C1—C2	1.5201 (13)	C4—N4	1.470 (2)
C2—N2	1.4819 (13)		
N2—Cu1—N2^{i}	91.09 (5)	O3—C3—C4	108.03 (9)
N2—Cu1—N4	85.46 (4)	O3—C3—C2	111.87 (9)
O1—C1—C2	109.74 (9)	C4—C3—C2	114.56 (10)
C2—C1—C2^{i}	113.97 (12)	N4—C4—C3	111.49 (8)
N2—C2—C1	111.20 (9)	C3—C4—C3^{i}	109.38 (13)
N2—C2—C3	111.96 (9)	C2—N2—Cu1	119.08 (7)
C1—C2—C3	109.78 (10)	C4—N4—Cu1	114.21 (10)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H21N···O3^{i}	0.785 (13)	2.347 (14)	3.1292 (13)	173.7 (14)
N2—H22N···Cl2^{ii}	0.864 (13)	2.668 (13)	3.4763 (9)	156.3 (12)
N4—H41N···O3^{iii}	0.796 (15)	2.673 (14)	3.4068 (15)	154.1 (13)
O1—H1O···O2*W*^{i}	0.755 (9)	2.029 (10)	2.7808 (15)	174 (3)
O3—H3O···O1*W*^{iv}	0.759 (8)	2.057 (9)	2.8026 (12)	167.2 (16)
O1*W*—H11*W*···Cl1^{v}	0.785 (12)	2.409 (12)	3.1836 (16)	169 (2)
O1*W*—H12*W*···Cl2^{v}	0.795 (12)	2.403 (15)	3.1389 (16)	154 (2)
O2*W*—H21*W*···Cl1^{vi}	0.791 (12)	2.360 (12)	3.146 (2)	173 (3)
O2*W*—H22*W*···O1	0.782 (12)	2.010 (14)	2.7808 (15)	169 (3)

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

The assignment of the centrosymmetric space group *Cmcm* instead of the non-centrosymmetric subgroup *Cmc*2_1 was based on arguments summarized by Marsh (1995). The atomic coordinates of all H atoms were taken from difference Fourier syntheses. Atomic coordinates and individual U_{iso} values for all H atoms belonging to the NH_2 groups were refined. The atomic coordinates for H atoms of OH groups were refined with the O—H distance restrained to a plausible value and the U_{iso} values set to $1.3U_{eq}(O)$. H atoms belonging to water molecules and the H atoms bonded to C atoms were refined with the O—H and C—H distances restrained to one common value for each type. The U_{iso} values were set to $1.5U_{eq}(O)$ or $1.2U_{eq}(C)$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS* for reducing diffractometer data and *X-RED* (Stoe & Cie, 1996) for absorption correction by indexed crystal faces. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1250). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 616–618

$[Ni(C_{10}H_8N_2)_3]_2[V_4O_{12}].11H_2O$

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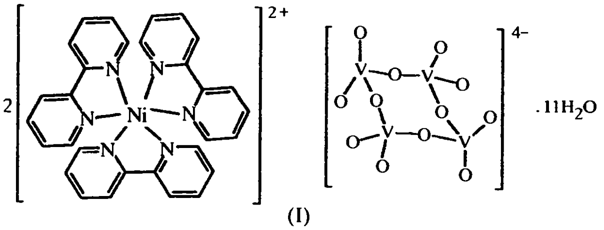
(*Received 27 August 1997; accepted 5 December 1997*)

Abstract

The crystal structure of the title compound, bis[tris(2,2′-bipyridyl-*N*,*N*′)nickel(II)] *cyclo*-tetravanadate undecahydrate, contains a centrosymmetric $[V_4O_{12}]^{4-}$ anion, which has an eight-membered ring structure formed by four VO_4 tetrahedra sharing vertices, and two complex cations containing octahedrally-coordinated Ni^{II} ions. The anion and coordinated Ni^{II} ions are isolated and make up anion and cation layers, respectively. The Ni—N distances range from 2.077 (3) to 2.112 (2) Å and the V—O distances range from 1.621 (2) to 1.803 (2) Å.

Comment

The isopolyanions $[(\eta\text{-}C_8H_{12})Ir(V_4O_{12})]^{3-}$ and $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$, which contain the ring anion $[V_4O_{12}]^{4-}$, were first synthesized by Day *et al.* (1990). Recently, some vanadium oxides consisting of $[V_4O_{12}]^{4-}$ clusters containing complex cations [transition metal cations coordinated by 2,2′-bipyridyl (bipy)], such as $[Cu(bipy)][V_2O_6]$ and $[Cu(bipy)_2][V_2O_6]$ (DeBord *et al.*, 1996), $[VO(VO_3)_6\{VO(bipy)_2\}_2]$ (Huan *et al.*, 1991), $[Zn(bipy)_2]_2[V_4O_{12}]$, $[Zn(phen)_2]_2[V_4O_{12}].H_2O$ and $[Zn(bipy)_3]_2[V_4O_{12}].11H_2O$ (Zhang *et al.*, 1997), have been reported. We report here the structure of a new compound, (I), built from complexed nickel cations, $[Ni(C_{10}H_8N_2)_3]^{2+}$, water molecules of crystallization and *cyclo*-tetravanadate anions, $[V_4O_{12}]^{4-}$.



(I)

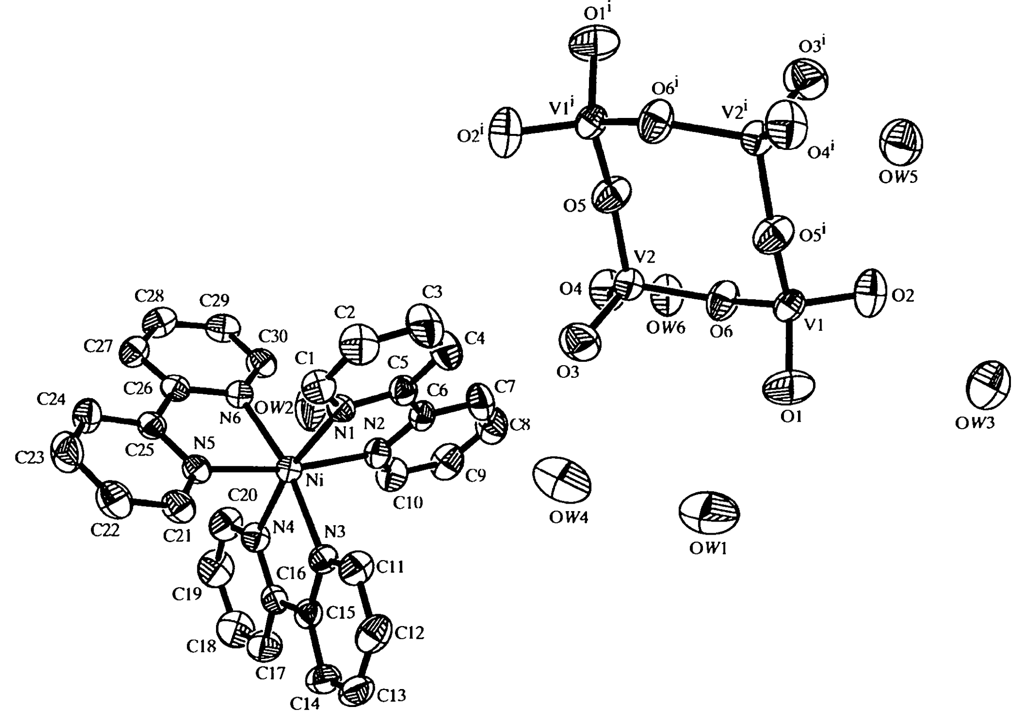


Fig. 1. View of the title compound with displacement ellipsoids at the 50% probability level. [Symmetry code: (i) $-x, 2-y, 1-z$.]

The structure of the *cyclo*-tetravanadate anion (Fig. 1) is essentially identical to that observed in $[Zn(bipy)_3]_2[V_4O_{12}].11H_2O$ (Zhang *et al.*, 1997). The Ni- and Zn-containing compounds are apparently isostructural. The $[V_4O_{12}]^{4-}$ anions and $[Ni(C_{10}H_8N_2)_3]^{2+}$ cations form layers separated by water molecules. The anion has a ring-like eight-membered centrosymmetric $\{V_4O_4\}$ core formed by corner-sharing of four distorted VO_4 tetrahedra. In the anion, each tetrahedron contains two terminal and two bridging O atoms, which have bond distances ranging from 1.621 (2) to 1.641 (3) and from 1.782 (2) to 1.803 (2) Å, respectively; these distances are similar to those found in $[Zn(bipy)_3]_2[V_4O_{12}].11H_2O$ (Zhang *et al.*, 1997).

Experimental

The synthesis of (I) was carried out by hydrothermal reaction of H_2O, V_2O_5, H_3PO_3, $H_2C_2O_4.2H_2O$, $Ni(CH_3COO)_2.4H_2O$, Ni powder, $H_2N(CH_2)_2NH_2$ and 2,2′-bipyridyl (molar ratio 900:6:20:4:2.5:2.5:20:1.6) in a 30 ml Teflon-lined stainless-steel autoclave for 3 d at 433 K. The pink crystals were isolated from a solution cooled to room temperature.

Crystal data

$[Ni(C_{10}H_8N_2)_3]_2[V_4O_{12}]$.-
$11H_2O$
$M_r = 1648.46$
Monoclinic
$C2/c$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 4.72$–$12.73°$
$a = 21.880 (2)$ Å
$b = 13.918 (1)$ Å
$c = 23.829 (2)$ Å
$\beta = 105.745 (1)°$
$V = 6984.3 (1)$ Å^3
$Z = 4$
$D_x = 1.568$ Mg m^{-3}
D_m not measured
$\mu = 1.126$ mm^{-1}
$T = 293 (2)$ K
Prism
0.50 × 0.42 × 0.36 mm
Pink

Data collection

Siemens *P*4 diffractometer
ω–2θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.563$, $T_{max} = 0.667$
7528 measured reflections
6153 independent reflections
4659 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 25°$
$h = -1 \rightarrow 26$
$k = -1 \rightarrow 16$
$l = -28 \rightarrow 27$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.108$
$S = 0.962$
6153 reflections
456 parameters
All H atoms except those of water were refined and assigned $U_{iso} = 0.08$ Å^2
$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 0.453$ e Å^{-3}
$\Delta\rho_{min} = -0.268$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni—N3	2.077 (3)	O5—V1^i	1.790 (2)
Ni—N6	2.085 (2)	N1—C1	1.340 (4)
Ni—N1	2.086 (2)	N1—C5	1.349 (4)
Ni—N5	2.095 (3)	N2—C10	1.338 (4)
Ni—N2	2.101 (3)	N2—C6	1.349 (4)
Ni—N4	2.112 (2)	C1—C2	1.376 (5)
V1—O1	1.621 (2)	C2—C3	1.367 (5)
V1—O2	1.638 (2)	C3—C4	1.382 (5)
V1—O5^i	1.790 (2)	C4—C5	1.388 (5)
V1—O6	1.803 (2)	C5—C6	1.474 (4)
V2—O4	1.638 (2)	C6—C7	1.380 (5)
V2—O3	1.641 (3)	C7—C8	1.379 (5)
V2—O5	1.782 (2)	C8—C9	1.375 (5)
V2—O6	1.784 (2)	C9—C10	1.370 (5)
N3—Ni—N6	168.80 (10)	O2—V1—O6	107.40 (12)
N3—Ni—N1	94.37 (10)	O5^i—V1—O6	111.30 (11)
N6—Ni—N1	95.40 (10)	O4—V2—O3	108.75 (14)
N3—Ni—N5	95.15 (10)	O4—V2—O5	109.73 (12)
N6—Ni—N5	78.53 (10)	O3—V2—O5	109.75 (13)
N1—Ni—N5	95.21 (10)	O4—V2—O6	109.60 (12)
N3—Ni—N2	92.07 (10)	O3—V2—O6	111.43 (13)
N6—Ni—N2	95.27 (10)	O5—V2—O6	107.56 (12)
N1—Ni—N2	78.21 (10)	V2—O5—V1^i	155.6 (2)
N5—Ni—N2	170.60 (10)	V2—O6—V1	135.64 (14)
N3—Ni—N4	78.74 (10)	C1—N1—C5	118.2 (3)
N6—Ni—N4	92.31 (10)	N1—C1—C2	122.9 (3)
N1—Ni—N4	169.35 (10)	C3—C2—C1	119.1 (3)
N5—Ni—N4	93.51 (10)	C2—C3—C4	119.0 (3)
N2—Ni—N4	93.80 (10)	C3—C4—C5	119.3 (4)
O1—V1—O2	107.92 (15)	N1—C5—C4	121.5 (3)
O1—V1—O5^i	109.31 (13)	N1—C5—C6	115.8 (3)
O2—V1—O5^i	109.75 (13)	C4—C5—C6	122.7 (3)
O1—V1—O6	111.07 (14)		

Symmetry code: (i) $-x, 2-y, 1-z$.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus* (Siemens, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

This work was supported by the National Natural Science Foundation of China, Development Project of Science and Technology of Jilin Province, and the Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1193). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 618–621

Potassium 3-Formyl-2,4-dinitrophenolate Dihydrate

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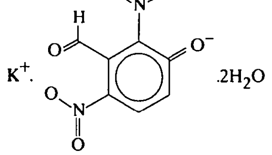
(*Received 28 October 1997; accepted 21 November 1997*)

Abstract

The extended conjugation of the phenoxide O atom in the title compound, $K^+.C_7H_3N_2O_6^-.2H_2O$, gives the ring a slight quinonoid character. The substituents deviate significantly from the plane of the ring, the largest deviations being those of the formyl, 2-nitro and 4-nitro groups, which are twisted by 81 (1), 45.06 (15) and 9.08 (12)°, respectively. The structure consists of infinite chains running along the *c* axis. These chains are stacked perpendicular to the shortest axis, *a*, in two alternating layers related by the 2_1 screw axis. The cation is coordinated by six O atoms at distances of 2.750 (2)–2.972 (2) Å. The phenoxide O atom does not belong to the first coordination shell; it is an acceptor with respect to the water molecules in a three-dimensional network of hydrogen bonds.

Comment

The title compound, (I), was synthesized as a precursor for the synthesis of *meso*-aryl-substituted porphyrins, designed to be used in the preparation of metalloporphyrins for oxidation catalysis.



(I)

Acta Crystallographica Section C
ISSN 0108-2701 © 1998