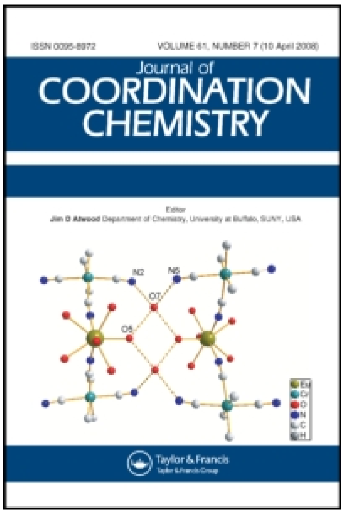

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A new cation induced chain-like complex $[Cu(H_2tea)(H_2O)(imi)][Cu(H_3tea)(imi)][Na\{Mo_8O_{26}\}] \cdot 4H_2O$

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A new complex $[Cu(H_2tea)(H_2O)(imi)][Cu(H_3tea)(imi)][Na\{Mo_8O_{26}\}] \cdot 4H_2O$ (H_3tea = triethanolamine, imi = imidazole) has been synthesized in aqueous solution and characterized by elemental analysis, IR spectroscopy, thermal gravimetric analysis, and single-crystal X-ray diffraction. X-ray diffraction reveals that β-$[Mo_8O_{26}]^{4-}$ polyanions are linked by sodium ions to form a chain. The coppers are five- and six-coordinate for $[Cu(H_3tea)(imi)]^{2+}$ and $[Cu(H_2O)(H_2tea)(imi)]^{+}$, respectively. Crystal packing is due to hydrogen bonds and $\pi \cdots \pi$ stacking interactions, giving a 3-D polymeric network. The magnetic properties of the title compound are also presented.

Keywords: Polyoxometalate; Hybrid material; Copper(II) complex; Magnetic property

1. Introduction

Design and assembly of organic–inorganic solid-state compounds have become a focus due to magnetic, electrical, and optical properties [1]. By using polyoxometalate anions as building blocks, assembly to form 1-D chain, 2-D layer, and 3-D network architectures has produced many new solid state materials with functional properties. Polyoxometalates (POMs) are extremely versatile inorganic building blocks with potential applications in medicine, materials, and catalysis [2–9]. Many inorganic–organic hybrid compounds including charge-transfer salts constructed from polyoxometalates and organic moieties were synthesized by molecular self-assembly [10]. Herein, we present synthesis, characterization, and crystal structure of $[Cu(H_2tea)(H_2O)(imi)][Cu(H_3tea)(imi)][Na\{Mo_8O_{26}\}] \cdot 4H_2O$, in which triethanolamine bond to Cu^{2+} forming two kinds of cations, and β-octamolybdates were linked by Na^+ in infinite chains. Crystal packing is due to hydrogen bonds and $\pi \cdots \pi$ stacking interactions, giving a 3-D polymeric network.

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2. Experimental

2.1. *Materials and physical measurements*

All reagents were purchased commercially and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Na, Cu, and Mo were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellets from 400–4000 $\mathrm{cm^{-1}}$. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$. Magnetic susceptibility was carried out using a Quantum Design MPMS-XL SQUID magnetometer at 1000 Oe. Diamagnetic correction was estimated from Pascal's constants [11].

2.2. *Synthesis of $[Cu(H_2tea)(H_2O)(imi)][Cu(H_3tea)(imi)][Na\{Mo_8O_{26}\}]\cdot 4H_2O$*

$Na_2MoO_4\cdot 2H_2O$ (0.56 g, 2.25 mmol) and $N(CH_2CH_2OH)_3$ (0.559 g, 3.75 mmol) was dissolved in H_2O (30 mL), and the pH was adjusted to 1 by addition of 1 M hydrochloric acid. After $CuSO_4\cdot 5H_2O$ (1 mL of 1 $\mathrm{mol\,L^{-1}}$ solution) and $C_3H_4N_2$ (0.034 g, 0.5 mmol) were added, the pH of solution was adjusted to 4.5 by addition of 1 M hydrochloric acid, and the mixture was refluxed for 2 h at 60°C. The solution was cooled to room temperature and, after 4 days, blue block crystals formed by evaporation of the filtrate at room temperature. Yield after 2 weeks: 220 mg (0.119 mmol, 73.33% based on Mo). Elemental analysis (%): Calcd (found) for the title compound: Na 1.24 (1.18), Cu 4.85 (4.84), C 11.64 (11.191), N 4.53 (4.86), H 2.50 (2.38), Mo 41.34 (40.36).

2.3. *Crystallographic data collection and structure determination*

A blue crystal of the title compound was glued on a glass fiber and data were collected on a Bruker SMART CCD single-crystal diffractometer using Mo-Kα radiation (0.71073 Å) at 273 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2, performed using the SHELXL-97 software package [12]. Hydrogens were not determined. The compound exhibits some disorder in counterions, as is often the case with polyoxometalates. A summary of crystal data and structure refinement for the title compound is provided in table 1 and selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Descriptions of the structures*

The title compound contains $[Mo_8O_{26}]^{4-}$, $[Cu(H_3tea)(imi)]^{2+}$, $[Cu(H_2O)(H_2tea)(imi)]^{+}$, Na^{+}, and crystallization water. The $[Mo_8O_{26}]^{4-}$ anion is a typical β-structure octamolybdate [13] (figure 1), built up from eight distorted $\{MoO_6\}$ edge-shared octahedra. They can be described alternatively as two cyclic Mo_4O_{12} units formed by

Table 1. Crystal data and structure refinement for the compound.

Formula	$H_{46}C_{18}N_6O_{37}NaCu_2Mo_8$
Formula weight	1856.10
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	13.6290(10)
b	14.3990(10)
c	14.4181(10)
α	73.7210(10)
β	86.5670(10)
γ	62.3100(10)
V (Å^3)	2396.7(3)
Z	2
Goodness-of-fit	1.034
T (K)	293
F(000)	1702.0
Wavelength (Å)	0.71073
Limiting indices	$-14 \leq h \leq 18$, $-11 \leq k \leq 19$, $-16 \leq l \leq 19$
Goodness-of-fit on F^2	1.034
Final R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0618, 0.1809
Final R_1[a], wR_2[b] [all data]	0.0822, 0.1983

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for the title compound.

O(2)–Mo(1)	2.301(6)	O(2)–Mo(7)	1.960(6)
O(3)–Mo(2)	1.703(6)	O(2)–Mo(2)	1.992(6)
O(4)–Mo(8)	1.955(6)	O(27)–Cu(1)	2.389(8)
O(5)–Mo(1)	1.972(6)	O(29)–Cu(2)	2.010(9)
O(4W)–Cu(1)	2.038(7)	O(36)–Cu(2)	2.249(9)
O(6)–Mo(4)	2.294(6)	O(37)–Cu(2)	1.975(9)
O(6)–Mo(5)	2.366(6)	O(39)–Mo(6)	1.720(7)
O(7)–Mo(3)	1.706(6)	O(41)–Mo(5)	1.708(7)
O(7)–Na(1)	2.547(8)	O(41)–Na(1)	2.807(10)
O(8)–Mo(7)	1.643(6)	O(42)–Mo(1)	1.699(7)
O(15)–Mo(1)	2.328(6)	N(1)–Cu(2)	1.992(9)
O(15)–Mo(6)	2.381(6)	N(2)–Cu(1)	2.032(8)
O(17)–Mo(6)	1.923(7)	N(3)–Cu(1)	1.954(9)
O(19)–Mo(6)	2.246(6)	N(4)–Cu(2)	1.932(10)
Mo(7)–O(2)–Mo(2)	108.6(3)	Mo(4)–O(11)–Na(1)	130.3(4)
Mo(7)–O(2)–Mo(1)	110.2(3)	Mo(8)–O(13)–Na(1)	128.9(4)
Mo(2)–O(2)–Mo(1)	102.4(2)	Mo(4)–O(14)–Mo(5)	115.6(3)
Mo(2)–O(3)–Na(1)	129.6(4)	Mo(7)–O(15)–Mo(6)	91.9(2)
Mo(8)–O(4)–Mo(3)	107.4(3)	Mo(1)–O(15)–Mo(6)	86.5(2)
Mo(1)–O(5)–Mo(2)	103.9(3)	Mo(1)–O(17)–Mo(6)	115.1(3)
Mo(8)–O(6)–Mo(4)	90.7(2)	N(3)–Cu(1)–O(23)	90.0(3)
Mo(8)–O(6)–Mo(3)	90.1(2)	N(3)–Cu(1)–N(2)	172.5(4)
Mo(4)–O(6)–Mo(3)	162.8(3)	N(3)–Cu(1)–O(27)	103.5(4)
Mo(8)–O(6)–Mo(5)	164.5(3)	O(23)–Cu(1)–O(27)	95.4(3)
Mo(4)–O(6)–Mo(5)	87.8(2)	N(2)–Cu(1)–O(27)	79.4(3)
Mo(3)–O(6)–Mo(5)	87.0(2)	N(4)–Cu(2)–O(37)	95.9(4)
Mo(3)–O(7)–Na(1)	130.7(4)	N(4)–Cu(2)–N(1)	174.1(5)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+2$, $-z$; #2: $-x+2$, $-y+1$, $-z+1$.

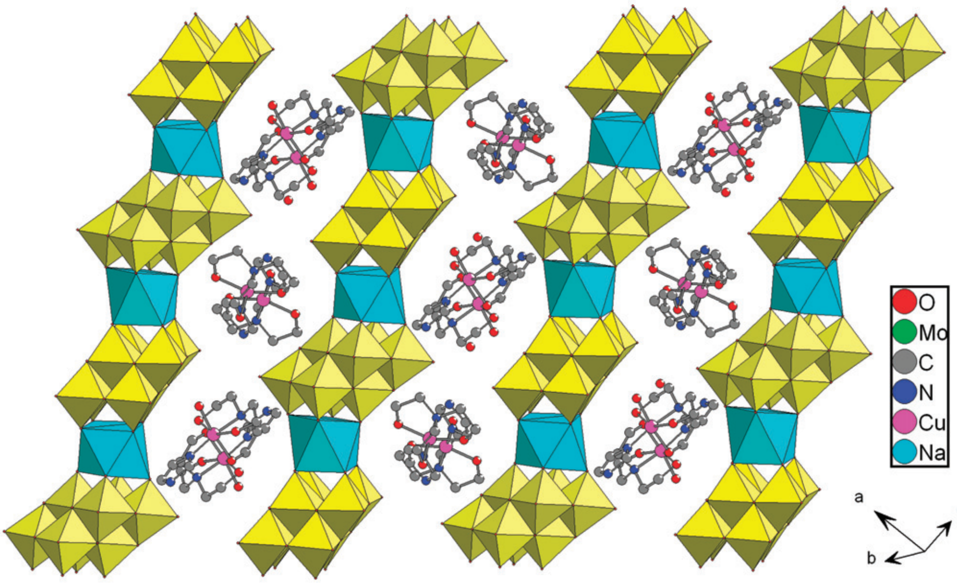

Figure 1. Combined polyhedral/ball-and-stick representation of the title compound. H atoms and water molecules are omitted for clarity.

distorted MoO_4 tetrahedra, cross-linked by long Mo–O bonds and by additional long bonds from Mo to two extra O^{2-} ions. The Mo–O bonds in this complex are terminal ($Mo–O_t$) and bridging (μ_2-O–Mo; μ_3-O–Mo; and μ_5-O–Mo). The Mo–O bond lengths vary from 1.646(7) Å for a terminal Mo=O bond to 2.179(6) Å for a bond to the unusual five coordinate oxygen [O(6)] that sits near the center of each Mo_4O_{12} half of the anion. Bond valence sum calculations [14] give values of 6.10, 6.00, 5.93, 5.94, 6.11, 5.98, 6.16, and 6.13 for Mo(1), Mo(2), Mo(3), Mo(4), Mo(5), Mo(6), Mo(7), and Mo(8), showing that all Mo sites are +6. The calculation shows values of 1.79 and 1.78 for Cu(1) and Cu(2), indicating Cu^{2+}. All oxygens have bond-valence sums close to 2.0.

As shown in figure 1, the β-$[Mo_8O_{26}]^{4-}$ are linked into a 1-D chain by Na^+ cations. In this chain, each sodium cation is coordinated by two β-$[Mo_8O_{26}]^{4-}$ units through eight terminal oxygens. The $Na–O_t$ bond distances range from 2.454(8) to 2.807(10) Å with an average value of 2.583(8) Å. The $[Cu(H_3tea)(imi)]^{2+}$ and $[Cu(H_2O)(H_2tea)(imi)]^+$ are charge balancing cations existing among inorganic chains.

The $[Cu(H_2O)(H_2tea)(imi)]^+$ and $[Cu(H_3tea)(imi)]^{2+}$ have different coordination geometries (figure 2). Cu2 is trigonal bipyramidal (figure 2a) with the trigonal plane defined by O29, O36, and O37 from triethanolamine, while axial positions are occupied by N1 from triethanolamine and N4 from imidazole, similar to $[Cu_2(nta)(bpe)]^{2-}$ in $[Cu_3(nta)_2(bpe)_2(H_2O)_4] \cdot bpe \cdot 10H_2O$ and $[Cu_2(nta)_2(azpy)]^{2-}$ in $[Cu(azpy)(H_2O)][Cu_2(nta)_2(azpy)] \cdot 6H_2O$ [15a]. However, the Cu1 has a distorted octahedral coordination (figure 2b) in $[Cu(H_2O)(H_2tea)(imi)]^+$, with monodeprotonated triethanolamine a tripod tetradentate ligand, one O from water and one N from imidazole, similar to $[Cu(azpy)(H_2O)_4]^{n+}{}_n$ in $[Cu(azpy)(H_2O)_4][Cu_2(nta)_2(azpy)] \cdot 6H_2O$ [15a]. The Cu1–O27 and Cu1–O39 lengths of *ca* 2.389–2.472 Å are unexceptional for protonated oxygen bonded to copper [15b, 15c] and are longer than Cu1–O23 [1.997(7) Å] with deprotonated oxygen.

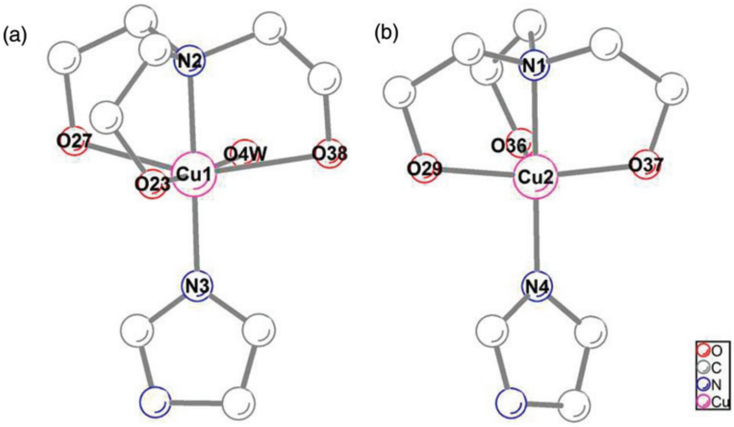

Figure 2. Ball-and-stick representation of the cations of the title compound: (a) $[Cu(H_3tea)(imi)]^{2+}$; (b) $[Cu(H_2O)(H_2tea)(imi)]^{+}$.

Table 3. The short O···O intermolecular hydrogen bonding distances.

O29···O1w	2.573(15)	O11···O1w	2.858(14)	O36···O2w	2.751(12)
O25···O3w	2.823(14)	O23···O3w	2.595(10)	O18···O4w	2.695(12)
O38···O4w	2.846(12)	O2···O40	2.816(14)	O37···O40	2.490(21)
O41···O40	2.76(1)				

The title compound contains hydrogen-bonding interactions among terminal oxygens of polyanions, oxygens coordinated to Cu, and oxygens from lattice water. The short O···O intermolecular distances, which can be interpreted as hydrogen bonds, are shown in table 3 and figure 3. The extensive hydrogen-bonding stabilizes both the polyanions and the cations and lead to a 3-D structure. Additionally, adjacent imidazole rings of two $[Cu(H_3tea)(imi)]^{2+}$ have $\pi\cdots\pi$ stacking interactions (see figure S3). The center-to-center distance and angle between the ring normal of the imidazole plane and the centroid vector is 3.91 Å and 15.68°, respectively, indicating weaker intramolecular $\pi\cdots\pi$ stacking interaction that stabilizes the complex.

3.2. *IR spectra*

The IR spectrum measured at room temperature (figure S1) exhibits broad bands at 3421 and 3259 cm^{-1} due to stretching of N–H and C–H groups of imidazole and triethanolamine. The bands from 1332 to 1619 cm^{-1} can be assigned to bending vibrations of C–H, N–H, or the ring stretching vibrations of the imidazole and triethanolamine. The sharp peaks at 931, 893, 840, 811, and 692 cm^{-1} are attributed to the Mo–O stretching, in agreement with three kinds of μ-O–Mo in the structure, μ_2-O–Mo, μ_3-O–Mo, and the unusual five-coordinate O atom in $[Mo_8O_{26}]^{4-}$ anion.

3.3. *Thermogravimetric analysis*

The thermogravimetric (TG) curve of the title compound exhibits three steps of weight loss from 25 to 600°C (figure S1). The weight loss of 5.45% from 25–154°C corresponds

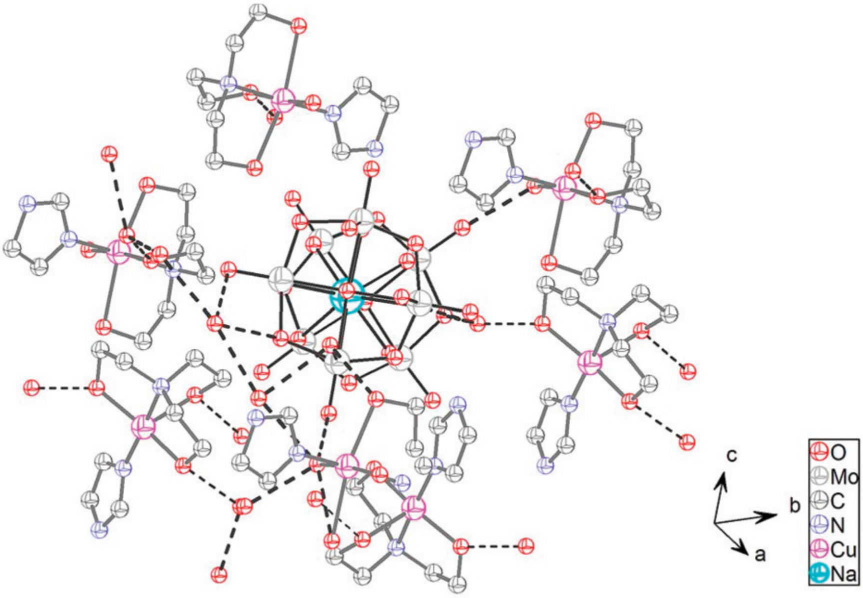

Figure 3. Ball-and-stick representation of the supramolecular interactions among imidazole molecules.

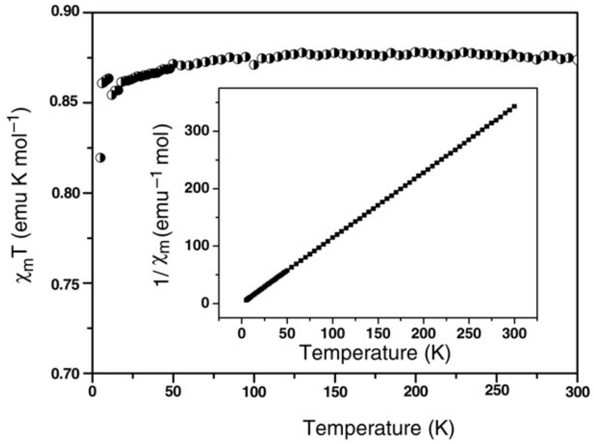

Figure 4. $1/\chi_m$ *vs.* T and $\chi_m T$ *vs.* T for the title compound.

to the release of four crystalline water molecules. The second stage from 154 to 314°C is attributed to the loss of six organic molecules; the observed weight loss (10.60%) is in agreement with the calculated value (11.9%). The third step occurs at 425°C, corresponding to decomposition of the polyanion.

3.4. *Magnetic properties*

The variable–temperature magnetic susceptibility, measured under applied magnetic field of 1000 Oe in the temperature range 5–300 K, follows the Curie–Weiss law,

$\chi = C/(T - \theta)$, with the Curie constant of $C = 0.88\,\text{emu}\,\text{K}\,\text{mol}^{-1}$ and the Weiss temperature of $\theta = -0.27\,\text{K}$. As shown in figure 4, $\chi_m T$ value of the title compound at room temperature is *ca* $0.87\,\text{emu}\,\text{K}\,\text{mol}^{-1}$ ($2.64\,\mu_B$), slightly smaller than that expected ($2.83\,\mu_B$) for two isolated Cu(II) ions ($S = 1$; $g = 2.00$).

4. Conclusions

A new complex based on POMs and copper complexes, $[Cu(H_2tea)(H_2O)(imi)][Cu(H_3tea)(imi)][Na\{Mo_8O_{26}\}] \cdot 4H_2O$, has been synthesized and structurally characterized. The β-$[Mo_8O_{26}]^{4-}$ polyanions are linked by sodium ions to form a 1-D chain. The two copper complexes have five- and six-coordinate geometries. Hydrogen bonds and $\pi \cdots \pi$ stacking interactions play an important role in crystal structure stabilization.

Supplementary material

Crystallographic data for the structure of the title compound reported in this article has been deposited in the Cambridge Crystallographic Data centre as supplementary publication number CCDC 672182. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.com.ac.uk).

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