Crystal Structures of Tris(*NN*-diethyldithiocarbamato)oxo-niobium(v) and -vanadium(v)

By **John C. Dewan, David L. Kepert, Colin L. Raston, Donald Taylor,** and **Allan H. White,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia
Edward N. Maslen, Department of Physics, University of Western Australia, Nedlands 6009, Western Australia

The crystal and molecular structures of the isomorphous and isostructural title compounds [MO(CS$_2$·NEt$_2$)$_3$] [(I), M = Nb; (II), M = V] have been determined by single crystal *X*-ray diffraction, the structures being solved by heavy-atom methods and refined by least-squares methods to *R* 0·096 [(I) 1680 visually estimated reflections] and 0·103 [(II) 671 diffractometer reflections]. Both are monoclinic, space group $P2_1/a$, Z = 4; (I): *a* = 17·28(1), *b* = 13·305(5), *c* = 10·774(5) Å; β = 90·09(6)°; (II): *a* = 17·27(1), *b* = 13·22(1), *c* = 10·72(1) Å, β = 90·5(1)°.

In each structure the seven-co-ordinate metal atom is surrounded by an oxygen atom [Nb=O, 1·74(1), V=O, 1·65(2) Å] and three bidentate dithiochelates, two lying in the equatorial plane of a distorted pentagonal bipyramid. The five equatorial distances are almost equal (Nb–S 2·547—2·596, V–S 2·46—2·50 Å) while that opposite to the oxygen is longer (Nb–S 2·753, V–S 2·63 Å). All O=M–S angles are greater than 90°.

We have recently described[1] the preparations and properties of a series of complexes of *NN*-dialkyldithiocarbamate ligands, L=CS$_2^-$·NR$_2$, with niobium(v) and vanadium(v), the complexes being formulated as MOL$_3$ monomers. The formulation and similarity of the two series of complexes remained in some doubt, however, owing to an inability to obtain accurate oxygen analyses, and the rather low metal–oxygen i.r. frequency which did not entirely preclude the possibility of co-ordinated peroxide; moreover, the vanadium derivative is an intense orange colour in comparison to the colourless niobium complex. In order to resolve these details and to determine the co-ordination number and stereochemistry of the metal-atom environment in each case, *X*-ray structure determinations were carried out on each of the two derivatives, the diethyl complex being chosen in each case and prepared as described previously.[1]

EXPERIMENTAL

Tris-(NN*-Diethyldithiocarbamato*)*oxoniobium*(v)

Crystals suitable for *X*-ray work were grown from chloroform by slow evaporation in air, crystals up to 0·5 mm being obtained with ease directly, the crystal being rather elongated along *a*, with *b* and *c* as section diagonals.

Non-integrated intensity data were collected about *a* and *b* on a crystal with axial dimensions 0·15 × 0·21 × 0·15 mm, by the multiple-film pack equi-inclination Weissenberg method for the layers 0—4*kl*, *h*0—4*l*, there being no evidence for crystal deterioration during data collection. Unit-cell dimensions were obtained from zero-layer Weissenberg photographs about *a* and *b*, calibrated with superimposed aluminium powder lines (*a* = 4·0494 Å).[2]

Crystal Data.—C$_{15}$H$_{30}$N$_3$NbOS$_6$, *M* = 554, Monoclinic, *a* = 17·28 ± 0·01, *b* = 13·305 ± 0·005, *c* = 10·774 ± 0·005 Å, β = 90·09 ± 0·06°, *U* = 2468 Å^3, D_m = 1·48 ± 0·01 (flotation), *Z* = 4, D_c = 1·48 g cm^{-3}, *F*(000) = 1144. Space group $P2_1/a$ (C_{2h}^5, No. 14)[3] (x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\bar{z}$; $\frac{1}{2} + x$, $\frac{1}{2} - y$, z) from systematic absences {*h*0*l*}, *h* = 2*n* + 1, {0*k*0}, *k* = 2*n* + 1. Ni-filtered Cu-K_α radiation: $\lambda(K_{\bar{\alpha}})$ = 1·5418 Å,[4] μ = 87·7 cm^{-1}, transmission coefficient range 0·317—0·497.

The intensities of 1680 independent observed reflections were estimated visually by use of a graded calibrated intensity strip; only these non-zero reflections were used in the subsequent structure determination. All intensities were corrected for absorption[5] and for Lorentz and polarization factors, and internally correlated and scaled.[6]

An unmodified three-dimensional Patterson synthesis was computed by use of all data; an ambiguous solution was obtained for the niobium atom (0·4, 0·25, 0·18) or (0·15, 0·25, 0·18). The situation was only resolved during location of the ethyl substituents when it became evident that the second solution was stereochemically impossible.

The structure was then refined by several cycles of block-diagonal (3 × 3, 6 × 6) least-squares (local SFLS1, 2 programs). A weighting scheme of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was introduced and found appropriate[7] and refinement was continued, $\Sigma w(|F_o| - |F_0|)^2$ being minimized and *a* and *b* being adjusted at successive stages. After refinement converged to *R* 0·128, anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ were introduced. With the niobium atom vibrating anisotropically, *R* converged to 0·107; with anisotropic thermal parameters for sulphur and oxygen *R* converged finally to 0·096, the weighted residual *R′* being 0·130 $[R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Ratio tests on *R* at each stage showed the introduction of thermal anisotropy to be significant.[8] During the final cycle of least-squares refinement, parameter shifts were < 0·1 σ for all atoms, final weighting scheme constants being *a* = 13·04, *b* = 0·0192. A final difference-Fourier map showed a ripple *ca.* 0·4 carbon atom in size at the niobium position, the remainder being flat to better than 0·2 carbon atoms. There was no evidence for disorder in the structure.

Tris-(NN*-diethyldithiocarbamato*)*oxovanadium*(v)

Unlike the niobium homologue, crystals of this complex proved very difficult to obtain in any considerable size. The slow evaporation of solutions of the substance in various

---

[1] A. T. Casey, D. J. Mackey, R. L. Martin, and A. H. White, *Austral. J. Chem.*, 1972, **25**, 477.

[2] B. W. Delf, *J. Appl. Phys.*, 1963, **14**, 345.

[3] 'International Tables for *X*-Ray Crystallography,' vol. I, 2nd edn., Kynoch Press, Birmingham, 1965, p. 99.

[4] Ref. 3, vol. III, 1962, p. 59.

[5] ABSCOR: N. W. Alcock, in 'Crystallographic Computing,' Munksgaard, Copenhagen, 1971, p. 271.

[6] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

[7] D. W. Cruickshank, in 'Computing Methods in *X*-Ray Crystallography,' ed. J. S. Rollett, Pergamon, Oxford, 1965, p. 114.

[8] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

solvents in air and under dry nitrogen, resulted in slow oxidation and/or hydrolysis by traces of oxygen and/or moisture to give an insoluble green material. A small flake of negligible size and of similar habit to that of the niobium derivative was eventually obtained from chloroform, yielding very weak and rather unsatisfactory data. Intensity data were collected on a Syntex $P\bar{1}$ four-circle automatic diffractometer; unit-cell dimensions were obtained by least-squares refinement of 14 reflections centred in the counter, being similar in size to that of the niobium derivative. The systematic extinctions in the observed data were identical. Data were collected by use of a θ—2θ scan rate of 0·5° min^{-1}, symmetrically over 2°, with stationary-counter–stationary-crystal background counts of 2 min at either end of the scan.

The $(2,0,-2)$ reflection was used to monitor the scan and varied during data collection by $\pm 7\%$ from the mean. A total of 1100 low-angle reflections were obtained, of which those having $I < 3\sigma(I)$ were considered unobserved, leaving 671 observed reflections (corrected for background) which were then corrected for Lorentz and polarization effects. No correction was made for absorption.

Crystal Data.—$C_{15}H_{30}N_3OS_6V$, $M = 508$, Monoclinic, $a = 17{\cdot}27 \pm 0{\cdot}01$, $b = 13{\cdot}22 \pm 0{\cdot}01$, $c = 10{\cdot}72 \pm 0{\cdot}01$ Å, $\beta = 90{\cdot}5 \pm 0{\cdot}1°$, $U = 2447$ Å^3, $D_m = 1{\cdot}38 \pm 0{\cdot}01$ (flotation, CCl_4–C_6H_{12}), $Z = 4$, $D_c = 1{\cdot}39$ g cm^{-3}, $F(000) = 1072$. Space group $P2_1/a$.[3] Ni-filtered Cu-K_α radiation, $\mu = 59{\cdot}2$ cm^{-1}.

An unmodified three-dimensional Patterson synthesis was computed on all data and found to be similar to that of the niobium derivative. Accordingly, all atoms were located in comparable positions and the structure refined by similar procedures with a similar treatment of the thermal anisotropy (all atoms isotropic, R 0·118; V anisotropic, R 0·112, R' 0·150; V,S anisotropic, R 0·112, R' 0·147) and a weighting scheme of the form $w = (a + |F_o| + b|F_o|^2 + c|F_o|^3)^{-1}$. At convergence R was 0·103 and R' 0·143, the final a being 3·70, b 0·0673, c 2×10^{-5} with similar atomic parameter shifts and a similarly flat difference-Fourier map.

Scattering factors employed were for the neutral atoms throughout: Nb[9] [corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$)[10]], V[11] (similarly corrected),[12] S, C, N, O.[11] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20809 (9 pp., 1 microfiche).* Final atomic positional and thermal parameters are given in Table 1, the atom numbering system being shown in Figure 1. Intramolecular distances and angles[13] are in Table 2, and ligand planes in Table 3.

Computing was carried out on the DEC PDP 10 computer at the University of Western Australia.

DISCUSSION

The two derivatives are isomorphous and isostructural, the asymmetric unit being the monomeric molecular species $[NbO(CS_2{\cdot}NEt_2)_3]$ (I), or $[VO(CS_2{\cdot}NEt_2)_3]$ (II), with four molecules in the unit cell (Figure 2).

TABLE 1

(*a*) Final atomic fractional cell parameters and isotropic thermal parameters; in this and the following Table, parameters pertaining to the vanadium derivative are given below the corresponding value for the niobium derivative. Block-diagonal least-squares estimated standard derivatives are given in parentheses

Atom	x	y	z	B/Å^2
Nb	0·4005(1)	0·2408(1)	0·1793(1)	
	0·4009(3)	0·2403(5)	0·1826(5)	
S(11)	0·5332(3)	0·2432(4)	0·2926(4)	
	0·5295(5)	0·2465(7)	0·2923(8)	
S(12)	0·4611(3)	0·0668(4)	0·1947(5)	
	0·4592(6)	0·0704(8)	0·1996(9)	
S(21)	0·3504(3)	0·2412(4)	0·4218(4)	
	0·3519(5)	0·2362(7)	0·4141(8)	
S(22)	0·4063(3)	0·4162(4)	0·2842(4)	
	0·4079(5)	0·4113(7)	0·2805(8)	
S(31)	0·2978(3)	0·1094(4)	0·1253(4)	
	0·3020(5)	0·1140(7)	0·1264(8)	
S(32)	0·2690(3)	0·3224(4)	0·1275(4)	
	0·2769(5)	0·3215(7)	0·1280(8)	
O	0·4389(7)	0·2810(10)	0·0387(10)	
	0·4365(11)	0·2714(16)	0·0454(17)	
N(1)	0·5938(8)	0·058(1)	0·325(1)	5·1(3)
	0·5974(13)	0·067(2)	0·329(2)	5·2(6)
N(2)	0·3780(9)	0·421(1)	0·526(1)	5·3(3)
	0·3768(13)	0·419(2)	0·524(2)	5·6(6)
N(3)	0·1750(9)	0·190(1)	0·014(1)	4·9(3)
	0·1760(13)	0·197(2)	0·018(2)	4·5(6)
C(11)	0·536(1)	0·115(1)	0·274(1)	5·3(4)
	0·534(2)	0·117(2)	0·280(2)	5·1(8)
C(12)	0·657(1)	0·101(1)	0·394(1)	5·1(4)
	0·663(2)	0·109(2)	0·399(3)	5·8(9)
C(13)	0·594(1)	−0·056(2)	0·305(2)	6·2(5)
	0·595(2)	−0·051(3)	0·313(3)	7·7(10)
C(14)	0·634(1)	0·101(2)	0·536(2)	7·7(6)
	0·644(2)	0·105(3)	0·540(3)	7·9(10)
C(15)	0·650(2)	−0·079(2)	0·195(3)	10·7(8)
	0·649(2)	−0·079(3)	0·198(3)	8·9(11)
C(21)	0·379(1)	0·365(1)	0·424(2)	5·1(4)
	0·379(2)	0·364(2)	0·425(2)	5·1(8)
C(22)	0·400(1)	0·529(1)	0·525(2)	5·9(4)
	0·402(2)	0·527(3)	0·524(3)	6·7(9)
C(23)	0·359(1)	0·376(2)	0·651(2)	6·9(5)
	0·359(2)	0·373(3)	0·647(3)	8·0(10)
C(24)	0·326(2)	0·593(2)	0·510(3)	10·5(8)
	0·325(2)	0·592(3)	0·508(3)	8·4(10)
C(25)	0·433(1)	0·343(2)	0·710(2)	6·8(5)
	0·437(2)	0·339(3)	0·710(3)	8·1(10)
C(31)	0·239(1)	0·204(1)	0·078(1)	4·4(3)
	0·241(2)	0·211(2)	0·077(2)	3·9(7)
C(32)	0·151(1)	0·087(2)	−0·029(2)	6·2(4)
	0·154(2)	0·091(3)	−0·028(3)	7·1(10)
C(33)	0·124(1)	0·278(2)	−0·023(2)	5·9(4)
	0·123(2)	0·281(2)	−0·017(3)	5·6(8)
C(34)	0·098(1)	0·041(2)	0·065(2)	8·3(6)
	0·097(2)	0·040(3)	0·065(3)	7·6(10)
C(35)	0·143(2)	0·312(2)	−0·158(2)	10·3(8)
	0·140(2)	0·312(3)	−0·155(3)	9·8(12)

(*b*) Anisotropic thermal parameters ($\times 10^4$)

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Nb	35(1)	− 2(2)	−3(1)	63(1)	1(2)	93(1)
	57(3)	10(7)	5(7)	66(6)	0(11)	127(8)
S(11)	37(2)	−12(6)	−24(5)	68(3)	−10(6)	125(4)
	49(5)	2(11)	−8(11)	66(10)	0(16)	120(12)
S(12)	49(2)	−1(7)	−37(6)	66(3)	−21(7)	149(3)
	58(6)	12(11)	−31(13)	75(11)	−6(17)	169(15)
S(21)	45(2)	−17(7)	10(4)	70(3)	15(6)	92(3)
	63(5)	−25(11)	10(11)	71(10)	25(15)	104(13)
S(22)	44(2)	−12(6)	−6(5)	58(3)	11(5)	99(4)
	61(5)	−14(11)	9(11)	51(10)	−3(15)	124(12)
S(31)	41(2)	−6(7)	−14(4)	66(3)	−11(6)	118(4)
	57(5)	9(10)	−14(11)	64(10)	−9(16)	125(13)
S(32)	39(2)	−1(7)	8(5)	65(3)	−17(6)	121(4)
	55(5)	−14(10)	28(12)	77(10)	−3(16)	123(14)
O	31(4)	−2(15)	25(12)	88(10)	10(11)	130(12)
	60(12)	47(25)	84(26)	104(24)	63(36)	97(27)

---

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[9] D. T. Cromer and A. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

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

[11] Ref. 3, p. 210.

[12] Ref. 3, p. 213.

[13] M. E. Pippy and F. R. Ahmed, Div. Pure and App. Physics, NRC, Ottawa, Canada, Program, NRC 12.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bonding distances and angles within the molecule

(i) the $NbOS_6$ core

Nb–O	1·74(1) 1·65(2)	S(11)–Nb–S(12)	67·5(2) 68·6(3)
Nb–S(11)	2·596(5) 2·505(10)	S(11)–Nb–S(21)	80·4(2) 81·3(4)
Nb–S(12)	2·547(6) 2·469(12)	S(11)–Nb–S(22)	75·6(2) 74·5(3)
Nb–S(21)	2·753(4) 2·629(10)	S(11)–Nb–S(31)	136·7(2) 138·4(4)
Nb–S(22)	2·594(5) 2·496(11)	S(11)–Nb–S(32)	151·0(2) 149·6(4)
Nb–S(31)	2·558(5) 2·460(10)	S(12)–Nb–S(21)	94·0(2) 92·6(3)
Nb–S(32)	2·578(5) 2·462(10)	S(12)–Nb–S(22)	140·7(2) 140·8(4)
O–Nb–S(11)	93·9(4) 94·3(7)	S(12)–Nb–S(31)	71·3(2) 71·5(3)
O–Nb–S(12)	100·3(4) 98·0(7)	S(12)–Nb–S(32)	139·4(2) 140·2(4)
O–Nb–S(21)	161·3(4) 166·2(8)	S(21)–Nb–S(22)	66·3(2) 68·7(3)
O–Nb–S(22)	95·1(4) 97·6(7)	S(21)–Nb–S(31)	89·9(2) 89·3(3)
O–Nb–S(31)	106·1(4) 102·4(7)	S(21)–Nb–S(32)	85·8(2) 86·9(3)
O–Nb–S(32)	91·1(4) 90·5(7)	S(22)–Nb–S(31)	137·8(2) 138·5(4)
		S(22)–Nb–S(32)	75·5(2) 75·1(3)
		S(31)–Nb–S(32)	68·1(2) 68·7(3)

(ii) Ligand(1)

C(11)–S(11)	1·72(2) 1·72(3)	Nb–S(11)–C(11)	87·4(6) 88·2(10)
C(11)–S(12)	1·67(2) 1·66(3)	Nb–S(12)–C(11)	90·0(7) 91·0(11)
C(11)–N(1)	1·37(2) 1·38(4)	S(11)–C(11)–S(12)	115(1) 112(2)
N(1)–C(12)	1·43(3) 1·46(4)	S(11)–C(11)–N(1)	121(1) 118(2)
N(1)–C(13)	1·54(2) 1·57(4)	S(12)–C(11)–N(1)	124(1) 129(2)
C(12)–C(14)	1·58(4) 1·55(4)	C(11)–N(1)–C(12)	123(1) 129(2)
C(13)–C(15)	1·57(3) 1·59(5)	C(11)–N(1)–C(13)	119(1) 114(2)
Nb · · · C(11)	3·04(2) 3·00(3)	C(12)–N(1)–C(13)	118(1) 117(2)
S(11) · · · S(12)	2·857(7) 2·805(13)	N(1)–C(12)–C(14)	108(2) 109(2)
		N(1)–C(13)–C(15)	108(2) 107(2)

(iii) Ligand (2)

C(21)–S(21)	1·72(2) 1·75(3)	Nb–S(21)–C(21)	85·6(6) 87·4(10)
C(21)–S(22)	1·72(2) 1·75(3)	Nb–S(22)–C(21)	90·9(6) 91·9(10)
C(21)–N(2)	1·32(2) 1·28(3)	S(21)–C(21)–S(22)	116(1) 111(2)
N(2)–C(22)	1·49(4) 1·50(4)	S(21)–C(21)–N(2)	123(1) 126(2)
N(2)–C(23)	1·51(2) 1·53(4)	S(22)–C(21)–N(2)	121(1) 122(2)
C(22)–C(24)	1·54(4) 1·59(5)	C(21)–N(2)–C(22)	122(1) 122(2)
C(23)–C(25)	1·58(3) 1·73(5)	C(21)–N(2)–C(23)	121(1) 120(2)
Nb · · · C(21)	3·14(2) 3·09(3)	C(22)–N(2)–C(23)	116(1) 118(2)
S(21) · · · S(22)	2·925(7) 2·894(13)	N(2)–C(22)–C(24)	109(2) 106(2)
		N(2)–C(23)–C(25)	106(2) 99(2)

TABLE 2 (*Continued*)

(iv) Ligand (3)

C(31)–S(31)	1·69(2) 1·75(3)	Nb–S(31)–C(31)	88·4(6) 89·7(9)
C(31)–S(32)	1·74(2) 1·68(3)	Nb–S(32)–C(31)	86·6(6) 91·1(10)
C(31)–N(3)	1·32(2) 1·29(3)	S(31)–C(31)–S(32)	114(1) 108(1)
N(3)–C(32)	1·50(2) 1·53(4)	S(31)–C(31)–N(3)	123(1) 124(2)
N(3)–C(33)	1·52(2) 1·49(4)	S(32)–C(31)–N(3)	122(1) 127(2)
C(32)–C(34)	1·50(3) 1·56(5)	C(31)–N(3)–C(32)	122(1) 120(2)
C(33)–C(35)	1·56(3) 1·57(5)	C(31)–N(3)–C(33)	121(1) 123(2)
Nb · · · C(31)	3·03(2) 3·01(3)	C(32)–N(3)–C(33)	117(1) 117(2)
S(31) · · · S(32)	2·877(7) 2·778(13)	N(3)–C(32)–C(34)	110(2) 110(2)
		N(3)–C(33)–C(35)	110(2) 108(2)

(*b*) Non-bonding distances <3·5 Å

C(33) · · · O(1^{II})	3·35(2) 3·36(3)

O(1^{II}) is at $x - \frac{1}{2}, \frac{1}{2} - y, z + 1$.

TABLE 3

Equations of least squares planes in the form $lX + mY + nZ = p$,* and atomic deviations (Å). Parameters corresponding to the vanadium derivative are given in parentheses. Atoms defining the plane are italicized

	l	*m*	*n*	*p*
Plane (i)	−0·370 (−0·382)	−0·213 (−0·201)	0·904 (0·902)	−1·225 (−1·279)
	[*Nb −0·27 (−0·23), S(11) −0·02 (−0·03), S(12) −0·01 (−0·00), S(22) 0·22 (0·22), S(31) 0·23 (0·21), S(32) −0·16 (−0·16),* O −1·99 (−1·88), S(21) 2·42 (2·35)]			
Plane (ii):	−0·524 (−0·506)	−0·108 (−0·099)	0·845 (0·857)	−2·502 (−2·245)
	[*S(11) 0·00 (0·00), S(12) 0·01 (−0·01), N(1) 0·01 (−0·02), C(11) −0·01 (0·02), C(12) 0·00 (−0·00), C(13) −0·01 (0·01),* Nb 0·17 (0·12), C(14) 1·50 (1·47), C(15) −1·49 (−1·48)]			
Plane (iii):	0·952 (0·938)	−0·259 (−0·272)	0·166 (0·216)	5·705 (5·766)
	[*S(21) −0·04 (0·01), S(22) 0·04 (−0·01), N(2) −0·02 (0·00), C(21) 0·01 (0·01), C(22) −0·04 (0·01), C(23) 0·05 (−0·01),* Nb 0·36 (0·27), C(24) −1·49 (−1·50), C(25) 1·57 (1·68)]			
Plane (iv):	−0·528 (−0·506)	−0·109 (−0·114)	0·842 (0·855)	−1·752 (−1·694)
	[*S(31) 0·02 (0·05), S(32) −0·01 (−0·03), N(3) 0·01 (0·02), C(31) −0·01 (−0·02), C(32) −0·01 (−0·05), C(33) 0·01 (0·04),* Nb −0·62 (−0·49), C(34) 1·39 (1·39), C(35) −1·44 (−1·43)]			

* Where X, Y, Z are orthogonal co-ordinates in Å, related to the crystal axes by: $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$.

There is no evidence to suggest that the stoicheiometry of either complex differs from this. The metal atom is seven-co-ordinate, being at the centre of a pentagonal bipyramid with the oxygen at one of the axial apices, the other six co-ordination sites being occupied by the sulphur atoms of the three bidentate dithiochelates, two of which lie approximately in the equatorial plane and the other [ligand (2)] spanning axial and equatorial sites (Figure 1). This co-ordination resembles that found in the tropolonate (trop) complexes [SnCl(trop)$_3$] and

$[Sn(OH)(trop)_3]$,[14] the acetylacetonate $[ZrCl(acac)_3]$,[15] and the oxalato-complex $[NbO(C_2O_4)_3]^{3-}$ (ref. 16). The Nb=O distance in (I) (1·74 Å) is comparable to that in $[NbO(C_2O_4)_3]^{3-}$ (1·71 Å) and $(Nb_6O_{19})^{8-}$ (1·76 Å).[17] The V=O distance is 1·65(2) Å, rather longer than in the five-co-ordinate $[VO(OMe)_3]_2$ (1·51 and 1·57 Å)[18] and comparable with that in the six-co-ordinate $(V_{10}O_{28})^{6-}$ (1·59—1·62 Å)[19,20] (*cf.* also many V^{IV}=O distances *ca.* 1·60 Å).[21] In (II), the V=O i.r. stretching frequency appears at 948 cm^{-1} (ref. 1); in (I) two sharp bands are found at 900vs and 913s (shoulder) cm^{-1}. The latter is probably a ligand skeletal vibration [a similar band being found at 917w cm^{-1} in (I)], the 900 cm^{-1} band presumably being the Nb=O frequency. This is comparable to that observed in $[NbO(C_2O_4)_3]^{3-}$ at 925 cm^{-1} (ref. 22) but slightly lower than that in a number of six-co-ordinate Nb^V=O compounds whose frequencies lie in the range 950 ± 20 cm^{-1} or in gaseous four-co-ordinate $NbOCl_3$ (997 cm^{-1}).[21] Similarly the V=O stretching frequency in (II) at 948 cm^{-1} is lower than that in four-co-ordinate vanadium(V) oxotrihalides in the range 1040 ± 20 cm^{-1} (ref. 21).

In the MOS_6 molecular cores of (I) and (II), the axial metal–sulphur distance is appreciably longer than the remaining equatorial metal–sulphur distances which do not differ appreciably from each other [M–S(21), 2·753 (I), 2·63 (II); M–S(eq), 2·547—2·598 (I), 2·47—2·50 Å (II)]. The only other structure determinations involving dithiochelates of V or Nb are those of $[V(S_2C_2(CN)_2)_3]^{2-}$ (V–S, 2·36 Å),[23] $[V(PS_2(OEt)_2)_3]$ (V–S, 2·43—2·47 Å),[24] and $[V(CS_2Ph)_4]$ (V–S, 2·47, 2·52 Å).[25] Only in the last-named, involving a CS_2 ligand and a high-co-ordination number (8), and with a lower oxidation state are the V–S distances comparable with the present complex.

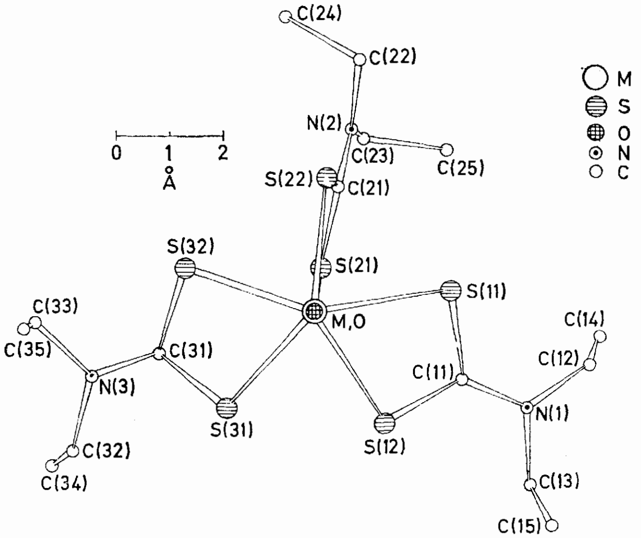

FIGURE 1 Molecular geometry and atomic numbering. Perspective down the O=M axis

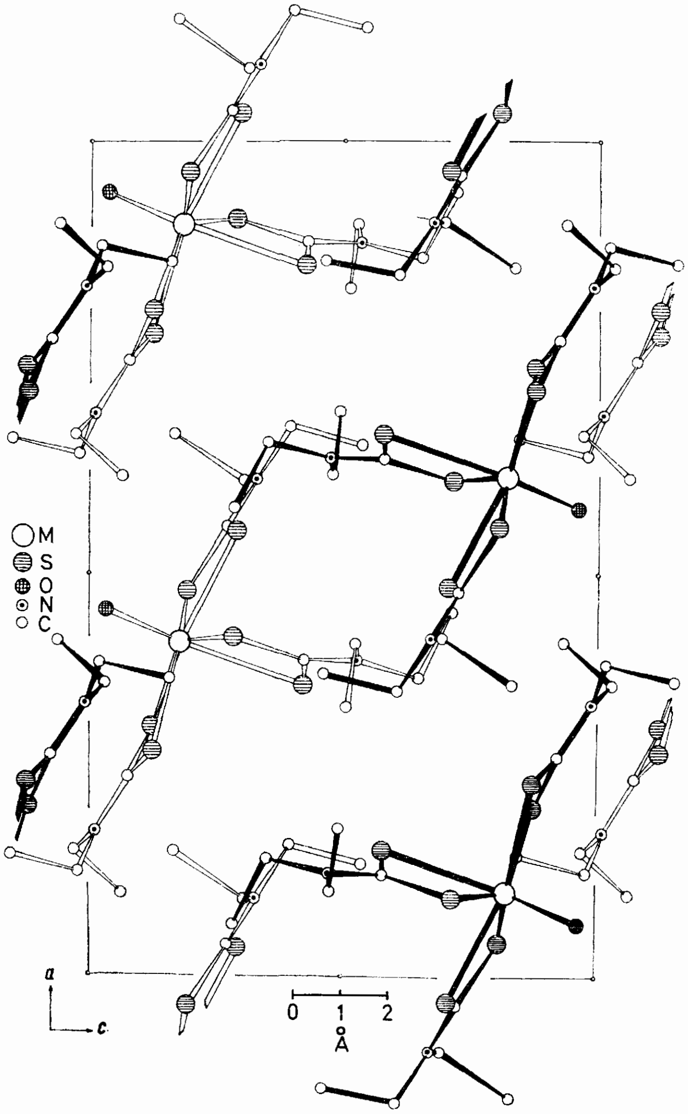

FIGURE 2 Unit-cell contents: perspective down *b*

The equatorial sulphur atoms are not coplanar (Table 3), nor are they coplanar with the metal atom, which lies well above the best plane through the remaining sulphur atoms with all O=M–S(eq) angles being greater than 90° [91—106° (I), 90—102° (II)]. All S(*i*1)–M–S(*i*2)

---

[14] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3636.

[15] R. B. von Dreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, 1971, **93**, 2887.

[16] G. Mattern and R. Weiss, *Acta Cryst.*, 1971, **B27**, 1610.

[17] C. M. Flynn and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 335.

[18] C. N. Caughlan, H. M. Smith, and K. Watenpaugh, *Inorg. Chem.*, 1966, **5**, 2131.

[19] A. G. Swallow, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1966, **21**, 397.

[20] H. T. Evans, *Inorg. Chem.*, 1966, **5**, 967.

[21] D. L. Kepert, 'The Early Transition Metals,' Academic Press, London, 1972.

[22] N. Brnicević and C. Djordjevic, *Inorg. Chem.*, 1968, **7**, 1936.

[23] E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 3353.

[24] G. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc.* (*A*), 1970, 2929.

[25] M. Bonamico, G. Dessy, V. Fares, P. Porta, and L. Scaramuzza, *Chem. Comm.*, 1971, 365.

angles are equal in (II) (68·7 ± 0·1°) and almost so in (I) (67·5, 66·3, 68·1°). Calculations of ligand–ligand repulsion energy for compounds of general stoicheiometry [M(unidentate)(bidentate)$_3$] shows that the stereochemistry observed in (I) and (II) occurs as a minimum on the potential-energy surface. The position of the minimum depends on the 'normalized bite' of the bidentate ligand, defined as the ratio of the distance between donor atoms of the same chelate to the metal-atom–donor-atom distance. As the normalized bite is increased, theory predicts that the unique bidentate ligand on the mirror plane swivels about the metal and away from the unidentate ligand, the stereochemistry for very large bites approaching that for the capped trigonal prism with the three bidentate ligands spanning the three parallel edges of the prism.[26] This prediction is correct for (I) and (II) where the increase in mean normalized bites rises from 1·108 (I) to 1·128 (II) as a result of decreased metal–sulphur distance, and is accompanied by an increase in O–M–S (22) from 95·1 to 97·6° and in O–M–S(21) from 161·3 to 166·2°. The M–S–C angles have large σ values and are not significantly different [85·6—90·0 (I), 87·4—91·9 (II)] between (I) and (II). Within the ligands the geometry is normal and although the difference in metal-atom size influences the S(*i*1)–C(*i*1)–S(*i*2) angles [114—116° (I), 108—112° (II)], the deviations from the mean in each compound are not significant. As usual, the S_2CNC_2 ligand fragments are exactly planar, although the metal atom deviates significantly in both complexes [0·17, 0·36, 0·62 (I); 0·12, 0·27, 0·49 Å (II)]. This is presumably indicative of the fact that only σ bonding is involved between ligand and metal in (I) and (II), since it is highly unusual for a metal atom chelated by a dithiocarbamate ligand to deviate markedly from the plane. The mean C(*i*1)–S(*i*1,2) is 1·71 Å which is usual, as is the mean $C \overset{...}{-} N$ distance (1·33 Å), the deviations from these not being significant. The geometries of the terminal substituents are as expected: the N–C distances (mean 1·50) and C–C distances [mean 1·56 Å, except for C(23)–C(25) (II)] are reasonable. The 'opposed' disposition of the terminal methyl substituents with respect to the ligand planes is also usual.

[2/2242 *Received*, 26*th September*, 1972]

---

[26] D. L. Kepert, to be published.