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Tris(1,10-phenanthroline)nickel(II) hexamolybdate

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Key indicators

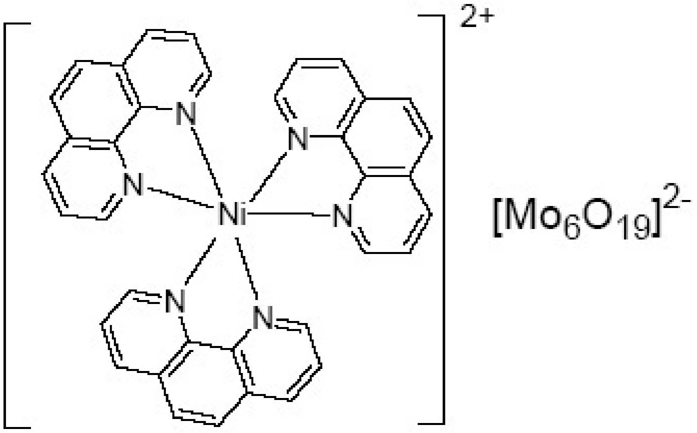
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.006 Å
R factor = 0.028
wR factor = 0.079
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $[Ni(C_8H_6N_2)_3][Mo_6O_{19}]$, contains centrosymmetric $[Mo_6O_{19}]^{2-}$ hexamolybdate anions, which are built up from distorted MoO_6 units by edge-sharing. The nickel atom in the $[Ni(phen)_3]^{2+}$ cation adopts distorted octahedral coordination with three *N*,*N*′-bidentate 1,10-phenanthroline (phen) ligands. The crystal packing is stabilized by some weak π–π stacking interactions between neighboring phen ligands, and some C—H···O interactions. The Ni atom occupies a special position with twofold symmetry.

Comment

Polyoxometalates have been attracting extensive interest in solid-state materials chemistry because of their potential applications in catalysis, electrochromism, magnetism and medicine, as well as the variety of their structures (Stein *et al.*, 1993; Hagrman *et al.*, 1997; Hagrman *et al.*, 1999). The introduction of transition metal–ligand units can not only enrich the frameworks of polyoxometalates, but also alter their electronic and magnetic properties (Hagrman & Zubieta, 1999; You *et al.*, 2001; Xu *et al.*, 2002). The secondary metal–ligand complex $[ML_3]^{n+}$ (M = transition metal and L = organic ligand) may be directly coordinated through bridging oxo groups, forming a bimetallic phase, or it may be present only as a discrete charge-balancing cation. In the latter case, an $[ML_3]^{n+}$-type counter-cation often occurs in the vanadium oxides with discrete clusters or one-dimensional chain-like structures, such as in the compounds $[Zn(2,2'\text{-bpy})_3]_2[V_4O_{12}]$ and $[Ni(en)_3][VO_3]_2$ (Zhang *et al.*, 1997; Liu *et al.*, 2000).



(I)

In the present work, we have prepared the molybdate-containing salt $[Ni^{II}(phen)_3][Mo_6O_{19}]$ (phen is 1,10-phenanthroline), (I), and determined its crystal structure. The nickel

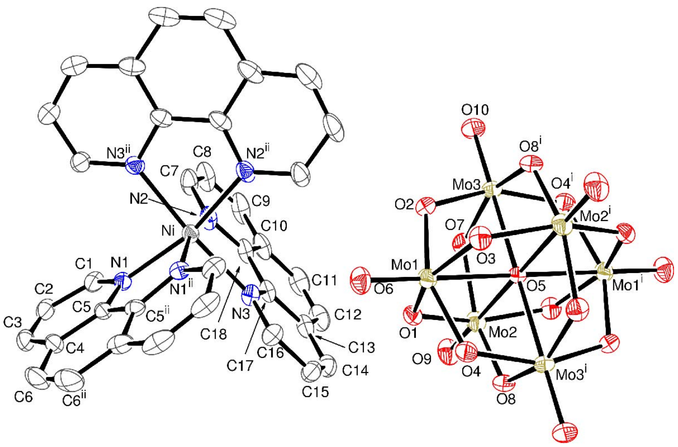


Figure 1
View of the component species in (I) showing 20% displacement ellipsoids (all H atoms are omitted for clarity). [Symmetry codes: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y$, $-x$; (ii) $-x$, y, $\frac{1}{2} - z$.]

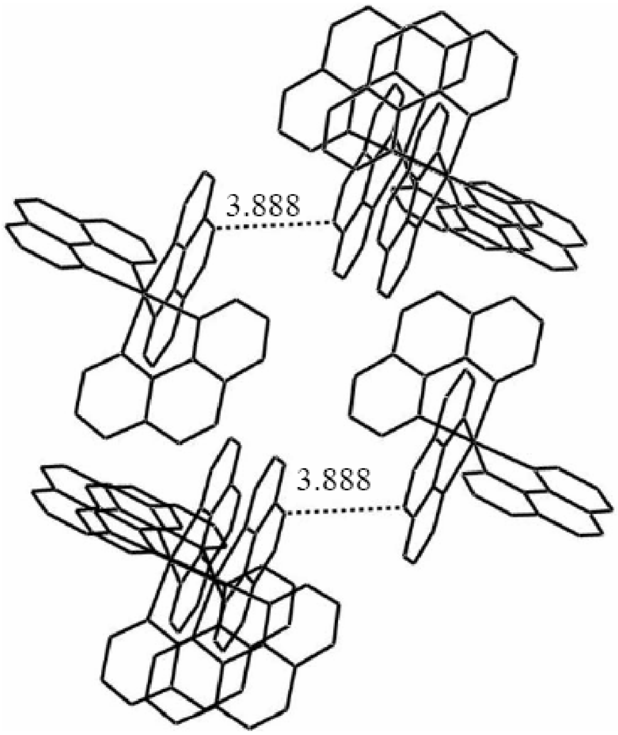


Figure 2
A view of the possible π–π stacking interactions (dashed lines) between the neighboring phen ligands in (I), with all H atoms omitted for clarity.

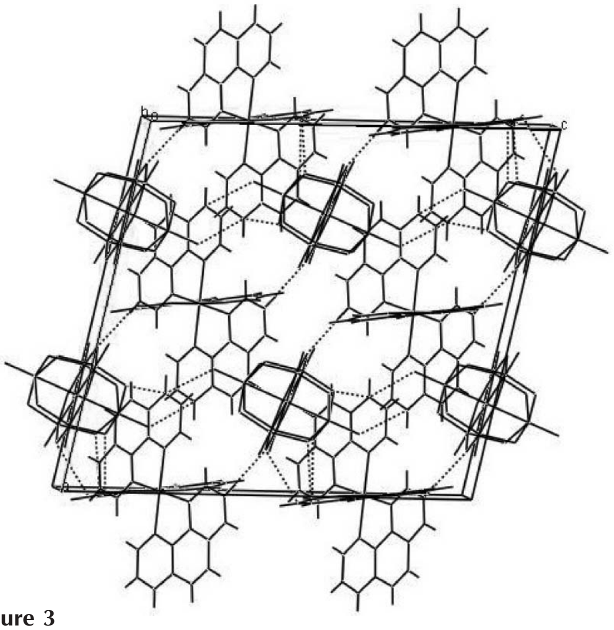


Figure 3
Packing diagram of (I), showing the possible C—H⋯O interactions (dashed lines), viewed along the *b* axis.

valence of +2 is in agreement with bond-valence calculations. The nickel cation adopts distorted octahedral coordination (Table 1 and Fig. 1), with six N atoms from three chelating bidentate phen ligands. The Ni atom occupies a special position with twofold symmetry. The bond distances and angles for the cation are comparable with those found in the complexes $[\mathrm{Ni(phen)_3}]\mathrm{I_2}$ and $[\mathrm{Ni(phen)_3}]_2[\mathrm{Cu_{10}H_2I_{16}}]$ (Gillard *et al.*, 1989). As for the anion, the discrete hexamolybdate is formed from six $\mathrm{MoO_6}$ units (Fig. 1). The complete anion is generated from the asymmetric unit by inversion symmetry, with the inversion centre occupied by atom O5. The geometrical parameters for the Mo atoms indicate substantial distortion from a regular octahedral shape, with *cis*–O—Mo—O bond angles in the range 75.67 (7)–104.23 (13)° and Mo—O bond lengths ranging from 1.674 (2)–2.332 (3) Å, which is consistent with the presence of three types of O atoms in the cluster, *viz*. terminal, bridging and octahedral (Fig. 1).

As well as electrostatic and van der Waals forces, the crystal packing in (I) appears to be influenced by π–π stacking involving some of the phen ligands (Fig. 2) with a ring separation of 3.888 Å. This distance is a little longer than that seen in comparable clusters. There are three possible C—H⋯O interactions in (I) (Table 2 and Fig. 3) in which the H⋯O separations vary from 2.41 to 2.59 Å. These weak interactions contribute to the three-dimensional network.

Experimental

A mixture of $\mathrm{Na_2MoO_4{\cdot}2H_2O}$ (0.493 g, 2.04 mmol), $\mathrm{NiSO_4}$ (0.143 g, 0.919 mmol), $\mathrm{H_2SeO_3}$ (0.259 g, 2.01 mmol) and 1,10-phenanthroline (0.157 g. 0.874 mmol) were fully dissolved in $\mathrm{H_2O}$ (10 ml) by stirring at room temperature in a 2.3:1:2.3:1:635 molar ratio. The mixture was adjusted to pH = 3.0 with 1 *M* hydrochloric acid. The solution was then sealed in a 30 ml Teflon-lined autoclave and was heated to 463 K for 3 d. The autoclave was cooled to room temperature at a rate of 10 K $\mathrm{h^{-1}}$. The resulting orange crystals of (I) were filtered off, washed with water and dried in air.

Crystal data

$[\mathrm{Ni(C_8H_6N_2)_3}][\mathrm{Mo_6O_{19}}]$
$M_r = 1478.96$
Monoclinic, $C2/c$
$a = 19.0062$ (18) Å
$b = 11.2552$ (11) Å
$c = 20.457$ (2) Å
$\beta = 102.273$ (2)°
$V = 4276.1$ (7) $\mathrm{Å^3}$
$Z = 4$
$D_x = 2.297$ Mg $\mathrm{m^{-3}}$
Mo $K\alpha$ radiation
Cell parameters from 12088 reflections
$\theta = 2.0$–26.4°
$\mu = 2.22$ $\mathrm{mm^{-1}}$
$T = 296$ (2) K
Block, orange
0.50 × 0.30 × 0.30 mm

Data collection

Bruker SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{\min} = 0.372$, $T_{\max} = 0.514$
12088 measured reflections
4355 independent reflections

3842 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 26.4°$
$h = -23 \rightarrow 12$
$k = -13 \rightarrow 14$
$l = -21 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.01$
4355 reflections
309 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 4P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.87$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mo1—O6	1.685 (2)	Mo2—O5	2.3223 (3)
Mo1—O2	1.912 (2)	Mo3—O10	1.690 (2)
Mo1—O1	1.913 (2)	Mo3—O7	1.899 (2)
Mo1—O4	1.936 (2)	Mo3—O4$^{\rm i}$	1.907 (2)
Mo1—O3	1.938 (2)	Mo3—O8$^{\rm i}$	1.933 (2)
Mo1—O5	2.3324 (3)	Mo3—O2	1.935 (2)
Mo2—O9	1.674 (2)	Mo3—O5	2.2942 (3)
Mo2—O8	1.908 (2)	Ni—N1	2.063 (2)
Mo2—O3$^{\rm i}$	1.916 (2)	Ni—N2	2.096 (3)
Mo2—O7	1.938 (2)	Ni—N3	2.144 (3)
Mo2—O1	1.945 (2)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$\cdots$O10$^{\rm ii}$	0.93	2.45	3.364 (7)	167
C9—H9$\cdots$O10$^{\rm iii}$	0.93	2.41	3.322 (5)	166
C11—H11$\cdots$O4$^{\rm iv}$	0.93	2.59	3.498 (5)	166

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

All H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding with the constraint $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ applied.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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