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A Novel Octanuclear Mixed-Metal Cluster: $Na_2[Cr_{0.5}Fe_{0.5}Mo_3O_4(O_2CEt)_8]_2$

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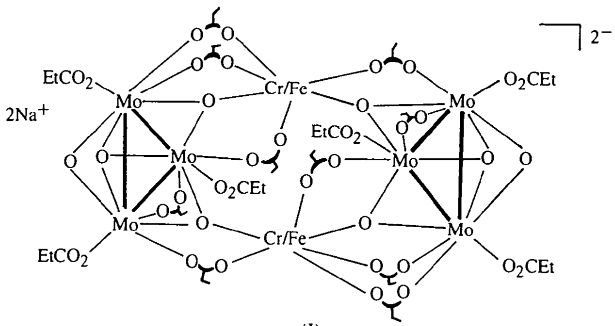
Abstract

The structure of disodium bis[μ-oxo-tri-μ_3-oxo-pentakis(μ-propionato-κO:$\kappa O'$)tris(propionato-κO)-0.5-chromium-0.5-irontrimolybdenum](3 *Mo—Mo*), $Na_2[Cr_{0.5}Fe_{0.5}Mo_3O_4(C_3H_5O_2)_8]_2$, consists of a centrosymmetric cluster anion, $[(EtCO_2)_8Mo_3O_4CrFeO_4Mo_3(O_2CEt)_8]^{2-}$, in which two Mo_3O_4 units are joined by the Fe and Cr atoms to complete a circular $[Mo_3O_4CrFeO_4Mo_3]^{14+}$ species. Each Na atom is coordinated to five O atoms to form a trigonal bipyramid with an average Na—O distance of 2.32 (2) Å. The anions are connected by Na cations to form a one-dimensional infinite chain structure.

Comment

Triangular trinuclear cluster species with an $[M_3O_4]^{4+}$ core (M = Mo, W) have been studied extensively (Mardon & Pernick, 1973; Murmann & Shelton, 1980). The sandwich-cubane type $[Mo_3S_4M'S_4Mo_3]$ and double-cubane type $[M_3S_4M'M'S_4M_3]$ species have been investigated by Shibahara, Akashi, Yamasaki & Hashimoto (1991), and Wolff, Berg, Hodgson, Frankel & Holm (1979). Here, we report a novel insoluble octanuclear mixed-metal cluster with a circular $[Mo_3O_4CrFeO_4Mo_3]^{14+}$ cation.

The black crystals of title compound, (I), were obtained from the redox reaction of $Na_2MoO_4.2H_2O$ with $Cr(CO)_6$ and $Fe(CO)_5$ in propionic anhydride. The crystals are very stable in air and difficult to dissolve in water, general organic solvents and acids.



(I)

The X-ray structure study indicates that Cr and Fe atoms are disordered in the crystal lattice. The structure of $Na_2[MMo_3O_4(O_2CEt)_8]_2$ (M = 0.5Cr + 0.5Fe) consists of an octanuclear centrosymmetric anion $[(EtCo_2)_8Mo_3O_4MMO_4Mo_3(O_2CEt)_8]^{2-}$, where the two $[Mo_3O_4(O_2CEt)_8]^{4-}$ units are joined by two M atoms through four μ_3-O (from μ_2-O atoms in both the Mo_3 units) and eight bridging $EtCO_2$ groups as shown in Fig. 1.

Each M atom is coordinated by six O atoms, two from μ_3-O atoms and four from propionate bridges. They complete regular octahedral coordination. The average M—μ_3-O bond length of 1.980 (9) Å is significantly longer than the Fe—μ_3-O length of 1.905 (5) Å found in the related cation $[Fe_3O(O_2CR)_6L_3]^+$ (Blake & Fraser, 1975) or the Cr—μ_3-O length of 1.89 Å in $[Cr_3O(O_2CR)_6L_3]^+$ (Chang & Jeffrey, 1970), as a result of the Fe_3O or Cr_3O four-centre *d–p–d* π-bonding found in the latter two.

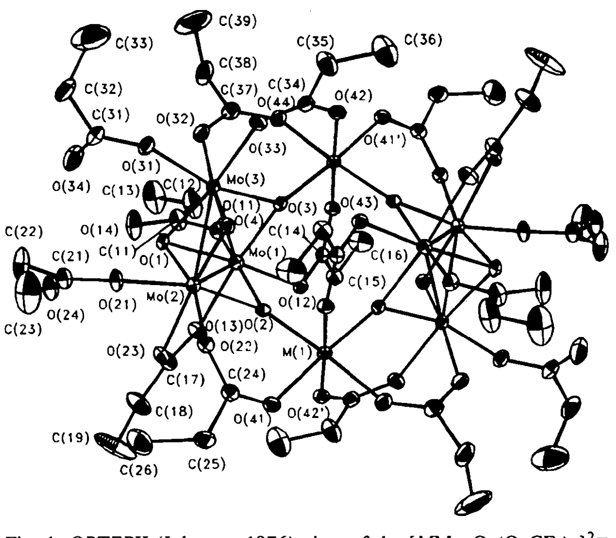


Fig. 1. *ORTEP*II (Johnson, 1976) view of the $[MMo_3O_4(O_2CEt)_8]_2^{2-}$ anion, where M = 0.5Cr + 0.5Fe. Displacement ellipsoids are drawn at the 20% probability level.

The $[Mo_3O_4(O_2CEt)_8]^{4-}$ unit is similar to other Mo_3O_4 species except for the propionate O(13)—C(17)—O(23) bridge spanning the Mo(1)—Mo(2) edge. Each Mo atom is bonded to six O atoms: three bridging O atoms [one μ_2-O and two μ_3-O atoms for Mo(2) and Mo(3), three μ_3-O atoms for Mo(1)], one O_t (terminal $EtCO_2$) and two O_{br} (bridging $EtCO_2$) atoms, forming a distorted octahedron. Bond lengths and angles of the Mo_3 unit in the octanuclear anion are similar to those in the discrete Mo_3O_4 species reported previously, except that Mo—μ_3-O (from μ_2-O atoms in both Mo_3 units) has an average bond length of 1.948 (9) Å, which is significantly longer than the corresponding Mo—μ_2-O bond lengths reported previously (*e.g.* 1.908 (7) Å; Benory, Bino, Gibson, Cotton & Dori, 1985). The average Mo—Mo distance [2.519 (3) Å] is comparable with those in $[Mo_3O_4(edta)_{3/2}]_2^{4-}$ [2.51 (1) Å; Bino, Cotton & Dori, 1979], suggesting that the formal oxidation states of the Mo atoms should be IV.

M(1), O(2), Mo(1) and O(3) form a nearly planar $Mo_2M_2O_4$ eight-membered ring about the symmetry centre. The average distance of the eight atoms from the least-squares plane is 0.30 Å. Each of the M metal atoms is also bonded to two bridging O atoms of each of the Mo_3O_4 units, thus forming four nearly planar MMo_2O units, *i.e.* the M(1)Mo(1)Mo(2)O(2) and M(1')Mo(1)Mo(3)O(3) units, in which the average M—Mo distance is 3.64 (9) Å, attesting to the absence of M—Mo bonding.

Each Na atom is five-coordinate. The coordination polyhedron is a trigonal bipyramid, consisting of one capping O, three O_t atoms from one anion and one O_t atom from another. The cluster anions are connected by Na atoms to constitute a chain structure characteristic of Na_2O_2 four-membered cycles about the unit-cell origin. The short Na—O distances [2.32 (2) Å] and the chain structure may be responsible for the insolubility of the compound.

Experimental

Preparation of the title compound was carried out in air. A mixture of $Na_2MoO_4.2H_2O$ and $Cr(CO)_6$ was heated and dissolved in propionic anhydride. $Fe(CO)_5$ was added to the solution which was kept heated at 393 K for 3 d. After cooling, well formed black crystals of the title compound were obtained. Analysis: calculated for $Na_2CrFeMo_6O_{40}C_{48}H_{80}$ Na 2.27, Cr 2.57, Fe 2.75, Mo 28.42, C 28.46, H 3.95%; found Na 2.16, Cr 2.70, Fe 2.80, Mo 27.1, C 25.93, H 3.36%.

Crystal data

$Na_2[Cr_{0.5}Fe_{0.5}Mo_3O_4$-$(C_3H_5O_2)_8]_2$
M_r = 2026.6
Triclinic
$P\bar{1}$
a = 12.981 (5) Å
b = 14.021 (4) Å
c = 12.356 (6) Å
α = 109.81 (4)°
β = 117.51 (3)°
γ = 90.36 (4)°
V = 1840 (2) Å^3
Z = 1
D_x = 1.83 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 20 reflections
θ = 5.29–10.48°
μ = 1.39 mm^{-1}
T = 296 K
Plate
0.40 × 0.20 × 0.10 mm
Black

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.249, T_{max} = 0.870
6811 measured reflections
6811 independent reflections

3118 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 25°
$h = 0 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -14 \rightarrow 13$
3 standard reflections monitored every 250 reflections
intensity decay: 0.8%

Refinement

Refinement on F
R = 0.056
wR = 0.064
S = 1.09
3118 reflections
443 parameters
H atoms not located
$w = 1/[\sigma^2(F_o) + (0.02F_o)^2 + 1.00]$

$(\Delta/\sigma)_{max}$ = 0.04
$\Delta\rho_{max}$ = 0.98 (2) e Å^{-3}
$\Delta\rho_{min}$ = −0.73 (2) 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)

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

	x	y	z	B_{eq}
Mo(1)	0.95285 (9)	0.35618 (8)	0.28112 (9)	2.16 (2)
Mo(2)	1.12590 (9)	0.27984 (8)	0.39368 (9)	2.14 (2)
Mo(3)	0.9360 (1)	0.23979 (8)	0.3928 (1)	2.37 (3)

M(1)*	1.2242 (2)	0.5560 (1)	0.5648 (2)	1.98 (4)
O(1)	0.9680 (7)	0.2073 (6)	0.2375 (7)	2.5 (2)
O(2)	1.1146 (7)	0.4249 (6)	0.4244 (7)	2.5 (2)
O(3)	0.8999 (7)	0.3760 (6)	0.4084 (7)	2.4 (2)
O(4)	1.0969 (7)	0.2829 (6)	0.5334 (7)	2.5 (2)
O(11)	0.7937 (8)	0.3131 (7)	0.1205 (8)	3.8 (3)
O(12)	0.9180 (7)	0.5020 (7)	0.2805 (7)	2.8 (2)
O(13)	1.0202 (8)	0.3523 (7)	0.1521 (8)	3.5 (2)
O(14)	0.766 (1)	0.1599 (9)	−0.035 (1)	5.7 (4)
O(21)	1.1774 (8)	0.1426 (7)	0.3623 (8)	3.0 (2)
O(22)	1.3098 (7)	0.3316 (7)	0.5279 (7)	2.7 (2)
O(23)	1.1778 (7)	0.2904 (7)	0.2570 (7)	3.1 (2)
O(24)	1.103 (1)	0.0472 (8)	0.1471 (9)	4.9 (3)
O(31)	0.9269 (8)	0.0901 (7)	0.3685 (8)	3.7 (3)
O(32)	0.7501 (8)	0.1857 (7)	0.2600 (9)	3.8 (3)
O(33)	0.8966 (8)	0.2549 (7)	0.5451 (8)	3.4 (2)
O(34)	0.867 (1)	−0.0138 (9)	0.162 (1)	7.0 (4)
O(41)	1.3563 (8)	0.4919 (7)	0.5498 (8)	3.5 (2)
O(42)	0.8052 (8)	0.3903 (7)	0.5746 (8)	3.1 (2)
O(43)	0.7518 (7)	0.4981 (6)	0.2987 (7)	2.6 (2)
O(44)	0.6569 (8)	0.3166 (7)	0.2961 (9)	3.5 (3)
C(11)	0.736 (1)	0.241 (1)	0.005 (1)	4.6 (5)
C(12)	0.617 (2)	0.267 (2)	−0.082 (2)	6.8 (7)
C(13)	0.545 (3)	0.183 (2)	−0.219 (2)	10 (1)
C(14)	0.818 (1)	0.5242 (9)	0.258 (1)	2.3 (3)
C(15)	0.769 (1)	0.584 (1)	0.167 (1)	3.9 (4)
C(16)	0.652 (2)	0.613 (1)	0.146 (2)	7.1 (6)
C(17)	1.114 (1)	0.319 (1)	0.166 (1)	3.6 (3)
C(18)	1.142 (1)	0.309 (1)	0.056 (1)	6.0 (5)
C(19)	1.274 (2)	0.298 (2)	0.103 (2)	10.2 (7)
C(21)	1.155 (1)	0.057 (1)	0.260 (1)	3.5 (4)
C(22)	1.206 (2)	−0.030 (1)	0.306 (2)	7.0 (6)
C(23)	1.331 (2)	0.002 (2)	0.421 (3)	8.9 (8)
C(24)	1.380 (1)	0.407 (1)	0.551 (1)	3.2 (3)
C(25)	1.506 (1)	0.396 (1)	0.583 (2)	4.8 (4)
C(26)	1.511 (2)	0.298 (2)	0.498 (2)	8.8 (8)
C(31)	0.890 (2)	0.000 (1)	0.274 (1)	4.6 (5)
C(32)	0.885 (2)	−0.090 (1)	0.314 (2)	7.2 (6)
C(33)	0.783 (3)	−0.094 (2)	0.338 (3)	12.7 (9)
C(34)	0.858 (1)	0.321 (1)	0.607 (1)	3.2 (3)
C(35)	0.874 (2)	0.313 (1)	0.731 (1)	6.4 (5)
C(36)	0.862 (2)	0.401 (2)	0.830 (2)	9.0 (8)
C(37)	0.660 (1)	0.223 (1)	0.240 (1)	3.6 (4)
C(38)	0.539 (2)	0.152 (2)	0.137 (2)	6.9 (7)
C(39)	0.513 (3)	0.082 (2)	0.188 (3)	14 (1)
Na(1)	0.8988 (5)	0.0612 (4)	0.0418 (5)	4.0 (2)

* *M*(1) = 0.5Cr + 0.5Fe.

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

Mo(1)—Mo(2)	2.506 (2)	Mo(3)—O(3)	1.937 (9)
Mo(1)—Mo(3)	2.533 (2)	Mo(3)—O(4)	1.915 (9)
Mo(2)—Mo(3)	2.519 (2)	Mo(3)—O(31)	2.01 (1)
Mo(1)—O(1)	2.007 (9)	Mo(3)—O(32)	2.14 (2)
Mo(1)—O(2)	1.964 (9)	Mo(3)—O(33)	2.11 (2)
Mo(1)—O(3)	1.931 (9)	*M*(1)—O(2)	1.984 (9)
Mo(1)—O(11)	1.99 (2)	*M*(1)—O(3′)	1.977 (9)
Mo(1)—O(12)	2.099 (9)	*M*(1)—O(41)	2.00 (2)
Mo(1)—O(13)	2.14 (2)	*M*(1)—O(42′)	1.99 (2)
Mo(2)—O(1)	1.987 (9)	*M*(1)—O(43′)	1.97 (1)
Mo(2)—O(2)	1.958 (9)	*M*(1)—O(44′)	1.99 (1)
Mo(2)—O(4)	1.917 (9)	O(1)—Na(1)	2.34 (2)
Mo(2)—O(21)	2.01 (1)	O(14)—Na(1)	2.28 (1)
Mo(2)—O(22)	2.12 (1)	O(24)—Na(1)	2.39 (1)
Mo(2)—O(23)	2.13 (1)	O(24′)—Na(1)	2.30 (1)
Mo(3)—O(1)	2.05 (1)	O(34)—Na(1)	2.26 (2)

Mo(1)—Mo(2)—Mo(3)	60.55 (5)	Mo(1)—Mo(3)—Mo(2)	59.47 (5)
Mo(2)—Mo(1)—O(1)	50.8 (3)	Mo(2)—Mo(1)—O(2)	50.2 (3)
Mo(2)—Mo(1)—O(3)	94.9 (3)	Mo(2)—Mo(1)—O(11)	139.8 (4)
Mo(2)—Mo(1)—O(12)	138.1 (3)	Mo(2)—Mo(1)—O(13)	86.2 (3)
Mo(3)—Mo(1)—O(1)	52.2 (3)	Mo(3)—Mo(1)—O(2)	92.2 (3)
Mo(3)—Mo(1)—O(3)	49.2 (3)	Mo(3)—Mo(1)—O(11)	101.7 (3)
Mo(3)—Mo(1)—O(12)	137.5 (3)	Mo(3)—Mo(1)—O(13)	135.9 (3)
O(1)—Mo(1)—O(2)	100.7 (4)	O(1)—Mo(1)—O(3)	100.8 (4)
O(1)—Mo(1)—O(11)	89.3 (5)	O(1)—Mo(1)—O(12)	167.1 (4)
O(1)—Mo(1)—O(13)	84.9 (4)	O(2)—Mo(1)—O(3)	90.6 (4)
O(2)—Mo(1)—O(11)	165.9 (4)	O(2)—Mo(1)—O(12)	88.1 (4)
O(2)—Mo(1)—O(13)	85.4 (4)	O(3)—Mo(1)—O(11)	97.3 (4)
O(3)—Mo(1)—O(12)	88.4 (4)	O(3)—Mo(1)—O(13)	173.6 (4)
O(11)—Mo(1)—O(12)	80.5 (5)	O(11)—Mo(1)—O(13)	85.8 (4)
O(12)—Mo(1)—O(13)	86.6 (4)	Mo(1)—Mo(2)—O(1)	51.6 (3)
Mo(1)—Mo(2)—O(2)	50.4 (3)	Mo(1)—Mo(2)—O(4)	96.7 (3)
Mo(1)—Mo(2)—O(21)	138.8 (3)	Mo(1)—Mo(2)—O(22)	137.4 (3)
Mo(1)—Mo(2)—O(23)	86.3 (3)	Mo(3)—Mo(2)—O(1)	52.6 (3)
Mo(3)—Mo(2)—O(2)	92.8 (3)	Mo(3)—Mo(2)—O(4)	48.9 (3)
Mo(3)—Mo(2)—O(21)	102.7 (3)	Mo(3)—Mo(2)—O(22)	139.8 (3)
Mo(3)—Mo(2)—O(23)	137.5 (3)	O(1)—Mo(2)—O(2)	101.7 (4)
O(1)—Mo(2)—O(4)	100.3 (4)	Mo(1)—Mo(3)—O(1)	50.6 (2)
Mo(1)—Mo(3)—O(3)	49.0 (3)	Mo(1)—Mo(3)—O(4)	95.9 (3)
Mo(1)—Mo(3)—O(31)	139.8 (4)	Mo(1)—Mo(3)—O(32)	93.1 (4)
Mo(1)—Mo(3)—O(33)	135.5 (3)	Mo(2)—Mo(3)—O(1)	50.3 (3)
Mo(2)—Mo(3)—O(3)	94.4 (3)	Mo(2)—Mo(3)—O(4)	48.9 (3)
Mo(2)—Mo(3)—O(31)	101.7 (3)	Mo(2)—Mo(3)—O(32)	140.9 (3)
Mo(2)—Mo(3)—O(33)	132.9 (3)	O(1)—Mo(3)—O(3)	99.1 (4)
O(1)—Mo(3)—O(4)	98.1 (4)	O(1)—Mo(3)—O(31)	89.6 (4)
O(1)—Mo(3)—O(32)	91.1 (4)	O(1)—Mo(3)—O(33)	173.4 (4)
O(3)—Mo(3)—O(4)	97.5 (4)	O(3)—Mo(3)—O(31)	163.7 (4)
O(3)—Mo(3)—O(32)	84.9 (4)	O(3)—Mo(3)—O(33)	86.7 (4)
O(4)—Mo(3)—O(31)	94.9 (4)	O(4)—Mo(3)—O(32)	169.9 (4)
O(4)—Mo(3)—O(33)	84.2 (4)	O(31)—Mo(3)—O(32)	81.1 (4)
O(31)—Mo(3)—O(33)	84.1 (4)	O(32)—Mo(3)—O(33)	86.2 (4)
O(2)—*M*(1)—O(41)	87.8 (4)	O(2)—*M*(1)—O(42′)	88.8 (4)
O(2)—*M*(1)—O(43′)	90.3 (4)	O(2)—*M*(1)—O(44′)	176.1 (5)
O(3′)—*M*(1)—O(41)	176.4 (5)	O(3′)—*M*(1)—O(42′)	89.7 (4)
O(3′)—*M*(1)—O(43′)	89.0 (4)	O(3′)—*M*(1)—O(44′)	88.9 (4)
O(41)—*M*(1)—O(42′)	92.5 (4)	O(41)—*M*(1)—O(43′)	89.0 (5)
O(41)—*M*(1)—O(44′)	88.3 (5)	O(42′)—*M*(1)—O(43′)	178.4 (4)
O(42′)—*M*(1)—O(44′)	91.0 (4)	O(43′)—*M*(1)—O(44′)	90.0 (5)
Mo(1)—O(1)—Na(1)	134.8 (5)	Mo(2)—O(1)—Na(1)	135.2 (5)
Mo(1)—O(2)—*M*(1)	147.3 (5)	Mo(2)—O(2)—*M*(1)	132.1 (5)
Mo(1)—O(3)—Mo(3)	81.8 (3)	Mo(1)—O(3)—Co(1′)	133.6 (5)
Mo(3)—O(3)—Co(1′)	132.9 (5)	O(1)—Na(1)—O(14)	80.9 (4)
O(24)—Na(1)—O(34)	117.1 (5)	O(1)—Na(1)—O(24)	81.3 (4)
O(1)—Na(1)—O(24′)	155.6 (5)	O(1)—Na(1)—O(34)	81.8 (4)
O(14)—Na—O(24)	146.7 (6)	O(14)—Na(1)—O(24)	102.3 (4)
O(14)—Na(1)—O(34)	115.3 (6)	O(24′)—Na(1)—O(24)	83.6 (4)

The structure was solved by direct methods using *MULTAN*11/82 (Main *et al.*, 1982) and refined by full-matrix least-squares techniques with anisotropic displacement parameters for all non-H atoms. All calculations were performed on a VAX 785 computer using the *SDP* package (Frenz, 1978). Molecular graphics were obtained using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(acetato)bis(pyridine-2-amidoxime-*N*,*N*′)nickel(II)–Ethanol (1/2)

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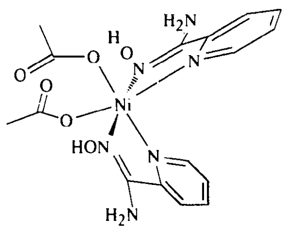
Abstract

The mononuclear complex of the title compound [alternative IUPAC name: bis(acetato-*O*)bis(pyridine-2-carboxamide oxime-*N*,*N*′)nickel(II)–ethanol (1/2)], $[Ni(C_2H_3O_2)_2(C_6H_7N_3O)_2].2C_2H_5OH$, crystallizes from ethanol as a disolvate. The coordination geometry at the Ni atom is distorted octahedral, with crystallographic twofold symmetry. The pyridine-2-carboxamide oxime ligands are coordinated to the metal through the N atoms of the pyridine ring and the oxime group. The acetate ligands are monodentate. The ethanol solvate molecule is linked to the non-coordinated O atom of the acetate ligand *via* a hydrogen bond.

Comment

Amidoximes and their complexes find a wide range of applications in technology, medicine and agriculture (Nicolaides & Varella, 1992). Recent attention has centred on the members of this group which form mono- or polynuclear chelate complexes (Pearse, Raithby & Maughan, 1994; Orama, Saarinen & Korvenranta, 1994). Pyridine-2-amidoxime (py2ao) is known to form stable complexes with various metals (Sanyal, Modak & Mudi, 1983), some of which are exploited in analytical chemistry (Losada del Barrio, Abad & Vicente-Perez, 1986). However, little or no attention has been paid to coordination compounds arising from reactions of py2ao with acetates of the 3*d* metals in organic solvents, despite the fact that the problem could be of interest in view of a possible deprotonation of py2ao in the presence of acetate ions.

The title complex, (I) (Fig. 1), is mononuclear and the central Ni atom is located on a twofold axis ($\frac{1}{2}$, *y*, $\frac{1}{4}$). The coordination geometry is distorted octahedral, the major distortions being N3—Ni—N3($1 - x, y, \frac{1}{2} - z$) 166.2 (2) and N3—Ni—N1 76.18 (11)°. Two mutually *cis* positions are occupied by the O2 atoms of the two monodentate acetato ligands and the two other pairs are occupied by the chelating pyridine N1 and oxime N3 atoms and their symmetry equivalents of the py2ao ligands. The N3 atoms are mutually *trans* and the N1 atoms mutually *cis*.



(I)

Electroneutrality requires that the py2ao ligand is not deprotonated during complex formation, as was confirmed by location of all H atoms. Since pyridine-2-aldoxime loses a proton on complexation to nickel(II) chloride in neutral aqueous solution, we suggest that the NH_2 group of py2ao stabilizes the oxime group

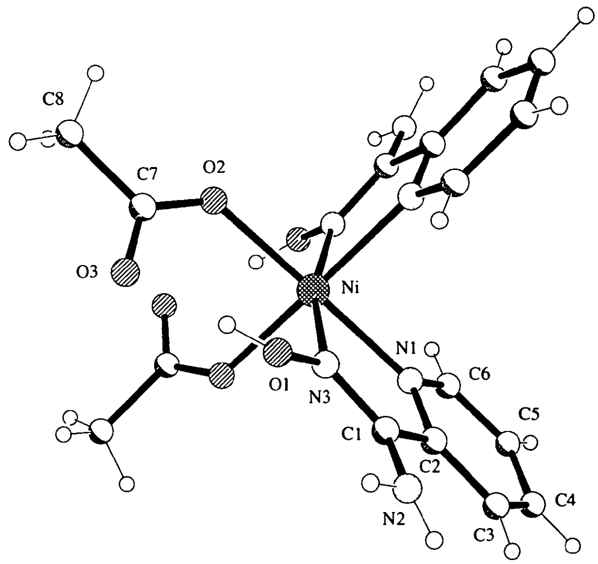


Fig. 1. The title complex in the crystal (solvent omitted). Radii are arbitrary and only the asymmetric unit is numbered.

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