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Structure of (*N,N*-Dipropyldithiocarbamato)[tris(3,5-dimethyl-1-pyrazolyl)-hydroborato]oxovanadium(IV)

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Abstract. [VO($C_{15}H_{22}BN_6$)($C_7H_{14}NS_2$)], $M_r = 540 \cdot 46$, monoclinic, $P2_1/n$, $a = 9 \cdot 838$ (2), $b = 20 \cdot 683$ (6), $c = 14 \cdot 029$ (2) Å, $\beta = 106 \cdot 365$ (2)°, $V = 2739 \cdot 1$ Å^3, $Z = 4$, $D_m = 1 \cdot 32$, $D_x = 1 \cdot 31$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71073$ Å, $\mu = 5 \cdot 24$ cm^{-1}, $F(000) = 1140$, $T = 295$ K, $R = 0 \cdot 049$, $wR = 0 \cdot 060$ for 2070 reflections. The central V atom adopts a distorted-octahedral coordination geometry in which one face of the octahedron is occupied by the tridentate tris(3,5-dimethyl-1-pyrazolyl)hydroborate ligand and the opposite face by oxo and dipropyldithiocarbamato ligands. The structure of the mononuclear complex is compared with that of the analogous diethyldithiocarbamato complex.

Introduction. Interest in metal oxo compounds has gained considerable momentum in recent years due to the role of metal-oxo species in certain catalytic processes of biological (Spiro, 1985) and industrial importance (Nugent & Mayer, 1988). These include the presence of mononuclear oxomolybdenum species in molybdenum hydroxylases (Bray, 1980; Spence, 1983). The bulky tris(3,5-dimethyl-1-pyrazolyl)hydroborate ligand (*L*) has been utilized to prepare oxomolybdenum complexes with unusual structural features and to prevent the formation of polynuclear species. Compounds such as $LMoOX_2$ (*X* = halide, pseudohalide, alkoxide, thiolate) (Cleland, Barnhart, Yamanouchi, Collison, Mabbs, Ortega & Enemark, 1987) and $LMoO(S_2CNR_2)$ (*R* = Me, Et, Pr, Bu) (Young, Roberts, Ortega & Enemark, 1987) have been prepared and characterized. We have recently prepared a series of vanadyl complexes of the form $LVO(S_2CNR_2)$ (*R* = Me, Et, Pr, Bu) (Sit, Collison, Mabbs & Cleland,

1989) and are investigating the detailed electron-spin-resonance spectra of these species in dilute single crystals. Crystals of the analogous $LMoO(S_2CNR_2)$ complexes serve as diamagnetic host lattices for these studies. We herein report the structure of one of these complexes, $LVO(S_2CNPr_2)$.

Experimental. The complex was prepared by the method of Sit *et al.* (1989). Violet crystals obtained by liquid–liquid diffusion of methanol into a methylene chloride solution of $LVO[S_2CN(C_3H_7)_2]$ at 298 K, dimensions $0 \cdot 30 \times 0 \cdot 25 \times 0 \cdot 10$ mm, mounted on a glass fiber with cyanoacrylate glue, D_m by flotation (ZnBr$_2$ and H$_2$O). Monoclinic crystal class, limiting conditions identified space group $P2_1/n$ (*h*0*l*: $h + l = 2n$; 0*k*0: $k = 2n$), 25 reflections for measuring lattice parameters, $13 \le 2\theta \le 28°$. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, no absorption correction applied. θ–2θ scans, $2\theta_{max} = 50°$, $0 \le h \le 11$, $0 \le k \le 24$, $-16 \le l \le 15$, standard reflection $\overline{2}20$, decay of 1%, no correction made. 4667 unique reflections, 2070 with $F_o > 3\sigma(F_o)$ used in refinement. $R_{int} = 0 \cdot 028$. Co-ordinates of V from Patterson, 34 non-H atoms from difference electron-density maps. Disorder was found in the last C atom of one of the propyl groups of the dithiocarbamate. Atom C47' was added at $0 \cdot 50$ occupancy; (Δ/σ) for this atom was zero after three cycles of refinement. Full-matrix least squares on F, all non-H atoms anisotropic. H atoms included at calculated positions but not refined. Final refinement of F (2070 reflections, 317 parameters) resulted in $R = 0 \cdot 049$, $wR = 0 \cdot 060$, where $w = 4F_o^2/[\sigma^2(I) + (pF_o^2)^2]$ with p set to $0 \cdot 06$, $(\Delta\rho)_{max} = 0 \cdot 34$, $(\Delta\rho)_{min} = -0 \cdot 38$ e Å^{-3}, $(\Delta/\sigma)_{max} = 0 \cdot 08$. Atomic scattering factors from Cromer & Waber (1974) and anomalous-dispersion factors from Cromer (1974). Programs *SDP* (Frenz, 1978) run on a MicroVAX II.

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Table 1. Refined positional parameters and thermal parameters and their e.s.d.'s

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B (Å^2)
V	0·8844 (1)	0·17078 (5)	0·89398 (7)	2·94 (2)
S1	0·9323 (2)	0·16946 (9)	1·0745 (1)	3·51 (4)
S2	0·7712 (2)	0·26659 (9)	0·9421 (1)	3·93 (4)
O	1·0288 (4)	0·2033 (2)	0·8894 (3)	3·8 (1)
N11	0·6666 (5)	0·1091 (2)	0·8819 (3)	3·0 (1)
N12	0·6330 (5)	0·0654 (2)	0·8054 (3)	2·8 (1)
N21	0·9478 (5)	0·0766 (2)	0·8727 (3)	3·0 (1)
N22	0·8747 (5)	0·0409 (2)	0·7913 (3)	3·3 (1)
N31	0·7862 (5)	0·1792 (2)	0·7402 (3)	3·0 (1)
N32	0·7239 (5)	0·1270 (2)	0·6845 (3)	3·2 (1)
N41	0·8520 (5)	0·2805 (3)	1·1397 (4)	3·8 (1)
C11	0·5694 (6)	0·1013 (3)	0·9316 (4)	3·3 (1)
C12	0·4765 (6)	0·0519 (3)	0·8876 (5)	4·0 (2)
C13	0·5190 (6)	0·0303 (3)	0·8089 (5)	3·5 (2)
C14	0·5690 (6)	0·1391 (3)	1·0216 (5)	4·2 (2)
C15	0·4568 (8)	−0·0219 (4)	0·7355 (6)	5·8 (2)
C21	1·0704 (6)	0·0453 (3)	0·9121 (4)	3·3 (1)
C22	1·0782 (6)	−0·0089 (3)	0·8570 (5)	3·9 (2)
C23	0·9537 (6)	−0·0111 (3)	0·7815 (5)	3·5 (1)
C24	1·1777 (7)	0·0698 (4)	1·0043 (5)	4·5 (2)
C25	0·9034 (8)	−0·0594 (3)	0·6985 (5)	5·3 (2)
C31	0·7780 (6)	0·2292 (3)	0·6776 (5)	3·3 (1)
C32	0·7062 (7)	0·2098 (4)	0·5825 (5)	4·2 (2)
C33	0·6741 (7)	0·1459 (3)	0·5874 (4)	3·8 (2)
C34	0·8374 (7)	0·2933 (4)	0·7112 (5)	4·7 (2)
C35	0·5982 (8)	0·1011 (4)	0·5059 (5)	5·6 (2)
C41	0·8514 (6)	0·2435 (3)	1·0627 (4)	3·1 (1)
C42	0·7823 (7)	0·3446 (4)	1·1270 (5)	4·7 (2)
C43	0·6262 (8)	0·3416 (4)	1·1201 (6)	6·7 (2)
C44	0·5602 (9)	0·4068 (5)	1·1024 (8)	9·1 (3)
C45	0·9312 (8)	0·2626 (4)	1·2421 (5)	5·1 (2)
C46	0·8490 (9)	0·2466 (6)	1·3144 (7)	9·1 (3)
C47	0·759 (1)	0·1951 (6)	1·2882 (8)	6·5 (3)
C47'	0·859 (3)	0·191 (2)	1·382 (2)	4·2 (9)
B	0·7196 (7)	0·0601 (4)	0·7312 (5)	3·3 (2)

Table 2. Selected interatomic distances (Å) and bond angles (°), with e.s.d.'s in parentheses

V—O	1·589 (4)		V—N31	2·108 (4)
C—S1	2·442 (2)		S1—C41	1·713 (6)
V—S2	2·459 (2)		S2—C41	1·721 (6)
V—N11	2·458 (4)		C41—N41	1·322 (8)
V—N21	2·092 (5)			

O—V—S1	97·7 (2)		V—S1—C41	86·7 (2)
O—V—S2	98·6 (2)		V—S2—C41	85·9 (2)
O—V—N11	171·3 (2)		S2—V—N31	95·8 (1)
O—V—N21	94·7 (2)		S2—V—N21	165·0 (2)
O—V—N31	94·6 (2)		N11—V—N21	78·2 (2)
S1—V—S2	72·20 (6)		N11—V—N31	80·4 (2)
S1—V—N11	88·6 (1)		N31—V—N21	90·0 (2)
S1—V—N31	164·0 (1)		S1—C41—N41	122·9 (4)
S1—V—N21	99·2 (1)		S2—C41—N41	122·6 (5)
S2—V—N11	89·1 (1)		S1—C41—S2	114·5 (3)

Discussion. Atomic coordinates with standard deviations are listed in Table 1 and selected interatomic distances and bond angles in Table 2.* The molecular structure is shown in Fig. 1. The structure consists of discrete mononuclear molecules of $[\{HB(C_5H_7N_2)_3\}VO\{S_2CN(C_3H_7)_2\}]$. Each V atom

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52992 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

adopts a distorted octahedral coordination geometry. The structural constraints of the ligand L require that it occupy a facial stereochemical position of an octahedron. This in turn requires the oxo group and each S atom of the dithiocarbamato ligand to be mutually *cis* to each other. The molecule has approximate C_s symmetry with the plane of symmetry passing through the pyrazole ring containing N11 of L, V, O and C41, N41 of the dithiocarbamate. Overall C_s symmetry is broken by the two different conformations of the propyl groups of the dithiocarbamate.

The V—O distance [1·589 (4) Å] is close to the average found for a substantial number of oxovanadium(IV) complexes and essentially equal to the V—O distance for the analogous diethyldithiocarbamato complex (Sit *et al.*, 1989). In a statistical treatment of the structural data on 58 vanadium monooxo complexes (Mayer, 1988), it was found that mean V—O distances for V^V and V^{IV} complexes are 1·582 and 1·598 Å, respectively. Further, the narrow range of V—O values was found to be relatively insensitive to coordination number as well as oxidation state. This phenomenon has been explained in terms of the high V—O bond strength (Mayer, 1988).

The V—N11 bond distance is elongated by 0·36 Å relative to V—N21 and V—N31 and is due to the *trans* labilizing effect of the oxo group. A lengthening of the V—N11 bond in $LVO(S_2CNEt_2)$ is also observed and is of comparable magnitude (0·33 Å). The V atom is displaced 0·245 Å toward the O atom above the plane defined by S1, S2, N21, N31 and is 0·354 Å above the plane containing S1, S2, C41, N41. Analogous displacements for the V atom in $LVO(S_2CNEt_2)$ are 0·256 and 0·300 Å, respectively (Sit *et al.*, 1989). Bond distances and angles within
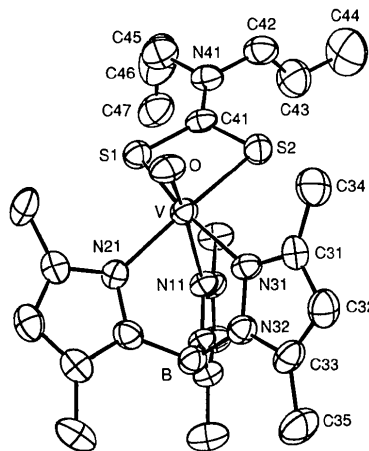

Fig. 1. The structure of $[\{HB(C_5H_7N_2)_3\}VO\{S_2CN(C_3H_7)_2\}]$. The atom numbering for the unlabeled pyrazole rings follows the same pattern as the labeled ring.

the S_2CNC_2 portions of the dipropyldithiocarbamato ligand are very similar to those of the analogous diethyldithiocarbamato complex (Sit *et al.*, 1989). The bond distances and angles in the trispyrazolyl-hydroborate ligand, *L*, are normal (Cleland *et al.*, 1987).

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Structure of Tetraphenylarsonium Heptanitrosyl-tri-μ_3-seleno-tetraferrate(1 −)

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Abstract. $C_{24}H_{20}As^+.[Fe_4Se_3(NO)_7]^-$, $M_r = 1053 \cdot 67$, triclinic, $P\bar{1}$, $a = 13 \cdot 122\,(9)$, $b = 13 \cdot 936\,(9)$, $c = 9 \cdot 908\,(8)$ Å, $\alpha = 99 \cdot 30\,(6)$, $\beta = 97 \cdot 04\,(6)$, $\gamma = 71 \cdot 94\,(5)°$, $V = 1694 \cdot 9$ Å^3, $Z = 2$, $D_x = 2 \cdot 065$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, $\mu = 58 \cdot 87$ cm^{-1}, $F(000) = 1016$, $T = 295$ K, $R = 0 \cdot 047$ for 5101 observations. The structure consists of isolated Ph_4As^+ cations and $[Fe_4Se_3(NO)_7]^-$ anions which exhibit approximate C_{3v} symmetry.

Introduction. It has been deduced from nuclear-magnetic-resonance spectroscopy (Butler, Glidewell, Hyde & McGinnis, 1985) that the iron–selenium–nitrosyl anion $[Fe_4Se_3(NO)_7]^-$ (Butler, Glidewell, Hyde, McGinnis & Seymour, 1983) has a structure, in solution, which is similar to that established by X-ray methods for the sulfur analogue $[Fe_4S_3(NO)_7]^-$ (Johansson & Lipscomb, 1958; Chu & Dahl, 1977). Structure analysis not only confirms

definitively the structure inferred from spectroscopy, but allows metrical comparison between $[Fe_4Se_3(NO)_7]^-$ and $[Fe_4S_3(NO)_7]^-$.

Experimental. Small black block crystals grown from methanol. Accurate cell dimensions and crystal orientation matrix determined on a Nicolet P3 diffractometer by least-squares refinement using the setting angles of 20 reflections in the range $15 \le \theta \le 18°$. Crystal dimensions $0 \cdot 24 \times 0 \cdot 40 \times 0 \cdot 40$ mm; intensities of reflections with indices $h - 17$ to $+17$, $k - 18$ to $+18$, $l 0$ to $+12$ with $2 \le 2\theta \le 55°$; ω–2θ scans, 2θ scan width $(2 \cdot 40$–$2 \cdot 75)°$, graphite-monochromated Mo $K\alpha$ radiation. 7830 reflections measured, 7828 unique, 5101 with $F \ge 4\sigma(F)$ labelled observed and used in structure solution and refinement. No intensity change was detected in two standard reflections measured after every 200 reflections. Data corrected for Lorentz and polarization effects and for absorption effects using a ψ-scan technique on the diffractometer (maximum and mini-

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