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Tris(ethylenediamine)nickel(II) tetraoxo-molybdate(VI)

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The crystal structure of the title compound, $[Ni(C_2H_8N_2)_3][MoO_4]$, is composed of tetrahedral $[MoO_4]^{2-}$ anions and octahedral $[Ni(en)_3]^{2+}$ cations (en is ethylenediamine), both ions lying on special positions of site symmetry 2. The components are held together in a three-dimensional network by hydrogen-bonding interactions.

Comment

In recent decades, organic–inorganic hybrid materials have attracted extensive interest owing to their potential applications in many fields such as catalysis, magnetism, and photochemistry (Braun *et al.*, 1999). Hydrothermal synthesis techniques, combined with amine-ligated transition metal complex cations, have proven to be a popular methodology for the isolation of such materials, *e.g.* $[\{Cu(pn)_2\}_7\{V_{16}O_{38}(H_2O)\}_2]$ (pn is 1,2-diaminopropane; Lin & Liu, 2002), $(H_2pn)_4(H_3O)[Ni(pn)_2][Na_3Mo_{12}O_{52}P_8(OH)_{10}]$ (Huang *et al.*, 2003), $[Co(bpy)Mo_3O_{10}]$ (bpy is 2,2'-bipyridine; Zapf *et al.*, 1997), $[\{Cu(bpy)_2\}\{Cu(bpy)(H_2O)\}(Mo_5O_{15})\{O_3P(CH_2)_4PO_3\}]$ (Finn *et al.*, 2001) and $[Cu(en)_2]_3[\{Cu(en)_2\}_2(H_2W_{12}O_{42})]$ (Lin *et al.*, 2003). More recently, several metal oxides including $[M(en)_3]^{n+}$ complex cations (en is ethylenediamine) have been synthesized, including $[Ni(en)_3][VO_3]_2$ (Liu *et al.*, 2000), $[Ni(en)_3]_2Na[Mo_8V_8O_{40}(PO_4)]\cdot H_2O$ (Xu *et al.*, 1999), $[Co(en)_3]H_3O[(CoO_6)Mo_6O_{18}(As_3O_3)_2]\cdot 2H_2O$ (He & Wang, 1999) and $[Co(en)_3][C_4H_{12}N_2]_{0.5}[(Mo_5O_{15})(HPO_4)_2]\cdot 3H_2O$ (He *et al.*, 2004). This paper presents the hydrothermal synthesis and crystal structure of a new organic–inorganic hybrid, *viz.* $[Ni(en)_3][MoO_4]$, (I).
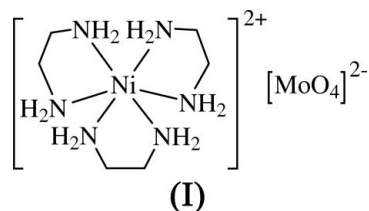
Compound (I) is isomorphous with the recently reported compound $[Zn(en)_3][MoO_4]$ (Han *et al.*, 2005). As shown in Fig. 1, the structure of (I) is made up of an $[MoO_4]^{2-}$ anion and a $[Ni(en)_3]^{2+}$ complex cation. The Mo atom, on a twofold axis, is in an MoO$_4$ tetrahedral environment, with the Mo—O bond distances (Table 1) in agreement with those observed in $[Co(en)MoO_4]$ (Lin, 2002) and $[Zn(en)_3][MoO_4]$ (Han *et al.*, 2005). The Ni atom, which also lies on a twofold axis, exhibits an octahedral coordination geometry completed by six N atoms from three ethylenediamine ligands; the Ni—N distances are also in accordance with those observed in
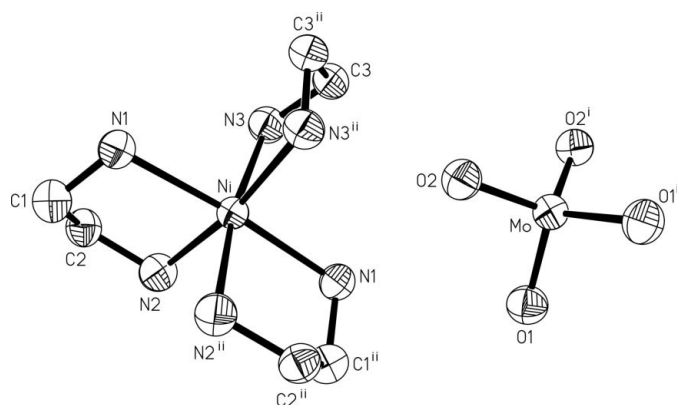
Figure 1
The structure of (I), showing the metal atom coordination environments, with 50% probability displacement ellipsoids. H atoms have been omitted. [Symmetry code: (i) $-x, -x + y, -z + \frac{1}{2}$; (ii) $y, x, -z + \frac{1}{2}$.]

[Ni(en)$_3$]$_2$Na[Mo$_8$V$_8$O$_{40}$(PO$_4$)]·H$_2$O (Xu *et al.*, 1999) and [Ni(en)$_3$][VO$_3$]$_2$ (Liu *et al.*, 2000).

The [MoO$_4$]$^{2-}$ anions and [Ni(en)$_3$]$^{2+}$ complex cations in the crystal structure of (I) interact with each other mainly through electrostatic interactions. There is extensive hydrogen bonding among the NH groups of the [Ni(en)$_3$]$^{2+}$ complex cations and the O atoms of the [MoO$_4$]$^{2-}$ anions, with N···O interatomic distances ranging from 2.765 (3) to 3.510 (3) Å (Table 2). These hydrogen-bonding interactions hold the [MoO$_4$]$^{2-}$ anions and [Ni(en)$_3$]$^{2+}$ complex cations together in a three-dimensional supramolecular network.

Experimental

Compound (I) was synthesized hydrothermally under autogenous pressure. A mixture of (NH$_4$)$_6$Mo$_7$O$_{24}$, Ni$_2$C$_2$O$_4$, ethylenediamine and water in the molar ratio 1:1:27.8:166.6 was sealed in a 17 ml Teflon-lined autoclave and heated at 403 K for 48 h. The reaction mixture was cooled slowly to room temperature at a rate of 10 K h^{-1} and violet block-shaped crystals of (I) were obtained. These crystals were filtered off, washed with distilled water and dried in air (87% yield, based on molybdenum). The pH values of the medium decreased from 11.2 before heating to 10.6 at the end of the reaction. The strong features at 982, 811 and 703 cm^{-1} in the IR spectrum of (I) are attributed to Mo—O stretching vibrations, and the bands at 1411, 1276, 1207, 1115 and 1043 cm^{-1} are related to the C—C and C—N stretching vibrations. The weight loss of (I) in the range 457–689 K is 44.57%, in agreement with the calculated removal of the en molecules associated with the Ni^{2+} cations (44.20%). Analysis calculated for C$_6$H$_{24}$MoN$_6$NiO$_4$: C 18.07, H 6.06, N 21.07, Ni 14.71, Mo 24.05%; found: C 17.92, H 6.15, N 21.14, Ni 14.58, Mo 23.87%.

Crystal data

[Ni(C$_2$H$_8$N$_2$)$_3$][MoO$_4$]	Mo $K\alpha$ radiation
$M_r = 398.96$	Cell parameters from 200
Trigonal, $P\bar{3}c1$	reflections
$a = 16.0024$ (16) Å	$\theta = 10$–$20°$
$c = 9.9608$ (19) Å	$\mu = 2.15$ mm^{-1}
$V = 2209.0$ (5) Å^3	$T = 291$ (2) K
$Z = 6$	Block, violet
$D_x = 1.799$ Mg m^{-3}	$0.20 \times 0.12 \times 0.08$ mm

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.037$
ω–2θ scans	$\theta_{max} = 28.0°$
Absorption correction: ψ scan	$h = -18 \rightarrow 18$
(North *et al.*, 1968)	$k = -21 \rightarrow 21$
$T_{min} = 0.674$, $T_{max} = 0.847$	$l = -13 \rightarrow 13$
5355 measured reflections	3 standard reflections
1785 independent reflections	every 150 reflections
1538 reflections with $I > 2\sigma(I)$	intensity decay: 0.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0867P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 1.4958P]$
$wR(F^2) = 0.153$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
1785 reflections	$\Delta\rho_{max} = 0.94$ e Å^{-3}
83 parameters	$\Delta\rho_{min} = -0.53$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni—N3	2.132 (3)	Mo—O1	1.6832 (18)
Ni—N2	2.140 (3)	Mo—O2	1.7326 (17)
Ni—N1	2.156 (2)		
N3—Ni—N3^i	79.28 (14)	N3^i—Ni—N1	90.24 (10)
N3—Ni—N2^i	170.85 (11)	N2—Ni—N1	82.65 (12)
N3—Ni—N2	95.32 (11)	N1^i—Ni—N1	175.32 (13)
N2^i—Ni—N2	90.95 (15)	O1^{ii}—Mo—O1	109.50 (13)
N3—Ni—N1^i	90.24 (10)	O1—Mo—O2^{ii}	107.42 (8)
N2—Ni—N1^i	94.05 (10)	O1—Mo—O2	108.27 (9)
N3—Ni—N1	93.36 (11)	O2^{ii}—Mo—O2	115.85 (11)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O2^{iii}	0.90	2.19	3.028 (3)	154
N2—H2C···O1^{iv}	0.90	2.04	2.934 (3)	170
N2—H2D···O1^v	0.90	2.64	3.510 (3)	164
N3—H3C···O2^{vi}	0.90	2.42	3.236 (3)	152
N3—H3D···O2^i	0.90	1.88	2.765 (3)	169

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

All H atoms were positioned geometrically and allowed to ride on their parent C and N atoms, with C—H distances of 0.97 Å and N—H of 0.90 Å, with U_{iso}(H) = 1.2U_{eq}(parent atom).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1987); cell refinement: *TEXSAN* (Molecular Structure Corporation, 1987); data reduction: *TEXSAN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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