Absorption correction:
ψ scan (North, Phillips & Mathews, 1968)
$T_{\rm min} = 0.74$, $T_{\rm max} = 1.00$
1721 measured reflections
1484 independent reflections
949 observed reflections
[$I \geq 3\sigma(I)$]

$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = -10 \rightarrow 9$
3 standard reflections
monitored every 97 reflections
intensity decay: 2%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.062$
$S = 2.04$
949 reflections
77 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0006F^2]$

$(\Delta/\sigma)_{\rm max} = 0.214$
$\Delta\rho_{\rm max} = 1.00$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.73$ 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)*

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

	x	y	z	$U_{\rm eq}$
U(1)	0	0.1515 (1)	0	0.075 (1)
O(1)	0.1310 (9)	0.1518 (12)	0.0996 (15)	0.095 (5)
O(2)	−0.0314 (10)	0	0.1518 (16)	0.075 (6)
O(3)	−0.0610 (15)	0.1860 (16)	0.2830 (19)	0.117 (7)
O(4)	−0.0327 (12)	0.3238 (13)	0.1453 (16)	0.110 (7)
O(5)	−0.0997 (19)	0.3348 (18)	0.380 (3)	0.175 (11)
O(6)	0.1043 (11)	0	0.4625 (19)	0.070 (4)
N(1)	−0.0668 (16)	0.281 (3)	0.274 (2)	0.131 (11)
N(2)†	0.2537 (13)	−0.0292 (12)	0.7602 (19)	0.045 (5)
C(1)	0.2141 (17)	0	0.446 (2)	0.090 (11)
C(2)†	0.279 (2)	0.037 (2)	0.617 (3)	0.081 (10)
C(3)†	0.281 (3)	−0.141 (2)	0.727 (4)	0.098 (16)
C(4)	0.3124 (17)	0	0.932 (2)	0.081 (9)

† Occupancy = 0.5.

Table 2. *Selected geometric parameters (Å)*

U(1)—O(1)	1.736 (11)	U(1)—O(2)	2.368 (8)
U(1)—O(3)	2.517 (17)	U(1)—O(4)	2.575 (17)
U(1)···U(1$^{\rm i}$)	3.930 (4)	O(3)—N(1)	1.23 (4)
O(4)—N(1)	1.29 (3)	O(5)—N(1)	1.22 (3)
O(6)—C(1)	1.43 (3)	N(2)—C(2)	1.50 (3)
N(2)—C(3)	1.52 (3)	N(2)—C(4)	1.49 (2)
C(1)—C(2)	1.54 (3)		

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

Data collection and cell refinement were performed using Nicolet *P*3 software (Nicolet XRD Corporation, 1980). The structure was solved by the heavy-atom method and refined using the *SHELXTL-Plus* program system (Sheldrick, 1990). H atoms except those belonging to the alcohol group and the water molecule were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The 2-dimethylaminoalcohol appears to be disordered about the mirror plane through O(6), C(1) and C(4). A population parameter of 0.5 was assigned to atoms C(2), C(3) and N(2).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1283). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Piperazine Metavanadate

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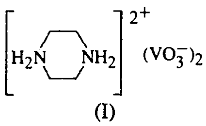
Abstract

The structure of the title compound {piperazinediium poly[trioxovanadate(2−)], $(C_4H_{12}N_2)(VO_3)_2$} is monoclinic, space group $P2_1/c$, and contains infinite $(VO_3^-)_n$ chains running parallel to the c axis. These chains form layers running parallel to the (100) plane. The protonated piperazine molecules are located between the $(VO_3^-)_n$ chains and form hydrogen bonds which contribute to the stabilization of the structure.

Comment

Anhydrous metavanadates typically adopt structures containing infinite chains of corner-sharing VO_4 tetrahedra, as found in the organic cation metavanadates $[(CH_2)_2(NH_3)_2](VO_3)_2$ (Bensch, Hug, Reller & Oswald, 1987), $[(CH_3)(CH_2)_5(NH_3)]VO_3$ (Roman, Aranzabe, Luque & Gutiérrez-Zorrilla, 1991), $[(CH_2)_6(NH_3)_2](VO_3)_2$ (Tyršelová & Pavelčík, 1992) and $[(CH_2)_4(NH_3)_2(NH)](VO_3)_2$ (Roman, Macias, Luque & Gutiérrez-Zorrilla, 1992). Structures containing a V_4O_{12} group based on a ring of four VO_4 tetrahedra have been reported for $[N(C_4H_9)_4]_3[HV_4O_{12}]$

(Fuchs, Mahjour & Pickardt, 1976) and $[(CH_3)_3CNH_3]_4[V_4O_{12}]$ (Roman, San José, Luque & Gutiérrez-Zorrilla, 1993). We describe here the structure of the title compound, (I).



(I)

The metavanadate anion in piperazine metavanadate is formed by corner-sharing VO_4 tetrahedra connected *via* the O1 atoms into infinite chains running parallel to the *c* axis. The bond lengths between V and the bridging O1 atoms [1.801 (3) and 1.803 (3) Å] are much longer than those between V and the unshared O atoms O2 and O3 [1.600 (3) and 1.629 (3) Å]. The O—V—O angles lie in the range 107.7 (2)–112.6 (1)°, indicating that the environment of the V atom is relatively undistorted. The doubly protonated piperazine molecules are located on centres of symmetry. The C—C and C—N distances in the piperazine cation are within the ranges observed in other structures containing the cations mentioned above (1.460–1.540 and 1.450–1.497 Å, respectively). Two hydrogen bonds, N1—H1···O1^{i} and N1—H2···O3^{ii} [symmetry codes: (i) $1-x$, $1-y$, $-z$; (ii) $2-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$], are formed: the former is longer than the latter as O1 is a bridging atom. The network of hydrogen bonds between the cations and the polyanions contributes to the stabilization of the structure.

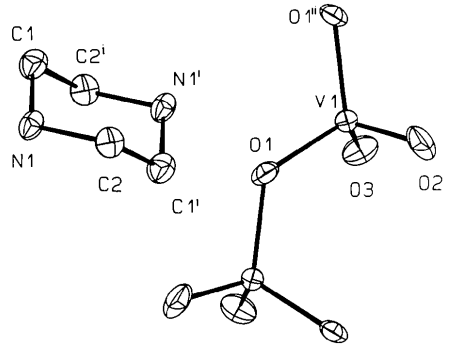


Fig. 1. *ORTEP* (Johnson, 1965) plot of the metavanadate anion and piperazine cation with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level for non-H atoms; H atoms are omitted for clarity. [Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) x, $\frac{3}{2}-y$, $z-\frac{1}{2}$.]

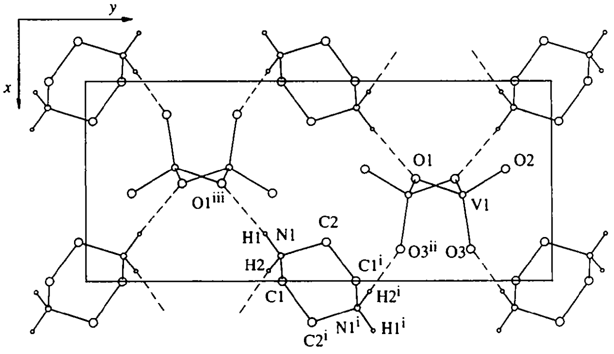


Fig. 2. A projection of the crystal structure onto the (001) plane. Hydrogen bonds are represented by dashed lines. [Symmetry codes: (i) $2-x$, $1-y$, $-z$; (ii) x, $\frac{3}{2}-y$, $z-\frac{1}{2}$; (iii) $1-x$, $1-y$, $-z$.]

Experimental

Piperazine metavanadate was prepared by dissolving V_2O_5 in an aqueous solution of piperazine. The resulting colourless solution was filtered (pH 7.0–8.0) and then acetone was slowly added. This solution was allowed to stand in a refrigerator. After several days colourless crystals of the title compound were obtained. The density D_m was measured by flotation in dioxane.

Crystal data

$(C_4H_{12}N_2)(VO_3)_2$
$M_r = 286.04$
Monoclinic
$P2_1/c$
$a = 6.132\,(5)$ Å
$b = 13.956\,(18)$ Å
$c = 5.507\,(9)$ Å
$\beta = 103.2\,(1)°$
$V = 458.9\,(10)$ Å^3
$Z = 2$
$D_x = 2.07$ Mg m^{-3}
$D_m = 2.1\,(2)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 3.42$–$8.22°$
$\mu = 2.043$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.3 × 0.3 × 0.15 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
ω–2θ scans
Absorption correction: none
1221 measured reflections
1050 independent reflections
920 observed reflections $[F_o^2 > 2\sigma(F^2)]$
$R_{int} = 0.036$

$\theta_{max} = 27.55°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 18$
$l = -7 \rightarrow 6$
2 standard reflections monitored every 98 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0340$
$wR(F^2) = 0.0861$
$S = 1.170$
1050 reflections
89 parameters
H atoms were located by difference Fourier syntheses and were refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.4240P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.031$
$\Delta\rho_{max} = 0.668$ e Å^{-3}
$\Delta\rho_{min} = -0.585$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0016 (35)
Atomic scattering factors from *SHELXL93*

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	$U_{\rm eq}$
V1	0.56793 (8)	0.80814 (3)	0.01302 (8)	0.0177 (2)
O1	0.4892 (3)	0.70755 (14)	0.1799 (3)	0.0231 (4)
O2	0.4410 (5)	0.9007 (2)	0.0830 (5)	0.0389 (6)
O3	0.8367 (4)	0.8252 (2)	0.1074 (4)	0.0316 (5)
N1	0.8699 (4)	0.4182 (2)	0.0292 (5)	0.0228 (5)
C1	1.0005 (5)	0.4211 (2)	−0.1645 (6)	0.0271 (6)
C2	0.8003 (5)	0.5155 (2)	0.0843 (6)	0.0248 (6)

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

V1—O2	1.600 (3)	N1—C1	1.473 (4)
V1—O3	1.629 (3)	N1—C2	1.476 (4)
V1—O1^{i}	1.801 (3)	C1—C2^{ii}	1.492 (4)
V1—O1	1.803 (3)		
O2—V1—O3	108.5 (2)	O1^{i}—V1—O1	112.6 (1)
O2—V1—O1^{i}	108.1 (2)	V1^{iii}—O1—V1	125.0 (1)
O3—V1—O1^{i}	111.1 (2)	C1—N1—C2	110.7 (2)
O2—V1—O1	107.7 (2)	N1—C1—C2^{ii}	110.2 (3)
O3—V1—O1	108.7 (2)	N1—C2—C1^{ii}	110.5 (3)
C1—N1—C2···C1^{ii}	−57.6 (4)	C2—C1^{ii}—N1^{ii}—C2^{ii}	−57.4 (4)
N1—C2—C1^{ii}—N1^{ii}	57.3 (4)	C1^{ii}—N1^{ii}—C2^{ii}—C1	57.6 (4)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
N1—H1···O1^{i}	2.04 (4)	2.85 (4)	170 (4)
N1—H2···O3^{ii}	1.88 (4)	2.70 (4)	168 (4)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $2-x, y-\frac{1}{2}, \frac{1}{2}-z$.

H atoms were refined isotropically, resulting in N—H bond lengths in the range 0.82–0.84 Å and C—H bond lengths in the range 0.92–0.96 Å. The values of $U_{\rm iso}$ for the H atoms lie in the range 0.019–0.042 Å^2.

Data reduction: *XP*21 (Pavelčík, unpublished program). Program(s) used to solve structure: *XFPS* (Pavelčík, Sivý, Rizzoli & Andreetti, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: BK1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Zirconocene Complex, $[\{\eta^5\text{-}C_5H_4\text{-}C(CH_2)_5(CH_2)_2CH(CH_3)_2\}_2ZrCl_2]$

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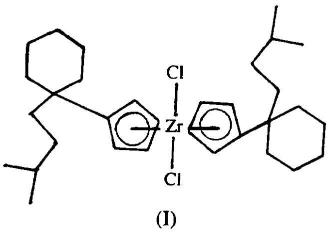
Abstract

The title compound, dichlorobis{η^5-[1-(3-methylbutyl)-cyclohex-1-yl]cyclopentadienyl}zirconium(IV), $[ZrCl_2(C_{16}H_{25})_2]$, has a pseudo-tetrahedral bent-metallocene structure in which the substituted cyclopentadienyl rings are asymmetrically bonded to the central Zr atom, due primarily to the interaction between the large substituents and the Cl atoms. The molecule has local C_2 symmetry with the substituents positioned in a *trans* arrangement and directed towards the lateral sectors of the bent-metallocene unit.

Comment

Studies on variations of the Group 4 metallocene structures (Erker *et al.*, 1989) are a topic of great interest, primarily because of their unprecedented behaviour as catalyst precursors of homogeneous Ziegler–Natta polymerization systems (Sinn, Kaminsky, Vollmer & Woldt, 1980; Sinn & Kaminsky, 1980). The addition of stereochemistry-controlling substituents to the cyclopentadienyl (Cp) rings of zirconocene catalyst precursors influences considerably their α-olefin-polymerization activity (Kaminsky, 1986; Kaminsky, Engehausen, Zoumis, Spaleck & Rohrmann, 1992; Chien & Razavi, 1988; Tian & Huang, 1994), their molecular weight and their specific stereoselectivity (Erker *et al.*, 1991). In this paper, we present the structural study of a new substituted zirconocene, dichlorobis{η^5-[1-(3-methylbutyl)cyclohex-1-yl]cyclopentadienyl}zirconium(IV), (I).



(I)

The molecular structure of the title compound has bent C_2-symmetric metallocene geometry, with the zirconium centre pseudo-tetrahedrally coordinated by two