

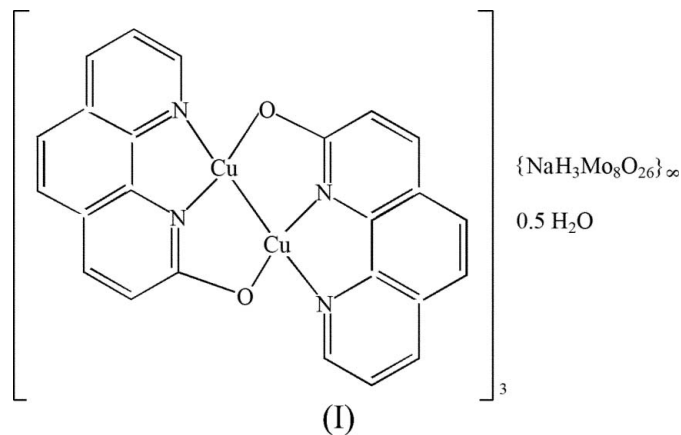
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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.015$ Å
H-atom completeness 92%
Disorder in solvent or counterion
 R factor = 0.058
 wR factor = 0.159
Data-to-parameter ratio = 11.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Tris[bis(μ -1,10-phenanthroline-2-olato)dicopper(I)]
monosodium trihydrogen β -octamolybdate hemi-
hydrateThe title compound, $\text{Na}[\text{H}_3\text{Mo}_8\text{O}_{26}][\text{Cu}_2(\text{C}_{12}\text{H}_7\text{N}_2\text{O})_2]_3 \cdot 0.5\text{H}_2\text{O}$, contains neutral dinuclear copper(I) complexes and infinite chain-like polyoxoanions comprising β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ units linked by Na^+ cations which lie on centres of inversion. The polyoxoanion chains are protonated, rendering them neutral.Received 20 August 2006
Accepted 14 September 2006

Comment

The polyoxomolybdate family exhibits diverse structures ranging from $\{\text{Mo}_4\text{O}_{13}\}_n^{2n-}$ (Hagrman & Zubieta, 1998) to the large $\{\text{Mo}_{248}\}$ cluster (Müller *et al.*, 1999). Of the various polyoxomolybdate structures, the octamolybdate family are of interest since they exhibit a variety of structural isomers, including α (Fuchs & Hartl, 1976), β (Wang *et al.*, 2006), γ (Niven *et al.*, 1991), δ (Xi *et al.*, 1994), ε (Hagrman *et al.*, 1997) and ζ (Xu *et al.*, 1999) isomers. The β -isomer in particular is a versatile building block for constructing organic-inorganic hybrid materials (Hagrman *et al.*, 1999).The title compound, (I), $\text{Na}[\text{H}_3\text{Mo}_8\text{O}_{26}][\text{Cu}_2(\text{C}_{12}\text{H}_7\text{N}_2\text{O})_2]_3 \cdot 0.5\text{H}_2\text{O}$ (Fig. 1), comprises infinite chain-like polyoxoanions (running along a) built from β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ units linked by Na^+ cations (Fig. 2). According to the manner of oxygen coordination, the $\text{Mo}-\text{O}$ bonds within $[\text{Mo}_8\text{O}_{26}]^{4-}$ can be divided into four categories: $\text{Mo}-\text{O}(t)$, 1.690 (7)–1.712 (6) Å; $\text{Mo}-\text{O}(\mu_2)$, 1.891 (6)–2.304 (6) Å; $\text{Mo}-\text{O}(\mu_3)$, 1.953 (5)–2.359 (6) Å; $\text{Mo}-\text{O}(\mu_5)$, 2.162 (5)–2.410 (5) Å. The Na^+ ions adopt approximately cubic coordination through eight terminal O atoms from two $\{\text{Mo}_4\text{O}_{13}\}$ subunits. Similar chains have been observed previously in $\{(\text{Bu}_4\text{N})_2\text{Ag}_2[\text{Mo}_8\text{O}_{26}]\}_n$ (Chen *et al.*, 2004), in that case with $[\text{Ag}-\text{Ag}]^{2+}$ units performing the linking role in place of Na^+ .In (I), neutral dicopper(I) complexes, $[\text{Cu}_2(\text{C}_{12}\text{H}_7\text{N}_2\text{O})_2]$, lie in stacks between the $\{\text{Na}[\text{Mo}_8\text{O}_{26}]\}^{3-}$ chains (Fig. 3). The

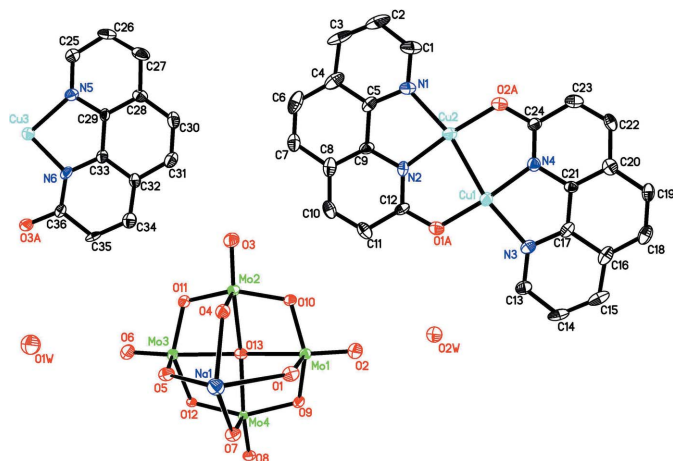


Figure 1
Asymmetric unit of (I), showing displacement ellipsoids at the 30% probability level. Only the unique half of the complex containing Cu3 and the unique half of the octamolybdate anion are shown. H atoms have been omitted.

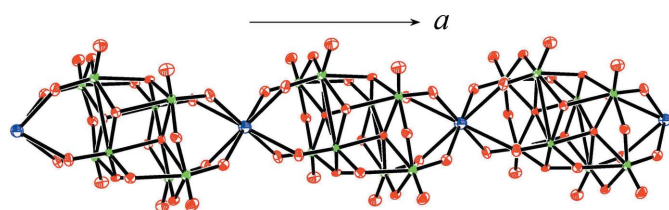


Figure 2
Perspective view of one $[\text{Na}[\text{Mo}_8\text{O}_{26}]]^{3-}$ chain running along a (30% displacement ellipsoids).

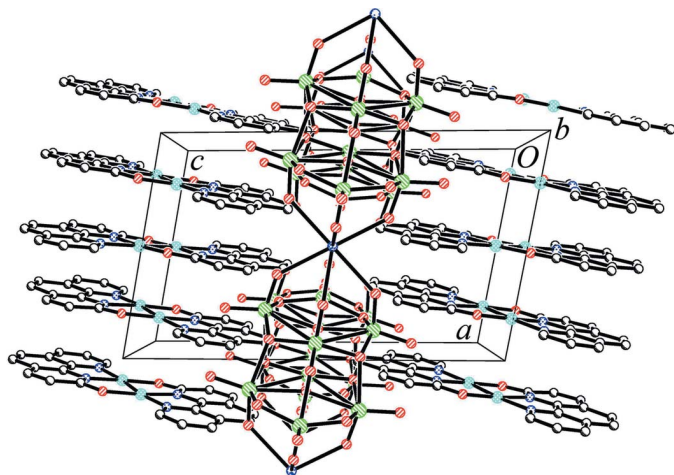


Figure 3
Perspective view of (I) along b showing stacks of $[\text{Cu}_2(\text{C}_{12}\text{H}_7\text{N}_2\text{O})_2]$ complexes between the $[\text{Na}[\text{Mo}_8\text{O}_{26}]]^{3-}$ chains. H atoms and solvent water molecules have been omitted.

complex containing Cu1 and Cu2 lies on a general position, while the complex containing Cu3 lies on a centre of inversion. Within the complexes, each Cu^{I} atom adopts a trigonal environment defined by two N donors and one O donor from two different deprotonated 2-hydroxy-1,10-phenanthroline ligands (Table 1). The Cu—Cu distances range from 2.417 (2) to 2.437 (2) Å, indicating $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$ bonding interactions

(Jones *et al.*, 1997) that complete an approximately square-planar coordination geometry. The hydroxylated 1,10-phenanthroline molecules were synthesized in the course of the reaction, in which phenanthroline acts to reduce Cu^{II} to Cu^{I} , becoming hydroxylated in the process (Zhang *et al.*, 2002).

Charge balance within the structure requires the presence of three protons per formula unit. It is likely that these are associated with the $[\text{Na}[\text{Mo}_8\text{O}_{26}]]^{3-}$ chains, rendering them neutral. These H atoms were not evident in difference Fourier maps, and bond-valence calculations also could not distinguish between any of the terminal O atoms. The three H atoms are therefore omitted from the structure model. Two solvent water molecules were evident, and these were included with fractional occupancy (0.125) to provide reasonable displacement parameters. The assignment of the complex as a hemihydrate is therefore approximate.

Experimental

A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.5 mmol), phenanthroline (1.5 mmol), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2 mmol) and water (18 ml) in a molar ratio of 3:3:4:1000 was placed in a Teflon-lined autoclave and the pH was adjusted to 6.36 using HCl (aq). The autoclave was heated to 458 K for four days and cooled to room temperature over two days, depositing green block crystals of (I).

Crystal data

$\text{Na}[\text{H}_3\text{Mo}_8\text{O}_{26}][\text{Cu}_2(\text{C}_{12}\text{H}_7\text{N}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$	$\gamma = 82.091 (2)^\circ$
$M_r = 2770.98$	$V = 2035.1 (11) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.640 (4) \text{ \AA}$	$D_x = 2.259 \text{ Mg m}^{-3}$
$b = 13.651 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 15.952 (5) \text{ \AA}$	$\mu = 2.82 \text{ mm}^{-1}$
$\alpha = 84.309 (4)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 78.972 (4)^\circ$	Block, green
	$0.18 \times 0.16 \times 0.15 \text{ mm}$

Data collection

Bruker SMART APEX CCD diffractometer	10029 measured reflections
φ and ω scans	6828 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4626 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.612$, $T_{\text{max}} = 0.657$	$R_{\text{int}} = 0.031$
	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.0899P)^2]$
$wR(F^2) = 0.159$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} < 0.001$
6828 reflections	$\Delta\rho_{\text{max}} = 2.28 \text{ e \AA}^{-3}$
600 parameters	$\Delta\rho_{\text{min}} = -0.99 \text{ e \AA}^{-3}$

H atoms bound to C atoms were placed in calculated positions and allowed to ride during subsequent refinement, with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms associated with the water molecules and the three H atoms associated with the polyoxoanion chains were not located. The largest peak in the difference density lies *ca* 1 Å from Mo3.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Specialized Research Fund for the Doctoral Programme of Higher Education (No. 20040475001), Henan Innovation Project for University Prominent Research Talents, the Foundation of Educational Department of Henan Province (No. 0524480020) and the Natural Science Foundation of Henan Province.

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