Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

One-dimensional chains in sodium tetraphenylphosphonium bis(2-mercapto-4-methylphenolato-*O*,*S*)oxovanadate(IV)

Paul R. Challen,[a]* David B. McConville[b] and Wiley J. Youngs[b]

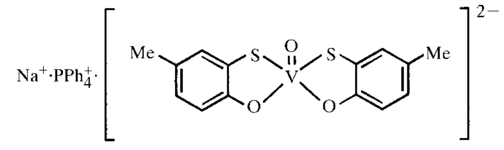
[a]Department of Chemistry, John Carroll University, Cleveland, OH 44118, USA, and [b]Department of Chemistry, University of Akron, Akron, OH 44325, USA
Correspondence e-mail: pchallen@jcvaxa.jcu.edu

Received 5 March 1999
Accepted 7 December 1999

The title compound, $Na(C_{24}H_{20}P)[V(C_7H_6OS)_2O]$, contains oxovanadium(IV) in a square-pyramidal coordination geometry with a basal plane consisting of a *cis*-S_2O_2 donor group. The $[VO(mmp)_2]^{2-}$ ($mmpH_2$ = 2-mercapto-4-methylphenol) units are linked into infinite chains by the sodium ions.

Comment

The controlled linking of discrete molecular building blocks into supramolecular aggregates can be achieved through utilizing a number of different kinds of inter-subunit interactions. For oxovanadium(IV) compounds, solid-state and solution structures have been stabilized by specific interactions including (i) V═O—V═O linkages (Zheng *et al.*, 1995; Aiello *et al.*, 1997; Sáez-Puche *et al.*, 1998), (ii) hydrogen bonds (Wen *et al.*, 1998), (iii) bridging ligands (Salta *et al.*, 1996) and (iv) alkali or alkaline earth ions functioning in a bridging mode (Garcia-Jaca *et al.*, 1993). We have reported (Klich *et al.*, 1996) the vanadyl(IV) complex $Na(Ph_4P)[VO(mp)_2]\cdot Et_2O$ containing the mixed O,S-donor ligand mp^{2-} [mpH_2 = 2-mercaptophenol, $C_6H_4(OH)(SH)$]. In this solid, a pair of $[VO(mp)_2]^{2-}$ anions are linked together through a pair of sodium ions into a centrosymmetric dimer. Each sodium ion is bonded to two ligand O atoms from one $[VO(mp)_2]^{2-}$ unit and to one ligand O atom plus the vanadyl O atom from the other. In the course of these studies, we also prepared the related compound $Na(Ph_4P)[VO(mmp)_2]$ ($mmpH_2$ = 2-mercapto-4-methylphenol), (I), which crystallized in a structure with anionic $[NaVO(mmp)_2^{-}]_\infty$ chains. We report herein upon this structure.



(I)

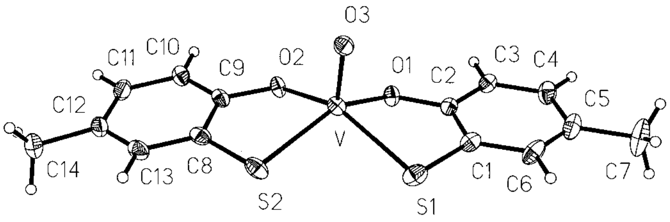


Figure 1
The structure of the $[VO(mmp)_2]^{2-}$ dianion. Displacement ellipsoids are drawn at the 50% probability level.

The square-pyramidal anion, $[VO(mmp)_2]^{2-}$, contains an apical O atom with a V═O bond length of 1.619 (2) Å, and an O_2S_2 basal plane with the two five-membered V—O—C—C—S chelate rings in a *cis* configuration (Fig. 1). This *cis* configuration has been seen in the other four oxovanadium(IV) complexes with an O_2S_2 donor set which have been structurally characterized (Higes-Rolando *et al.*, 1994; Tsagkalidis *et al.*, 1994; Preuss *et al.*, 1990; Klich *et al.*, 1996; Wen *et al.*, 1998). The $V(O_2S_2)$ core thus displays pseudo-C_s symmetry with the σ plane passing through the V—O3 bond and bisecting the O1—O2 and S1—S2 vectors. The V atom is displaced 0.598 (1) Å from the O_2S_2 least-squares plane, giving a slightly flatter pyramid than in $[VO(mp)_2]^{2-}$, where the corresponding displacement is 0.638 Å. The V—S and V—O basal plane bond lengths average to 2.375 and 1.963 Å, respectively, and are very similar to those in $[VO(mp)_2]^{2-}$ (2.365 and 1.959 Å, respectively) and the other three $VO(OS)_2$ complexes. The two five-membered chelate rings are folded about the O—S vector, with the aromatic rings bending toward the apical O atom and making angles of 24.54 (9) and 12.60 (8)° with the O1—V—S1 and O2—V—S2 planes, respectively. While this bending is also observed in the related complexes $[VO(mp)_2]^{2-}$ (Klich *et al.*, 1996) and $VO(Hmpp)_2$ (Wen *et al.*, 1998), it is more pronounced in the title compound.

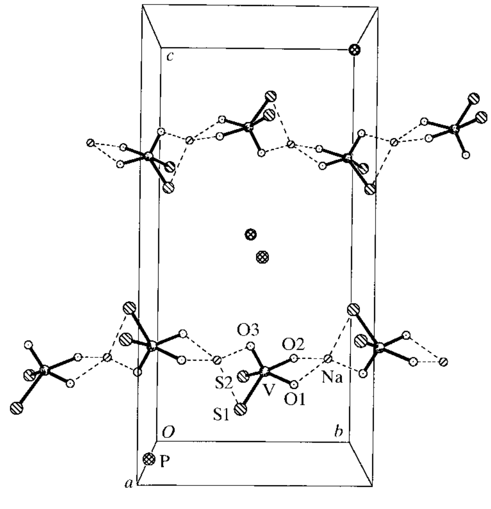


Figure 2
View of the $[NaVO(mmp)_2^{-}]_\infty$ chains down the *a* axis. The chains can be seen running parallel to **b**. C and H atoms have been omitted for clarity.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

The $[VO(mmp)_2]^{2-}$ ions are linked through sodium ions into one-dimensional polymeric chains (Fig. 2). Each Na^+ bridges two $[VO(mmp)_2]^{2-}$ ions, coordinating through the two ligand O atoms from one unit and the ligand S atom plus the vanadyl O atom from the other. The chains run parallel to the *b* axis, along the crystallographic twofold screw, so that each $[VO(mp)_2]^{2-}$ unit is rotated 180° to the next. The chains are well isolated from each other, being separated by Ph_4P^+ ions. The sodium ions are four-coordinate, with no solvent molecules attached, in contrast to the dimeric units in $Na(Ph_4P)[VO(mp)_2]\cdot Et_2O$, where a molecule of ether completes the five-coordination of each sodium ion. In the title compound, a phenyl ring from Ph_4P^+ blocks one side of each Na^+ where a solvent molecule might otherwise have been located. The Na—O bond lengths are significantly shorter in the title compound than in $Na(Ph_4P)[VO(mp)_2]\cdot Et_2O$, probably reflecting an opening up of the dimeric structure relative to the infinite chain due to close proximity of the sodium ions held between pairs of $[VO(mp)_2]^{2-}$ ions.

Experimental

$Na(Ph_4P)[VO(mmp)_2]$ was prepared under an atmosphere of prepurified N_2. To a stirred suspension of $VO(acac)_2$ (0.76 g, 2.9 mmol) in EtOH (35 ml) was added a solution of Na_2mmp in MeOH (15 ml) [prepared from reaction of 2-mercapto-4-methylphenol (1.0 g, 7.1 mmol) with NaOMe in MeOH]. The $VO(acac)_2$ dissolved in the reaction mixture and an olive-green solution resulted. After 2 h of stirring at ambient temperature, the mixture was filtered to remove small amounts of undissolved material and Ph_4PCl was added. Some pale solid (NaCl) precipitated and was removed by filtration. Addition of a small amount of diethyl ether to the green filtrate and subsequent standing led to formation of well formed green crystals, which were isolated by filtration. The IR spectrum showed a strong band at 951 cm^{-1} indicative of the presence of the V═O group.

Crystal data

$Na(C_{24}H_{20}P)[V(C_7H_6OS)_2O]$
$M_r = 705.66$
Monoclinic, $P2_1/n$
$a = 13.888$ (3) Å
$b = 10.947$ (2) Å
$c = 22.330$ (5) Å
$\beta = 90.01$ (2)°
$V = 3394.9$ (13) Å^3
$Z = 4$

$D_x = 1.381$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 30 reflections
$\theta = 20.77$–28.90°
$\mu = 0.512$ mm^{-1}
$T = 129$ K
Block, green
0.42 × 0.38 × 0.28 mm

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.789$, $T_{\max} = 0.841$
13 312 measured reflections
5977 independent reflections
4301 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\max} = 25.01°$
$h = -16 \rightarrow 16$
$k = -1 \rightarrow 13$
$l = -26 \rightarrow 26$
3 standard reflections every 97 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.072$
$S = 1.00$
5977 reflections
417 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.01$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V—O3	1.6194 (15)	Na—O2	2.256 (2)
V—O2	1.959 (2)	Na—O1	2.260 (2)
V—O1	1.967 (2)	Na—O3$^{\rm i}$	2.281 (2)
V—S2	2.3652 (8)	Na—S1$^{\rm i}$	2.9371 (12)
V—S1	2.3853 (8)		
O2—V—S2	84.09 (5)	C8—S2—V	95.52 (8)
O1—V—S1	82.93 (5)	C2—O1—V	119.26 (14)
C1—S1—V	94.50 (8)	C9—O2—V	120.61 (14)

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

A peak representing 0.76 e Å^{-3} was observed in the final difference map at a distance of 1.32 Å from V, 1.92 Å from O1, 2.28 Å from O2, 2.14 Å from S1 and 2.43 Å from S2. However, in a refinement carried out on another data set on the same crystal, collected using a Bruker 1K CCD detector, the peak was not observed. The 20 highest peaks in the difference map were all found in the vicinity of the aromatic rings of the ligands and the tetraphenylphosphonium cation, with none greater than 0.41 e Å^{-3}. It was concluded that the peak near V was spurious. The H-atom isotropic displacement parameters were fixed at either 1.5 (methyl) or 1.2 (aryl) times the equivalent isotropic displacement parameters of their parent atoms.

Data collection: *P*3/*P*4–*PC* (Siemens, 1991); cell refinement: *P*3/*P*4–*PC*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *XS* (Siemens, 1994); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1473). Services for accessing these data are described at the back of the journal.

References

Aiello, I., Ghedini, M. & Zanchini, C. (1997). *Inorg. Chim. Acta*, **255**, 133–137.
Garcia-Jaca, J., Rojo, T., Pizarro, J. L., Goñi, A. & Arriortua, M. I. (1993). *J. Coord. Chem.* **30**, 327–336.
Higes-Rolando, F. J., Perez-Florindo, A., Valenzuela-Calahorro, C., Martin-Ramos, J. D. & Romero-Garzon, J. (1994). *Acta Cryst.* C**50**, 1049–1052.
Klich, P. R., Daniher, A. T., Challen, P. R., McConville, D. B. & Youngs, W. J. (1996). *Inorg. Chem.* **35**, 347–356.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Preuss, F., Steidel, M. & Exner, R. (1990). *Z. Naturforsch. Teil B*, **45**, 1618–1624.
Sáez-Puche, R., Romero, J., González-Baró, A. C. & Baran, E. J. (1998). *Chem. Phys. Lett.* **282**, 273–275.
Salta, J., O'Connor, C. J., Li, S. & Zubieta, J. (1996). *Inorg. Chim. Acta*, **250**, 303–310.
Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.
Siemens (1991). *P3/P4–PC Diffractometer Program* (Version 4.23) and *XDISK* (Version 4.21). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *XP* and *XS*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tsagkalidis, W., Rodewald, D., Rehder, D. & Vergopoulos, V. (1994). *Inorg. Chim. Acta*, **219**, 213–215.
Wen, T.-B., Shi, J.-C., Huang, X., Chen, Z.-N., Liu, Q.-T. & Kang, B.-S. (1998). *Polyhedron*, **17**, 331–339.
Zheng, H., Lai, C. K. & Swager, T. M. (1995). *Chem. Mater.* **7**, 2067–2077.