Refinement of the crystal structure of *catena*-[(1,10-phenanthroline-*N*,*N'*)-(μ_3-molybdato(VI))copper(II)] monohydrate, $Cu(C_{12}H_{10}N_2)(MoO_4) \cdot H_2O$

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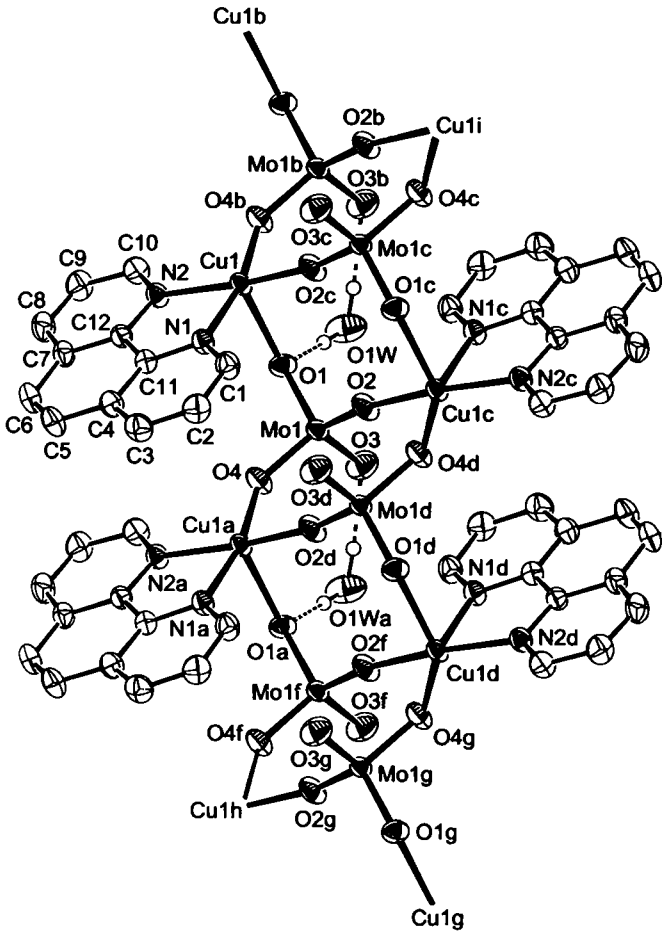

Abstract

$C_{12}H_{10}CuMoN_2O_5$, monoclinic, $P12_1/n1$ (no. 14), a = 14.147(3) Å, b = 5.890(1) Å, c = 16.221(3) Å, β = 103.27(1)°, V = 1315.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.023, $wR_{ref}(F^2)$ = 0.061, T = 298 K.

Source of material

A mixture of $Cu(NO_3)_2 \cdot 2H_2O$ (0.302 g, 1.25 mmol), V_2O_5 (0.115 g, 1.25 mmol), As_2O_5 (0.144 g, 1.25 mmol), $Na_2MoO_4 \cdot 2H_2O$ (3.326 g, 13.75 mmol), 1,10-phenanthroline monohydrate (0.248 g, 1.25 mmol) and H_2O (18 ml, 1 mol) was sealed in a Teflon-lined stainless steel vessel (25 ml), and the vessel was heated at 393 K for 7 d, then cooled to room temperature. Block shaped blue crystals were isolated (yield 20 % based on the initial $Cu(NO_3)_2 \cdot 2H_2O$ amount).

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Discussion

The crystal structure of the title complex, $[Cu(C_{12}H_{10}N_2)(MoO_4)] \cdot H_2O$, was redetermined with more precise structural parameters than those in the formerly reported [1] ($R_{gt}(F)$ = 0.075, $N(hkl)_{gt}$ = 2135, $N(hkl)_{unique}$ = 3063).

The title compound consists of $[Cu(C_{12}H_{10}N_2)(MoO_4)]$ polymeric chains and lattice water molecules, in which the Cu atoms are each square pyramidally coordinated by two nitrogen atoms from the 1,10-phenanthroline ligand and three oxygen atoms from three molybdate anions (O1, O2$^{\#1}$, O4$^{\#2}$) with the apex positions occupied by O1 atoms (#1: $-x+2,-y+1,-z$; #2: $x,y+1,z$). The chelating aromatic ligand resides on the basal plane with the Cu—N bond distances of 2.0398(2) Å and 2.0061(2) Å, respectively, which are according with those of the corresponding $[Cu(phen)(H_2O)_2]^{2+}$ subunits in the $[(Cu(phen)(H_2O)_2)_2Mo_6O_{18}(O_3AsOH)_2]$ [2]. The apical Cu—O bond length (2.2677(2) Å) is obviously longer than the basal Cu—O bond lengths (d(Cu1—O2$^{\#1}$) = 1.9049(2) Å and d(Cu1—O4$^{\#2}$) = 1.9269(2) Å, respectively). The *cis* bond angles at the central Cu atom from the apical O1 atom fall in the range of 93.59(7)° – 100.37(7)°, indicating a significant deviation from the value for an ideal square pyramid, which maybe due to d^9 cation Jahn-Teller effect. The tetrahedral MoO_4 groups exhibit slight distortion with Mo—O bond lengths ranging from 1.7256(2) Å to 1.7711(2) Å and O–Mo–O angles being between 107.63(8)° and 111.35(8)°. The MoO_4 groups adopt tridentate bridging mode, and the $[Cu(phen)]^{2+}$ subunits are linked by the MoO_4 groups into one dimensional ladder-shape double chains. Within the crystal structure, the lattice water molecules act as hydrogen bonding acceptors receiving hydrogen atoms from 1,10-phenanthroline groups to form intra-chain hydrogen bonds. The chains are further hold together by inter-chain hydrogen-bonding interactions, where the water molecules donate hydrogen atoms to the O1 atoms and the uncoordinated O3 atoms of MoO_4 groups to generate O1w–H1···O1$^{\#3}$ and O1w–H2···O3$^{\#4}$ hydrogen bonds, respectively (#3: $-½+x,½-y,-½+z$; #4: $-½+x,½-y,-½+z$, d(O1w···O1$^{\#3}$) = 2.898 Å, ∠O1w–H1···O1$^{\#3}$ = 171.1°, d(O1w···O3$^{\#4}$) = 2.767 Å, ∠O1w–H2···O3$^{\#4}$ = 174.0°).

Table 1. Data collection and handling.

Crystal:	blue block, size 0.20 × 0.25 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	25.92 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD II, ω
$2\theta_{max}$:	56.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11008, 3304
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2860
$N(param)_{refined}$:	191
Programs:	SHELXS-97 [3], SHELXL-97 [4]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	1.1270	0.3714	0.1090	0.039
H(2A)	4e	1.1987	0.0607	0.1854	0.044
H(3A)	4e	1.1627	−0.0270	0.3128	0.044
H(5A)	4e	1.0621	0.0651	0.4218	0.045
H(6A)	4e	0.9488	0.2858	0.4616	0.044
H(8A)	4e	0.8351	0.6345	0.4326	0.043
H(9A)	4e	0.7745	0.9299	0.3439	0.044
H(10A)	4e	0.8290	0.9862	0.2212	0.039
H(2)	4e	0.7081	−0.1361	−0.0491	0.075
H(1)	4e	0.7330	−0.3562	−0.0073	0.075

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}
Mo(1)	4e	0.87203(1)	0.22461(3)	0.01528(1)	0.0269(1)	0.0202(1)	0.0252(1)	0.00067(7)	0.01237(8)	0.00192(7)
O(1)	4e	0.8518(1)	0.4868(3)	0.0598(1)	0.0317(8)	0.0243(8)	0.0373(9)	0.0015(6)	0.0132(7)	−0.0026(7)
O(2)	4e	0.9658(1)	0.2517(3)	−0.0392(1)	0.046(1)	0.034(1)	0.040(1)	0.0048(7)	0.0299(8)	0.0077(7)
O(3)	4e	0.7657(1)	0.1475(3)	−0.0549(1)	0.040(1)	0.044(1)	0.046(1)	−0.0051(8)	0.0012(8)	−0.0069(9)
O(4)	4e	0.9009(1)	0.0179(3)	0.0965(1)	0.048(1)	0.0296(9)	0.0357(9)	0.0112(7)	0.0238(8)	0.0113(7)
Cu(1)	4e	0.96654(2)	0.73343(4)	0.12792(2)	0.0285(1)	0.0230(2)	0.0237(2)	0.0035(1)	0.0132(1)	0.0043(1)
N(1)	4e	1.0475(1)	0.4678(3)	0.1864(1)	0.0285(9)	0.029(1)	0.0246(9)	0.0035(7)	0.0097(7)	0.0039(8)
N(2)	4e	0.9177(1)	0.7289(3)	0.2347(1)	0.0286(9)	0.029(1)	0.0254(9)	0.0031(7)	0.0117(8)	0.0027(7)
C(1)	4e	1.1110(2)	0.3369(4)	0.1601(2)	0.035(1)	0.036(1)	0.029(1)	0.006(1)	0.013(1)	0.002(1)
C(2)	4e	1.1548(2)	0.1492(5)	0.2061(2)	0.035(1)	0.037(1)	0.039(1)	0.011(1)	0.011(1)	−0.001(1)
C(3)	4e	1.1330(2)	0.0961(4)	0.2813(2)	0.037(1)	0.035(1)	0.037(1)	0.010(1)	0.006(1)	0.006(1)
C(4)	4e	1.0651(2)	0.2296(4)	0.3109(2)	0.030(1)	0.033(1)	0.028(1)	0.0027(9)	0.0042(9)	0.0043(9)
C(5)	4e	1.0351(2)	0.1863(5)	0.3877(2)	0.042(1)	0.041(1)	0.029(1)	0.007(1)	0.007(1)	0.014(1)
C(6)	4e	0.9679(2)	0.3193(5)	0.4118(2)	0.042(1)	0.045(2)	0.024(1)	0.001(1)	0.013(1)	0.010(1)
C(7)	4e	0.9259(2)	0.5093(4)	0.3623(1)	0.029(1)	0.035(1)	0.024(1)	−0.0021(9)	0.0090(9)	0.0019(9)
C(8)	4e	0.8564(2)	0.6570(5)	0.3831(2)	0.036(1)	0.047(2)	0.028(1)	−0.001(1)	0.017(1)	0.000(1)
C(9)	4e	0.8205(2)	0.8324(5)	0.3306(2)	0.034(1)	0.042(2)	0.038(1)	0.007(1)	0.018(1)	−0.002(1)
C(10)	4e	0.8533(2)	0.8649(4)	0.2563(2)	0.035(1)	0.032(1)	0.034(1)	0.008(1)	0.013(1)	0.003(1)
C(11)	4e	1.0247(2)	0.4130(4)	0.2609(1)	0.025(1)	0.028(1)	0.023(1)	0.0001(8)	0.0057(8)	0.0015(9)
C(12)	4e	0.9541(2)	0.5546(4)	0.2866(1)	0.026(1)	0.026(1)	0.022(1)	−0.0011(8)	0.0067(8)	0.0016(8)
O(1W)	4e	0.6861(2)	−0.2763(3)	−0.0418(2)	0.043(1)	0.041(1)	0.078(2)	−0.0051(9)	0.005(1)	−0.007(1)

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