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Synthesis, properties and crystal structure of some polyoxometallates containing the tris(hydroxymethyl)aminomethane cation

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Abstract

Polyoxometallates $[(CH_2OH)_3CNH_3]_3PMo_{12}O_{40} \cdot 5H_2O$, $[(CH_2OH)_3CNH_3]_3PW_{12}O_{40} \cdot 11H_2O$, $[(CH_2OH)_3CNH_3]_2H_2SiW_{12}O_{40} \cdot 10H_2O$, $[(CH_2OH)_3CNH_3]_4GeW_{12}O_{40} \cdot 9H_2O$, $[C_4H_{12}NO_3]_4SiMo_{12}O_{40} \cdot 5H_2O$, $[(CH_2OH)_3CNH_3]_2H_4P_2W_{18}O_{62} \cdot 3H_2O$ and $[(CH_2OH)_3CNH_3]_3H_3As_2W_{18}O_{62} \cdot 4H_2O$ have been synthesized for the first time, purified, and structurally characterized by means of elemental analyses, IR spectrum, electronic spectrum, cyclic voltammogram, ³¹P NMR and X-ray diffraction. The crystal structure of $[(CH_2OH)_3CNH_3]_4PMo_{12}O_{40} \cdot 5H_2O$ has been determined by X-ray diffraction. Hydrogen bonding between $(CH_2OH)_3CNH_2$ and $PMo_{12}O_{40}^{3-}$ was inferred from heavy atom distances. The solid reflectance electronic spectra and IR spectra indicate that there is interaction between the $H_3PMo_{12}O_{40}$ and the organic substrate. The complexes have photosensitivity under irradiation of sunlight to result in charge transfer by oxidation of $(CH_2OH)_3CNH_2$ and the reduction of the polyoxometallates. We also found that $[(CH_2OH)_3CNH_3]_3PMo_{12}O_{40} \cdot 5H_2O$ and $[(CH_2OH)_3CNH_3]_3PW_{12}O_{40} \cdot 11H_2O$ exhibited substantial catalytic activity toward the electro-reduction of bromate and nitrite, respectively. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Polyoxometallate complexes; Electro-catalysis; Molybdenum complexes; Tungsten complexes; Crystal structures

1. Introduction

A recent development of polyoxometallate anions in materials science deals with the use of these soluble metal-oxide clusters as inorganic components of new organic–inorganic hybrid molecular materials based on electron donor molecules. Most hybrids of this kind are based on π -electron and organic amine [1]. The donors combined with polyoxometallate clusters of various nuclearities, shapes, and charges have resulted in the preparation of new types of insulating, semiconducting, or even metallic charge transfer salts having unusual structural and/or electronic features [2]. The charge transfer salts have attracted much interest since they have electrical [3], magnetic [4], optical properties [5], and the same character as liquid crystals [6]. According to 'charge-transfer theory' and 'molecule engineering',

we know that if there is a donor and a acceptor in a molecule, it is easy for a charge transfer to happen in the molecule, and the molecule will probable show good photochromism and nonlinear optical properties [7]. We have reported the photochromism and nonlinear optical properties of the charge transfer salts formed by the H₃PMo₁₂O₄₀ and the quinolin-8-ol and 1,10-phenanthroline [8]. Base on the previous work, we choose tris(hydroxymethyl)aminomethane as electron donors which combine with Keggin and Dawson to form seven organic-inorganic salts, among which three salts exhibit good photochromism under the sunlight to become charge-transfer salts. And they will be the base of the new photochromism materials. The tris(hydroxymethyl)aminomethane molecule is a kind of biochemical reagent and chiral molecule. The combination of seven organic-inorganic salts will supply information for the break of DNA and the designation of anti-HIV drugs, antineoplastic drugs, and anti-viral drugs [9].

Although a large amount of literature has reported the photochromism of polyoxometallates in solution

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and discussed its mechanism [10,11], the photochromism of solid materials made of polyoxometallates has been studied rarely. Here we characterized the charge-transfer salts by IR spectra, solid electronic spectra and ESR spectra. The results indicated that electron transfer occurred between the organic ions and the heteropolyanions under the sunlight; in the same time the heteropolyanion were reduced and the organic donors were oxidized. So we can find that not only the substance formed by the solvent molecules and the heteropolyanions but also the ionic salts formed by the organic cations and the heteropolyanions can become charge-transfer salts.

2. Experimental

2.1. Materials and methods

 $H_3PMo_{12}O_{40} \cdot nH_2O$, $H_3PW_{12}O_{40} \cdot nH_2O$, $H_4SiW_{12}O_{40} \cdot nH_2O$, $H_4GeW_{12}O_{40} \cdot nH_2O$, $H_4SiMo_{12}O_{40} \cdot nH_2O$, $H_6P_2 \cdot W_{18}O_{62} \cdot nH_2O$ and $H_6As_2W_{18}O_{62} \cdot nH_2O$ were prepared by literature methods [12] and characterized by means of elemental analyses and IR spectra. Other reagents used were of analytical grade.

The elemental analyses were carried out by means of an ICP-AES analyzer. The IR spectra (2% sample, in KBr) were recorded on an Alpha Centaurt FT/IR spectrometer. The electronic absorption spectra were measured on a Beckman DU-8B spectrometer. The cyclic voltammograms were obtained with a CH Instrument (Model 600V) analyzer and an X-Y recorder. A typical three-electrode cell was used with a glassy carbon working electrode, a platinum counter electrode, and a silver | silver chloride reference electrode for the voltammetry experiments. The glassy carbon electrode was polished with 1.0 and 0.3 µm Al₂O₃ powders in turn and then washed ultrasonically. ³¹P NMR spectra were recorded on a Varian Unity-400NMR spectrometer. The spectra were obtained with the sample in the 10 mm sample tubes put on the equipment and reported with respect to external H₃PO₄ at the operating temperature. TG were measured on a Perkin-Elemer TG-7 thermal analysis system.

2.2. Preparation of $[(CH_2OH)_3CNH_3]_3$ ·PMo₁₂-O₄₀·5H₂O (1), $[(CH_2OH)_3CNH_3 = tris(hydroxymethyl)-aminomethane]$

 $(CH_2OH)_3CNH_2$ (0.1g) was dissolved in a HCl solution (20 ml, 1.0 M), to which $H_3PMo_{12}O_{40} \cdot nH_2O$ (0.5 g) was added. The solution was stirred for 1 h, and then filtered. The filtrate was kept in a refrigerator. A large quantity of yellow octahedral crystals was isolated after several days. After drying in air, 0.3 g (60%) of 1 was obtained. *Anal.* Calc. for $C_{12}H_{46}Mo_{12}N_3O_{53}P$: C, 6.32;

N, 1.84; P, 1.36; Mo, 50.54; H₂O, 3.94. Found: C, 6.19; N, 1.72; P, 1.34; Mo, 50.46; H₂O, 4.15%.

The following polyoxometallate salts were obtained by the same procedure as described above.

 $[(CH_2OH)_3CNH_3]_4$ ·GeW₁₂O₄₀·9H₂O (4), yield 65%. Anal. Calc. for C₁₆H₆₆GeN₄O₆₁W₁₂: C, 5.38; N, 1.57; Ge, 2.03; W, 61.81; H₂O, 4.54. Found: C, 5.42; N, 1.63; Ge, 2.08; W, 61.76; H₂O, 4.48%.

[(CH₂OH)₃CNH₃]₄·SiMo₁₂O₄₀·SH₂O (**5**), yield 52% *Anal.* Calc. for $C_{16}H_{58}Mo_{12}N_4O_{57}Si: C, 8.01; N, 2.34;$ Si, 1.17; Mo, 48.01; H₂O, 3.75. Found: C, 7.95; N, 2.38; Si, 1.23; Mo, 47.95; H₂O, 3.83%.

 $\label{eq:constraint} \begin{array}{l} [(CH_2OH)_3CNH_3]_2 \cdot H_4P_2W_{18}O_{62} \cdot 3H_2O\ (6), \ yield\ 43\%. \\ Anal. \ Calc. \ for\ C_8H_{34}N_2O_{71}P_2W_{18} \cdot C,\ 2.06;\ N,\ 0.60;\ P, \\ 1.33;\ W,\ 70.93;\ H_2O,\ 1.16. \ Found:\ C,\ 2.21;\ N,\ 0.66;\ P, \\ 1.29;\ W,\ 71.08;\ H_2O,\ 1.21\%. \end{array}$

[(CH₂OH)₃CNH₃]₃·H₃As₂W₁₈O₆₂·4H₂O (7), yield 46%. *Anal.* Calc. for As₂C₁₂H₄₇N₃O₇₅W₁₈: C, 2.94; As, 3.07; N, 0.86; W, 67.64; H₂O, 1.47. Found: C, 2.69; As, 3.15; N, 0.88; W, 67.85; H₂O, 1.43%.

2.3. X-ray crystallography

A crystal with approximate dimensions of $0.52 \times 0.42 \times 0.38$ mm was mounted on a glass fiber in an arbitrary orientation. Data collection were performed on a Siemens diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The heavy atoms were located by the direct method and the other non-hydrogen atoms were found from Fourier synthesis. Structure refinement was carried out by the full-matrix least-squares method and the crystal and refinement parameters are listed in Table 1.

3. Results and discussion

3.1. Synthesis, chemical formula, and properties of 1

The dodecamolybdophosphoric anion forms readily in an acidic medium and has been well characterized both in solution and in the solid state. Mixing a solution of dodecamolybdophosphoric anions and an acidic solution of $(CH_2OH)_3CNH_2$ yielded a crystalline material characterized as **1** (see above). The N–H distances (0.890 Å) observed for the $(CH_2OH)_3CNH_2$ are in the range of protonated amines, suggesting that the $(CH_2OH)_3CNH_2$ existed in protonated form in **1**. If the overall charges of $(CH_2OH)_3CNH_3^+$ are thus considered to be one, the most possible formula of 1 consistent

Table 1Crystal data and structure refinement for 1

Empirical formula	$C_{12}H_{46}Mo_{12}N_3O_{54}P$
Formula weight	2278.77
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	Cc
Unit cell dimensions	
a (Å)	15.148(3)
b (Å)	25.866(5)
c (Å)	15.067(3)
α (°)	90
β (°)	118.77(3)
γ (°)	90
$V(Å^3)$	5175(2)
Z	4
$D_{\rm calc}$ (Mg m ⁻³)	2.925
Absorption coefficient (mm^{-1})	2.968
F(000)	4360
Crystal size (mm)	$0.52 \times 0.42 \times 0.38$
θ Range for data collection (°)	1.57-28.02
Limiting indices	$-1 \le h \le 20, -1 \le k \le 34,$
e	$-19 \le l \le 17$
Reflections collected	7559
Independent reflections	6930 ($R_{int} = 0.0143$)
Max. and min. transmission	0.59644 and 0.38580
Refinement method	full-matrix least-squares on F^2
Data/refinement/parameters	6930/2/749
Goodness-of-fit on F^2	1.047
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0249, wR_2 = 0.0649$
R indices (all data)	$R_1 = 0.0262, wR_2 = 0.0653$
Absolute structure parameter	0.41(3)
Extinction coefficient	0.00133(4)
Largest difference peak and hole	0.688 and -0.655
$(\tilde{e} \tilde{A}^{-3})$	



Fig. 1. Structure and labeling scheme for $[PMo_{12}O_{40}]^{3-}$.



Fig. 2. Drawing of the structure **1**. Hydrogen bonds between the $[PMo_{12}O_{40}]^3$ anion and the $[(CH_2OH)_3CNH_3]^+$ cations are indicated by dashed lines.

with the elemental analysis and mass and charge balance would be $[(CH_2OH)_3CNH_3]_3PMo_{12}O_{40}$ ·5H₂O. This formula is also consistent with the results of the X-ray structure determination (see below). The IR spectrum is similar to that reported for other trianionic molybdophosphate compounds [13].

3.2. Structure of 1

Fig. 1 shows the structure and labeling scheme of the dodecamolybdophosphoric anion, while Fig. 2 shows the hydrogen-bonding interactions in the dodecamolybdophosphoric anion and (CH₂OH)₃CNH₂ units. The selected bond lengths and bond angles are listed in Table 2. The bond angles and distances observed for the $PMo_{12}O_{40}^{3-}$ unit indicate that the geometry is quite similar to that found in previously reported dodecamolybdophosphoric salt. It is of Keggin structure [14]: the central P atom is surrounded by a tetrahedron whose oxygen vertices are each linked to one of the four W₃O₁₃ groups. Each W₃O₁₃ is consisted of three MoO₆ octahedra linked in a triangular arrangement by sharing edges, and the four W3O13 are linked together by sharing corners. The P-O bond lengths are in the normal range of 1.530-1.538 Å and the Mo-O(terminal) bond lengths 1.661-1.694 Å. The Mo-O(bridge) bonds in each MoO₆ unit fall into two well resolved categories: the long pair (1.923-2.057 Å) and the short pair (1.793-1.914 Å) of Mo-O bonds which are in the cis positions. The mean bond order is 0.8 for the long ones and 1.2 for the short ones. The Mo-O-Mo bond angles are in the range of 122.2-157.4°.

It is interesting to compare bond lengths and angles of 1 with those of some other phosphomolybdates [15]. As shown in Table 3, the increasing sequence of the mean bond length of the long (l) Mo–Ob/c bonds [Mo–Ob/c(l)] for the three compounds is C_4H_9 -NO–PMo₁₂ < (CH₂OH)₃CNH₂–PMo₁₂ < C₁₀H₈S₈–P-Mo₁₂, whereas the mean bond length of the short (s) Mo–Ob/c bonds [Mo–Ob/c(s)] are in the sequence of C_4H_9NO –PMo₁₂ > (CH₂OH)₃CNH₂–PMo₁₂ > C₁₀H₈S₈–PMo₁₂, i.e. the distortion of the MoO₆ octahedra in 1 is in the middle position of the sequence. Probably the extent of distortion is roughly parallel to the volumes of the organic molecules [4]. The distortion of the MoO₆ octahedron has made the symmetry of the heteropolyanion decreased.

Table 2 Selected bond distances (Å) and bond angles (°)

Mo(2)-O(40)	1.684(5)	Mo(2)-O(6)	1.817(5)
Mo(2)-O(28)	1.868(5)	Mo(2)–O(29)	1.970(5)
Mo(2)-O(36)	2.018(5)	Mo(2)–O(13)	2.403(4)
Mo(8)-O(35)	1.690(5)	Mo(8)–O(8)	1.793(5)
Mo(8)–O(34)	1.906(5)	Mo(8)–O(24)	1.924(5)
Mo(8)-O(30)	2.057(5)	Mo(8)–O(3)	2.404(4)
P-O(14)	1.530(5)	P-O(18)	1.533(4)
P–O(3)	1.538(5)	P-O(13)	1.531(4)
O(41)–C(2)	1.446(13)	O(42)–C(3)	1.405(11)
O(43)–C(4)	1.429(11)	O(44)–C(6)	1.423(9)
O(45)-C(7)	1.426(9)	O(46)–C(8)	1.426(8)
O(47)-C(10)	1.425(10)	O(48)–C(11)	1.424(8)
O(49)-C(12)	1.403(10)	N(1)-C(1)	1.511(9)
N(2)–C(5)	1.487(9)	N(3)-C(9)	1.504(9)
C(1)–C(2)	1.511(10)	C(1)–C(4)	1.507(12)
C(1)–C(3)	1.521(11)	C(5)–C(6)	1.530(9)
C(5)-C(8)	1.526(10)	C(5)–C(7)	1.521(9)
C(9)-C(10)	1.528(10)	C(9)–C(12)	1.527(10)
C(9)–C(11)	1.541(10)		
		$O(40) = M_O(2) = O(6)$	103.4(2)
O(40)-Mo(2)-O(28)	100.9(2)	O(6)-Mo(2)-O(28)	97.4(2)
O(40)-Mo(2)-O(29)	101.2(2)	O(6)-Mo(2)-O(29)	87.3(2)
O(6)-Mo(2)-O(36)	157.5(2)	O(40)-Mo(2)-O(36)	98.2(2)
O(29)-Mo(2)-O(36)	82.6(2)	O(28)-Mo(2)-O(36)	84.2(2)
O(6)-Mo(2)-O(13)	86.0(2)	O(40)-Mo(2)-O(13)	170.0(2)
O(29)-Mo(2)-O(13)	82.5(2)	O(28)-Mo(2)-O(13)	74.1(2)
O(35)-Mo(8)-O(34)	101.3(2)	O(36)-Mo(2)-O(13)	72.9(2)
O(35)-Mo(8)-O(24)	100.6(2)	O(35)-Mo(8)-O(8)	104.8(3)
O(34)-Mo(8)-O(24)	154.9(2)	O(8)-Mo(8)-O(34)	95.8(2)
O(8)–Mo(8)–O(30)	159.8(2)	O(8)-Mo(8)-O(24)	90.3(2)
O(24)-Mo(8)-O(30)	83.7(2)	O(35)-Mo(8)-O(30)	95.3(2)
O(8)–Mo(8)–O(3)	87.6(2)	O(34)–Mo(8)–O(30)	82.3(2)
O(24) - Mo(8) - O(3)	82.5(2)	O(35)-Mo(8)-O(3)	167.1(2)
N(1)-C(1)-C(2)	107.3(6)	O(34)-Mo(8)-O(3)	73.5(2)
C(2)-C(1)-C(4)	111.4(7)	O(30)-Mo(8)-O(3)	72.5(2)
C(2)-C(1)-C(3)	110.7(7)	N(1)-C(1)-C(4)	107.4(7)
O(41)-C(2)-C(1)	110.4(7)	N(1)-C(1)-C(3)	108.2(6)
O(43)-C(4)-C(1)	111.3(7)	N(4)-C(1)-C(3)	111.6(7)
C(12)-C(9)-N(3)	109.1(6)	O(42)-C(3)-C(1)	113.8(7)
C(12)-C(9)-C(11)	110.8(6)	N(2)-C(5)-C(6)	107.8(6)
	. /	O(46)-C(8)-C(5)	111.2(6)
		C(10)-C(9)-N(3)	108.1(6)

Table 3 Comparison of bond distances (Å) and angles (°) in $[PMo_{12}O_{40}]^{3-\epsilon}$

	1	2	3	4
Mo-Ob/c(l)	1.923–2.057 (0.134) [1.983]	1.929–1.974 (0.045) [1.953]	1.97–2.01 (0.04) [1.99]	1.96–1.97 (0.01) [1.965]
Mo–Ob/c(s)	1.793–1.914 (0.121) [1.858]	1.842–1.879 (0.037) [1.861]	1.81–1.82 (0.01) [1.815]	1.85–1.87 (0.02) [1.86]
Mo-Ob/c(l-s)	0.125	0.092	0.175	0.105
Mo–Ob/c–Mo	122.2–157.4 (35.2) [138.08]	125.1–152.1 (27) [138.55]		125–152 (27) [138.5]

^a () differences; [] averages. [(CH₂OH)₃CNH₃]₃PMo₁₂O₄₀ (1) (this work), [H₃PMo₁₂O₄₀ $^{\circ}$ 6DMA $^{\circ}$ CH₃CN] (2) [15], [C₁₀H₈S₈]₈[PMo₁₂O₄₀] (3) [13] and H₃PMo₁₂O₄₀ (4) [13].

It is interesting to observe the interactions between the three protonated (CH₂OH)₃CNH₂ units and the five water molecules found in a single crystal and their interactions with the dodecamolybdophosphoric anion too. As the three neutral organic molecules with the same structure were protonated, they reacted with $PMo_{12}O_{40}^{3-}$ anion and form a polyoxometallate salt, which displays the following characters: (i) There are intra- and inter-molecular hydrogen-bonds among the three organic molecules (N1...O41, 2.790; N1...O43, 2.377; N2···O45, 2.749; N2···O46, 2.833; N3···O47, 2.878; N1···O44, 2.824; N2···O48, 2.710; O44···O48, 2.966; O46…O49, 2.783; O42…OW3, 2.907; O43…OW2, 2.783 Å). Three organic molecules exibit the action of hydrogen-bonds to the water molecules as well: O42...OW3, 2.907; O43...OW2, 2.783; O44...OW2, 2.704; N3…OW1, 2.825; O48…OW5, 2.652; O47…OW5, 2.759; O49…OW4, 2.757 Å. (ii) The inter-molecular hydrogen bonds in the organic molecules are not destroyed, indicating weak interaction between the organic molecules and the heteropolyanion. (iii) Among the three organic molecules, only one of them exhibits weak action of hydrogen-bond to the $PMo_{12}O_{40}^{3-}$ anion (O49...O40, 2.936), while the other two form much weaker hydrogen-bonds to the heteropolyanion (O43...O35, 3.340; O46...O36, 3.475; O46...O40, 3.663 Å).

Day and Klemperer found that the triple (Oc) and double (Ob) bridged oxygen atoms are more basic than terminal oxygen atoms, and that in turn Oc sites are more basic than Ob sites [16]. Kempf et al. confirmed that the triple bridged oxygen atoms are more basic than the double bridged oxygen atoms by means of ab initio and electrostatic potential calculations [17].We have studied and reported hydrogen bonding interactions between the $C_4H_{11}O_3N$ unit and terminal oxygen atom in dodecamolybdophosphoric anion (O49...O40,

Tabl	le 4				
The	IR	spectral	data	of	compounds

Compounds		X–Oa	M–Od	M-Ob-M	M–Oc–M	$({\rm \ddot{N}H_3})_{\rm as}$	$({\rm \ddot{N}H_3})_{\rm s}$
$\overline{H_3PMo_{12}O_{40}}$		1064	964	867	788		
[(CH ₂ OH) ₃ CNH ₃] ₃	yellow	1060	962	882	788	1613	1460
PMo ₁₂ O ₄₀	blue	1058	959	879	783	1622	1468
$H_{3}PW_{12}O_{40}$		1081	984	889	810		
[(CH ₂ OH) ₃ CNH ₃] ₃	white	1080	982	897	812	1625	1463
PW ₁₂ O ₄₀	blue	1079	978	898	805	1622	1471
$H_4SiW_{12}O_{40}$		926	980	881	785		
[(CH ₂ OH) ₃ CNH ₃] ₃	white	923	973	886	798	1620	1470
$H_2SiW_{12}O_{40}$	blue	921	972	883	795	1629	1479
$H_4GeW_{12}O_{40}$		827	977	894	776		
$[(CH_2OH)_3CNH_3]_4GeW_{12}O_{40}$		826	972	882	770	1625	1466
H ₄ SiMo ₁₂ O ₄₀		910	964	862	776		
[(CH ₂ OH) ₃ CNH ₃] ₄ SiMo ₁₂ O ₄₀		903	955	860	785	1627	1490
$H_6P_2W_{18}O_{62}$		1091	996	916	796		
[(CH ₂ OH) ₃ CNH ₃] ₂ H ₄ P ₂ W ₁₈ O ₆₂		1088	980	892	780	1632	1481
$H_6As_2W_{18}O_{62}$		864	971	828	775		
[(CH ₂ OH) ₃ CNH ₃] ₃ H ₃ As ₂ W ₁₈ O ₆₂		862	968	882	770	1628	1485
(CH ₂ OH) ₃ CNH ₂						1589	1460

2.936 Å). We also observed this phenomenon for the decavanadate guanidinium salt [18].

3.3. ³¹P NMR spectrum

The ³¹P NMR spectrum of an aqueous solution of 1 showed a resonance peak -3.58 ppm with a very slight shift (0.3 ppm) compared with the ³¹P NMR spectrum of an aqueous solution of H₃PMo₁₂O₄₀ at -3.9 ppm [19]. Although (CH₂OH)₃CNH₂ is a chiral molecule, the doubling lines as described in the literature [20] did not appear in the ³¹P NMR spectrum of 1, implying that the intermolecular interaction between [(CH₂OH)₃-CNH₃]⁺ and [PMo₁₂O₄₀]³⁻ is weak.

3.4. IR spectra

The IR spectral data of polyoxometallate salts are listed in Table 4.

The title compounds possess characteristic absorption bands similar to those of HPAs by Table 4 except that the positions of characteristic bands have shifted a little. This shows that their primary structures haven't been destroyed, but each bond becomes stronger or weaker in different extents in these organic-inorganic salts, which agrees with the behaviors of those organicinorganic salts formed by HPAs and other electron donors [20]. Comparing the IR spectra of the irradiated samples with that of the original salts, the characteristic vibrational bands appeared in red shifts. The results indicate that HPAs have obtained some electrons and formed heteropoly blues [21].

The vibrational bands in the range of 1200-1700 cm⁻¹ are similar to that of neutral organic molecules,

and part of their vibrational bands have shifted, which indicate the existence of the organic molecules in the compounds. These changes are related to the charges of protonated organic molecules.

The IR spectra indicate that polyoxometallate anions and the organic substrates have interactions in the solid state.

3.5. Electronic spectra

Comparison of the UV spectra of $[(CH_2OH)_3$ -CNH₃]₃·PW₁₂O₄₀ with that of H₃PW₁₂O₄₀ dissolved in an aqueous solution indicates that the interactions between (CH₂OH)₃CNH₂ and polyoxometallate are rather weak and the complexes are almost entirely disrupted in solution (Fig. 3), but if the solution is concentrated (Fig. 4), we find that the low-energy tail of the charge-transfer absorption band has a little red shift, which is similar to the spectrum of the HMPA solution of PW₁₂O₄₀³⁻ [22]. The results indicate that



Fig. 3. Comparison of the electronic spectra of $H_3PW_{12}O_{40}$ and $[(CH_2OH)_3CNH_3]_3 PW_{12}O_{40}$ in aqueous solution: (a) $H_3PW_{12}O_{40}$; (b) $[(CH_2OH)_3CNH_3]_3 PW_{12}O_{40}$. All spectra were obtained on 2×10^{-6} M solutions in a 1 cm cell at r.t.



Fig. 4. Comparison of the electronic spectra of $H_3PW_{12}O_{40}$ and $[(CH_2OH)_3CNH_3]_3 PW_{12}O_{40}$ in aqueous solution: (a) $H_3PW_{12}O_{40}$; (b) $[(CH_2OH)_3CNH_3]_3 PW_{12}O_{40}$. All spectra were obtained on 5×10^{-4} M solutions in a 1 cm cell at r.t.



Fig. 5. Solid electronic spectra of the compounds: (a) $H_3PW_{12}O_{40}$; (b) $[(CH_2OH)_3CNH_3]_3PW_{12}O_{40}$.



Fig. 6. Solid electronic spectra of the compounds: (a) $[(CH_2OH)_3CNH_3]_3PMo_{12}O_{40};$ (b) $[(CH_2OH)_3CNH_3]_3 PW_{12}O_{40};$ (c) $[(CH_2OH)_3CNH_3]_2H_2SiW_{12}O_{40};$ (d) $[(CH_2OH)_3CNH_3]_3 PW_{12}O_{40}.$ —: before irradiation; \cdots : after irradiation.



Fig. 7. ESR spectra of the irradiated. $[(CH_2OH)_3CNH_3]_3\ PW_{12}O_{40}$ at 77 K.

there is a interaction between the organic molecules and the polyanions and the charge-transfer of polyoxometallate anion is obviously influenced by the presence of $(CH_2OH)_3CNH_2$. Fig. 5 compares the reflectance electronic spectrum of $[(CH_2OH)_3-CNH_3]_3 \cdot PW_{12}O_{40}$ with that of $H_3PW_{12}O_{40}$. It is interesting to note that the low-energy tail of the charge-transfer absorption band of $[(CH_2OH)_3CNH_3]_3$ ·PW₁₂O₄₀ has quite a large red-shift, which is similar to the spectrum of H₄SiW₁₂O₄₀ HMPA [5]. This suggests that the interaction between the organic substrate and the polyoxometallate anion must play a role in the observed CT effect if the distance of both is short enough (in concentrated solution or the solid state) [23].

The electronic spectra in the solid ulteriorly indicate that $H_3PW_{12}O_{40}$ and $(CH_2OH)_3CNH_2$ have an interaction in the solid state.

3.6. Photochromism

By irradiation of three pure solid sample under the sunlight, [(CH₂OH)₃CNH₃]₃PMo₁₂O₄₀, [(CH₂OH)₃CN-H₃]₃PW₁₂O₄₀, and [(CH₂OH)₃CNH₃]₂H₂SiW₁₂O₄₀ immediately induces intense photochromism in solid state. The solid reflectance electronic spectra of three irradiated and original samples are listed in Fig. 6. We found that the $O \rightarrow W$ charge transfer transition bands show no evident changes of the position, but only a little decrease of its intensity. In addition, several new aborption bands appear in visible region, which are assigned to the intervalence charge transfer $(M^{5+} \rightarrow M^{6+})$ band of the heteropoly anions and are characteristic bands of heteropoly blues [24]. This indicates that electron transfer occurs between organic substrates and heteropoly anions, resulting in the reduction of heteropoly anion $(M^{VI}O_6)$ into heteropoly blue $(M^VO_5(OH))$ with simultaneous oxidation of the organic substrate. This case has been verified by the ESR spectra of the irradiated sample. The paramagnetic signals were not observed in the ESR spectrum at room temperature (r.t.), but they were observed at 77 K. The paramagnetic signals of sample [(CH₂OH)₃CNH₃]₃PMo₁₂O₄₀ and [(CH₂OH)₃-CNH₃]₂H₂SiW₁₂O₄₀ are very weak. The signal of sample [(CH₂OH)₃CNH₃]₃PW₁₂O₄₀ is shown as Fig. 7 and g = 1.826, and this is the signal of W⁵⁺. The polyoxometallate anions are in the section of one electron reduction. The paramagnetic signals of sample [(CH₂-OH)₃CNH₃]₃PMo₁₂O₄₀ and [(CH₂OH)₃CNH₃]₂H₂Si- $W_{12}O_{40}$ are reduced probably because their lives are too short or they coupled with each other.

From the above results, it turns out that under sunlight, charge transfer between the organic substrates and the polyoxometallate anions can take place in the compounds.

When the irradiated samples are placed in the air and sheltered from the light, they turn back to their original color, and recover again when exposed to sunlight. But if color-changed samples are put under nitrogen atmosphere and sheltered from light, their color does not fade, indicating that the fading process is a chemical one and that it is the oxygen in the air that has reoxidized M^{V} into M^{VI} , not the self redox occurring in

the system. Thus it can be speculated that the whole process may be proceed in the following way [25].



3.7. Electrocatalytic reduction of bromate and nitrite

In order to characterize electrocatalytic properties of compound 1 in an aqueous solution, bromate was chosen as test reactant for catalytic reduction. The bromate reduction does not occur at a bare GC electrode, at least not, before the onset of hydrogen evolution [26]. We found that the compound 1 exhibited



Fig. 8. Cyclic voltammograms for the electrocatalytic reduction of bromate in 1.0 mM [$(CH_2OH)_3CNH_3$]_3PMo_{12}O_{40}, pH 1.0 solutions containing different concentration bromate: (a) 0; (b) 0.2 mM; (c) 0.4 mM; (d) 0.6 mM; (e) 0.8 mM. Scan rate = 50 mV s⁻¹.



Fig. 9. Cyclic voltammograms for the electrocatalytic reduction of nitrite in 1.0mM [(CH₂OH)₃CNH₃]₃PW₁₂O₄₀ and before (—) and after (…) addition 5.0 mM NO₂⁻. pH 2.0. Scan rate = 50 mV s⁻¹.

substantial catalytic activity toward the electro-reduction of bromate, but only very weak activity toward chlorate, which is known otherwise to be more inert than bromate.

The catalytic reactions were conducted in pH 1.0 solution. The cyclic voltammograms for the reduction of bromate in 1 solution containing different concentration of bromate are shown in Fig. 8. From Fig. 8 it can be seen that by the addition of an equimolar quantity of NaBrO₃ to a solution of 1, the cathodic peak current of the second wave is enhanced while its anodic counterpart is greatly diminished. It seems clear that the reduced forms of 1 react with the added bromate. As the bromate concentration increases, the enhancement of the second peak current increases, so that the reduction of bromate appears to be catalyzed by the four-electron reduction of 1.

According to the work of Kulesza and Faulkner [27] and others [28], the catalytic reduction of bromate is accompanied by the removal of oxygen from the bromate, but only the initial oxygen abstraction step is considered to be the slowest. Br_2 is not a final product, because at the potentials of the catalytic reduction of Br_2 must be reduced to Br^- [29]. In order to verify the bromide as the final catalytic product, the controlled potential-electrolysis was performed in the presence of 1 and BrO_3^- at the potential where the catalytic effect was observed. The solution subjected to the electrolysis reacted with silver nitrate to yield the yellow precipitates of silver bromide.

Thus, we expect the catalytic reaction to proceed as follows [30]:

 $PMo_{12}O_{40}^{3-} + 2e^{-} + 2H^{+} \rightleftharpoons H_{2}PMo_{12}O_{40}^{3-}$ $H_{2}PMo_{12}O_{40}^{6-} + 2e^{-} + 2H^{+} \rightleftharpoons H_{4}PMo_{12}O_{40}^{3-}$ $H_{4}PMo_{12}O_{40}^{3-} + BrO_{3}^{-} \rightarrow H_{2}PMo_{12}O_{40}^{3-} + Br^{-} + H_{2}O_{40}^{3-}$

The direct electroreduction of nitrite ion to ammonia requires a large overpotential at most electrode surfaces but the reduction can be catalyzed in aqueous solution by various transition-metal complexes [31]. By contrast, the heteropoly compounds examined in this study appear to accomplish a multiple-electron reduction of nitrite and nitric oxide to ammonia entirely, while hydroxylamine is not. In addition, controlled-potential electrolyses involving a large number of catalyst turnovers showed that these anions have excellent longterm durability [32].

With addition of an equimolar quantity of $NaNO_2$ to a solution of **2**, no changes occur in IR and UV spectra of the reaction between two anions. However, there are significant changes in the voltammetry of the mixed solution as shown in Fig. 9. At pH 2 the cathodic peak current of the third wave is enhanced while its anodic counterpart is greatly diminished. These results indicate that the **2** have good electrocatalytic activities for NO_2^- reduction [33].

4. Conclusions

Seven organic-inorganic salts have been synthesized and the crystal structure of [(CH₂OH)₃CNH₃]₃P-Mo₁₂O₄₀·5H₂O was determined. By comparing [(CH₂-OH)₃CNH₃]₃[PMo₁₂O₄₀]·5H₂O with a series of organicinorganic salts containing the same anion, we found that the volume of the organic molecules contained in the organic-inorganic salts influences the symmetry of the heteropolyanion. In our study on [(CH₂- O_{40} ·11H₂O and [(CH₂OH)₃CNH₃]₂H₂SiW₁₂O₄₀·10H₂O, we found that they are charge transfer polyoxometallates (CTPS) with photochromism. Two kinds of organic-inorganic salts $[(CH_2OH)_3CNH_3]_3PMo_{12}$ -O40.5H2O and [(CH2OH)3CNH3]3PW12O40.11H2O show high catalytic activity towards the electrocatalytic reduction of bromate in pH 1.0 and nitrite in pH 2.0 solutions, respectively. With the increased concentration of bromate and nitrite, the cathodic peak current increased, and the anodic peak current decreased.

5. Supplementary material

Tables of atomic coordinates, anisotropic thermal parameters, and complete bond distances and angles have been deposited.

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