

**Bis[diacquabis(2,2-bipyridine  
*N,N'*-dioxide- $\kappa^2O,O'$ )cobalt(II)]  
 $\xi$ -octamolybdate dihydrate**

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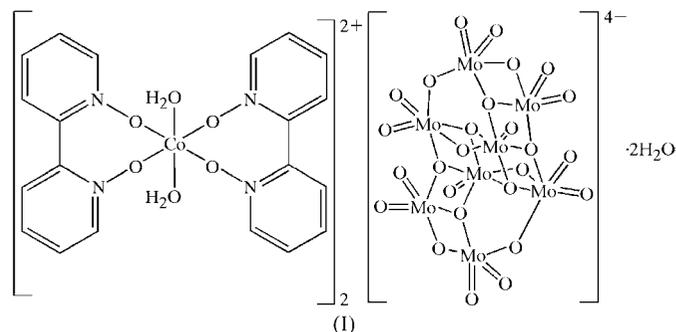
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The title organic–inorganic hybrid compound,  $[\text{Co}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_2][\text{Mo}_8\text{O}_{26}]\cdot 2\text{H}_2\text{O}$ , consists of  $[\text{Co}(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2+}$  (bpdo is 2,2-bipyridine *N,N'*-dioxide) and  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  groups in a 2:1 ratio, plus two water solvent molecules. The independent Co atom in the cation is coordinated by four O atoms from two bpdo ligands and two water molecules, in a distorted octahedral geometry. The counter-anions, built up around a symmetry center, are linked by solvent water molecules through O–H···O hydrogen bonds to generate two-dimensional layers, which are in turn linked by coordinated water molecules from the cationic units through further O–H···O hydrogen bonds, forming a three-dimensional supramolecular structure.

**Comment**

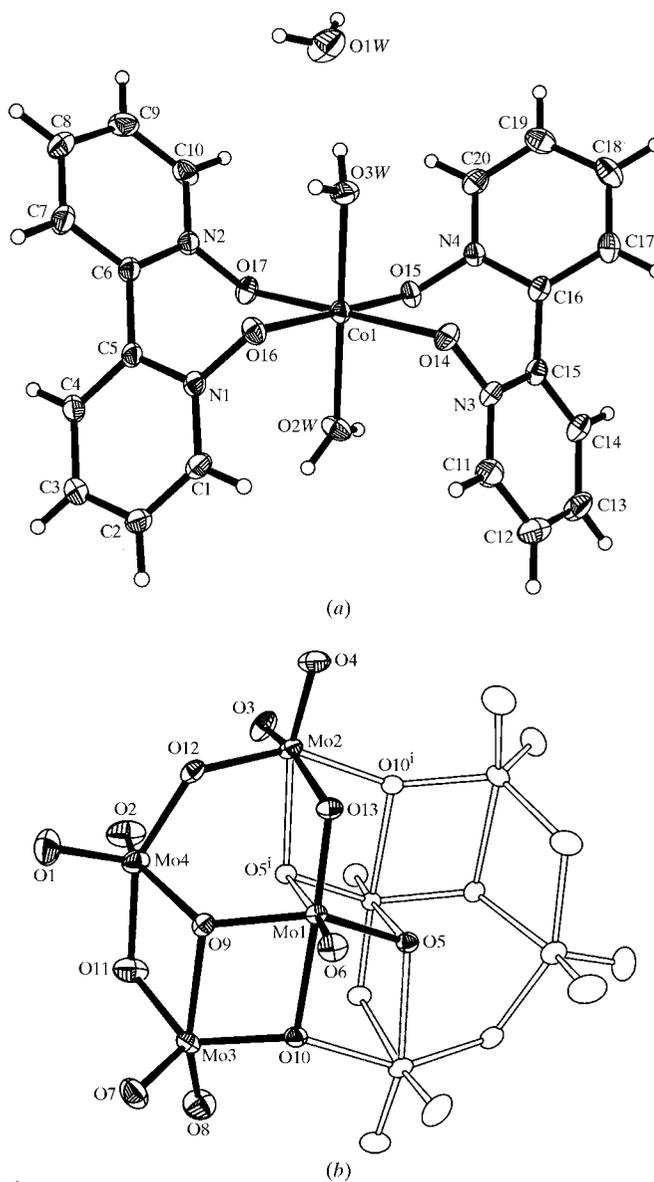
Polyoxometalates (Pope, 1983; Hill, 1998; Fukaya & Yamase, 2003), as a unique class of metal–oxide clusters, have many properties that make them attractive for applications in catalysis, biology, magnetism, optics and medicine (Kögerler &



Cronin, 2005; Yamase, 1998). Recently, important advances have been achieved in the coordination chemistry of polyoxoanions with classical transition metal coordination complexes or fragments. Among the various polyoxometalate structures of interest, octamolybdate is a particularly attrac-

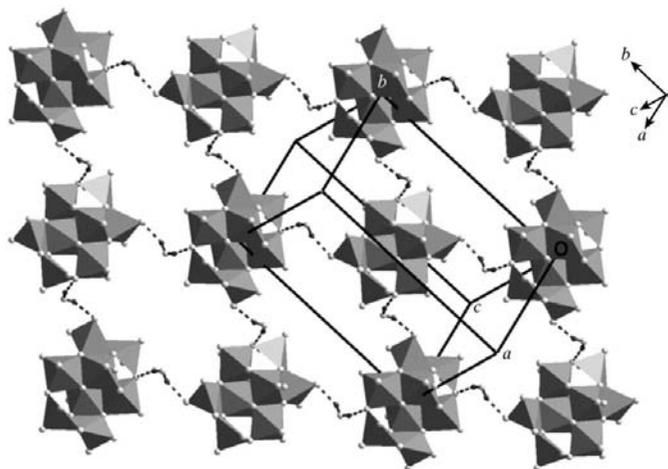
tive cluster with a variety of structural isomers (Hagrman *et al.*, 1997; Yang *et al.*, 2002). As reported previously (Finn & Zubietta, 2001; Liu *et al.*, 2001), much of the work has been focused on transition metal complexes with  $\alpha\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  and  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  clusters. However, research on the  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  cluster with metal complexes is comparatively scarce. In the present work, the assembly by the hydrothermal method of  $\text{Na}_2\text{MoO}_4$ , 2,2-bipyridine *N,N'*-dioxide (bpdo) and cobalt(II) nitrate resulted in the complex  $[\text{Co}(\text{bpdo})_2(\text{H}_2\text{O})_2]_2\text{-}[\text{Mo}_4\text{O}_{13}]\cdot 2\text{H}_2\text{O}$ , (I).

As shown in Fig. 1, the compound contains two subunits (in a 2:1 ratio), *viz.* a cationic group,  $[\text{Co}(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2+}$ , and its anionic counterpart, a  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  cluster which lies around an inversion center. The structure is completed by a water



**Figure 1**  
A split view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. (a) The  $[\text{Co}(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2+}$  unit and a solvent water molecule and (b) the  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  cluster. Full (empty) ellipsoids represent independent (symmetry-related) atoms. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]

solvent molecule. The  $\text{Co}^{\text{II}}$  ion exhibits a distorted octahedral geometry and is coordinated by four O atoms from two bpdo ligands, with Co—O distances ranging from 2.061 (2) to 2.069 (2) Å, and two water molecules, with coordination distances of 2.098 (2) and 2.109 (2) Å (Table 1), similar to other Co—O distances in the literature (*viz.* Zhang *et al.*, 2005). Two kinds of bpdo ligands coordinate the  $\text{Co}^{\text{II}}$  ion as bidentate ligands. The dihedral angles between two rings from the same bpdo ligand are 29.1 (1) and 29.4 (1)°, respectively.

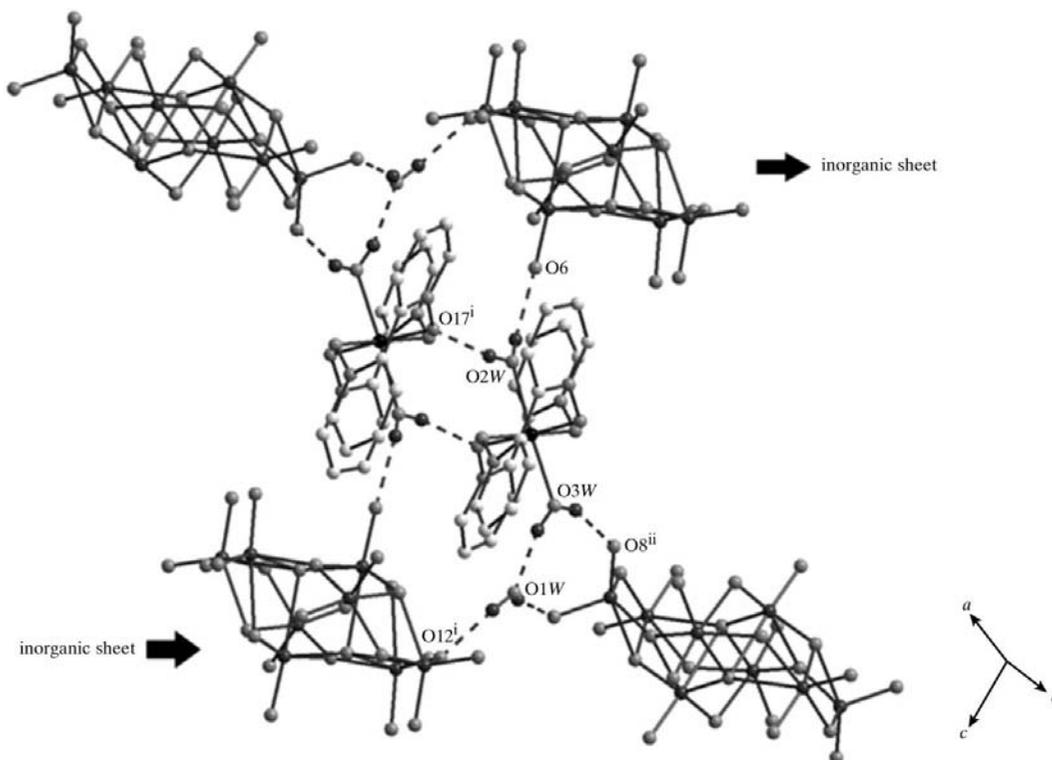


**Figure 2**  
The inorganic layer, composed of hydrogen-bonded  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  clusters and solvent water molecules.

The  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  octamolybdate anion exhibits an open structure (Xu *et al.*, 1999; Bridgeman, 2002). Each cluster contains an  $\text{Mo}_6\text{O}_6$  ring capped on opposite faces by  $\text{MoO}_6$  octahedra. In the ring, the linkage between any two  $\text{MoO}_5$  trigonal bipyramids is edge shared, while that between any  $\text{MoO}_6$  and  $\text{MoO}_5$  groups is corner shared. Each capping  $\text{MoO}_6$  octahedron is linked to four groups in the ring, *viz.* two  $\text{MoO}_6$  octahedra and one  $\text{MoO}_5$  pyramid by edge sharing and a second  $\text{MoO}_5$  bipyramid by corner sharing. In addition, the capping  $\text{MoO}_6$  octahedra are attached to one another by edge sharing. Therefore, three types of O atoms exist in the cluster, according to their coordination behavior, *viz.* six  $\text{O}(\mu_3)$ , six  $\text{O}(\mu_2)$  and 14 terminal  $\text{O}(t)$  atoms. The Mo—O distances are similar to those in other reported  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  clusters (Xu *et al.*, 1999).

The structure presents an interesting water cluster. As shown in Table 2, one coordinated ( $\text{O}3\text{W}$ ) and one solvent water molecule ( $\text{O}1\text{W}$ ) assemble into a dimer with an  $\text{O}\text{W}\cdots\text{O}\text{W}$  distance of 2.689 (4) Å, shorter than those in regular ice, liquid water and water vapor (2.74, 2.85 and 2.98 Å, respectively). Each  $\text{O}1\text{W}$  molecule, in turn, links two different  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anions to form a two-dimensional anionic layer (Table 2 and Fig. 2).

In addition, the  $[\text{Co}(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2+}$  units form hydrogen-bonded dimers through  $\text{O}2\text{W}\cdots\text{O}17^{\text{ii}}$  hydrogen bonds (Table 2). These dimers, in turn, link four  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anions from adjacent two-dimensional inorganic sheets to generate a three-dimensional supramolecular structure (Fig. 3).



**Figure 3**  
A view of a cationic dimer connecting four  $\xi\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  clusters from adjacent inorganic sheets into a three-dimensional structure. The symmetry codes are as in Tables 1 and 2.

Experimental

The bpdo ligand was synthesized according to the method reported by Simpsox *et al.* (1963). A mixture of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.146 g, 0.5 mmol), Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.484 g, 2.0 mmol), bpdo (0.188 g, 1.0 mmol) and water (10 ml) was adjusted to approximately pH 3 with HNO<sub>3</sub> (6 mol l<sup>-1</sup>) and stirred for 1 h, and then transferred to and sealed in a 25 ml Teflon-lined stainless steel container. The container was heated to 423 K and held at that temperature for 72 h, then cooled to 373 K at a rate of 5 K h<sup>-1</sup> and held for 8 h, followed by further cooling to 303 K at a rate of 3 K h<sup>-1</sup>. Pink crystals of the title compound were collected in 76.2% yield based on Co(NO<sub>3</sub>)<sub>2</sub>. Elemental analyses calculated for C<sub>20</sub>H<sub>22</sub>CoMo<sub>4</sub>N<sub>4</sub>O<sub>20</sub>: C 22.22, H 2.05, N 5.18%; found: C 22.35, H 2.03, N 5.21%.

Crystal data

[Co(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>  
[Mo<sub>8</sub>O<sub>26</sub>]<sup>2-</sup>·2H<sub>2</sub>O  
M<sub>r</sub> = 2162.22  
Monoclinic, P2<sub>1</sub>/n  
a = 12.603 (3) Å  
b = 18.014 (3) Å  
c = 14.658 (4) Å  
β = 110.392 (5)°  
V = 3119.3 (11) Å<sup>3</sup>  
Z = 2  
Mo Kα radiation  
μ = 2.18 mm<sup>-1</sup>  
T = 293 (2) K  
0.43 × 0.30 × 0.19 mm

Data collection

Bruker APEX CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
T<sub>min</sub> = 0.466, T<sub>max</sub> = 0.661  
18887 measured reflections  
7333 independent reflections  
5992 reflections with I > 2σ(I)  
R<sub>int</sub> = 0.033

Refinement

R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.028  
wR(F<sup>2</sup>) = 0.062  
S = 1.04  
7333 reflections  
460 parameters  
10 restraints  
H atoms treated by a mixture of independent and constrained refinement  
Δρ<sub>max</sub> = 0.45 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.61 e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

Co1—O15	2.061 (2)	Mo2—O12	1.8991 (19)
Co1—O16	2.0614 (19)	Mo2—O10 <sup>i</sup>	2.0089 (19)
Co1—O14	2.067 (2)	Mo2—O5 <sup>i</sup>	2.2307 (18)
Co1—O17	2.069 (2)	Mo2—O13	2.312 (2)
Co1—O3W	2.098 (2)	Mo3—O8	1.692 (2)
Co1—O2W	2.109 (2)	Mo3—O7	1.697 (2)
Mo1—O6	1.693 (2)	Mo3—O11	1.846 (2)
Mo1—O13	1.7475 (19)	Mo3—O10	1.9117 (19)
Mo1—O5	1.8811 (18)	Mo3—O9	2.2898 (19)
Mo1—O9	1.9021 (19)	Mo4—O1	1.682 (3)
Mo1—O10	2.2527 (19)	Mo4—O2	1.696 (2)
Mo1—O5 <sup>i</sup>	2.458 (2)	Mo4—O12	1.927 (2)
Mo2—O4	1.692 (2)	Mo4—O11	1.974 (2)
Mo2—O3	1.698 (2)	Mo4—O9	2.1676 (19)

Symmetry code: (i) -x + 1, -y + 1, -z + 1.

All H atoms of water molecules were located in difference maps and refined isotropically, with U<sub>iso</sub>(H) values of 1.5U<sub>eq</sub>(O) (O—H distances are given in Table 2). Other H atoms were positioned

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1A...O12 <sup>ii</sup>	0.843 (17)	2.00 (2)	2.819 (3)	163 (3)
O1W—H1B...O7 <sup>iii</sup>	0.836 (17)	2.14 (2)	2.927 (4)	158 (3)
O2W—H2B...O17 <sup>ii</sup>	0.830 (17)	1.88 (2)	2.681 (3)	162 (3)
O2W—H2A...O6	0.84 (4)	2.16 (2)	2.930 (3)	154 (3)
O3W—H3A...O1W	0.837 (17)	1.87 (2)	2.689 (4)	166 (3)
O3W—H3B...O8 <sup>iii</sup>	0.843 (17)	2.00 (2)	2.799 (3)	157 (3)

Symmetry codes: (ii) -x + 1, -y + 1, -z + 2; (iii) x - 1/2, -y + 3/2, z + 1/2.

geometrically and allowed to ride on their parent atoms at C—H distances of 0.93 Å and with U<sub>iso</sub>(H) values of 1.2U<sub>eq</sub>(C).

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus (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: BG3034). Services for accessing these data are described at the back of the journal.

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