Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.74$, $T_{\max} = 1.56$
2787 measured reflections
2684 independent reflections
2089 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.028$
$\theta_{\max} = 60°$
$h = -32 \rightarrow 31$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 20$
2 standard reflections
frequency: 30 min
intensity variation: ±0.82%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.049$
$S = 1.79$
2089 reflections
272 parameters
H atoms refined in fixed positions with one overall $U_{\text{iso}} = 0.081(4)$ Å^2

$w = 1/[\sigma^2(F_o) + 0.0003F_o^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}
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)

$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Cu	0.0142 (1)	0.2193 (1)	0.5054 (1)	3.01 (2)
O(1)	−0.0259 (1)	0.3025 (4)	0.4152 (2)	3.3 (1)
O(2)	−0.1605 (1)	0.5466 (5)	0.2482 (2)	4.6 (1)
O(3)	−0.1502 (1)	0.5447 (4)	0.5077 (2)	3.6 (1)
N(1)	−0.0263 (1)	0.3009 (5)	0.5644 (2)	3.1 (1)
C(1)	−0.0668 (1)	0.3789 (6)	0.4056 (2)	2.8 (1)
C(2)	−0.0873 (1)	0.4232 (6)	0.4651 (2)	2.6 (1)
C(3)	−0.1323 (2)	0.5094 (6)	0.4474 (3)	2.7 (1)
C(4)	−0.1555 (1)	0.5484 (6)	0.3754 (3)	3.0 (2)
C(5)	−0.1343 (2)	0.5027 (7)	0.3184 (3)	3.1 (2)
C(6)	−0.0915 (1)	0.4180 (7)	0.3313 (2)	3.0 (2)
C(7)	−0.0659 (2)	0.3832 (7)	0.5415 (3)	3.1 (2)
C(8)	−0.1415 (2)	0.5128 (9)	0.1867 (3)	5.3 (2)
C(9)	−0.1967 (2)	0.6167 (7)	0.4918 (3)	4.0 (2)
C(10)	−0.0066 (2)	0.2736 (8)	0.6456 (3)	5.0 (2)
O(1′)	0.0565 (1)	0.1380 (5)	0.4502 (2)	3.6 (1)
O(2′)	0.1941 (1)	−0.1015 (5)	0.3973 (2)	4.3 (1)
O(3′)	0.1797 (1)	−0.0854 (5)	0.6470 (2)	4.3 (1)
N(1′)	0.0512 (1)	0.1237 (5)	0.5969 (2)	3.0 (1)
C(1′)	0.0978 (1)	0.0613 (6)	0.4756 (3)	3.1 (2)
C(2′)	0.1170 (1)	0.0217 (6)	0.5518 (3)	2.7 (1)
C(3′)	0.1627 (1)	−0.0578 (7)	0.5721 (3)	3.2 (2)
C(4′)	0.1874 (1)	−0.0982 (7)	0.5206 (3)	3.3 (2)
C(5′)	0.1669 (1)	−0.0584 (7)	0.4457 (3)	3.2 (2)
C(6′)	0.1234 (1)	0.0203 (7)	0.4223 (3)	3.3 (2)
C(7′)	0.0925 (2)	0.0491 (6)	0.6087 (3)	3.2 (2)
C(8′)	0.1777 (2)	−0.0462 (8)	0.3217 (3)	5.8 (2)
C(9′)	0.2255 (2)	−0.1603 (9)	0.6713 (3)	6.0 (2)
C(10′)	0.0274 (2)	0.1292 (8)	0.6578 (3)	4.5 (2)
O(*W*)	0.0387 (2)	0.3101 (7)	0.3131 (2)	8.8 (2)

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

Cu—O(1)	1.892 (3)	Cu—O(1′)	1.898 (3)
Cu—N(1)	1.908 (4)	Cu—N(1′)	1.912 (4)
O(1)—Cu—N(1)	93.3 (1)	N(1)—Cu—O(1′)	177.7 (2)
O(1)—Cu—O(1′)	88.8 (1)	N(1)—Cu—N(1′)	85.1 (2)
O(1)—Cu—N(1′)	175.9 (1)	O(1′)—Cu—N(1′)	92.8 (1)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. All H atoms were found in a difference synthesis and included as fixed contributors with an overall isotropic temperature parameter. Refinement was by full-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos. Programs used were: *SHELXS*86 (Sheldrick, 1985), *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: MU1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Potassium (5-Nitro-1,10-phenanthroline-N^1,N^{10})oxodiperoxovanadate(V) Dihydrate: an Insulin-Mimetic Peroxovanadate

ALAN SHAVER,* JESSE B. NG, ROSEMARY C. HYNES AND BARRY I. POSNER

Departments of Chemistry and Medicine,
McGill University, 801 Sherbrooke Street West,
Montreal, Quebec, Canada H3A 2K6

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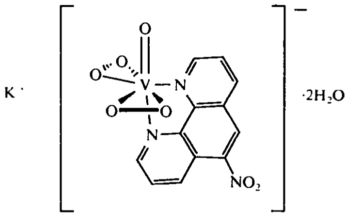
Abstract

The structure of the title compound, $K[VO(O_2)_2(C_{12}H_7N_3O_2)].2H_2O$, was determined. The geometry about the V atom is pentagonal bipyramidal with the pentagonal plane defined by the two peroxo groups and one N atom from the phenanthroline ligand [N(2)]. The oxo ligand lies in the plane of the

vanadium–phenanthroline moiety, *trans* to the second phenanthroline N atom [N(1)]. The planes formed by the two peroxo groups and the V atom are bent towards each other with a dihedral angle of 22.1 (3)° and are roughly perpendicular to the phenanthroline ligand. Of the two potential positions for the nitro group, that found puts the greatest possible distance between the nitro group and the oxo ligand.

Comment

Peroxovanadium compounds of the type M[VO(O$_2$)$_2$(L)], M = NH$_4$ or K, are stabilized when L is a bidentate ligand such as 1,10-phenanthroline (Vuletic & Djordjevic, 1973). These systems are of interest in that they mimic the activity of insulin in their reaction with certain model substrates (Posner *et al.*, 1984). The biological significance of vanadium complexes has been reviewed recently (Rehder, 1991). The structure of the title compound (I) is analogous to those of other known peroxovanadates (Shaver, Ng, Hall, Soo Lum & Posner, 1993, Stomberg, 1985, 1986; Szentivanyi & Stomberg, 1983).



(I)

The compound crystallizes with two molecules of solvent water which are hydrogen-bonded to the oxo and peroxo O atoms and are coordinated to the K counterion. Their reasonable displacement parameters reflect the extent of their interactions. One of the solvent molecules is disordered across two positions with 50% occupancy at each site. The K ions are surrounded by a coordination sphere of eight O atoms at distances of less than 3 Å.

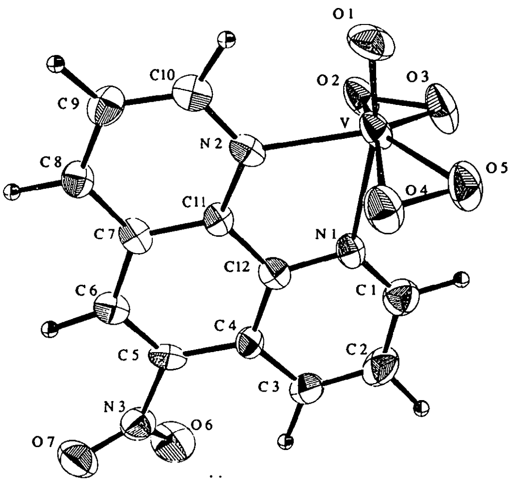


Fig. 1. *ORTEP*II plot (Johnson, 1976) of the [VO(O$_2$)$_2$(C$_{12}$H$_7$N$_3$O$_2$)] anion showing the numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn with an arbitrary radius.

While the possibility exists for a second isomer of this compound – one with the nitro group at position six relative to N(1) – this isomer was not observed and there was no evidence to suggest that the two isomers had co-crystallized.

Experimental

The complex was synthesized according to the literature method (Shaver, Ng, Hall, Soo Lum & Posner, 1993). Crystals were grown from a water-ethanol mixture.

Crystal data

K[VO(O$_2$)$_2$(C$_{12}$H$_7$N$_3$O$_2$)].2H$_2$O
M_r = 431.27
Triclinic
$P\overline{1}$
a = 6.972 (3) Å
b = 10.058 (6) Å
c = 12.131 (6) Å
α = 73.08 (4)°
β = 75.90 (4)°
γ = 77.04 (4)°
V = 778.5 (7) Å^3

Z = 2
D_x = 1.840 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 18 reflections
θ = 10–13°
μ = 0.94 mm^{-1}
T = 294 K
Needle
0.35 × 0.10 × 0.10 mm
Orange-yellow

Data collection

Rigaku AFC-6*S* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2252 measured reflections
2052 independent reflections
1260 observed reflections [$I > 2.5\sigma(I)$]

$R_{\rm int}$ = 0.048
$\theta_{\rm max}$ = 22.5°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = -12 \rightarrow 13$
3 standard reflections monitored every 150 reflections intensity variation: 8.3%

Refinement

Refinement on F
R = 0.056
wR = 0.059
S = 1.65
1260 reflections
229 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.0001(F_o)^2]$
$(\Delta/\sigma)_{\rm max}$ = 0.076
$\Delta\rho_{\rm max}$ = 0.61 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.46 e Å^{-3}
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)

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

	x	y	z	$B_{\rm eq}$
V	0.26692 (23)	0.80614 (15)	0.18312 (12)	2.70 (7)
K	0.2997 (3)	1.01641 (21)	−0.10659 (17)	3.59 (11)
O(1)	0.2544 (9)	0.9662 (5)	0.1888 (5)	4.0 (3)

O(2)	−0.0052 (8)	0.7926 (6)	0.2054 (5)	3.6 (3)
O(3)	0.0931 (9)	0.8203 (6)	0.0827 (5)	4.3 (3)
O(4)	0.5482 (9)	0.7433 (6)	0.1732 (5)	3.7 (3)
O(5)	0.4857 (9)	0.7874 (6)	0.0597 (5)	4.0 (3)
O(6)	0.2488 (10)	0.0679 (6)	0.5145 (5)	4.5 (4)
O(7)	0.4023 (9)	0.0891 (6)	0.6403 (5)	3.9 (3)
N(1)	0.2891 (9)	0.5610 (6)	0.2229 (5)	2.3 (3)
N(2)	0.2351 (9)	0.7227 (6)	0.3693 (5)	2.3 (3)
N(3)	0.3184 (11)	0.1392 (6)	0.5566 (6)	2.9 (3)
C(1)	0.3189 (13)	0.4850 (9)	0.1479 (7)	3.3 (5)
C(2)	0.3441 (15)	0.3367 (9)	0.1800 (8)	3.8 (5)
C(3)	0.3423 (14)	0.2680 (9)	0.2953 (7)	3.4 (5)
C(4)	0.3055 (12)	0.3447 (8)	0.3801 (6)	2.2 (4)
C(5)	0.2980 (12)	0.2912 (7)	0.5044 (7)	2.2 (4)
C(6)	0.2677 (12)	0.3725 (8)	0.5807 (7)	2.3 (4)
C(7)	0.2409 (12)	0.5217 (8)	0.5373 (6)	2.2 (4)
C(8)	0.2062 (12)	0.6113 (8)	0.6118 (6)	2.4 (4)
C(9)	0.1833 (13)	0.7542 (8)	0.5636 (7)	2.9 (4)
C(10)	0.1990 (12)	0.8066 (8)	0.4421 (7)	2.7 (4)
C(11)	0.2520 (11)	0.5809 (8)	0.4162 (6)	1.9 (4)
C(12)	0.2849 (12)	0.4922 (8)	0.3380 (7)	2.2 (4)
O(*W*1)	0.1207 (12)	0.8325 (7)	−0.1756 (6)	6.26 (18)
O(*W*2)†	0.1848 (22)	0.5085 (14)	0.8933 (11)	5.5 (3)
O(*W*2′)†	0.1076 (24)	0.4131 (15)	0.9188 (13)	6.5 (4)

† Disordered: an occupancy of 0.5 was assumed for each.

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

V—O(1)	1.614 (6)	V—N(2)	2.142 (6)
V—O(2)	1.880 (6)	O(2)—O(3)	1.452 (8)
V—O(3)	1.875 (6)	O(4)—O(5)	1.460 (8)
V—O(4)	1.906 (6)	O(6)—N(3)	1.225 (9)
V—O(5)	1.878 (6)	O(7)—N(3)	1.219 (9)
V—N(1)	2.347 (6)		
O(1)—V—O(2)	102.0 (3)	O(5)—V—N(1)	86.10 (25)
O(1)—V—O(3)	104.4 (3)	O(5)—V—N(2)	131.7 (3)
O(1)—V—O(4)	99.5 (3)	N(1)—V—N(2)	72.18 (23)
O(1)—V—O(5)	102.1 (3)	V—O(2)—O(3)	67.0 (3)
O(1)—V—N(1)	166.2 (3)	V—O(3)—O(2)	67.4 (3)
O(1)—V—N(2)	94.2 (3)	V—O(4)—O(5)	66.3 (3)
O(2)—V—O(3)	45.51 (25)	V—O(5)—O(4)	68.3 (3)
O(2)—V—O(4)	157.8 (3)	V—N(1)—C(1)	127.7 (5)
O(2)—V—O(5)	132.9 (3)	V—N(1)—C(12)	114.3 (5)
O(2)—V—N(1)	79.68 (24)	C(1)—N(1)—C(12)	117.7 (7)
O(2)—V—N(2)	85.80 (24)	V—N(2)—C(10)	121.6 (5)
O(3)—V—O(4)	132.5 (3)	V—N(2)—C(11)	120.1 (5)
O(3)—V—O(5)	89.3 (3)	C(10)—N(2)—C(11)	118.3 (6)
O(3)—V—N(1)	86.7 (3)	O(6)—N(3)—O(7)	122.8 (6)
O(3)—V—N(2)	130.2 (3)	O(6)—N(3)—C(5)	118.3 (6)
O(4)—V—O(5)	45.39 (25)	O(7)—N(3)—C(5)	118.9 (7)
O(4)—V—N(1)	78.12 (24)	N(2)—C(11)—C(12)	118.0 (6)
O(4)—V—N(2)	87.39 (24)	N(1)—C(12)—C(11)	115.2 (6)

The structure was solved by direct methods and refined by a full-matrix least-squares method with all non-H atoms anisotropic except for the water O atoms. H-atom positions were calculated assuming a C—H distance of 1.08 Å. Solvent protons were omitted. All computing was performed using the *NRCVAX* system (Gabe, Le Page, Charland, Lee & White, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: BR1055). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis[*m*-(trifluoromethyl)phenyl]tin(IV)

F. E. Smith*

Chemistry Department, Laurentian University, Sudbury, Ontario, Canada P3E 2C6

Rosemary C. Hynes

Chemistry Department, McGill University, Montreal, Quebec, Canada H3A 2TS

Ying Z. Zhang and George Eng

Agricultural Experiment Station and Department of Chemistry, The University of the District of Columbia, Washington, DC 20005, USA

L. E. Khoo

School of Science, National Institute of Education, Nanyang Technological University, Bukit Timah Road, Singapore 1025

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Abstract

The crystal structure of tetrakis[*m*-(trifluoromethyl)-phenyl]tin(IV), $[Sn(C_6H_4CF_3)_4]$, has been determined. The Mössbauer spectrum of the compound shows a single peak with an isomer shift of 1.20 mm s^{-1}. The molecule is tetrahedral with no short intermolecular contacts. The Sn atom is located at a special position and the four Sn—C bond lengths [2.143 (5) Å] are equal by symmetry.

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