Monoclinic
$P2_1/n$
$a = 6.5940\,(10)$ Å
$b = 10.763\,(2)$ Å
$c = 11.649\,(2)$ Å
$\beta = 105.360\,(10)°$
$V = 797.2\,(2)$ Å^3
$Z = 2$
$D_x = 2.850$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 15$–$30°$
$\mu = 18.367$ mm^{-1}
$T = 293\,(2)$ K
Rhombohedral block
$0.40 \times 0.15 \times 0.05$ mm
Yellow

Data collection

Nicolet *R*3*m*/*V* diffractometer with locally modified ψ box
Profile data from $\theta/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scan (*SHELXTL-Plus*; Sheldrick, 1987)
$T_{\min} = 0.261$, $T_{\max} = 1.000$
2668 measured reflections
1936 independent reflections

1479 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0990$
$\theta_{\max} = 28.07°$
$h = -1 \rightarrow 8$
$k = -14 \rightarrow 1$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0426$
$wR(F^2) = 0.1131$
$S = 1.032$
1936 reflections
67 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 2.14$ e Å^{-3}
$\Delta\rho_{\min} = -1.62$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Pt1	0.11762 (6)	0.10541 (4)	0.11383 (3)	0.0335 (2)
Cl1	−0.1500 (5)	−0.0395 (4)	0.0794 (3)	0.0600 (9)
Cl2	0.3836 (5)	0.2455 (4)	0.1314 (3)	0.0578 (8)
P1	0.0863 (4)	0.1609 (3)	0.2905 (2)	0.0359 (6)
C1	0.040 (2)	0.3240 (12)	0.3008 (14)	0.064 (4)
C2	−0.1192 (18)	0.0845 (14)	0.3373 (12)	0.057 (3)
C3	0.318 (2)	0.1269 (17)	0.4093 (11)	0.067 (4)

Table 2. *Selected geometric parameters (Å, °)*

Pt1—P1	2.205 (3)	Pt1—Cl1	2.309 (3)
Pt1—Cl2	2.281 (3)	Pt1—Cl1$^{\rm i}$	2.423 (3)
P1—Pt1—Cl2	89.81 (11)	Cl1—Pt1—Cl1$^{\rm i}$	83.81 (10)
P1—Pt1—Cl1	95.10 (10)	Pt1—Cl1—Pt1$^{\rm i}$	96.19 (10)
Cl2—Pt1—Cl1$^{\rm i}$	91.28 (11)		

Symmetry code: (i) $-x, -y, -z$.

Data collection: *P*3 software. Cell refinement: *P*3 software. Data reduction: *XDISK* (Siemens, 1991). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1987). Software used to prepare material for publication: *SHELXL*93.

The authors thank the EPSRC for a studentship (to MSR).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Mixed-Valence Tetranuclear Vanadium(IV,V) Complex, $[V_4O_4(\mu\text{-OEt})_2(\mu\text{-O})_2(OEt)_4(phen)_2]$

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(*Received 17 January 1996; accepted 3 May 1996*)

Abstract

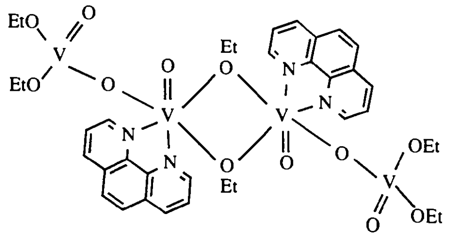
The mixed-valence tetranuclear title complex, di-μ-ethoxo-1:2κ^4O-tetraethoxo-3κ^2O,4κ^2O-di-μ-oxo-1:3κ^2O;-2:4κ^2O-tetraoxo-1κO,2κO,3κO,4κO-bis(1,10-phenanthroline)-1κ^2N,N';2κ^2N,N'-tetravanadium, $[V_4O_6(C_2H_5O)_6(C_{12}H_8N_2)_2]$, was prepared and the crystal structure analysis showed it to have an alkoxo-bridged dinuclear oxovanadium core. The complex has a crystallographic inversion centre.

Comment

The coordination chemistry of polynuclear vanadium complexes has received considerable attention in recent

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

years as a consequence of its relevance to such diverse fields of interest as the role of vanadium in biological systems (Rehder, 1991; Cornman, Kampf, Lah & Pecoraro, 1992), the properties of inorganic solid phases (Gatteschi, Pardi, Barra & Mueller, 1994; Gatteschi, Pardi, Barra, Mueller & Doering, 1991) and the structure of polyoxo anion clusters (Pope & Mueller, 1991). In particular, polynuclear μ-alkoxo, μ-oxo and μ-hydroxo vanadium complexes are interesting as models for metal oxide surfaces. Several examples of organometallic units incorporated into polyoxovanadate frameworks have been structurally characterized (Hayashi, Ozawa & Isobe, 1989, 1991; Chae, Klemperer & Day, 1989). We found that a dinuclear oxovanadium core is a good acceptor for dialkoxide vanadium(V) compounds. The present study is concerned with the preparation and crystallographic structure of the mixed-valence tetranuclear complex $[V_4O_4(\mu\text{-OEt})_2(\mu\text{-O})_2(OEt)_4(phen)_2]$, (I).



(I)

The crystal of (I) consists of independent neutral molecules containing four vanadium ions with a crystallographic inversion centre midway between V(1) and V(1′) (Fig. 1). Charge-balance considerations indicate that the molecule is a mixed-valence V^V/V^{IV} complex. Bond-valence calculations (Brese & O'Keefe, 1991) give bond-valence sums of 4.1 and 5.3 for V(1) and V(2), respectively. Consequently, we assigned V(1) to the V^{IV} state and V(2) to the for V^V state.

The four V atoms, V(2), V(1), V(1′) and V(2′), are bridged by μ-alkoxo and μ-oxo groups to afford an approximately linear tetranuclear arrangement. The V(1) ion is coordinated in a distorted octahedral geometry by the VN_2O_4 donor set. The V=O(1) and V—O(2) distances, and the V(1)—O(2)—V(1′) angle have values of 1.592 (3), 1.990 (3) Å and 104.6 (1)°, respectively, falling within normal values for corresponding V^{IV} compounds (Das, Nanda, Mukherjee, Mukherjee, Hellivell & Nag, 1993). The two V=O groups adopt *anti* positions with respect to the V(1), O(2), V(1′), O(2′) plane. The V—N_{cis} distances with respect to the oxo group range from 2.1 to 2.2 Å in six-coordinate vanadyl complexes, while the V—N_{trans} distances are longer than the V—N_{cis} distances due to the *trans* influence of the oxo group (Wieghardt, Bossek, Volckmar, Swiridoff & Weiss, 1984). For this complex, the V—N(1) bond distance [2.336 (4) Å] in the position *trans* to the oxo group is also longer than the V—N(2) distance [2.168 (4) Å]. The V(2) ion has two different types of oxo groups, namely, bridging O(3) and terminal O(4). As shown in Fig. 1, the complex crystallizes as a μ-alkoxo- and μ-oxo-bridged tetranuclear V^V/V^{IV} complex through the linkage of two four coordinate $[VO_2(OEt)_2]^-$ moieties to the central dinuclear $[V_2O_2(\mu\text{-OEt})_2]^{2+}$ unit in a vertex-sharing fashion. The V(2)=O(4), V(2)—O(5) and V(2)—O(6) distances have normal values.

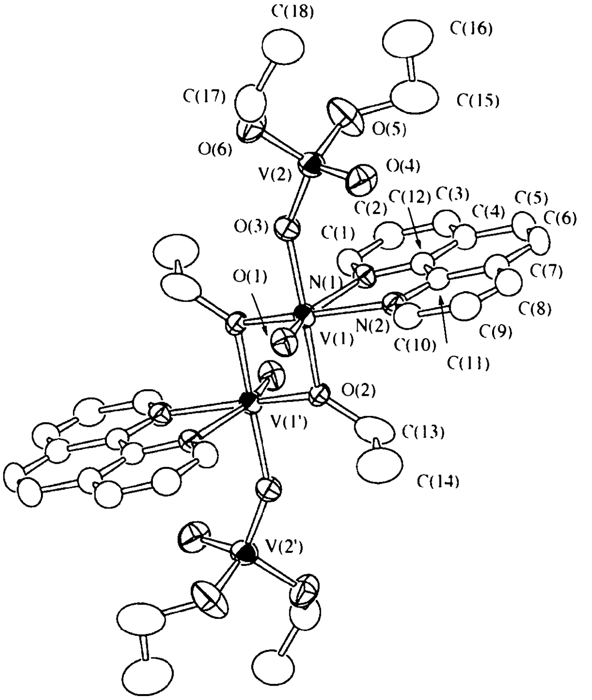


Fig. 1. An *ORTEP* (Johnson, 1965) representation of the title complex showing the atom-labelling scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

Experimental

The reaction of $[VCl_3(thf)_3]$ (0.1 g, 0.27 mmol) with phen (0.1 g, 0.54 mmol) and NaSPh (0.07 g, 0.54 mmol) in tetrahydrofuran/ethanol solution yields orange microcrystals of the title compound.

Crystal data

$[V_4O_6(C_2H_5O)_6(C_{12}H_8N_2)_2]$
M_r = 465.27
Triclinic
$P\bar{1}$
a = 8.971 (1) Å
b = 15.511 (2) Å
c = 8.329 (1) Å
α = 102.85 (1)°
β = 111.46 (1)°
γ = 73.67 (1)°
V = 1025.7 (3) Å^3
Z = 1
D_x = 1.51 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 26.07–33.15°
μ = 0.946 mm^{-1}
T = 293 K
Plate
0.20 × 0.20 × 0.10 mm
Orange

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.88$, $T_{\max} = 1.00$
5048 measured reflections
5048 independent reflections
3100 observed reflections $[I > 2.5\sigma(I)]$
$\theta_{\max} = 27.6°$
$h = 0 \rightarrow 11$
$k = -18 \rightarrow 20$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 150 reflections
intensity decay: 3.85%

Refinement

Refinement on F
$R = 0.060$
$wR = 0.054$
$S = 3.530$
3100 reflections
253 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{\max} = 0.22$
$\Delta\rho_{\max} = 0.79$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
V(1)	0.0415 (1)	−0.09957 (5)	0.0388 (1)	0.0459 (2)
V(2)	0.0846 (1)	−0.32199 (6)	−0.1568 (1)	0.0623 (3)
O(1)	−0.0824 (4)	−0.1042 (2)	0.1315 (4)	0.060 (1)
O(2)	0.0837 (4)	0.0231 (2)	0.1458 (4)	0.0470 (9)
O(3)	0.0250 (4)	−0.2091 (2)	−0.1322 (4)	0.062 (1)
O(4)	0.1572 (5)	−0.3586 (2)	0.0280 (5)	0.083 (1)
O(5)	0.2436 (6)	−0.3550 (3)	−0.2492 (6)	0.114 (2)
O(6)	−0.0855 (5)	−0.3716 (2)	−0.2862 (5)	0.089 (1)
N(1)	0.2837 (4)	−0.1169 (2)	−0.0216 (5)	0.050 (1)
N(2)	0.2402 (5)	−0.1764 (2)	0.2298 (5)	0.052 (1)
C(1)	0.3045 (6)	−0.0876 (3)	−0.1470 (7)	0.060 (2)
C(2)	0.4537 (7)	−0.1071 (4)	−0.1772 (7)	0.066 (2)
C(3)	0.5878 (6)	−0.1586 (4)	−0.0715 (8)	0.068 (2)
C(4)	0.5730 (6)	−0.1905 (3)	0.0631 (7)	0.060 (2)
C(5)	0.7062 (6)	−0.2448 (4)	0.1815 (8)	0.075 (2)
C(6)	0.6840 (7)	−0.2732 (4)	0.3093 (8)	0.078 (2)
C(7)	0.5272 (7)	−0.2524 (3)	0.3322 (7)	0.062 (2)
C(8)	0.4940 (8)	−0.2814 (4)	0.4592 (7)	0.076 (2)
C(9)	0.3405 (9)	−0.2602 (4)	0.4692 (7)	0.076 (2)
C(10)	0.2149 (7)	−0.2075 (3)	0.3509 (7)	0.064 (2)
C(11)	0.3939 (6)	−0.1993 (3)	0.2185 (6)	0.051 (1)
C(12)	0.4178 (6)	−0.1680 (3)	0.0843 (6)	0.051 (1)
C(13)	0.210 (1)	0.0474 (4)	0.306 (1)	0.095 (3)
C(14)	0.160 (1)	0.0537 (5)	0.444 (1)	0.127 (3)
C(15)	0.430 (1)	−0.4036 (6)	−0.165 (1)	0.141 (4)
C(16)	0.429 (1)	−0.4808 (7)	−0.266 (1)	0.177 (5)
C(17)	−0.1352 (8)	−0.4433 (5)	−0.246 (1)	0.105 (3)
C(18)	−0.034 (1)	−0.5301 (5)	−0.278 (1)	0.120 (3)

Table 2. *Selected geometric parameters* (Å, °)

V(1)—O(1)	1.592 (3)	V(2)—O(4)	1.601 (3)
V(1)—O(2)	1.990 (3)	V(2)—O(5)	1.762 (4)
V(1)—O(3)	1.962 (3)	V(2)—O(6)	1.781 (4)
V(1)—O(2′)	1.957 (3)	V(1)—N(1)	2.336 (4)
V(2)—O(3)	1.670 (3)	V(1)—N(2)	2.168 (4)
O(1)—V(1)—O(2)	99.6 (1)	N(1)—V(1)—N(2)	72.1 (1)
O(1)—V(1)—O(3)	100.1 (2)	O(3)—V(1)—N(1)	81.8 (1)
O(1)—V(1)—O(2′)	106.9 (1)	O(3)—V(1)—N(2)	90.9 (1)
O(1)—V(1)—N(1)	161.4 (2)	O(3)—V(2)—O(4)	110.6 (2)
O(1)—V(1)—N(2)	89.3 (2)	O(3)—V(2)—O(5)	109.3 (2)
O(2)—V(1)—O(2′)	75.4 (1)	O(3)—V(2)—O(6)	110.3 (2)
O(2)—V(1)—O(3)	158.5 (1)	O(4)—V(2)—O(5)	107.1 (2)
O(2)—V(1)—N(1)	82.3 (1)	O(4)—V(2)—O(6)	107.8 (2)
O(2)—V(1)—N(2)	97.8 (1)	O(5)—V(2)—O(6)	111.8 (2)
O(2′)—V(1)—O(3)	90.7 (1)	V(1)—O(2)—V(1′)	104.6 (1)
O(2′)—V(1)—N(1)	91.5 (1)	V(1)—O(3)—V(2)	143.7 (2)
O(2′)—V(1)—N(2)	163.1 (1)		

Symmetry code: (′) $-x, -y, -z$.

Weak reflections $[I<10\sigma(I)]$ were rescanned (maximum of 4 rescans) and the counts accumulated to insure good counting statistics. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques (*PATTY* in *DIRDIF*92; Beurskens *et al.*, 1992). H atoms were placed in calculated positions. Non-H atoms were refined anisotropically. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1993), and *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) was used for data collection and cell refinement.

This research was supported by a Grant-in-Aid for scientific research (area number 07640757) from the Ministry of Education, Science and Culture, Japan.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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