Crystal Structure of Bis(diethyldithiocarbamato)oxovanadium(IV)

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The crystal structure of the title compound, $[VO(CS_2 \cdot NEt_2)_2]$, has been determined by direct methods and refined by full-matrix least-squares to R 0.056 for 2 017 reflections. Crystals are monoclinic, space group $P2_1/c$, a = 12.863(4), b = 14.023(5), c = 9.558(3) Å, β = 104.05(3)°, Z = 4. The molecular core has the expected C_{2v} symmetry [V–O 1.591(4), V–S 2.387(2)—2.410(2) Å]. The V–O axis is almost parallel to c.

THE VOX_4 (X = unidentate) or VOL_2 (L = bidentate ligand) systems containing the d^1 configuration in a C_{2v} or C_{4v} crystal field have been the subject of considerable electronic and crystallographic study, but almost exclusively on ligands with first-row donor atoms. This paper describes the crystal structure determination of $[VO(CS_2 \cdot NEt_2)_2]$,[1] and gives an improved method of preparation, by use of solvents dried by distillation through a stream of dry nitrogen and manipulations by the Schlenk technique.

EXPERIMENTAL

$VOSO_4 \cdot 2H_2O$ (3.98 g, 0.02 mol) was dissolved in warm water (25 ml) and ethanol (25 ml) added; the solution was immediately added slowly to a stirred solution of sodium diethyldithiocarbamate trihydrate (9.01 g, 0.04 mol) in ethanol (50%, 50 ml) yielding a pale grey precipitate of the complex. Chloroform (150 ml) was added and the green organic layer separated and dried ($MgSO_4$). Cyclohexane (25 ml) was added and the solution kept at 0 °C overnight, when it had deposited shining crystals, blue-grey with a pink dichroism, which were collected and dried under nitrogen. A crystal 0.30 × 0.17 × 0.30 mm was used for the crystallographic work.

Unit-cell calibration was carried out by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 20° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 45°$ was gathered by a conventional 2θ—θ scan, yielding 2 206 independent reflections, of which 2 017 with $I > \sigma(I)$ were used in the structure solution and refinement. No correction for absorption was found necessary.

Crystal Data.—$C_{10}H_{20}N_2OS_4V$, $M = 363.5$, Monoclinic, $a = 12.863(4)$, $b = 14.023(5)$, $c = 9.558(3)$ Å, $\beta = 104.05(3)°$, $U = 1\,672(1)$ Å^3, $D_m = 1.44(1)$, $Z = 4$, $D_c = 1.444$, $F(000) = 756$, Mo-K_α radiation (monochromatic, $\lambda = 0.710\,69$ Å); μ(Mo-K_α) = 11.0 cm^{-1}, neutral-atom scattering factors,[2] those for V and S being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[3] Space group $P2_1/c$ (C_{2h}^5, No. 14).

The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters of the form $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$. Hydrogen atoms were located in a difference map; not all would refine satisfactorily and they were eventually included as invariants with $U = 0.10$ Å^2. Refinement converged at R 0.056, $R'[= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ being 0.064, a weighting scheme of the form $w = (\sigma^2(F_o) + 6 \times 10^{-4}(F_o)^2)^{-1}$ being found appropriate.

Structure amplitudes and hydrogen parameters are available as Supplementary Publication No. SUP 21499 (11 pp., 1 microfiche).† Computation was carried out on the local CDC 6 200 machine, using a local variant of the '*X*-Ray' system.[4] Ligand numbering is as shown, the atom

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† For details, see Notice to Authors, No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[1] For previous work on vanadyl dithiocarbamates, $[VO(CS_2 \cdot NR_2)_2]$ see: H. J. Stoklosa and J. R. Wasson, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 377; B. J. McCormick, *Inorg. Chem.*, 1965, **7**, 19; *Canad. J. Chem.*, 1969, **47**, 4283; G. M. Larin, V. V. Zelentsov, Yu. V. Rakitin, and M. E. Dyatkina, *Russ. J. Inorg. Chem.*, 1972, **17**, 1110; V. M. Byr'ko, M. B. Polinskaya, A. I. Busev, and T. A. Kuz'mina, *ibid.*, 1973, **18**, 820.

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

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

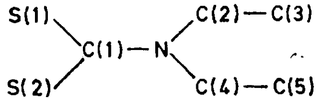
TABLE 1

Atomic fractional cell co-ordinates, (x,y,z) (V $\times 10^5$, others $\times 10^4$), and thermal parameters ($\times 10^3$ Å^2), with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	26 273(7)	−02 199(6)	11 613(9)	53.2(6)	35.9(5)	48.3(6)	0.9(4)	15.8(4)	5.8(4)
O	2 776(4)	0 277(3)	2 694(4)	97(3)	57(3)	47(2)	−1(2)	17(2)	2(2)
Ligand (1)									
S(1)	3 525(1)	0 759(1)	−0 246(1)	46.3(8)	41.5(8)	52.6(9)	−1.4(6)	12.6(7)	7.1(6)
S(2)	1 226(1)	0 606(1)	−0 539(1)	47.2(8)	53.1(9)	59.0(9)	1.0(7)	18.5(7)	11.5(7)
C(1)	2 259(4)	1 143(4)	−1 112(5)	54(3)	35(3)	37(3)	1(2)	15(2)	−8(2)
N	2 096(3)	1 771(3)	−2 173(4)	50(3)	42(3)	36(2)	−1(2)	9(2)	8(2)
C(2)	3 007(4)	2 202(4)	−2 651(6)	67(4)	37(3)	57(4)	−4(3)	24(3)	7(3)
C(3)	3 268(5)	1 642(4)	−3 870(6)	77(5)	67(4)	57(4)	0(3)	32(3)	3(3)
C(4)	1 016(5)	2 082(5)	−2 953(6)	61(4)	75(4)	42(3)	−7(3)	0(3)	13(3)
C(5)	0 663(5)	2 989(5)	−2 374(7)	57(4)	84(5)	64(4)	14(4)	19(3)	22(4)
Ligand (2)									
S(1)	1 644(1)	−1 674(1)	1 209(2)	45.2(9)	42.6(9)	98.7(1)	4.2(7)	29.0(8)	10.9(8)
S(2)	3 901(1)	−1 475(1)	1 297(2)	47.6(9)	46.1(9)	131.7(16)	2.7(7)	32.0(9)	23.4(9)
C(1)	2 861(4)	−2 224(4)	1 394(7)	48(3)	38(3)	99(5)	9(3)	32(3)	18(3)
N	3 006(4)	−3 144(4)	1 676(7)	51(3)	48(3)	158(6)	10(2)	47(3)	27(3)
C(2)	2 111(5)	−3 786(5)	1 808(9)	65(4)	57(4)	112(6)	4(3)	24(4)	31(4)
C(3)	1 536(6)	−4 170(6)	0 427(11)	74(5)	87(6)	149(8)	7(4)	7(5)	−17(6)
C(4)	4 165(6)	−3 602(6)	2 031(9)	103(6)	81(5)	90(6)	−17(4)	24(5)	15(4)
C(5)	4 288(8)	−3 876(6)	0 656(9)	160(8)	80(6)	109(7)	−26(6)	55(6)	−21(5)

number being preceded where necessary by the ligand number [(1) or (2)]; S(1) and C(2) are on the same side of the ligand.

Atomic co-ordinates and molecular dimensions are given in Tables 1 and 2.



DISCUSSION

The crystal is composed of discrete molecules (Figure) of $[VO(CS_2{\cdot}NEt_2)_2]$ with the expected five-co-ordinate rectangular pyramidal vanadium environment with the oxygen at the apex at the usual V^{IV}=O distance of 1.59_1 Å. The vanadium atom lies approximately in the ligand planes but 0.75 Å above the basal ' plane ' of the four sulphur atoms (Table 3). The V=O molecular axis lies approximately parallel to *c* and the pseudomirror plane through OVN_2 approximately parallel to the *bc* plane.

TABLE 2

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

(*a*) Vanadium geometry

V–O	1.591(4)	O–V–S(22)	110.2(2)
V–S(11)	2.404(2)	S(11)–V–S(12)	74.36(6)
V–S(12)	2.410(2)	S(11)–V–S(21)	145.14(7)
V–S(21)	2.406(2)	S(11)–V–S(22)	92.00(7)
V–S(22)	2.387(2)	S(12)–V–S(21)	96.31(6)
O–V–S(11)	107.4(2)	S(12)–V–S(22)	141.46(7)
O–V–S(12)	108.3(2)	S(21)–V–S(22)	74.39(6)
O–V–S(21)	107.4(2)		

(*b*) Ligands: values for ligand (2) follow those for ligand (1)

S(1)–C(1)	1.727(5), 1.715(6)	V–S(1)–C(1)	85.7(2), 85.0(2)
S(2)–C(1)	1.732(6), 1.721(6)	V–S(2)–C(1)	85.4(2), 85.4(2)
S(1) · · · S(2)	2.909(2), 2.897(2)	S(1)–C–S(2)	114.5(3), 115.0(3)
C(1)–N	1.314(6), 1.323(8)	S(1)–C(1)–N	122.4(4), 122.7(4)
N–C(2)	1.486(8), 1.490(9)	S(2)–C(1)–N	123.0(4), 122.2(4)
N–C(4)	1.475(7), 1.582(9)	C(1)–N–C(2)	121.1(4), 122.2(5)
C(2)–C(3)	1.51(1), 1.45(1)	C(1)–N–C(4)	122.7(5), 121.3(5)
C(4)–C(5)	1.50(1), 1.40(1)	C(2)–N–C(4)	116.2(4), 116.3(5)
		N–C(2)–C(3)	111.4(4), 112.4(7)
		N–C(4)–C(5)	113.4(4), 102.1(6)

(*c*) Intermolecular O · · · H contacts (<3 Å). (*cf.* van der Waals estimate, 2.6 Å)

O^I · · · H(13)	2.74	O^{II} · · · H(23)	2.71
O^I · · · H(14)	2.73	O^{II} · · · H(25)	2.68

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $x, \frac{1}{2} - y, \frac{1}{2} + z$ II $x, -\frac{1}{2} - y, \frac{1}{2} + z$

TABLE 3

Equations of least-squares planes [(i) and (ii) defined by the S_2CNC_2 ligand fragments (1) and (2) and (iii) by the S_4 basal ' plane '] in the form $pX + qY + rZ = S$, where $X = ax \sin\beta + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$. σ Å is the estimated standard deviation of the defining atoms from the plane; atomic deviations (Å) are in square brackets

	10^4p	10^4q	10^4r	S	σ	χ^2
Plane (i)	−1 204	7 346	6 677	0.0873	0.01	24.8

[S(1) −0.01, S(2) −0.01, C(1) 0.01, N 0.01, C(2) −0.01, C(4) 0.00, C(3) 1.35, C(5) −1.41, V 0.03]

	10^4p	10^4q	10^4r	S	σ	χ^2
Plane (ii)	−0 696	1 951	9 783	0.4592	0.04	284.1

[S(1) 0.05, S(2) −0.01, C(1) −0.04, N −0.04, C(2) −0.02, C(4) 0.06, C(3) −1.34, C(5) −1.29, V 0.32]

	10^4p	10^4q	10^4r	S	σ	χ^2
Plane (iii)	−0 918	4 298	8 983	−0.2051	0.04	1 715.0

[S(11) 0.036, S(12) −0.034, S(21) 0.035, S(22) −0.036, V 0.75]

Angles (°) between planes: (i)–(ii) 36.4, (i)–(iii) 22.1, (ii)–(iii) 14.3

While in ligand (1), the terminal methyl groups are disposed in the usual fashion above and below the ligand plane, in ligand (2), the less usual arrangement is found with both terminal methyl groups on the same side of the ligand plane. The latter is sterically a less-favoured disposition; this is reflected in the higher thermal motion of the terminal carbon atoms and in the curious apparent distortion of the NEt_2 geometry whereby the

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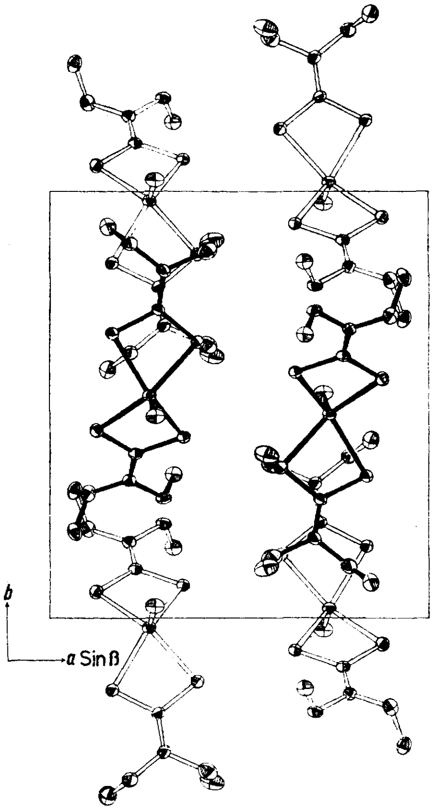
[4] ' *X*-Ray ' System, version of June, 1972,' Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A.

N–C and C–C distances differ significantly from their usual values, exemplified in ligand (1) whose geometry is as expected. It is probable that this is a result of some disordering rather than of lack of correction for thermal motion.



Unit cell contents projected down *c* showing 20% thermal ellipsoids

The vanadium–sulphur distances are considerably shorter than those found in the other vanadium 1 : 1 dithiolate complexes so far reported (Table 4), probably a consequence of the low co-ordination number, but are still longer than those of the 1 : 2 dithiolates; one of the distances [V–S(22)] is shorter than the other three, but the reason for this is probably not distortion due to intermolecular sulphur–hydrogen bonds, as is reported in other structures. In the present complex, the principal intermolecular contacts appear to be O $\cdots$ H distances, there being no S $\cdots$ H contacts <3.0 Å. These O $\cdots$ H distances, however, are all greatei than the van der Waals distances.

TABLE 4

A comparison of V–S distances, *r* Å, with literature values

Complex	$\langle r \rangle$	Ox. state	Co-ord. no.
$[VO(CS_2{\cdot}NEt_2)_2]$ [a]	2.40	IV	5
$[VO(CS_2{\cdot}NEt_2)_3]$ [b]	2.55—2.75	V	7
$[V(CS_2{\cdot}C_6H_5)_4]$ [c]	2.45, 2.56	IV	8 (4 + 4)
$[V(CS_2{\cdot}CH_2{\cdot}C_6H_5)_4]$ [c]	2.47, 2.53	IV	8 (4 + 4)
$[V(CS_2{\cdot}CH_3)_4]$ [d]	2.46, 2.50	IV	8 (4 + 4)
$[V(S_2P(OEt)_2)_3]$ [e]	2.45	III	6
$[V(S_2C_2(C_6H_5)_2)_3]$ [f]	2.33	III	6
$[V(C_4N_2S_2)_3]^{2-}$ [g]	2.36	I	6

[a] This work. [b] J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White, and E. N. Maslen, *J.C.S. Dalton*, 1973, 2082. [c] M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J.C.S. Dalton*, 1974, 1258. [d] L. Fanfani, A. Nunzi, P. F. Zanazzi, and A. R. Zanzari, *Acta Cryst.*, 1972, **B28**, 1298. [e] C. Furlani, A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J.C.S. Dalton*, 1970, 2929. [f] R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 1967, **6**, 1844. [g] E. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, 1967, **89**, 3353.

Consideration of the ' plane ' through the four sulphur atoms reveals a considerable deviation from planarity; this probably arises as a distortion associated with the disposition and packing of ligand (2), the vanadium atom deviating considerably (0.32 Å) from the ligand plane, while V–S(22) is short (see earlier).

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