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Synthesis and Characterization of Two Charge-Transfer Salts Based on Keggin-Type Polyoxometalates and Morpholinebiguanide[1]

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Abstract—Two new inorganic-organic salts, formulated as $(C_6H_{13}N_5OH)_2[HPMo_{12}O_{40}] \cdot 5H_2O$ and $(C_6H_{13}N_5OH)_3[PW_{12}O_{40}]$, were synthesized and characterized by elemental analysis, IR, ESR, diffuse reflectance spectra, thermogravimetry, and X-ray photoelectron spectroscopy. Solid diffuse reflectance spectra showed charge-transfer interactions between the inorganic and organic moieties in the solid state. Salt I had strong photosensitivity for UV light or X-ray irradiation, and its photochromic reaction under UV light was found to exhibit first-order kinetics.

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The polyoxometalate-based inorganic-organic charge-transfer salts have special properties and potential applications in catalysis, biology, and material science [1–3] and have drawn tremendous attention in the past decade [4]. Heteropolyacids with Keggin structure are among the most important polyoxometalates and usually used as inorganic building blocks to form charge-transfer salts with a number of organic substrates containing N, S, and O atoms by ionic interactions as well as by hydrogen bonds or van der Waals interactions [5–9]. In our past investigation, we have prepared a few charge-transfer salts based on heteropolyacids with Dawson structure [10, 11].

Morpholinebiguanide (N',N'-anhydrobis(2-oxyethyl)biguanide) contains both delocalized π electrons and a lone pair of electrons and is expected to combine with heteropolyacids to obtain charge-transfer salts *via* proton transfer reactions and electrostatic and hydrogen-bonding interactions. To the best of our knowledge, the charge-transfer salts of morpholinebiguanide associated with heteropolyacids have not been reported so far. In this work, we choose morpholinebiguanide hydrochloride ($C_6H_{13}N_5O \cdot HCl$) as the source of organic cations. Herein, we report the synthesis and properties of two charge-transfer salts based on Keggin-type polyoxometalates and morpholinebiguanide.

EXPERIMENTAL

All reagents used for the synthesis and physical measurements were reagent grade and used without further purification.

Elemental analyses were performed on a Varia EL III Elemental analyzer and an ICP-AES (Inductively Coupled Plasma-Atomic Emission spectroscopy) analyzer. IR spectra were measured on a Nicolet 380 FT-IR spectrometer using KBr pellets in the 4000–400 cm^{-1} region. Solid diffuse reflectance spectra (DRS) were registered on a VARIAN Cary 5000 UV-Vis-NIR spectrophotometer with $BaSO_4$ as reference. A 125-W high-voltage mercury lamp was used as radiation light source for photochromism experiments. Samples were maintained in contact with air and placed below the mercury lamp at a distance of 15 cm during irradiation. X-ray photoelectron spectra (XPS) were recorded on a KRATOS XSAM 800 spectrometer with a MgK_α (1253.6 eV) achromatic X-ray source. ESR spectrum was recorded on a JES-FE3AX spectrometer. Experimental conditions used: microwave frequency, 9.205 GHz; modulation frequency, 100 KHz, modulation amplitude, 0.5 mT, microwave power, 1.00 mW. Thermogravimetry (TG) measurements were carried out on a Netzsch STA 449C thermal analyzer in static air with a heating rate of 10°C/min.

Synthesis of $(C_6H_{13}N_5OH)_2$ $[HPMo_{12}O_{40}] \cdot 5H_2O$ (I) and $(C_6H_{13}N_5OH)_3[PW_{12}O_{40}]$ (II). $C_6H_{13}N_5O \cdot HCl$ (0.83 g, 4.0 mmol) was added to a solution of $H_3PMo_{12}O_{40} \cdot 20H_2O$ (2.19 g, 1.0 mmol) in 80 cm^3 of distilled water. The mixture was stirred for 30 min, giving a large quantity of light yellow precipitate. The precipitate was filtered out, washed repeatedly with distilled water until the pH of the wash water approximated to 7, and dried in an evacuated desiccator. The similar procedure was applied for the synthesis of salt **II** to obtain its light yellow powder. Salt **I** must be protected from light

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during preparation and conserved in light-protective containers because of its photosensitivity.

For $C_{12}H_{39}N_{10}PMo_{12}O_{47}$ (**I**)
anal. calcd, %: C, 6.38; H, 1.74; N, 6.20; P, 1.37; Mo, 50.99; H_2O, 3.99.
Found, %: C, 6.25; H, 1.81; N, 6.25; P, 1.39; Mo, 49.56; H_2O, 4.15.

For $C_{18}H_{42}N_{15}PW_{12}O_{43}$ (II)
anal. calcd, %: C, 6.37; H, 1.25; N, 6.19; P, 0.91; W, 65.01.
Found, %: C, 6.45; H, 1.22; N, 6.02; P, 0.94; W, 65.35.

RESULTS AND DISCUSSION

Double replacement reactions between morpholinebiguanide hydrochloride and two Keggin-type heteropolyacids produced two charge-transfer salts. They are soluble in acetone but insoluble in water, which makes it possible to filter off the unreacted precursors by water washing.

The main IR spectral data of the two charge-transfer salts are presented in comparison with those of morpholinebiguanide hydrochloride (Table 1). The IR spectra of both salts have the characteristic bands of the Keggin anions in a region of 790–1100 cm^{-1} assigned to P–O, M=O, and M–O–M (M=Mo, W) stretching vibrations [9], which indicates that the polyoxoanions in both salts retain Keggin structure. The bands higher than 1100 cm^{-1} are assigned to morpholinebiguanide [12].

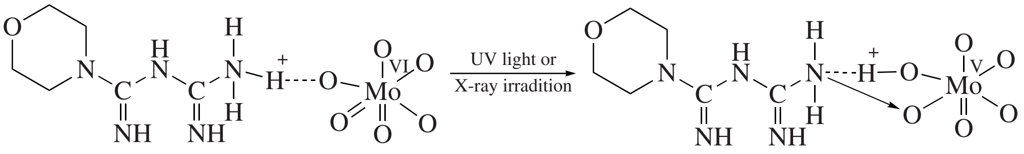
Figure 1 compares the reflectance electronic spectra of salts **I** and **II** with those of the corresponding heteropolyacids. For heteropolyacids (Fig. 1, curve *1*), the bands at lower wavelengths are assigned to the $O_d \longrightarrow M$, while those at higher wavelengths are ascribed to the $O_{b/c} \longrightarrow M$. From $H_3PW_{12}O_{40}$ to salt **II**, the low-energy tail of the absorption band shows quite a large redshift. From $H_3PMo_{12}O_{40}$ to **I**, the low-energy tail of the absorption band has such a large blueshift that the $O_{b/c} \longrightarrow Mo$ band disappears. In fact, the low-energy bands at *ca*. 400–500 nm are characteristic of the synthesized charge-transfer salts and responsible for their yellow color, which are assigned to the charge transfer between morpholinebiguanide and heteropolyacid anions and, thus, give direct evidence for the intermolecular electronic interactions between the inorganic and organic moieties in the solid state [13].

Salt **I** shows no significant absorption from 500 to 800 nm before UV irradiation (Fig. 2a). After UV irradiaion, two bands at around 520 and 720 nm are observed, which are characteristic of reduced Keggin heteropolyanions, attributed to *d–d* transition and intervalence charge transfer (IVCT, $Mo^{5+} \longrightarrow Mo^{6+}$), respectively [14]. The *d–d* band appears as an unobvious shoulder because of being obscured by the IVCT band [15]. The appearance of the IVCT band shows that electron transfer occurs between the organic substrate and $[PMo_{12}O_{40}]^{3-}$, resulting in the reduction of the heteropoly anion $[PMo_{12}O_{40}]^{3-}$ into heteropoly blue $[PMo_{12}O_{40}]^{4-}$ with the simultaneous oxidation of the organic substrate [5]. This has been verified by the ESR spectra (Fig. 3). At 77 K no ESR signal is observed for the nonirradiated sample, but the irradiated sample shows one defined Mo^{5+} isotropic signal with $g = 1.9486$, which is close to the value reported in the literature [16]. Observation of the ESR signal also suggests that the electron transfer takes place and that $[PMo_{12}O_{40}]^{3-}$ gains electrons as an acceptor during UV irradiaion.

After UV irradiation, the IR spectra of salt I shows a little difference from the nonirradiated one (Fig. 4). The bands of $Mo–O_b–Mo$ and $Mo–O_c–Mo$ have red shift by 15 and 9 cm^{-1}, respectively. However, the $P–O_a$ and $Mo=O_d$ characteristic vibration bands remain almost unshifted. This indicates that the bridged oxygen atoms are chemically active and play a key role in the photochemical process [17].

The charge transfer in salt I during the photochromic process was further investigated using XPS spectroscopy. The molybdenum 3*d* XPS spectra of salt **I** before and after UV irradiation are almost identical (Fig. 5). The binding energies of Mo 3*d* can be resolved into the Mo 3*d*5/2 and Mo 3*d*3/2 doublet caused by the spin-orbit coupling through the Gaussian deconvolution. However, the Mo 3*d* XPS spectra before UV irradiation (Fig. 5, curve *1*) show the binding energies of 232.8 and 235.6 eV for the Mo 3d doublet of Mo^{6+} and 231.5 and 234.3 eV for that of Mo^{5+}. Meanwhile, the nonirradiated sample changes to blue after XPS measurement, which suggests that the photoreduction of $[PMo_{12}O_{40}]^{3-}$ occurs when the sample is exposed to the X-ray source during XPS measurement [14].

When the colored powder of salt **I** is exposed in air, it cannot return to its original color even if it has been placed in the dark for three months, indicating that its photochromism is almost irreversible. The photochromic mechanism can be described as follows:



This is similar to the photochromic mechanism proposed by Yamase [18]. Photoexcitation results in the ligand-to-metal (O ⟶ Mo) charge-transfer (LMCT) transition, which produces a hole at the oxygen atom and the transfer of a proton from hydrogen-bonded amino nitrogen towards the bridge oxygen atom at the photoreduced site in the MoO_6 octahedral lattices. Simultaneously, the hole resulting from the LMCT transition interacts with the nonbonding electrons on the amino nitrogen atom to form a charge-transfer complex [19] in which Mo^{5+} is produced.

Referring to the method used in the solid photochromic kinetics by Kawato et al. [20] and Liu et al. [21], provided that the production of the reduced heteropolyanions is proportional to the absorbance at 720 nm for salt **I**, the experimental data are treated with the following integrated equations:

$$A_t - A_\infty = kt + b, \quad (1)$$

$$-\ln(A_\infty - A_t) = kt + b, \quad (2)$$

$$1/(A_\infty - A_t) = kt + b, \quad (3)$$

$$1/(A_\infty - A_t)^2 = 2kt + b, \quad (4)$$

where k is rate constant, A_∞, and A_t are the observed reflection data measured at the beginning, at the end and at time t of the reaction, respectively. The linear regression data based on Eqs. (1)–(4) are presented in Table 2.

Table 1. Most important IR bands (cm^{-1}) and their assignment*

Vibration	$C_6H_{13}N_5O \cdot HCl$	Salt **I**	Salt **II**
$\nu_{as}(M–O_d)$		960 s	978 v.s
$\nu_{as}(X–O_a)$		1061s	1079 v.s
$\nu_{as}(M–O_b–M)$		883 s	894 s
$\nu_{as}(M–O_c–M)$		796 v.s	816 v.s
ν(C=N)	1646 v.s	1633 s	1630 s
δ(NH)	1446 m	1444 m	1555 v.s, 1434 m
$\nu(C–NH_3^+)$	1514 s	1508 m	1504 m
ν(OH or NH)	3318 b.s; 3147 v.s	3429 b.s	3473 m, 3437 m, 3380 m, 3186 m

* b is broad; s is strong; v.s is very strong; m is medium; w is weak.

A good linear fit is found only between $-\ln(A_\infty - A_t)$ and t from Table 2 (also see Fig. 6), indicating that the photochromic reaction exhibits first-order or pseudo-first-order kinetics with rate constant $k = 1.20 \times 10^{-4}$ s^{-1}. Here, the last three measurement data are not used for kinetic analysis in view of errors caused by possible sub-

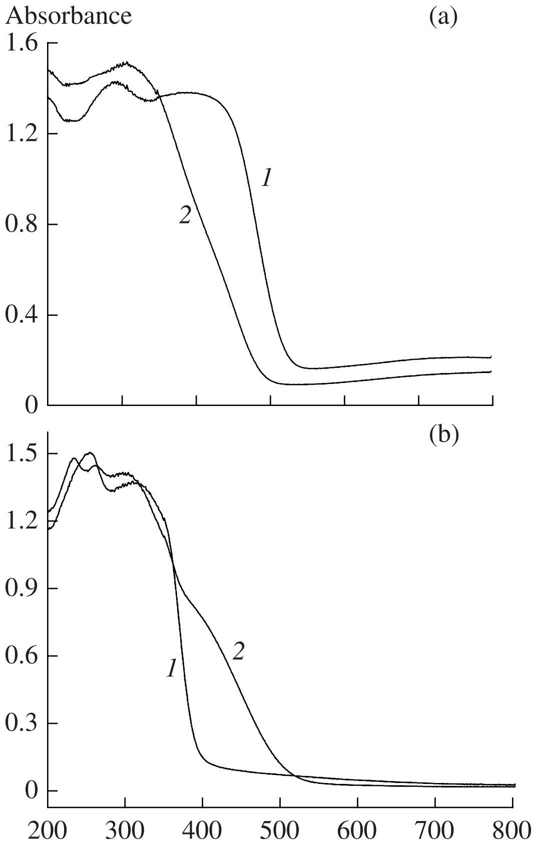


Fig. 1. Diffuse reflectance spectra of: a—$H_3PMo_{12}O_{40}$ (*1*) and $(C_6H_{13}N_5OH)_2[HPMo_{12}O_{40}] \cdot 5H_2O$ (*2*), b—$H_3PW_{12}O_{40}$ (*1*) and $C_6H_{13}N_5OH)_3[PW_{12}O_{40}]$ (*2*).

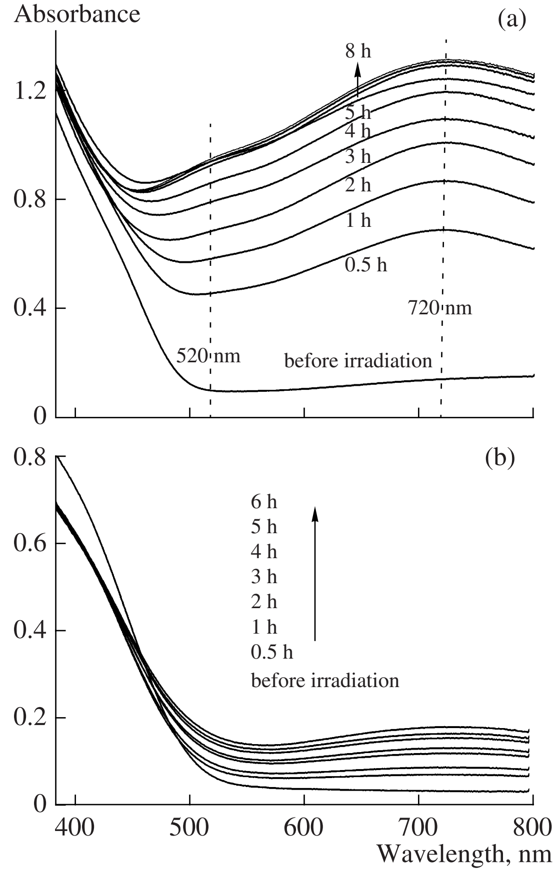


Fig. 2. Time dependences of the diffuse reflectance spectra of **I** (a) and **II** (b).

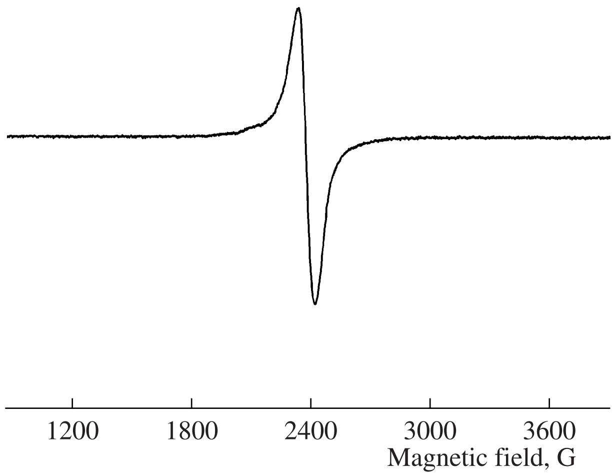


Fig. 3. ESR spectrum of the irradiated solid sample of **I** at 77 K.

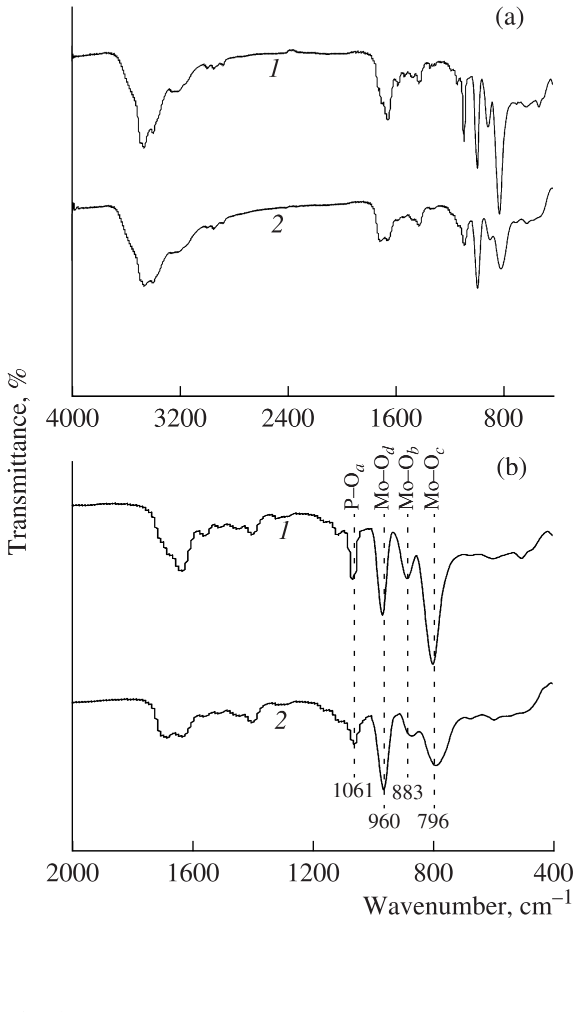


Fig. 4. IR spectra of **I** before coloration (*1*) and after UV irradiation for 30 min (*2*) between 4000 and 400 cm^{-1} (a) and between 2000 and 400 cm^{-1} (b).

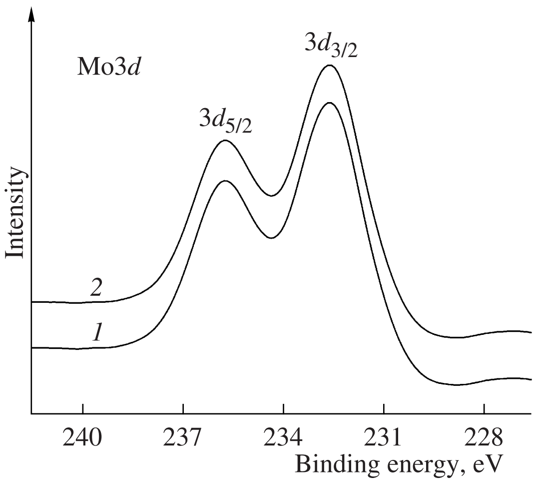


Fig. 5. XPS spectra of molybdenum 3*d* of **I** without UV irradiation (*1*) and with UV irradiation for 1 h (*2*).

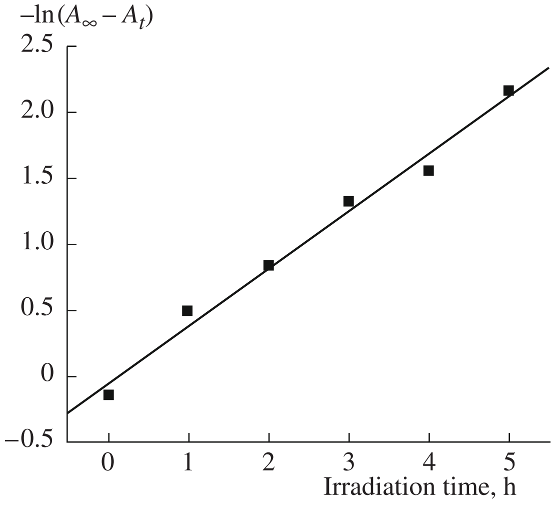


Fig. 6. First-order kinetics plot of photochromic reaction of **I**.

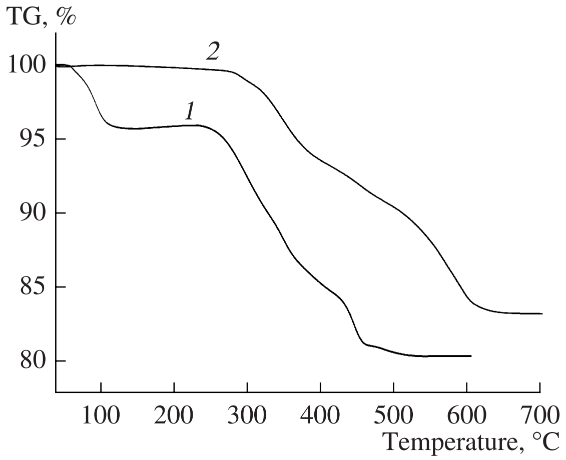


Fig. 7. TG curves of **I** (*1*) and **II** (*2*).

Table 2. Linear regression data for the photochromic kinetics of salt **I***

y (= $kt + b$)	k/h^{-1}	b	r
$A_t - A_\infty$	0.1866	–0.9314	0.9231
$-\ln(A_\infty - A_t)$	0.4328	–0.0457	0.9933
$1/(A_\infty - A_t)$	1.4172	0.1120	0.9402
$1/(A_\infty - A_t)^2$	0.1878	0.8579	0.9811

* A is absorbance; t is irradiation time (h); r is correlation coefficient; $1/(A_\infty - A_t)^2 = 2kt$.

sidiary reactions, variation in temperature for radiation, and repeating interrupt of irradiation for measurements.

The TG curves of salts **I** and **II** are showed in Fig. 7. The TG curve of salt **I** shows three stages. The first stage occurs in a temperature range of 25–130°C, which corresponds to the loss of five crystallization water molecules (found 4.15%, calcd 3.99%). The mass of salt I remains unchanged in the temperature range 130–230°C. The second stage (at about 230–455°C) has a mass loss of 14.55% due to the oxidative decomposition of two $C_6H_{13}N_5O$ molecules. The last mass loss stage (at about 455–520°C) is attributed to the removal of one constitution water molecule. The total mass loss (19.65%) is in good agreement with that of the calculated (20.35%).

The TG curve of salt **II** includes two stages. The first stage (at about 260–385°C) corresponds to the oxidative decomposition of one $C_6H_{13}N_5O$ molecule. The second stage (at about 385–635°C) is attributed to the oxidative decomposition of two $C_6H_{13}N_5O$ molecules and the loss of 1.5 water molecules. The total mass loss (16.59%) is in accordance with the calculated value (15.93%).

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