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Electrochromism and X-ray Crystal Structure of a Mixed-Valence Charge-Transfer Complex $[(CH_3)_2NC_6H_4NH(CH_3)_2]_4[(C_4H_9)_4N]SiMo_{12}O_{40}$

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The study of electrochromic materials has attracted great interest in recent years due to their potential applications in displays, imaging devices, smart windows, and energy conservation.[1−5] Previous papers on electrochromism have emphasized organic materials, and metal oxides such as WO_3, MoO_3, V_2O_5, and NiO.[6−11] An electrochromic material is one whose absorption spectrum changes reversibly when it is subjected to a redox reaction. Organic materials have some advantages in terms of their easily designed structural diversity as well as the broad range of decoloring and fast coloration processes. But they are generally not very stable, and the repetition lifetime is short. Compared with organic materials, metal oxides are very stable even at high temperatures; however, they generally possess only a single color change. To obtain a new type of electrochromic material that can overcome the above disadvantages of these two kinds of materials, we have tried to combine organic materials and inorganic materials. The electrochromism of heteropolyacids has been reported.[12−14] Here, we have chosen an organic cation as the electron donor and a polyoxoanion as an electron acceptor to afford a novel type of mixed-valence, charge-transfer (CT) salt. The complex does not dissolve in water and common organic solvents, and the polyanion $SiMo_{12}O_{40}^{4-}$ can reversibly accept several electrons while keeping its gross structure unchanged. The above characteristics suggest that such CT salts could be quite interesting for a wide range of applications. A spin-coated film of the title complex was made from its DMF solution. Its electrochromism was studied, and shows good characteristics. As far as we know, this is the first example of a CT salt whose electrochromism was investigated.

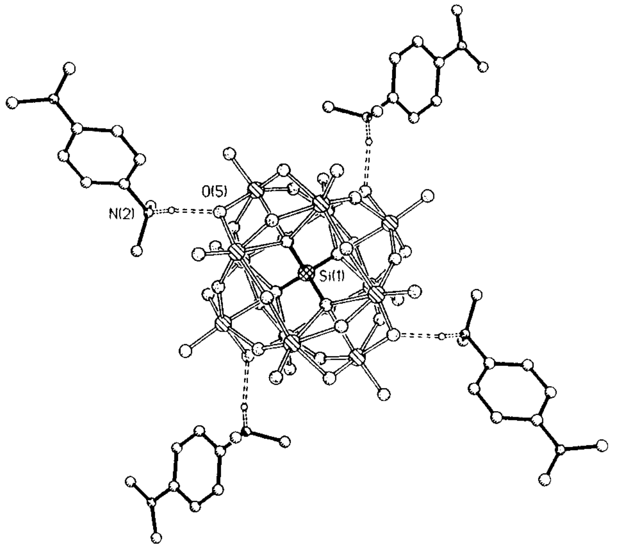

Figure 1. Molecular structure of the complex (the disordered $(C_4H_9)_4N^+$ has been omitted for clarity).

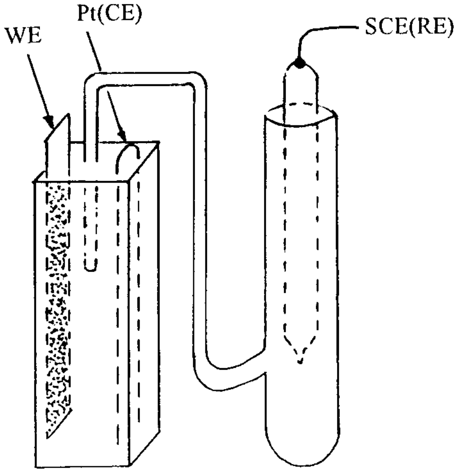

Figure 2. Spectroelectrochemical cuvette cell showing the working electrode (WE), the saturated calomel reference electrode (RE), and the platinum counter electrode (CE).

The $(Bu_4N)_4SiMo_{12}O_{40}$[15] (0.23 g, 0.1 mmol), and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (tmpd, 0.066 g, 0.4 mmol) were mixed in 25 cm^3 acetonitrile. The mixture was refluxed for 2 h with stirring. After cooling to room temperature, a green precipitate was filtered off by suction and washed three times with acetonitrile, yield 90%. Green prismatic crystals of the title complex were obtained from DMF solution by diffusion of ether. Anal. Calcd for $C_{56}H_{104}Mo_{12}N_9O_{40}Si$: C, 24.7; H, 3.8; N, 4.6. Found: C, 24.8; H, 3.6; N, 4.5%. A single-crystal X-ray diffraction study showed that the structure of the complex is tetragonal with space group *I*41/*a* (unit-cell constants $a = 24.359(4)$ Å, $c = 14.384(5)$ Å, $V = 8535(5)$ Å^3, $Z = 4$, $d_{calc} = 2.119$ g cm^{-3}. $\mu = 1.804$ mm^{-1}, 3582 reflections collected, 2042 observed ($F > 4.0\sigma(F)$), $F_{gof} = 1.20$, $R = 3.75\%$ and $Rw = 4.38\%$).

An ORTEP of the complex is shown in Figure 1. The X-ray crystal structure analysis indicates that the complex contains a reduced polyanion $SiMo_{12}O_{40}^{5-}$, four tmpd$^+$ cations and one $(C_4H_9)_4N^+$ cation. Thus, there are two types of organic cations in the complex, tmpd$^+$ and $(C_4H_9)_4N^+$. The $(C_4H_9)_4N^+$ cation is severely disordered and is not discussed here. The other cation,

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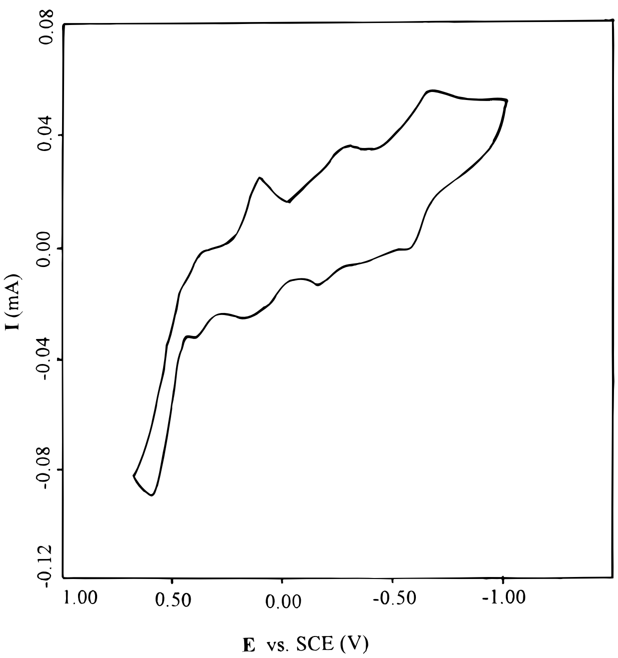

Figure 3. Cyclic voltammogram for the film of the title compound on ITO glass (1.5 cm^2) in 0.5 M $LiClO_4$, $\nu = 50$ mV/s.

tmpd$^+$, forms strong hydrogen bonding with a protonated hydrogen atom of a $NHMe_2$ group. The corresponding N(2) atom actually assumes psuedotetrahedral symmetry,[16] which is clearly shown by a Fourier difference map. Such sp^3 hybridization of the N(2) atom is also in accord with the bond distances N(2)−C(5) 1.484(9) Å and N(2)−C(9) 1.490(9) Å. On the other hand, the related nonprotonated N(1)−C(1) and N(1)−C(2) distances are 1.409 and 1.403 Å, respectively. The hydrogen bonds distances are N(2)···O(5) (2.861 Å) and C(4)···O(9) (3.158 Å), which indicate the presence of strong interactions between the polyanion and the tmpd$^+$ cations.

The ESR spectrum of the CT salt at 110 K indicates the presence of a single isotropic signal $g = 1.948$, line width $\Delta H = 33$ G, which is ascribed to the Mo^{5+}. The value is close to those observed in similar polyoxoanions containing Mo^{5+} ($S = {}^1/_2$) species.[18,19] No hyperfine split ESR signal of Mo^{5+} of the complex has been observed, probably due to a rapid intraionic hopping of the unpaired electron, comparable with the ESR time scale.[17]

Electrochromism Measurement. A film of the title complex was prepared by spin-coating its solution in DMF on a cleaned indium−tin oxide (ITO) coated glass substrate. A classical three-electrode electrochemical cell was used for electrochemical measurements. A three-electrode cuvette cell, as shown in Figure 2, was used for the spectroelectrochemical measurements. The spin-coated film of the complex was used as the working electrode. The conductivity of the ITO glass substrate was about 50 (Ω cm)$^{-1}$. A calomel reference electrode and a platinum counter electrode were used. The electrical conductivity was measured by the Vander Pauw method on compressed pellets by the two-probe d.c. method at room temperature.[20]

Table 1. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)[a]

	x	*y*	*z*	*U*(eq)
Mo(1)	4698(1)	6511(1)	3009(1)	40(1)
Mo(2)	5747(1)	6266(1)	1159(1)	39(1)
Mo(3)	4007(1)	7703(1)	2975(1)	41(1)
Si(1)	5000	7500	1250	32(1)
O(1)	5205(2)	6220(2)	2029(3)	41(1)
O(2)	4259(2)	7018(2)	3620(3)	44(1)
O(3)	3501(2)	7170(2)	2328(3)	42(1)
O(4)	3898(2)	8196(2)	2015(3)	40(1)
O(5)	4112(2)	6248(2)	2266(3)	40(1)
O(6)	4654(2)	8054(2)	3312(3)	41(1)
O(7)	6148(2)	5715(2)	1379(3)	52(1)
O(8)	4741(2)	6001(2)	3787(3)	56(1)
O(9)	4539(2)	7214(2)	1904(3)	30(1)
O(10)	3564(2)	7919(2)	3789(3)	54(1)
N(1)	8546(3)	5070(3)	−1078(5)	93(1)
N(2)	7335(3)	6605(3)	1005(4)	59(1)
C(1)	9109(4)	5137(4)	−1275(6)	142(1)
C(2)	8271(4)	4701(5)	−1665(5)	182(1)
C(3)	8511(3)	5806(3)	56(5)	68(1)
C(4)	8222(3)	6174(3)	576(5)	57(1)
C(5)	7655(3)	6200(3)	457(4)	51(1)
C(6)	7393(3)	5863(3)	−138(4)	56(1)
C(7)	7680(3)	5490(3)	−666(5)	67(1)
C(8)	8258(3)	5449(3)	−584(5)	61(1)
C(9)	7357(3)	6478(4)	2017(5)	93(1)
C(10)	7495(3)	7179(3)	839(5)	98(1)
N(3)	5000	7500	6250	81(1)
C(11)	4783(5)	7857(4)	5525(5)	91(1)
C(14)	4342(6)	9370(4)	5740(6)	124(1)
C(12)	4744(5)	8425(4)	5982(6)	111(1)
C(13)	4305(5)	8760(4)	5469(6)	105(1)
C(13′)	4531(5)	9052(4)	5783(6)	109(1)
C(11′)	4830(5)	8041(4)	5745(6)	97(1)
C(14′)	4012(5)	8943(5)	5177(6)	118(1)
C(12′)	4595(6)	8524(5)	6287(6)	101(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. The s.o.f = ${}^1/_2$ for atoms C(11), C(12), C(13), C(14), C(11′) C(12′), C(13′), C(14′).

Electrochromic Properties. The electrical conductivity of the title compound at room temperature was $\sigma(300\ \mathrm{K}) = 3.6 \times 10^{-4}$ (Ω cm)$^{-1}$.

A cyclic voltammogram of the CT salt in the region +0.6 to −1.0 V is displayed in Figure 3. The diagram is complicated and shows five groups of oxidized and reduced peaks that correspond to various color changes. From Figure 3, it can be seen that the complex exhibits three reduction steps and two oxidation steps. This indicates that different reduced states of the polyoxoanion exist under different applied potentials:

$$[SiMo_{12}O_{40}]^{4-} \xrightarrow[+0.346]{-e} [SiMo_{12}O_{40}]^{5-} \xrightarrow[+0.138]{+e} [SiMo_{12}O_{40}]^{6-} \xrightarrow[-0.191]{+e} [SiMo_{12}O_{40}]^{7-} \xrightarrow[-0.628]{+e} [SiMo_{12}O_{40}]^{8-}$$

The oxidation peak at +0.54 V has no corresponding reduction peak, which may be due to the formation of the N$^{\bullet+}$ cation radical, where the radical is very unstable and converts to N quickly by reaction with the solvent. The color of the salt changes from green to violet when

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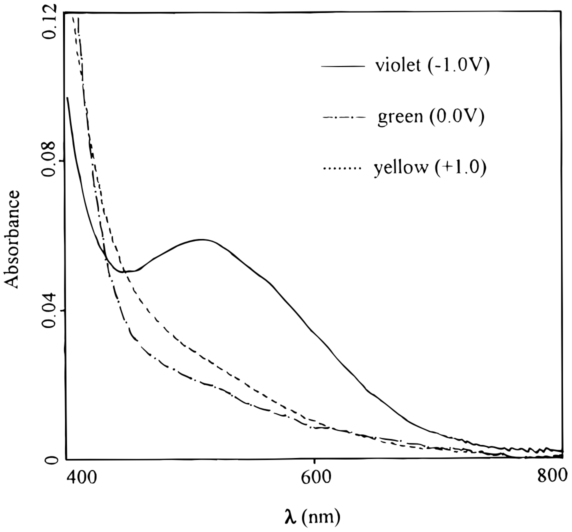

Figure 4. Absorption spectra of the title compound film at different voltage.

it is reduced, and turns into yellow upon oxidation. The color change is very sensitive and highly varied.The UV spectra of the spin-coated film at various potentials are shown in Figure 4. The UV curve does not show a large difference when the applied potential is 0.0 and +1.0 V, but the color change from green to yellow is distinct. When the applied potential is −1.0 V, the film has a broad absorption at 518 nm, and the film then appears violet. The entire electrochromic process can be discribed as follows:

$$\text{yellow} \xrightarrow{+1.0\text{ V}} \text{green} \xrightarrow{-1.0\text{ V}} \text{violet}$$

The rich and varied color change is similar to that of phthalocyanine, which has been extensively investigated:[21]

$$\text{red} \xrightarrow[+1.0\text{ V}]{} \text{green} \xrightarrow[-0.8\text{ V}]{} \text{blue} \xrightarrow[-1.20\text{ V}]{} \text{violet}$$

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, complete bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and isotropic thermal parameters for (8 pages); structure factor table (7 pages). Ordering information is given on any current masthead page.

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