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Tris(ethylenediamine)zinc(II) molybdate(VI), $[Zn(en)_3][MoO_4]$

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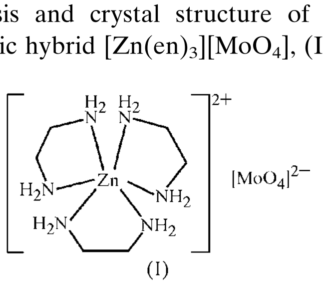
The crystal structure of the title compound, $[Zn(C_2H_8N_2)_3]$-$[MoO_4]$, is composed of $[MoO_4]^{2-}$ anions and $[Zn(en)_3]^{2+}$ complex cations (en is ethylenediamine), both with symmetry 2, which are held together in a three-dimensional network *via* hydrogen-bonding interactions. The $[Zn(en)_3]^{2+}$ cations in the crystal structure exhibit two configurations, *viz*. $\Lambda(\delta\delta\delta)$ and $\Delta(\lambda\lambda\lambda)$, as a pair of enantiomers.

Comment

There has been extensive interest in organic–inorganic hybrid materials in the past few years, reflecting their potential application in catalysis, conductivity and photochemistry, as well as their interesting structural features (Braun *et al.*, 1999). Exploitation of hydrothermal techniques, combined with amine-ligated transition metal complex cations, has been demonstrated as an effective strategy to obtain such materials, for example, $[Co(dien)_2][VO_3]_3\cdot H_2O$ (dien is diethylenetriamine; Lin, Li *et al.*, 2003), $[Co(bpy)Mo_3O_{10}]$ (bpy is 2,2′-bipyridine; Zapf *et al.*, 1997), $[Cu(en)_2]_2[Mo_8O_{26}]$ (en is ethylenediamine; DeBord *et al.*, 1997) and $[Cu(en)_2]_3$-$[\{Cu(en)_2\}_2(H_2W_{12}O_{42})]$ (Lin, Chen & Liu, 2003). More recently, several metal oxides, including $[M(en)_3]^{n+}$ complex cations, have been synthesized, including $[Ni(en)_3][VO_3]_2$ (Liu *et al.*, 2000) and $(C_4H_{12}N_2)_{0.5}[Co(en)_3][(Mo_5O_{15})(HPO_4)_2]$ (He *et al.*, 2004), but hybrids including $[Zn(en)_3]^{2+}$ complex cations are yet to be studied. This paper presents the hydrothermal synthesis and crystal structure of the title novel organic–inorganic hybrid $[Zn(en)_3][MoO_4]$, (I).



(I)

As shown in Fig. 1, the molecular structure of (I) is made up of an $[MoO_4]^{2-}$ anion and a $[Zn(en)_3]^{2+}$ complex cation. The Mo atom, on a twofold axis, is in an almost regular MoO_4 tetrahedral environment, with Mo—O bond distances ranging from 1.7243 (15) to 1.7354 (15) Å (Table 1), which are in accordance with those observed in $[Co(en)MoO_4]$ (Lin, 2002). The Zn atom, which also lies on a twofold axis, exhibits a distorted octahedral coordination geometry defined by six N atoms from three ethylenediamine ligands, with Zn—N distances ranging from 2.1573 (16) to 2.2079 (16) Å, which are in agreement with those observed in $[Zn(en)_3]_2[Sn_2Te_6]$ (Li *et al.*, 1998).

The $[MoO_4]^{2-}$ anions and $[Zn(en)_3]^{2+}$ complex cations in the crystal structure of (I) mainly interact with each other through electrostatic interactions, in which each anion is surrounded by five cations and each cation is surrounded by five anions.

The packing arrangement of (I) along the *c* axis is depicted in Fig. 2. There is extensive hydrogen bonding between the

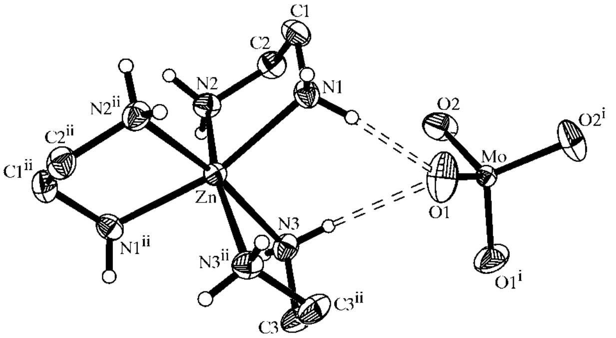


Figure 1
The molecular structure of (I), showing the metal-atom coordination environments and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, dashed lines denote the hydrogen-bonding interactions in the asymmetric unit and H atoms have been omitted for clarity. [Symmetry codes: (i) $x-y, -y, \frac{1}{2}-z$; (ii) $y, x, \frac{1}{2}-z$].

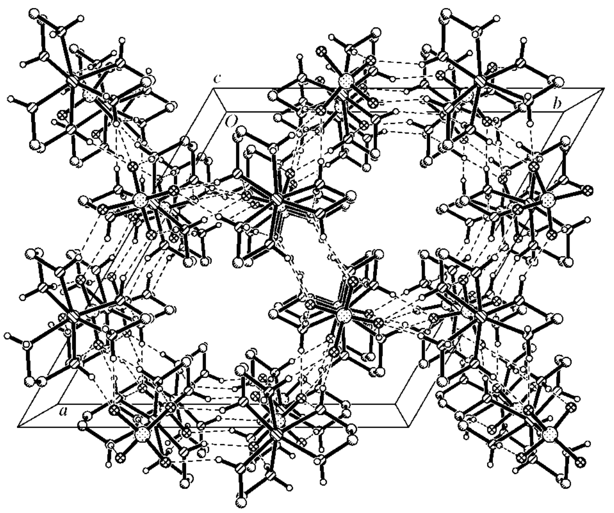


Figure 2
A packing view of (I) along the *c* axis, showing the extended three-dimensional network formed *via* the hydrogen-bonding interactions (dashed lines). The large striped, cross-hatched, small striped, large open, shaded and small open circles denote Mo, Zn, O, N, C and H atoms, respectively.

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N−H groups of the $[Zn(en)_3]^{2+}$ complex cations and the O atoms of the $[MoO_4]^{2-}$ anions, with N···O interatomic distances ranging from 2.894 (2) to 3.225 (3) Å (Table 2). These hydrogen-bonding interactions hold $[MoO_4]^{2-}$ anions and $[Zn(en)_3]^{2+}$ complex cations together in a three-dimensional network.

The $[MoO_4]^{2-}$ anions and $[Zn(en)_3]^{2+}$ cations in the crystal structure of (I) are arranged alternately along the *c* axis into one-dimensional linear chains *via* hydrogen-bonding interactions. All $[Zn(en)_3]^{2+}$ complex cations in a linear chain have a uniform configuration, and those in adjacent chains have the other configuration.

Experimental

Compound (I) was synthesized hydrothermally under autogenous pressure. A mixture of $(NH_4)_6Mo_7O_{24}$, $ZnCl_2$, $C_2H_2O_4$, ethylenediamine and water in the molar ratio 1:4:4:34.8:833 was sealed in a 17 ml Teflon-lined autoclave and heated at 393 K for 72 h. The reaction mixture was cooled slowly to room temperature at a rate of 12 K h^{-1} and green plate-like crystals of (I) were obtained. The resultant crystals were filtered off, washed with distilled water and dried in air (75% yield, based on molybdenum). The pH of the medium decreased from 10.2 before heating to 9.3 at the end of the reaction. The strong features at 934, 909, 861 and 653 cm^{-1} in the IR spectrum of (I) are attributed to Mo−O stretching vibrations, and the bands at 1407, 1223, 1199, 1118 and 1046 cm^{-1} are related to the C−C and C−N stretchings. The weight loss of (I) in the range 457–689 K is 44.77%, in agreement with the calculated removal of the en molecules associated with the Zn^{2+} cations (44.45%). Analysis calculated for $C_6H_{24}MoN_6O_4Zn$: C 17.76, H 5.96, N 20.72, Zn 16.12, Mo 23.65%; found: C 17.82, H 6.05, N 20.64, Zn 16.29, Mo 23.73%.

Crystal data

$[Zn(C_2H_8N_2)_3][MoO_4]$
M_r = 405.62
Trigonal, $P\bar{3}c1$
a = 15.8791 (19) Å
c = 9.905 (2) Å
V = 2163.0 (6) Å^3
Z = 6
D_x = 1.868 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 100 reflections
θ = 10–15°
μ = 2.55 mm^{-1}
T = 293 (2) K
Needle, colourless
0.42 × 0.17 × 0.09 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω/2*θ* scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
T_{min} = 0.414, T_{max} = 0.803
11 127 measured reflections
1658 independent reflections
1361 reflections with $I > 2\sigma(I)$

R_{int} = 0.052
θ_{max} = 27.5°
h = −20 → 17
k = −14 → 20
l = −12 → 12
3 standard reflections every 150 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.099
S = 1.03
1658 reflections
84 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.578P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0037 (3)

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

Table 1
Selected geometric parameters (Å, °).

Mo−O1	1.7243 (15)	Zn−N2	2.1845 (16)
Mo−O2	1.7354 (15)	Zn−N3	2.2079 (16)
Zn−N1	2.1573 (16)		
O1−Mo−O1^{i}	110.76 (15)	N2^{ii}−Zn−N2	103.83 (10)
O1−Mo−O2^{i}	108.08 (9)	N1−Zn−N3	93.59 (7)
O1−Mo−O2	110.14 (9)	N2−Zn−N3	89.10 (6)
O2^{i}−Mo−O2	109.65 (11)	N1−Zn−N3^{ii}	97.33 (7)
N1−Zn−N1^{ii}	165.94 (10)	N2−Zn−N3^{ii}	166.81 (7)
N1−Zn−N2^{ii}	91.27 (7)	N3−Zn−N3^{ii}	78.12 (9)
N1−Zn−N2	80.02 (8)		

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

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

D−H···*A*	*D*−H	H···*A*	*D*···*A*	*D*−H···*A*
N1−H1*A*···O2^{iii}	0.90	2.01	2.905 (2)	172
N1−H1*B*···O1	0.90	2.02	2.918 (2)	173
N2−H2*B*···O2^{iv}	0.90	2.06	2.894 (2)	154
N3−H3*A*···O1^{v}	0.90	2.11	2.989 (2)	166
N3−H3*B*···O1	0.90	2.46	3.225 (3)	143

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

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1492). Services for accessing these data are described at the back of the journal.

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