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catena-Poly[[[μ-pyridinium-3-carboxylato-bis[dioxomolybdenum(VI)]]-di-μ_3-oxo] monohydrate]

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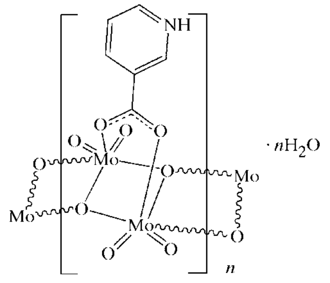
A novel chain molybdenum compound, $\{[Mo_2O_6(C_6H_5NO_2)]\cdot H_2O\}_n$, which was synthesized under hydrothermal conditions, consists of an infinite rail-like chain formed by molybdenum oxide units linked by zwitterionic nicotinic acid ligands. Each Mo atom is coordinated octahedrally by six O atoms and the MoO_6 octahedra are linked to one another *via* edge-sharing to produce a zigzag polymeric chain, with nicotinic acid ligands located, alternately, on each side of the rail-like chain plane.

Comment

Chemists are becoming increasingly interested in topics concerning transition metal oxides, owing mainly to their structural variety and promising potential applications in catalysis, biology, medicine and materials science (Pope & Müller, 1991). The molybdenum oxides are an important subclass and have been reported frequently (Rarig & Zubieta, 2001). It has been recognized that molybdenum in its higher oxidation states readily forms polynuclear anionic metal–oxygen clusters, and many giant polymolybdates have been reported (Müller & Kögerler, 1999). However, the number of dimeric structures of molybdenum oxides that are known is much smaller; only a few compounds, such as $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ (Strukan & Cindric, 2000) and $[Mo_2(i\text{-PrO})_6(Cat)_2]$ (*i*-PrO is isopropoxy and Cat is tetrachloro-*o*-catecholate; Timothy *et al.*, 1988), have been reported. Recently, compounds based on polyoxometalates linked by clusters, organic ligands and so on have been a hot topic in this research area (Müller *et al.*, 1999), but solid materials of one-dimensional structure with only molybdenum oxide frameworks have rarely been reported. On the other hand, nicotinic acid has often been used as a ligand to prepare transition metal cations. To our knowledge, only one Mo compound, $[Mo_2Cl_2(C_6H_4NO_2)_4]Cl_2\cdot 6H_2O$ (Cotton *et al.*, 1990), in which molybdenum is directly coordinated by nicotinate has been reported. Recently, we have launched a systematic program aimed at linking polyoxometalates by organic ligands and (or) transition metal fragments, in order to generate distinctive architectures. We have succeeded in obtaining an infinite rail-like chain compound, $\{[Mo_2O_6(nic)]\cdot H_2O\}_n$ (nic is nicotinic acid), (I), by hydrothermal reaction. The preparation, elemental analysis, IR spectrum and crystal structure of this compound are presented here.



(I)

Compound (I) consists of an infinite rail-like chain formed by molybdenum oxide units linked by zwitterionic nicotinic acid ligands. As shown in Figs. 1 and 2, every Mo atom is coordinated octahedrally by six O atoms, which can be divided into three groups according to their Mo—O distances (Table 1); two short terminal bonds [Mo—O = 1.683 (5) and 1.714 (5) Å], two medium-length bonds [1.956 (5) and 1.957 (5) Å] and two longer bonds [2.230 (5) and 2.295 (5) Å] are observed. It is known that nicotinic acid can offer three coordination atoms, namely two O atoms and one N atom, and has several coordination modes (Chen *et al.*, 2001). In (I), each nicotinic acid ligand bridges two Mo centers *via* the two O atoms of its carboxylate group. The most interesting structural feature of (I), however, is that all nicotinic acid ligands are coordinated to Mo atoms in a bridging mode [Mo1···Mo2 = 3.3965 (9) Å].

As shown in Fig. 2, the MoO_6 octahedra are linked to one another *via* edge-sharing to produce a zigzag polymeric chain. In this one-dimensional structural motif, nicotinic acid ligands

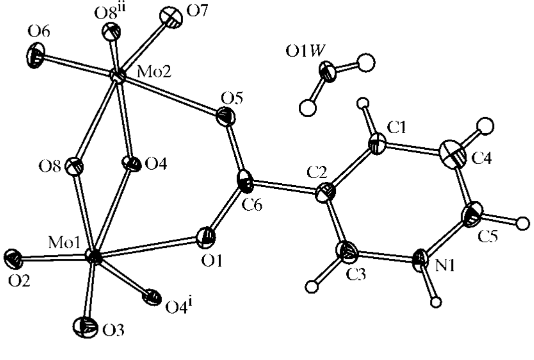


Figure 1
The independent unit in (I), shown with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.]

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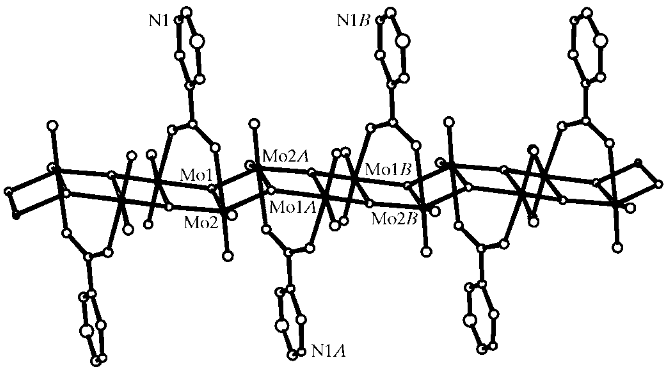

Figure 2
A view of the extended structure of (I), with 30% probability displacement ellipsoids, showing the rail-like chain. H atoms and water molecules have been omitted for clarity. Atoms with the suffixes *A* and *B* are at the symmetry positions $(1 - x, 1 - y, 1 - z)$ and $(x, 1 + y, z)$, respectively.

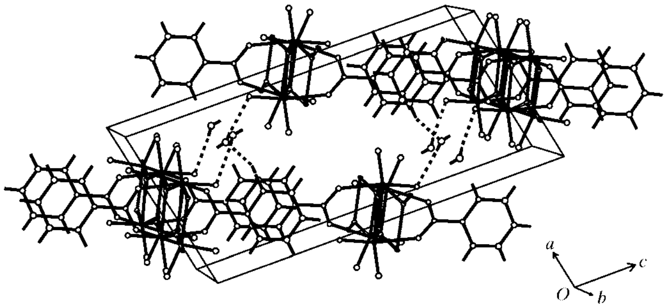

Figure 3
The crystal structure of (I), with the one-dimensional chains viewed approximately end-on. Intermolecular hydrogen bonds are shown as dotted lines.

are located, alternately, on each side of the rail-like chain plane. Such a coordination mode for the nicotinic acid ligand has been reported previously but infrequently for related compounds (Chen *et al.*, 2001).

Fig. 3 shows the structure of (I), with the one-dimensional chains viewed end-on. It can be seen that the chains are held together in two-dimensional layers by weak π–π stacking contacts between interleaved pyridine rings from adjacent chains. One pyridine ring of one chain and another pyridine ring of an adjacent chain form π–π stacks with a dihedral angle of 18.2°, and the shortest and longest atom-to-centroid distances are 3.761 (3) and 4.639 (3) Å, respectively. This two-dimensional structure is further extended into a three-dimensional structure by interlayer hydrogen-bonded water molecules (Table 2).

Experimental

A mixture of $Na_2MoO_4 \cdot H_2O$ (0.24 g, 1 mmol), nicotinic acid (0.25 g, 2.0 mmol), $(C_2H_5)_4NCl \cdot H_2O$ (0.18 g, 1.0 mmol) and $NH_2OH \cdot HCl$ (0.18 g, 2.5 mmol) in water (10 ml) was heated at 413 K for 3 d. After the reaction had been cooled to room temperature over a period of 72 h, colorless crystals of (I) were produced (yield 51% based on Mo). Analysis calculated for $C_6H_7Mo_2NO_9$: C 16.80, H 1.64, N 3.26%; found: C 16.99, H 1.48, N 3.11%. IR (KBr, cm^{-1}): 3541 (*m*), 1637 (*s*), 1585 (*m*), 1416 (*s*), 953 (*vs*), 924 (*s*), 544 (*s*).

Crystal data

$[Mo_2O_6(C_6H_5NO_2)] \cdot H_2O$
$M_r = 429.01$
Monoclinic, $P2_1/n$
$a = 8.5404$ (6) Å
$b = 7.3459$ (5) Å
$c = 18.3735$ (11) Å
$\beta = 103.045$ (2)°
$V = 1122.95$ (13) Å^3
$Z = 4$
$D_x = 2.538$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1888 reflections
$\theta = 2.3$–25.1°
$\mu = 2.28$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.28 × 0.10 × 0.06 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.761$, $T_{max} = 0.872$
3942 measured reflections
1987 independent reflections

1501 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 25.1°$
$h = -10 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -17 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.126$
$S = 0.99$
1987 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 10.3372P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -1.12$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O3	1.683 (5)	Mo2—O6	1.688 (5)
Mo1—O2	1.714 (5)	Mo2—O7	1.688 (5)
Mo1—O8	1.956 (5)	Mo2—O4	1.943 (5)
Mo1—O4^{i}	1.957 (5)	Mo2—O8^{ii}	1.965 (5)
Mo1—O1	2.230 (5)	Mo2—O8	2.291 (5)
Mo1—O4	2.295 (5)	Mo2—O5	2.300 (5)
Mo1—Mo2	3.3965 (9)		
O3—Mo1—O2	102.3 (3)	O6—Mo2—O7	103.8 (3)
O3—Mo1—O8	106.0 (2)	O6—Mo2—O4	98.3 (2)
O2—Mo1—O8	96.8 (2)	O7—Mo2—O4	104.0 (2)
O3—Mo1—O1	87.4 (2)	O6—Mo2—O8	93.0 (2)
O2—Mo1—O1	170.2 (2)	O7—Mo2—O8	163.2 (2)
O8—Mo1—O1	81.0 (2)	O4—Mo2—O8	74.00 (19)
O3—Mo1—O4	166.5 (2)	O6—Mo2—O5	172.5 (2)
O2—Mo1—O4	91.1 (2)	O7—Mo2—O5	83.7 (2)
O8—Mo1—O4	73.70 (19)	O4—Mo2—O5	78.9 (2)
O1—Mo1—O4	79.16 (19)	O8—Mo2—O5	79.59 (18)

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WB···O7^{iii}	0.82 (6)	2.39 (7)	3.059 (8)	141 (10)
O1W—H1WB···O5^{iii}	0.82 (6)	2.47 (7)	3.151 (9)	142 (10)
O1W—H1WA···O2^{i}	0.82 (8)	2.07 (6)	2.809 (8)	151 (11)
N1—H1A···O1W^{iv}	0.86	1.93	2.727 (9)	154

Symmetry codes: (i) $1 - x, -y, 1 - z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $x - 1, y, z$.

H atoms attached to C and N atoms were positioned geometrically and included in the refinement using a riding model [C—H = 0.93 Å, N—H = 0.86 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N)]. The water H atoms were located from difference maps and their positions were refined isotropically, with O—H distances fixed at 0.82 (6) and 0.82 (8) Å [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O)]. The −1.12 Å^{-3} hole in the final difference map is 1.05 Å from atom Mo1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1466). Services for accessing these data are described at the back of the journal.

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