The Crystal Structure of a Dianionic Molybdenum Tris-(1,2-dithiolate) Complex

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Summary *X*-Ray studies reveal the diamagnetic complex anion in $[Ph_4As]_2[Mo(mnt)_3]$, $[(mnt) = S_2C_2(CN)_2]$ to have a structure midway between octahedral and trigonal-prismatic limiting geometries.

RECENT structural work on tris-(1,2-dithiolate) complexes has shown that while the neutral complexes possess trigonal prismatic co-ordination,[1] the dianionic and trianionic complexes of first-row transition elements have octahedral or severely distorted structures.[2,3] However, despite the large number of complexes which have been characterized,[4,5] structural evidence on anionic complexes of second- and third-row elements has been lacking. It has been suggested,[6] however, that the diamagnetism of ML_3^{2-} species ($M = Mo$, W; $L = S_2C_6F_4$) favours assigning them the trigonal-prismatic structure. To provide the needed structural information we report the *X*-ray determined crystal structure of the diamagnetic complex $Mo(mnt)_3^{2-}$ in its bis(tetraphenylarsonium) salt.

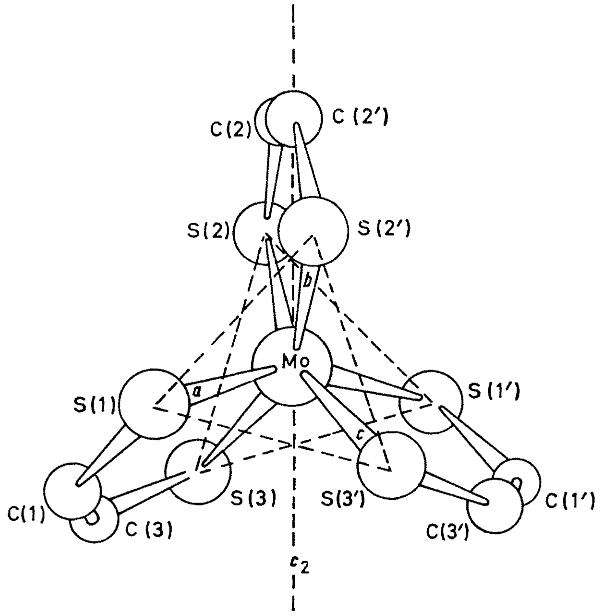

FIGURE. *A perspective drawing of the co-ordination sphere of* $Mo(mnt)_3^{2-}$.

[$a = 2{\cdot}405(5)$, $b = 2{\cdot}362(5)$, $c = 2{\cdot}390(5)$, S(1)–S(2′) = 3·123(7), S(2′)–S(3′) = 3·279(8), S(1)–S(3′) = 3·223(7) Å; ∠S(1)–Mo–S(1′) = 156(2), ∠S(2)–Mo–S(3′) = 155(2)°].

Crystal data: $C_{60}H_{40}N_6As_2MoS_6$ (green crystals from Me_2CO–Pr^iOH) $M = 1283{\cdot}2$; orthorhombic, $a = 20{\cdot}10(2)$, $b = 15{\cdot}30(2)$, $c = 18{\cdot}73(2)$ Å, $U = 5760$ Å^3, $D_m = 1{\cdot}47(1)$ g/cm^3, $Z = 4$, $D_c = 1{\cdot}479$ g/cm^3; space group P_{bcn} (No. 60). Intensities were measured by visual–photographic methods, using Mo-K_α radiation, for 1643 non-zero reflections. The structure was solved by the heavy-atom method and has been refined to $R = 0{\cdot}087$ by full-matrix least-squares analysis using anisotropic thermal parameters for Mo, As, and S. The analogous tungsten compound $[Ph_4As_2]_2[W(mnt)_3]$ crystallizes in the same space group, with $a = 20{\cdot}16(2)$, $b = 15{\cdot}27(2)$, $c = 18{\cdot}69(2)$ Å, and is assumed to be isomorphous.

As seen in the Figure, Mo lies on a two-fold axis which bisects one of the ligands and relates the other two. Six sulphur atoms surround the Mo at an average distance of 2·385 Å and form a polyhedron which is not close to either the trigonal-prismatic or octahedral geometries. Although the molecule in fact possesses only the crystallographically-required C_2 symmetry, we refer to an idealized D_3 structure for the purpose of description and discussion. In this context the structure consists of two approximately parallel (dihedral angle = 178°), roughly equilateral triangles separated by a distance of 3·00 Å. The triangles are twisted from each other by an averaged angle of 27° from the trigonal prism. The bite angle in the chelates is 82(1)° in each case while the bite distances are 3·15(1) Å on the two-fold and 3·12(1) Å in the independent ligand. Within the ligands the S–C and C–C distances average 1·76 and 1·30 Å, respectively, indicating the net closeness of the ligands to the dithiolato-form. The CN groups and the tetraphenylarsonium counter-ions have their expected dimensions.

The $Mo(mnt)_3^{2-}$ structure can be compared to that of $Mo(S_2C_2H_2)_3$ in which Smith *et al.*[1] find a perfect MoS_6 prism with Mo–S distance of 2·33, S–S intraligand (intertriangle) distance of 3·11, and S–S interligand (intratriangle) distance of 3·10 Å. The $Mo(mnt)_3^{2-}$ structure can be looked upon as derived from that of $Mo(S_2C_2H_2)_3$ by three steps; (i) a trigonal twist of 27°, (ii) an axial trigonal compression of 0·11 Å, and (iii) a radial trigonal expansion wherein the S_3 triangles expand from a side of 3·10 to an average side of 3·21 Å. These departures from the trigonal prism along with the increase in M–S bond length can be viewed as a direct consequence of the addition of two electrons to an orbital which is antibonding in the trigonal prism. However, the complex has not twisted all the way to the octahedral limit and the important effect caused by the rigid nature of the chelating ligand cannot be overlooked at this point. Amidst great structural variety in all 1,2-dithiolate (or 1,2-dithiolene) complexes the bite of the ligand varies only from 3·03 to 3·15 Å.[7] Thus, considering the observed Mo–S bond length and taking the ligand constraint into account, it is apparent that the complex could not move farther towards the octahedron without additional trigonal axial compression and trigonal radial expansion (both being necessary to keep Mo–S the same). It seems reasonable that these changes are not favoured by M–L bonding considerations in the Mo complex. On the other hand, in $Fe(mnt)_3^{2-}$ the shorter Fe–S distance of 2·26 Å allows[2] a near octahedral structure to be reached without these disadvantages. Calculations are in progress to clarify these points.

Finally, we recall the diamagnetism of the Mo and W complexes and note that it cannot be used as a structural diagnostic in this or similar cases. It is clear that while diamagnetism, in these formally d^2 systems, would seem to preclude a strictly octahedral (O_h co-ordination) geometry it does not require a fully prismatic structure either. Rather, as has been discussed elsewhere,[5,8] either D_{3h} or D_3 symmetry can accommodate the observed magnetic properties.

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