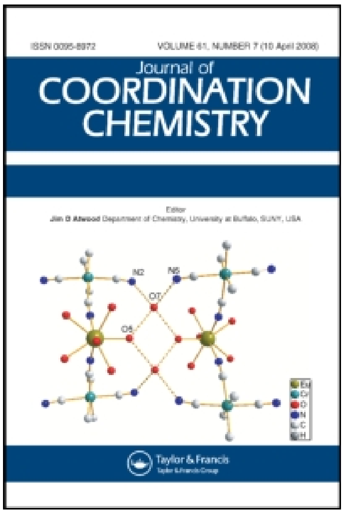

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Novel wavy chain structure

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A novel wavy molybdenum oxide chain structure

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A novel one-dimensional coordination polymer $[Mo_3O_9(phen)_2]_n$ (phen = 1,10-phenanthroline) has been synthesized by hydrothermal methods and characterized by single-crystal X-ray diffraction analysis. The complex exhibits an infinite, one-dimensional wavy chain with phen coordinated directly to the molybdenum oxide framework, where binuclear units consisting of binuclear octahedral $[MoO_4N_2]$ groups are linked by $[MoO_4]$ tetrahedra through corner-sharing oxygen atoms.

Keywords: Molybdenum; 1,10-Phenanthroline; Crystal structure; Wavy chain

1. Introduction

The synthesis and characterization of novel hybrid materials have significant interest, owing to the enormous variety of intriguing topological structures and properties as well as potential applications in many fields such as catalysis, material science, electrical conductivity, magnetism and photochemistry [1,2]. In past decades, there has been much interest in molybdenum oxides and molybdates in terms of polymeric oxoanion chemistry and model systems [3–7].

Recently, the use of hydrothermal techniques and organic structure-directing agents has led to the production of various molybdenum oxides with discrete clusters or one-, two- and three-dimensional structures [8–11]. However, published literature concerning molybdenum is mainly focused on metal clusters with Mo–Mo bonds. On the other hand, the use of carboxylic acids and organodiamines, which can be extensively linked to inorganic oxide backbones, has a dramatic effect on the oxide structures and offers a powerful synthetic route for the design of novel materials [12–14]. Here, the bidentate ligand phen was used to link to molybdate in a hydrothermal synthesis to prepare $[Mo_3O_9(phen)_2]_n$ (phen = 1,10-phenanthroline). It exhibits an infinite one-dimensional wavy chain with phen coordinated directly to the molybdenum oxide

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framework, where binuclear octahedral [MoO_4N_2] units are linked by tetrahedral [MoO_4] groups through corner-sharing oxygen atoms.

2. Experimental

2.1. *Synthesis*

A mixture of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (371.0 mg), phen (119.1 mg) and 15 cm^3 water was added to a Teflon-lined autoclave (25 cm^3), then the pH was adjusted to 4 with nitric acid (5 M). The reaction mixture was kept at 180° C for 3 days. After slow cooling to room temperature, pink crystals were filtered off, washed with distilled water and dried in vacuum at room temperature. Yield: 40%. Found (Calcd) for $[Mo_3O_9(phen)_2]_n$: C, 36.05 (36.39); H, 1.82 (2.04); N, 7.59 (7.07)%.

2.2. *Physical measurements*

Analyses for C, H and N were carried out on a Perkin-Elmer instrument at the Institute of Organic Chemistry, Nankai University. Thermogravimetric analyses were made using a Netzsch TG 209 instrument.

2.3. *Crystal structure determination*

A red single crystal having approximate dimensions $0.15 \times 0.06 \times 0.04$ mm was mounted on a glass fiber. Determination of the unit cell and data collection were performed with Mo Kα adiation ($\lambda = 0.71073$ Å) on a Bruker SMART 1000 diffractometer equipped with a CCD camera. Cell parameters were determined from least-squares refinement of the setting angles of 25 well-centered reflections in the range 2.23 to 25.02° at 293 K. Intensities of the $\pm hkl$ reflections were measured up to $\theta_{max} = 25.02°$; ; the ω–2θ scan technique was used. The index range was $-15 \le h \le 17$, $-9 \le k \le 11$ and $-12 \le l \le 10$. The structure was solved by direct methods using the program SHELXS-97 [15] and subsequent difference Fourier syntheses, and refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [16]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Crystal parameters and structure refinement details are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of the structure*

The structure analysis revealed the formation of a one-dimensional Mo–O–Mo chain with phen coordinated directly to the Mo1 and Mo2 sites of the skeleton. The molecular structure is depicted in figure 1. There are two crystallographically unique molybdenum atoms. Mo1 and Mo1A sites both exhibit distorted octahedral geometries defined by two N atoms of phen with an average Mo–N bond distance of 2.349(9) Å,

Table 1. Crystal data and structure refinement details for $[Mo_3O_9(phen)_2]_n$.

Empirical formula	$C_{24}H_{16}Mo_3N_4O_9$
Formula weight	792.23
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2
a (Å)	14.983(5)
b (Å)	9.715(3)
c (Å)	10.332(3)
β (°)	118.100(5)
Volume ($Å^3$)	1326.7(7)
Z	2
Density (calculated) ($mg\,m^{-3}$)	1.983
Absorption coefficient (mm^{-1})	1.456
F(000)	772
Crystal size (mm^3)	0.15 × 0.06 × 0.04
θ range for data collection (°)	2.23–25.02
Limiting indices	$-15 \le h \le 17$
	$-9 \le k \le 11$
	$-12 \le l \le 10$
Reflections collected	2773
Independent reflections	2037 [*R*(int) = 0.0295]
Max. and min. transmission	1.000000 and 0.800074
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2037/115/183
Goodness-of-fit on F^2	1.051
$R1$, $wR2$ [$I > 2\sigma(I)$][a]	0.0374, 0.0832
$R1$, $wR2$ (all data)	0.0442, 0.0867
Largest diff. peak and hole ($e\,Å^{-3}$)	0.726 and −0.580

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2)^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 5.2547P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for $[Mo_3O_9(phen)_2]_n$.

Mo(1)–O(2)	1.689(7)	Mo(2)–O(4)	1.805(6)
Mo(1)–O(3)	1.699(6)	Mo(2)–O(4)#1	1.805(6)
Mo(1)–O(1)	1.8765(10)	O(1)–Mo(1)#2	1.8765(10)
Mo(1)–O(4)	2.003(6)	C(2)–C(3)	1.366(13)
Mo(1)–N(1)	2.343(7)	N(1)–C(11)	1.367(9)
Mo(1)–N(2)	2.354(7)	N(1)–C(1)	1.340(10)
Mo(2)–O(5)	1.687(9)	N(2)–C(10)	1.326(11)
Mo(2)–O(5)#1	1.687(9)	N(2)–C(12)	1.350(10)
O(2)–Mo(1)–O(1)	100.6(3)	O(2)–Mo(1)–O(3)	106.4(3)
O(3)–Mo(1)–O(1)	100.0(2)	O(2)–Mo(1)–N(2)	90.4(3)
O(2)–Mo(1)–O(4)	93.7(3)	O(3)–Mo(1)–N(2)	162.5(3)
O(3)–Mo(1)–O(4)	95.9(3)	O(1)–Mo(1)–N(2)	81.3(2)
O(1)–Mo(1)–O(4)	154.6(3)	O(4)–Mo(1)–N(2)	77.7(2)
O(3)–Mo(1)–N(1)	92.4(3)	O(5)–Mo(2)–O(5)#1	107.4(7)
O(1)–Mo(1)–N(1)	83.4(3)	O(5)–Mo(2)–O(4)	109.7(3)
O(4)–Mo(2)–O(4)#1	106.5(4)	O(5)#1–Mo(2)–O(4)	111.8(3)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+2$; #2 $-x, y, -z+1$.

two bridging oxygen atoms [Mo1–O1 1.8765(10) Å, Mo1–O4 2.003(6) Å] and two terminal oxygen atoms [Mo1–O2 1.689(7) Å, Mo1–O3 1.699(6) Å]. The bridging Mo–O bonds are longer than the terminal coordinated Mo–O bonds, which is common for MoO_6 octahedra [17]. The equatorial plane of the octahedron is defined by

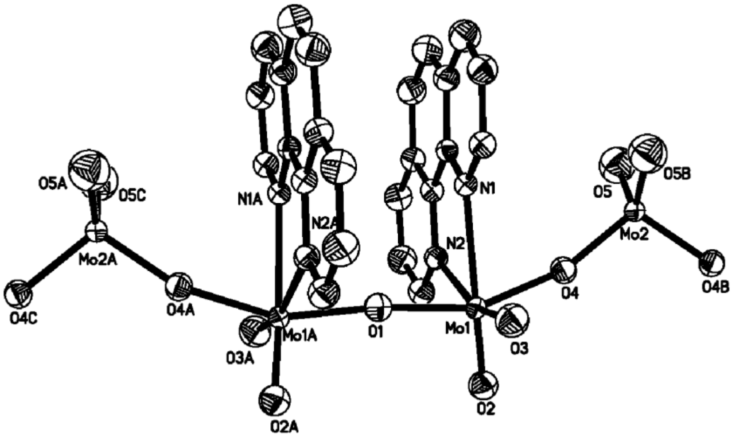

Figure 1. Structure of the complex showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

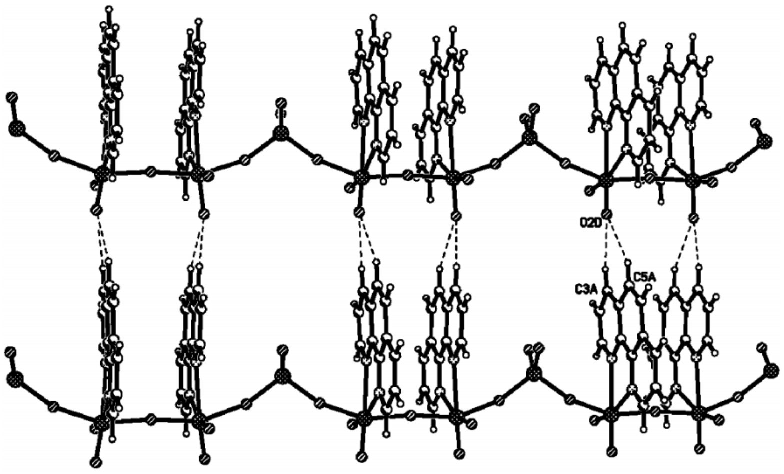

Figure 2. The one-dimensional chain structure in $[Mo_3O_9(phen)_2]_n$, showing the hydrogen bonds that link the chains into a two-dimensional network.

N1N2O2O3, with the largest deviation of 0.1145 Å for O3. Mo1 deviates from the plane by 0.1298 Å. Two MoN_2O_4 octahedra are linked through an oxygen atom as a bridge with an Mo1–O1–Mo1A bond angle of 173.8(6)° to form a dinuclear unit. The distance Mo1···Mo1A is 3.748(7) Å. The aromatic rings of the two phen ligands coordinated to Mo1 and Mo1A are almost parallel with a dihedral angle of 2.9°, and suggest a significant $\pi \cdots \pi$ interaction.

The Mo2 site exhibits distorted tetrahedral geometry and is coordinated by two bridging oxo groups [1.805(6) Å] and two terminal oxo groups [1.687(9) Å]. The average O–Mo2–O bond angle is 109.5° and Mo1–O4–Mo2 is 155.4(3)°. A view of the molybdenum oxide chain is shown in figure 2. The one-dimensional wavy chain is composed of the binuclear units of MoN_2O_4 octahedra linked by MoO_4 tetrahedra through corner-sharing. The Mo1A···Mo2A distance is 3.721 Å.

The one-dimensional wavy chains are linked together by hydrogen bonds [C3A–H···O2D = 3.353(6) Å, C5A–H···O2D = 3.329(6) Å] to form a two-dimensional network as shown in figure 2. The closest Mo···Mo distance between neighboring chains is 8.642(4) Å. McGowan *et al.* [18] have reported a related series of molybdenum trioxides containing 1,4,7-triazacyclononane and its derivatives, in which simple mononuclear molybdenum oxides are used as a template for hydrogen-bonding interactions with monofunctionalized triazacyclononane ligands with a longest N–H···O distance of 3.395(7) Å. The TG trace of the title compound shows a total weight loss of 22.2% up to 600° C. This loss is due to release of the phen ligand.

The successful isolation of this compound shows that the hydrothermal technique offers a powerful method for the creation of novel inorganic oxide materials. We are exploring other organonitrogen chelating ligands in similar hydrothermal systems with the aim of synthesizing novel molybdenum oxides with interesting topological structures and properties.

Supplementary material

Additional material, consisting of atomic coordinates and equivalent isotropic displacement parameters, is available from the Cambridge Crystallographic Data Centre, CCDC No. 188069. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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