Crystal structure of bis[(1,3-bis(4-pyridinium)propane)]- β -hexacosaoxooctamolybdate(VI), $(C_{13}H_{16}N_2)_2[Mo_8O_{26}]$

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Received July 17, 2006, accepted and available on-line August 7, 2006; CCDC no. 1267/1841

Source of material

Yellow block-shaped crystals of the title compound were obtained by hydrothermal reaction of $CoCl_2 \cdot 6H_2O$ (0.2 mmol, 0.0476 g), 1,3-bis(4-pyridyl)propane (0.4 mmol, 0.0792 g), MoO_3 (0.40 mmol, 0.0580 g), and water (15 mL) in a 23 mL Teflon-lined reaction vessel at 140 °C for 72 h (yield 91 % based on initial MoO_3 input). $CoCl_2$ acts probably as catalyst, the synthesis did not succeed without this compound.

Discussion

The polyoxometalates (POMs) have been of great interest because of their so-called "value-adding properties" and conventional applications in photochemical response, conductivity, catalysis and medicine [1–3]. POMs are found to be extremely versatile inorganic building blocks for construction of inorganic-organic hybrid materials with novel structures and unusual properties [4–5]. The $[Mo_8O_{26}]^{4-}$ octamolybdates are well-known POMs, which are incorporated into extended structures by covalent linkages between secondary metal sites and polydentate nitrogen donor ligands or only modified by organic components [6–9].

The structure of the title compound contains one discrete β -octamolybdate anion $[Mo_8O_{26}]^{4-}$ and two protonized bpp ligands (bpp = 1,3-bis(4-pyridyl)propane). Each $[Mo_8O_{26}]^{4-}$ polyanion is built up from eight distorted MoO_6 octahedra by sharing edges and corners with local C_{2h} symmetry. Eight molybdenum atoms can be visualized as an edge-sharing double O-centered trigonal bipyramid. According to the different coordination number, the oxygen atoms in the $[Mo_8O_{26}]^{4-}$ polyanion can be classified into four types: terminal oxygen atoms (O_t); two-coordinated oxygen atoms (O_{2c}); three-coordinated oxygen atoms (O_{3c}) and five-coordinated oxygen atoms (O_{5c}). On the other hand, the molybdenum atoms in $[Mo_8O_{26}]^{4-}$ can also be classified into three types according to their environment: the class I Mo atoms are coordinated to one O_t , one O_{2c} , two O_{3c} and two O_{5c} atoms, such as Mo1; the class II Mo atoms are coordinated to two O_t , one O_{2c} , two O_{3c} and one O_{5c} atoms, such as Mo2 and Mo4; and the class III Mo atoms are coordinated to two O_t , three O_{2c} , and one O_{5c} atoms, such as Mo3. Therefore, there are four kinds of Mo—O bonds in this polyanion, which can be named as Mo— O_t (bond lengths: 1.6906 Å – 1.7220 Å), Mo— O_{2c} (bond lengths: 1.7425 Å – 2.3326 Å), Mo— O_{3c} (bond lengths: 1.9456 Å – 2.3298 Å) and Mo— O_{5c} (bond lengths: 2.1650 Å – 2.4692 Å). The overall dimensions of the present octamolybdate polyanion are consistent with those reported compounds containing the same type polyanion [8–10], in spite of slightly difference in Mo—O bond lengths due to the different cation-polyanion interactions. The protonized bpp ligands in this compound play a role of counteraction to balance the charge of the $[Mo_8O_{26}]^{4-}$ polyanions. The protonized bpp ligands are linked to $[Mo_8O_{26}]^{4-}$ via strong hydro-

Abstract

$C_{26}H_{32}Mo_8N_4O_{26}$, monoclinic, $P12_1/c1$ (no. 14), $a = 10.589(2)$ Å, $b = 10.007(2)$ Å, $c = 19.662(4)$ Å, $\beta = 100.85(3)^\circ$, $V = 2046.2$ Å³, $Z = 2$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.056$, $T = 293$ K.

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gen bonds ($d(\text{N} \cdots \text{O}) = 2.766(3) \text{ \AA} - 2.786(3) \text{ \AA}$), while each [Mo₈O₂₆]⁴⁻ polyanion is linked to four adjacent bpp through its four terminal oxygen atoms, and the bpp ligands are further linked to adjacent [Mo₈O₂₆]⁴⁻ polyanions to build up 3D supramolecular structure.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.33 × 0.34 × 0.55 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	24.67 cm ⁻¹
Diffractometer, scan mode:	Rigaku R-Axis RAPID IP, φ/ω
$2\theta_{\text{max}}$:	51°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	16318, 3801
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3568
$N(\text{param})_{\text{refined}}$:	253
Programs:	SHELXS-97 [11], SHELXL-97 [12]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	4e	0.2862	0.1179	0.2222	0.047
H(2A)	4e	0.2001	0.2586	0.2939	0.068
H(3A)	4e	0.4793	0.1775	0.4484	0.069
H(4A)	4e	0.5735	0.0364	0.3808	0.050
H(6A)	4e	0.4422	-0.0725	0.2149	0.042
H(6B)	4e	0.5684	-0.0784	0.2714	0.042
H(7A)	4e	0.6013	0.0196	0.1634	0.043
H(7B)	4e	0.5142	0.1395	0.1770	0.043
H(8A)	4e	0.6656	0.1856	0.2801	0.045
H(8B)	4e	0.7549	0.0758	0.2580	0.045
H(10A)	4e	0.8986	0.2868	0.2816	0.049
H(11A)	4e	0.9925	0.4528	0.2273	0.060
H(12A)	4e	0.7362	0.4065	0.0573	0.053
H(13A)	4e	0.6336	0.2412	0.1082	0.044
H(1B)	4e	0.3017	0.2818	0.4021	0.073
H(2B)	4e	0.9056	0.5044	0.1196	0.055

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mo(1)	4e	0.97335(2)	0.02620(2)	0.08681(1)	0.0222(1)	0.0172(1)	0.0157(1)	0.00124(9)	0.00594(9)	0.00102(8)
Mo(2)	4e	1.07307(2)	-0.26391(2)	0.04851(1)	0.0272(2)	0.0150(1)	0.0209(1)	0.00094(9)	0.0038(1)	0.00289(8)
Mo(3)	4e	1.17963(2)	0.29367(2)	0.07494(1)	0.0278(2)	0.0177(1)	0.0248(1)	-0.00220(9)	0.0042(1)	-0.00165(9)
Mo(4)	4e	1.27515(2)	-0.00259(2)	0.03585(1)	0.0193(1)	0.0202(1)	0.0238(1)	0.00114(9)	0.0045(1)	0.00093(9)
O(1)	4e	0.88927(6)	-0.04649(6)	0.14276(3)	0.035(1)	0.033(1)	0.024(1)	-0.0002(9)	0.0117(9)	0.0056(8)
O(2)	4e	0.83990(6)	0.12772(6)	0.02707(3)	0.023(1)	0.0165(9)	0.0211(9)	0.0040(7)	0.0067(8)	-0.0014(7)
O(3)	4e	1.05120(6)	0.16154(6)	0.13223(3)	0.032(1)	0.022(1)	0.023(1)	0.0008(8)	0.0059(8)	-0.0025(8)
O(4)	4e	0.99104(6)	-0.35029(6)	-0.03361(3)	0.031(1)	0.017(1)	0.025(1)	0.0032(8)	0.0049(8)	-0.0010(7)
O(5)	4e	1.21636(6)	-0.34415(6)	0.06426(3)	0.034(1)	0.025(1)	0.040(1)	0.0069(9)	0.001(1)	0.0032(9)
O(6)	4e	0.98880(6)	-0.32618(6)	0.10839(3)	0.048(1)	0.027(1)	0.028(1)	-0.009(1)	0.011(1)	0.0034(9)
O(7)	4e	1.21422(6)	0.38932(6)	0.14750(3)	0.048(1)	0.031(1)	0.035(1)	-0.005(1)	0.002(1)	-0.0101(9)
O(8)	4e	1.28501(6)	0.13907(6)	0.10097(3)	0.027(1)	0.024(1)	0.025(1)	-0.0002(8)	-0.0018(8)	-0.0022(8)
O(9)	4e	1.26244(6)	0.36219(6)	0.01703(3)	0.043(1)	0.031(1)	0.044(1)	-0.004(1)	0.016(1)	0.004(1)
O(10)	4e	1.38442(6)	-0.11060(6)	0.07911(3)	0.027(1)	0.031(1)	0.044(1)	0.0052(9)	0.003(1)	0.0037(9)
O(11)	4e	1.34625(6)	0.06762(6)	-0.02664(3)	0.033(1)	0.035(1)	0.038(1)	-0.002(1)	0.014(1)	0.005(1)
O(12)	4e	1.12315(6)	-0.09072(6)	0.09678(3)	0.022(1)	0.020(1)	0.0189(9)	0.0006(7)	0.0028(7)	0.0017(7)
O(13)	4e	0.9185(2)	-0.1096(2)	0.00058(8)	0.024(1)	0.0190(9)	0.0193(9)	0.0010(8)	0.0047(8)	0.0014(7)
C(1)	4e	0.3277(2)	0.1299(2)	0.26783(8)	0.042(2)	0.046(2)	0.033(2)	0.006(2)	0.016(2)	0.007(1)
C(2)	4e	0.2761(4)	0.2130(4)	0.3106(2)	0.061(3)	0.046(2)	0.073(3)	0.015(2)	0.038(2)	0.014(2)
C(3)	4e	0.4418(5)	0.1650(4)	0.4022(2)	0.074(3)	0.066(3)	0.036(2)	-0.042(2)	0.020(2)	-0.021(2)
C(4)	4e	0.4981(3)	0.0813(4)	0.3620(2)	0.035(2)	0.054(2)	0.037(2)	-0.017(2)	0.006(2)	-0.003(2)
C(5)	4e	0.4420(3)	0.0632(3)	0.2928(1)	0.030(2)	0.025(2)	0.029(2)	-0.009(1)	0.011(1)	0.001(1)
C(6)	4e	0.5062(3)	-0.0186(3)	0.2446(2)	0.037(2)	0.026(2)	0.044(2)	-0.004(1)	0.015(2)	-0.004(1)
C(7)	4e	0.5746(3)	0.0729(3)	0.1994(2)	0.035(2)	0.040(2)	0.034(2)	0.001(1)	0.012(1)	-0.007(1)
C(8)	4e	0.6908(3)	0.1428(3)	0.2404(2)	0.036(2)	0.037(2)	0.037(2)	-0.003(1)	0.005(1)	0.011(1)
C(9)	4e	0.7524(3)	0.2463(3)	0.2017(2)	0.036(2)	0.027(2)	0.033(2)	0.005(1)	0.016(1)	0.002(1)
C(10)	4e	0.8632(3)	0.3108(4)	0.2363(2)	0.043(2)	0.044(2)	0.036(2)	-0.003(2)	0.010(2)	0.004(1)
C(11)	4e	0.9196(4)	0.4091(4)	0.2040(2)	0.049(2)	0.050(2)	0.055(2)	-0.012(2)	0.018(2)	-0.000(2)
C(12)	4e	0.7670(4)	0.3819(4)	0.1030(2)	0.062(2)	0.043(2)	0.033(2)	0.015(2)	0.023(2)	0.008(2)
C(13)	4e	0.7059(4)	0.2832(3)	0.1334(2)	0.044(2)	0.034(2)	0.035(2)	0.002(2)	0.013(2)	-0.002(1)
N(1)	4e	0.3348(4)	0.2284(3)	0.3759(2)	0.094(3)	0.039(2)	0.066(2)	-0.017(2)	0.056(2)	-0.019(2)
N(2)	4e	0.8697(3)	0.4417(3)	0.1391(2)	0.059(2)	0.030(2)	0.058(2)	-0.005(1)	0.039(2)	0.005(1)

Acknowledgment. The author gratefully acknowledges the financial support of Young Teacher Research Fund of Beijing Institute of Civil Engineering and Architecture(1005014).

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