metal-organic papers

Bis[bis(2,2′-bipyridine-κ^2N,$N′$)(nitrato-κ^2O,$O′$)-cobalt(II)] molybdate heptahydrate

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The crystal structure of the title compound, [Co(NO$_3$)(bipy)$_2$]$_2$[MoO$_4$]·7H$_2$O (bipy is 2,2′-bipyridine, C$_{10}$H$_8$N$_2$), contains the isomers Δ and Λ of the cation [Co(NO$_3$)(bipy)$_2$]$^+$, self-assembled through complementary π–π, C—H$\cdots\pi$ and C—H$\cdots$O interactions, leading to an intricate two-dimensional array. The final three-dimensional network is sustained *via* extensive hydrogen bonding among the cations, uncoordinated water molecules and molybdate anions, which are accommodated in between adjacent cationic two-dimensional arrays. In the cations, the metal centres adopt a distorted octahedral geometry due to the coordination of the N atoms of two bipy molecules and one bidentate nitrate ligand.

Comment

Research on organic–inorganic hybrid materials based on oxometalates has attracted much attention owing to their importance for the development of new materials with unusual properties (Hagrman *et al.*, 1999, 2001; Hill, 1998; Pope & Müller, 1991, 1994). Oxomolybdates, particularly, have found industrial applications in the hydroprocessing of oil feedstock, such as hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) (Topsøe *et al.*, 1996). The catalysts commonly used nowadays for HDS correspond to a bimetallic combination of Mo(W) and a promoter, such as Co(Ni). A striking feature of the oxometalates is their anionic nature, which means that they can be combined with cationic metal complexes that act as charge compensating agents. Recently, we have explored this alternative to synthesize bimetallic compounds as new catalytic precursors for HDS (Briceño, 2003). We report here the synthesis and structural characterization of the bimetallic compound [Co(NO$_3$)(bipy)$_2$]-[MoO$_4$]·7H$_2$O (where bipy = 2,2′-bipyridine), (I).

(I)
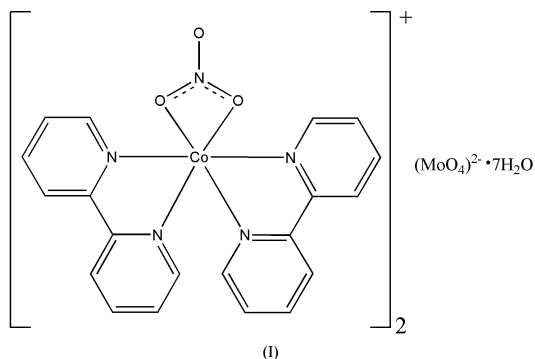
The asymmetric unit of (I) contains two crystallographically independent cationic complexes, [Co(NO$_3$)(bipy)$_2$]$^+$, one anion [MoO$_4$]$^{2-}$ and seven water molecules of crystallization.
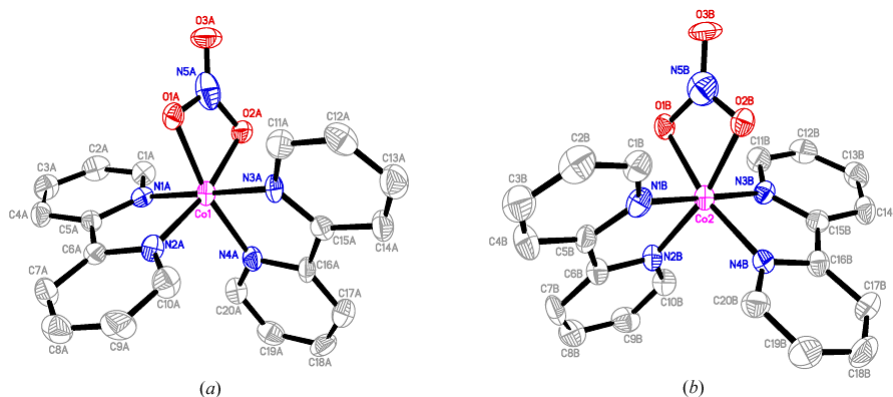
Figure 1
View of (*a*) the Δ isomer and (*b*) the Λ isomer of the cation in the crystal structure of (I), showing anisotropic displacement parameters at the 50% probability level. H atoms have been omitted.
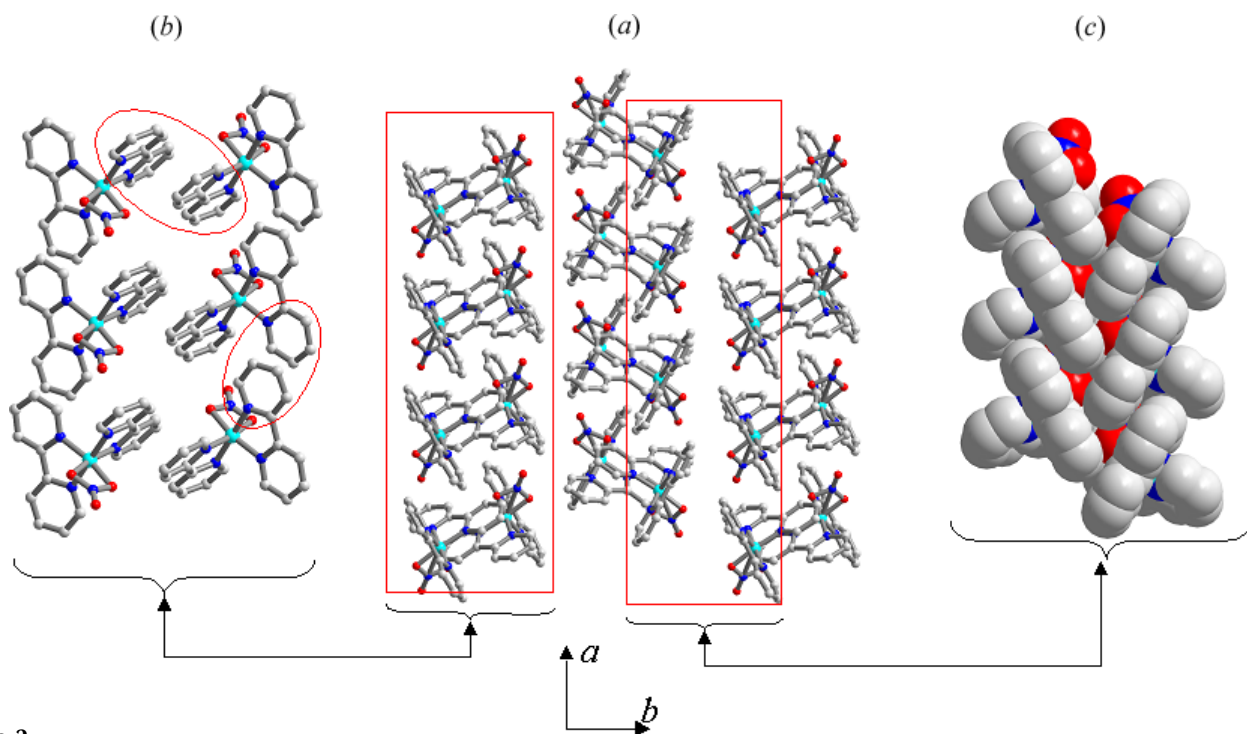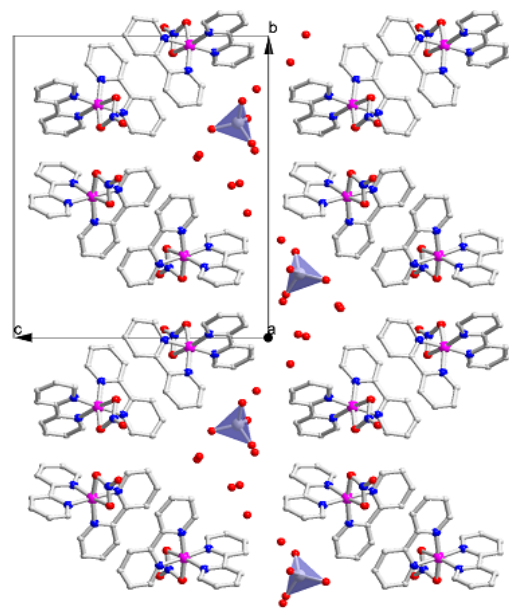

Figure 2
(*a*) The two-dimensional array in the crystal structure of (I), which is generated by direct cation–cation interactions. (*b*) The π–π overlapping between pyridine rings along the *a* axis. (*c*) The herring-bone arrangement due to the C—H···π interactions.

In both cationic complexes, the coordination environment may be considered as distorted octahedral, with the cobalt(II) ion coordinated by four N atoms of two bipy molecules and two O atoms of one bidentate nitrate ligand. The complexes, however, may be assigned to the isomers Δ (Fig. 1*a*) and Λ (Fig. 1*b*), respectively.

Selected geometric parameters are given in Table 1. The Co—N bond distances in the Δ isomer (labelled Co1) lie in a very narrow range [1.925 (5)–1.938 (6) Å], while in the Λ isomer (Co2), the range is wider [1.916 (6)–1.943 (6) Å]. In contrast, the nitrate ligand is symmetrically coordinated to the metal centre in both isomers with essentially equal Co—O bond lengths [average 1.891 (6) Å]. These cations appear to be similar to that previously reported for [Co(NO₃)(bipy)₂]-NO₃·5H₂O (Zheng & Lin, 2002). In this latter compound, however, the complex possesses crystallographic C_2 symmetry,

whereas the cations of (I) show a slight deviation from this twofold symmetry. A striking feature of this cation is that the only symmetry possible is C_2, which makes it a chiral entity. On the other hand, the anionic moiety $[MoO_4]^{2-}$ also shows asymmetry in its Mo—O bond distances [range 1.743 (6)–1.773 (5) Å].

In the crystal structure of (I), the cations form a wave-like two-dimensional array parallel to the *ab* plane (Fig. 2*a*), which is sustained by π–π, C—H···π and C—H···O interactions. Firstly, two different π–π overlaps (average 3.55 Å) of pyridine rings of adjacent cations are observed in the *a* direction (Fig. 2*b*), whence a herring-bone arrangement along the *a* axis is observed due to C—H···π interactions (Fig. 2*c*). Finally, all the O atoms, coordinated and non-coordinated, of the nitrate ligands are involved in C—H···O(nitrate) interactions [C···O range 2.886 (10)–3.226 (9) Å].
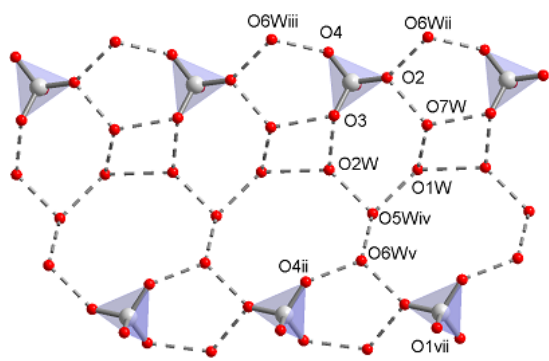
Figure 3
(a) View of the final three-dimensional array, showing the position of the uncoordinated water molecules and the anions $[MoO_4]^{2-}$ between adjacent cationic two-dimensional arrays. (b) The hydrogen-bond network formed between water molecules and the anions. Water molecules O3W and O4W (omitted) are located above and below the mean plane of the network. [Symmetry code: (vii) $1 - x$, $y - \frac{1}{2}$, $-z$.]

The water molecules of crystallization and the anions are accommodated in between adjacent cationic two-dimensional arrays (Fig. 3a) via an extensive hydrogen-bonding network (Fig. 3b), which is built up from O(water)—H···O(water) and Mo—O···O(water) interactions (see Table 2). Intricate sets of C—H···O(water) and C—H···O(molybdate) hydrogen bonds help to hold together this anion–water arrangement and the cationic two-dimensional arrays.

Experimental

To a solution of Co(NO₃)·6H₂O (0.100 mg, 0.34 mmol) in water (50 ml) was added bipy (0.107 mg, 0.69 mmol). The mixture was stirred until dissolution was complete. Na₂MoO₄ (0.049 mg, 0.34 mmol) was then added and the mixture was left to evaporate at

room temperature. After 2–3 weeks, deep-red crystals of the title compound, (I), were obtained.

Crystal data

[Co(NO₃)(C₁₀H₈N₂)₂]₂[MoO₄]·7H₂O	$D_x = 1.692$ Mg m^{-3}
$M_r = 1152.67$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 22
$a = 6.996$ (3) Å	reflections
$b = 19.569$ (4) Å	$\theta = 20.6–28.5°$
$c = 16.659$ (2) Å	$\mu = 1.08$ mm^{-1}
$\beta = 97.328$ (19)°	$T = 298$ (2) K
$V = 2262.3$ (11) Å^3	Prism, red
$Z = 2$	$0.50 \times 0.20 \times 0.20$ mm

Data collection

Rigaku AFC-7S diffractometer	$\theta_{max} = 25.0°$
ω–2θ scans	$h = 0 \to 8$
Absorption correction: none	$k = 0 \to 23$
4482 measured reflections	$l = -19 \to 19$
4117 independent reflections	3 standard reflections
3579 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.040$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$+ 0.9871P]$
$wR(F^2) = 0.091$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
4117 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
631 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983),
	354 Friedel pairs
	Flack parameter = 0.01 (2)

Table 1
Selected geometric parameters (Å, °).

Mo1—O4	1.743 (6)	Co2—O2B	1.895 (5)
Mo1—O1	1.757 (6)	Co2—N1B	1.916 (6)
Mo1—O3	1.765 (6)	Co2—N3B	1.929 (6)
Mo1—O2	1.773 (6)	Co2—N2B	1.934 (6)
Co1—O1A	1.887 (5)	Co2—N4B	1.943 (6)
Co1—O2A	1.891 (5)	O1A—N5A	1.319 (8)
Co1—N3A	1.925 (5)	O2A—N5A	1.327 (8)
Co1—N1A	1.928 (6)	O3A—N5A	1.229 (8)
Co1—N2A	1.935 (6)	O1B—N5B	1.310 (8)
Co1—N4A	1.938 (6)	O2B—N5B	1.337 (8)
Co2—O1B	1.888 (5)	O3B—N5B	1.226 (8)
O4—Mo1—O1	110.7 (3)	N1A—Co1—N5A	87.6 (2)
O4—Mo1—O3	107.7 (3)	N2A—Co1—N5A	133.0 (2)
O1—Mo1—O3	109.1 (3)	N4A—Co1—N5A	133.5 (2)
O4—Mo1—O2	109.5 (3)	O1B—Co2—O2B	69.9 (2)
O1—Mo1—O2	109.7 (3)	O1B—Co2—N1B	88.5 (2)
O3—Mo1—O2	110.1 (3)	O2B—Co2—N1B	92.1 (2)
O1A—Co1—O2A	70.0 (2)	O1B—Co2—N3B	91.3 (2)
O1A—Co1—N3A	92.0 (2)	O2B—Co2—N3B	86.8 (2)
O2A—Co1—N3A	88.9 (2)	N1B—Co2—N3B	178.9 (3)
O1A—Co1—N1A	86.5 (2)	O1B—Co2—N2B	97.8 (2)
O2A—Co1—N1A	91.8 (2)	O2B—Co2—N2B	166.9 (2)
N3A—Co1—N1A	178.1 (3)	N1B—Co2—N2B	83.1 (2)
O1A—Co1—N2A	98.4 (2)	N3B—Co2—N2B	98.0 (2)
O2A—Co1—N2A	167.7 (2)	O1B—Co2—N4B	167.1 (2)
N3A—Co1—N2A	95.8 (2)	O2B—Co2—N4B	98.1 (2)
N1A—Co1—N2A	83.2 (2)	N1B—Co2—N4B	96.8 (3)
O1A—Co1—N4A	167.6 (2)	N3B—Co2—N4B	83.2 (2)
O2A—Co1—N4A	98.4 (2)	N2B—Co2—N4B	94.6 (2)
N3A—Co1—N4A	83.2 (2)	O1B—Co2—N5B	91.8 (3)
N1A—Co1—N4A	98.5 (2)	N3B—Co2—N5B	87.4 (2)
N2A—Co1—N4A	93.5 (2)	N2B—Co2—N5B	132.3 (3)
N3A—Co1—N5A	91.9 (2)	N4B—Co2—N5B	133.1 (2)

Table 2
Contact distances (Å).

O1···O3W^i	2.832 (10)	O1W···O7W^i	2.785 (10)
O2···O6W^{ii}	2.784 (8)	O2W···O5W^{iv}	2.772 (9)
O2···O7W	2.780 (9)	O3W···O4W	2.879 (11)
O3···O2W	2.727 (9)	O4W···O1^v	2.871 (10)
O4···O6W^{iii}	2.702 (9)	O5W···O6W^{vi}	2.828 (9)

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

The H atoms bound to carbon were included in calculated positions and refined using a riding model [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The water H atoms were not observed in Fourier difference maps and were therefore not included.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT* and *DIAMOND* (Brandenburg, 1996–2001); software used to prepare material for publication: *SHELXTL-NT*.

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