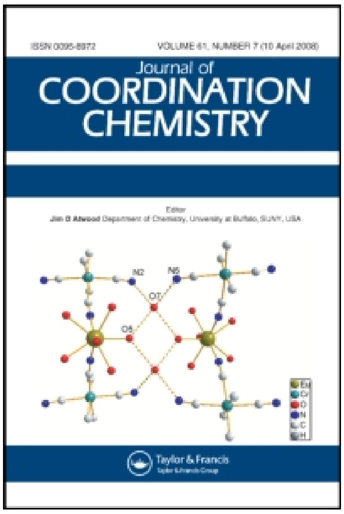

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Crystal Structure and Properties of Novel Composite Complex: $[La(Nmp)_4(H_2o)_4][HsiMo_{12}O_{40}]\cdot 2nmp\cdot H_2o$

Jingyang Niu[ab]; Qiuxia Han[a]; Jingping Wang[a]
[a] School of Chemistry and Chemical Engineering, Henan University, Kaifeng, P.R. China [b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, P.R. China

To cite this Article Niu, Jingyang , Han, Qiuxia and Wang, Jingping(2003) 'Synthesis, Crystal Structure and Properties of Novel Composite Complex: $[La(Nmp)_4(H_2o)_4][HsiMo_{12}O_{40}]\cdot 2nmp\cdot H_2o$', Journal of Coordination Chemistry, 56: 11, 1003 — 1012

To link to this Article: DOI: 10.1080/00958972310001593415

URL: http://dx.doi.org/10.1080/00958972310001593415

J. Coord. Chem. Vol. 56, No. 11, 20 July 2003, pp. 1003–1012

Taylor & Francis
Taylor & Francis Group

SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF NOVEL COMPOSITE COMPLEX: $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}]\cdot 2NMP\cdot H_2O$

JINGYANG NIU[a,b,*], QIUXIA HAN[a] and JINGPING WANG[a,†]

[a]*School of Chemistry and Chemical Engineering, Henan University,*
Kaifeng 475001, P.R. China; [b]*State Key Laboratory of Coordination Chemistry,*
Nanjing University, Nanjing 210093, P.R. China

(Received 20 November 2002; Revised 17 February 2003; In final form 15 May 2003)

A new composite complex of $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}]\cdot 2NMP\cdot H_2O$ (NMP = *N*-methyl-2-pyrrolidone) was synthesized and characterized by IR, UV, ESR, TG-DTA and single crystal structural analysis. The water and organic ligands (NMP) coordinate directly with La(III) to form a dodecahedral complex and the $SiMo_{12}O_{40}^{4-}$ anion is the counter ion. IR and X-ray analysis show that there is strong interaction between the polyoxometalate and organic donors. The complex is strongly photosensitive under irradiation with sunlight, resulting in a charge-transfer complex by oxidation of the *N*-methyl-2-pyrrolidone and reduction of the polyoxometalate. Low temperature ESR spectra indicate thermal electron delocalization among the Mo atoms in the title compound.

Keywords: Crystal structure; Composite complex; Hydrogen bonding

INTRODUCTION

Polyoxometalates (POMs) are molecular blocks of metal oxide formed by MoO_6 and WO_6 octahedra sharing vertices or edges [1,2]. Due to the richness of their structural and electronic properties, the polyoxometalates are extremely versatile inorganic building blocks for the construction of functionally active solids [3–6]. In previous work, we have succeeded in taking polyoxometalates as inorganic electron acceptor components of charge-transfer salts, to examine the novel structural and, in particular, the photochromism and non-linear optical properties [7,8]. Recently, we focused our attention on the combinations of heteropolyacid anions with organic-coordinated metallic cations to give rise to molecule-based materials having electrical and/or photochromism properties. Reports of d-block transition metal and alkaline earth metal complexes [9,10] are more common than those of lanthanide complexes. The high coordination numbers of lanthanide ions make it difficult to control synthetic

---

[†] Author for correspondence. Fax: +86-378-2853650. *E-mail: jyniu@henu.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/00958972310001593415

reactions and, thereby, the structures of the products. However, the fascinating coordination geometry and interesting structures along with the special properties of lanthanide complexes have attracted increasing attention from chemists, and lanthanide heteropoly complexes have been reported extensively since their first preparation by Peacock and Weakley in 1971 [11]. Most are complexes of rare earth elements in complexes with vacant Keggin or Wells–Dawson polyoxoanions, such as: $Ln(As_2W_{17}O_{61})^{17-}$ [12], $[Ce(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ and $[La(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$ [13], and some other compounds [14–16].

From the standpoint of molecular design, we recently began to assemble *N*-methyl-2-pyrrolidone (NMP), lanthanide ions and heteropolyacids into complexes. Herein we report the synthesis, crystal structure, physical characterization and thermal properties of the complex $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$.

EXPERIMENTAL

Materials

All organic solvents used for synthesis and physical measurements were reagent grade and used without further purification. Lanthanum chloride was prepared from La_2O_3 in over 99.9% purity. The $H_4SiMo_{12}O_{40} \cdot nH_2O$ complex was prepared by the literature method and confirmed by IR and UV spectra [17].

Physical Measurements and Analyses

C, H and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrometer in the range of $4000–500\,cm^{-1}$. The UV spectra were observed in acetonitrile–water (2:1 v/v) solution with an England Heλiosα spectrometer. Thermogravimetric analysis (TG-DTA) was performed in air on a Perkin Elmer-7 instrument with a heating rate of $10°C\,min^{-1}$ from room temperature to 600°C. The ESR spectra of the powder after it became dark blue owing to exposure to sunshine, were recorded on a Bruker ER-200-D-SRC spectrometer at X-band at 110 K.

Preparation of the Title Compound

Single crystals of the title compound suitable for single-crystal structure analysis were synthesized as follows: a solution of $H_4SiMo_{12}O_{40} \cdot nH_2O$ (4.0 g, 2.0 mmol) in water (20 mL) was added to $LaCl_3 \cdot 6H_2O$ powders (1.0 g, 2.7 mmol) at 90°C with stirring until the solution was nearly dry. *N*-Methyl-2-pyrrolidone (2 mL) was immediately added with vigorous stirring and a pasty solid appeared. The paste was dissolved in suitable acetonitrile–water mixture (2:1 v/v), filtered and left to evaporate at room temperature. One or two days later, crystals suitable for X-ray diffraction were obtained; yield based on $H_4SiMo_{12}O_{40} \cdot nH_2O$ is about 75%. Anal. Calcd. for $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$(%): C, 13.63; H, 2.48; N, 3.18. Found: C, 13.69; H, 2.47; N, 3.21. The excess $LaCl_3$ in the preparation ensures a high yield of the desired product.

X-ray Structure Determination of the Title Compound

The crystal data for $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$ (monoclinic, space group $P2_1/c$): $a = 17.421(4)$ Å, $b = 18.199(4)$ Å, c=23.002(5) Å, $\beta = 105.75(3)°$, $V = 7019(2)$ Å^3, $D = 2.399$ Mg/m^3, Z=4, $F(000) = 4756$. A single crystal of dimensions 0.28 × 0.24 × 0.21 mm was used for the data collection on a Rigaku RAXIS-IV image plate area detector with Mo Kα ($\lambda = 0.71073$ Å). A total of 27 838 reflections were collected ($2.15 < \theta < 25.00°$, $-20 \leq h \leq 20$, $-21 \leq k \leq 21$, $-27 \leq l \leq 27$); 11 018 reflections were unique. The structure was solved by direct methods and refined using full-matrix least-squares calculations with anistropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. The refinement converged at $R = 0.0833$ for 11 018 reflections with $I \geq 2\sigma(I)$, $wR = 0.1270$, $w^{-1}=[\sigma^2(F_o^2) + (0.0315\,P)^2 + 78.4137\,P]$ (where $P = (F_o^2 + 2F_c^2)/3$). The largest remaining difference peak and hole were 3.050 and -1.922 eÅ^{-3}, respectively. All calculations were performed using the SHELXTL-97 program [18].

RESULTS AND DISCUSSION

Synthesis

Charge-transfer complexes formed by POMs and organic donors have attracted much interest, with many investigations and some crystal structures reported, but crystals are usually unstable at room temperature. Applying molecular design principles, we attempted to introduce metal ions into the structure to make the organic–inorganic complex more stable. Several stable and common organic-coordinated metallic cation salts of Keggin-type complexes have been reported and a number of widely differing syntheses have been used [9]. In order to coordinate more NMP molecules, in our synthesis NMP was added as soon as the heteropoly salt formed; that is, NMP and the salt reacted in the solid state. Though the coordination potency of NMP is stronger than that of water, the exposed portion of La^{3+} can be conveniently occupied by smaller water molecules, which displace the larger NMP molecules.

The crystals are sensitive to sunlight because the POM anion is good electron acceptor, while NMP is a rich electron donor. Thus they can interact through electron transfer, and the final result is some heavy atoms of high oxidation state and the POM anions reduced in mixed-valence compounds. Exposure of the solution to sunlight should be avoided.

IR and UV Spectra

Infrared spectra of the title compound exhibit four characteristic terminal Mo=O$_d$ (950 cm^{-1}), corner-sharing Mo–O$_b$–Mo (864 cm^{-1}), edge-sharing Mo–O$_c$–Mo (793 cm^{-1}) and Si–O (902 cm^{-1}) asymmetric vibration peaks for the heteropolyanion with a Keggin structure. Comparing the IR spectra of the compound with those of α-$H_4SiMo_{12}O_{40}$ [14], the vibration peaks of the Mo=O$_d$ and Si–O bonds have red-shifted slightly, while the Mo–O$_b$–Mo and Mo–O$_c$–Mo bonds have blue-shifted 9 and 23 cm^{-1}, respectively. The results indicate that the polyanion of the compound still maintains a basic Keggin structure, but is distorted by coordination. These infrared spectra are also in agreement with the results of the single-crystal X-ray diffraction analysis. In additional, features at about 1639, 1512 and 1118 cm^{-1} are characteristic of *N*-methyl-2-pyrrolidone, assigned to $\nu_{as}(C{=}O)$, $\nu_{as}(C–N)$ and $\nu(N–CH_3)$ stretching vibrations. Compared with the standard spectra of free NMP, $\nu_{as}(C{=}O)$ decreased 27 cm^{-1}, whereas $\nu_{as}(C–N)$ and $\nu(N–CH_3)$ increase slightly, verifying that the NMP ligands coordinate with lanthanide(III) ions through the oxygen atoms of C=O bonds. Decreasing the charge density over the oxygen of the C=O bonds, lead to an increase in the electron-donating effect of methyl. The IR spectral studies indicate that there is strong interaction between the polyanion and organic groups in the solid state.

The near-UV spectra of the title complex are found from 200 to 400 nm in acetonitrile–water (v/v = 2:1) solution. In this range the complex reveals two peaks at about 240 and 305 nm. The absorption peak at 305 nm is weak and assigned to the $O_{b,c} \rightarrow Mo$ charge-transfer absorption band of the polyanion, and that at 240 nm is the strong $O_d \rightarrow Mo$ charge-transfer band due to absorption of NMP molecules. The results indicate that interactions between the heteropolyanion and coordinated ion are rather weak and the complex almost decomposes in dilute solution. This was also reported in a previous paper [9a].

X-ray Structure of the Title Compound

The crystal structure along with the atomic numbering scheme of the title compound is given in Fig. 1. The structure of the polyanion and coordination polyhedron of Mo are given in Fig. 2. The packing diagram of the compound is given in Fig. 3. Selected bond lengths and angles are listed in Table I.

As can be seen from Fig. 1, the complex consists of discrete organic groups coordinated to a lanthanum(III) cation and an α-Keggin heteropolyanion, $SiMo_{12}O_{40}^{4-}$, combined by static electrical forces; one free water molecule and two

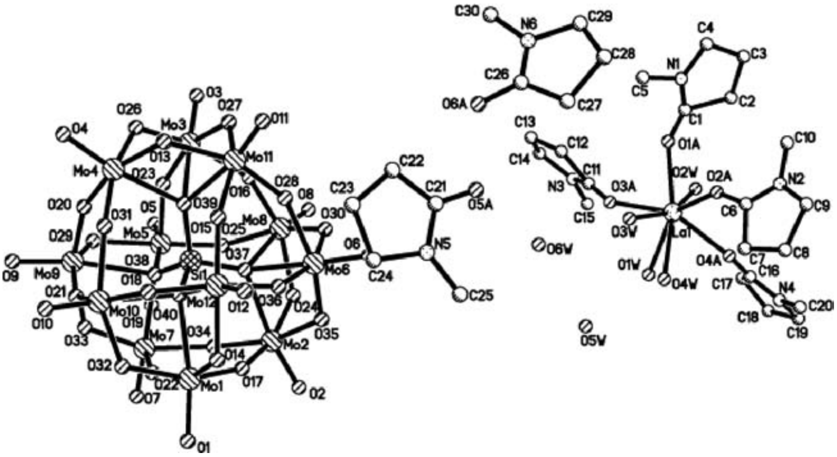

FIGURE 1 The structure of $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$ with labeling scheme. Hydrogen atoms are omitted for clarity.

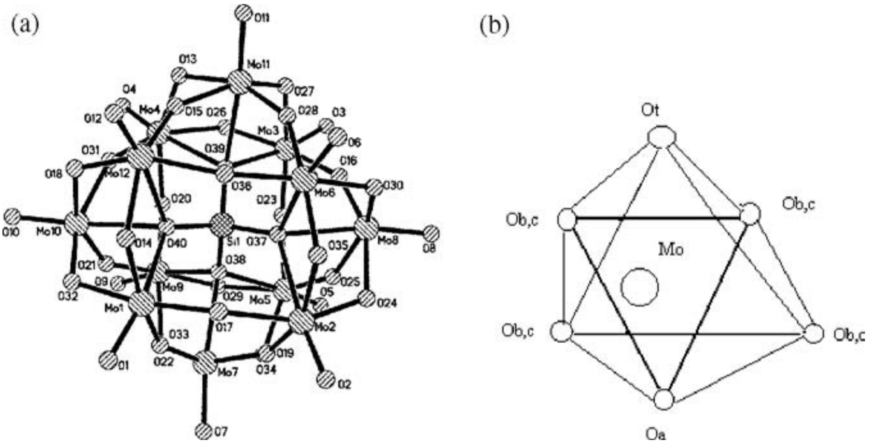

FIGURE 2 (a) Crystal structure of the polyanion; (b) coordination polyhedron of Mo.

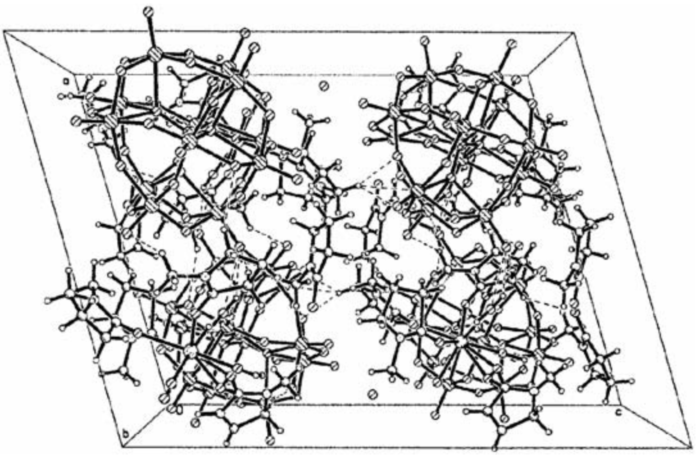

FIGURE 3 Packing diagram of $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$ viewed down the *b*-axis.

NMP molecules which do not directly interact with the metal ions are also present. The La(III) cation is coordinated to eight oxygen atoms with an irregular geometry.

The $SiMo_{12}O_{40}^{4-}$ anion exhibits well-known Keggin structures [1a] and is formed from a central SiO_4 tetrahedron whose O atoms are part of the cage of twelve MoO_6 octahedra linked by sharing corners and edges [Fig. 2(a)]. The Si–O bond distances within the cage range from 1.619(7) to 1.628(6) Å, with an average bond distance of 1.623 Å, and O–Si–O mean bond angles of 109.4°, in good agreement with previously reported values [9a]. Within the MoO_6 octahedron, the Mo–O distances can be grouped into three sets: (i) Mo$=$O$_d$ (O atom coordinated to one Mo atom only); (ii) Mo–O$_a$ (O atom coordinated to Si as well as to three Mo atoms); and (iii) Mo–O$_{b,c}$ (O atom coordinated to two Mo atoms). There are alternating "short" and "long" Mo–O$_{b,c}$–Mo bonds, which result from small displacements of Mo atoms from the mirror planes of the Mo_3O_{13} triplets [1a]. O atoms in group (i) are always *trans* relative to

TABLE I Selected bond lengths (Å) and angles (°) of $[La(NMP)_4(H_2O)_4][HSiMo_{12}O_{40}] \cdot 2NMP \cdot H_2O$

La(1)–O(3W	2.20(6)	La(1)–O(3A)	2.24(4)
La(1)–O(2A)	2.288(14)	La(1)–O(1A)	2.314(9)
La(1)–O(4A)	2.317(9)	La(1)–O(2W)	2.336(10)
La(1)–O(1W)	2.422(10)	La(1)–O(4W)	2.75(3)
Si(1)–O(40)	1.628(6)	Si(1)–O(38)	1.619(7)
Si(1)–O(39)	1.623(7)	Si(1)–O(37)	1.624(6)
Mo(1)–O(1)	1.698(7)	Mo(1)–O(14)	1.826(8)
Mo(1)–O(17)	1.792(7)	Mo(1)–O(22)	2.007(7)
Mo(1)–O(32)	2.006(8)	Mo(2)–O(2)	1.663(7)
Mo(1)–O(40)	2.321(6)	Mo(2)–O(24)	1.845(7)
Mo(2)–O(34)	1.829(7)	Mo(2)–O(35)	2.040(7)
Mo(2)–O(17)	2.030(8)	Mo(3)–O(3)	1.688(7)
Mo(2)–O(37)	2.357(6)	Mo(3)–O(23)	1.828(7)
Mo(3)–O(26)	1.826(7)	Mo(3)–O(16)	2.016(7)
Mo(3)–O(27)	2.001(8)	Mo(4)–O(4)	1.688(8)
Mo(3)–O(39)	2.340(6)	Mo(4)–O(13)	1.844(7)
Mo(4)–O(31)	1.822(6)	Mo(4)–O(26)	2.028(7)
Mo(4)–O(20)	2.021(8)	Mo(5)–O(5)	1.702(8)
Mo(4)–O(39)	2.329(6)	Mo(5)–O(19)	1.852(7)
Mo(5)–O(25)	1.828(7)	Mo(5)–O(29)	2.033(8)
Mo(5)–O(23)	1.998(7)	Mo(6)–O(6)	1.682(7)
Mo(5)–O(38)	2.351(7)	Mo(6)–O(35)	1.820(7)
Mo(6)–O(36)	1.815(8)	Mo(6)–O(30)	2.038(8)
Mo(6)–O(28)	2.003(7)	Mo(6)–O(37)	2.330(6)
O(3W)–La(1)–O(2A)	79.5(15)	O(3A)–La(1)–O(2A)	142.0(11)
O(3W)–La(1)–O(1A)	90(2)	O(3A)–La(1)–O(1A)	79.3(11)
O(2A)–La(1)–O(1A)	73.5(4)	O(3W)–La(1)–O(4A)	121.6(15)
O(3A)–La(1)–O(4A)	140.7(11)	O(2A)–La(1)–O(4A)	76.9(4)
O(1A)–La(1)–O(4A)	131.1(4)	O(3W)–La(1)–O(2W)	157.1(13)
O(3A)–La(1)–O(2W)	85.6(8)	O(2A)–La(1)–O(2W)	111.6(5)
O(1A)–La(1)–O(2W)	74.9(4)	O(4A)–La(1)–O(2W)	81.1(4)
O(3W)–La(1)–O(1W)	93(2)	O(3A)–La(1)–O(1W)	70.7(11)
O(2A)–La(1)–O(1W)	138.9(4)	O(1A)–La(1)–O(1W)	147.5(4)
O(4A)–La(1)–O(1W)	72.6(3)	O(2W)–La(1)–O(1W)	90.4(4)
O(1W)–La(1)–O(4W)	66.4(7)	O(38)–Si(1)–O(39)	109.3(3)
O(38)–Si(1)–O(37)	109.9(4)	O(39)–Si(1)–O(37)	109.4(3)
O(38)–Si(1)–O(40)	109.7(4)	O(39)–Si(1)–O(40)	109.8(4)
O(37)–Si(1)–O(40)	108.6(3)	O(1)–Mo(1)–O(17)	103.1(4)
O(1)–Mo(1)–O(14)	102.1(4)	O(17)–Mo(1)–O(14)	97.5(3)
O(1)–Mo(1)–O(32)	96.2(4)	O(17)–Mo(1)–O(32)	158.5(3)
O(14)–Mo(1)–O(32)	87.5(3)	O(1)–Mo(1)–O(22)	98.5(4)
O(17)–Mo(1)–O(22)	85.9(3)	O(14)–Mo(1)–O(22)	157.8(3)
O(32)–Mo(1)–O(22)	81.9(3)	O(1)–Mo(1)–O(40)	169.3(4)
O(17)–Mo(1)–O(40)	87.6(3)	O(14)–Mo(1)–O(40)	76.0(3)
O(32)–Mo(1)–O(40)	73.3(2)	O(22)–Mo(1)–O(40)	82.2(3)
O(2)–Mo(2)–O(34)	103.6(4)	O(2)–Mo(2)–O(24)	102.6(4)
O(34)–Mo(2)–O(24)	98.2(3)	O(2)–Mo(2)–O(17)	100.0(4)
O(34)–Mo(2)–O(17)	84.9(3)	O(24)–Mo(2)–O(17)	155.7(3)
O(2)–Mo(2)–O(35)	98.0(4)	O(34)–Mo(2)–O(35)	155.8(3)
O(24)–Mo(2)–O(35)	87.4(3)	O(17)–Mo(2)–O(35)	80.7(3)
O(2)–Mo(2)–O(37)	169.9(3)	O(34)–Mo(2)–O(37)	86.5(3)
O(24)–Mo(2)–O(37)	74.8(3)	O(17)–Mo(2)–O(37)	81.4(3)

those in group (iii), while in group (ii) those "long" are in a *trans* position relative to those that are "short". A schematic representation of this is given in Fig. 2(b). For the MoO_6 octahedron, Mo–O_d distances range from 1.659(8) to 1.702(8) Å, average 1.684 Å; Mo–O_a distances varied between 2.321(6) and 2.366(6) Å, average 2.340 Å; Mo–$O_{b,c}$ distances varied between 1.792(7) and 2.043(8) Å, average 1.922 Å. As can be seen from the distance and angle values, the mean Mo=O_d and Mo–O_a distances are longer, while the mean Mo–$O_{b,c}$ distances are shorter than those of the literature [10a]; the results show that the MoO_6 octahedra are somewhat distorted and attest to strong interactions between the polyanions and the outer coordination environment. The differences in Mo–O distances in the octahedra result from varying π-bond contributions to the bonds [19].

It is of interest to study in detail bond lengths involving La(III), and hydrogen bonding in the title compound. As can be seen from the bond distances and angles relevant to the La(III) coordination sphere, the La is eight-coordinate with a dodecahedral environment of oxygen atoms; four O atoms are from the NMP ligands, and the remaining four O atoms are from four-coordinate water molecules. The molecular geometry of the cation is constrained by the fact that the La^{3+} ion lies at the center of the coordination polyhedron. The La–O bond distances range from 2.20(6) to 2.75(3) Å and the average bond distance for all eight La–O is 2.358 Å. The average $La{-}O_{(NMP)}$ bond distance, 2.290 Å, is 0.137 Å shorter than the average $La{-}O_{(H_2O)}$ bond distance, 2.427 Å, indicating stronger coordination. This stronger coordination arises because the electron density of C=O is larger than that of water, resulting in stronger linkage between NMP and La^{3+}.

There are extensive intermolecular H-bonding interactions involving coordinated water, coordinated NMP and the oxygen atoms of the polyanion (Fig. 3). The free NMP molecules do not participate in H-bonding. The coordinated water O(1W) forms two H-bonds with the coordinated water O(4W) (O···O distance 2.845 Å) and coordinated NMP O(4A) (O···O distance 2.807 Å), the O(1W) is also H-bonded to the terminal oxygen of polyanion O(9) (O···O distance 2.778 Å)$[-x+1,\ -y+3,\ -z+1]$. The O(2W) also forms two H-bonds with the coordinated NMP O(1A)(O···O distance 2.829 Å) and the terminal oxygen of polyanion O(6) (O···O distance 2.860 Å)$[-x,\ -y+3,\ -z+1]$. Van der Waals contact is also observed between O(2W) and O(3A) at a distance of 3.111 Å.

The presence of numerous heavy atoms in the structure precludes determination of the hydrogen atom positions. Although we cannot determine the site of the H^+ of the title compound from the X-ray structure, based on the bond valence parameters [20], the bond orders for the N atoms in the molecule are determined by fitting Eq. (1)

$$V_i = \sum_j S_{ij} = \sum_j \exp\left(\frac{r'_o - r_{ij}}{B}\right) \tag{1}$$

The bond orders for N atoms of two free NMP molecules are 2.418 (N5) and 3.305 (N6), respectively, suggesting that the N atoms are not protonated. The bond orders for O atoms of two free NMP molecules are 1.583 [O(5A)] and 1.528 [O(6A)], respectively, so presumably the H atom is located between the two O atoms.

Thermogravimetric Analysis

The thermal stability of the title compound was confirmed by TG and DTA analysis taking 2.000 mg and performing the experiment at a heating rate of 10°C min^{-1} in the range 20 to 600°C in air. The result of the thermogravimetric analysis is basically in agreement with that of the structure determination. The TG analysis of the compound

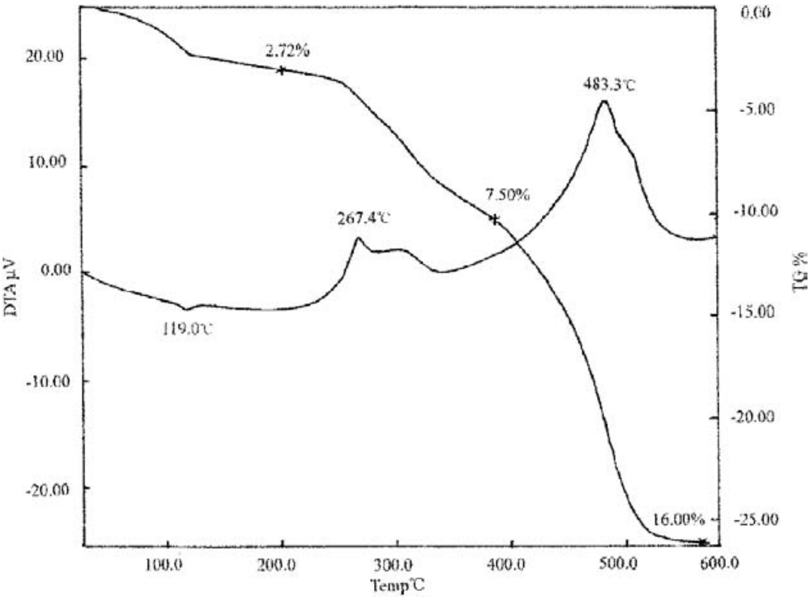

FIGURE 4 Thermogravimetric curves for the title compound.

shows three steps for weight loss (see Fig. 4). The first step, heated from about 20 to 120°C leads to the loss of one free water and three coordinated water molecules (weight loss *ca.* 2.74%), and one exothermic peak at 119.0°C is observed in the DTA. The second step in the range 120 to 390°C leads to the loss of two free NMP molecules (weigh loss *ca.* 7.50%), and one exothermic peak at 267.4°C corresponding to oxidation of NMP. The last step, from 390 to 575°C leads to the loss of four coordinated NMP, one coordinated water and half a constitution water (weigh loss *ca.* 15.2%). In the last step, one strong exothermic peak at 483.3°C is observed, due to La–O bonds breaking with oxidation of organics and initial decomposition of the heteropoly anionic cage to the lower oxides of the metals like MoO_3, and their slow volatilization [21]. Complete decomposition is finished at 593.5°C, comparison with the decomposition temperature of $H_4SiMo_{12}O_{40}$ [22], indicates that the thermal stability of the $SiMo_{12}O_{40}^{4-}$ anion is greater in the compound than in the acid; the strong interaction between the polyanion and organic groups in the solid state and the H-bonding make the compound more stable. In addition, the temperatures for loss of coordinated water are lower than for loss of coordinated NMP, further confirming a stronger linkage between NMP and La^{3+} than between water and La^{3+}.

ESR Spectra

The title compound is sensitive to visible light. The intense photochromism exhibited by irradiating the pure solid sample in sunlight is assigned to the intervalence charge transfer ($Mo^{5+} \rightarrow Mo^{6+}$) IVCT band of $SiMo_{12}O_{40}^{4-}$, indicating that electron transfer occurred between the organic cation and the inorganic anion, reducing $SiMo_{12}O_{40}^{4-}$ to heteropoly blue $SiMo_{12}O_{40}^{5-}$ with simultaneous oxidation of the organic coordinated cation. This has been verified by ESR spectra of the irradiated sample. The low

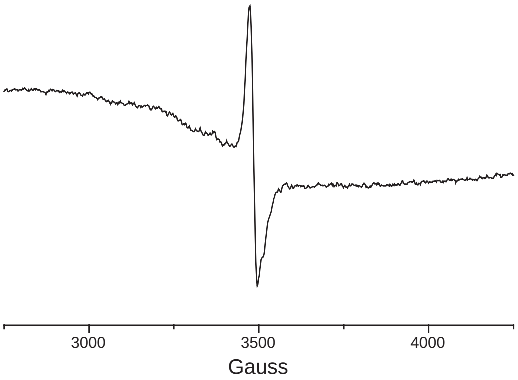

FIGURE 5 ESR spectra of the title compound at 110 K.

temperature (110 K) ESR spectrum of the irradiated sample is shown in Fig. 5. The spectrum is typical of molybdenum(V) at 110 K [23,24], $g = 1.9392$. It has been reported that charge transfer between an organic donor and a polyanion acceptor is carried by means of H-bonding [25].

Acknowledgments

This work was supported by the Natural Science Foundation of Henan Province and the Outstanding Youth Foundation of Henan Province.

References

[1] (a) M.T. Pope, Heteropoly and Isopoly Oxometalates (Springer-Verlag: New York, 1983); (b) H.T. Evans, *J. Perspect. Struct. Chem.* **4**, 1 (1971); (c) M.T. Pope and G.M. Varga, *Inorg. Chem.* **5**, 1249 (1966); (d) M.T. Pope and A. Muller, *Angew. Chem., Int. Ed. Engl.* **30**, 34 (1991).
[2] (a) L.C.W. Baker, V.S. Baker, A.H. Wasfi, G.A. Candela and A.H. Kahn, *J. Am. Chem. Soc.* **94**, 5499 (1972); (b) C.L. Hill (Guest Ed). *Chem. Rev* **98**, 1–389 (1998); (c) D. Attanasio, C. Bellitto, M. Bonamico, V. Fares and S. Patrizo, *Synth. Met*, **41–43**, 2289 (1991).
[3] E. Coronado and C.J. Gomez-Garcia, *Chem. Rev.* **98**, 273 (1998).
[4] C.J. Gomez-Garcia, E. Coronado and J. Borras-Almenar, *J. Inorg. Chem.* **31**, 1667 (1992).
[5] E. Coronado and C.J. Gomez-Garcia, *Comments Inorg. Chem.* **17**, 255 (1995).
[6] E. Coronado, P. Delhaes, J.R. Galan Mascaros, C. Gimenez-Saiz and C.J. Gomez-Garcia, *Synth. Met.* **85**, 1647 (1997).
[7] (a) J.Y. Niu, X.Z. You, C.Y. Duan, H.K. Fun and Z.Y. Zhou, *Inorg. Chem.* **14**, 4211 (1996); (b) J.Y. Niu, J.P. Wang, W. Chen, C.H.L. Kennard and K.A. Byriel, *J. Coord. Chem.* **53**,153 (2001).
[8] (a) J.Y. Niu, B.Z. Shan, X.Z. You, H.K. Fan and B.C. Yip, *Transition Met. Chem.* **24**, 108 (1999); (b) J.Y. Niu, J.P. Wang, Y. Bo, D.B. Dang and Z.Z. Yuan. *J. Chem. Crystallog.* **30**, 43 (2000).
[9] (a) J.Y. Niu, Q. Wu and J.P. Wang, *J. Chem. Soc., Dalton Trans.* 2512 (2002); (b) J.P. Wang, Q. Wu and J.Y. Niu, *Sci. China (B)* **323**, 210 (2002); (c) J.Y. Niu, Q.X. Han and J.P. Wang, *J. Coord. Chem.*, **56**, 523 (2003).
[10] (a) A.S.J. Wery, J.M. Gutierrez-Zorrilla, A. Luque, P. Vitoria, P. Roman and M. Martinez-Ripoll, *Polyhedron* **17**, 1247 (1998); (b) W.S. You, E.B. Wang, Y. Xu, Y.G. Li, L. Xu and C.W. Hu, *Inorg. Chem.* **40**, 5468 (2001); (c) A.R. Siedle, R.A. Newmark, P.A. Lyon, S.L. Hunt and V.W. Day, *Inorg. Chim. Acta* **259**, 241 (1997).
[11] (a) R.D. Peacock and T.J.P. Weakley, *J. Chem. Soc. (A)* **18**, 1836 (1971). (b) L.C.W. Baker and D.C. Glick, *Chem. Rev.* **8**, 4 (1998); (c) E.B. Wang, C.W. Hu and L. Xu, Introduction to Polyacid Chemistry (Chemical Industry Press, Beijing, 1998), Vol. 4 .
[12] X.D. Xi, G. Wang, B.F. Liu and S.J. Dong, *Electrochem. Acta* **408**, 1025 (1995).
[13] M.T. Pope, M. Sadakane and M.H. Dickman, *Angew. Chem., Int. Ed.*, **3916**, 2914 (2000).

[14] Q.H. Luo, R.C. Howell, M. Dankova, J. Bartis, C.W. Williams, W. De W. Horrocks Jr., V.G. Young Jr., A.L. Rheingold, L.C. Francesconi and M.R. Antonio, *Inorg. Chem.* **40**, 1894 (2001).
[15] N. Haraguchi, Y. Okaue, T. Isobe, and Y. Matsuda, *Inorg. Chem.* **33**, 1015 (1994).
[16] J.F. Liu, Z.P. Zu, B.L. Zhao and Z. Liu, *Inorg. Chem. Acta* **104**, 119 (1989).
[17] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.* **22**, 207 (1983).
[18] G.M. Sheldrick, SHELXTL 97, Program for the Refinement of Crystal Structures (University of Göttingen, Göttingea, 1997).
[19] Rolf Strandberg, *Acta Crystallogr* **B33**, 3090 (1977).
[20] I.D. Brown and D. Altermatt. *Acta Crystallogr.* **B41**, 244 (1985).
[21] R.C. Mackenjie, Differential Thermal Analysis (Academic, Press New York, 1970), Vol. 1.
[22] Z.P. Wang, J.Y. Niu and L. Xu, *Acta Chim. Sin.* **53**, 757 (1995).
[23] C. Sanchez, J. Livage, J.P. Launay, M. Fournier and Y. Jeannin, *J. Am. Chem. Soc.* **104**, 3194 (1982).
[24] J.N. Barrows and M.T. Pope, *Adv. Chem. Ser.* **226**, 403 (1990).
[25] M.M. Williamson, D.A. Bouchard and C.L. Hill, *Inorg. Chem.* **26**, 1436 (1987).