Layered (ethylenediamine-$\kappa^2 N$,N')-cobalt(II) molybdate(VI)

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The structure of poly[[(ethylenediamine-$\kappa^2 N$,N')cobalt(II)]-μ-tetraoxomolybdato(VI)], [Co(C$_2$H$_8$N$_2$)MoO$_4$]$_n$ or [CoMoO$_4$(C$_2$H$_8$N$_2$)]$_n$, is composed of puckered layers constructed from MoO$_4$ tetrahedra and CoN$_2$O$_4$ octahedra, with the ethylenediamine ligand coordinated to the Co atom in a *cis* fashion. Each pair of cobalt sites forms a binuclear edge-sharing unit through a {Co$_2$O$_2$} interaction. The binuclear octahedral units are interconnected through the bridging MoO$_4$ tetrahedra into a layer structure.

Comment

The hydrothermal technique, in the presence of organic and/or metal coordination templating species, has been demonstrated to be a versatile approach for the synthesis of inorganic/organic hybrids (Lin & Liu, 2000). One subclass of these hybrids consists of the molybdenum oxides, or polyanionic clusters covalently coordinated to heterometal–diamine coordination complexes or fragments (Hagrman *et al.*, 1999); these include [{Ni(bpy)$_2$}$_2$Mo$_4$O$_{14}$] (bpy is 2,2′-bipyridine; Zhang *et al.*, 1997), [Ni(bpy)$_2$Mo$_4$O$_{13}$], [Cu(bpy)Mo$_2$O$_7$] and [Co(bpy)Mo$_3$O$_{10}$] (Zapf *et al.*, 1997), [{Cu(en)$_2$}$_2$Mo$_8$O$_{26}$] (en is ethylenediamine; DeBord *et al.*, 1997), [{Cu$_3$(phen)$_3$}$_2$-Mo$_{14}$O$_{45}$] (phen is 4,7-phenanthroline; Hagrman, Pazf & Zubieta, 1998), [Fe(bpy)Mo$_4$O$_{15}$] (Zapf *et al.*, 1998) and [Cu(bpa)$_{0.5}$MoO$_4$] (bpa is 4,4′-bipydridylamine; Hagrman, Warren *et al.*, 1998). This paper reports the hydrothermal synthesis and crystal structure of a new layered inorganic/organic hybrid, namely [Co(en)MoO$_4$], (I).

(I)
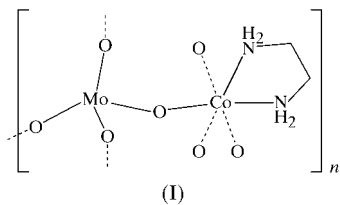
The coordination environments around the Mo and Co atoms in the asymmetric unit of (I) are shown in Fig. 1. The Mo atom exhibits a tetrahedral geometry involving a terminal

(O2), two doubly bridging (O1 and O2) and a triply bridging O atom (O4). The Mo—O bond distances range from 1.731 (2) to 1.8007 (16) Å. The Co atom is in a distorted octahedral environment involving the two N atoms from the ethylenediamine ligand and four O atoms from four MoO$_4$ tetrahedra, with Co—O and Co—N bond lengths in the range 2.0601 (17)–2.1735 (16) Å; these values are in agreement with other bond lengths observed previously (Zapf *et al.*, 1997).

As illustrated in Fig. 2, the crystal structure of (I) consists of puckered layers fused by MoO$_4$ tetrahedra and CoN$_2$O$_4$ octahedra, with each ethylenediamine ligand coordinated to each Co atom in a *cis* fashion. Two adjacent cobalt sites form a binuclear edge-sharing unit through a {Co$_2$O$_2$} interaction. The binuclear octahedral units are interconnected through bridging MoO$_4$ tetrahedra to produce a double chain along the *c* axis (Fig. 3), where two neighbouring Co octahedral units and two MoO$_4$ tetrahedra are linked through shared corners and generate an eight-membered Co$_2$Mo$_2$O$_4$ ring. The chains are further held together through Co—O—Mo corner linkages into a two-dimensional network structure parallel to the (100) plane. Consequently, each Co atom forms three corner-sharing linkages to neighbouring Mo atoms of the chain and one to an Mo atom of an adjacent chain, along with one edge-sharing linkage in a Co binuclear unit. Each Mo atom bridges three Co binuclear units and a terminal oxo group protrudes into the interlamellar region. As shown in Fig. 3, a second kind of four-polyhedral ring, built from two MoO$_4$ tetrahedra and two CoN$_2$O$_4$ octahedra, is observed in the plane of the layer. In the Co$_2$Mo$_2$O$_4$ ring of the chains, the two terminal oxo groups of the MoO$_4$ tetrahedra are oriented toward opposite sides of the plane of the ring defined by the four metal atoms. In contrast, the two terminal groups of the ring in the layer project onto the same side of the plane.

The title compound provides an example of a new layer structure constructed from molybdenum oxide polyhedra and heterometal coordination units. The layers found in [{Cu(en)$_2$}$_2$Mo$_8$O$_{26}$] (DeBord *et al.*, 1997), [{Cu$_3$(phen)$_3$}$_2$-Mo$_{14}$O$_{45}$] (Hagrman, Pazf & Zubieta, 1998) and [{Cu$_2$(tpz)-(H$_2$O)$_2$}(Mo$_5$O$_{15}$)(C$_2$H$_4$O$_6$P$_2$)]·5.5H$_2$O [tpz is tetra(2-pyri-
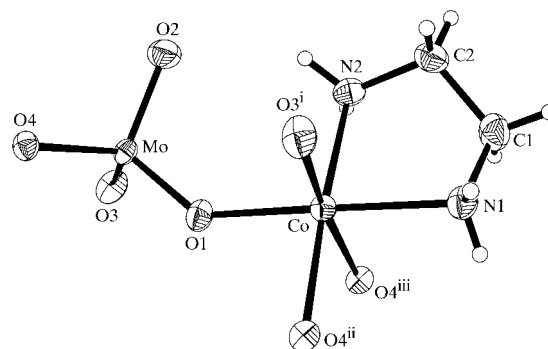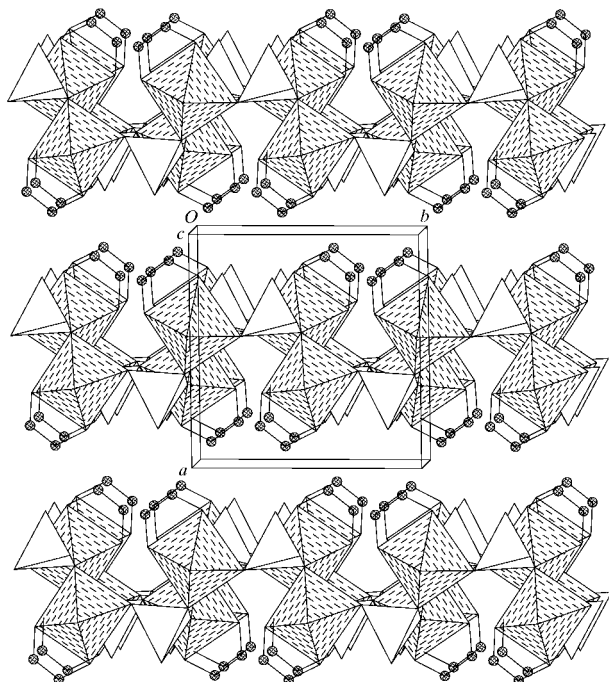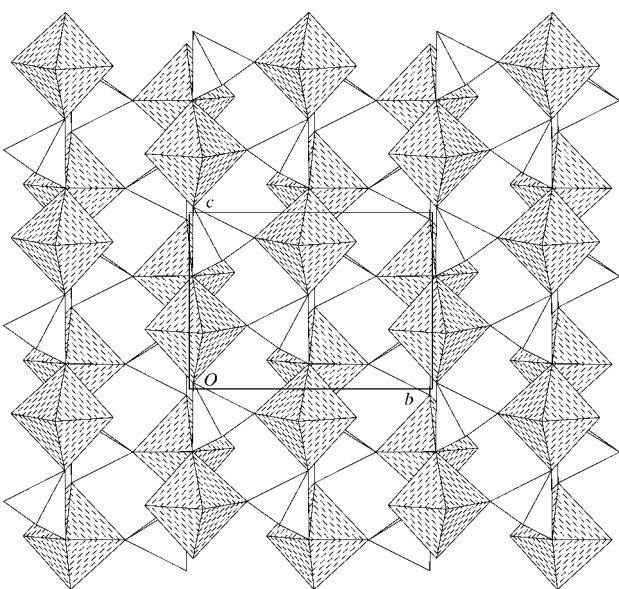

Figure 1
The asymmetric unit in the structure of (I), with ellipsoids at the 50% probability level, showing the coordination environment around the metal atoms [symmetry codes: (i) x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (ii) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (iii) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$].

Figure 2
A view of the structure of (I) along the c axis, showing the puckered layers fused by MoO_4 tetrahedra and CoN_2O_4 octahedra, where each ethylenediamine ligand is coordinated to each Co atom in a *cis* fashion and hatched circles denote C atoms. H atoms have been omitted for clarity.

dyl)pyrazine; Finn *et al.*, 2001] are composed of poly-oxomolybdate clusters and bridging organodiamine-ligated copper groups. The layers in $[Co(bpy)Mo_3O_{10}]$ are built up from molybdenum oxide chains interconnected through CoN_2O_4 octahedra (Zapf *et al.*, 1997). However, the layers in

Figure 3
A view of (I) perpendicular to one of the vanadium oxide layers, showing the connectivities between the MoO_4 tetrahedra and CoN_2O_4 octahedra.

(I) are constructed from 'isolated' MoO_4 tetrahedra and $Co(en)^{2+}$ fragments.

Experimental

The hydrothermal synthesis of (I) was carried out in a 17 ml Teflon-lined stainless steel vessel with a *ca* 40% fill factor. A mixture of $NaMoO_4 \cdot 2H_2O$ (0.243 g), $CoC_2O_2 \cdot 2H_2O$ (0.152 g), ethylenediamine (0.105 ml) and water in a molar ratio of 1:1:1.75:278 was heated at 413 K for 48 h. Violet plate-shaped crystals of (I) were formed in a yield of 75% based on molybdenum. The pH decreased from 8.2 before heating to 7.5 at the end of the reaction. Analysis calculated for $C_2H_8CoMoN_2O_4$ (%): C 8.61, H 2.89, N 10.04, Co 21.13, Mo 34.39; found: C 8.63, H 2.87, N 9.96, Co 21.25, Mo 34.41.

Crystal data

$[CoMoO_4(C_2H_8N_2)]$	$D_x = 2.670$ Mg m^{-3}
$M_r = 278.97$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 300
$a = 10.3955$ (6) Å	reflections
$b = 9.7127$ (8) Å	$\theta = 10–25°$
$c = 7.1234$ (4) Å	$\mu = 4.15$ mm^{-1}
$\beta = 105.236$ (6)°	$T = 293$ (2) K
$V = 693.96$ (8) Å^3	Plate, violet
$Z = 4$	$0.12 \times 0.10 \times 0.08$ mm

Data collection

Rigaku AFC-5R diffractometer	$R_{int} = 0.038$
$\omega–2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -13 \rightarrow 13$
(North *et al.*, 1968)	$k = -12 \rightarrow 0$
$T_{min} = 0.614$, $T_{max} = 0.716$	$l = 0 \rightarrow 9$
6370 measured reflections	3 standard reflections
1590 independent reflections	every 150 reflections
1461 reflections with $I > 2\sigma(I)$	intensity decay: 0.2%

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.023$	$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$
$wR(F^2) = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.002$
1590 reflections	$\Delta\rho_{max} = 0.82$ e Å^{-3}
91 parameters	$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo—O2	1.731 (2)	Co—O3^i	2.1048 (17)
Mo—O1	1.7607 (17)	Co—O4^{ii}	2.1095 (18)
Mo—O3	1.7606 (17)	Co—N1	2.129 (2)
Mo—O4	1.8007 (16)	Co—N2	2.135 (2)
Co—O1	2.0601 (17)	Co—O4^{iii}	2.1735 (16)
O2—Mo—O1	108.36 (9)	O3^i—Co—N2	89.90 (8)
O2—Mo—O3	109.18 (10)	O4^{ii}—Co—N2	176.27 (8)
O1—Mo—O3	109.85 (8)	N1—Co—N2	82.25 (9)
O2—Mo—O4	106.94 (8)	O1—Co—O4^{iii}	89.33 (7)
O1—Mo—O4	109.92 (8)	O3^i—Co—O4^{iii}	171.11 (7)
O3—Mo—O4	112.47 (8)	O4^{ii}—Co—O4^{iii}	84.50 (7)
O1—Co—O3^i	98.16 (7)	N1—Co—O4^{iii}	85.03 (7)
O1—Co—O4^{ii}	87.94 (7)	N2—Co—O4^{iii}	94.16 (7)
O3^i—Co—O4^{ii}	90.96 (7)	Mo—O1—Co	139.83 (11)
O1—Co—N1	173.76 (8)	Mo—O3—Co^{iii}	146.09 (10)
O3^i—Co—N1	87.69 (8)	Mo—O4—Co^{iv}	122.58 (9)
O4^{ii}—Co—N1	94.16 (8)	Mo—O4—Co^i	130.40 (9)
O1—Co—N2	95.54 (8)	Co^{iv}—O4—Co^i	95.50 (7)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$A$$\cdots$O1[i]	0.90	2.62	3.192 (3)	122
N1—H1$B$$\cdots$O1[ii]	0.90	2.29	3.089 (3)	148
N2—H2$A$$\cdots$O2	0.90	2.40	3.127 (3)	138
N2—H2$B$$\cdots$O2[iii]	0.89	2.15	3.022 (3)	167

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

All H atoms were located in a difference Fourier map and were fixed at calculated positions (C—H = 0.91–0.96 Å and N—H = 0.89–0.90 Å), with a common isotropic displacement parameter (U_{iso} = 0.05 Å^2).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1987); cell refinement: *TEXSAN* (Molecular Structure Corporation, 1987); data reduction: *TEXRAY* in *TEXSAN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1361). Services for accessing these data are described at the back of the journal.

References

DeBord, J. R. D., Haustalter, R. C., Meyer, L. M., Rose, D. J., Zapf, P. J. & Zubieta, J. (1997). *Inorg. Chim. Acta*, **256**, 165–167.
Finn, R. C., Burkholder, E. & Zubieta, J. (2001). *Chem. Commun.* pp. 1852–1853.
Hagrman, D., Pazf, P. J. & Zubieta, J. (1998). *Chem. Commun.* pp. 1283–1284.
Hagrman, D., Warren, C. J., Haushalter, R. C., Raring, R. S. Jr, Johnson, K. M. III, LaDuca, R. L. & Zubieta, J. (1998). *Chem. Mater.* **10**, 3294–3296.
Hagrman, P. J., Hagrman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2648.
Lin, B.-Z. & Liu, S.-X. (2000). *Polyhedron*, **19**, 2521–2527.
Molecular Structure Corporation (1987). *MSC/AFC Diffractometer Control Software* and *TEXSAN* (Version 2.0). MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Philips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**42**, 351–359.
Sheldrick, G. M. (1990a). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990b). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Zapf, P. J., Hammond, R. P., Haushalter, R. C. & Zubieta, J. (1998). *Chem. Mater.* **10**, 1336–1339.
Zapf, P. J., Warren, C. J., Haushalter, R. C. & Zubieta, J. (1997). *Chem. Commun.* pp. 1543–1544.
Zhang, Y., Zapf, P. J., Meyer, L. M., Haushalter, R. C. & Zubieta, J. (1997). *Inorg. Chem.* **36**, 2159–2165.