving the quasiprismatic part of the complex are similar to those observed in the Nb structure, i.e., 3.204 (3) and 3.265 (4) Å compared to an average of 3.23 (2) Å.

Another feature of the present structure that is worthy of mention is the nonplanarity of two of the benzenedithiolate ligand systems. In Table VI one can see that the two ligands retaining nearly the prismatic configuration are also folded about the S–S axis. The third ligand system, approaching the octahedral limit, is planar. Furthermore, the ligand dihedral angles are 22.8, 22.6, and 21.8° in $Nb(S_2C_6H_6)_3^-$ and 13.1, 21.1, and 30.0° in $Mo(S_2C_6H_4)_3$, respectively, both complexes being trigonal prismatic, whereas in the nearly octahedral $Zr(S_2C_6H_4)_3^{2-}$, the ligands are folded by only 3.9, 3.9, and 0.5°. The variable nature of the ligand folding [viz., the angles in $Mo(S_2C_6H_4)_3$ and the observation of folded ligands in $Mo(S_2C_2H_2)_3$,[2] whereas trigonal-prismatic complexes containing $S_2C_2(C_6H_5)_2$[1,3] have planar ligands] tempts one to ascribe these affects to packing forces. But, at the same time, the existence of a rough correlation between twist angle and folding angle of a ligand system, in our complexes, must be recorded.

A similar variation in ligand folding has also been observed in bis(cyclopentadienyl)metal–dithiolene complexes. Köpf and Kotoglu have invoked π bonding to explain the bending of the ligands in these complexes.[34–38] For example, the $d^0$ systems $(\eta^5\text{-}C_5H_5)_2Ti(S_2C_6H_4)$ and $(\eta^5\text{-}C_5H_5)_2Ti(S_2C_2H_2)$ have ligands folded by 46° about the S–S axis and short M–S and C–S distances,[36,34,39] whereas the $d^2$ systems $(\eta^5\text{-}C_5H_5)_2M(S_2C_6H_4)$, M = Mo and W, exhibit folding of 9 and 8°, respectively, and relatively longer M–S and C–S distances.[37,38] However, in our case, the direction of the apparent correlation is just the opposite of that normally expected from π-bonding arguments. That is, out-of-plane π bonding, if important in stabilizing trigonal-prismatic geometry, should also favor planar ligands. As yet, no explanation has been advanced which seems to explain all of the above observations.

## Discussion

Clearly, the major importance of the present study is the unambiguous demonstration of structural differences between the niobium and tantalum complexes, establishing that at least for some compounds spectral differences are accompanied by structural changes. A few comments are in order about the diagnostic value of uv–visible spectra as a structural probe for these complexes. As mentioned previously,[15] the presence of low-energy, high-intensity bands in these complexes was taken as the indication of prismatic geometry. Based on major differences both as far as band position and intensity (the extinction coefficient in the tantalum complex is less than half the value observed in the niobium derivative) are concerned, $Ta(S_2C_6H_4)_3^-$ was assumed to be distorted from the prismatic geometry observed in $Nb(S_2C_6H_4)_3^-$. The applicability of such reasoning was recently questioned when spectral differences between $Mo(mnt)_3^{2-}$ and $W(mnt)_3^{2-}$ were shown, by X-ray diffraction methods, not to correspond to structural changes.[14] However, in the above complexes the intensities of the bands are quite low and, assuming the previous argument about intensities is valid, imply gross distortion from trigonal-prismatic geometry. It is perhaps not surprising that band position changes in such cases do not correspond to different structures. Furthermore, it is apparent that the diagnostic check must involve both intensity and energy changes. We would also hasten to add and emphasize the qualitative and restrictive utility of uv–visible spectra. It appears that first-row transition metals are in a different class since the similarities in spectra between $Ti(S_2C_6H_3CH_3)_3^{2-}$ and $Nb(S_2C_6H_4)_3^-$ did not translate into identical structures; indeed the titanium complex[40] proved to be more octahedral than $Zr(S_2C_6H_4)_3^{2-}$. In addition, we are the first to admit that our postulation of the distortion for the tantalum complex did not visualize the type that the present study established. In fact, we are at a loss to give a satisfactory explanation for its occurrence. However, an examination of existing structural data reveals that the distortion seen is not as surprising as it first looks.

**Table VIII.** Dihedral Angles (deg) Made by Polyhedron Faces[a]

| δ's at $b_1$ | δ's at $b_2$ | Remaining δ's |
|---|---|---|
| 24.2 | 90.3 | 59.6, 60.5 |
| 48.8 | 92.7 | 81.0, 82.7 |
| 49.3 | 95.3 | 87.4, 89.8 |

[a] δ's are chosen as described in ref 41.

In a recent discussion,[41] Muetterties and Guggenberger favored the coordination polyhedron as a means of describing the geometry of a large number of complexes including six-coordination. The coordination polyhedron was described by the angles δ between adjacent faces, and these angles were subsequently tabulated for a large number of complexes between the octahedral and trigonal-prismatic extremes. It was pointed out that few examples are known in the region from the midpoint of this series to the trigonal-prismatic extreme. The present study is then of interest since the Ta complex falls within this region. Table VIII gives the values of the dihedral angles describing the $Ta(S_2C_6H_4)_3^{2-}$ coordination polyhedron. Comparison of these values with those reported by Muetterties and Guggenberger brings out several interesting points. For complexes near the trigonal-prismatic limit the δ's at the $b_1$ edges, as defined by Muetterties et al.,[41] show a wide range of values, often with two being similar in magnitude; δ's at $b_2$ are nearly constant, and the remaining δ's may be grouped into three pairs of nearly equal values. The groupings above arise due to the fact that the molecules in question have at most $C_2$ symmetry. That the $Ta(S_2C_6H_4)_3^-$ polyhedron has approximately $C_2$ symmetry is even more evident when one compares the intraionic angles, Table V, which would be required to be identical if a twofold axis bisecting chelate $S_1S_6$ and passing through Ta were present. These pairs have been coded with the same letter in Table V; the similarities are indeed obvious. It should be noted that other compounds, not contained in Muetterties' list, $V(mnt)_3^{3-}$,[42,43] $Mo(mnt)_3^{2-}$,[14] $W(mnt)_3^{2-}$,[14] and $Zr(S_2C_6H_4)_3^{2-}$,[13] with relatively small average twist angles all have $C_2$ symmetry, albeit the molybdenum and tungsten structures are quite close to $D_3$ symmetry.

The unique distortion observed for the Ta complex and a reexamination of the shape parameters for other tris-chelated complexes brings two points into focus. First, it most dra-

**Table IX.** Least-Squares Planes[a]

| Atoms defining the plane | Equation of the plane | Distances of atoms from the plane, Å | | | |
|---|---|---|---|---|---|
| Ta, S(1), S(6) | $0.9952X - 0.0542Y - 0.0815Z = 0$ | | | | |
| Ta, S(4), S(5) | $-0.2576X + 0.9307Y - 0.2598Z = 0$ | | | | |
| Ta, S(2), S(3) | $0.2407X + 0.2872Y - 0.9271Z = 0$ | | | | |
| S(1), S(2), C(1), C(2) | $0.9937X - 0.0962Y - 0.0581Z + 0.0968 = 0$ | S(1) | −0.007 | C(3) | 0.026 |
| C(3), C(4), C(5), C(6) | | S(6) | 0.030 | C(4) | −0.012 |
| | | C(1) | −0.019 | C(5) | −0.012 |
| | | C(2) | 0.012 | C(6) | −0.017 |
| S(2), S(3), C(7), C(8) | $0.4134X + 0.0340Y - 0.9099Z - 0.5479 = 0$ | S(2) | 0.046 | C(9) | 0.037 |
| C(9), C(10), C(11), C(12) | | S(3) | −0.025 | C(10) | −0.022 |
| | | C(7) | −0.0019 | C(11) | −0.029 |
| | | C(8) | 0.026 | C(12) | −0.014 |
| S(4), S(5), C(13), C(14) | $0.0816X + 0.7801Y - 0.6203Z + 0.9075 = 0$ | S(4) | 0.006 | C(15) | 0.011 |
| C(15), C(16), C(17), C(18) | | S(5) | −0.046 | C(16) | −0.043 |
| | | C(13) | 0.032 | C(17) | −0.008 |
| | | C(14) | 0.021 | C(18) | 0.028 |
| S(2), S(4), S(6) | $-0.6619X - 0.4519Y - 0.5981Z - 1.4608 = 0$ | | | | |
| S(1), S(3), S(5) | $0.6515X + 0.6034Y + 0.4598Z - 1.4388 = 0$ | | | | |
| S(1), S(4), S(5) | $-0.6462X + 0.6447Y + 0.4085Z - 1.3948 = 0$ | | | | |
| S(1), S(3), S(6) | $0.7283X + 0.4472Y - 0.5193Z - 1.2393 = 0$ | | | | |
| S(1), S(4), S(6) | $-0.7426X + 0.5336Y - 0.4048Z - 1.2551 = 0$ | | | | |
| S(2), S(3), S(5) | $0.2257X - 0.6918Y + 0.6859Z - 1.1519 = 0$ | | | | |
| S(2), S(3), S(6) | $0.6553X - 0.3714Y - 0.6577Z - 1.3823 = 0$ | | | | |
| S(2), S(4), S(5) | $-0.1936X - 0.7029Y + 0.6844Z - 1.1573 = 0$ | | | | |

[a] The equations of the planes are in the form $LX + MY + NZ = D$, where $L, M,$ and $N$ are direction cosines referred to the orthogonal coordinate system where $X$ is $a$, $Y$ is in the $ab$ plane, and $Z$ is $c^*$.

matically demonstrates the inappropriateness of trigonal distortion in transition metal–dithiolene complexes. Such a description might be qualitatively applicable in certain cases, for instance, in Mo(mnt)$_3^{2-}$ and W(mnt)$_3^{2-}$, but distortion which is initiated by individual twist of the chelate rings about the $C_2$ axes of the trigonal prism is a more preferable description and is the one that will maintain the, at most, $C_2$ symmetry of the complexes. Describing the distortion in this way necessitates the knowledge of individual twist angles, or alternatively Muetterties and Guggenberger's dihedral angles, and the reporting of an average value should therefore be discouraged. Second, the observation of at most $C_2$ symmetry for distorted dithiolene complexes, and even for other tris chelates which are severely distorted from octahedral geometry, raises questions about the $D_{3d} \leftrightarrow D_{3h}$ trigonal twist reaction path or at least about the possibility of correlating the observed distortions in the solid state to the above idealized reaction path.[41] Of course there are well-documented cases of intramolecular rearrangements which proceed by a trigonal twist type process.[44,45] However, the absence of real examples representing that half of the geometric reaction path which is closer to the $D_{3h}$ limit may not in fact be a function of lack of synthetic studies or the high energy of the trigonal twist process. It may well be that further examples of complexes close to the trigonal-prismatic geometry will mirror the distortions observed in transition metal dithiolenes.[46,47]

Finally, we wish to comment upon the structural difference observed between the Nb and Ta complexes and its relevance to our understanding the factors stabilizing the trigonal-prismatic geometry in these complexes. It is important to reiterate, even at the risk of being repetitive, that the significance of the observed structural change is that it happened between two complexes where everything but the central transition metal ion remained constant. That is, at least for these complexes, it establishes unequivocally a property of the metal ion as the dominant contribution toward the stabilization of trigonal-prismatic geometry. It obviously follows that the importance of interligand sulfur–sulfur bonding, albeit often invoked, can only be secondary in this respect. The property of the central ion that can have a profound effect on the remaining factors believed to be responsible for the prismatic geometry is the energy of the d orbitals. Indeed, in their respective molecular orbital study, both Gray[10] and Schrauzer[11] assumed the highly delocalized nature of the 4e' MO, made up from the overlap of the metal d$_{x^2-y^2}$, d$_{xy}$ and ligand $\pi$ orbitals of proper symmetry, to be singularly important in this respect. However, the validity of this conclusion is debatable since in a separate study Huisman et al.[48] concluded that, based solely on $\sigma$ bonding, the trigonal-prismatic coordination would be favored over the octahedral one for highly covalent 4d and 5d transition metal complexes containing metal ions in the d$^0$, d$^1$, and d$^2$ electronic configurations.[49] Although, at the present time, it is premature to argue about the relative importance of $\sigma$ and $\pi$ bonding, one can easily see that as the metal d-orbital energy is raised (destabilized), the delocalized nature of the bonding, both $\sigma$ and $\pi$, is decreasing and distortion from prismatic geometry should result. The finding that the calculated d-orbital energies of tantalum are consistently less stable than those of niobium[50] is completely consistent with the above argument and, we believe, is a clear corroboration of the postulate of Bennett et al.[13] that matching ligand orbital and metal d-orbital energies is the most important factor in maintaining the trigonal-prismatic geometry in tris(dithiolene) complexes of the transition metals.

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**Registry No.** $[(C_6H_5)_4As][Ta(S_2C_6H_4)_3]$, 52882-44-7.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40561D.

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(20) The function being minimized was $\sum w(|F_o| - |F_c|)^2$ where $F_o$ and $F_c$ are the observed and calculated structure factors, respectively, and $w = [\sigma(F_o)]^{-2}$.

(21) Scattering factors for the neutral atoms were used as tabulated by Cromer and Mann[23] for Ta, S, and C and by Stewart, Davidson, and Simpson[24] for H.

(22) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ while $R_2 = \{\sum w[|F_o| - |F_c|]^2 / \sum w|F_o|^2\}^{1/2}$; $w$, $F_o$, and $F_c$ are as previously defined.[20]

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(29) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **7**, 2140 (1968).

(30) Individual ligand twist angles were calculated by first defining an idealized threefold axis as the normal to the plane formed by the midpoints of the three ligand S–S vectors. Ta–S vectors were then defined and the cross product of each of these with the idealized threefold axis resulted in a new set of six vectors from which the twist angles could be calculated as the angle between the appropriate pairs.

(31) Tilt angles were calculated as the angle between the chelate S–S vectors and the idealized threefold axis as previously defined.[30]

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

(33) The possibility also remains that there is some systematic error present which causes the observed variations in these distances. We cannot eliminate all possibilities. However, an obvious candidate, errors in the unit cell dimensions, can be discounted based on the following argument. The Ta–S bonds follow roughly the direction of the unit cell axes; clearly then, the alternating long–short pattern of lengths for transoid bonds [Ta–S(1) = 2.396 (2) Å, Ta–S(2) = 2.467 (3) Å; Ta–S(3) = 2.398 (2) Å, Ta–S(4) = 2.440 (2) Å; Ta–S(5) = 2.427 (2) Å, Ta–S(6) = 2.449 (2) Å] is not reconcilable with this type of an error.

(34) H. Köpf, *Z. Naturforsch.*, **236**, 1531 (1968).

(35) A. Kutoglu, *Acta Crystallogr., Sect. B*, **29**, 2891 (1973).

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(39) These complexes by virtue of an empty MO, according to the Ballhausen–Dahl bonding scheme, are capable of accepting additional electrons from the ligands and hence we have the observed dihedral angle. In $d^2$ complexes this MO is filled.

(40) M. J. Bennett, personal communication.

(41) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1749 (1974).

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

(43) The electronic origin of the highly distorted nature of the $[(CH_3)_4N]_2[V(mnt)_3]$ structure was recently questioned[14] when it was found that $[(C_6H_5)_4As][V(mnt)_3]$ is isomorphous with the structure of the corresponding molybdenum and tungsten complexes which are only slightly distorted from the ideal $D_3$ symmetry. The possibility that the observed distortion is the result of the small size and more stringent packing requirements of the tetramethylammonium cation was raised. In view of our results, which we find hard to believe to be solely due to packing forces, the structure of $[(C_6H_5)_4As]_2[V(mnt)_2]$ takes on a special significance. It is clearly important to establish for this complex whether its isomorphic relation to molybdenum and tungsten indicates an identical structure or not. The obtained results will have bearings on the relative importance of packing forces vs. electronic factors in determining the coordination geometry in these complexes.

(44) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Am. Chem. Soc.*, **93**, 360 (1971).

(45) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 6411 (1972).

(46) The recently published[47] structure of $Fe[S_2CC(COOC_2H_5)_2]_3^{2-}$ bears remarkable similarity to the tantalum structure. In the former complex, as in the latter one, one of the chelating ligands suffers a much more severe twisting than the other two. As a result the following interligand sulfur–sulfur distances are observed: 3.468 (3), 3.332 (2), and 3.226 (2) Å. The trend mirrors quite closely the one we are observing. The asymmetric type distortion must of course produce triangles of sulfur atoms which are no longer parallel; the observed dihedral angle of 6° of the iron structure is consistent with this and compares well with the 12° found in the present structure. The manifestation of this unusual type of distortion with a more innocent chelating ligand is indeed quite interesting.

(47) F. J. Hollander, R. Pedelty, and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 4032 (1974).

(48) R. Huisman, R. DeJonge, C. Haas, and F. Jellinek, *J. Solid State Chem.*, **3**, 56 (1971).

(49) Of course in the M.O. studies it was recognized that $\sigma$ and $\pi$ bonding are not separable in $D_{3h}$ symmetry, however, the $\pi$ component of the bonding was apparently favored for the occurrence of prismatic geometry.

(50) (a) S. Fraga, personal communication. (b) A reference to the experimental ionization potentials[51] might look somewhat less convincing since the first and second ionization potentials of niobium are actually smaller than those of tantalum; however, there is an inversion in the order at the next value. That is by assuming a charge of 1.5 or somewhat higher (cf. charge on titanium in $TiCl_6^{2-}$ is 2.61[52]) on the central ion in these complexes, we conclude that, as required, the "experimental" d-orbital energy of tantalum is smaller than that of niobium.

(51) C. W. Allen, "Astrophysical Quantities", 3rd ed, University of London, The Athlone Press, London, 1973, pp 36–40.

(52) E. Tondello, *Inorg. Chim. Acta*, **10**, 65 (1974).