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Preliminary communication

Structural and spectral characterization of novel charge-transfer salts of polyoxometalates and the cationic ferrocenyl donor [☆]

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Abstract

The first charge-transfer salts containing the cationic ferrocenyl donor cpFecp$CH_2N^+(CH_3)_3$ and polyoxometalate acceptors of the Lindqvist structural type ($M_6O_{19}^{2-}$; M = Mo, W) have been isolated in high yields (87–88%). The X-ray structure of the charge-transfer salt shows the close (interionic) interaction of the hydrogen atoms of the cyclopentadienyl ligand with the surface of the polyoxometalate. Furthermore, the UV-vis diffuse reflectance spectrum in the solid state indicates the presence of a new charge-transfer band at $\lambda_{max} = 550$ nm; and laser-flash photolysis spectroscopy establishes $cpFe^+cpCH_2N^+(CH_3)_3$ and $M_6O_{19}^{3-}$ as short-lived transients in the direct photoactivation of the charge-transfer salt.

Keywords: Ferrocene; Polyoxometalate; Charge-transfer salts; Laser-flash photolysis; Spectral CT transients; Time-resolved spectrum

Polyoxometalates have experienced revived attention in recent years as viable models for metal oxides of relevance to heterogeneous catalysis [1], and their remarkable ability to function as oxidants as well as oxygen transfer agents is potentially applicable to the development of oxidation catalysts [2]. In particular, the low reduction potentials of Lindqvist-type polyoxometalates [3] have been exploited in their use as electron acceptors in the oxidation of electron-rich aromatic compounds, such as tetramethylphenylendiamine, tetrathiafulvalene, etc. [4] via an initial electron transfer. Despite extensive studies on various redox systems involving polyoxometalates and organic donors [5], limited attention has been paid to understanding how they undergo electron transfer [6]. Because the latter has recently elicited our interest in connection with the use of organometallic donors to probe the charge-transfer (CT) interactions inherent to electron acceptors in various types of electron donor-acceptor complexes [7], we now report the synthesis, isolation and structural elucidation of the EDA complexes of the donor ferrocenylmethyltrimethylammonio (**1**) cation with the polyoxometalate acceptors $M_6O_{19}^{2-}$ with M = Mo, **2** and W, **3**. X-ray crystallography coupled with time-resolved (laser-flash) spectroscopy has revealed the relevant charge-transfer interactions between the ferrocenyl and polyoxometalate moieties in the EDA complexes.

The spatial origin of the charge-transfer transition was established by an X-ray crystallographic study (see Experimental details) of the single salt grown from a dilute (1–2 mM) solution of **4** in acetonitrile at 25°C.

The molecular structure of the charge-transfer salt **4** was solved in the monoclinic space group *I2/c* as a 2:1 mixture of (trimethylammonio)methylferrocene$^+$ and $Mo_6O_{19}^{2-}$ units. The hexamolybdate anion [9] shows three distinct types of Mo–O bond lengths. The Mo–O1 distances average 2.317 Å, the Mo=O distances average 1.677 Å, and the remaining Mo–O distances to the bridging oxygens average 1.924 Å. The cationic trimethylammonio group stands almost perpendicular to the plane of the cyclopentadienyl ring (114.4(3)°) to allow optimal interaction with the hexamolybdate anion. The cations and the anions arrange themselves in alternating layers in the crystals, as can be seen from the packing diagram shown in Fig. 1. The ammonio groups penetrate partly into the anion layers, where two hydrogen atoms are close to the hexamolybdate

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[☆] Dedicated to Professor Fausto Calderazzo on his 65th birthday for his pioneering and seminal research on organometallic charge-transfer salts.

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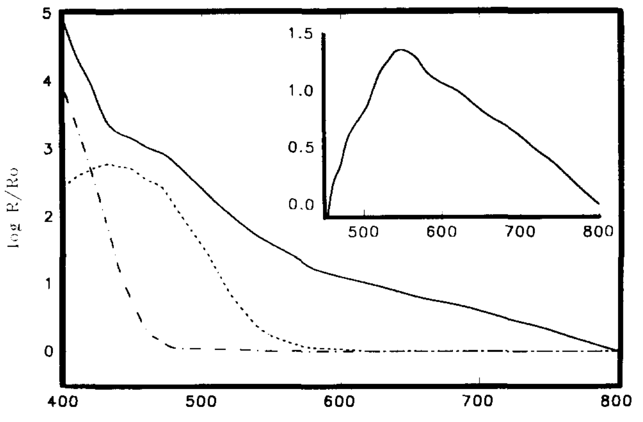


Fig. 1. Charge-transfer absorption spectrum of [cpFecpCH$_2$NMe$_3$]$_2$-Mo$_6$O$_{19}$, **4** (———) as a 2.5% dispersion in alumina in comparison with the absorption spectra of [Bu$_4$N]$_2$Mo$_6$O$_{19}$, **2** (·–·–·) and cpFecpCH$_2$NMe$_3$CF$_3$SO$_3$, **1** (------). The inset elicits the charge-transfer band of **4** by the spectral (digital) subtraction of cpFecpCH$_2$NMe$_3$CF$_3$SO$_3$, **1** (------) from [cpFecpCH$_2$4-NMe$_3$]$_2$-Mo$_6$O$_{19}$, **4** (———).

anion at 2.56–2.60 Å. The cyclopentadienyl rings of the ferrocene moiety are almost parallel, having a dihedral angle of 3.5°. The rings are twisted by about 11° relative to each other about the axis connecting the two ring centroids. This structure indicates that they are much closer to an eclipsed conformation (0°) rather than to an ideal staggered conformation (36°). As detailed in the Fig. 2, the charge-transfer transition in **4** is centered about the three hydrogen atoms of the cyclopentadienyl ligand, which have four close separations from the surface of oxygen atoms of the hexamolybdate. They are observed between C3′H3′-O3, C4′H4′-O2, C9′H9′-O4 and C9′H9′-O8 at distances between 2.66 Å and 2.76 Å. Most importantly, the critical Fe-O2 and O3 separations average about 4.2 Å, and there are no other oxygen atoms closer.

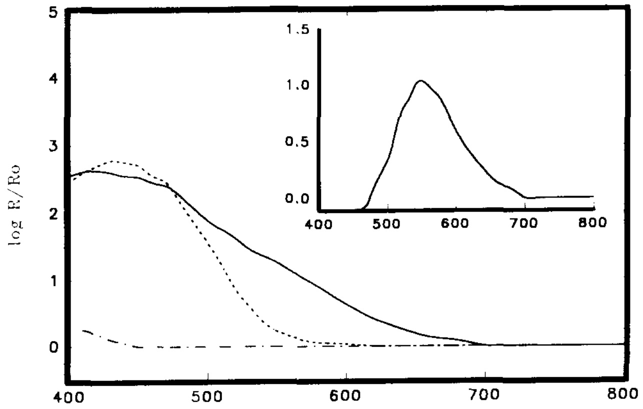
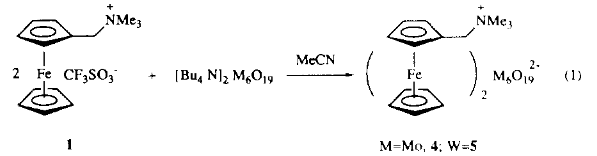


Fig. 2. Charge-transfer absorption spectrum of [cpFecpCH$_2$NMe$_3$]$_2$-W$_6$O$_{19}$, **5** (———) obtained by a procedure similar to that in Fig. 3.

1. Charge-transfer complexes of the ferrocenyl cation and the Lindqvist-type polyoxometalate $M_6O_{19}^{2-}$ (M = Mo, W). Spectral characterization and X-ray crystal structure

When dilute yellow solutions of cpFecpCH$_2$N-(CH$_3$)$_3^+$CF$_3$SO$_3^-$ **1** (see Experimental details), and (Bu$_4$N)$_2$Mo$_6$O$_{19}$ **2** [10] in acetonitrile were mixed at 25°C, dark red-brown crystals of **4** were formed according to the stoichiometry in Eq. 1.



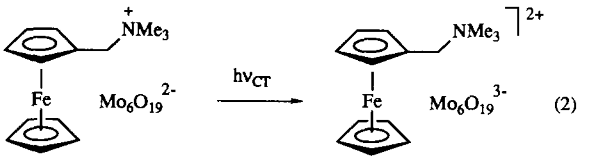
Similarly, treatment of the hexatungstate salt (Bu$_4$N)$_2$-W$_6$O$_{19}$ **3** [10] under the same conditions led to separation of bright red crystals of the corresponding ferrocenyl–tungstate salt **5** in ca. 90% yield.

The diffuse reflectance (UV-VIS) spectrum of the dark red-brown charge-transfer salt **4** in Fig. 3 (as a 2.5% dispersion in neutral alumina) showed a pronounced low-energy tail that extended from 550 nm to well beyond 750 nm. Spectral (digital) subtraction of the component spectra (i.e. of **1** and **2** individually) yielded the difference spectrum (Fig. 1, inset) consisting of a very broad featureless charge-transfer band of **4** with $\lambda_{max} = 550 \pm 5$ nm (fwhm ca. 6,000 cm^{-1}). The corresponding hexatungstate salt **5** afforded a similar set of diffuse reflectance spectra (Fig. 4); indeed, the visual distinction of the bright red CT salt **5** is reflected in a rather sharp CT band ($\lambda_{max} = 550 \pm 5$ nm, fwhm ca. 3,000 cm^{-1}) in which the 550–750 nm component is absent. The spectral red-shift of the hexamolybdate CT salt **4** relative to the hexatungstate analogue **5** is consistent with the enhanced strength of the acceptor moiety as indicated by the more positive value of the cyclic voltammetric reduction wave of $Mo_6O_{19}^{2-}$ compared to $W_6O_{19}^{2-}$ in Table 1. [It is interesting to note that donor strength of the ferrocenyl group in **1** is reduced by 0.2 V by the attachment of the cationic trimethylammonio substituent].

The charge-transfer transition in **4** and **5** are inherent to the crystalline state because the red-brown colors are bleached when the salts are dissolved in dimethylformamide. The latter indicates that the electrostatic binding of the trimethylammonio group to the anionic polyoxometalate in the solid state represents the primary donor-acceptor attraction in **4** and **5** [11]. As such, we believe the charge-transfer character of the salts is enforced by the proximal tethering of the ferrocenyl group. The latter is consistent with the singular absence of charge-transfer absorption bands when either the $Mo_6O_{19}^{2-}$ or $W_6O_{19}^{2-}$ salt is exposed to ferrocene itself, even at very high donor concentrations.

2. Transient intermediates from the laser-flash photolysis spectroscopy of charge-transfer salts

The charge-transfer character of **4** and **5** was confirmed by the laser-flash photolysis of the crystalline salts (as 10% dispersions in neutral alumina). The application of a 25 ps laser pulse at 532 nm (obtained by the frequency doubling of the output of the Nd^{3+} : YAG laser) was utilized to excite specifically the charge-transfer band of $[cpFecpCH_2N(CH_3)_3]_2Mo_6O_{19}$, **4** and $[cpFecpCH_2N(CH_3)_3]_2W_6O_{19}$, **5**. Thus the transient difference spectrum in Fig. 5 obtained by diffuse reflectance is a spectral composite representing the charge-transfer excited state, i.e.:



(2)

For the spectral comparison, the absorption spectrum of the reduced $Mo_6O_{19}^{3-}$ **2**$^-$, was obtained spectroelectrochemically by cathodic reduction of **2** at −0.45 V in acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$. Analogously, the absorption spectrum of the oxidized ferricinium dication **1**$^+$ was determined independently by the anodic oxidation of the ferrocenyl-methyl(trimethylammonio) salt **1** at 0.65 V vs. SCE. The transient absorption in Fig. 5 is thus consistent with the superposition of the weak absorption band of **1**$^+$ (1 mM) with $\lambda_{max} = 628$ nm ($\epsilon = 340$ M^{-1} cm^{-1}) and **2**$^-$ (1 mM) with $\lambda_{max} = 502$ nm ($\epsilon = 365$ M^{-1} cm^{-1}). The very broad band of **2**$^-$ ($\lambda_{max} = 790 \pm 10$ nm; $\epsilon = 170$ M^{-1} cm^{-1}) continues into the near IR and is responsible for the grey-brown aspect of $Mo_6O_{19}^{3-}$ salts [6]. The negative absorbance in the transient spectrum at ca. 550 nm is caused by the bleaching of the ground-state CT absorption upon laser excitation. The very short-lived transient disappeared within the laser pulse width, indicative of a rapid back-electron transfer in Eq. 2. A similar spectral transient with the same spectral features was also observed when the charge-transfer salt **5** was subjected to the 532 nm laser-flash photolysis under similar conditions.

3. Experimental details

Methyl triflate (2.71 g, 16.50 mmol) was added dropwise under argon to a stirred solution of dimethylaminomethylferrocene (4.00 g, 16.45 mmol) in dry THF (40 mL). The mixture was stirred for 20 min and the solvent was then removed in vacuo. The solid was filtered off and washed with Et_2O (50 mL). Recrystallization from THF (180 ml) gave a yellow solid: 5.70 g, 86% yield (based on dimethylaminomethyl-ferrocene). ^1H NMR (300 MHz, CD_3CN) δ 2.88 (s, CH_3, 9H), 4.23 (s, cp, 5H), 4.30 (s, CH_2, 2H), 4.37 (t, cp, 2H), 4.44 (t, cp, 2H).

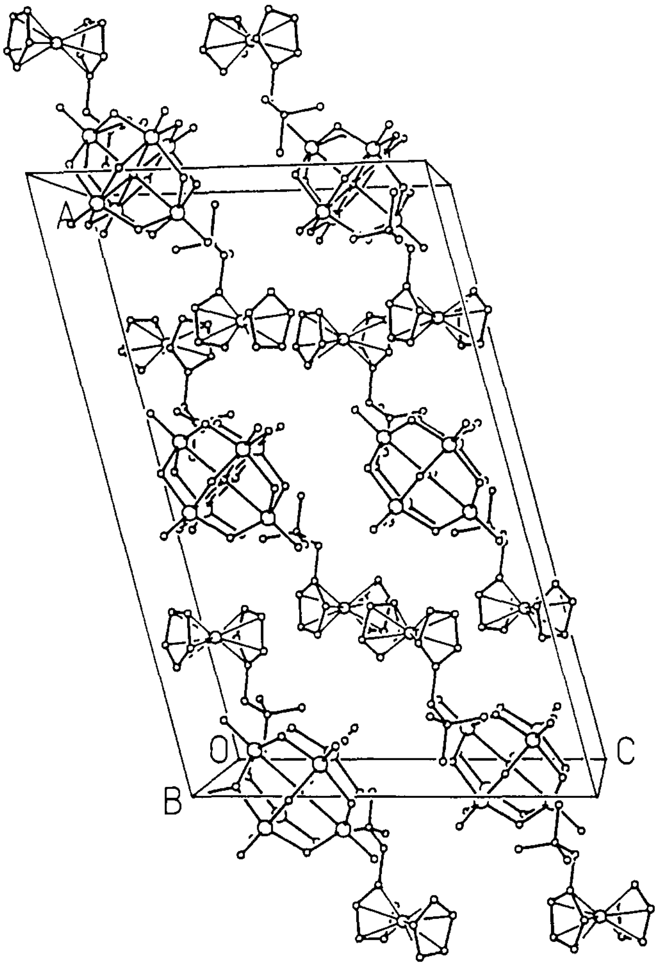


Fig. 3. Unit cell of the charge transfer salt $[cpFecpCH_2NMe_3]_2Mo_6O_{19}$, **4** showing the alternating layers of the cationic donor and anionic acceptor in the crystal.

Crystal data: $[C_{14}H_{20}NFe]_2Mo_6O_{19}$, dark-brown wedge, 0.60 × 0.35 × 0.20 mm, monoclinic, $I2/c$; a =

Table 1

The reduction potentials of the polyoxometalates acceptors **2** and **3**, and the oxidation potential of the ferrocenyl cation **1** in relation to that of ferrocene [a]

Donor/Acceptor	E_{ox}/V [b]	E_{red}/V
$Mo_6O_{19}^{2-}(Bu_4N^+)$		−0.42
$W_6O_{19}^{2-}(Bu_4N^+)$		−0.92
$cpFecpCH_2N(CH_3)_3^+(CF_3SO_3^-)$	+0.62	
cpFecp [c]	+0.41	

[a] By cyclic voltammetry with Pt electrodes at 0.5 V sec^{-1} of 5 mM solutions in acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ as the supporting electrolyte. [b] Volts vs. SCE. [c] Ref. [8].

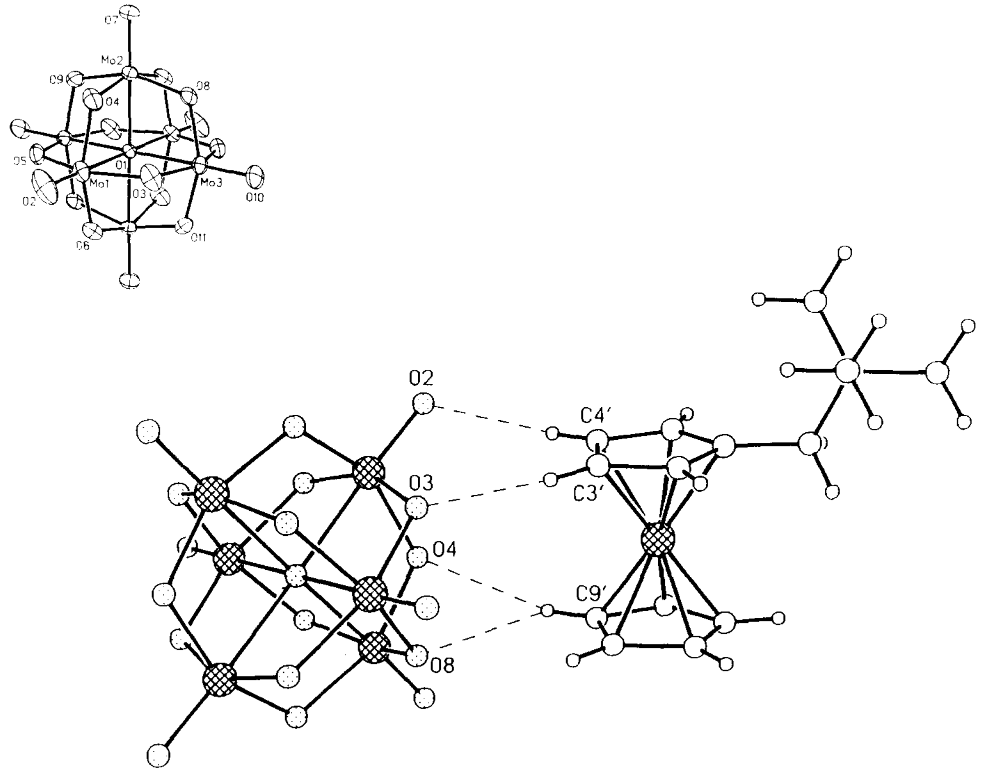


Fig. 4. ORTEP diagram of the electron donor-acceptor salt obtained as the 2:1 charge-transfer complex of $cpFecpCH_2N^+Me_3$ and $Mo_6O_{19}^{2-}$, showing the nearest interactions between the hydrogen atoms of the cyclopentadienyl ligand and the oxygen atoms on the surface of the hexamolybdate acceptor. Inset: complete atom labelling scheme for the polyoxometalate moiety.

24.861(8) Å, $b = 10.444(2)$ Å, $c = 15.649(4)$ Å, $\beta = 104.10(2)°$, $Z = 4$; $V = 3941$ Å^3; $T = 223$ K; $F.W. = 1396.04$ g mol^{-1}; $D_c = 2.35$ Mg m^{-3}; absorption coefficient $\mu = 2.60$ cm^{-1}; radiation (Mo-Kα) $\lambda = 0.71073$ Å; collection range $4° \leq 2\theta \leq 50°$; scan width $\Delta\theta = 1.25 + (K\alpha_2 - K\alpha_1)°$; total data collected 3817; independent data $I > 3\ \sigma(I)$ 3463, total variables 260; $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, 0.027; $R_w = [\Sigma w(| F_o | - | F_c |)^2 / [\Sigma w | F_o |^2]^{1/2}$, 0.027; weights $w = \sigma(F)^{-2}$. The structure was solved by the SHELXTL direct methods program.

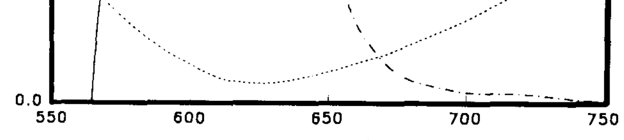


Fig. 5. Transient absorption spectrum taken at 25 ps (———) following the application of the 532 nm laser pulse to a 10% dispersion of $[cpFecpCH_2NMe_3]_2Mo_6O_{19}$ **4** in neutral alumina. The reduced hexamolybdate acceptor $Mo_6O_{19}^{3-}$, **2**$^-$ (- - - - - -), $\lambda_{max} = 628$ nm ($\epsilon = 340$ M^{-1} cm^{-1}) and the oxidized ferrocenyl donor $cpFe^+cpCH_2N^+Me_3$, **1**$^+$ (·—·—·), $\lambda_{max} = 502$ nm ($\epsilon = 365$ M^{-1} cm^{-1}) units are presented as the component spectra.

Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

Aknowledgements

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