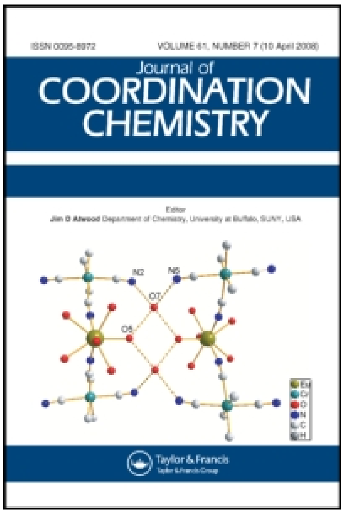

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Jing-Ping Wang[a]; Jun-Wei Zhao[a]; Su-Zhi Li[a]; Jing-Yang Niu[ab]
[a] Institute of Molecule and Crystal Engineering, School of Chemistry and Chemical Engineering, University of Henan, Kaifeng 475001, China [b] State Key Laboratory of Coordination Chemistry, University of Nanjing, Nanjing 210093, China

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JING-PING WANG†, JUN-WEI ZHAO†, SU-ZHI LI†
and JING-YANG NIU*†‡

†Institute of Molecule and Crystal Engineering, School of Chemistry and
Chemical Engineering, University of Henan, Minglun Street, Kaifeng 475001, China
‡State Key Laboratory of Coordination Chemistry, University of Nanjing,
Nanjing 210093, China

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A new B-Anderson-type heteropoly compound $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2]$ $[HAl(OH)_6(Mo_6O_{18})]\cdot 2.5H_2O$ containing binuclear copper(II) coordination ions has been synthesized by reaction of $AlCl_3\cdot 6H_2O$, $Na_2MoO_4\cdot 2H_2O$, glacial acetic acid, 1,10-phenanthroline and $CuCl_2\cdot 2H_2O$ in methanol–water mixed solution and characterized by IR, UV-Vis spectra, TG-DTA analysis and X-ray crystallography. From X-ray single-crystal structural analysis, the title compound crystallizes in a triclinic lattice, $P\bar{1}$ space group, with $a = 13.379(3)$, $b = 17.388(4)$, $c = 18.063(4)$ Å, $\alpha = 85.97(3)$, $\beta = 69.79(3)$, $\gamma = 69.22(3)^\circ$, $V = 3680.4(13)$ Å^3, $Z = 2$, $R_1 = 0.0797$, $wR_2 = 0.1787$. In the title compound, the two Cu^{2+} coordination cations are combined with each other through two acetate bridges and have five-coordinate, distorted square-pyramid geometry with N2O3 bonding at each metal. In addition, there are also two crystallographically independent 'one-half' Anderson-type polyanions in the title compound lattice.

Keywords: Anderson structure; Polyoxometalates; Hybrid materials; Heteropoly compounds

1. Introduction

Crystal engineering of inorganic/organic hybrid materials has provoked significant interest in new structural architectures and potential applications to the fields of photochemistry, electromagnetism, catalysis, sorption, analytical chemistry, materials science, nanotechnology, chemical recognition, environmental decontamination, biochemical and geochemical processes, and medicine [1–14]. Syntheses of

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*Corresponding author. Fax: +86-378-2853650. Tel.: +86-378-2192443. Email: jyniu@henu.edu.cn

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inorganic/organic hybrid materials built by polyoxometalate building blocks and metal coordination complexes are well developed [15–18]. Among them, Anderson-type polyanions as a building unit are drawing attraction [19]. According to the differences of the chemical valence and distinctions of combined groups for the central atoms, Anderson-type polyaions can be divided into two types: (1) $[X^{n+}M_6O_{24}]^{(12-n)-}$ ($X = Te^{VI}$, I^{VII}, etc., $M = Mo^{VI}$, W^{VI}); (2) $[X^{n+}M_6O_{24}H_6]^{(6-n)-}$ ($X = Cr^{III}$, Co^{III}, etc., $M = Mo^{VI}$, W^{VI}), the former is defined as A-Anderson-type polyanion, the latter is described as B-Anderson-type polyanion [19]. Anderson-type inorganic polyoxometalate compounds with rare earth metal cations were reported [20–21]. To date, however, the investigation of the organic-inorganic hybrid compounds with Anderson-type polyanions as building blocks is very limited [22–24]. In this article, we report for the first time the synthesis, characterization, thermal properties and crystal structural determination of $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2][HAl(OH)_6(Mo_6O_{18})] \cdot 2.5H_2O$.

2. Experimental

All chemicals used for synthesis were of reagent grade and used without further purification.

2.1. *Synthesis of* $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2][HAl(OH)_6(Mo_6O_{18})] \cdot 2.5H_2O$

A 50 mL aqueous solution containing 1.75 g (7.23 mmol) of $Na_2MoO_4 \cdot 2H_2O$ was added to a 20 mL aqueous solution containing 0.75 g (3.10 mmol) of $AlCl_3 \cdot 6H_2O$. Then a solution of glacial acetic acid was added slowly under vigorous stirring until the pH of the mixed solution was adjusted to 3.16. A solution of 20 mL methanol–water (1 : 1, volume ratio) containing 0.13 g (0.64 mmol) 1,10-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$) and 0.25 g (1.03 mmol) $CuCl_2 \cdot 2H_2O$ was added dropwise. The pH of the resulting solution was adjusted to 2.72 with glacial acetic acid. The obtained blue solution was filtered and slowly evaporated at ambient temperature. Three days later, blue stick-shaped crystals suitable for X-ray diffraction were collected. Yield based on Al is about 65%. Anal. Calcd (%): C, 20.01; H, 2.78; N, 3.33; Al, 1.61; Cu, 7.56; Mo, 34.26. Found: C, 20.45; H, 2.39; N, 3.17; Al, 1.65; Cu, 7.50; Mo, 34.40.

2.2. *Physical measurements*

C, H, N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Jarrel-Ash J-A1100 spectrometer. The IR spectra (KBr pellets) were recorded on a Nicolet 170 SXFT-IR spectrometer (4000–400 cm^{-1}). UV-Vis spectra were obtained on Unican UV-500 spectrometer (900–190 nm, distilled water as solvent). TG-DTA measurements were carried out on a Exstar 6000 thermal analysis system in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$.

2.3. *Crystal structure determination*

A blue stick-shaped single crystal of the title compound with $0.23 \times 0.16 \times 0.14\,\text{mm}^3$ was mounted on a glass fiber capillary. The data were collected on a Rigaku RAXIS-IV diffractometer with Mo Kα ($\lambda = 0.71073\,\text{Å}$) at 293(2) K in the range of $2.41 < \theta < 24.99°$. An empirical absorption correction was applied. A total of 8468 (8468 unique, $R_{\text{int}} = 0.0000$) reflections were measured ($-14 \le h \le 15$, $-20 \le k \le 20$, $0 \le l \le 21$). The structure of the title compound was solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 software [25]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in calculated positions. A summary of crystal data and structure refinement for the title compound is provided in table 1. Selected bond distances are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of the title compound*

A ball-and-stick structural representation of the title compound with labeling scheme is shown in figure 1. The molecular asymmetric unit of the title compound consists of two crystallographically independent 'one-half' B-Anderson-type $[\text{HAl(OH)}_6(\text{Mo}_6\text{O}_{18})]^{2-}$ polyanions, a discrete dimer $[\text{Cu}_2(\text{phen})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]^{2+}$ and 2.5 water molecules. In 2002, Manikumari and co-workers investigated a near-linear supramolecular water dimer, $(\text{H}_2\text{O})_2$, in the channel of an inorganic framework material based on the B-Anderson polyanion [26]. In the same year, Shivaiah *et al.* reported

Table 1. Crystallographic data and structure refinement for the title compound.

Empirical formula	$\text{C}_{28}\text{H}_{38}\text{AlCu}_2\text{Mo}_6\text{N}_4\text{O}_{32.50}$
Formula weight	1680.32
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 13.379(3)\,\text{Å}$, $\alpha = 85.97(3)°$ $b = 17.388(4)\,\text{Å}$, $\beta = 69.79(3)°$ $c = 18.063(4)\,\text{Å}$, $\gamma = 69.22(3)°$
Volume (Å^3), Z	3680.4(13), 2
Density (calculated) (Mg m^{-3})	1.510
Absorption coefficient (mm^{-1})	1.634
$F(000)$	1620
Crystal size (mm^3)	$0.23 \times 0.16 \times 0.14$
θ range for data collection (°)	2.41 to 24.99
Limiting indices	$-14 \le h \le 14$, $-20 \le k \le 20$, $0 \le l \le 21$
Reflections collected	8468
Independent reflections	8468 ($R_{\text{int}} = 0.0000$)
Absorption correction	Empirical
Max. and min. transmission	0.8035 and 0.7050
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8468/12/697
Goodness-of-fit on F^2	1.016
R_1^9□ 0.0797, wR_2^6□0.1787	Largest diffraction peak and hole (eÅ^{-3})
Largest diffraction peak and hole (e Å^{-3})	1.039 and −0.664

$R_1^9 = \Sigma||F_o - F_c||/\Sigma|F_o|$, $wR_2^6 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond distances (Å).

Cu(2)–N(3)	1.904(9)	Cu(2)–O(4 Å)	1.928(10)
Cu(2)–N(4)	2.006(11)	Cu(2)–O(2W)	2.203(9)
Cu(2)–Cu(1)	3.038(2)	Cu(1)–O(1 Å)	1.892(9)
Cu(1)–O(3 Å)	1.927(9)	Cu(1)–N(1)	1.942(9)
Cu(1)–N(2)	2.002(10)	Cu(1)–O(1w)	2.211(10)
Al(1)–O(12)	1.846(7)	Al(1)–O(12)#1	1.846(7)
Al(1)–O(11)	1.904(8)	Al(1)–O(11)#1	1.904(8)
Al(1)–O(10)#1	1.917(7)	Al(1)–O(10)	1.917(7)
Al(2)–O(22)#2	1.827(7)	Al(2)–O(22)	1.827(7)
Al(2)–O(23)#2	1.900(7)	Al(2)–O(23)	1.900(7)
Al(2)–O(24)#2	1.907(8)	Al(2)–O(24)	1.907(8)
Mo(1)–O(1)	1.656(8)	Mo(1)–O(2)	1.667(10)
Mo(1)–O(8)	1.883(8)	Mo(1)–O(7)	1.943(8)
Mo(1)–O(11)	2.241(7)	Mo(1)–O(12)#1	2.244(8)
Mo(2)–O(3)	1.636(12)	Mo(2)–O(4)	1.725(12)
Mo(2)–O(9)	1.884(8)	Mo(2)–O(8)	1.904(8)
Mo(2)–O(10)#1	2.272(8)	Mo(2)–O(11)	2.303(8)
Mo(3)–O(6)	1.662(9)	Mo(3)–O(9)	1.867(10)
Mo(3)–O(5)	1.708(10)	Mo(3)–O(10)#1	2.251(7)
Mo(3)–O(7)#1	1.909(9)	Mo(4)–O(14)	1.582(11)
Mo(3)–O(12)	2.290(8)	N(1)–C(1)	1.321(16)
N(1)–C(5)	1.298(14)	N(2)–C(12)	1.357(16)
N(2)–C(9)	1.292(13)	N(3)–C(17)	1.394(14)
N(3)–C(13)	1.317(15)	N(4)–C(21)	1.366(13)
N(4)–C(24)	1.256(15)		

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

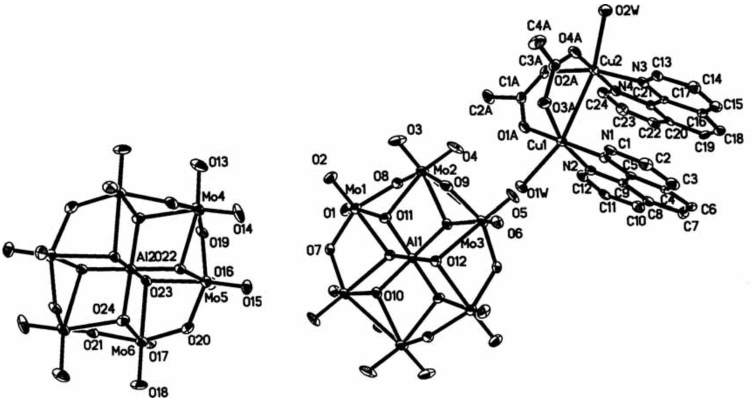

Figure 1. Perspective drawing of $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2][HAl(OH)_6(Mo_6O_{18})] \cdot 2.5H_2O$ with labeling scheme. The hydrogen atoms and crystal water molecules are omitted for clarity. Displacement ellipsoids are scaled to enclose 30% probability.

an unprecedented 1D chain rare earth metal derivative $[La(H_2O)_7Al(OH)_6 Mo_6O_{18}]_n \cdot 4nH_2O$ supported by B-Anderson-type polyanions $[Al(OH)_6Mo_6O_{18}]^{3-}$ as building blocks [20]. In 2003, Shivaiah *et al.* firstly provided a helical suprastructure of B-Anderson compound [22]. In 2004, Drewes *et al.* again reported the 1D chain lanthanide derivatives $[Ln(H_2O)_5(TeMo_6O_{24})]_n^{3n-}$ – $(Ln = Tb^{III}, Dy^{III}, Ho^{III}, Er^{III})$ with A-Anderson-type polyanions [21]. To the best of our knowledge, our B-Anderson-type heteropoly compound containing a binuclear metal coordination cations bridged by two acetate anions is reported for the first time.

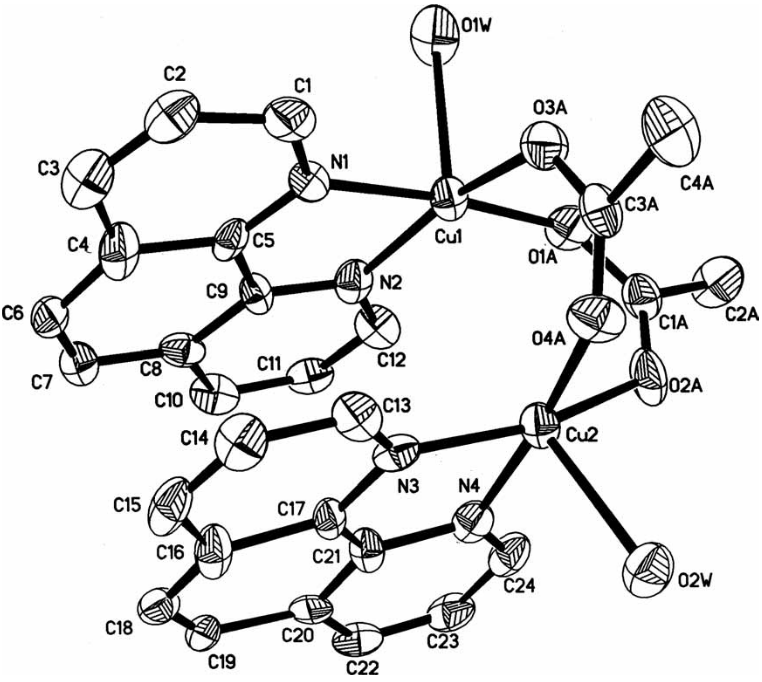

Figure 2. Ball-and-stick representation of $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2]^{2+}$ coordination cation showing 30% probability ellipsoids and the labeling scheme.

Figure 2 demonstrates coordination environment of the dimer $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2]^{2+}$ cation. Cu1 and Cu2 coordination cations are twinned toward each other and bridged through two CH_3COO^- bridges by means of oxygen atoms from carboxyl groups and carbonyl groups. The two 1,10-phenanthroline rings are parallel with a separation distance of ca 3 Å, approximately equal to the distance between two Cu^{2+} spheres (3.038 Å). The π–π packing interactions from the 1,10-phenanthrolines enhance the molecular stability. Both Cu1 and Cu2 coordination cations reside in the five-coordinate, distorted square pyramid configuration. Among the coordination atoms of every Cu^{2+} ion, two are from nitrogen atoms of 1,10-phenanthroline cycle, two from oxygen atoms of CH_3COO^- and one from coordinated water. In the coordination sphere of Cu1, the Cu–N, Cu–O distances in the bottom plane range from 1.942(9) to 2.002(10) Å and from 1.892(9) to 1.927(9) Å, respectively. N1, N2, O3A, O1A constitutes the plane of the square pyramid, with average deviation of 0.1005 Å. The O1W atom occupies the 'top' position over the plane, and the distance between the 'top' oxygen atom and the bottom plane is 2.3271 Å. Moreover, the Cu1 atom is not in the bottom plane, and the distance of Cu1 from the bottom plane is 0.1208 Å. In the coordination sphere of Cu2, the Cu–N, Cu–O bond lengths in the bottom plane range from 1.904(9) to 2.006(11) Å and from 1.888(8) to 1.928(10) Å, respectively. N3, N4, O2A, O4A form the plane of the square pyramid with average deviation from ideal of 0.0967 Å. The O2W atom is situated on the 'top' site over the bottom plane, and the distance of the 'top' oxygen atom and the bottom plane is 2.3228 Å. The Cu2 atom is not in the bottom plane, and the distance of Cu2 from the bottom plane is 0.1227 Å. These data show that the two Cu^{2+} cations are distorted to some degree.

The polyanion structure of the title compound is illustrated in figure 3. The polyanion exhibits a classical B-Anderson-type structure approaching D_{3h} point symmetry. The polyanion is composed of seven edge-shared octahedra, six of which are MoO_6 octahedra arranged hexagonally around the central AlO_6 octahedron. In the central AlO_6 octahedron, the Al–O distances range from 1.827(7) to 1.917(7) Å. In the B-Anderson-type polyanion, the Mo–O distances can be classified into three groups according to the number and types of oxygen atoms: (a) There are twelve terminal O (O_t) atoms only bonded to one Mo atom, and the Mo–O distances vary from 1.582(11) to 1.725(12) Å; (b) There are six O (O_b) atoms shared by two Mo atoms, and the Mo–O distances are in the range of 1.864(10) and 1.943(8) Å; (c) There are six O (O_c) atoms combined with the central Al and two Mo atoms, and the Mo–O distances vary between 2.241(7) and 2.333(8) Å. From the above-mentioned analyses, the coordination geometry of AlO_6 and MoO_6 octahedra are all distorted to some extent. In addition, based on the band valence parameters [27], the summations of bond valences of O(1–6, 13–18) atoms in the anion of the title compound are 2.02, 1.91, 2.14, 1.68, 1.76, 1.99, 1.83, 2.47, 2.17, 1.84, 2.17 and 2.02, according to these analytical results, the terminal oxygen atom (O4) may be protonated. Therefore, the title polyanion can be described as $[HAl(OH)_6(Mo_6O_{18})]^{2-}$, rather than $[Al(OH)_6(Mo_6O_{18})]^{3-}$.

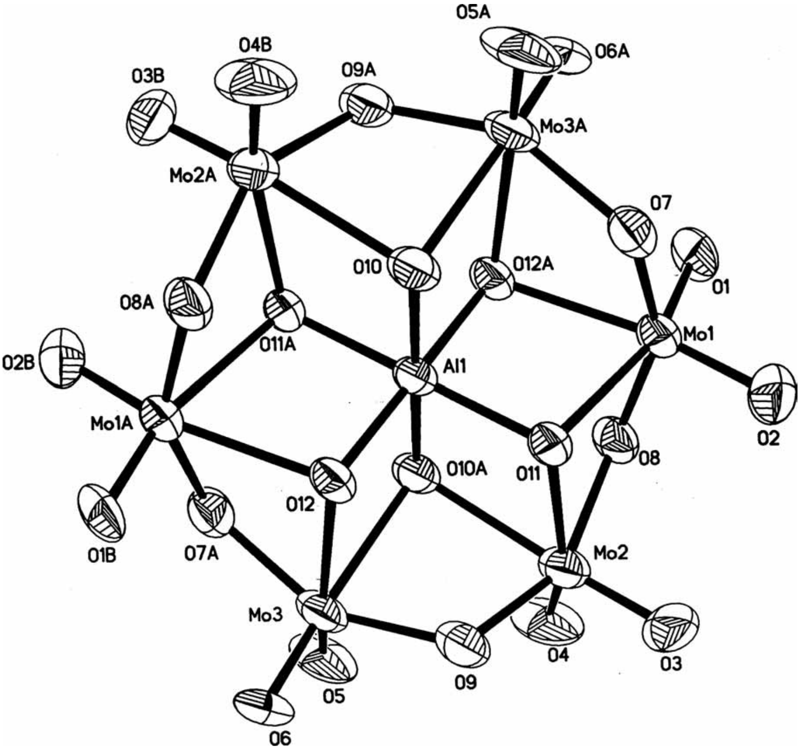

Figure 3. Perspective drawing of $[HAl(OH)_6(Mo_6O_{18})]^{2-}$ ployanion with labeling scheme. The hydrogen atoms are omitted for clarity. Displacement ellipsoids are scaled to enclose 30% probability.

As shown in figure 4, the crystal structure of the title compound shows that the B-Anderson polyoxometalate clusters lined up along the crystallographic *a* axis to give "rectangle" columns, which are arranged with straight channels of 16 × 23 Å, whereas parallel to the crystallographic *b* and *c* axes, the title polyanions $[HAl(OH)_6(Mo_6O_{18})]^{2-}$ are capsulated into the gap generated by the dimer copper(II) coordination cations. Interestingly, this structure motif along the crystallographic *a* axis may act as useful model for the design and assembly of functional molecule-based compounds, especially in the field of molecular sieve materials.

3.2. *Spectroscopic properties*

The IR spectral data of the title compound reveal the characteristic vibration bands. The characteristic peaks centered at 941, 920, 898; 831; 703, 665, 640; and 570 cm^{-1} are attributed to $\nu as(Mo–O_t)$, $\nu as(Mo–O_b–Mo)$, $\nu as(Mo–O_c–Mo)$ and $\nu as(Al–O)$, respectively, showing that the title polyanion still retains an B-Anderson-type structure [19]. A series of bands at 3030; 1573; and 1649, 1426 cm^{-1} are assigned to C–H stretching vibration of aryl groups, asymmetric stretching vibration from aryl ring backbone and $R–COO^-$ stretching vibration of CH_3COO^- anion, respectively, which suggests the existence of 1,10-phenanthroline and acetate ligands in the title compound.

The UV spectra of the title compound in aqueous solution reveal a strong absorption at 208 nm and a shoulder absorption centered at 242 nm, the former is attributable to the $d\pi–p\pi$ charge transfer absorption band of an $O_t \rightarrow Mo$ bond, and the latter, which is the characteristic absorption band of B-Anderson polyanion, is assigned to the $d\pi–p\pi$ charge transitions of $O_{b,c} \rightarrow Mo$ bond. In addition, according to molecular orbital theory of MOL_5 model with C_{4V} symmetry [28], the two absorption bands can be attributed to the $e \rightarrow e^*$ and $e \rightarrow b_2$ electron transitions, respectively. Because the $e \rightarrow e^*$ electron transitions are symmetry-allowed and have larger transition energy

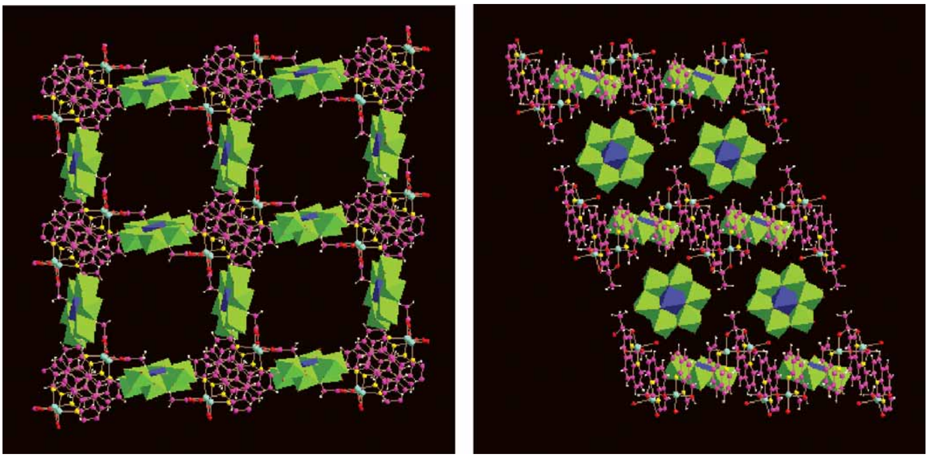

Figure 4. Packing arrangement of $[Cu_2(phen)_2(CH_3COO)_2(H_2O)_2][HAl(OH)_6(Mo_6O_{18})] \cdot 2.5H_2O$ viewed down the crystallographic *a* (left) and *c* (right) axis. The hydrogen atoms and crystal water molecules are omitted for clarity.

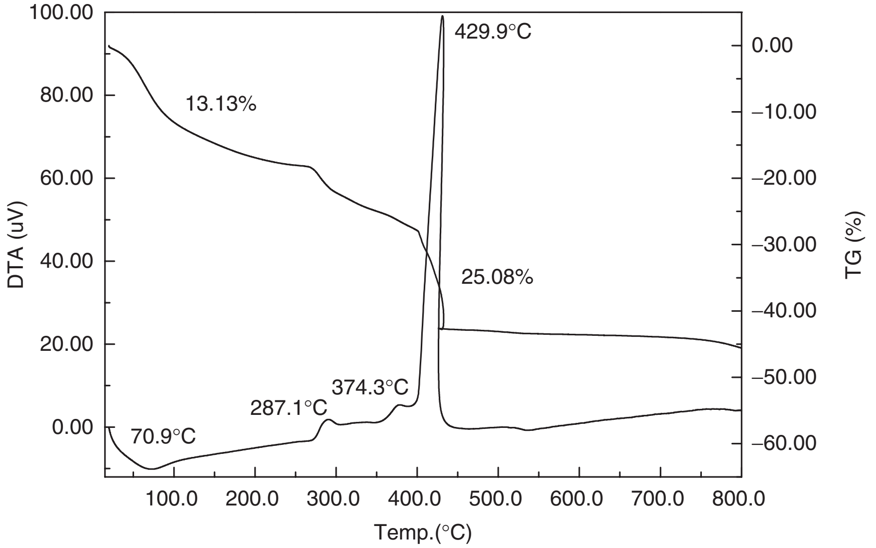

Figure 5. Thermal analytical curves (TG-DTA) of the title compound in flowing N_2 with a heating rate of 10°C min^{-1} at the temperature range of 15 and 800°C.

while the $e \rightarrow b_2$ electron transitions are symmetry-forbidden, the absorption intensity at 208 nm is stronger than that at 242 nm. Moreover, the broad absorption band centered at 762 nm can be attributed to the d–d charge transfer transitions of Cu^{2+} coordination cations in square pyramidal geometry.

3.3. *Thermal property*

The TG curve of the title compound shows two stage weight loss (figure 5), giving a total loss of 38.21% of its initial weight in the range of 15–600°C, which approximately corresponds to the release of 2.5 crystal water molecules, two coordination water molecules, 3.5 structural water molecules, two CH_3COO^- ligands and two 1,10-phenanthroline molecules (37.50% calculated) per formula unit of the title compound. The first weight loss is 13.13% in the temperature range of 15–145°C, corresponding to the release of 2.5 crystal water, 2 coordination water, 0.5 structural water and $2CH_3COO^-$ ligands. There is an endothermal peak at 70.9°C in the corresponding DTA curve. The second weight loss of 25.08% from 145 to 600°C, is attributed to the removal of three structural waters and two 1,10-phenanthroline molecules. In the corresponding DTA curve, two weak exothermal peaks appear at 287.1 and 374.3°C, and another very strong exothermal peak appears at 429.9°C, probably resulting from oxidation and combustion of organic groups and the framework decomposition of the title polyanion.

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References

[1] M.T. Pope, *Heteropoly and Isopoly Oxometalates*, p. 31, Springer, New York (1983).
[2] E. Coronado, C.J. Gomez-Garcia. *Chem. Rev.*, **98**, 273 (1998).
[3] M. Sadakane, E. Steckhan. *Chem. Rev.*, **98**, 219 (1998).
[4] C.L. Bowes, G.A. Ozin. *Adv. Mater.*, **8**, 13 (1996).
[5] S.R. Batten, R. Robson. *Angew. Chem. Int. Ed. Engl.*, **37**, 460 (1998).
[6] M.J. Zaworotko. *Angew. Chem. Int. Ed. Engl.*, **37**, 1211 (1998).
[7] C. Janiak. *Angew. Chem. Int. Ed. Engl.*, **36**, 1431 (1997).
[8] D. Hagrman, R.P. Hammond, R. Haushalter, J. Zubieta. *Chem. Mater.*, **10**, 2091 (1998).
[9] M. Fujita, Y.J. Kwon, K. Sasake, K. Yamaguchi, K. Ogura. *J. Am. Chem. Soc.*, **117**, 7287 (1995).
[10] G.B. Gardner, Y.H. Kiang, S. Lu, A. Asgaonker, D. Venketaraman. *J. Am. Chem. Soc.*, **118**, 6946 (1996).
[11] M.J. Zaworotko, P. Losier. *Angew. Chem. Int. Ed. Engl.*, **35**, 2779 (1996).
[12] C.S. Hong, Y. Do. *Inorg. Chem.*, **37**, 4470 (1998).
[13] C.M. Liu, D.Q. Zhang, D.B. Zhu. *Crystal Growth & Design*, **3**, 363 (2003).
[14] M.I. Khan. *J. Solid State Chem.*, **152**, 105 (2000).
[15] Z. Shi, L.R. Zhang, G.S. Zhu, G.Y. Yang, J. Hua, H. Ding, S.H. Feng. *Chem. Mater.*, **11**, 3565 (1999).
[16] D. Hagrman, C. Sangregorio, C.J. O'Connor, J. Zubieta. *J. Chem. Soc., Dalton Trans.*, 3707 (1999).
[17] A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot, F. Sécheresse. *Chem. Eur. J.*, **9**, 2914 (2003).
[18] J.Y. Niu, D.J. Guo, J.P. Wang, J.W. Zhao. *Crystal Growth & Design*, **4**, 241 (2004).
[19] B. Xiang, Y.R. Guo, H.Y. Ma, B.B. Zhou, X.Q. Xu. *Chemistry Online*, **65**, 1 (2002) (in Chinese).
[20] V. Shivaiah, P.V.N. Reddy, L. Cronin, S.K. Das. *J. Chem. Soc., Dalton Trans.*, 3781 (2002).
[21] D. Drewes, E.M. Limanski, B. Krebs. *J. Chem. Soc., Dalton Trans.*, 2087 (2004).
[22] V. Shivaiah, M. Nagaraju, S.K. Das. *Inorg. Chem.*, **42**, 6604 (2003).
[23] B. Krebs, I. Loose, M. Bösing, A. Nöh. *C. R. Acad. Sci. Ser. IIc: Chim.*, 351 (1998).
[24] H. Yan, Y.Q. Guo, Y.G. Li, E.B. Wang, J. Lü, L. Xu, C.W. Hu. *Inorg. Chem. Commun.*, **7**, 521 (2004).
[25] G.M. Sheldrick. *SHELXL 97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[26] S. Manikumari, V. Shivaiah, S.K. Das. *Inorg. Chem.*, **41**, 6953 (2002).
[27] I.D. Brown, D. Altermatt. *Acta Crystallogr.*, **B41**, 244 (1985).
[28] E.B. Wang, C.W. Hu, L. Xu. *Introduction of Heteroplyacid Chemistry*, p. 45, Chemical Industry Press, Beijing (1998).