Table 4. *Least-squares planes and deviations* (Å) *of individual atoms*

The equations of the planes are in the form $Ax + By + Cz = D$, where x,y,z are fractional coordinates.

Plane through N(1), N(2), O(1) and O(3)

$$-1{\cdot}557x - 2{\cdot}715y + 25{\cdot}370z = 14{\cdot}663$$

Cu(1)	0·261 (1)	C(3)	−0·587 (10)
N(1)	−0·257 (8)	C(4)	0·298 (11)
N(2)	0·259 (8)	O(1)	−0·269 (6)
C(1)	−0·217 (11)	O(3)	0·266 (8)
C(2)	0·133 (11)		

Plane through N(3), N(4), O(6) and O(8)

$$-6{\cdot}923x + 6{\cdot}765y + 7{\cdot}140z = 6{\cdot}164$$

Cu(2)	0·044 (1)	C(12)	−0·192 (11)
N(3)	0·044 (8)	C(13)	0·437 (10)
N(4)	−0·044 (9)	O(6)	−0·046 (7)
C(10)	−0·165 (11)	O(8)	0·046 (7)
C(11)	−0·095 (11)		

Cu(1)–O(3), 149·8 (2) and 179·2 (2)° respectively. N(1)–Cu(1)–O(3) is distorted towards the trigonal angle 120°, while N(2)–Cu(1)–O(3) is distorted towards 180° so that the coordination of Cu(1) is nearly trigonal bipyramidal.

The coordination of Cu(2) is square planar. Two N atoms from the other diamine molecule and two O atoms from the bridging oxalate ion are coordinated to Cu(2) in almost regular square-planar arrangement. Cu(2) deviates only 0·044 (1) Å from the N(3), N(4), O(6), O(8) plane.

Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H···*A*	H···*A*	*D*···*A*	*D*–H···*A*
N(1)–H(N1)···O(8^{i})	2·18 (5)	3·014 (6)	165 (5)
N(2)–H′(N2)···O(9)	2·09 (6)	2·874 (8)	160 (5)
N(3)–H(N3)···O(4^{ii})	2·27 (6)	2·987 (7)	140 (4)
N(4)–H′(N4)···O(5^{iii})	2·05 (5)	2·907 (6)	139 (4)
O(9)–H(O9)···O(2^{iv})	2·04 (7)	2·804 (7)	169 (7)
O(9)–H′(O9)···O(1)	2·22 (6)	3·000 (7)	127 (5)

Symmetry code

(i) $-x, \frac{1}{2} + y, \frac{3}{2} - z$
(ii) $-1 + x, y, z$
(iii) $-x, -\frac{1}{2} + y, \frac{3}{2} - z$
(iv) $-x, -y, 1 - z$

Bond lengths and angles in the diamine molecules and oxalate ions are as expected. The packing is determined by intermolecular hydrogen bonds involving the water molecule, the diamine N atoms, and O atoms from the oxalate ions. The parameters of the hydrogen bonds are listed in Table 5.

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N,N,N′,N′-Tetramethylethylenediammonium Aquabis(malonato)oxovanadate(IV) Dihydrate

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Abstract. $C_6H_{18}N_2^{2+}.C_6H_6O_{10}V^{2-}.2H_2O$, orthorhombic, *Pnma*, $a = 11{\cdot}185\,(3)$, $b = 18{\cdot}512\,(3)$, $c = 9{\cdot}434\,(4)$ Å, $Z = 4$. The structure was refined to $R = 0{\cdot}038$ for 1409 observed reflections. The crystal structure is formed from $C_6H_{18}N_2^{2+}$ cations, $[VO(H_2O)(C_3H_2O_4)_2]^{2-}$ anions and water molecules. The V atom is coordinated to six O atoms in the form of a distorted octahedron. The malonate ions are chelated in a *trans* arrangement, the lengths of the equatorial bonds being 1·981 (2) and 1·995 (2) Å. The apical sites are taken by the oxo O atom and by a water O atom at 1·589 (4) and 2·281 (4) Å, respectively. The remaining water molecules link the complex anions by hydrogen bonding.

Introduction. The magnetic properties of oxovanadium(IV) complexes with carboxylic acids have been

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extensively studied (Syamal, 1975), but crystal structures of only a few oxovanadium(IV) carboxylate complexes have been reported (Forrest & Prout, 1967; Bernsted, Belford & Paul, 1968; Tapscott, Belford & Paul, 1968; Oughtred, Raper & Shearer, 1976; Rieskamp & Mattes, 1976).

Oxovanadium(IV) carbonate (prepared from $VOSO_4.5H_2O$ and $BaCO_3$), malonic acid and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine were mixed in the molar ratio 1:1:1 in aqueous methanol and warmed. After cooling, the olive-green precipitate was filtered off and the mother liquor evaporated to dryness, leaving blue crystals of the title compound.

Cell parameters and the intensities of 1784 reflections were measured with a Syntex $P2_1$ automatic four-circle diffractometer (graphite monochromator, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, ω-scan method, $3 < 2\theta < 55°$). The intensities of 1409 independent reflections with $I > 3\sigma(I)$ were adopted for the structure determination. The structure was solved with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the full-matrix least-squares technique (Stewart, 1976). Anisotropic temperature factors were used for all non-hydrogen atoms. The H atoms were determined from a difference map and included in the refinement with fixed isotropic temperature factors of $U = 0{\cdot}06$ Å^2. Scattering factors, and corrections for anomalous dispersion for V, were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w||F_o| - |F_c||^2$ where $w = (20{\cdot}0 + |F_o| + 0{\cdot}0133|F_o|^2 + 0{\cdot}0002|F_o|^3)^{-1}$. Three low-angle intense reflections (020, 101, 002) were considered to be affected by extinction and were removed from the last cycles. A final difference synthesis was featureless. The final R and R_w were 0·038 and 0·052, respectively.* The atomic coordinates, interatomic distances and bond lengths are listed in Tables 1, 2 and 3, the complex anion is

Table 1. *Fractional atomic coordinates* (×10^4) *and* U_{eq} (×10^2) *for the non-hydrogen atoms*

	x	y	z	U_{eq} (Å^2)
V	4813·8 (5)	2500	5914·3 (7)	3·5
O(1)	6026 (2)	1738 (1)	5588 (2)	4·9
O(2)	7743 (2)	1248 (1)	5023 (3)	5·0
O(3)	3583 (2)	1736 (1)	5605 (2)	4·3
O(4)	1974 (2)	1242 (1)	4682 (3)	5·0
O(5)	4810 (3)	2500	7598 (5)	6·2
O(6)	4747 (4)	2500	3498 (4)	4·7
O(7)	4767 (2)	1318 (1)	1726 (2)	6·8
N(1)	5538 (2)	5443 (1)	3298 (2)	3·3
C(1)	7106 (2)	1784 (1)	5173 (3)	3·7
C(2)	7646 (5)	2500	4833 (9)	7·7
C(3)	2535 (2)	1779 (1)	5045 (3)	3·5
C(4)	1935 (4)	2500	4882 (7)	5·8
C(5)	4725 (2)	5030 (2)	4271 (3)	3·3
C(6)	6676 (3)	5056 (2)	2985 (4)	4·7
C(7)	4900 (3)	5635 (2)	1961 (3)	4·6

Table 2. *Fractional atomic coordinates* (×10^3) *of the* H *atoms*

	x	y	z
H(O6)	473 (3)	210 (2)	301 (4)
H(O7)	534 (3)	131 (2)	127 (4)
H′(O7)	423 (3)	131 (2)	123 (4)
H(N1)	573 (3)	586 (2)	374 (4)
H(C2)	850 (5)	250	504 (5)
H′(C2)	773 (5)	250	390 (6)
H(C4)	161 (5)	250	403 (5)
H′(C4)	126 (5)	250	553 (5)
H(C5)	398 (3)	529 (2)	434 (3)
H′(C5)	464 (3)	455 (2)	388 (4)
H(C6)	649 (3)	459 (2)	260 (4)
H′(C6)	713 (3)	497 (2)	383 (4)
H″(C6)	703 (3)	527 (2)	233 (4)
H(C7)	418 (3)	592 (2)	217 (3)
H′(C7)	473 (3)	519 (2)	148 (4)
H″(C7)	546 (3)	594 (2)	137 (4)

Table 3. *Bond lengths* (Å) *and angles* (°)

V–O(1)	1·981 (2)	C(3)–O(3)	1·287 (3)
V–O(3)	1·995 (2)	C(3)–O(4)	1·226 (3)
V–O(5)	1·589 (4)	C(3)–C(4)	1·502 (3)
V–O(6)	2·281 (4)	C(5)–C(5$^{\rm i}$)	1·511 (4)
C(1)–O(1)	1·272 (3)	N(1)–C(5)	1·501 (3)
C(1)–O(2)	1·231 (3)	N(1)–C(6)	1·491 (4)
C(1)–C(2)	1·491 (4)	N(1)–C(7)	1·492 (4)

O(1)–V–O(1$^{\rm ii}$)	90·8 (1)	O(1)–C(1)–C(2)	120·7 (3)
O(1)–V–O(3)	86·9 (1)	O(2)–C(1)–C(2)	117·2 (3)
O(1)–V–O(3$^{\rm ii}$)	162·6 (1)	C(1)–C(2)–C(1$^{\rm ii}$)	125·4 (4)
O(1)–V–O(5)	99·1 (1)	O(3)–C(3)–O(4)	122·1 (2)
O(1)–V–O(6)	82·4 (1)	O(3)–C(3)–C(4)	120·3 (3)
O(3)–V–O(3$^{\rm ii}$)	90·2 (1)	O(4)–C(3)–C(4)	117·6 (3)
O(3)–V–O(5)	98·3 (1)	C(3)–C(4)–C(3$^{\rm ii}$)	125·4 (2)
O(3)–V–O(6)	80·3 (1)	N(1)–C(5)–C(5$^{\rm i}$)	110·3 (2)
O(5)–V–O(6)	178·0 (1)	C(5)–N(1)–C(6)	113·2 (2)
V–O(1)–C(1)	130·5 (2)	C(5)–N(1)–C(7)	110·4 (2)
V–O(3)–C(3)	130·1 (2)	C(6)–N(1)–C(7)	110·8 (2)
O(1)–C(1)–O(2)	122·1 (2)		

Symmetry code

(i) $1-x, 1-y, 1-z$ (ii) $x, \frac{1}{2}-y, z$

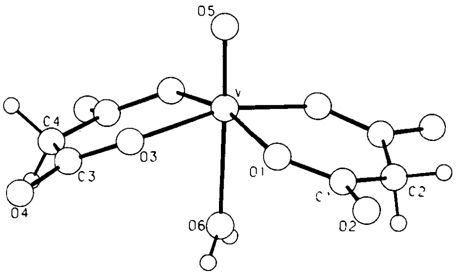

Fig. 1. Perspective view of the complex anion.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35422 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

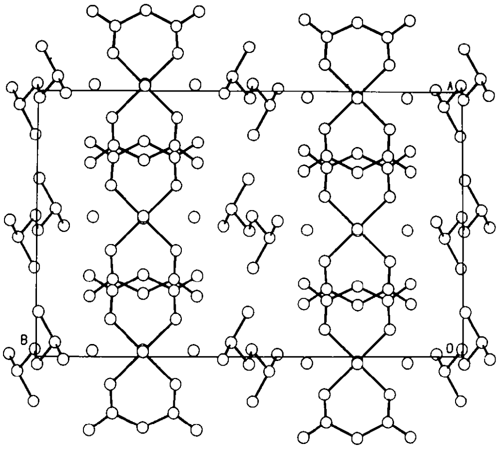

Fig. 2. Projection of the structure along **c**.

depicted in Fig. 1, and a projection of the structure along **c** appears in Fig. 2.

Discussion. The structure consists of *N,N,N′,N′*-tetramethylethylenediammonium cations, aquabis(malonato)oxovanadate(IV) anions and water molecules. As can be seen in Fig. 1, the two malonate ions are coordinated in a *trans* arrangement. This coordination differs from that in bis(oxalato)vanadate complexes, where the two oxalate ions coordinate in a *cis* arrangement, *e.g.* in diammonium aquabis(oxalato)oxovanadate(IV) (Oughtred, Raper & Shearer, 1976), triammonium bis(oxalato)dioxovanadate(V) dihydrate (Scheidt, Tsai & Hoard, 1971) and tripotassium bis(oxalato)dioxovanadate(V) (Drew, Einstein & Gransden, 1974). The anion has exact *m* and almost *mm* symmetry. The two six-membered V–malonate rings have different conformations, one having a boat and the other a chair conformation (Table 4).

The V atom is coordinated by six O atoms in the form of a distorted octahedron with four equatorial V—O(carbonyl) distances of 1·981 (2) and 1·995 (2) Å. The apical sites are taken by the oxo O and by a water molecule. The short V—O(5) bond of 1·589 (4) Å is typical for oxovanadate compounds. The long apical distance of 2·281 (4) Å is also comparable with values in similar structures. The V atom is elevated from the equatorial plane (plane I, Table 4) by 0·300 (2) Å.

The bond lengths in the malonate ions are normal. The C—O lengths vary according to whether or not the O atom is coordinated or uncoordinated. This variance has previously been observed in bis(oxalato)-oxovanadate complexes (Oughtred *et al.*, 1976). The C—O distances for coordinated O atoms, C(1)—O(1) 1·272 (3) and C(3)—O(3) 1·287 (3) Å, are longer than the corresponding uncoordinated distances, C(1)—O(2) 1·231 (3) and C(3)—O(4) 1·226 (3) Å.

Table 4. *Distances* (10^{-3} Å) *of atoms from different planes in the anion*

Atoms with an asterisk are used to define the plane.

Equations of planes with reference to the cell axes

Plane (I): $0.066X + 9.434Z = 5.311$
Plane (II): $3.446X + 8.975Z = 7.092$
Plane (III): $-4.593X + 8.602Z = 3.176$

Plane (I)		Plane (II)		Plane (III)	
V	300 (2)	V	−125 (2)	V	−299 (2)
O(1)*	0	O(1)*	0	O(3)*	0
O(1^{i})*	0	O(1^{i})*	0	O(3^{i})*	0
O(3)*	0	O(2)	84 (7)	O(4)	−55 (7)
O(3^{i})*	0	C(1)*	0	C(3)*	0
C(1)	−384 (9)	C(1^{i})*	0	C(3^{i})*	0
C(2)	−701 (20)	C(2)	−119 (20)	C(4)	135 (16)
C(3)	−534 (9)				
C(4)	−693 (16)				

Symmetry code

(i) $x, \frac{1}{2}-y, z$

Table 5. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H···*A*	*D*···*A*	H···*A*	∠*D*–H···*A*
O(6)–H(O6)···O(7)	2·753 (3)	1·89 (4)	172 (3)
O(7)–H(O7)···O(4^{i})	2·806 (3)	2·04 (4)	172 (4)
O(7)–H′(O7)···O(2^{ii})	2·804 (3)	2·05 (4)	176 (4)
N(1)–H(N1)···O(3^{iii})	2·788 (3)	1·89 (4)	168 (3)

Symmetry code

(i) $\frac{1}{2}+x, \quad y, \frac{1}{2}-z$ (ii) $-\frac{1}{2}+x, y, \frac{1}{2}-z$
(iii) $1-x, \frac{1}{2}+y, 1-z$

The *N,N,N′,N′*-tetramethylethylenediammonium cation is in a *trans* configuration and the cation has $\bar{1}$ symmetry.

All water H atoms participate in hydrogen bonding (Table 5). H atoms of the apical water molecule [O(6)] form hydrogen bonds to O(7) and this O atom links two symmetry-related anions. H atoms bonded to O(7) form hydrogen bonds involving the uncoordinated malonate atoms O(2) and O(4). These bonds link the anions into layers parallel to the *ac* plane. The layers of anions and cations are held together by hydrogen bonding between N(1) and the coordinated malonate O(3).

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trans-Diamminebis[dimethylglyoximato(1−)]cobalt(III) Nitrate *and* Thiocyanate*

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Abstract. $[Co(C_4H_7N_2O_2)_2(NH_3)_2]NO_3$, *trans*-$[(NH_3)_2\,Co(Hdmg)_2]NO_3$, Hdmg = the monoanion of dimethylglyoxime, monoclinic, $P2_1/c$, $a = 9{\cdot}940\,(2)$, $b = 6{\cdot}3847\,(7)$, $c = 12{\cdot}558\,(2)$ Å, $\beta = 99{\cdot}872\,(3)°$, $U = 785{\cdot}2$ Å^3, $Z = 2$, $d_m = 1{\cdot}629\,(12)$, $d_c = 1{\cdot}629$ Mg m^{-3} $R_1 = 0{\cdot}026$, $R_2 = 0{\cdot}038$. $[Co(C_4H_7N_2O_2)_2(NH_3)_2]SCN.H_2O$, *trans*-$[(NH_3)_2Co(Hdmg)_2]SCN.H_2O$, orthorhombic, $Pmmn$, $a = 7{\cdot}0346\,(8)$, $b = 10{\cdot}528\,(2)$, $c = 11{\cdot}476\,(3)$ Å, $U = 849{\cdot}9$ Å^3, $Z = 2$, $d_m = 1{\cdot}563\,(8)$, $d_c = 1{\cdot}568$ Mg m^{-3}, $R_1 = 0{\cdot}036$, $R_2 = 0{\cdot}022$. The six-coordinate cobalt complexes have the expected *trans* geometry with coplanar Hdmg ligands joined by a strong hydrogen bond between oxime O atoms. There is no evidence favoring formulation as $[(NH_3)_2(H_2dmg)Co(dmg)]^+$. The two cation structures are essentially identical and the Co—N(NH$_3$) bonds are 1·951 (2) (NO_3^- salt) and 1·957 (2) Å (SCN^- salt).

Introduction. To extend the 'Structural *trans* Effect' (STE) series which has been established (Heeg, Elder & Deutsch, 1980) for octahedral complexes of the type $[(NH_3)_5CoX]^{n+}$, we have begun a program to determine structures of the type $[(NH_3)Co(Hdmg)_2X]^{+,0,-}$. To define a zero for this STE series we determined the structures of *trans*-$[(NH_3)_2Co(Hdmg)_2]Br$ (Heeg & Elder, 1980) as well as *trans*-$[(NH_3)_2Co(Hdmg)_2]NO_3$ and *trans*-$[(NH_3)_2Co(Hdmg)_2]SCN.H_2O$ which we report here.

Amber-colored crystals of *trans*-$[(NH_3)_2Co(Hdmg)_2]NO_3$ were formed by simple metathesis from a solution of the Cl^- salt (Nakatsuka & Iinuma, 1936) using NH_4NO_3. Replacement of the Cl^- by NO_3^- was shown both by the lack of AgCl precipitate when $AgNO_3$ was added to a solution of the NO_3^- crystals and the presence of a strong NO_3^- absorption band in the IR spectrum. A crystal (0·21 × 0·15 × 0·30 mm) of the NO_3 salt was mounted and a Syntex $P\bar{1}$ diffractometer used with Mo radiation to measure unit-cell constants (14 pairs of reflections), systematic absences and intensity data in our usual manner (Heeg & Elder, 1980). Intensities for 1803 reflections (hkl, $hk\bar{l}$, $2{\cdot}5 \leq 2\theta \leq 50°$) were averaged where necessary to yield 1295 unique, observed reflections [$I > 2\sigma(I)$]. Other details of data collection were as follows: scan rate 1·0–6·0° min^{-1}; scan range 1·5° in 2θ; max h 12; max k 8; max l 15. Examination of the intensity data showed systematic absences for $h0l$, l odd and $0k0$, k odd in agreement with space group $P2_1/c$. With $Z = 2$, this requires that both the complex cation and the NO_3^- anion have site symmetry $\bar{1}$ as found for a previous determination of this structure from projections (Viswanathan & Kunchur, 1961). An independent solution derived from a Patterson vector map was consistent with the published solution (Co at 0,0,0 and N at $\frac{1}{2}$,0,0), and confirmed the space-group assignment. Electron density maps showed positions for all non H atoms including six O atoms of one-half weight about N(4), yielding a static, disordered NO_3^-. This model was refined without difficulty. H atoms were found from a difference electron density map (ΔF map). Those on NH_3 and the oxime H atom were well behaved on refinement. A ΔF map at this point showed a second set of H atoms on CH_3 staggered between holes at the sites of the original H-atom positions for CH_3. Further investigation showed that the final model with six fixed H atoms each of half-weight on CH_3 was clearly

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* Dimethylglyoxime ≡ 2,3-butanedione dioxime.

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