Journal of Molecular Structure 920 (2009) 284–288

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

# Synthesis and characterization of B-type Anderson polyoxoanions supported copper complexes with mixed ligands

Shiwei Zhang [a], Yuxin Li [b,*], Ying Liu [a], Ruige Cao [a], Chunyan Sun [a], Hongmei Ji [a], Shuxia Liu [a,*]

[a] *Key Laboratory of Polyoxometalates Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun City, JiLin 130024, PR China*
[b] *Institute of Genetics and Cytology, Northeast Normal University, Changchun City, JiLin 130024, PR China*

ARTICLE INFO

*Article history:*
Received 23 September 2008
Received in revised form 8 November 2008
Accepted 10 November 2008
Available online 27 November 2008

*Keywords:*
Organic–inorganic hybrids
Anderson-type polyoxoanion
Photoluminescence properties
Mixed ligands

ABSTRACT

Two novel compounds constructed by Anderson-type polyoxoanions and copper complexes with mixed ligands, $(H_3O^+)[Cu(C_6NO_2H_4)(phen)(H_2O)]_2[Al(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (1) and $(H_3O^+)[Cu\ (C_6NO_2H_4)(phen)(H_2O)]_2[Cr(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (2) have been isolated by conventional solution method, and characterized by elemental analyses, IR spectra, thermal stability analyses, X-ray powder diffraction and single-crystal X-ray diffraction. Compounds **1** and **2** are isomorphic and reveal an example of three-dimensional supramolecular organic–inorganic hybrids based on copper complexes with mixed 1,10-phenanthroline and pyridine-4-carboxylic acid ligands supported on Anderson-type polyoxoanions. Furthermore, both of the compounds exhibit photoluminescent properties at ambient temperature, and to elucidate the electronic properties of the metal ions ($Cu^{2+}$ or $Cu^{2+}/Cr^{3+}$), EPR studies have been performed, and the results are in good agreement with the structural feature of these compounds.

## 1. Introduction

Over the past decades, organic–inorganic hybrid compounds have been attracting considerable interest as a promising new class of materials owing to the possibility of combining the different features of the components to get unexpected structures, properties, or applications [1]. Polyoxometalates (POMs) are discrete anionic metaloxygen clusters, because their electronic versatility and structural diversity [2] have been extensively employed as inorganic building blocks for the construction of organic–inorganic hybrid materials with various transition-metal complexes as bridging ligands [3]. Among the versatile polyoxoanions, the Anderson-type polyoxoanions holding charming planar structures has been extensively employed as inorganic building blocks in recent years, due to each Mo (or W) atom of the Anderson-type polyoxoanions has two terminal oxygen atoms with high reactivity [4], which may facilitate the construction of novel organic–inorganic hybrid compounds. The successful syntheses of hybrid compounds holding 1D (one-dimensional), 2D, and even 3D structures [5] have further inspired our research interest to construct the novel architectures based on this kind of polyoxoanions.

More recently, much attention has been focused on developing coordination polymers with mixed organoamine and carboxylate ligands or two different organoamine ligands incorporating the various polyoxoanion for structural reasons, as well as for their properties [6]. But up to now, the examples of hybrid compounds based on Anderson-type POM building blocks and coordination polymers with mixed organoamine and carboxylate ligands have rarely been reported [7]. Taking into account these, we choose the 1,10-phenanthroline and pyridine-4-carboxylic acid as organic ligands to combine the transition-metal centers because of their multifold electronic properties and coordination modes.

In this paper, we isolated two organic–inorganic hybrid compounds, namely $(H_3O^+)[Cu(C_6NO_2H_4)(phen)]_2[Al(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (**1**) and $(H_3O^+)[Cu\ (C_6NO_2H_4)(phen)]_2[Cr(OH)_6\ Mo_6O_{18}]\cdot 5H_2O$ (**2**), which are built up of Anderson-type polyoxoanions and copper coordination polymers with mixed 1,10-phenanthroline and pyridine-4-carboxylic acid ligands, extensive π–π interactions and hydrogen bonding interactions form the 3D supramolecular structures. Herein, the syntheses, structures, photoluminescence properties and the X-band powder EPR spectra studies for the compounds have been reported.

## 2. Experimental

### 2.1. Materials

All chemicals were used as purchased without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Cr, Al, Cu and Mo were determined by a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 $cm^{-1}$ on an

---

* Corresponding authors. Tel./fax: +86 431 85099502 (Y. Li), +86 431 85099328 (S. Liu).
*E-mail addresses:* liyx486@nenu.edu.cn (Y. Li), liusx@nenu.edu.cn (S. Liu).

0022-2860/$ - see front matter Crown Copyright © 2008 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2008.11.031

Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermal stability analyses were performed on a Perkin-Elmer TGA-7 instrument in $N_2$ atmosphere with a heating rate of 10 °C/min. Powder X-ray diffraction measurements were performed on a Rigaku D/MAX-3 instrument with Cu-Kα radiation in the angular range $2\theta = 3–50°$ at 293 K. Luminescence measurement was carried out on a Hitachi F-4500 Fluorescence Spectrophotometer. The electron paramagnetic resonance (EPR) spectra were recorded on a Japanese JES-FE3AX spectrometer at room temperature and liquid nitrogen temperature, respectively.

### *2.2. Syntheses of compounds **1** and **2***

#### *2.2.1. $(H_3O^+)[Cu(C_6NO_2H_4)(phen)(H_2O)]_2[Al(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (**1**)*

Both the cationic complex $[Cu(C_6NO_2H_4)(phen)(H_2O)]^+$ (**A**) and the anion $[Al(OH)_6Mo_6O_{18}]^{3-}$ (**B**) were prepared in situ. For **A**, pyridine-4-carboxylic acid (0.073 g, 0.27 mmol) was dissolved in 20 mL hot water, after cooling to room temperature, 10 mL methanol solution of 1,10-phenanthroline (0.11 g, 0.60 mmol) and 10 mL aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.14 g, 0.60 mmol) were added in succession under stirring. For **B**, $Na_2MoO_4\cdot 2H_2O$ (0.90 g, 3.72 mmol) was dissolved in 30 mL water and the pH of the solution was adjusted with the dilute $HNO_3$ solution (3 M) to approximately 4.5, and 10 mL aqueous solution containing $Al(NO_3)_3\cdot 9H_2O$ (0.56 g, 1.50 mmol) was added with stirring, the final pH of the solution was adjusted to 2.6 with the dilute $HNO_3$ solution (3 M). The solution of **A** was quickly added into that of **B** with stirring, immediately blue precipitate formed and the pH of resulting solution was about 2.6. The mixture was stirred for 30 min and then filtered. The filtrate was allowed to evaporate for 10 days at room temperature and blue block crystals of compound **1** were isolated (53% yield based on Mo). Anal. Calcd for $C_{36}H_{47}AlCu_2N_6Mo_6O_{36}$: C, 23.13; H, 2.53; N, 4.50; Al, 1.44; Cu, 6.79; Mo, 30.79 (%). Found: C, 23.34; H, 2.38; N, 4.67; Al, 1.65; Cu, 7.13; Mo, 31.05 (%). IR (KBr, $cm^{-1}$): 3440 (br), 3049 (m), 1606 (m), 1558 (m), 1518 (m), 1424 (m), 1370 (m), 1342 (m), 1238 (w), 1199 (w), 1150 (w), 1107 (w), 1014 (w), 936 (s), 919 (s), 830 (m), 773 (m), 723 (m), 647 (s), and 444 (m).

#### *2.2.2. $(H_3O^+)[Cu(C_6NO_2H_4)(phen)(H_2O)]_2[Cr(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (**2**)*

The synthesis of **2** was prepared following the procedure described above, except that $Cr(NO_3)_3\cdot 6H_2O$ (0.42 g, 1.12 mmol) was used instead of $Al(NO_3)_3\cdot 9H_2O$. Yield: 61% (based on Mo). Anal. Calcd for $C_{36}H_{47}CrCu_2N_6Mo_6O_{36}$: C, 22.82; H, 2.50; N, 4.44; Cr, 2.74; Cu, 6.71; Mo, 30.37 (%). Found: C, 22.64; H, 2.36; N, 4.61; Cr, 2.85; Cu, 6.94; Mo, 30.68 (%). IR (KBr, $cm^{-1}$): 3440 (br), 3049 (m), 1605 (m), 1541 (m), 1518 (m), 1425 (m), 1370 (m), 1342 (m), 1223 (w), 1201 (w), 1150 (w), 1109 (w), 1014 (w), 934 (s), 909 (m), 830 (m), 773 (m), 723 (m), 643 (s) and 414 (m).

### *2.3. X-ray crystallography*

Diffraction intensities for compounds **1** and **2** were collected on a SMART CCD diffractometer equipped with graphite monochromatic MoKα radiation ($\lambda = 0.71073$ Å) at 293 K. The linear absorption coefficient, scattering factor for the atom, and anomalous dispersion correction were taken from International Tables for X-ray Crystallography. The structure was solved by the direct method and refined by the full-matrix least-squares method on $F^2$ using the SHELXTL crystallographic software package [8]. Empirical absorption correction by SADABS was applied to the intensity data. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms on the 1,10-phenanthroline and pyridine-4-carboxylic acid ligands were placed on calculated positions and included in the refinement riding on their respective parent atoms. Details of the crystal data and final structure refinements of compounds **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles are provided in Table S1 and Table S2 of the Supplementary material. The experimental and simulated X-ray powder diffraction patterns (XRPD) of both compounds are shown in Fig. S5. The diffraction peaks on both experimental and simulated patterns match well in position, indicating their phase purity. Additionally, the XRPD patterns of **1** and **2** are similar, which are in agreement with their isomorphic structures determined by single-crystal X-ray diffraction.

## 3. Results and discussion

### *3.1. Synthesis and structure*

The compounds **1** and **2** were synthesized by the conventional solution method. We propose the following formation process scheme for compounds **1** and **2**. ($C_6NO_2H_5$ = pyridine-4-carboxylic acid, $C_{12}H_8N_2$ = 1,10-phenanthroline = phen).

$$\begin{aligned}&Cu^{2+} + phen + H_2O/CH_3OH + C_6NO_2H_5\\&\quad \rightarrow H^+ + [Cu(C_6NO_2H_4)(phen)(H_2O)_n(CH_3OH)_{3-n}]^+ \qquad (1)\end{aligned}$$

$$6[MoO_4]^{2-} + M^{3+} + 6H^+ \rightarrow [M(OH)_6Mo_6O_{18}]^{3-} \quad (M = Al,\ Cr) \qquad (2)$$

$$\begin{aligned}&2[Cu(C_6NO_2H_4)(phen)(H_2O)_n(CH_3OH)_{3-n}]^+ + [M(OH)_6Mo_6O_{18}]^{3-}\\&\quad + H^+ + (6-n)H_2O\\&\rightarrow (H_3O^+)[Cu(C_6NO_2H_4)(phen)(H_2O)[M(OH)_6Mo_6O_{18}]\cdot 5H_2O\\&\quad + (3-n)CH_3OH \qquad (3)\end{aligned}$$

It was noted that, by plenty of parallel experiments, we found that the adjustment of the pH of the mixture to 2.6 was crucial for the formation of the final product.

For that compounds $(H_3O^+)[Cu(C_6NO_2H_4)(phen)(H_2O)]_2$-$[Al(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (**1**) and $(H_3O^+)[Cu(C_6NO_2H_4)(phen)(H_2O)]_2$-$[Cr(OH)_6Mo_6O_{18}]\cdot 5H_2O$ (**2**) are isomorphic only with slight differences in bond lengths and bond angles, **1** is described as an example below. The unit cell of **1** contains one Anderson-type polyoxoanions supported copper complex with mixed 1,10-phenanthroline and pyridine-4-carboxylic acid ligands (Fig. 1) and six lattice water molecules. The building block $[Al(OH)_6Mo_6O_{18}]^{3-}$ belongs to B-type Anderson structure, which consists of seven

**Table 1**
Crystal data and structure refinement parameters for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{36}H_{47}AlCu_2N_6Mo_6O_{36}$ | $C_{36}H_{47}CrCu_2N_6Mo_6O_{36}$ |
| *M* | 1869.49 | 1894.51 |
| Crystal system | Triclinic | Triclinic |
| Space group | *P*–1 | *P*–1 |
| θ range (°) | 2.21–28.13 | 2.11–25.60 |
| *a* (Å) | 9.9403(10) | 9.9418(9) |
| *b* (Å) | 9.9424(10) | 9.9459(9) |
| *c* (Å) | 14.2362(14) | 14.2493(12) |
| α (°) | 83.1470(10) | 81.4570(10) |
| β (°) | 81.4550(10) | 83.0140(10) |
| γ (°) | 77.1910(10) | 77.2240(10) |
| *V* ($Å^3$) | 1351.3(2) | 1353.1(2) |
| *Z* | 1 | 1 |
| *F* (000) | 936 | 1170 |
| $D_c$ (g $cm^{-3}$) | 2.294 | 2.327 |
| Abs coeff., ($mm^{-1}$) | 5.085 | 8.000 |
| Total data collected | 7159 | 7275 |
| Unique data | 4942 | 5025 |
| $R_{int}$ | 0.0143 | 0.0163 |
| GOF | 1.021 | 1.046 |
| $R_1$ $[I > 2\sigma(I)]$[a] | 0.0257 | 0.0304 |
| $wR_2$ (all data)[b] | 0.0651 | 0.0781 |

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_0^2 - Fc^2)^2/\sum w(F_0^2)^2]^{1/2}$.