Crystal structure of oxonium 4,4′-bipyridinium chromium-molybdate(VI) trihydrate, $[H_3O][C_{10}H_{10}N_2][CrMo_6H_6O_{24}] \cdot 3H_2O$

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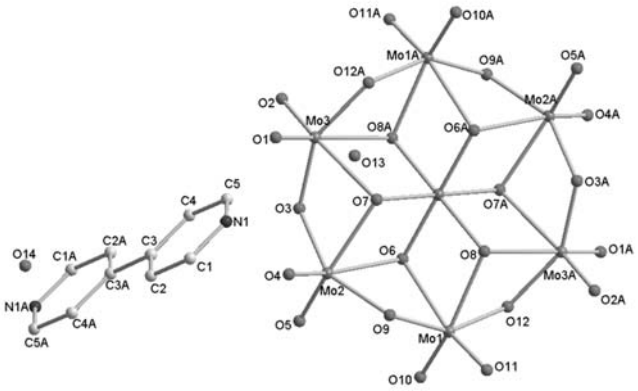

Abstract

$C_{10}H_{10}CrMo_6N_2O_{28}$, triclinic, $P\bar{1}$ (no. 2), a = 7.9590(3) Å, b = 8.6394(3) Å, c = 11.6502(5) Å, α = 91.559(1)°, β = 103.539(1)°, γ = 95.664(1)°, V = 774.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.080, T = 273 K.

Source of material

A mixture of $Na_2MoO_4 \cdot 2H_2O$ (1.86 mmol), $MnCl_2 \cdot 2H_2O$ (0.3 mmol), $CrCl_3 \cdot 6H_2O$ (0.75 mmol), 1,10-phenanthroline (0.2 mmol), 4,4′-bipyridine (0.2 mmol), and H_2O (10 mL) was stirred for 30 minutes at 75 °C. After the pH value of the solution was adjusted to 3.54 with diluted NaOH solution it was transferred to a 23 mL Teflon-lined stainless steel reactor. The solution was heated under autogenous pressure at 165 °C for 120 h. After slow cooling to room termperature at a rate of 10 °C/h, pink platelet crystals were filtered off, washed with distilled water and dried in air.

Discussion

Polyoxometalates (POMs) have become a subject of general interest which not only originates from their intriguing variety of architectures and geometric topologies [1,2], but also from their promising potential applications in catalysis, medicine, ion exchange, molecular materials, photochemical, electrochemistry, and magnetism [3-6].

The title crystal structure is composed of $[CrMo_6H_6O_{24}]^{3-}$ Anderson-type polyoxoanions, 4,4′-bipyridinium cations and waters molecules. The $[CrMo_6H_6O_{24}]^{3-}$ anionic cluster has a B-type Anderson structure consisting of seven edge-shared octahedra, six of which are $[MoO_6]$ octahedra arranged around the central Cr^{3+} octahedron. According to the coordination mode, the oxygen atoms within $[CrMo_6H_6O_{24}]^{3-}$ clusters can be divided into three different groups: the terminal oxygen atoms O_t, the oxygen atoms O_b coordinated to two Mo atoms, the oxygen atoms O_c coordinated to a Cr atom and two Mo atoms. Thus, the Mo—O distances can be divided into three groups: d(Mo—O_t) = 1.687(3) - 1.722(2) Å, d(Mo—O_b) = 1.905(2) - 1.997(2) Å and d(Mo—O_c) = 2.270(2) - 2.332(2) Å. The central distances d(Cr—O_c) range from 1.956(2) to 1.980(2) Å. The bond angles ∠O–Cr–O_{cis} vary from 83.31(9)° to 96.3(1)°, and ∠O–Cr–O_{trans} is 180.0°. The cations interact with the $[CrMo_6H_6O_{24}]^{3-}$ anion to give rise to a three-dimensional hydrogen-bonded network.

Table 1. Data collection and handling.

Crystal:	pink platelet, size 0.12 × 0.20 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	27.97 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID IP, ω
$2\theta_{max}$:	56.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5658, 3692
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3438
$N(param)_{refined}$:	214
Programs:	SHELXS-97, SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(01A)	2*i*	0.3411	0.7541	0.3382	0.055
H(2)	2*i*	0.0457	0.7602	0.5589	0.051
H(1)	2*i*	0.2241	0.6320	0.4675	0.056
H(4)	2*i*	0.1219	1.1290	0.3716	0.098
H(5)	2*i*	0.2999	0.9953	0.2861	0.106

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(14)	2*i*	0.2184(8)	0.8003(7)	0.7960(4)	0.178(5)	0.148(5)	0.053(2)	0.141(5)	0.017(3)	0.005(2)
Cr(1)	1*e*	½	½	0	0.0154(3)	0.0170(3)	0.0238(3)	0.0032(2)	0.0057(2)	–0.0011(2)
Mo(1)	2*i*	0.14248(3)	0.24786(3)	–0.04168(3)	0.0174(1)	0.0185(1)	0.0399(2)	0.00236(9)	0.0081(1)	–0.0018(1)

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Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(2)	2*i*	0.33770(4)	0.38927(4)	0.23009(3)	0.0238(1)	0.0346(2)	0.0300(2)	0.0029(1)	0.0104(1)	0.0038(1)
Mo(3)	2*i*	0.68953(3)	0.64402(3)	0.27380(2)	0.0231(1)	0.0315(2)	0.0265(2)	0.0043(1)	0.0029(1)	–0.0054(1)
O(7)	2*i*	0.4191(3)	0.5789(3)	–0.1588(2)	0.021(1)	0.023(1)	0.028(1)	0.0059(8)	0.0056(8)	0.0022(8)
O(6)	2*i*	0.2725(3)	0.4859(2)	0.0416(2)	0.0171(9)	0.021(1)	0.030(1)	0.0046(7)	0.0075(8)	–0.0007(8)
O(8)	2*i*	0.4081(3)	0.2951(2)	–0.0816(2)	0.021(1)	0.018(1)	0.031(1)	0.0031(8)	0.0064(8)	–0.0040(8)
O(3)	2*i*	0.4468(3)	0.6005(3)	0.2746(2)	0.026(1)	0.035(1)	0.033(1)	0.0051(9)	0.0112(9)	–0.008(1)
O(5)	2*i*	0.1375(4)	0.4184(4)	0.2525(3)	0.032(1)	0.069(2)	0.054(2)	–0.005(1)	0.023(1)	–0.010(2)
O(1)	2*i*	0.7902(4)	0.5493(4)	0.3908(2)	0.040(2)	0.063(2)	0.034(1)	0.006(1)	0.000(1)	0.010(1)
O(2)	2*i*	0.7127(4)	0.8347(3)	0.3186(3)	0.042(2)	0.040(1)	0.046(2)	0.000(1)	0.007(1)	–0.018(1)
O(4)	2*i*	0.4367(4)	0.2908(4)	0.3454(3)	0.050(2)	0.055(2)	0.037(2)	–0.002(1)	0.004(1)	0.017(1)
C(3)	2*i*	0.0598(4)	0.9583(4)	0.4731(3)	0.028(2)	0.033(2)	0.032(2)	0.001(1)	0.013(1)	–0.008(1)
N(1)	2*i*	0.2742(5)	0.8031(4)	0.3710(3)	0.041(2)	0.048(2)	0.054(2)	0.012(1)	0.023(2)	–0.012(2)
C(2)	2*i*	0.0948(6)	0.8094(5)	0.5026(3)	0.052(2)	0.049(2)	0.035(2)	0.021(2)	0.022(2)	0.007(2)
C(1)	2*i*	0.2025(6)	0.7332(5)	0.4487(4)	0.056(2)	0.050(2)	0.043(2)	0.028(2)	0.020(2)	0.007(2)
C(4)	2*i*	0.1403(9)	1.0276(6)	0.3919(6)	0.120(5)	0.034(2)	0.133(5)	0.024(3)	0.105(5)	0.021(3)
C(5)	2*i*	0.2467(9)	0.9484(6)	0.3412(7)	0.122(5)	0.053(3)	0.135(6)	0.020(3)	0.112(5)	0.018(3)
O(10)	2*i*	–0.0560(3)	0.2864(3)	–0.0193(2)	0.020(1)	0.029(1)	0.051(2)	0.0042(9)	0.012(1)	0.002(1)
O(11)	2*i*	0.1139(3)	0.0615(3)	–0.0983(3)	0.033(1)	0.023(1)	0.053(2)	0.0009(9)	0.008(1)	–0.004(1)
O(9)	2*i*	0.2725(3)	0.2138(3)	0.1131(2)	0.027(1)	0.023(1)	0.038(1)	0.0019(8)	0.0070(9)	0.0055(9)
O(12)	2*i*	0.1180(3)	0.3589(3)	–0.1906(2)	0.021(1)	0.032(1)	0.036(1)	0.0047(9)	0.0043(9)	0.001(1)
O(13)	2*i*	0.3768(5)	0.9103(4)	0.0935(4)	0.053(2)	0.046(2)	0.093(3)	0.023(2)	0.012(2)	–0.001(2)

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