Crystal structure of bis(4-aminopyridinium) oxonium chromo(III)-hexamolybdate(VI) dihydrate, $[C_5H_7N_2]_2[H_3O][CrMo_6(OH)_6O_{18}] \cdot 2H_2O$

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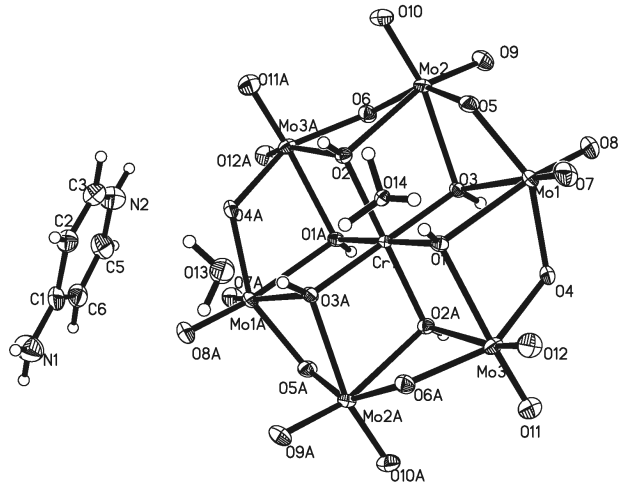

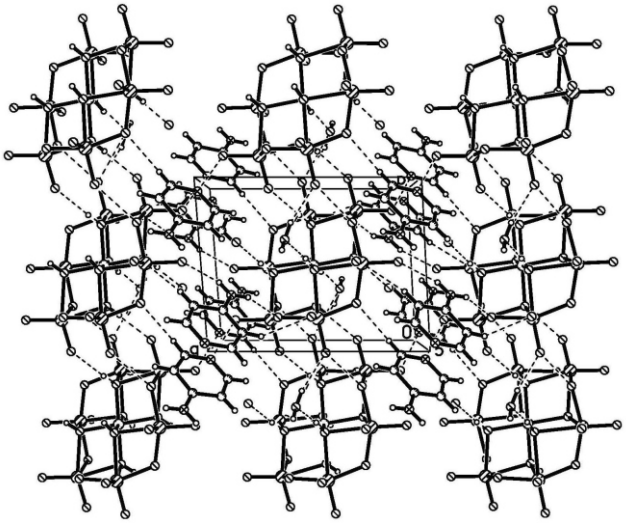

Abstract

$C_{10}H_{27}CrMo_6N_4O_{27}$, triclinic, $P\bar{1}$ (no. 2), a = 7.951(5) Å, b = 10.036(5) Å, c = 10.345(5) Å, α = 88.976(5)°, β = 78.016(5)°, γ = 86.207(5)°, V = 805.7 Å^3, Z = 1, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.116, T = 293 K.

Source of material

A mixture of $CrCl_3 \cdot 6H_2O$ (0.060 g, 2.252 mmol), MoO_3 (0.600 g, 4.167 mmol), $Na_2MoO_4 \cdot 2H_2O$ (0.120 g, 0.496 mmol), 4-aminopyridine (0.030 g, 0.032 mmol), H_2SO_4 (0.4 ml, 1:1, *v*/*v*)), H_2O (14 ml) was sealed in a 25 ml Teflon-lined bomb at 170 °C for 120 h, then solwly cooled to room temperature. Red block-like crystals were collected by filtration, washed by distilled water, and air-dried in a yield of 35 % based on the initial $CrCl_3 \cdot 6H_2O$ input.

Experimental details

The hydrogen atoms positions of 4-aminopyridinium were generated geometrically, but for the Anderson type polyoxoanion and all free oxygen, the hydrogen atoms were located from difference Fourier maps. Especially for the free oxygen O14, there were three Q peaks around it, and the peaks value was approximately. So we named the three Q peaks to three hydrogen atoms, which also can be used to interpret the balance of valence.

Discussion

The title crystal structure consists of $C_5H_7N_2^+$ and H_3O^+ cations, water molecules and $[CrMo_6(OH)_6O_{18}]^{3-}$ polyoxoanions (figure, top), which belong to B-type Anderson with a center of symmetry. The polyanion consists of seven edge-sharing octahedra, six of which are $[MoO_6]$ octahedra, arranged around the central $[Cr(OH)_6]$ octahedron. Cr^{3+} and Mo^{6+} often form B-type Anderson polyoxoanions, e.g. $[CrMo_6(OH)_6O_{18}]^{3-}$ [2]. The Cr—O and Mo—O bond lengths are in the range of 1.961(4) - 1.976(4) Å and 1.605(1) - 2.280(4) Å, respectively. The *cis* bond angles of O–Cr–O and O–Mo–O range from 83.1(2)° to 96.9(2)° and 69.7(1)° to 106.7(2)°, respectively, and the *trans* bond angle of O–Cr–O and O–Mo–O are 180.00° and 149.2(2)° to 161.9(2)°, respectively, suggesting a significant deviation from the perfect octahedral coordination. All of the bond lengths and bond angles are within the normal ranges and are consistent with those described in the literature [1]. The water molecules donor hydrogen atoms to the $[CrMo_6(OH)_6O_{18}]^{3-}$ polyoxoanion oxygen atoms O8 and O10 to form strong inter-molecular hydrogen bonds (figure, bottom). The title compound forms a layer supramolecular structure via hydrogen-bonding interactions.

Table 1. Data collection and handling.

Crystal:	red block, size 0.17 × 0.24 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	26.89 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6917, 2751
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2601
$N(param)_{refined}$:	224
Programs:	SHELXS-97, SHELXL-97 [3]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(14A)	2*i*	0.50	0.3740	0.1550	0.3367	0.020
H(14B)	2*i*	0.50	0.3909	0.0628	0.4355	0.020
H(14C)	2*i*	0.50	0.2543	0.1588	0.4554	0.020
H(2A)	2*i*		0.0904	0.7550	0.0281	0.044
H(3B)	2*i*		–0.0472	0.8279	0.2264	0.058
H(5A)	2*i*		0.1937	1.1506	0.1973	0.060
H(6A)	2*i*		0.3492	1.1008	–0.0034	0.052
H(1A)	2*i*		0.3077	0.8095	–0.1718	0.072
H(1B)	2*i*		0.4001	0.9349	–0.1824	0.072
H(2C)	2*i*		0.0128	1.0156	0.3057	0.065
H(1)	2*i*		0.4890	0.2486	0.4876	0.028
H(2B)	2*i*		0.1920	0.4477	0.5043	0.029
H(3A)	2*i*		0.5412	0.5350	0.7328	0.027
H(13A)	2*i*		0.4104	0.3616	0.0856	0.059
H(13B)	2*i*		0.2501	0.4082	0.1565	0.059

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(14)	2*i*	0.50	0.3599(9)	0.1431(7)	0.4197(7)	0.013(2)	0.013(2)	0.015(2)	–0.001(1)	–0.004(1)	–0.002(1)
C(1)	2*i*		0.242(1)	0.9181(9)	–0.0212(8)	0.043(4)	0.070(5)	0.031(4)	0.011(4)	–0.014(3)	0.012(4)
C(2)	2*i*		0.1149(9)	0.8364(7)	0.0592(7)	0.037(4)	0.034(3)	0.041(4)	–0.009(3)	–0.012(3)	0.004(3)
C(3)	2*i*		0.036(1)	0.8799(9)	0.1765(8)	0.035(4)	0.060(5)	0.049(5)	–0.003(3)	–0.010(3)	0.007(4)
C(5)	2*i*		0.178(1)	1.0704(8)	0.1593(8)	0.061(5)	0.045(4)	0.045(5)	–0.001(4)	–0.012(4)	0.003(4)
C(6)	2*i*		0.270(1)	1.0428(8)	0.0402(8)	0.043(4)	0.047(4)	0.044(4)	–0.016(3)	–0.017(3)	0.018(3)
Cr(1)	1*h*		½	½	½	0.0115(6)	0.0165(6)	0.0134(6)	–0.0013(4)	–0.0009(5)	0.0015(5)
Mo(1)	2*i*		0.51291(6)	0.27655(5)	0.73863(5)	0.0227(3)	0.0220(3)	0.0183(3)	–0.0026(2)	–0.0022(2)	0.0067(2)
Mo(2)	2*i*		0.18301(6)	0.49662(5)	0.76878(5)	0.0168(3)	0.0333(3)	0.0173(3)	–0.0016(2)	0.0023(2)	0.0017(2)
Mo(3)	2*i*		0.83648(6)	0.27902(5)	0.46775(5)	0.0160(3)	0.0210(3)	0.0282(3)	0.0015(2)	–0.0027(2)	–0.0007(2)
N(1)	2*i*		0.326(1)	0.8836(8)	–0.1382(7)	0.065(5)	0.062(5)	0.050(5)	–0.018(4)	–0.004(4)	–0.003(4)
N(2)	2*i*		0.0663(9)	0.9929(7)	0.2274(7)	0.050(4)	0.054(4)	0.054(4)	–0.002(3)	–0.002(3)	–0.002(3)
O(1)	2*i*		0.5468(5)	0.3053(4)	0.5166(4)	0.019(2)	0.016(2)	0.019(2)	–0.003(1)	–0.001(2)	–0.000(2)
O(2)	2*i*		0.2479(5)	0.5000(4)	0.5407(4)	0.018(2)	0.020(2)	0.020(2)	–0.002(2)	–0.004(2)	–0.001(2)
O(3)	2*i*		0.4739(5)	0.4973(4)	0.6931(4)	0.019(2)	0.021(2)	0.014(2)	–0.003(2)	–0.002(2)	0.000(2)
O(4)	2*i*		0.7579(5)	0.3075(4)	0.6592(4)	0.026(2)	0.030(2)	0.017(2)	0.002(2)	–0.006(2)	0.005(2)
O(5)	2*i*		0.2735(5)	0.3130(4)	0.7440(4)	0.022(2)	0.023(2)	0.028(2)	–0.006(2)	–0.001(2)	0.006(2)
O(6)	2*i*		0.1865(5)	0.6823(4)	0.7081(4)	0.028(2)	0.028(2)	0.019(2)	0.001(2)	–0.002(2)	–0.003(2)
O(7)	2*i*		0.5216(6)	0.1068(4)	0.7231(5)	0.042(3)	0.021(2)	0.040(3)	–0.002(2)	–0.003(2)	0.009(2)
O(8)	2*i*		0.5235(6)	0.3063(5)	0.8971(4)	0.039(3)	0.045(3)	0.022(2)	0.001(2)	–0.007(2)	0.007(2)
O(9)	2*i*		0.2003(6)	0.5251(5)	0.9258(4)	0.040(3)	0.052(3)	0.018(2)	0.002(2)	0.001(2)	–0.003(2)
O(10)	2*i*		–0.0259(6)	0.4699(5)	0.7738(5)	0.022(2)	0.049(3)	0.039(3)	–0.002(2)	0.003(2)	0.009(2)
O(11)	2*i*		1.0334(2)	0.3101(5)	0.4621(5)	0.031(2)	0.047(3)	0.038(3)	0.004(2)	–0.004(2)	–0.001(2)
O(12)	2*i*		0.8376(6)	0.1090(4)	0.4625(5)	0.038(3)	0.019(2)	0.040(3)	0.002(2)	–0.003(2)	0.000(2)
O(13)	2*i*		0.3497(6)	0.3759(5)	0.1624(5)	0.039(1)	0.041(1)	0.039(1)	–0.0014(9)	–0.0095(9)	–0.0006(9)

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