

Structure and two-dimensional correlation infrared spectroscopy study of two isomeric forms of the octamolybdate cluster

Yiping Chen^a, Hanhui Zhang^{a,b,*}, Xuezhen Wang^a, Changcang Huang^a,
Yanning Cao^a, Ruiqing Sun^a

^aDepartment of Chemistry, Fuzhou University, Fuzhou, Fujian, 350002, PR China

^bState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian, 350002, PR China

Received 15 November 2005; received in revised form 17 February 2006; accepted 18 February 2006
Available online 6 March 2006

Abstract

Two isomeric forms of the octamolybdate cluster, $(\text{NH}_4)_2(\text{Hbpy})_2[\text{Mo}_8\text{O}_{26}](\text{bpy})_3$ **1** (bpy = bipydine), and $[\text{Cu}_2(\text{imi})_4]_2[\text{Mo}_8\text{O}_{26}]$ **2** (imi = imidazole), were synthesized by hydrothermal method and characterized by X-ray single analysis, one-dimensional (1D) infrared spectroscopy and two-dimensional (2D) correlation infrared spectroscopy under thermal perturbation. In compound **1**, the $[\text{Mo}_8\text{O}_{26}]$ units are β -structure, and octamolybdate anion is ζ -structure in compound **2**. The 2D IR correlation spectroscopy study indicates that the intensity changes of Mo=O band are more sensitive to the temperature variation than that of the Mo–O bond. The μ -Mo–O bond and framework vibrations in compound **1** are more sensitive to the temperature variation than that for compound **2**. As the vibrations of μ -Mo–O bond accompanied by the transfer of an oxygen atom, the catalysis ability of compound **1** may be higher than that of compound **2**.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Polyoxometalate; Octamolybdate; Crystal structure; Two-dimensional infrared (2D IR) correlation spectroscopy

1. Introduction

Generalized two-dimensional (2D) correlation spectroscopy proposed by Noda [1–4], which is an extension of the original 2D correlation spectroscopy, has become a very powerful and versatile tool for elucidating subtle spectral changes induced by an external perturbation such as light, heat, electricity, magnetism, chemistry, or mechanical force. 2D infrared (IR) correlation spectroscopy could not only enhance spectral resolution and identify overlapped peaks but also probe the specific order of certain events taking place under the influence of a controlled physical variable. This has proven as valuable, especially in IR spectroscopic studies of biomolecules, as this enables

one, for example, to identify discrete and unique protein secondary structure conformations as well as interconversion of one form to another as a result of changes in external environment [5–9]. 2D IR correlation analysis has also been used to analyze structure in monomolecular films [10]. The phase behavior of phospholipid monolayer has been studied using 2D IR, and how these methods could distinguish bands due to co-existing phases in a disorder–order phase transition in the monolayer was shown [10,11]. 2D IR techniques have been used to investigate the coupled carbonyl stretches of $\text{Rh}(\text{CO})_2$ ($\text{C}_5\text{H}_7\text{O}_2$) [12–14] and water transportation in epoxy resin was studied [15].

Polyoxometalates (POMs) have recently received much attention, owing to their fascinating properties and great potential applications in many fields (such as catalysis, material science, bio- and nanotechnology, medicine, and magneto chemistry) as well as their unusual topological properties [16–19]. But there is obviously a lack of

*Corresponding author. Department of Chemistry, Fuzhou University, Fuzhou, Fujian, 350002, PR China. Fax: +86 591 8789 3239.

E-mail addresses: zhanghh1840@hotmail.com, hhzhang@fzu.edu.cn (H. Zhang).

physico-chemical methods characterizing POM catalyst. Even though some of the POMs have been put into practice, the mechanism of the POM remains incompletely understood. Thus, some new technologies and methods are needed to resolve these problems. 2D IR spectroscopy, recently the subject of extensive theoretical and experimental study, has shown promise for providing new information about evolving structures [20,21]. The 2D IR spectroscopy can represent an interesting way to check the presence or the breaking of the POM structure during the chemical reactions by an external perturbation, such as heating, changing reagent concentration, increasing pressure or altering intensity of additional magnetic field. And the 2D correlation IR spectroscopy will become a new method to promote the deep study of the POMs.

On the other hands, POMs often have kinds of isomeric forms. For example, there are eight kinds of isomeric forms for octamolybdate anion [22–26]. Sometimes, X-ray single crystallography diffraction was employed to determine their exact structure, but single crystal is usually difficult to obtain. And it is difficult to distinguish their configuration by other routine physico-chemical methods. 2D IR correlation spectroscopy could enhance spectral resolution and identify overlapped peaks. It would become a new powerful tool to recognize the POM configuration.

We firstly apply 2D correlation IR spectroscopy for investigation on POMs [27–30]. Now, we herein report two isomeric forms of the octamolybdate cluster, $(\text{NH}_4)_2(\text{Hbpy})_2[\text{Mo}_8\text{O}_{26}](\text{bpy})_3$ **1** (bpy = 4,4'-bipyridine), and $[\text{Cu}_2(\text{imi})_4]_2[\text{Mo}_8\text{O}_{26}]$ **2** (imi = imidazole), and use 2D correlation IR spectroscopy to study the structure changes induced by thermal perturbation. The objective of this study was to enrich the POM structure chemistry and spectroscopy and to promote theory studies on practice application of POMs.

2. Experimental

2.1. Synthesis of compound 1

A mixture of MoO_3 (0.10 g, 0.41 mmol), bpy (0.05 g, 1.5 mmol) and NH_4Cl (0.5 M 2 ml) in H_2O (10 ml) was adjusted to pH 7–8 with $\text{NH}_3 \cdot \text{H}_2\text{O}$ (1.0 M solution in water) and was heated at 180°C for 18 h in a sealed 30 ml Teflon-lined stainless-steel vessels under autogeneous pressure. After the mixture was slowly cooled to room temperature, colorless parallelepiped crystals (yield 85%, based on bpy) were produced. The single crystals were selected carefully under a microscope to be measured. Anal. calc. For 1: C 29.96%; H 2.52%; N 8.39%. Found: C 28.16%; H 2.36%; N 8.25%.

2.2. Synthesis of compound 2

A mixture of MoO_3 (0.3 g, 1.23 mmol), imi (0.1 g, 1.5 mmol), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.3 g, 1.5 mmol) and H_3BO_3 (0.4 g) in H_2O (5 ml) was adjusted to pH 6.5 with

NaOH (1.0 M solution in water) and was heated at 140°C for 4 days in a sealed 30 ml Teflon-lined stainless-steel vessels under autogeneous pressure. After the mixture was slowly cooled to room temperature, black block crystals (yield 50%, based on Mo) and little brown crystals were produced. The black block single crystals were selected carefully under a microscope to be measured. Anal. calc. For 1: C 14.54%; H 1.61%; N 11.30%. Found: C 14.44%; H 2.06%; N 10.85%.

2.3. Data collection, structure solution and refinement

The data collection of compound **1** was performed on a Rigaku Weissenberg IP diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) at 293(2) K. And the data of compound **2** were collected on Bruker MART APEX area-detector diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K. The structure of the two compounds was solved by direct methods using SHELXS-97 [31] and refined by full-matrix least-square techniques using SHELXL-97 [32]. Each non-hydrogen atom was treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data are summarized in Table 1.

2.4. Apparatus

IR spectra were recorded in the range of $4000\text{--}400 \text{ cm}^{-1}$ on a Perkin-Elmer FT-IR spectrum 2000 spectrometer using KBr pellets. Spectra were calculated from a total of 32 scans. In order to get the dynamic IR spectra, the temperature was varied from 50 to 120°C at an interval of 10°C by a Portable programmable temperature controller (Model 50-886, Love Control Corporation). 2D IR correlation spectra were obtained by treatment of the series of dynamic spectra with 2D IR correlation analysis software provided by Tsinghua University.

3. Results and discussion

3.1. The molecular and crystal structure

Compound **1** contains the $[\text{Mo}_8\text{O}_{26}]^{4-}$ anions, ammonium ions, protonized bpy cations, and bpy molecules. $[\text{Mo}_8\text{O}_{26}]^{4-}$ anion is a typical β -structure octamolybdate [24,33,34] (Fig. 1a), which is built up from eight distorted $\{\text{MoO}_6\}$ edge-shared octahedra. They can be described alternatively as two cyclic Mo_4O_{12} units formed by distorted MoO_4 tetrahedra, which is cross-linked by long Mo–O bonds and by additional long bonds from Mo to two extra O^{2-} ions. The Mo–O bond lengths vary from $1.68(1) \text{ \AA}$ for one of terminal $\text{Mo}=\text{O}$ bonds to $2.38(1) \text{ \AA}$ for one of the bonds to the unusual five-coordinate O atom [O(3)] that sits near the center of each Mo_4O_{12} half of the anion. There are four kinds of M–O bond: namely $\text{M}=\text{O}$, $\mu_2\text{-O-Mo}$, $\mu_3\text{-O-Mo}$, and the unusual five-coordinate O atom in $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ anion.

Table 1
Crystal data and structure refinement for compounds **1** and **2**

Salt	Compound 1	Compound 2
Molecule formula	C ₅₀ H ₅₀ Mo ₈ N ₁₂ O ₂₆	C ₂₄ H ₃₂ Cu ₄ Mo ₈ N ₁₆ O ₂₆
Molecule weight	2002.54	1982.34
Crystal size (mm)	0.38 × 0.30 × 0.28	0.18 × 0.16 × 0.14
Crystal color	Colourless	Black
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ /n
<i>a</i> (Å)	10.2024(6)	13.0101(7)
<i>b</i> (Å)	32.4188(16)	14.0014(7)
<i>c</i> (Å)	18.8355(12)	15.0610(8)
β (°)	102.033(19)	108.4730(10)
<i>V</i> (Å ³)	6093(2)	2602.1(2)
<i>Z</i>	4	2
<i>D</i> _{calc} /Mg × m ⁻³	2.183	2.530
θ range (°)	2.54–27.48	1.81–28.29
Index ranges	0 ≤ <i>h</i> ≤ 13 0 ≤ <i>k</i> ≤ 42 −24 ≤ <i>l</i> ≤ 23	−16 ≤ <i>h</i> ≤ 17 −18 ≤ <i>k</i> ≤ 17 −19 ≤ <i>l</i> ≤ 19
<i>F</i> (000)	3912	1896
μ (mm ⁻¹)	1.686	3.549
Reflections collected/unique	23,838/6598	29,758/6267
Reflections with <i>I</i> > 2 σ (<i>I</i>)	2108	5882
<i>R</i> ₁ indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0604	<i>R</i> ₁ = 0.0350
w <i>R</i> ₂ indices (all data) ^b	w <i>R</i> ₂ = 0.1755	w <i>R</i> ₂ = 0.0924
Largest diff. peak and hole (e Å ⁻³)	1.242 and −1.369	1.245 and −1.029

Bond-valence sum (BVS) [35,36] calculations show that the Mo atom exhibits a BVS of +6. Terminal oxygen atom of β -octamolybdate unit links to ammonium ions through hydrogen bonds (N⋯O: 2.897(4) 2.94(2) 2.926(3) 3.02(3) Å) to form chain structure.

The overall neutral 3D framework of **1** clearly shows the presence of large channels (Fig. 1b) that are built by protonized bpy cations, 4,4'-bpy and lattice crystalline water molecules. In reverse, infinite chains of [NH₄(Mo₈O₂₆)]³⁻ blocks are surrounded by protonized bpy cations, bpy and ammonium ion. The distance between centers of two pyridine rings is 3.86(7), 3.93(2) or 3.99(1) Å, which suggests the existence of π - π stacking between parallel bpy chains.

Compound **2** consists of [Mo₈O₂₆]⁴⁻ anions, imi and copper(I) ions. [Mo₈O₂₆]⁴⁻ anion is a typical ζ -structure octamolybdate [26] (Fig. 2), which consists of four {MoO₆} octahedral and four {MoO₅} square pyramids linked through corner and edge-sharing interactions. The structure may be described as a ring constructed from two pairs of edge-sharing octahedral linked through two edge- and corner-sharing square pyramidal sites and capped on either face by square pyramids. The octahedral and square pyramids of the equatorial ring all exhibit two terminal oxo-groups, while the two capping square pyramids have a single terminal oxo-group. Differently from compound **1**, there are only three kinds of M–O bond in [Mo₈O₂₆]⁴⁻ anion: namely M=O, μ_2 -O–Mo, and μ_3 -O–Mo. BVS

[35,36] calculations also show that the Mo and Cu atom exhibits a BVS of +6 and +1, respectively. Two Cu(I) atoms are bonded to two nitrogen atoms of imidazole ligands, respectively. Two [Cu(imidazole)₂]⁺ units are connected to the terminal oxygen of [Mo₈O₂₆]⁴⁻ anion by weak interactions, Cu–O distance ranges from 2.457(1) to 2.840(1) Å. The intermolecular hydrogen bonds lead to the short contacts of N2⋯O11 2.933(1) Å, N4⋯O9 (−*x*+2, −*y*+2, −*z*+1) 2.821(2) Å, N5⋯O1 (*x*−1/2, −*y*+3/2, *z*−1/2) 2.847(2) Å and N7⋯O8 (*x*+1/2, −*y*+3/2, *z*+1/2) 3.114(2) Å.

CCDC-280065 for compound **1** and CCDC-268703 for compound **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

3.2. Assignments of the 1D IR spectra

Fig. 3 shows IR spectra of compounds **1** and **2** measured at room temperature. The IR spectrum of compound **1** exhibits broad bands at 3242, 3176, and 3098 cm⁻¹ due to stretching vibrations of N–H and C–H groups of bpy. The bands from 1406 to 1636 cm⁻¹ can be assigned to the bending vibrations of the C–H, N–H, or the ring stretching vibrations of the bpy. The strong bands at 936 and 912 cm⁻¹ are assigned to asymmetry and symmetry stretching vibrations, respectively, of the terminal Mo=O. The sharp peaks at 842, 806, 711, 719, and 672 cm⁻¹ are

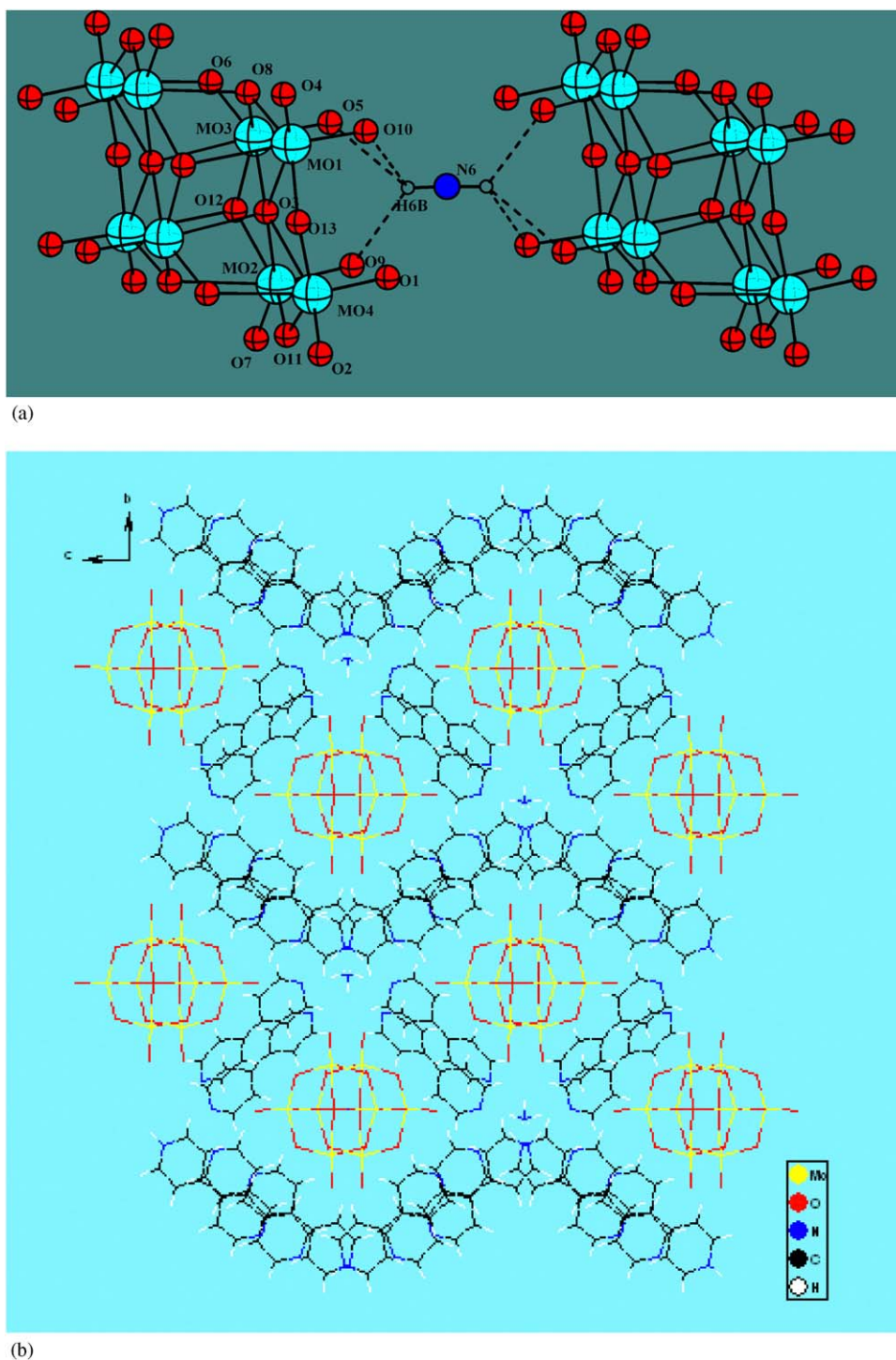


Fig. 1. (a) A perspective view of anions of **1**, with displacement ellipsoids drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. (b) Packing diagram of **1** along *a*-axis.

attributed to the Mo–O stretching, in agreement with three kinds of μ -O–Mo in the structure, namely μ_2 -O–Mo, μ_3 -O–Mo, and the unusual five-coordinate O atom in $[\text{Mo}_8\text{O}_{26}]^{4-}$ anion.

The IR spectrum of compound **2** exhibits broad bands at 3535 and 3254 cm^{-1} due to stretching vibrations of N–H of imi, which agree with N–H of hydrogen bond to terminal oxygen of octamolybdate or no hydrogen bond to it. The

3137 cm^{-1} peak would be attributed to C–H of imi ligands. The bands from 1428 to 1613 cm^{-1} can be assigned to the bending vibrations of the C–H, N–H, or the ring stretching vibrations of the imi ligand. The sharp peaks at 937, 927, 904, 857, and 745 cm^{-1} are attributed to the Mo–O stretching, in agreement with three kinds of Mo–O in the structure, namely terminal $\text{Mo}=\text{O}$, μ_2 -O–Mo, and μ_3 -O–Mo.

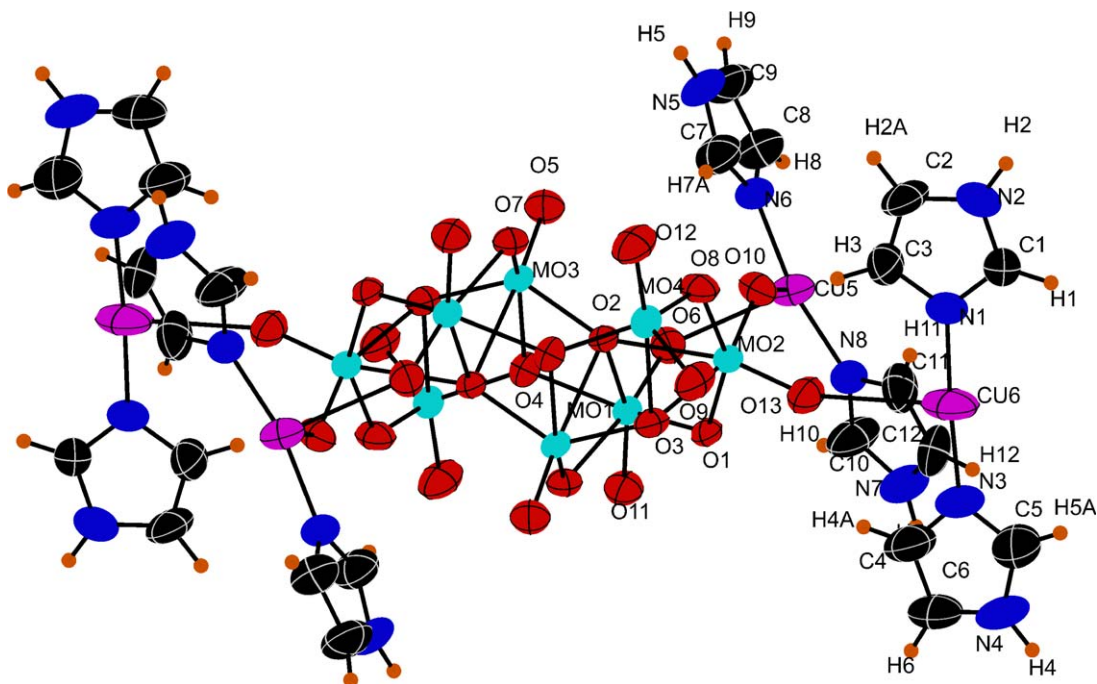


Fig. 2. A perspective view of one molecule of **2**, with displacement ellipsoids drawn at the 50% probability level.

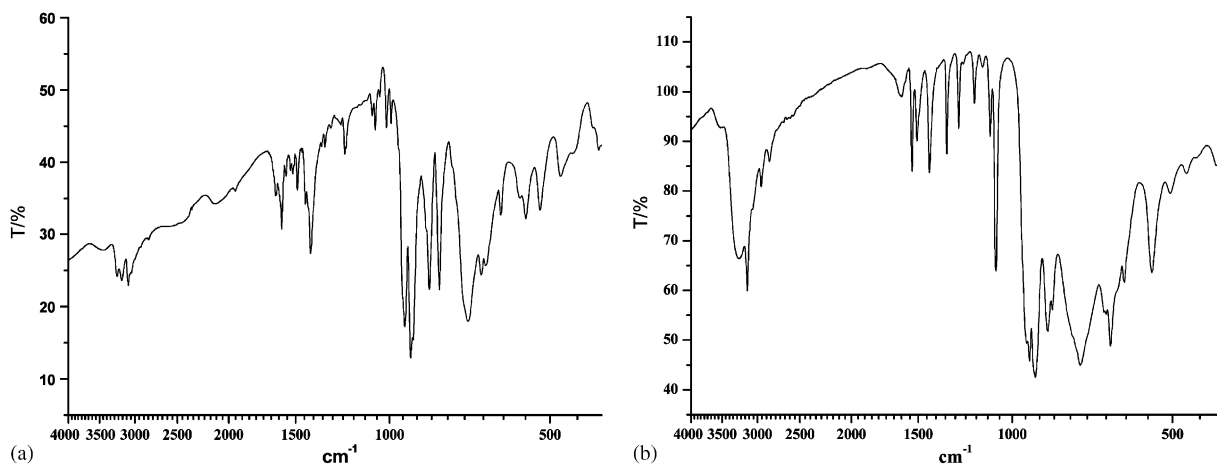


Fig. 3. FTIR spectra of compounds measured at room temperature: (a) compound **1**; (b) compound **2**.

3.3. Temperature-induced structural variations in the compounds revealed by 2D IR correlation spectroscopy

In order to clarify the structural changes of the cluster units in compounds more efficiently, 2D correlation IR spectra of the temperature-dependent were introduced.

Fig. 4 depicts the synchronous and asynchronous 2D correlation spectra of compound **1** over the temperature range from 50 to 120 °C in 400–1000 cm^{-1} , calculated from the dynamic spectra. In the synchronous spectrum, two auto peaks along the diagonal line can be detected at 948 and 918 cm^{-1} unambiguously, which are assigned to

asymmetry and symmetry stretching vibrations, respectively, of the terminal $\text{Mo}=\text{O}$. Furthermore, it can be concluded that the position at 936 cm^{-1} (wide) in 1D spectrum in fact contains the 948 cm^{-1} peak. The strong positive cross peak at (918, 948) cm^{-1} indicates the same direction of the intensity variations in these two correlated stretching vibrations modes. As the terminal oxygen atom of β -octamolybdate unit connected ammonium ions through hydrogen bonds, stretching vibrations of the terminal $\text{Mo}=\text{O}$ give birth to a new weak auto-peak at 930 cm^{-1} . The weak auto-peaks at 842, 813, 733, and 660 cm^{-1} are ascribed to the symmetry stretching

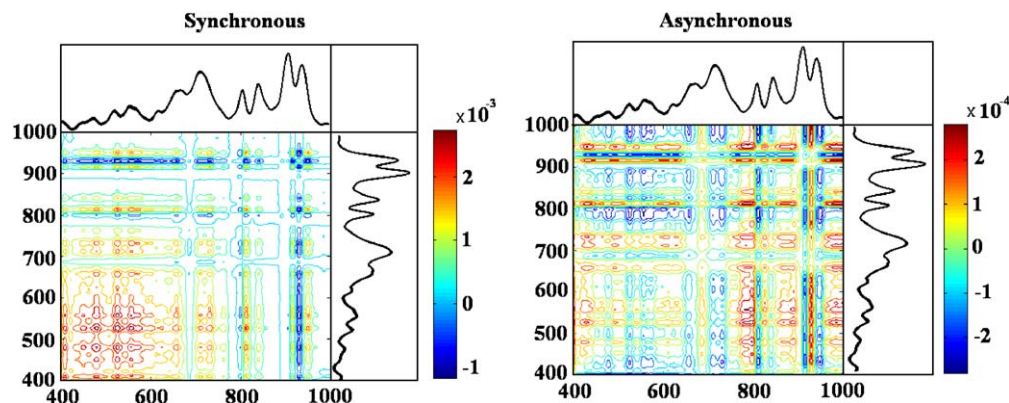


Fig. 4. Synchronous and asynchronous correlation spectra of compound **1** over a temperature range from 50 to 120 °C in the range of 400–1000 cm^{-1} .

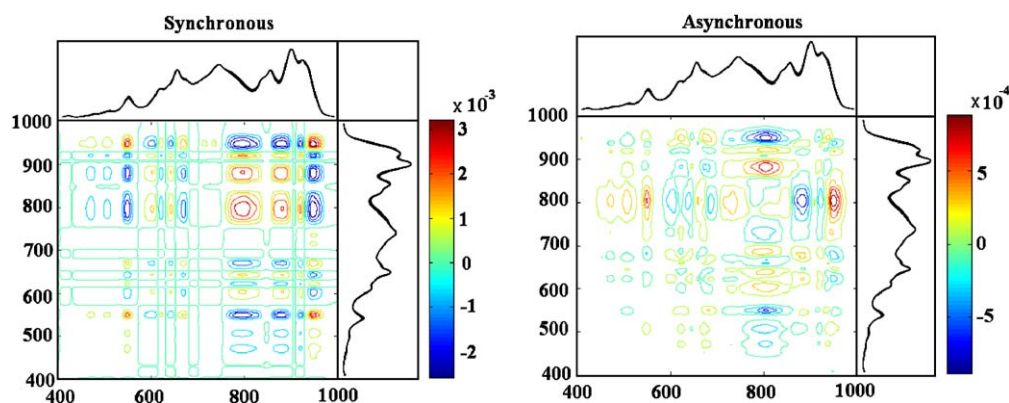


Fig. 5. Synchronous and asynchronous correlation spectra of compound **2** over a temperature range from 50 to 120 °C in the range of 400–1000 cm^{-1} .

vibrations of the $\mu\text{-O-Mo}$ stretching, which indicates that the intensity variation of the Mo=O stretching vibrations occurs more predominantly due to heating effect than that of the $\mu\text{-O-Mo}$ stretching. There are negative cross-peaks at (948, 842), (948, 813), (948, 733), and (948, 660) cm^{-1} and positive cross-peaks at (918, 842), (918, 813), (918, 733), and (918, 660) cm^{-1} . The peak group from 400 to 600 cm^{-1} could be recognized as framework vibrations under thermal perturbation, which is consistent with the structure that the octamolybdate anion is in isolation, and connected to cations only by hydrogen bond. In the asynchronous spectrum, according to the rule of Noda [1], the positive sign of the cross-peak at (948, 918) cm^{-1} reveals that the intensity changes of asymmetry stretching vibration of the terminal Mo=O occur prior to that of symmetry stretching vibration of the terminal Mo=O .

In the synchronous spectrum (Fig. 5 for compound **2**), two auto-peaks along the diagonal line can be inspected at 947 and 925 cm^{-1} , which result from asymmetry and synchronous stretching vibrations of the terminal Mo=O . Furthermore, it can be concluded that the position at 937 cm^{-1} (wide) in 1D spectrum in fact contains the 947 cm^{-1} peak. The strong negative cross peak at (925, 947) cm^{-1} indicates the reverse direction of the intensity

variations in these two correlated stretching vibrations modes. Differently from compound **1**, only two weak auto peaks at 880, and 795 cm^{-1} are ascribed to the stretching vibration of $\mu\text{-O-Mo}$ stretching, which agrees with the structure that the types of $\mu\text{-O-Mo}$ in ζ -octamolybdate are less than that in β -octamolybdate of compound **1**. But the same as compound **1**, there are also negative cross-peaks at (947, 880) and (947, 795) cm^{-1} and positive cross-peaks at (925, 880) and (925, 795) cm^{-1} . In the asynchronous spectrum, according to the rule of Noda [1], the positive sign of the cross-peak at (925, 947) cm^{-1} reveals that the intensity changes of asymmetry stretching vibration of the terminal Mo=O occur prior to that of symmetry stretching vibration of the terminal Mo=O .

4. Conclusions

The present study has demonstrated the structure of $(\text{NH}_4)_2(\text{Hbpy})_2[\text{Mo}_8\text{O}_{26}](\text{bpy})_3$ and $[\text{Cu}_2(\text{C}_3\text{H}_4\text{N}_2)_4]_2[\text{Mo}_8\text{O}_{26}]$. The 1D IR spectra and 2D IR correlation spectroscopy of the compound has been analyzed. All the results are in a fairly good agreement with the predictions deduced from the structural analysis. From the 2D IR correlation spectroscopy analyses, we discover that in

compound **1**, the intensity changes of Mo=O band are more sensitive to the temperature variation than that of the Mo–O bond. As the β -octamolybdate anion is connected to cations only by hydrogen bond for compound **1**, μ -Mo–O bond and framework vibrations are more sensitive to the temperature variation than that for compound **2**. As the vibrations of μ -Mo–O bond accompanied by the transfer of an oxygen atom [37,38], the catalysis ability of compound **1** may be higher than that of compound **2**. The results indicate that the subtle structural changes of POMs can be probed by the generalized 2D IR correlation spectroscopy. 2D IR correlation spectroscopy can not only improve to recognize the structure of POMs but also provide valuable dynamic information for the in-depth study of POMs, such as exploring the mechanism of their catalysis, investigating the magnetic exchange process for magnetic POMs, and researching the interaction during the building blocks of POMs.

Acknowledgments

This work is supported by grants from the Natural Science Foundation of Fujian Province (Project nos. JB04049 and K02028), the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, and Fuzhou University Science and Technology Foundation. We thank Prof. Sun Suqin (Tsinghua University, Beijing, China) for providing the 2D IR correlation analysis software.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2006.02.023](https://doi.org/10.1016/j.jssc.2006.02.023).

References

- [1] I. Noda, *Appl. Spectrosc.* 47 (1993) 1329.
- [2] I. Noda, *Vib. Spectrosc.* 36 (2004) 143.
- [3] I. Noda, *Appl. Spectrosc.* 54 (2000) 994.
- [4] I. Noda, *Appl. Spectrosc.* 57 (2003) 1049.
- [5] S. Gnanakaran, R.M. Hochstrasser, *J. Am. Chem. Soc.* 123 (2001) 12886.
- [6] Y. Ozaki, K. Murayama, Y. Wang, *Vib. Spectrosc.* 20 (1999) 127.
- [7] V.G. Gregoriou, S.E. Rodman, B.R. Nair, P.T. Hammond, *J. Phys. Chem.* 106 (2002) 11108.
- [8] S. Sasic, D.A. Clark, J.C. Mitchell, M.J. Snowden, *Appl. Spectrosc.* 59 (2005) 630.
- [9] Y. Shen, E.Q. Chen, C. Ye, H.L. Zhang, P.Y. Wu, I. Noda, Q.F. Zhou, *J. Phys. Chem.* 109 (2005) 6089.
- [10] S. Shanmukh, R.A. Dluhy, *Vib. Spectrosc.* 36 (2004) 167.
- [11] S. Shanmukh, P. Howell, J.E. Baatz, R.A. Dluhy, *Biophys. J.* 83 (2002) 2126.
- [12] M.K.N. Demirdoven, A. Tokmakoff, *Phys. Rev. Lett.* 89 (2002) 237401.
- [13] M.K.N. Demirdoven, O. Golonzka, A. Tokmakoff, *J. Phys. Chem. A* 105 (2001) 8025.
- [14] M.K.O. Golonzka, N. Demirdoven, A. Tokmakoff, *J. Chem. Phys.* 115 (2001) 10814.
- [15] L.N. Li, S.Y. Zhang, Y.H. Chen, M.J. Liu, Y.F. Ding, X.W. Luo, Z. Pu, W.F. Zhou, S.J. Li, *Chem. Mater.* 17 (2005) 839.
- [16] J.T. Rhule, C.L. Hill, D.A. Judd, *Chem. Rev.* 98 (1998) 327.
- [17] U. Kortz, F. Hussain, M. Reicke, *Angew. Chem. Int. Ed.* 44 (2005) 3773.
- [18] S.S. Mal, U. Kortz, *Angew. Chem. Int. Ed.* 44 (2005) 3777.
- [19] Y. Yang, M.H. Cao, C.W. Hu, Y.H. Guo, E.B. Wang, *J. Nanosci. Nanotechnol.* 4 (2004) 833.
- [20] M. Cho, *J. Chem. Phys.* 115 (2001) 4424.
- [21] H.L.K. Kwac, M. Cho, *J. Chem. Phys.* 120 (2004) 1477.
- [22] X.B. Cui, K. Lu, Y. Fan, J.Q. Xu, L. Ye, Y.H. Sun, Y. Li, H.H. Yu, Z.H. Yi, *J. Mol. Struct.* 743 (2005) 151.
- [23] E. Burkholder, J. Zubieta, *Solid State Sci.* 6 (2004) 1421.
- [24] D.G. Allis, E. Burkholder, J. Zubieta, *Polyhedron* 23 (2004) 1145.
- [25] E. Burkholder, J. Zubieta, *Inorg. Chim. Acta* 358 (2005) 116.
- [26] D.G. Allis, R.S. Rarig, E. Burkholder, J. Zubieta, *J. Mol. Struct.* 688 (2004) 11.
- [27] Y. Cao, H. Zhang, C. Huang, Q. Yang, Y. Chen, R. Sun, F. Zhang, W. Guo, *J. Solid State Chem.* 178 (2005) 3563.
- [28] Y. Chen, H. Zhang, C. Huang, Y. Cao, R. Sun, W. Guo, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 63 (2006) 536.
- [29] Y. Chen, X. Shen, H. Zhang, C. Huang, Y. Cao, R. Sun, *Vib. Spectrosc.* 40 (2006) 142.
- [30] Y.P. Chen, H.H. Zhang, D.M. Ke, X.M. Shen, C.C. Huang, R.Q. Sun, *Chin. J. Struct. Chem.* 24 (2005) 1033.
- [31] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
- [32] G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [33] L.D. Chen, Y.H. Wang, C.W. Hu, L.Y. Feng, E.B. Wang, N.H. Hu, H.Q. Jia, *J. Solid State Chem.* 161 (2001) 173.
- [34] R.Q. Fang, X.M. Zhang, H.S. Wu, S.W. Ng, *Acta Crystallogr. E-Structure Reports Online* 60 (2004) M359.
- [35] I.D. Brown, K.K. Wu, *Acta Crystallogr. B* 32 (1976) 1957.
- [36] I.D. Brown, D. Altermatt, *Acta Crystallogr. B* 41 (1985) 244.
- [37] I. Kawafune, G.E. Matsubayashi, *Inorg. Chim. Acta* 188 (1991) 33.
- [38] Z.Z. Lin, H.H. Zhang, R.S. Yang, R.Q. Sun, X.F. Yu, D.G. Chen, S.L. Zhao, X.L. Zheng, *Spectrosc. Spectral Anal.* 20 (2000) 593.