Crystal Structure of Tris(quinoxaline-2,3-dithiolato)molybdate(V); a Distorted Trigonal Prismatic Complex†

Stephen Boyde and C. David Garner *
The Chemistry Department, Manchester University, Manchester M13 9PL
John H. Enemark, Michael A. Bruck, and John G. Kristofzski
Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.

The anion $[Mo(qdt)_3]^-$ (qdt = quinoxaline-2,3-dithiolate) has been prepared by iodine oxidation of the corresponding dianion. The compound $[PPh_4][Mo(qdt)_3]$ crystallizes in triclinic space group $P\bar{1}$ with $a = 12.077(5)$, $b = 12.519(5)$, $c = 15.297(6)$ Å, $\alpha = 89.76(3)$, $\beta = 81.09(3)$, $\gamma = 80.50(3)$°, and $Z = 2$. The complex has a distorted trigonal prismatic MoS_6 core with a mean Mo–S distance of 2.393(1) Å and a mean twist angle of 14.6°. This monoanion is more significantly distorted from ideal trigonal-prismatic geometry than is the dianion, $[Mo(qdt)_3]^{2-}$, contrary to the results expected on the basis of previous molecular orbital calculations for tris(dithiolene) complexes.

Recently, we reported the crystal structure of $[PPh_4]_2[Mo(qdt)_3]\cdot H_2O$ (qdt = quinoxaline-2,3-dithiolate, see Figure 1) and showed that the (formally) molybdenum(IV) tris(dithiolene) dianion had an almost perfectly trigonal prismatic MoS_6 core.[1] This result was unexpected, as the isoelectronic complex $[Mo(mnt)_3]^{2-}$ (mnt = maleonitriledithiolate) has a MoS_6 core with a structure intermediate between trigonal prismatic and octahedral geometries,[2] and this distorted structure had been rationalized by consideration of a molecular orbital scheme for trigonal prismatic tris(dithiolene) complexes.[2,3]

Therefore, to provide further information concerning the relationship between the electronic configuration and the molecular geometry of these complexes, we have structurally characterized the (formally) molybdenum(V) complex, $[Mo(qdt)_3]^-$, in order to obtain a direct structural comparison between the two components of the redox couple $[Mo(qdt)_3]^-$–$[Mo(qdt)_3]^{2-}$. To facilitate the direct comparison, we determined the structure of the monoanion as the salt of the $[PPh_4]^+$ cation as was used in the earlier study of the dianion.[1] However, despite repeated attempts we were unable to obtain satisfactory elemental analyses for the bulk material $[PPh_4][Mo(qdt)_3]$ and, therefore, we also prepared $[Mo(qdt)_3]^-$ as the $[NBu_4]^+$ salt, which *was* isolable as analytically pure material. The latter compound was used for spectroscopic characterization of the anion.

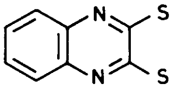

Figure 1. The structure of quinoxaline-2,3-dithiolate (qdt)

Experimental

Instrumentation and Analyses.—Chemical analyses were performed by the University of Manchester, Microanalytical Laboratory. U.v.–visible spectra were recorded on a Shimadzu UV-260 spectrophotometer and e.s.r. spectra on a Varian 112 instrument.

Materials and Methods.—All reactions were carried out in dry, de-oxygenated solvents under a purified dinitrogen atmosphere. The compound $[PPh_4]_2[Mo(qdt)_3]\cdot H_2O$ was prepared by the previously published procedure[1] and $[NBu_4]_2[Mo(qdt)_3]$ was prepared similarly, using $[NBu_4]Br$ in place of $[PPh_4]Br$ and recrystallized from CH_2Cl_2–hexane.

Syntheses.—$[NBu_4][Mo(qdt)_3]$. The compound $[NBu_4]_2[Mo(qdt)_3]$ (0.50 g, 0.43 mmol) was dissolved in CH_2Cl_2 (50 cm^3), chilled to 0 °C, and stirred as a solution of I_2 (0.054 g, 0.21 mmol) in CH_2Cl_2 (10 cm^3) was added, dropwise, over a 5 min period. The solution changed colour from purple to olive-green. Hexane (100 cm^3) was added and the solution was filtered to isolate a dark powder, which was washed with cold MeOH (0 °C, 3 × 10 cm^3 portions) and recrystallized from CH_2Cl_2–hexane to give $[NBu_4][Mo(qdt)_3]$ (0.27 g, 70%) as a dark green, microcrystalline powder (Found: C, 52.7; H, 5.4, Mo, 10.5; N, 11.0; S, 20.5. $C_{40}H_{48}MoN_7S_6$ requires C, 52.5; H, 5.3; Mo, 10.5; N, 10.8; S, 21.0%). U.v.–visible: $\lambda_{max.}(CH_2Cl_2)$ 800 (ε 10 500), 687 (23 500), 500 (37 900), 435 (47 000), 401 (54 400), and 255 nm (136 700 dm^3 mol^{-1} cm^{-1}). E.s.r. (CH_2Cl_2): $g = 2.002$, A(Mo) = 32.9 G.

$[PPh_4][Mo(qdt)_3]$. The compound $[PPh_4][Mo(qdt)_3]$ was prepared by iodine oxidation of $[PPh_4]_2[Mo(qdt)_3]$, as described for $[NBu_4][Mo(qdt)_3]$. For the $[PPh_4]^+$ salt, analytically pure material could not be obtained due to co-precipitation of $[PPh_4]I_3$, but recrystallization from CH_2Cl_2–hexane by solvent diffusion gave a few well formed crystals which were separated by hand. These crystals proved suitable for structure analysis by *X*-ray diffraction. The u.v.–visible and e.s.r. spectra of $[PPh_4][Mo(qdt)_3]$ in CH_2Cl_2 solution were identical with those of $[NBu_4][Mo(qdt)_3]$.

Crystal-structure Determination.—A dark crystal of $[PPh_4][Mo(qdt)_3]$ was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed, with Mo-K_α radiation on a Nicolet $P2_1$ diffractometer equipped with a graphite-crystal incident-beam monochromator and controlled by locally modified *P*3 software. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 24 reflections in the range $17 < 2\theta < 27$°. Omega scans of several intense reflections were measured; the width at half-height was 0.38°, indicating moderate crystal quality. There were no systematic absences; the space group was determined to be $P\bar{1}$ (no. 2). The details of data collection and corrections applied to the data are summarized in Table 1.

The structure was solved using the Patterson heavy-atom method which revealed the position of the Mo atom. The

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: G = 10^{-4} T.

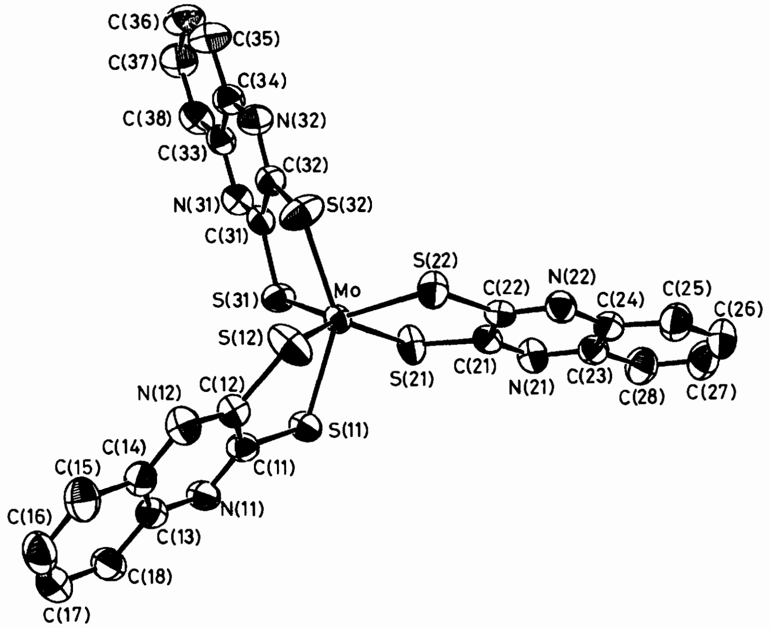

Figure 2. The structure of the anion in [PPh$_4$][Mo(qdt)$_3$], showing the crystallographic atom numbering

Table 1. Experimental details for the *X*-ray crystallographic study of [PPh$_4$][Mo(qdt)$_3$]

Crystal data	
$C_{48}H_{32}MoN_6PS_6$, M = 1 012.1, $F(000)$ = 1 030	
Crystal dimensions: 0.40 × 0.40 × 0.70 mm	
Peak width at half-height 0.38°	
Mo-K_α radiation (λ = 0.710 73 Å)	
Triclinic, space group $P\bar{1}$	
a = 12.077(5), b = 12.519(5), c = 15.297(6) Å	
α = 89.76(3), β = 81.09(3), γ = 80.50(3)°	
U = 2 252.9 Å^3, Z = 2	
D_c = 1.49 g cm^{-3}, μ = 6.3 cm^{-1}, T = 23(1) °C	
Intensity measurements	
Instrument	Nicolet/Syntex $P2_1$ diffractometer running locally modified $P3$ software
Monochromator	Graphite crystal, incident beam
Crystal–detector distance	21 cm
Incident beam collimator	0.75 mm diameter
Scan type	2θ–θ
Scan rate	2–8° min^{-1}
Scan width	from (2θ – 0.9°) to (2θ + 1.5°)
Maximum 2θ	60°
Number of reflections measured	9 188 total, 7 982 unique
Corrections	Lorentz-polarization Reflection averaging (agreement on I for 550 observed and accepted reflections, 6.6%)
Structure refinement	
Refinement	Full-matrix least squares
Minimization functions	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares weights	$4F_o^2/[\sigma^2(I) + 0.04F_o^2]^2$
Reflections included	6 018 with $F_o^2 > 3.0\sigma(F_o)^2$
Parameters refined	559
Unweighted agreement factor	0.035
Weighted agreement factor	0.043
E.s.d. of observation of unit weight	1.49
Convergence, largest shift	0.39
Highest peak in final difference Fourier map	0.67(6) e Å^{-3}

remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were observed in the difference maps and included in the refinement but were constrained to ride on the atom to which they were bonded, with fixed isotropic thermal parameters. The geometry of the hydrogens was idealized and the C–H bond lengths were fixed at 0.95 Å. The details of the refinement of the structure are included in Table 1. The weights for each reflection were calculated using $w = 4F^2/[\sigma^2(I) + pF^2]^2$ with the uncertainty factor, p, set to 0.04. Scattering factors were taken from Cromer and Waber.[4] Anomalous dispersion effects were included in F_c;[5] the values for $\Delta f''$ were those of Cromer.[6] Plots of $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ *versus* F_o, reflection order in data collection, (sin θ)/λ, and various classes of indices showed no unusual trends. All calculations were performed on a PDP-11/34a computer using SDP-PLUS.[7]

The final refined atomic co-ordinates are presented in Table 2.

Results and Discussion

Positional parameters for [PPh$_4$][Mo(qdt)$_3$] are listed in Table 2 and the structure of the anion, showing the crystallographic atom numbering, is illustrated in Figure 2. Selected interatomic distances and interbond angles for the anion are listed in Tables 3 and 4, respectively.

The co-ordination geometry of the MoS$_6$ core of [Mo(qdt)$_3$]$^-$ is that of a slightly distorted trigonal prism, with an average Mo–S distance of 2.393(1) Å. The three qdt ligands are each virtually planar; the largest displacement of any atom from the least-squares plane of the appropriate $C_8N_2S_2$ group is 0.009, 0.036, and 0.070 Å for ligands 1, 2, and 3, respectively. The ligand $C_8N_2S_2$ planes are folded with respect to the MoS$_2$ planes, along the S–S vector, at angles of 25, 8, and 13°, respectively. The dimensions of the ligands do not differ significantly from each other and are similar to those found for qdt in other complexes.[1,8,9]

Metal tris(dithiolenes) were the first non-octahedral, six-co-ordinate transition-metal complexes to be structurally characterized[3] and much of the interest shown in these complexes has concentrated on attempts to explain the observed trigonal-prismatic geometry.[10] It is generally considered that the unusual structures of these complexes are due to electronic, rather than steric effects, as octahedral tris(dithiolenes) have

Table 2. Positional parameters with estimated standard deviations for $[PPh_4][Mo(qdt)_3]$

Atom	x	y	z	Atom	x	y	z
Mo	0.196 82(2)	0.197 94(2)	0.291 70(2)	C(33)	0.4369(3)	0.5321(3)	0.1608(2)
S(11)	0.151 39(7)	0.082 18(7)	0.183 60(6)	C(34)	0.3765(3)	0.5865(3)	0.2392(2)
S(12)	−0.008 22(8)	0.2443(1)	0.323 99(6)	C(35)	0.3945(4)	0.6920(3)	0.2579(3)
S(21)	0.359 00(8)	0.058 97(8)	0.282 13(6)	C(36)	0.4686(4)	0.7408(3)	0.2008(3)
S(22)	0.182 07(8)	0.159 44(7)	0.444 76(6)	C(37)	0.5293(3)	0.6865(3)	0.1242(3)
S(31)	0.313 69(8)	0.260 09(7)	0.166 45(6)	C(38)	0.5150(3)	0.5833(3)	0.1040(3)
S(32)	0.1843(1)	0.381 04(8)	0.340 97(7)	P	0.097 58(8)	0.316 60(7)	0.740 28(6)
N(11)	−0.0173(2)	0.1099(2)	0.0905(2)	C(41)	0.1928(3)	0.3933(3)	0.6738(2)
N(12)	−0.1614(2)	0.2551(2)	0.2170(2)	C(42)	0.1812(3)	0.4219(3)	0.5882(2)
N(21)	0.4412(2)	−0.0847(2)	0.3916(2)	C(43)	0.2528(4)	0.4876(3)	0.5425(3)
N(22)	0.2817(2)	0.0058(2)	0.5390(2)	C(44)	0.3347(4)	0.5236(3)	0.5818(3)
N(31)	0.4203(2)	0.4297(2)	0.1385(2)	C(45)	0.3489(4)	0.4928(4)	0.6666(3)
N(32)	0.3015(3)	0.5384(2)	0.2960(2)	C(46)	0.2787(3)	0.4274(3)	0.7127(3)
C(11)	0.0149(3)	0.1381(3)	0.1642(2)	C(51)	0.0192(3)	0.2473(3)	0.6745(2)
C(12)	−0.0581(3)	0.2121(3)	0.2279(2)	C(52)	0.0337(3)	0.1344(3)	0.6705(3)
C(13)	−0.1251(3)	0.1543(3)	0.0772(2)	C(53)	−0.0269(4)	0.0838(3)	0.6182(3)
C(14)	−0.1968(3)	0.2268(3)	0.1407(2)	C(54)	−0.0996(3)	0.1445(4)	0.5690(3)
C(15)	−0.3070(3)	0.2705(3)	0.1236(3)	C(55)	−0.1153(3)	0.2553(4)	0.5732(3)
C(16)	−0.3426(3)	0.2428(3)	0.0482(3)	C(56)	−0.0574(3)	0.3073(3)	0.6266(3)
C(17)	−0.2707(3)	0.1718(3)	−0.0148(3)	C(61)	0.1811(3)	0.2193(3)	0.8006(2)
C(18)	−0.1639(3)	0.1283(3)	−0.0008(3)	C(62)	0.2744(3)	0.1506(3)	0.7534(3)
C(21)	0.3620(3)	−0.0009(3)	0.3849(2)	C(63)	0.3391(3)	0.0739(3)	0.7976(3)
C(22)	0.2824(3)	0.0463(3)	0.4596(2)	C(64)	0.3135(4)	0.0669(4)	0.8876(3)
C(23)	0.4420(3)	−0.1280(3)	0.4737(2)	C(65)	0.2229(4)	0.1344(4)	0.9345(3)
C(24)	0.3614(3)	−0.0832(3)	0.5473(2)	C(66)	0.1562(3)	0.2106(3)	0.8910(2)
C(25)	0.3637(4)	−0.1328(3)	0.6304(3)	C(71)	−0.0016(3)	0.4073(3)	0.8175(2)
C(26)	0.4457(4)	−0.2191(3)	0.6393(3)	C(72)	0.0188(3)	0.5102(3)	0.8371(2)
C(27)	0.5264(4)	−0.2613(3)	0.5681(3)	C(73)	−0.0557(4)	0.5743(3)	0.9016(3)
C(28)	0.5246(3)	−0.2180(3)	0.4861(3)	C(74)	−0.1486(4)	0.5357(3)	0.9472(3)
C(31)	0.3452(3)	0.3862(3)	0.1937(2)	C(75)	−0.1699(3)	0.4346(4)	0.9277(3)
C(32)	0.2853(3)	0.4413(3)	0.2735(2)	C(76)	−0.0978(3)	0.3704(3)	0.8628(3)

Table 3. Bond lengths (Å)* for the anion of $[PPh_4][Mo(qdt)_3]$

Mo–S(11)	2.387(1)	S(11)–C(11)	1.750(3)
Mo–S(12)	2.421(1)	S(12)–C(12)	1.745(3)
Mo–S(21)	2.382(1)	S(21)–C(21)	1.742(3)
Mo–S(22)	2.374(1)	S(22)–C(22)	1.744(3)
Mo–S(31)	2.404(1)	S(31)–C(31)	1.751(1)
Mo–S(32)	2.389(1)	S(32)–C(32)	1.740(3)
Mean Mo–S	2.393(1)	Mean S–C	1.745(4)
N(11)–C(11)	1.316(3)	C(16)–C(17)	1.402(5)
N(11)–C(13)	1.374(3)	C(17)–C(18)	1.363(5)
N(12)–C(12)	1.309(4)	C(21)–C(22)	1.433(4)
N(12)–C(14)	1.372(4)	C(23)–C(24)	1.419(4)
N(21)–C(21)	1.313(4)	C(23)–C(28)	1.410(4)
N(21)–C(23)	1.368(4)	C(24)–C(25)	1.415(4)
N(22)–C(22)	1.315(4)	C(25)–C(26)	1.362(5)
N(22)–C(24)	1.366(4)	C(26)–C(27)	1.386(5)
N(31)–C(31)	1.324(4)	C(27)–C(28)	1.366(5)
N(31)–C(33)	1.383(4)	C(31)–C(32)	1.434(4)
N(32)–C(32)	1.318(4)	C(33)–C(34)	1.416(4)
N(32)–C(34)	1.368(4)	C(33)–C(38)	1.413(5)
C(11)–C(12)	1.434(4)	C(34)–C(35)	1.412(4)
C(13)–C(14)	1.415(4)	C(35)–C(36)	1.368(5)
C(13)–C(18)	1.405(4)	C(36)–C(37)	1.396(6)
C(14)–C(15)	1.415(4)	C(37)–C(38)	1.374(5)
C(15)–C(16)	1.357(4)		

* Numbers in parentheses are estimated standard deviations in the least significant digits.

also been characterized.[11] Previously, we have reported the structure of $[PPh_4]_2[Mo(qdt)_3]\cdot H_2O$.[1] This dianion, and the monoanion, $[Mo(qdt)_3]^-$ described in this work, comprise the first redox-related pair of tris(dithiolene) complexes to be structurally characterized. Thus, comparison of the two structures provides a test of the explanations which have been advanced for the dependence of the molecular geometry of tris(dithiolenes) upon their electron configuration.

Selected structural parameters for $[Mo(qdt)_3]^-$ and $[Mo(qdt)_3]^{2-}$ are compared in Table 5. It is apparent that the only significant structural differences between the two complexes lie in the degree to which their MoS_6 cores are distorted from ideal trigonal-prismatic geometry and the extent of folding of the ligand planes with respect to the MoS_2 planes.

Several workers[12–14] have attempted to define parameters which would allow a quantitative description of the shapes of distorted or irregular polyhedra; the approach of Stiefel and Brown[14] is the most appropriate to the present case. These workers define a regular trigonal prism as one in which the separation between the triangular faces is equal to the length of their sides. Six-co-ordinate structures may then be described in terms of two distortions from the regular trigonal prism: (*i*) a rotation of one triangular face with respect to the other, about an axis defined by the centroids of the two triangles, through an angle described as the twist angle; and (*ii*) a compression along the same axis defined in terms of the compression ratio, s/h, where s is the length of side of a triangular face and h is the perpendicular distance between the triangular faces. Thus, a twist angle of 0° and a compression ratio of 1.0 defines a regular trigonal prism, while a twist of 60° accompanied by a 1.22-fold compression generates a regular octahedron. This analysis is strictly valid only if the two triangular faces are parallel, regular, and isodimensional. This is not generally the case for real complexes, for which calculated twist angles and compression ratios are only approximate. In this work, individual twist angles have been calculated for each ligand, defined as the dihedral angle between the lines joining the sulphur atoms and

Table 4. Interbond angles (°) for the anion of $[PPh_4][Mo(qdt)_3]$

S(11)–Mo–S(12)	81.77(3)	Mo–S(31)–C(31)	108.7(1)	N(11)–C(11)–C(12)	122.0(2)	N(22)–C(22)–C(21)	121.8(3)
S(11)–Mo–S(21)	80.88(3)	Mo–S(32)–C(32)	109.2(1)	S(12)–C(12)–N(12)	118.9(2)	N(21)–C(23)–C(24)	121.1(3)
S(11)–Mo–S(22)	123.81(3)	C(11)–N(11)–C(13)	116.9(2)	S(12)–C(12)–C(11)	118.8(2)	S(31)–C(31)–N(31)	119.1(3)
S(11)–Mo–S(31)	83.34(3)	C(12)–N(12)–C(14)	116.7(2)	N(12)–C(12)–C(11)	122.3(3)	S(31)–C(31)–C(32)	118.8(3)
S(11)–Mo–S(32)	145.53(3)	C(21)–N(21)–C(23)	116.4(3)	N(11)–C(13)–C(14)	120.7(2)	N(31)–C(31)–C(32)	122.0(3)
S(12)–Mo–S(21)	146.89(4)	C(22)–N(22)–C(24)	116.7(3)	N(11)–C(13)–C(18)	119.5(3)	S(32)–C(32)–N(32)	118.6(2)
S(12)–Mo–S(22)	84.10(3)	C(24)–C(23)–C(28)	119.7(3)	C(14)–C(13)–C(18)	119.8(3)	S(32)–C(32)–C(31)	119.4(2)
S(12)–Mo–S(31)	124.93(3)	N(21)–C(23)–C(28)	119·2(3)	N(12)–C(14)–C(13)	121.4(3)	N(32)–C(32)–C(31)	121.9(3)
S(12)–Mo–S(32)	81.77(3)	N(22)–C(24)–C(23)	121.3(3)	N(12)–C(14)–C(15)	120.1(3)	N(31)–C(33)–C(34)	121.0(3)
S(21)–Mo–S(22)	82.48(3)	N(22)–C(24)–C(25)	119.8(3)	C(13)–C(14)–C(15)	118.4(3)	N(31)–C(33)–C(38)	119.3(3)
S(21)–Mo–S(31)	80.58(3)	C(23)–C(24)–C(25)	119.0(3)	C(14)–C(15)–C(16)	120.4(3)	C(34)–C(33)–C(38)	119.7(3)
S(21)–Mo–S(32)	126.48(4)	C(24)–C(25)–C(26)	119.7(3)	C(15)–C(16)–C(17)	120·8(3)	N(32)–C(34)–C(33)	121.0(3)
S(22)–Mo–S(31)	144.93(3)	C(25)–C(26)–C(27)	121.5(3)	C(16)–C(17)–C(18)	120·4(3)	N(32)–C(34)–C(35)	120.1(3)
S(22)–Mo–S(32)	84.17(3)	C(26)–C(27)–C(28)	120.5(3)	C(13)–C(18)–C(17)	120.1(3)	C(33)–C(34)–C(35)	118.8(3)
S(31)–Mo–S(32)	81.64(3)	C(23)–C(28)–C(27)	120.1(3)	S(21)–C(21)–N(21)	118.2(3)	C(34)–C(35)–C(36)	120.3(3)
Mo–S(11)–C(11)	106.06(9)	C(31)–N(31)–C(33)	116.6(3)	S(21)–C(21)–C(22)	119.1(2)	C(35)–C(36)–C(37)	120.8(3)
Mo–S(12)–C(12)	105.8(1)	C(32)–N(32)–C(34)	117.4(3)	N(21)–C(21)–C(22)	122.6(3)	C(36)–C(37)–C(38)	120.7(3)
Mo–S(21)–C(21)	109.1(1)	S(11)–C(11)–N(11)	118.0(2)	S(22)–C(22)–N(22)	118.8(2)	C(33)–C(38)–C(37)	119.7(3)
Mo–S(22)–C(22)	109.2(1)	S(11)–C(11)–C(12)	119.9(2)	S(22)–C(22)–C(21)	119.4(2)		

Table 5. Structural parameters for $[Mo(qdt)_3]^{2-}$ and $[Mo(qdt)_3]^-$

Parameter	$[Mo(qdt)_3]^{2-}$	$[Mo(qdt)_3]^-$
Mo–S/Å	2.393(1)	2.393(1)
Intraligand S–S (bite)/Å	3.126(7)	3.138(7)
Interligand S–S (side, *s*)/Å	3.141(7)	3.154(7)
Height of trigonal prism (*h*)/Å	3.122(4)	3.103(4)
Compression ratio (*s*/*h*)	1.01	1.02
Twist angles[a]/°		
Ligand 1	5.2	16.2
Ligand 2	3.8	14.4
Ligand 3	4.6	13.2
Mean	4.5	14.6
Ligand folding angles[b]/°		
Ligand 1	12	25
Ligand 2	3	7
Ligand 3	12	10

[a] For ligand *N*, the twist angle is the dihedral angle between the lines S(*N*1)–X(1) and S(*N*2)–X(2) where X(1) and X(2) are the centroids of the triangles defined by S(11), S(21), S(31) and S(12), S(22), S(32), respectively. [b] Angle between MoS_2 and $C_8N_2S_2$ planes.

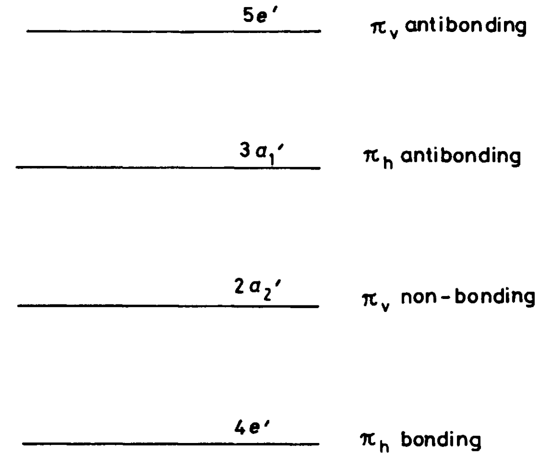

Figure 3. The frontier molecular orbitals for trigonal prismatic tris(dithiolene) complexes

the centroids of the triangular faces. The agreement of these individual values provides a measure of the regularity of the complex.

The anion $[Mo(qdt)_3]^{2-}$ has an average twist angle of 4.5° and a compression ratio of 1.01 and, therefore, is virtually perfectly trigonal prismatic, while $[Mo(qdt)_3]^-$ has an average twist angle of 14.6° (and a compression ratio of 1.02) and thus can be described as distorted one quarter of the way towards the octahedral limit, according to the twist-angle criterion.

Molecular orbital schemes for trigonal-prismatic tris(dithiolene) complexes have been presented by Gray and co-workers[3] and by Schrauzer and Mayweg;[15] the two schemes differ slightly in the ordering of the valence orbitals and the former model has been found to give better agreement with the results of spectroscopic studies. Gray assumed D_{3h} symmetry and attributed the stability of the trigonal-prismatic geometry to two π-bonding interactions:[3] first, the π_h interaction which results from overlap of the metal d_{z^2} orbital with the sulphur sp^2 lone-pair orbitals at 120° to the M–S and S–C bonds and, secondly, the π_v bonding which arises from overlap of the metal d_{xy} and $d_{x^2-y^2}$ orbitals with the butadienoid π orbitals of the ligand S_2C_2 groups. The ordering of the frontier molecular orbitals in this model is shown in Figure 3.

In this model, the optimal electron configuration for trigonal-prismatic geometry is that of the neutral tris(dithiolene) complexes of the Group 6 transition metals, for which the h.o.m.o. (highest occupied molecular orbital) is the $2a_2$ level, *i.e.* the bonding π_h and π_v orbitals are filled and their antibonding counterparts unoccupied. The l.u.m.o. (lowest unoccupied molecular orbital) in these complexes is an antibonding π_h orbital; therefore, the occupation of this orbital in monoanionic and dianionic tris(dithiolene) complexes of the Group 6 transition metals {*e.g.* $[Mo(qdt)_3]^-$ and $[Mo(qdt)_3]^{2-}$} was expected to destabilize the trigonal-prismatic structure and allow distortion towards octahedral geometry. In support of this argument, the structures of the dianionic complexes $[Mo(mnt)_3]^{2-}$ and $[W(mnt)_3]^{2-}$ have been determined and found to be severely distorted from trigonal-prismatic geometry;[2] these latter complexes are isostructural, with a twist angle of 25° and a compression ratio of 1.07, indicative of a geometry midway between the octahedral and trigonal prismatic limits.[2]

The twist angle of 14.6° for $[Mo(qdt)_3]^-$ is consistent with the above arguments. Thus, one-electron occupation of the π_h antibonding orbital in $[Mo(qdt)_3]^-$ induces a distortion from trigonal-prismatic geometry almost exactly half that found for the dianionic mnt complexes, in which this orbital is fully occupied. However, these arguments predict that $[Mo(qdt)_3]^{2-}$ should be more distorted towards the octahedral limit than $[Mo(qdt)_3]^-$. Therefore, the observation of nearly perfect trigonal-prismatic geometry for the former complex is unexpected. Recently, another dianionic molybdenum tris(dithiolene) complex, $[Mo\{S_2C_2(CO_2Me)_2\}_3]^{2-}$, has been structurally characterized,[16] and found to have an average twist angle of 10.6° (calculated from published atomic co-ordinates), significantly different from the value of this parameter for either $[Mo(qdt)_3]^{2-}$ or $[Mo(mnt)_3]^{2-}$. Thus, it is apparent that the structures of these complexes are not as simply related to the degree of occupation of the π_h antibonding orbital as the early results appeared to suggest and that the geometries of dianionic molybdenum tris(dithiolene) complexes are significantly dependent upon the nature of the substituents on the metalladithiolene (MS_2C_2) rings.

Another feature of the structures of metal dithiolene complexes which has attracted attention is that in most,[17] although not all,[2,18,19] of these complexes the ligand planes are folded with respect to the planes defined by the MoS_2 groups, *i.e.* the metalladithiolene groups are puckered. This folding has been variously attributed to maximization of overlap between ligand π-donor and metal π-acceptor orbitals, to sulphur hybridization intermediate between sp^2 and sp^3, and to solid-state packing interactions.[13,20] However, the wide range of folding angles observed for the individual ligands of $[Mo(qdt)_3]^{2-}$ and $[Mo(qdt)_3]^-$ is not reflected in, for example, variations in the Mo–S bond lengths. Therefore, it appears that steric (crystal packing) rather than electronic factors provide a more probable explanation for the adoption of a particular folding angle in this case.

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