Journal of Organometallic Chemistry 695 (2010) 1863–1868

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Synthesis of 1-(1-ferrocenylethyl)-pyridinium chloride and its hybrid materials with lindquist-type polyoxometalates

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ARTICLE INFO

*Article history:*
Received 2 February 2010
Received in revised form
22 April 2010
Accepted 30 April 2010
Available online 6 May 2010

*Keywords:*
Charge-transfer salts
Ferrocene
Polyoxometalates
Reflectance spectra

ABSTRACT

A new ferrocene derivative, 1-(1-ferrocenylethyl)-pyridinium (fep = CpFeCp–CH($CH_3$)–$Py^+$) chloride, and two charge-transfer salts (CTSs) based on the cationic fep donor and Lindqvist-type polyoxometalate acceptors, $[fep]_2[Mo_6O_{19}]$ (**1**) and $[fep]_2[W_6O_{19}]$ (**2**), were synthesized. fepCl was characterized by elemental analysis, IR spectroscopy and $^1H$ NMR and the two CTSs were characterized by elemental analysis, IR spectroscopy, UV–vis diffuse reflectance spectrum, cyclic voltammetry, fluorescence spectrum and single crystal X-ray diffraction. X-ray crystallographic studies of the brownish red CTSs **1** and **2** reveal that they are isostructural and crystallize in the monoclinic space group $P2_1/n$. In salts **1**–**2**, fep and polyoxoanions are cocrystallized by Coulombic forces, and there also exist the complex C–H···π and π···π stacking interactions between the adjacent fep cations and C–H···O hydrogen bonds between the adjacent fep cations and polyanions. The UV–vis diffuse reflectance spectra indicate the presence of a broad charge-transfer band between 500 and 850 nm for **1**–**2**, and CT character of **1** and **2** is also confirmed by the Mulliken correlation between the CT transition energies and the reduction potentials of the polyoxometalate acceptors.

## 1. Introduction

Polyoxometalates (POMs) or metal oxide clusters are versatile in many aspects, and in recent years new efforts have been made to explore their applications in catalysis, medicine, and material sciences [1,2], which is based on the ability of POMs to act as electron reservoirs as well as the extreme variability of their molecular properties, including size, shape, charge, charge density, redox potential, acidity, solubility and so on [3,4]. In particular, the potentialities of molecular materials of these metal oxide clusters are exemplified by the POMs in their use as electron-accepting moieties in charge-transfer materials prepared by cocrystallization with electron-rich organic donors, such as tetrathiafulvalene and their derivatives via an initial electron-transfer [5]. The ferrocene and its derivatives are an excellent type of organicmetallic electron donors, and recent years some charge-transfer salts (CTSs) based on ferrocene-type donor and POM acceptor have been synthesized and structurally characterized [6–13]. The first charge-transfer salt containing the cationic ferrocenyl donor $CpFeCpCH_2N^+(CH_3)_3$ and polyoxometalate acceptors of the Lindqvist structural type ($[M_6O_{19}]^{2-}$) (M = Mo, W) was reported by Professor Kochi in 1995 [10], and he revealed the relevant charge-transfer interactions between POM acceptors and organic donors in the $[C_5H_5FeC_5H_4CH_2N(CH_3)_3]_2M_6O_{19}$ (M = Mo, W) by the UV–vis diffuse reflectance spectrum and time-resolved (laser-flash) spectroscopic method. Recently, our group reported the charge-transfer salts based on the cationic ferrocenyl donor $CpFeCpCH_2N^+(CH_3)_3$ and Keggin-type acceptors, $[CpFeCpCH_2N(CH_3)_3]_4[PMo_{12}O_{40}]\cdot CH_3CN$ and $[CpFeCpCH_2N(CH_3)_3]_4[GeMo_{12}O_{40}]$ [8], in which the Keggin polyanion $\{PMo_{12}O_{40}\}$ was reduced to −4 from the original −3, and $[GeMo_{12}O_{40}]^{4-}$ remains its original oxidation state. The charge-transfer salts composed of cationic donors and anion acceptors can be described as outer-sphere (OS) charge-transfer complexes [14] in which the main interaction between the cation and anion are coulomb force, and the charge-transfer transitions are highly related to the contacts interactions between the cation and anion, and also to the structures and composition of cationic donor and polyoxometalate acceptors. In this direction, we have recently utilized cationic ferrocenylmethylpyridinium donor

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doi:10.1016/j.jorganchem.2010.04.033

**Table 1**
Crystallographic parameters and refinement details for $[fep]_2[Mo_6O_{19}]$ (**1**) and $[fep]_2[W_6O_{19}]$ (**2**).

| Compounds | 1 | 2 |
|---|---|---|
| Formula | $C_{34}H_{36}Fe_2Mo_6N_2O_{19}$ | $C_{34}H_{36}Fe_2W_6N_2O_{19}$ |
| $M$, g mol$^{-1}$ | 1463.99 | 1991.45 |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 12.4674(11) | 12.516(2) |
| $b$, Å | 13.6294(12) | 13.681(2) |
| $c$, Å | 14.0077(13) | 14.053(2) |
| $A$ | 90 | 90 |
| $B$ | 114.681(1) | 114.705(3) |
| $\Gamma$ | 90 | 90 |
| $V$, Å$^3$ | 2162.8(3) | 2186.1(6) |
| $Z$ | 2 | 2 |
| $d_{calc}$, g cm$^{-3}$ | 2.248 | 3.025 |
| $\mu$, mm$^{-1}$ | 2.409 | 16.436 |
| Total reflns | 10,541 | 10,774 |
| Indep reflns | 3834 | 3878 |
| Parameters | 287 | 263 |
| GOF | 1.180 | 0.932 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0252 | 0.0378 |
| $wR_2$ ($I > 2\sigma(I)$) | 0.0763 | 0.0948 |
| $R_1$ (all data) | 0.0319 | 0.0612 |
| $wR_2$ (all data) | 0.0966 | 0.1151 |
| Difference in peak and hole, e Å$^{-3}$ | 0.569, −0.920 | 1.565, −1.323 |

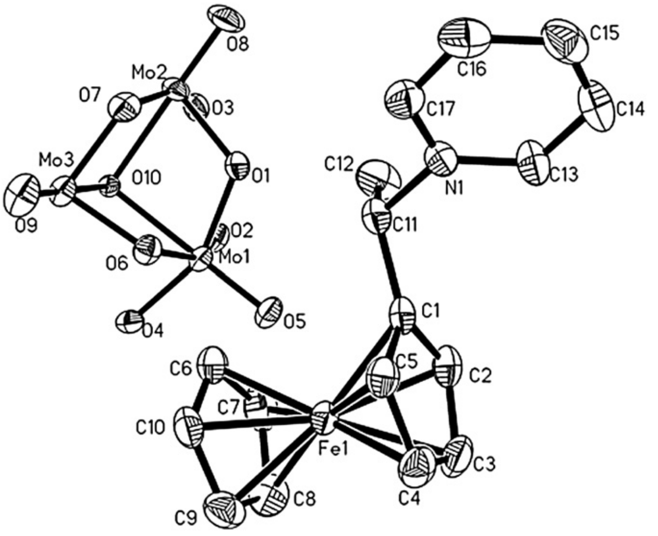


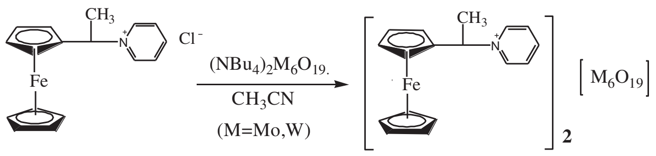
**Fig. 1.** ORTEP diagram of the asymmetric unit of **1** with the atomic numbering scheme and 30% thermal ellipsoids. H atoms are omitted for clarity.

($CpFeCp{-}CH_2{-}Py^+$) as cations to obtain four new outer-sphere charge-transfer complexes, $[CpFeCp{-}CH_2{-}Py]_2[Mo_6O_{19}]$, $[CpFeCp{-}CH_2{-}Py]_2[W_6O_{19}]$, $[CpFeCp{-}CH_2{-}Py]_4[W_{10}O_{32}]$ and $(NBu_4)[CpFeCp{-}CH_2{-}Py]_2[PMo_{12}O_{40}]$ [13]. In these salts, the ferrocenylmethylpyridinium ($CpFeCp{-}CH_2{-}Py^+$) and the polyoxoanions are cocrystallized by Coulombic forces, and there also exist the complex $C{-}H\cdots\pi$ and $\pi\cdots\pi$ stacking interactions between the adjacent ferrocenylmethylpyridinium cations. The orbital overlap between the π-donor plane of the pyridyl ring and one oxygen facet of the acceptor octahedron in the solid state is observed in salts $[CpFeCp{-}CH_2{-}Py]_2[Mo_6O_{19}]$ and $[CpFeCp{-}CH_2{-}Py]_2[W_6O_{19}]$. As a part of our continuing efforts to find new and more suitable cationic donor to tune the crystal stacking structure of charge-transfer complexes based on ferrocenyl cationic donors and polyoxometalate acceptors, herein we report the synthesis of a new cationic ferrocenyl containing pyridinium group, 1-(1-ferrocenylethyl)-pyridinium chloride, and its CTSs with Lindquist-type polyoxometalates.

## 2. Experimental

### 2.1. General methods

$(NBu_4)_2M_6O_{19}$ ($M = Mo$ or $W$) was prepared according to the literature [15]. The solvents used in preparations of fepCl (fep = $CpFeCp{-}CH(CH_3){-}Py^+$) were all dried, especially THF was distilled from Na and pyridine was distilled from NaOH just prior to use, other starting materials were AR grade and used as purchased. $^1H$ NMR spectra were recorded on a Varian INOVA-400 MHz spectrometer with TMS as an internal standard. IR spectra were obtained on an EQUINOX55 IR spectrometer with KBr pellets. Solid state diffuse reflectance spectra between 300 and 850 nm were obtained for the dry pressed disk samples using a Shimazu UV-2550 spectrophotometer, equipped with an integrating sphere coated with polytetrafluoroethylene (PTFE). Absorption spectra were referenced to barium sulfate. 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 [16]. SCE (saturated calomel electrode) was as the reference electrode, and a platinum wire as the counter electrode, $NBu_4Br$ was the supporting electrolyte, and the scan rate was 100 mV s$^{-1}$. Luminescent spectra were measured at room temperature on a Hitachi F4500 fluorescence spectrophotometer. Magnetic measurements were carried out using a Quantum Design MPMS-XL SQUID magnetometer.



**Scheme 1.**

### 2.2. Synthesis of 1-(1-ferrocenylethyl)-pyridinium chloride (fepCl)

A solution of 46.2 g (0.2 mol) of acetylferrocene [17] in 200 ml of ethanol was added dropwise, at room temperature, to a solution of

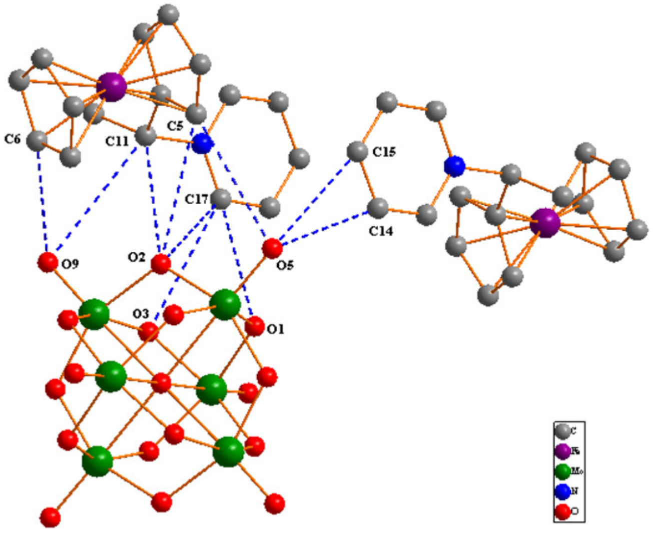


**Fig. 2.** A representation showing the linkages of hydrogen bonding between the polyoxoanions and the ferrocenyl cations in **1**, H atoms are omitted for clarity.