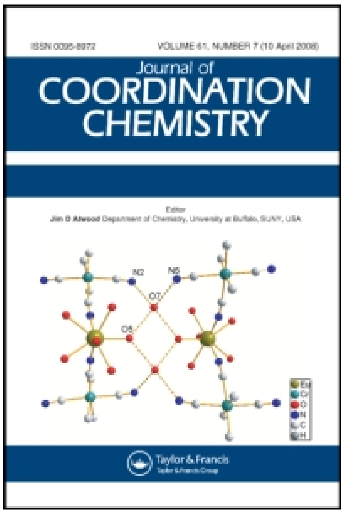

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SYNTHESIS, CHARACTERIZATION, PHOTOCHROMISM AND CRYSTAL STRUCTURE OF A CHARGE-TRANSFER COMPLEX BETWEEN AN ORGANIC SUBSTRATE AND A POLYOXOMETALATE $[C_{10}H_{10}N]_4GeMo_{12}O_{40} \cdot 6DMF$ ($C_{10}H_{10}N$ = 7-METHYL-QUINOLINE)

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SYNTHESIS, CHARACTERIZATION, PHOTOCHROMISM AND CRYSTAL STRUCTURE OF A CHARGE-TRANSFER COMPLEX BETWEEN AN ORGANIC SUBSTRATE AND A POLYOXOMETALATE $[C_{10}H_{10}N]_4GeMo_{12}O_{40} \cdot 6DMF$ ($C_{10}H_{10}N$ = 7-METHYL-QUINOLINE)

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A charge-transfer complex, $[C_{10}H_{10}N]_4GeMo_{12}O_{40} \cdot 6DMF$, between the heteropolymolybdate anion, $GeMo_{12}O_{40}^{4-}$ and the organic cation, protonated 7-methyl-quinoline has been synthesized and characterized. Light yellow crystals of the title compound as a DMF solvate of formula $[C_{10}H_{10}N]_4GeMo_{12}O_{40} \cdot 6DMF$ were crystallized from DMF by diffusing acetone vapor into the solution. Spectroscopic data support the presence of a significant electronic interaction between the electron-rich aromatic organic cations and the inorganic anion in the solid state. The complex is strongly photosensitive under irradiation with sunlight, resulting in charge-transfer by oxidation of the 7-methyl-quinoline and reduction of the polyoxometalate. The variable temperature ESR spectra indicate thermal electron delocalization occurs among the Mo atoms in the title compound.

Keywords: Photochromism; Crystal structure; Charge-transfer; Polyoxometalate

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INTRODUCTION

Polyoxometalates have received increasing attention due to their extensive usage and special properties, particularly in homogeneous catalysts and photochromism [1–3]. Most studies of photochromism have been made in solution [4–7]. The study of photochromism in the solid state is relatively less common; only a few polyoxometalates with photosenstivity properties have been studied crystallographically [8–11]. Hill and co-workers did original work in the field [10]. The title compound is light yellow in the dark and greenish when exposed to sunlight in an irreversible process. In order to ascertain the mechanism of photoreduction, the crystal structure of the title compound was analyzed and the photochromism properties investigated.

EXPERIMENTAL

Materials

All organic solvents used for synthesis and physical measurements were reagent grade and used without further purification. The $H_4GeMo_{12}O_{40}$ was prepared by the literature method [12].

Physical Measurements and Analyses

C, H and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra of samples were obtained as KBr pellets on a Nicolet 170SX FT-IR spectrometer. Solid state diffuse reflectance spectra were recorded on a Shimadzu UV-240 spectrometer. An ESR spectrum was recorded on a Bruker ER200-D-SRC spectrometer at X-band.

Preparation of the Title Compound

20 mL of 100 mM alcohol solution of $H_4GeMo_{12}O_{40}$ was added to 0.2 mL of an alcohol solution of 7-methyl-quinoline (50% V/V) while stirring. A yellow precipitate formed immediately. The precipitate was collected and dried on a fritted-glass funnel and recrystallized from DMF by diffusing acetone vapor into the solution. The crystals are sensitive to sunlight. Anal. Found: C, 24.6; H, 2.8; N, 4.5, Calcd. for $[C_{10}H_{10}N]_4GeMo_{12}O_{40} \cdot 6DMF$, C, 24.2; H, 2.9; N, 4.9%.

X-ray Structure Determination of the Title Compound

A light yellow crystal of the title compound was affixed to the end of a glass capillary and then mounted on the goniometer head of a CAD4 four-circle diffractometer. Accurate cell dimensions were obtained by least-squares refinement of 19 centered reflections ($\lambda(\text{MoK}\alpha) = 0.7103\,\text{Å}$). Crystal and data collection parameters along with the values for the residuals after final refinement are summarized in Table I.

Computations for data refinement and structure solution were performed on an IBM486 PC using the SHELXS86/SHELXL93 programs. The structure was solved by direct methods and completed by a series of Fourier synthesis and least-squares refinements. Hydrogen positions were not readily discernible from the electron density difference maps. All non-hydrogen atoms except the disordered atoms and the solvent molecules were refined anisotropically. Residual electron densities were observed around the solvent molecules which were believed to be DMF molecules although the oxygen atoms in some of them could not be located from the difference Fourier maps. The final extrema in the difference map are 1.695 to $-0.988\,\text{eÅ}^3$. Least-squares refinement of 300 parameters gave final reliability factors $R = 0.0789$, $R_w = 0.2011$ and GOF = 1.159. The data were corrected for absorption by a semiempirical (ψ scan) method. A weighting

TABLE I Crystallographic data for the title compound

Molecule formula	$C_{40}H_{40}N_4GeMo_{12}O_{40} \cdot 6DMF$
Molecule weight	2879.21
Color and habit	yellow polyhedral
Crystal size	$0.5 \times 0.5 \times 0.5\,\text{mm}^3$
Crystal system	Orthorhombic
Space group	Cmca
Unit cell parameters	$a = 14.323(1)$, $b = 30.552(9)$, $c = 20.177(3)$ Å $\alpha = \beta = \gamma = 90°$ $V = 8829(3)\,\text{Å}^3$ $Z = 4$
D_{calcd}	$1.836\,\text{gcm}^{-3}$
Radiation	graphite-monochromatized MoKα $\lambda = 0.71073$ Å
R_{int}	0.0061
Absorption coefficient	$2.050\,\text{mm}^{-1}$
Scan range	1.33° to 25.01°
Collection range	$0 \leq h \leq 17$, $0 \leq k \leq 36$, $0 \leq l \leq 23$
Reflection	4056
Unique data measured	4055
Data/restraints/parameters	4055/19/300
Goodness-of-fit on	1.159
Final R indices ($I > 2.0\sigma(I)$)	$R = 0.0789$, $R_w = 0.2011$
R indices (all data)	$R = 0.0919$, $R_w = 0.2093$
Residual extrema in final difference map	$+1.695$ to $-0.988\,\text{eÅ}^{-3}$

scheme utilizing weights of the form $w=[\sigma^2(Fo)^2+(0.0626P)^2+283P]^{-1}$ $(P=(Fo^2+2Fc^2)/3)$ was implemented. Scattering factors used were those for neutral atoms. Hydrogen atoms on the organic molecules were generated, those on the mirror plane were allowed to ride on their parent C atoms and those about the two-fold axis were fixed and given $U=0.08\,\text{Å}^2$. The bond parameters were not ideal particularly so in the disordered molecule on the two-fold axis. The molecules were constrained by fixing them to be regular naphthalene in the refinement procedure. The C(1)—C(10), C(1′)—C(10′) and N(b)—C(b2) bonds were also restrained by fixing the distances. The final atomic coordinates, bond distances and angles and a list of observed and calculated structure factors have been deposited as supplementary material with Jing-Ping Wang from whom copies are available.

RESULTS AND DISCUSSION

Synthesis

Dissolved polyoxometalate acids in an organic donor solvent induce a sizable red-shift in the charge-transfer absorption spectrum of the polyanion indicating an electronic interaction between the organic substrate and the inorganic anion [13]. Usually, it is difficult to isolate a stable solid product using alkylaromatics as the organic substrate [14, 15]. However by the introduction of a basic function, such as an amino group in the organic moiety, it is easy to separate the salt of the polyoxometalate. Among several organic substrates, 7-methyl-quinoline was chosen due to it strong basicity. When the heteropolymolybdate, $H_4GeMo_{12}O_{40}$, solution was mixed with the 7-methyl-quinoline, a new material far less soluble in alcohol than either of the components precipitated. This complex was recrystallized from DMF by diffusing acetone vapor into the solution to yield yellow solvated polyhedral crystals.

IR Spectra

Comparing the IR spectra of the title compound with that of $H_4GeMo_{12}O_{40}\cdot nH_2O$, the vibrational band of the Mo=Od bond in the title compound has a red-shift from 950 cm^{-1} to 948 cm^{-1}; the Ge—Oa bond has a blue-shift from 798 to 800 cm^{-1}; the Mo—Ob bond has a blue-shift from 870 to 871 cm^{-1}; and the Mo—Oc bond has a blue-shift from 760 cm^{-1} to 766 cm^{-1}. The results indicated that the bonds of Ge—O, Mo—Ob and Mo—Oc are strengthened while the Mo═Od bonds are weakened in the title compound. After the sample was irradiated under 300 W high pressure Hg lamp for two hours, the Mo—Ob and the Ge—O bonds have red-shifted 2 cm^{-1} and 1.3 cm^{-1}, respectively while the other bonds have a little shift, indicating that the Mo—Ob and Ge—O bonds were weakened after the anion was reduced.

UV Spectra

Figure 1 compares the diffuse reflectance electronic spectra of the title compound and the irradiated sample with $H_4GeMo_{12}O_{40}$. It is interesting to note that the low-energy tail of the charge-transfer absorption band of the title compound has a red-shift. This suggests that the interaction between the organic substrate and the polyoxometalate anion must play a role in the observed C.T. effect. There is a new absorption band in the spectrum of the

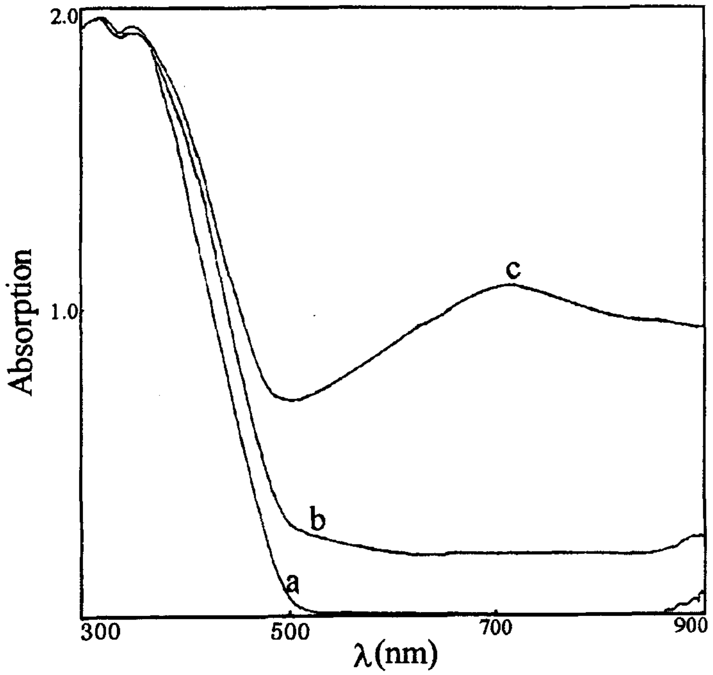

FIGURE 1 Reflectance electronic spectra of $H_4GeMo_{12}O_{40} \cdot nH_2O$ (a) the title compound (b) and the irradiated title compound (c). All spectra were obtained from a pellet which consisted of 90% sample and 10% MgO by weight. The base of the pellet is MgO.

irradiated sample at ca. 720 nm, ascribed to the IVCT ($Mo^{5+} \rightarrow Mo^{6+}$) band of the reduced anion $GeMo_{12}O_{40}^{5-}$.

ESR Spectra

The title compound appeared sensitive to visible light. The intense photochromism exhibited by irradiating the pure solid sample in sunlight is assigned to the intervalence charge transfer ($Mo^{5+} \rightarrow Mo^{6+}$) IVCT band of $GeMo_{12}O_{40}^{5-}$, indicating that electron transfer occurred between the organic cation and the inorganic anion, reducing $GeMo_{12}O_{40}^{4-}$ to heteropoly blue $GeMo_{12}O_{40}^{5-}$ with simultaneous oxidation of the organic cation. This has been verified by ESR spectra of the irradiated sample. The low temperature (110 K) ESR spectrum of the irradiated sample is shown in Figure 2(f) whereas the unirradiated sample has no signal. The signal of

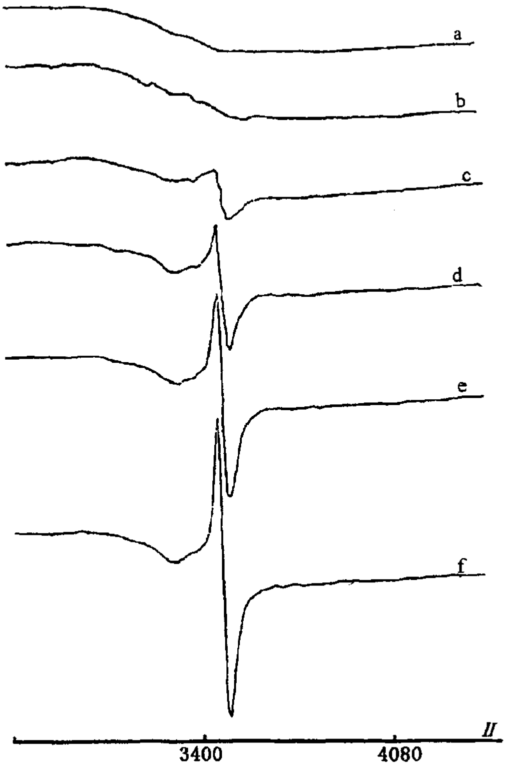

FIGURE 2 X-band ESR spectra of the title compound at different temperatures. a: 294 K; b: 240 K; c: 180 K; d: 150 K; e: 130 K; f: 110 K. The powder sample was irradiated for 30 min. by a 300 W Hg lamp.

$g = 1.94$ is ascribed to Mo^{5+}[9]. The ESR line widths are different at different temperatures (Fig. 2). Hyperfine lines appeared on the spectra at the low temperature. The broadening of the ESR spectra with temperature indicates thermal electron delocalization among the Mo atoms in a molecule [16].

X-crystal Structure of the Title Compound

Diffraction-quality crystals of the title compound were grown from DMF solution in the dark. A plot with the numbering scheme of all the non-hydrogen atoms in the asymmetric unit is given in Figure 3. The packing diagram viewed down the *b*-axis is given in Figure 4. Selected bond distances and angles are given in Tables II and III, respectively.

There are four molecules of $[C_{10}H_{10}N]_4GeMo_{12}O_{40} \cdot 6DMF$ in a unit cell. The Ge atom is situated on a 2/m special position with Ge—O bonds varying between 1.68 – 1.81 Å. The mean value of 1.726 Å is close to the reported value of 1.73 Å [17]. The Mo—O bond distances vary widely from 1.638(8) Å to 2.424(12) Å. The shortest Mo—O bonds are in the

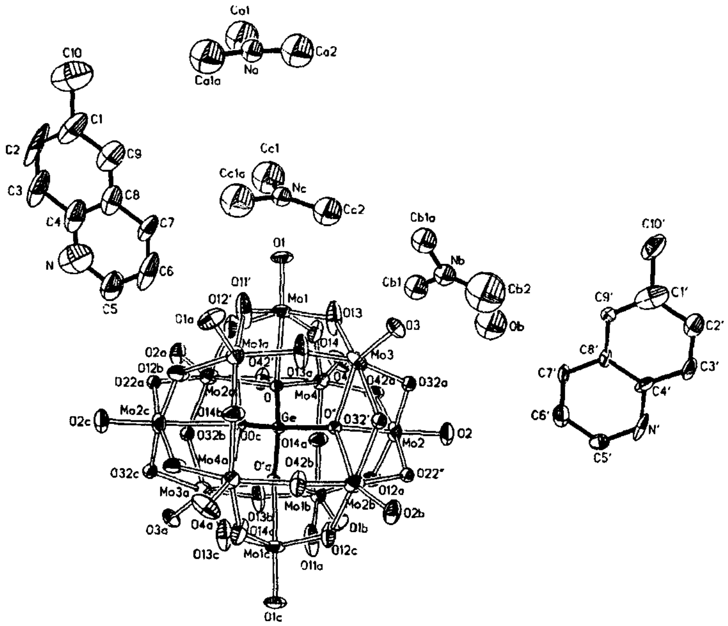

FIGURE 3 ORTEP plot of the compound showing 20% probability displacement ellipsoids.

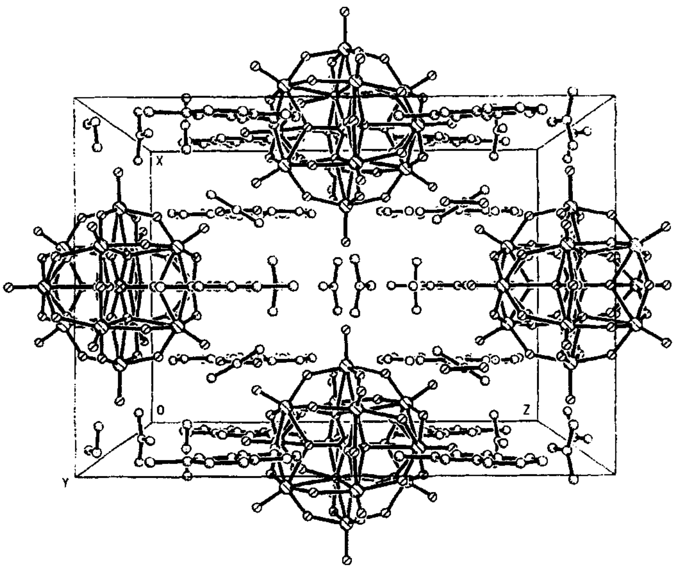

FIGURE 4 Packing diagram of the compound viewed down the *b* axis.

TABLE II Selected bond lengths (Å)

Mo(1)—O(1)	1.638(8)	Mo(1)—O(14)	1.871(11)
Mo(1)—O(13)	1.899(9)	Mo(1)—O(12′)	1.893(9)
Mo(1)—O(11′)	1.929(10)	Mo(1)—O′	2.285(10)
Mo(1)—O	2.366(12)	Mo(2)—O(2)	1.650(9)
Mo(2)—O(22′)	1.824(5)	Mo(2)—O(32′)^1	1.883(14)
Mo(2)—O(42′)^2	1.888(10)	Mo(2)—O(12′)^2	1.904(9)
Mo(2)—O(32′)^1	2.000(20)	Mo(2)—O(2)	2.077(11)
Mo(2)—O″	2.296(11)	Mo(2)—O^2	2.424(12)
Mo(3)—O(3)	1.668(11)	Mo(3)—O(32″)	1.785(14)
Mo(3)—O(13)	1.890(10)	Mo(3)—O(32′)	2.090(20)
Mo(3)—O″	2.340(20)	Mo(3)—O′	2.420(20)
Mo(4)—O(4)	1.652(13)	Mo(4)—O(14)	1.888(9)
Mo(4)—O(42′)	1.909(9)	Mo(4)—O	2.316(13)
Ge—O	1.678(13)	Ge—O′	1.740(20)
Ge—O″	1.810(20)		

Symmetry transformations used to generate equivalent atoms:
$^1 -x, y, z$; $^2 x, -y, -z$.

range of 1.638(8)–1.668(11) Å for the terminal O atoms. The mean value of 1.652 Å for Mo═Od is 0.038 Å shorter than the value of this bond in literature. The longest Mo—O bond distances are in the range of 2.316(13)–2.424(12) Å for those O atoms connecting Mo and the Ge atoms, the mean value of 2.382 Å for these bonds is 0.092 Å longer than

TABLE III Selected bond angles (°)

O(1)—Mo(1)—O(14)	101.9(6)	O(1)—Mo(1)—O(13)	102.3(7)
O(13)—Mo(1)—O(14)	88.2(5)	O(1)—Mo(1)—O(12′)	98.7(6)
O(14)—Mo(1)—O(12′)	88.0(4)	O(13)—Mo(1)—O(12′)	158.9(6)
O(1)—Mo(1)—O(11′)	97.2(8)	O(14)—Mo(1)—O(11′)	160.8(8)
O(13)—Mo(1)—O(11′)	89.2(5)	O(12′)—Mo(1)—O(11′)	87.7(6)
O(1)—Mo(1)—O′	155.3(6)	O(14)—Mo(1)—O′	98.3(5)
O(13)—Mo(1)—O′	64.1(6)	O(12′)—Mo(1)—O′	96.0(6)
O(11′)—Mo(1)—O′	63.6(7)	O(1)—Mo(1)—O	155.1(6)
O(14)—Mo(1)—O	61.1(5)	O(13)—Mo(1)—O	95.5(5)
O(12′)—Mo(1)—O	64.6(6)	O(11′)—Mo(1)—O	100.3(8)
O—Ge—O^{1}	113.7(8)	O′—Ge—O^{2}	110.6(5)
O—Ge—O″	108.3(5)	O″—Ge—O′^{3}	104.8(8)

Symmetry transformations used to generate equivalent atoms:
$^{1}-x, y, z$; $^{2}x, -y, -z$; $^{3}-x, -y, -z$.

TABLE IV The shortest intermolecular contact distance (Å) for nitrogen to oxygen and oxygen to oxygen in the crystal

O(1)···O(1)	(1)	3.02(2)	O(B)···O(32)′	(4)	3.15(5)
C(10)···O(22)″	(2)	2.92(5)	O(7)′···O(B)	(4)	2.60(6)
C(10)′···C(10)′	(3)	3.36(4)	O(B)···C(B1)	(1)	3.32(6)

(1): $1/2-x, +y, 1/2-z$; (2): $x, 1/2+y, 1/2-z$; (3), $1/2-x, -y-1/2, 1-z$; (4): $-x, y, z$.

the value of this bond in literature. The Mo—O bond distances for the bridging oxygen atoms are in the range of 1.785–2.09 Å. The H atoms of the acid were not located, but are from the bond length/bond order calculation [18], which shows that bond order of N and N′ are 2.52 and 2.32, respectively. So we presume that the N atom in each 7-methyl-quinoline is protonated to form the $[C_{10}H_{10}N]^+$ cation. Two bridging O atoms of the anion (namely O(22) and O(32)) are two-fold disordered.

The organic cations were stacked in a channel between the heteropoly anions parallel to the *a*-axis. The two crystallographically independent cations were planar, one lies on a mirror plane while the other one lies on a two-fold rotation axis.

There is no hydrogen bond in the molecules. The shortest distances between each of the organic molecules and the anions are summarized in Table IV. We found that there are four types of shortest contact in the molecules, but only one type of shortest contact involves the methyl carbon atom of 7-methyl-quinoline and the oxygen atom of anion. The shortest intermolecular cation–anion contact is larger than the sum of the appropriate shared-bond radii of H, C and O atoms.

Photochromism studies indicate that the photoexcitation of the ligand to the metal charge-transfer band O → Mo of MoO_6 octahedra in the polyoxometalate lattice leads to the formation of the localized $MoO_5(OH)$ center as a result of transfer of a hydrogen-bonding proton of the cation to the bridging oxygen atom [19]. IR, UV and ESR spectra confirm that the anion of the title compound obtained charge under irradiation. The lack of hydrogen bond interactions between the organic moieties and the polyoxometalate anion, similar to the compound α-$H_3PMo_{12}O_{40} \cdot 6DMF \cdot 0.5H_2O$, is unexpected. The results support the conclusion proposed by Hill that the cause of the electronic and photochemical spectra of the title compound does not have a simple structural basis [10], and the electronic transitions in the title compound may involve delocalized excited states or intermolecular donor acceptor character.

Acknowledgment

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