Structural Studies of Eight-co-ordinate Metal Complexes. Part II.[1] Crystal and Molecular Structure of Tetrakis(dithiobenzoato)molybdenum(IV)

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The crystal and molecular structure of the title compound has been determined by X-ray methods. The compound crystallizes in the tetragonal space group $I4_1/a$, with a = 21.486(1), c = 6.73(2) Å, Z = 4. The structure was solved using 1 267 reflections collected by atomatic diffractometry, *via* Patterson and Fourier techniques, and refined by least-squares to R 0.033. The dodecahedral geometry of co-ordination (subclass D_{2d}, $\bar{4}2m$) and the general ligand conformation closely approximate to those of the vanadium analogue.

As part of a continuing study of the factors affecting the geometry of eight-co-ordinate complexes of transition metals with bidentate sulphur donor ligands, we have performed a relatively accurate crystal-structure determination on [Mo(PhCS$_2$)$_4$]. The aim of this work is to allow a closer comparison of the experimental results with the detailed predictions arrived at from theoretical calculations, and to extend the sparse structural information on eight-co-ordinate Mo^{IV} complexes with bidentate ligands.

EXPERIMENTAL

The compound was synthesized as in ref. 2. Cell dimension a was determined by an improved version of Christ's method[3] from a zero-layer Weissenberg film about the c axis, whilst c was determined from experimental values of equi-inclination angles determined on an automatic diffractometer.

Crystal Data.—$C_{28}H_{20}MoS_8$, M = 708.89, Tetragonal, a = 21.486(1), c = 6.73(2) Å, U = 3107 Å^3, D_m = 1.52 (by flotation), Z = 4, D_c = 1.53, $F(000)$ = 2091.9. Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 82.7 cm.$^{-1}$ Space group $I4_1/a$ (C^6_{4h}, No. 88), from systematic absences and structure determination.

Intensities were measured on a STOE automatic Weissenberg diffractometer. The crystal used, average radius 0.01 cm, was mounted along the needle axis c. Nickel-filtered Cu-K_α radiation was monochromatized by a plane graphite crystal.

Two sets of data were collected from seven layers, $hk0$—6: the first in 2θ-scan ($12° \leqslant 2\theta \leqslant 152°$; $1.5° \leqslant \Delta\theta \leqslant 2.5°$), and the second, for low-angle reflections only, in ω-scan ($3.5° \leqslant \Delta\omega \leqslant 10.0°$). A single reference reflection for each layer was monitored during both data collections. A background count for every reflection was determined by two stationary-crystal–stationary-counter measurements at the beginning and end of each scan. The low-angle data for the two data collections were compared *via* peak profiles and integrated intensities (first corrected for background, Lorentz, and polarisation[4] effects, and absorption). On the basis of this comparison, the 2θ data collection was used for the zero and first layers, whereas an increasing number of ω-scan low-angle data were preferred for the upper layers. 1 267 independent reflections (36%), of which *ca.* 100 were collected in ω-scan, were considered significant ($I > 3C^{1/2}$, where C is the integrated intensity not corrected for background). Independent layer scales were refined during the isotropic phase of the structure refinement.

Structure Determination and Refinement.—The general features of the structure became apparent on comparison of the $hk0$ Weissenberg films with those for the analogous vanadium dithiobenzoate.[1] Virtually all the strongest reflections in the two films coincided. In addition, the a axis in the molybdenum complex coincided with an evident direction in the film of the vanadium complex, at *ca.* 26° to the a axis of the latter. A relationship between the two cells, consistent with these results and with the space group, is apparent, as shown in the [001] projection of the two cells (Figure 1), in which the black circles are vanadium atoms in the special position 4(a) in space group $I4_1/a$, and the other circles are vanadium atoms in general positions. The space group requires that the molybdenum atoms all lie in the special position 4(a). Shaded circles, together with the

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[1] Part I, M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1974, 1258.

[2] O. Piovesana and L. Sestili, *Inorg. Chem.*, 1974, **13**, 2745.

[3] G. Mazzone, A. Vaciago, and M. Bonamico, *Ricerca Sci.*, 1963, **33**, (II*A*), 1113.

[4] H. A. Levy and R. D. Ellison, *Acta Cryst.*, 1960, **13**, 270.

central black circle, show the positions of the molybdenum atoms in this projection.

The relative layer scale factors were assumed equal to 1 for Fourier syntheses, then refined during the isotropic least-squares calculations.

TABLE 1

Co-ordinates ($\times$ 10^4) and temperature factors,* with standard deviations in parentheses

	x/a	y/b	z/c	B/b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Mo	0(0)	2 500(0)	1 250(2)	17(0)	0(0)	0(0)	17(0)	0(0)	181(2)
S(1)	237(0)	3 187(0)	4 231(2)	31(0)	−10(0)	−2(1)	18(0)	8(1)	213(2)
S(2)	360(1)	3 554(0)	314(2)	34(0)	−9(0)	15(1)	21(0)	17(1)	223(3)
C(1)	439(1)	3 770(1)	2 699(6)	19(1)	0(1)	8(4)	17(1)	12(4)	257(10)
C(2)	668(2)	4 380(2)	3 365(7)	26(1)	−4(1)	8(5)	19(1)	1(4)	295(11)
C(3)	657(2)	4 540(2)	5 349(7)	26(1)	−2(1)	−14(5)	20(1)	7(5)	330(13)
C(4)	875(2)	5 117(2)	5 959(8)	37(1)	0(2)	−49(7)	24(1)	−37(6)	363(14)
C(5)	1 087(3)	5 540(2)	4 598(10)	57(2)	−29(3)	44(11)	25(1)	−39(8)	495(21)
C(6)	1 090(5)	5 382(3)	2 627(13)	110(4)	−62(4)	177(18)	30(1)	−21(10)	571(26)
C(7)	883(4)	4 799(3)	2 016(9)	88(3)	−51(3)	104(12)	30(1)	−13(8)	355(17)
H(3)	492	4 239	6 352	6.00					
H(4)	878	5 225	7 404	6.00					
H(5)	1 238	5 958	5 037	6.00					
H(6)	1 242	5 689	1 618	6.00					
H(7)	892	4 687	574	6.00					

* Exponential coefficients b_{ij} as given here are defined by $T = \exp 10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

A Patterson map was necessary to locate the two independent sulphur atoms, and one electron-density map led to the location of all carbon atoms. Block-diagonal least-squares refinement with isotropic temperature factors converged at R 0.089. Anisotropic refinement for all non-hydrogen atoms gave R 0.038. At this stage, the co-ordinates of the five independent hydrogen atoms were calculated and an isotropic refinement carried out to refine layer scales. The positional co-ordinates of the hydrogen atoms were fixed during the refinement, which gave virtually the same R factor as before.

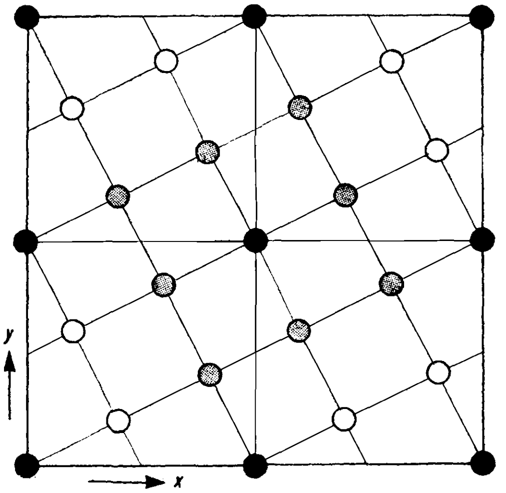

FIGURE 1 [001] Projection of the lattices of tetrakis(dithiobenzoato)-vanadium(IV) and -molybdenum(IV). All circles represent vanadium atoms in the first complex, whereas the molybdenum atoms in the latter only occupy the shaded positions and the central black circle

Final refinement with the new layer scales had anisotropic temperature factors for all non-hydrogen atoms and fixed positional co-ordinates for hydrogen atoms; their isotropic temperature factors were also fixed at a constant value, roughly similar to the mean temperature factors of the phenyl group. It converged at R 0.033. At the end of refinement, shifts in atomic parameters were $\leqslant 0.11\,\sigma$. The weighting scheme used was $w = (3.0 + |F_o| + 0.002\,|F_o|^2)^{-1}$.

Table 1 gives final atomic parameters with standard deviations within the asymmetric unit. The values of b_{13}, b_{23}, and b_{33} are virtually without significance because of restrictions in the intensity data. Structure factors, based on the final atomic parameters, compared with the observed structure amplitudes, are listed in Supplementary Publication No. SUP 21351 (5 pp., 1 microfiche).*

TABLE 2

Molecular geometry within the chemical unit, with estimated standard deviations in parentheses

(*a*) Distances (Å)

Mo–S(1)	2.543(1)	C(2)–C(7)	1.36(1)
Mo–S(2)	2.475(1)	C(3)–C(4)	1.39(1)
S(1)–C(1)	1.680(3)	C(4)–C(5)	1.37(1)
S(2)–C(1)	1.679(4)	C(5)–C(6)	1.37(1)
C(1)–C(2)	1.469(5)	C(6)–C(7)	1.39(1)
C(2)–C(3)	1.38(1)		

(*b*) Angles (°)

S(1)–Mo–S(2)	66.8(1)	S(2)–C(1)–C(2)	124.9(3)
S(1)–Mo–S(2^{I})	142.6(1)	C(1)–C(2)–C(3)	120.8(3)
S(1)–Mo–S(1^{II})	128.5(1)	C(1)–C(2)–C(7)	120.0(4)
S(2)–Mo–S(1^{II})	78.3(1)	C(3)–C(2)–C(7)	119.2(4)
S(1)–Mo–S(2^{II})	78.5(1)	C(2)–C(3)–C(4)	120.2(4)
S(2)–Mo–S(2^{II})	93.7(1)	C(3)–C(4)–C(5)	120.5(5)
Mo–S(1)–C(1)	90.0(1)	C(4)–C(5)–C(6)	119.1(5)
Mo–S(2)–C(1)	92.4(1)	C(5)–C(6)–C(7)	120.5(6)
S(1)–C(1)–S(2)	110.8(2)	C(2)–C(7)–C(6)	120.5(6)
S(1)–C(1)–C(2)	124.3(3)		

Roman numeral superscripts are defined in the caption to Figure 2.

Bond distances and angles within the asymmetric unit, with estimated standard deviations, are listed in Table 2.

Calculations.—Calculations were carried out on a Univac 1108 computer of Rome University using the system of programs of the Laboratorio di Strutturistica Chimica [5] del

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10pp. are supplied as full size copies).

[5] A. Domenicano, R. Spagna, and A. Vaciago, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1969, **47**, 331.

C.N.R. and our own programs for the processing of automatic diffractometer data. Scattering factors (neutral atoms) for the listed final structure factors were taken from ref. 6 and corrections for anomalous scattering from ref. 7.

RESULTS AND DISCUSSION

The crystal contains discrete monomolecular units (Figure 2). The molybdenum atom lies on the $\bar{4}$ axis, so there is only a single crystallographically independent ligand molecule and the structure is strictly related to that of the vanadium atom [V(1)] in tetrakis(dithiobenzoato)vanadium(IV).[1] Table 3 gives the parameters used to describe the shape of the co-ordination dodecahedron (D_{2d} isomer), following the usual notation.

TABLE 3

Stereochemical parameters of the dodecahedron

$Mo-S_A$	2.543(1) Å	a edge	3.124(1) Å
$Mo-S_B$	2.475(1)	b edge	3.612(1)
$Mo-S_A/Mo-S_B$	1.03	g edge	3.176(1)
θ_A	37.90° (3)	m edge	2.764(1)
θ_B	75.26° (3)		

TABLE 4

Results of least-squares planes calculation. Deviations (Å) of the atoms from the planes are given in square brackets

Plane (i): Dodecahedral trapezoid, S(1), S(2), Mo, S(1^I), S(2^I)

$$20.33x - 6.96y + 1.74 = 0$$

[S(1) −0.003, S(2) 0.002]

Plane (ii): Chelating portion of ligand, S(1), S(2), C(1), C(2)

$$20.20x - 7.33y - 0.052z + 1.88 = 0$$

[S(1) −0.003, S(2) −0.003, C(1) 0.009, C(2) −0.003]

Plane (iii): Ph ring, C(1)—(7)

$$19.83x - 7.99y + 0.68z + 1.95 = 0$$

[C(1) 0.005, C(2) −0.007, C(3) 0.006, C(4) −0.007, C(5) 0.003, C(6) 0.006, C(7) −0.007]

Dihedral angles: (*a*) between planes (ii) and (iii), 6.6°; (*b*) between planes Mo, S(1), S(2), and Mo, S(1^I), S(2^I), 0.2°.

TABLE 5

Details of the co-ordination polyhedra of some eight-co-ordinate complexes containing bidentate sulphur ligands

	b	Stereochemistry	θ_A/°	θ_B/°	Interligand S · · · S contacts/Å
$[Mo(S_2CPh)_4]$ [a]	1.10	D_{2d}(dodec.)	37.90	75.26	3.1, 3.2 [b]
$[V(S_2C{\cdot}CH_2Ph)_4]$ [c]	1.10	D_{2d}(dodec.)	37.5	76.0	3.1, 3.2 [b]
$[V(S_2CPh)_4]$ [c]	1.12	D_{2d}(dodec.)	37.9	74.4	3.2, 3.2 [b]
$[V(S_2CMe)_4]$ [d]	1.11	D_{2d}(dodec.)	35.7	77.0	2.9, 3.1 [b]
$[V(S_2CMe)_4]$ [d]	1.11	C_2(dodec.)			3.1, 3.1, 3.1 [e]
$[Ti(S_2CNEt_2)_4]$ [f]	1.11	D_{2d}(dodec.)	35.1	77.5	3.0, 3.3 [b]
$[Zr(S_2CNEt_2)_4]$ [g]	1.09	D_{2d}(dodec.)	35.4	79.3	3.1, 3.8, 3.5 [h]
$[W(S_2CNEt_2)_4Br]$ [i]	1.12	D_{2d}(dodec.)	34.7	77.6	2.9, 3.6 [j]
$[Th(S_2CNEt_2)_4]$ [k]	1.04	Intermediate	44	66	3.9, 4.0 [j]
$[Et_4N][Np(S_2CNEt_2)_4]$	1.02	(See text)			3.6. 4.1 [j]

[a] This work. [b] Along edges *a* and *g* respectively. [c] Ref. 1. [d] Ref. 9. [e] Along edges *a*, *g*, and *m*. [f] Ref. 10. [g] Ref. 11. [h] Mean values from two independent molecules along edges *a*, *b*, and *g*. [i] Ref. 12. [j] Range limits for all interligand S · · · S contacts. [k] Ref. 13 (*a*). [l] Ref. 13 (*b*).

Table 4 gives several least-squares planes and dihedral angles relevant to the discussion. The angle between the least-squares plane of the chelating part of the ligand, [−C·C(⁚S)S⁻], and the phenyl ring is 6.56°. The two sulphur–carbon distances are the same (1.68 Å) and agree with those in the analogous vanadium complex.

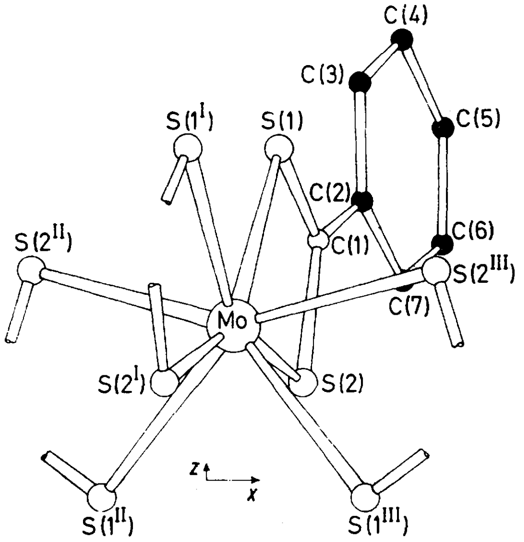

FIGURE 2 [010] Projection of the asymmetric unit of tetrakis(dithiobenzoato)molybdenum(IV), together with all the crystallographically equivalent sulphur atoms of the co-ordination polyhedron. Roman numeral superscripts refer to the following equivalent positions: I $-x, \frac{1}{2} - y, z$; II $\frac{3}{4} - y, \frac{3}{4} + x, \frac{3}{4} - z$; III, $\frac{1}{4} + y, \frac{3}{4} - x, \frac{3}{4} - z$

The major result arising from this study is that, at least so far as the chromophores $[MS_8]$ are concerned, the stereochemistry about the metal is influenced neither by variation in electronic configuration, going from d^0 (refs. 10 and 11) through d^1 (refs. 1, 9, and 12) to d^2 (present work) nor by changes in conjugation in the ligand. It is thus most probable that the most important effect operating is ligand–ligand repulsion, even though not all the structural details calculated by Blight and Kepert[8] are observed experimentally. In

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[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

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[9] L. Fanfani, A. Nunzi, P. F. Zanazzi, and A. R. Zanzari, *Acta Cryst.*, 1972, **B28**, 1298.

[10] M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *J.C.S. Dalton*, 1972, 1052.

[11] M. Colapietro and A. Vaciago, personal communication.

[12] J. C. Wijnhoven, *Cryst. Struct. Comm.*, 1973, **2**, 637.

particular, in the present compound the dihedral angle α, due to the 'longitude' difference between the two sulphur atoms, is virtually zero.

Table 5 gives the experimental shape parameters of some eight-co-ordinate complexes [1,9-13] with bidentate sulphur ligands for comparison with theoretical values calculated [8] as a function of a normalised 'bite', b, also shown in the Table.

The listed structures may, roughly, be divided into two groups: complexes with small metal ions, in which the distances between sulphur atoms not belonging to the same ligand are smaller than van der Waals contacts (3.7 Å), and the thorium and neptunium complexes, where these distances are $\geqslant$3.7 Å. In the first group, the co-ordination polyhedra are rather regular and the calculations [8] agree well with the experimental results, with the exception of the C_2–2 isomer of $[V(dta)_4]$. In the second group, ligand–ligand repulsions are not in all cases the main energy term necessary to rationalise the observed stereochemistry. In particular, the distortion in $[Et_4N][Np(S_2CNEt_2)_4]$ is not explained by the calculations [8] and there is close similarity between the stereochemistry of this complex with those of neptunyl and uranyl complexes, if the co-ordination pattern is regarded as being as suggested in ref. 13(*b*).

[4/2728 *Received*, 30*th December*, 1974]

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[13] D. Brown, D. G. Holah, and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, (*a*) p. 423, (*b*) p. 786.