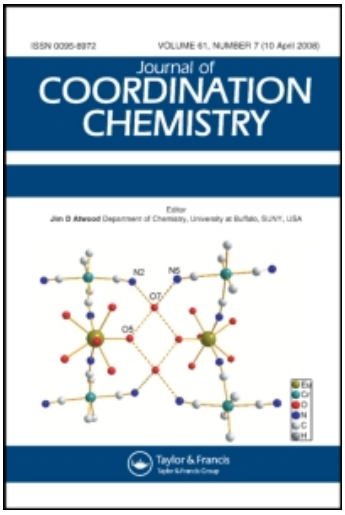

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Synthesis, structure and absorption spectrum of a new charge transfer salt $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}]\cdot CH_3CN\cdot H_2O$

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A new charge-transfer (CT) salt based on $Fe(C_5H_5)_2$ and Keggin-type anion $[GeMo_{12}O_{40}]^{4-}$, $[Fe(C_5H_5)_2]_4HGeMo_{12}O_{40}\cdot CH_3CN\cdot H_2O$, was electrochemically synthesized and its structure was determined by single-crystal X-ray diffraction. Triclinic, *P1*, $M = 2668.07$, $a = 12.600(9)$ Å, $b = 13.033(4)$ Å, $c = 13.298(5)$ Å, $\alpha = 116.312(6)^\circ$, $\beta = 101.244(9)^\circ$, $\gamma = 92.919(9)^\circ$, $V = 1896.4(16)$ Å^3, $Z = 1$, $R_1 = 0.0673$, $wR_2 = 0.1667(I > 2\sigma)$. $Fe(C_5H_5)_2^+$ moieties are stacked to form quadrangle channels with distances of $d_1' = 3.242(3)$ Å and $d_2' = 3.500(3)$ Å between the cyclopentadienyl rings of two adjacent ferrocene cations along the [0 1 1] direction that accommodate the polyanions, and each polyanion is surrounded by eight adjacent $[Fe(C_5H_5)_2]^+$ units with the nearest distance of framework oxygens of Keggin anions and carbon atoms of $[Fe(C_5H_5)_2]^+$ cations from 2.996 Å to 3.201 Å. The UV–Vis spectrum in concentrated solution indicates the presence of a new band at $\lambda_{max} = 620$ nm, ascribed to CT transitions between the ferrocenyl donors and the Polyoxometalate acceptors. IR, EPR, and CV properties of the salts were also discussed.

Keywords: Polyoxometalates; Charge-transfer; Ferrocene; Structure

1. Introduction

Charge-transfer (CT) salts involving organic donors and inorganic acceptors are of interest due to special electrical, optical, and magnetic properties [1]. Polyoxometalates (POMs) are anionic clusters commonly based on molybdenum or tungsten oxides. One application of POMs is based on their potential as electron acceptors [2]. Tetrathiafulvalene (TTF) and its derivatives as organic metallic electron donors are widely used to study CT interactions between POM acceptors and organic donors [3]. Other electroactive donor molecules can also be combined with POM acceptors to prepare donor–acceptor hybrid materials. Ferrocene and its derivatives are potential candidates as organometallic electron donors and some charge transfer complexes based on decamethylferrocene have been synthesized and structurally characterized,

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$Fe(Cp^*)_2 \cdot TCNE \cdot MeCN$ [4], $(Fe(Cp^*)_2)_4(POM) \cdot n(solv)$ ($POM = [SiMo_{12}O_{40}]^{4-}$, $[SiW_{12}O_{40}]^{4-}$, $[PMo_{12}O_{40}]^{4-}$, $[HFeW_{12}O_{40}]^{4-}$; $solv = H_2O$, DMF, CH_3CN) [5], $(Fe(Cp^*)_2)_3Cr(OH)_6Mo_6O_{18} \cdot 20H_2O$, $Na[Fe(Cp)_2]_2[Cr(OH)_6Mo_6O_{18}] \cdot 3H_2O$ ($Cp =$ ferrocene), $[Fe(Cp^*)_2]_4[HPCu(H_2O)W_{11}O_{39}] \cdot 6CH_3CN$ [6], $(Fe(Cp^*)_2)_2[M(mnt)_2]_2$ ($M = Fe^{III}, Co^{III}$) [7], and $Fe(Cp^*)$ $[Fe^{III}(CN)_6]_3 \cdot 2CH_2Cl_2 \cdot 6H_2O$ ($M^{II} = Mn, Fe, Co, Ni, Cu, Zn$) [8]. Veya and Kochi [9] reported two charge transfer salts based on $[FcCH_2N^+(CH_3)_3]_4$ electron donor and Lindquist-type polyanion $M_6O_{19}^{2-}$ ($M = Mo, W$); their CT interactions between POM acceptors and organic donors were revealed by time-resolved (laser-flash) spectroscopic method. Four charge transfer salts based on ferrocene and POMs have been reported: $Na[Fe(C_5H_5)_2]_2[Cr(OH)_6Mo_6O_{18}] \cdot 3H_2O$ was reported by Golhen *et al.* [6], prepared in an aqueous concentrated solution of $[Fe(C_5H_5)_2]BF_4$ and $Na_3[Cr(OH)_6Mo_6O_{18}] \cdot 8H_2O$; $[Fe(Cp)_2]_4PMo_{12}O_{40}$ [10] was prepared via solid phase synthesis at room temperature and exhibited nonlinear optical properties, however its structure was not determined; $(Fe(C_5H_5)_2)_3[W^VW_5^{VI}O_{19}]$ [11] was prepared via a conventional chemical reaction and its structure was determined; and $[NBu_4]_6H[Fe(C_5H_5)_2]$ $[PMo^VMo_{11}^{VI}O_4]_2$ was synthesized electrochemically by our team in 2006 [12]. The novelty of the four salts is that the POMs are mixed valence as a result of one electron reduction by the organic donor. Herein, we report a new CT salt-based Keggin anion $[GeMo_{12}O_{40}]^{4-}$ and ferrocene, $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}] \cdot CH_3CN \cdot H_2O$, which was electrochemically synthesized in CH_3CN and its structure was determined by X-ray diffraction analysis. The title complex has non-centrosymmetric character and probably possesses non-linear optical properties.

2. Experimental

2.1. *Materials and instruments*

IR spectra were obtained on an EQUINOX55 IR spectrometer with KBr pellets. UV–Visible spectra were recorded on a Shimadzu UV-2550 spectrometer. EPR spectra of powder samples were run on a JES-FE3AX spectrometer at 9.2 GHz. Cyclic voltammetry (CV) studies were carried out in CH_3CN at ambient temperature under N_2 using an EG & G 273A apparatus with M270 software. The source, mounting, and polishing of the glassy carbon (GC, 3 mm diameter) have been described [13]. Calomel electrode was used 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 $100\,mV\,s^{-1}$. The $(NBu_4)_4[GeMo_{12}O_{40}]$ was prepared according to the literature procedures [14], and other starting materials were of AR grade and were used as purchased.

2.2. *Syntheses*

The crystals of $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}] \cdot CH_3CN \cdot H_2O$ were prepared by anodic oxidation of ferrocene ($5 \times 10^{-3}\,mol\,L^{-1}$) dissolved in 10 mL CH_3CN in an H-shaped electrocrystallization cell (platinum wire electrode ($\phi = 0.5$ mm)) under a low constant current intensity *ca* $1.8\,\mu A\,cm^{-2}$. Solution of $(NBu_4)_4[GeMo_{12}O_{40}]$ ($5 \times 10^{-3}\,mol\,L^{-1}$) in

10 mL CH_3CN was used as electrolyte. After 1 month, the electrolyte was filtered with brown black block crystals of $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}]\cdot CH_3CN\cdot H_2O$ separated from filtrate in about 72% yield (based on Mo). Anal. Calcd (%) for $C_{42}H_{46}Fe_4GeMo_{12}NO_{41}$: H, 1.74; C, 18.91; N, 0.53; Fe, 8.37; Ge, 2.72; Mo, 43.15. Found: H, 1.81; C, 18.20; N, 0.49; Fe, 8.51; Ge, 2.64; Mo, 43.3.

2.3. *Crystallography*

A selected crystal of $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}]\cdot CH_3CN\cdot H_2O$ was mounted on a glass fiber capillary which was put on a BRUKER SMART APEX II CCD diffractometer equipped with graphite monochromatic radiation and used for data collection. A total of 9430 (7920 independent, $R_{int}=0.0347$) reflections were collected at 293(2) K from $1.67^\circ \le 2\theta \ge 25.05^\circ$. The crystal structure belongs to triclinic, space group *P1*, with cell dimensions $a=12.600(9)$ Å, $b=13.033(4)$ Å, $c=13.298(5)$ Å, $\alpha=116.312(6)^\circ$, $\beta=101.244(9)^\circ$, $\gamma=92.919(9)^\circ$, $V=1896.4(16)$ Å^3, $Z=1$, $D_{Calcd}=2.336$ g cm^{-3}, $F(000)=1273$. The structure was solved by direct methods (SHELXTL-97) and refined by full-matrix least-squares on F^2. The heavy atoms (Mo, Fe, Ge) were refined with anisotropic displacement parameters and O, C, and N were refined isotropically. Hydrogen atoms were not included. Structure solution and refinement based on 3761 reflections with $I>2\sigma(I)$ and on 393 parameters gave $R_1=0.0673$, $wR_2=0.1667$. In the final difference map, the maximum and minimum residuals were 1.418×10^3 and -0.834×10^3 e nm^{-3}, respectively. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No: 699463 for $C_{42}H_{46}Fe_4GeMo_{12}NO_{41}$.

3. Results and discussion

3.1. *Structure description*

The title compound was composed of one crystallographic asymmetric Keggin anion, one water, one acetonitrile, and four ferrocenyl cations (figure 1). The ratio of Keggin ion and ferrocenyl cation at 1 : 4 is different from 2 : 1 in $[NBu_4]_6H[Fe(C_5H_5)_2][PMo^{V}Mo^{VI}_{11}O_4]_2$ [12]. Figure 2 shows the packing of **1** in solid state along *b*. Two of four independent ferrocenyl cations stack to form infinite chains along the [0 1 1] direction with intrachain Fe···Fe distances of $d_1=6.927(3)$ Å and $d_2=7.047(3)$ Å, and the distances between the cyclopentadienyl rings of two adjacent Fe are $d_1'=3.242(3)$ Å and $d_2'=3.500(3)$ Å. Four chains provide quadrangle channels (figure 3) that incorporate the polyanions forming inorganic chains with the closest terminal oxygens distance between the neighboring polyanions of 3.501 Å, and two other crystallographic asymmetric $Fe(Cp)_2^+$ moieties with Fe···Fe distances of $d_3=7.552(3)$ Å are perpendicular to the aforesaid ferrocenyl cation infinite chains. Each Keggin anion is surrounded by eight adjacent $[Fe(C_5H_5)_2]^+$ units, four coming from the infinite chains and four others, forming an irregular cube with the nearest distance of framework oxygens of Keggin anions and carbon atoms of $[Fe(C_5H_5)_2]^+$ cations from 2.996 Å to 3.201 Å. All these data indicate that the intrachain ferrocenyl cations, intrachain anions and neighboring ferrocenes have strong interaction. The Fe···Fe

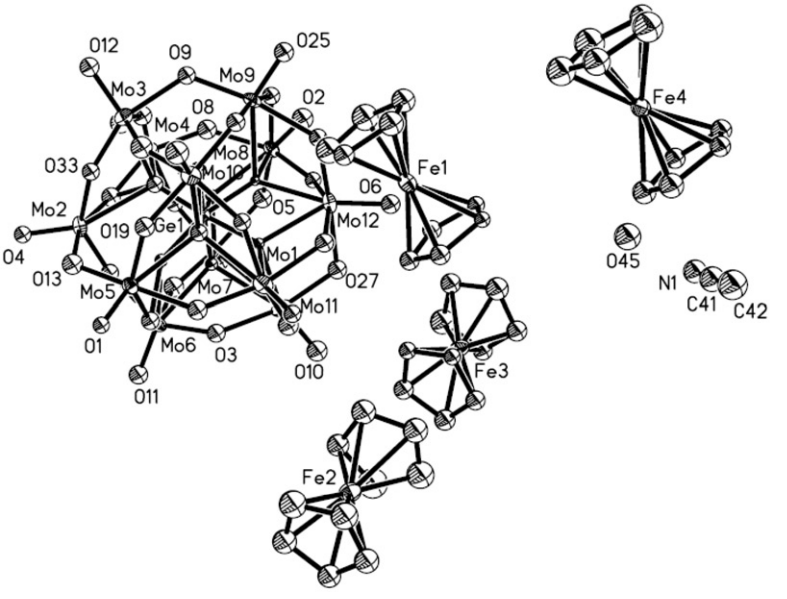

Figure 1. ORTEP drawing of the asymmetric unit in $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}] \cdot CH_3CN \cdot H_2O$ with displacement ellipsoids shown at 30% probability.

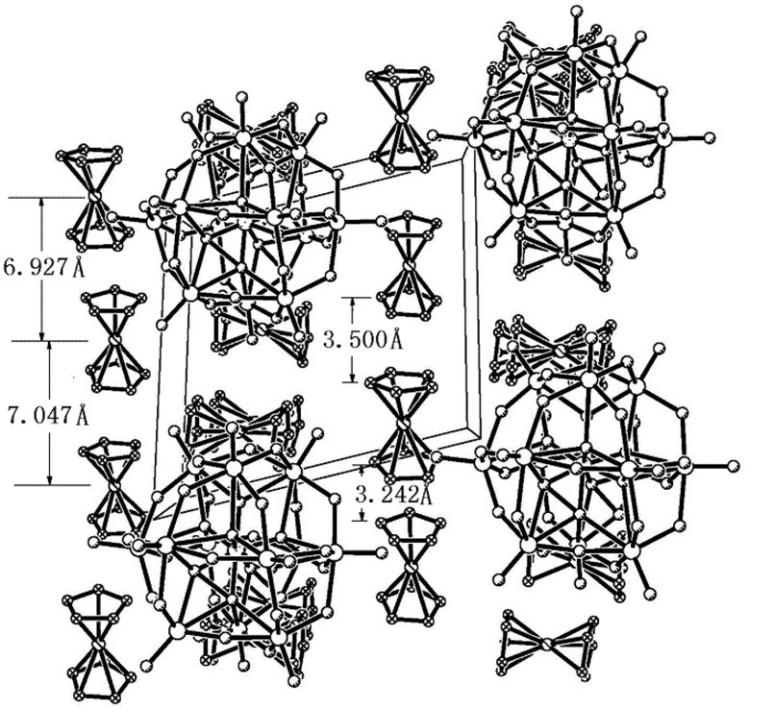

Figure 2. Projection of the structure in the *b* direction showing two of four independent ferrocenyl cations stack to form infinite chains.

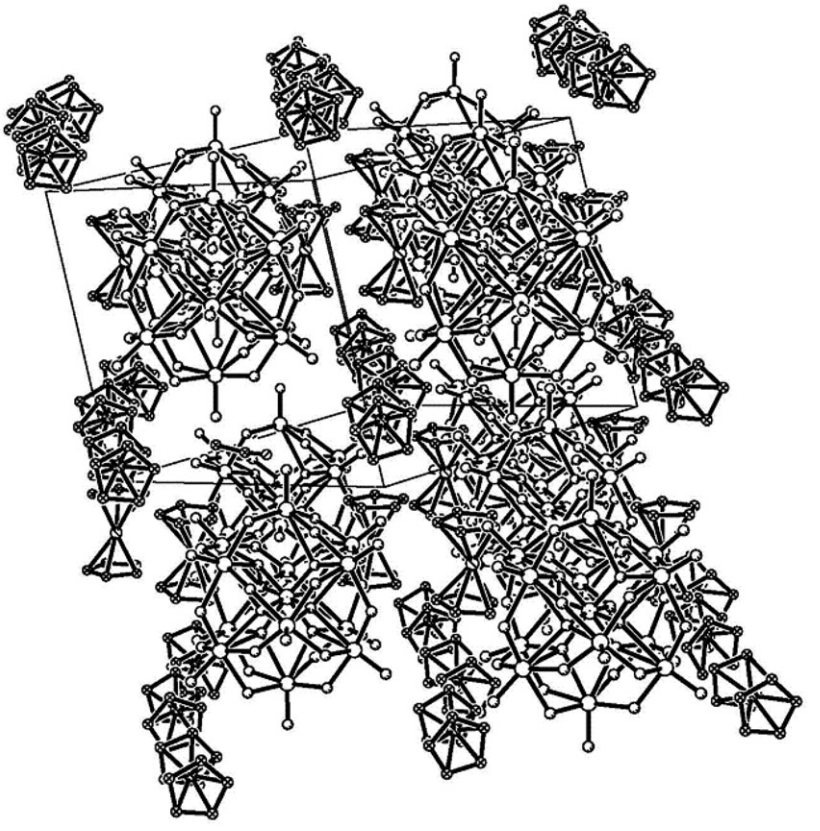

Figure 3. Four chains along [0 1 1] direction provide quadrangle channels that incorporate the polyanions. Water and acetonitrile molecules are omitted for clarity.

distances are much shorter than the closest distance of 12 Å in $[NBu_4]_6H[Fe(C_5H_5)_2][PMo^{V}Mo^{VI}_{11}O_{40}]_2$ [12]. As found in many other crystal structures [15] with the disordered a-Keggin anion, Ge is surrounded by a cube of eight oxygens with each oxygen site half occupied.

3.2. *IR and UV–Vis spectra*

Comparing the IR spectrum of the title compound with that of *a*-$[NBu_4]_4[GeMo_{12}O_{40}]$, the vibrational bands of $Mo=O_d$, $Mo–O_b$, $Ge–O_a$, and $Mo–O_c$ bonds shifted from 939 to 943, 873 to 871, 812 to 805, and 778 to 772 cm^{-1}, respectively, due to strong interaction between the framework oxygen of POM and ferrocene; and the presence of CT between the organic donor and POM acceptor was verified by EPR spectra. The result is consistent with the structure data that the framework of polyanion deformed greatly and indicates that the Mo = Od bond was strengthened and the Ge–Oa, Mo–Ob, and Mo–Oc bonds were all weakened in the CT salt.

Comparing the UV–Vis spectrum of the title compound with that of $[NBu_4]_4[GeMo_{12}O_{40}]$ dissolved in a weakly coordinating solvent, acetonitrile, we find that the UV–Vis spectrum of the brown black title compound in 1×10^{-4} mol L^{-1}

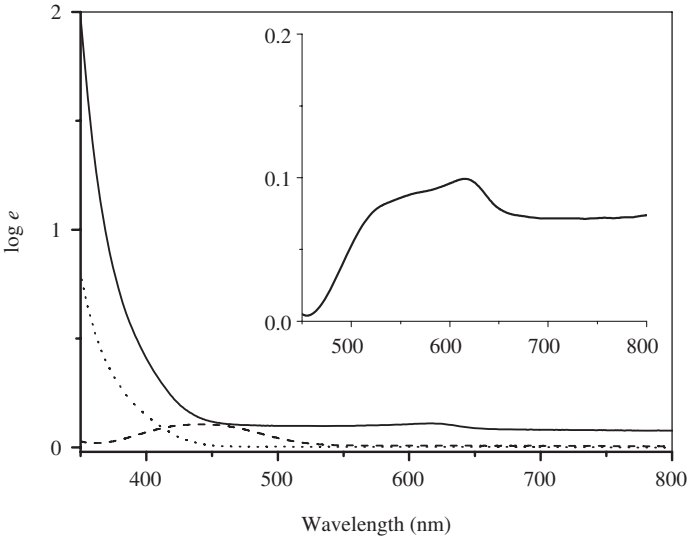

Figure 4. Charge-transfer absorption spectrum of $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}]\cdot CH_3CN\cdot H_2O$ (——) in 1×10^{-4} mol L^{-1} acetonitrile solution in comparison with the absorption spectra of 1×10^{-4} mol L^{-1} $[NBu_4]_4[GeMo_{12}O_{40}]$ (–·–·–·) and 4×10^{-4} mol L^{-1} $[Fe(C_5H_5)_2]$ (·····) acetonitrile solutions. The inset shows the CT band of $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}]\cdot CH_3CN\cdot H_2O$ by the spectral (digital) subtraction of the $[NBu_4]_4[GeMo_{12}O_{40}]$ (–·–·–·) and the $[Fe(C_5H_5)_2]$ (·····) solutions individually from the $[Fe(C_5H_5)_2]_4H[GeMo_{12}O_{40}]\cdot CH_3CN\cdot H_2O$ solution.

acetonitrile (figure 4) showed a pronounced low-energy tail that extended from 500 nm to well beyond 800 nm. Spectral (digital) subtraction of the component spectrum (i.e., of 1×10^{-4} mol L^{-1} $[NBu_4]_4[GeMo_{12}O_{40}]$ and 4×10^{-4} mol L^{-1} $[Fe(C_5H_5)_2]$ acetonitrile solution individually) yielded the difference spectrum (figure 4 inset) consisting of a very broad CT band with $\lambda_{max}=620$ nm. Thus, in accord with Mulliken theory [16, 17], the new (visible) absorption bands were ascribed to CT transitions between the ferrocenyl donors and the POM acceptors ($[GeMo_{12}O_{40}]^{4-}$), and the strongly colored crystals were identified as CT salts [18, 19].

3.3. *Cyclic voltammogram*

The voltammetry curves of $[Fe(C_5H_5)_2]_4HGeMo_{12}O_{40}\cdot CH_3CN\cdot H_2O$ exhibits two redox pairs (figure 5). The first couple could be assigned to ferrocene($+1/0$) and the second could be assigned to Mo(VI/V). The E_{mid} values ($E_{mid}=(E_{pa}+E_{pc})/2$, E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively) of redox pair for ferrocene and $GeMo_{12}$ in the charge transfer salt is 0.41 V and -0.34 V, compared with 0.455 V of free ferrocene and -0.31 V of $(NBu_4)_4[GeMo_{12}O_{40}]$, respectively.

3.4. *EPR spectra*

EPR spectrum (figure 6) of powdered samples of $[Fe(C_5H_5)_2]_4HGeMo_{12}O_{40}\cdot CH_3CN\cdot H_2O$ at 77 K has one signal at $g=1.921$ from the presence of one unpaired electron in the reduced $[GeMo_{12}O_{40}]^{5-}$ anion as found in other related charge transfer salts [5, 10, 12].

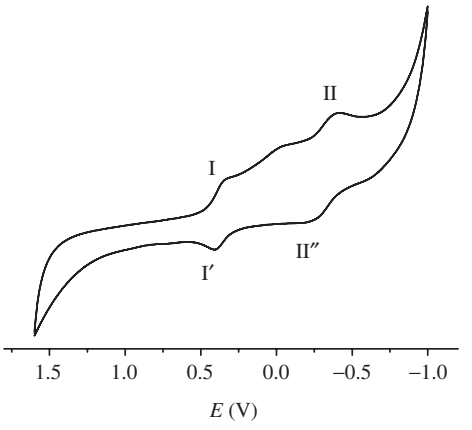

Figure 5. Cyclic voltammetry of $[Fe(C_5H_5)_2]_4HGeMo_{12}O_{40} \cdot CH_3CN \cdot H_2O$ in 1×10^{-4} mol L^{-1} acetonitrile solution and 0.1 mol L^{-1} $(NBu_4)ClO_4$ as the supporting electrolyte at 100 mV $\cdot$ s^{-1}.

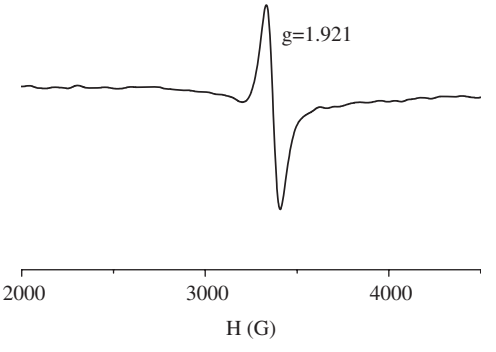

Figure 6. The EPR spectrum of the charge transfer salt at 77 K.

4. Conclusion

A new charge transfer salt based on $Fe(C_5H_5)_2$ and Keggin-type anion $[GeMo_{12}O_{40}]^{4-}$ with the ratio of Keggin ion and ferrocenyl cation of 1 : 4 was electrochemically synthesized. The $Fe(C_5H_5)_2^+$ moieties are stacked to form quadrangle channels that accommodate the polyanions in the crystal structure. UV–Vis spectra in concentrated solution indicate the presence of a CT band at $\lambda_{max} = 620$ nm. The title complex has non-centrosymmetric character and its non-linear optical properties appear to be promising.

Acknowledgments

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