Preparation, crystal structures, EPR and reflectance spectra of two new charge-transfer salts, [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$[XMo$_{12}$O$_{40}$] · nCH$_3$CN (n = 0 for X = P or n = 1 for X = Ge)

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ARTICLE INFO

ABSTRACT

Two new charge-transfer salts, [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$[PMo$_{12}$O$_{40}$] · CH$_3$CN (**1**) and [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$ [GeMo$_{12}$O$_{40}$] (**2**), were synthesized by the traditional solution synthetic method and their structures were determined by single-crystal X-ray analysis. Salt **1** belongs to the triclinic space group $P1$, and salt **2** belongs to the triclinic space group $P\bar{1}$. There exist the complex interactions of the cationic ferrocenyl donor and Keggin polyanion in the solid state. The solid state UV–Vis diffuse reflectance spectra indicate the presence of a charge-transfer band climbing from 450 nm to well beyond 900 nm for **1**, a charge-transfer band from 460 to 850 nm with λ_{max} = 630 nm for **2**. The EPR spectra of salts **1** and **2** at 77 K show a signal at g = 2.0048 and 1.9501, respectively, ascribed to the delocalization of one electron in reduced Keggin ion [PMo^{V}Mo$^{VI}_{11}$O$_{40}$]$^{4-}$ in salt **1** and the Mo^{VI} in [GeMo$_{12}$O$_{40}$]$^{4-}$ is partly reduced to Mo^V owing to the charge-transfer transitions taking place between the ferrocenyl donors and the POM acceptors. The two compounds were also characterized by IR spectroscopy and cyclic voltammetry.

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1. Introduction

Polyoxometalates (POMs), a large class of anionic and discrete molecular metal–oxygen clusters, have attracted great attention in recent years due to their versatility and utility in many fields of research such as catalysis, medicine, and material sciences [1–3]. Some POMs can be reversibly reduced to mixed-valence species (heteropoly "blues" and "browns") by addition of various specific numbers of electrons, which are delocalized over a significantly large number of atoms of the heteropoly framework [4]. For instance, the Keggin polyanion [XM$_{12}$O$_{40}$]$^{n-}$ with proper size, shape and electronic properties can accept up to 32e– [5]. This offers the opportunity to prepare organic donor inorganic acceptor (ODIA) materials with a mixed valence state on the organic and inorganic units [6]. Therefore, POMs have been widely used as electron-acceptors in charge-transfer materials and cocrystallized with electron-rich organic donors, such as tetrathiafulvalene and its derivatives [7–14]. The ferrocene and its derivatives are also a type of potential candidates as organic metallic electron donors, and recent years some CTs based on ferrocene-type donor and POM acceptor have been synthesized and structurally characterized, such as, [Fe(C$_5$Me$_5$)$_2$]$_4$(POM) · n(solv) (POM = [SiMo$_{12}$O$_{40}$]$^{4-}$, [SiW$_{12}$O$_{40}$]$^{4-}$,

[PMo^{V}Mo$^{VI}_{11}$O$_{40}$]$^{4-}$, [HFeW$_{12}$O$_{40}$]$^{4-}$; solv = H$_2$O, DMF, CH$_3$CN) [15], [Fe(C$_5$Me$_5$)$_2$]$_3$[Cr(OH)$_6$Mo$_6$O$_{18}$] · 20H$_2$O, Na[Fe (Cp)$_2$]$_2$[Cr(OH)$_6$-Mo$_6$O$_{18}$] · 3H$_2$O, and [Fe(C$_5$Me$_5$)$_2$]$_4$[HPCu(H$_2$O)W$_{11}$O$_{39}$] · 6CH$_3$CN [16], [Fe(Cp)$_2$]$_3$[W$^V_5$W^{VI}O$_{19}$] [17], [NBu$_4$]$_6$ [Fe(Cp)$_2$][HPMo^{V}Mo$^{VI}_{11}$O$_{40}$]$_2$ [18]. And the charge-transfer salts based on the cationic ferrocenyl donor CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ and polyoxometalate acceptors of Lindqvist structural type (M$_6$O$^{2-}_{19}$), [CpFeCpCH$_2$N(CH$_3$)$_3$]$_2$M$_6$O$_{19}$ (M = Mo, W), were reported in 1995 by Kochi and co-worker [19], the UV–Vis diffuse reflectance spectrum in the solid state indicated the presence of a new charge-transfer band at λ_{max} = 550 nm. In this paper we report the synthesis, crystal structures, UV–Vis diffuse reflectance spectra, UV–Vis spectra in CH$_3$CN solution, CV and EPR properties of two new charge-transfer salts based on CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ units and Keggin polyanion [XM$_{12}$O$_{40}$]$^{n-}$ (X = P or Ge), [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$[PMo$_{12}$O$_{40}$] · CH$_3$CN (**1**) and [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$[GeMo$_{12}$O$_{40}$] (**2**).

2. Experimental

2.1. General methods

The experimental procedure was carried out in open air. The (NBu$_4$)$_3$[PMo$_{12}$O$_{40}$], (NBu$_4$)$_4$[GeMo$_{12}$O$_{40}$] and CpFeCpCH$_2$N(CH$_3$)$_3$I were prepared according to the literature procedures [20,21], and other starting materials were AR grade used as purchased. EPR

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spectra of powder samples were run on a JES-FE3AX spectrometer at 9.2 GHz at 77 K. IR spectra were obtained on an EQUINOX55 IR spectrometer with KBr pellets. Electronic spectra ($\lambda = 280$–600 nm) were recorded on a Shimazu UV-2550 spectrophotometer in acetonitrile solution. Solid state diffuse reflectance spectra of the samples were obtained for the dry pressed disk samples using a Shimazu UV-2550 spectrophotometer, equipped with an integrating sphere coated with polytetrafluoroethylene (PTFE), between 400 and 850 nm. Absorption spectra were referenced to $BaSO_4$. Cyclic voltammetry (CV) studies were carried out in acetonitrile solution at ambient temperature under the protection of N_2 using an EG & G 273A apparatus under computer control (M270 software). The source, mounting, and polishing of the glassy carbon (GC, 3 mm diameter) have been described [22]. Calomel electrode was as the reference electrode, and a platinum wire as the counter electrode. Potentials are quoted against a saturated calomel electrode (SCE). NBu_4ClO_4 was the supporting electrolyte, and the scan rate was 100 mV s^{-1}.

2.2. Synthesis of $[CpFeCpCH_2N(CH_3)_3]_4[PMo^VMo_{11}^{VI}O_{40}]CH_3CN$ (1)

$(NBu_4)_3[PMo_{12}O_{40}]$ (0.62 g, 0.25 mmol) was dissolved in 20 mL of acetonitrile. To the solution $CpFeCpCH_2N(CH_3)_3I$ (0.38 g, 1.0 mmol) dissolved in 10 mL of acetonitrile was added with stirring for 30 min at r.t. The brown-yellow solution was filtered and allowed to stand in a closed container at r.t. After a few days, the brown black crystalline product of **1** was collected (yield: 0.42 g, 69% based on $(NBu_4)_3[PMo_{12}O_{40}]$). Elemental Anal. Calc. for $C_{58}H_{83}Fe_4Mo_{12}N_5O_{40}P$: C, 24.03; H, 2.91; N, 2.42; Fe, 7.71; Mo, 39.76. Found: C, 24.12; H, 2.93; N, 2.40; Fe, 7.76; Mo, 39.74%. IR (KBr): 3447.6(vs), 1633.8(m), 1467.1 (w), 1404.9 (w), 1380.6(w), 1240.6(w), 1100.8(w), 1056.1(s), 947.8(vs), 866.2(w), 780.4(s), 481.9(m) cm^{-1}.

2.3. Synthesis of $[CpFeCpCH_2N (CH_3)_3]_4[GeMo_{12}O_{40}]$ (2)

The synthetic procedure for **2** is similar to that of **1** except for using $(NBu_4)_4[GeMo_{12}O_{40}]$ (0.71 g, 0.25 mmol) instead of $(NBu_4)_3[PMo_{12}O_{40}]$. The yield (0.46 g) of black green crystal **2** was 65% (based on $(NBu_4)_4[GeMo_{12}O_{40}]$). Elemental Anal. Calc.

for $C_{56}H_{80}Fe_4GeMo_{12}N_4O_{40}$: C, 23.20; H, 2.76; N, 1.93; Fe, 7.71; Mo, 39.75. Found: C, 23.24; H, 2.74; N, 1.91; Fe, 7.72; Mo, 39.78%. IR (KBr): 3444.3(vs), 3094.4(w), 3031.4 (w), 1639.0 (m), 1467.6(s), 1406.1(m), 1378.7(w), 1240.6(w), 1101.8(w), 1043.6(w), 946.1(vs), 875.5(vs), 806.7(vs), 772.5(vs), 634.3(m), 485.4(m), 445.4(m) cm^{-1}.

2.4. Crystallography

The X-ray crystallographic data of **1** and **2** were collected on a BRUKER SMART APEX II CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) radiation at 293(2) K. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package. A summary of the crystal data, experimental details, and refinement results for **1–2** are given in Table 1. All heavy atoms (Mo, Fe and Ge) of compounds **1** and **2** were refined with anisotropic displacement parameters. Other atoms (C, N, P and O) were refined isotropically. Hydrogen atoms were included at calculated positions and refined with a riding model.

## 3. Results and discussion

3.1. Synthesis and crystal structures

The charge-transfer salts **1–2** were synthesized in high yields (65–69%) by reaction of the corresponding Keggin anions $[NBu_4]_n[XMo_{12}O_{40}]$ ($n = 3$ for X = P; $n = 4$ for X = Ge) with $CpFeCpCH_2N(CH_3)_3I$ in CH_3CN solution (Scheme 1). Salts **1** and **2** are the strongly colored crystalline materials which are soluble in most of organic solvents, such as acetonitrile, CH_2Cl_2 and THF, but almost insoluble in n-hexane, and all of them are stabile to air and moisture.

Salt **1** crystallizes in the triclinic space group $P\bar{1}$ and is composed of one crystallographic asymmetric Keggin ion, four ferrocenylmethyltrimethylammonio cations and one acetonitrile molecule (Fig. 1). 4:1 ratio of $CpFeCpCH_2N^+(CH_3)_3$ and Keggin polyanion clearly indicates that the Keggin ion $[PMo_{12}O_{40}]^{3-}$ is reduced by one electron to $[PMo^VMo_{11}^{VI}MoO_{40}]^{4-}$. The cations and the anions arrange themselves in alternating layers in (001) plane (Fig. 2). The $CpFeCpCH_2N^+(CH_3)_3$ moieties stack to form infinite chains along a direction with the distances of 3.43(2) or 3.63(2) Å between the cyclopentadienyl rings of two adjacent $CpFeCpCH_2N^+(CH_3)_3$ units, and the Fe···Fe distances between two adjacent $CpFeCpCH_2N^+(CH_3)_3$ units are 6.14 or 6.58(2) Å, much shorter than the closest distance of 12 Å in $[NBu_4]_6[Fe(Cp)_2][HPMo^VMo_{11}^{VI}O_{40}]_2$ [18]. Different from the almost parallel arrangement of the cyclopentadienyl rings of the ferrocene moiety in $[CpFeCpCH_2N(CH_3)_3]_2M_6O_{19}$ (M = Mo, W) [19], $CpFeCpCH_2N^+(CH_3)_3$ cations adopt different packing, and the cyclopentadienyl rings of the adjacent chains stand almost perpendicular to another one with the dihedral angle of the cyclopentadienyl rings of ca. 75.68 or 69.20°. Six chains fit quadrangle channels that incorporate the polyanions. Each Keggin anion is surrounded by ten adjacent $CpFeCpCH_2N^+(CH_3)_3$ units with the nearest distance of framework oxygens of Keggin anions and carbon atoms of the cyclopentadienylammonio from 3.27(2) to 3.72(2) Å. The cationic trimethylammonio group stands almost perpendicular to the plane of the cyclopentadienyl ring (84.88°) to allow optimal interaction with the Keggin anion. And the ammonium groups penetrate partly into the anion layers, where two hydrogen atoms are close to the framework oxygens of Keggin anion at 2.38(2) and 2.66(2) Å (Fig. 2). All these data indicate that the strong interactions exist not only between the neighboring cations but also between the neighboring anions and cations.

Table 1
Crystallographic data for $[CpFeCpCH_2N(CH_3)_3]_4[PMo^VMo_{11}^{VI}O_{40}] \cdot CH_3CN$(**1**) and $[CpFeCpCH_2N(CH_3)_3]_4[GeMo_{12}O_{40}]$ (**2**).

Compounds	1	2
Formula	$C_{58}H_{83}Fe_4Mo_{12}N_5O_{40}P$	$C_{56}H_{80}Fe_4GeMo_{12}N_4O_{40}$
M (g mol^{-1})	2895.94	2896.51
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.631(6)	12.287(2)
b (Å)	13.210(6)	12.673(2)
c (Å)	14.780(7)	15.739(3)
α (°)	93.801(9)	67.872(3)
β (°)	111.478(8)	81.361(3)
γ (°)	101.942(8)	64.976(3)
V (Å^3)	2217.7(17)	2056.9(6)
Z	1	1
D_{calc} (g cm^{-1})	2.168	2.338
μ (mm^{-1})	2.367	2.888
Total reflections	11052	10084
Independent reflections	9297	6977
Parameters	466	293
Goodness-of-fit	0.943	1.058
R_1 ($I > 2\sigma(I)$)	0.0642	0.0966
wR_2 ($I > 2\sigma(I)$)	0.1603	0.1999
R_1 (all data)	0.1351	0.1442
wR_2 (all data)	0.2104	0.2168
Difference in peak and hole (A^{-3})	1.225, −1.046	1.719, −1.119

Scheme 1.

($n = 3$ for X = P; $n = 4$ for X = Ge)
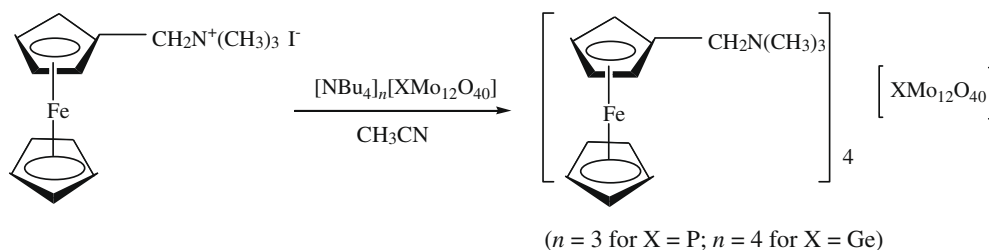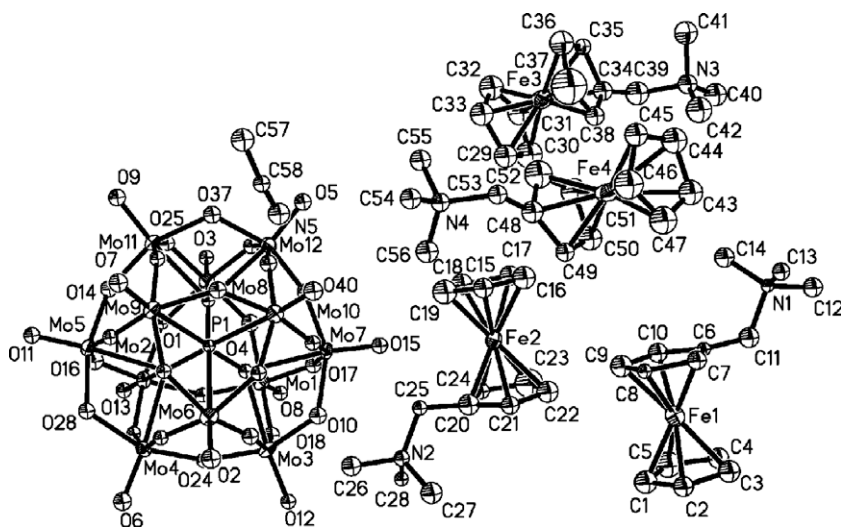
Fig. 1. ORTEP diagram of the asymmetric unit of **1** with the atomic numbering scheme and 30% thermal ellipsoids. H atoms are omitted for clarity.

Salt **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit contains half of Keggin ion and two ferrocenylmethyltrimethylammonio cations (Fig. 3). The crystal structure also presents a 3D packing, and the layers of the organic donor and inorganic acceptor are alternatively arranged in $(0\,0\,1)$ plane (Fig. 4). Each polyanion is surrounded by 12 adjacent $CpFeCpCH_2N^+(CH_3)_3$ units with the nearest distance of framework oxygens of Keggin anion and carbon atoms of $CpFeCpCH_2N^+(CH_3)_3$ from 3.01 to 3.52(2) Å.
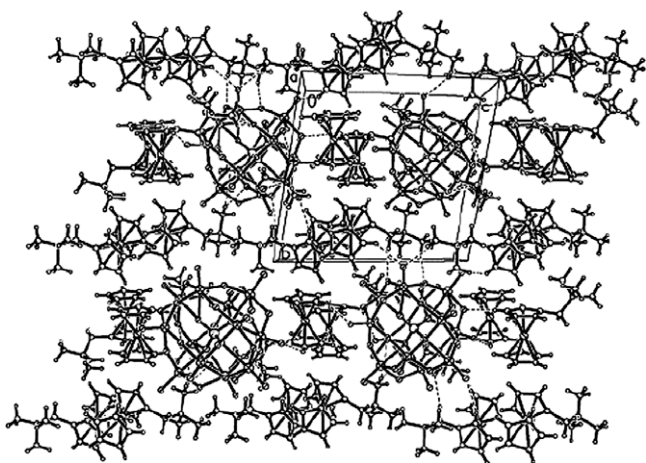
Fig. 2. Projection of the crystal structure of **1** in the bc plane showing the layers of the organic donor and inorganic acceptor alternatively arranged in $(0\,0\,1)$ plane. All CH_3CN molecules are omitted for clarity.

It is noticeable that there are strong interactions between adjacent anions in **2**, and the nearest distance of framework oxygens of the neighboring Keggin anions is 3.03(2) Å for **2**, far shorter than 4.43(2) Å for **1**. Different from T_d symmetry of Keggin ions in **1** the Keggin ions in salt **2** show the same type of crystallographic disorder as found in some other crystal structures with the Keggin anion [23,24]. The central Ge atom is surrounded by a cube of eight oxygen atoms with each oxygen site half occupied, and the central atom and these oxygen atoms form two group tetrahedra.

The central P–O and Ge–O distances of polyoxometallates in **1-2** vary from 1.42(2) to 1.53(2) Å, and 1.72(2) to 1.83(2) Å, and the range of bond angles of O–P–O and O–Ge–O vary from 106.4(11) to 112.2(11)°, and 107.6 to 111.4(11)°, respectively, which are all far depart from the regular tetrahedral angle. All of these show that the Keggin anions in **1** and **2** are severely distorted. The cyclopentadienyl rings of most ferrocene moieties in **1–2** are essentially parallel with a dihedral angle within 6°, except one in **1** with a dihedral angle of 15.3°.

3.2. IR spectra

The absorption peaks (Mo=Od, Mo–Ob, Mo–Oc and X–Oa) in the range 1100–500 cm^{-1} arising from the polyoxoanion in compounds **1–2** are compared in Table 2, which change slightly either in intensities, or in positions compared with those of the starting materials, α-$(NBu_4)_3[PMo_{12}O_{40}]$ and α-$[NBu_4]_4[GeMo_{12}O_{40}]$ due to the interactions among the cyclopentadienyl ligands and the framework oxygen atoms of polyoxometalates. The results are consistent with the structure data that the Keggin anions in **1** and **2** have a large distortion.
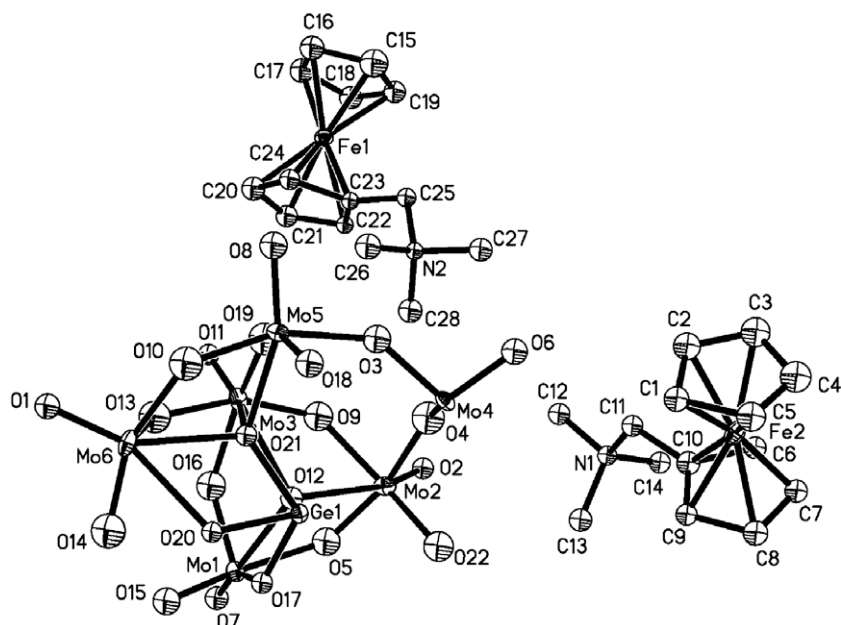
Fig. 3. ORTEP diagram of the asymmetric unit of **2** with the atomic numbering scheme and 30% thermal ellipsoids. H atoms are omitted for clarity.
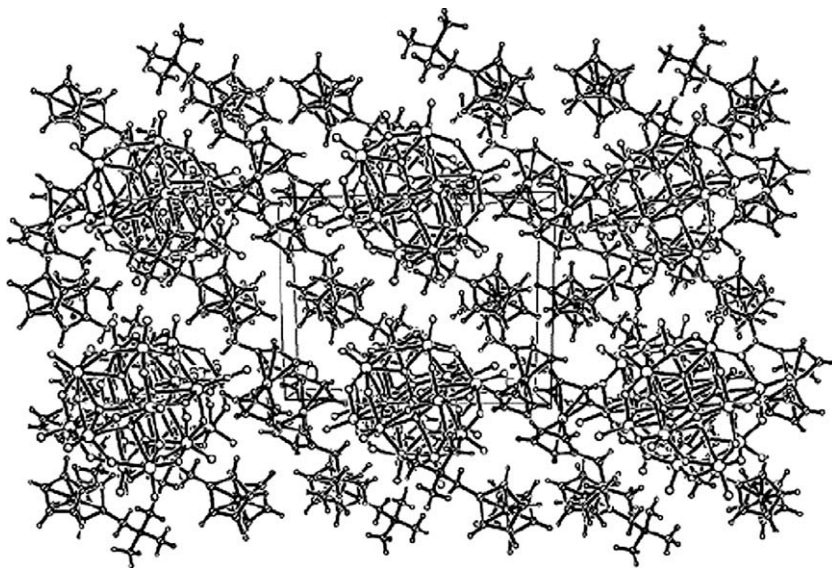

Fig. 4. Projection of the crystal structure of **2** in the *ac* plane showing the layers of the organic donor and inorganic acceptor alternatively arranged in (0 0 1) plane.

3.3. Electronic absorption spectra

UV–Vis absorption spectra were obtained by the diffuse reflectance technique [19,25]. The reflectance electronic spectra of the title compounds and starting materials (α-[NBu$_4$]$_n$[XMo$_{12}$O$_{40}$]

Table 2
Comparison of the IR spectrum of the title compounds with that of their starting materials.

Compounds	$\nu_{as(Mo=Od)}$	$\nu_{as(X-Oa)}$	$\nu_{as(Mo-Ob)}$	$\nu_{as(Mo-Oc)}$
α-(NBu$_4$)$_3$[PMo$_{12}$O$_{40}$]	965, 955	1063	880	805
1		947	1056	866	780
α-(NBu$_4$)$_4$[GeMo$_{12}$O$_{40}$]	939	812	873	778
2	946	806	875	772

($n = 3$ for X = P; $n = 4$ for X = Ge) and CpFeCpCH$_2$N$^+$(CH$_3$)$_3$I$^-$) are compared in Fig. 5. The diffuse reflectance spectrum of the brown black charge-transfer salt **1** in the solid state (Fig. 5a) showed a strong climbing absorption band from 500 to 850 nm. Spectral (digital) subtraction of the component spectra (i.e. of [NBu$_4$]$_3$[P-Mo$_{12}$O$_{40}$] and CpFeCpCH$_2$N(CH$_3$)$_3$I, individually) of salt **1** in the solid state yielded the difference spectrum (Fig. 5a inset) consisting of a very climbing band from 450 to beyond 850 nm. The diffuse reflectance spectrum of the black green salt **2** in the solid state (Fig. 5b) showed a low-energy tail from 500 to 850 nm, which is similar to the spectra of the charge-transfer salts [CpFeCpCH$_2$N(CH$_3$)$_3$]$_2$M$_6$O$_{19}$ (M = Mo, W) [19]. The difference spectrum (Fig. 5b inset) of salt **2** shows a band from 460 to 850 nm with λ_{max} = 630 nm. Thus, in accord with Mulliken theory [26–28], the new (visible) absorption bands should be ascribed to

charge-transfer transitions between the cationic ferrocenyl donor $CpFeCpCH_2N^+(CH_3)_3$ and the POM acceptors, and the strongly colored crystals were identified as charge-transfer salts [25,29]. It is interesting to note that salt **1** has a broader and higher-energy absorptions compared with those of salt **2** perhaps owing to Keggin ion was reduced by one electron in **1**.

The UV–Vis spectra in weak coordination acetonitrile solution of the title compounds and the starting materials are showed in Fig. 6. Compared with solid state UV–Vis diffuse reflectance spectra the absorption over 450 nm of the title compounds in solution is very weak, and the absorption gets weaker with the concentration reduced, meaning that the charge-transfer absorption band of the title compounds in the solid state has quite a large red-shift as compared to that in acetonitrile solution. All those suggest that the interaction between the cationic ferrocenyl donor and the polyoxometalate anion must play a role in the observed CT effect if the distance of both is short enough (in concentrated solution [30,31] or the solid state [32]). Indeed in a very dilute solution the complexes are almost entirely disrupted and the absorption bands vanish.

3.4. Cyclic voltammetry

Cyclic voltammetry of the charge-transfer salts **1–2** are showed in Fig. 7. The cathodic, anionic peak potentials (E_{pc}/E_{pa}) and corresponding E_{mid} ($E_{mid} = (E_{pa} + E_{pc})/2$) value of redox pair for the starting materials, $CpFeCpCH_2N(CH_3)_3I$, $(NBu_4)_3[PMo_{12}O_{40}]$, $(NBu_4)_4$ $[GeMo_{12}O_{40}]$ and the charge-transfer salts **1–2** are compared in table 3. The voltammetry curve of **1** exhibits three redox pairs (see Fig. 7a), which could be assigned to $CpFeCpCH_2N^+(CH_3)_3$ (+2/+1),
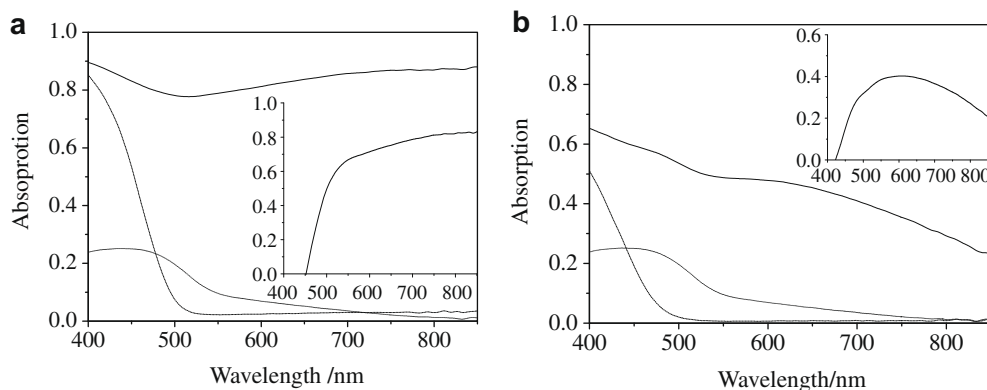

Fig. 5. Charge-transfer absorption spectra of CTs **1** (a) and **2** (b) (——) dispersed in barium sulfate in comparison with the absorption spectra of $[NBu_4]_n[XMo_{12}O_{40}]$ ($n = 3$ for $X = P$; $n = 4$ for $X = Ge$) (– – – –), respectively, and $CpFeCpCH_2N(CH_3)_3I$ (·······). The inset elicits the charge-transfer band by the spectral (digital) subtraction of $[[NBu_4]_n[XMo_{12}O_{40}]$ and $CpFeCpCH_2N(CH_3)_3$ I individually from **1** to **2**, respectively.
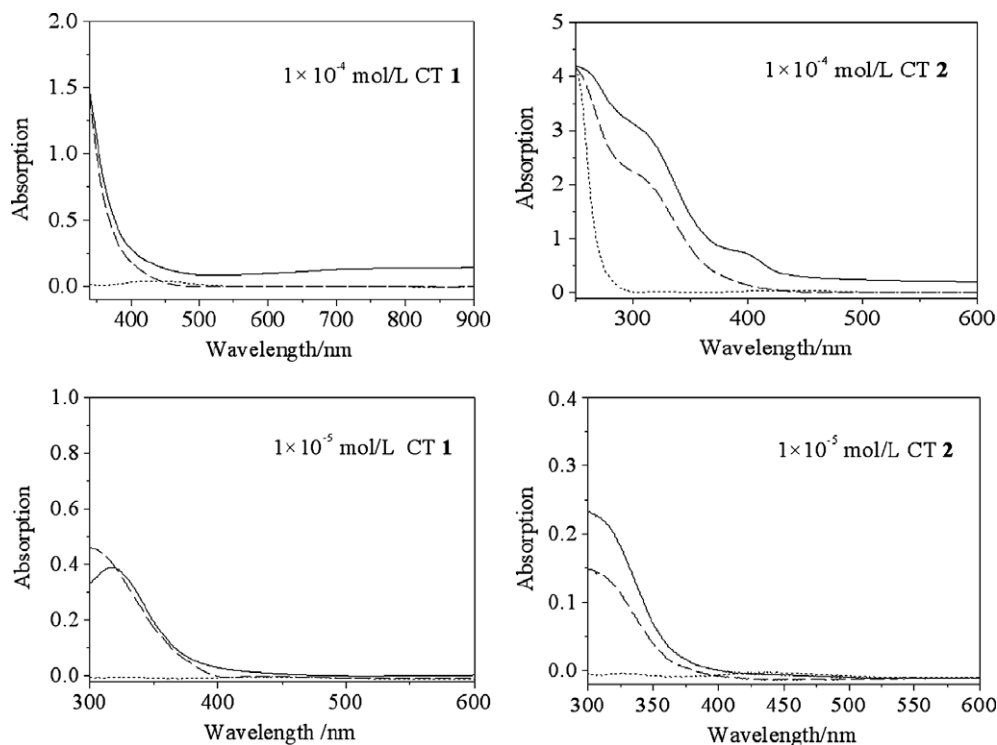

Fig. 6. Charge-transfer absorption spectra of CTs **1** and **2** (——) in 1×10^{-4} mol/L and 1×10^{-5} mol/L acetonitrile solutions in comparison with the absorption spectra of 1×10^{-4} mol/L and 1×10^{-5} mol/L $[NBu_4]_n[XMo_{12}O_{40}]$ ($n = 3$ for $X = P$; $n = 4$ for $X = Ge$) (– – – –),and 4×10^{-4} mol/L and 4×10^{-5} mol/L $CpFeCpCH_2N^+(CH_3)_3I^-$ (·······) acetonitrile solutions, respectively. All spectra were obtained in a 1 cm cell at 25 °C.
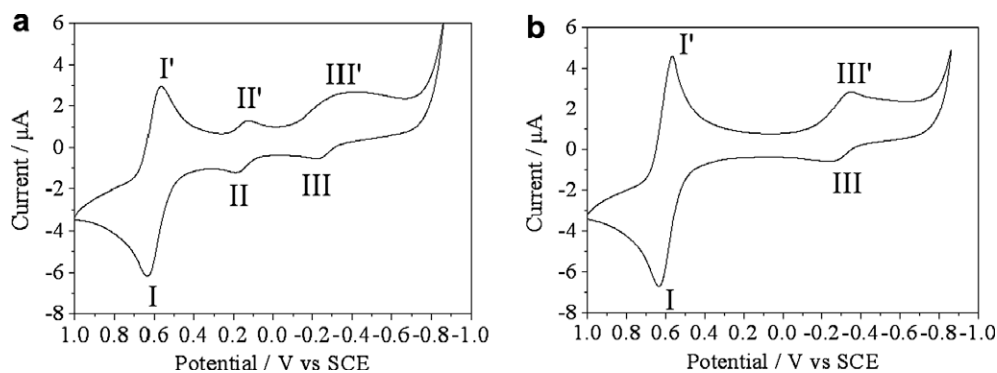
Fig. 7. Cyclic voltammetry of CTs **1** (a) and **2** (b) in 1×10^{-4} mol/L acetonitrile solution and 0.1 mol/L NBu$_4$ClO$_4$ as the supporting electrolyte.

Table 3
Cathodic peak potentials (E_{pc}/V), anionic (E_{pa}/V) and E_{mid} ($E_{mid} = (E_{pa}+E_{pc})/2$ for the starting materials and CTs **1–2**.

Compounds	E_{cp}/E_{ap}, E_{mid}		
	I/ I′	II/II′	III/III′
CpFeCpCH$_2$N(CH$_3$)$_3$I	0.62/0.56, 0.59	–	–
(NBu$_4$)$_3$[PMo$_{12}$O$_{40}$]	–	0.18/0.11, 0.145	−0.22/−0.30, −0.26
(NBu$_4$)$_4$[GeMo$_{12}$O$_{40}$]	–	–	−0.23/−0.35, −0.29
1	0.63/0.56, 0.595	0.18/0.12, 0.15	−0.22/−0.32, −0.27
2	0.63/0.56, 0.595	–	−0.24/−0.35, −0.295

PMo$_{12}$O$_{40}$(-3/-4) and PMo$_{12}$O$_{40}$(-4/-5) systems, respectively. E_{mid} value of redox pair for CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ in the charge-transfer salt **1** is 0.595 V compared with 0.59 V of free CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ cation, and those of two pairs for PMo$_{12}$ are 0.15 and −0.27 V compared with 0.145 and −0.26 V of (NBu$_4$)$_3$[PMo$_{12}$O$_{40}$]. The voltammetry curve (Fig. 7b) of **2** exhibits two redox pairs, the first could be assigned to CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ (+2/+1), and the second to Mo(VI/V). E_{mid} value of redox pair for CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ in salt **2** is 0.595 V, and that for GeMo$_{12}$O$_{40}$ in salt **2** is −0.295 V compared with −0.290 V of (NBu$_4$)$_4$[GeMo$_{12}$O$_{40}$]. The small difference of the corresponding E_{mid} value and of redox pair for the starting materials and charge-transfer salts means that the electrochemical behaviors of both Keggin ions and the cationic ferrocenyl donor CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ in salts are the same as those of the starting materials, that is, there are very weak interactions between the cationic ferrocenyl donor CpFeCpCH$_2$N$^+$(CH$_3$)$_3$ and polyoxometalate acceptors in the solution, which is also consistent with those of the UV–Vis spectra. Furthermore, the symmetric shape of anodic and cathodic current peaks in the charge-transfer salts **1–2** reveals that ratios of the anodic and cathodic current peak heights are

rather closed to 1, indicating reversible redox reaction of the cationic ferrocenyl donor occurred in both the Keggin anion systems.

3.5. EPR spectra

The EPR spectra of powdered samples of salts **1** and **2**, at 77 K and in the measured range, show a single, respectively at $g = 2.0048$ for **1** and $g = 1.9501$ for **2** (Fig. 8a and b). The signal for **1** should be ascribed to the delocalization of the electron in reduced Keggin ions [PMo^{V}Mo$^{VI}_{11}$O$_{40}$]$^{4-}$ in salt **1**. The signal for salt **2** is close to those observed in similar polyoxoanions containing Mo^V in other related charge-transfer salts [15,18], which means the anion [GeMo$_{12}$O$_{40}$]$^{4-}$ is partly reduced and the charge-transfer transition took place between the cationic ferrocenyl donor and the POM acceptor.

4. Conclusion

In summary, two new charge-transfer salts based on ferrocenylmethyltrimethylammonio cations and Keggin polyanions, [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$[XMo$_{12}$O$_{40}$] (X = P or Ge), were synthesized by the traditional solution synthetic method which are easily controlled and in high yields (65–69%) compared with the electrochemical synthetic method. There exist the complex interactions of the cyclopentadienyl ligands and polyanions in the solid state. The electronic spectra of the title compounds show the charge-transfer absorption band between the cationic ferrocenyl donor and the POM acceptors. The EPR spectra of the title compounds at 77 K show a signal of Mo^V, which ascribed to the delocalization of one electron in reduced Keggin ions [PMo^{V}Mo$^{VI}_{11}$O$_{40}$]$^{4-}$ in salt **1** and the Mo^{VI} in [GeMo$_{12}$O$_{40}$]$^{4-}$ is partly reduced to Mo^V owing to the charge-transfer transitions taking place between the ferrocenyl donors and the POM acceptors. The compound **1** has non-centro-
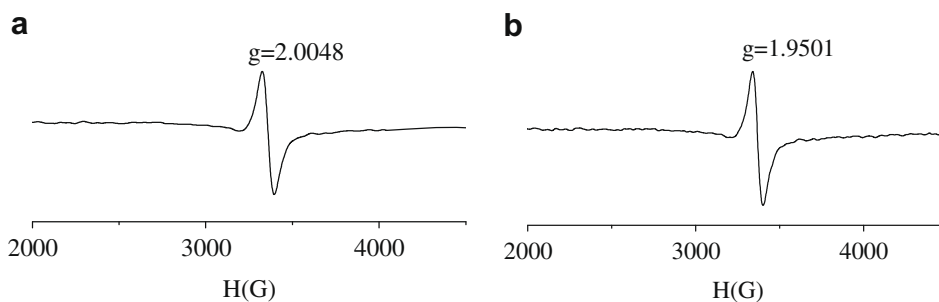

Fig. 8. EPR spectra of powder samples of the [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$[PMo^{V}Mo$^{VI}_{11}$O$_{40}$] · CH$_3$CN (a) and [CpFeCpCH$_2$N(CH$_3$)$_3$]$_4$[GeMo$_{12}$O$_{40}$] (b) at 77 K.

symmetric character, and probably possesses non-linear optical property.

Acknowledgments

This work was supported by Funded projects of independent innovation of Northwest University Postgraduates (07YZZ21) and the Education Commission of Shaanxi Province (07JK404).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.02.029.

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