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Tetrahedral Transition Metal Complexes of $[MW_{12}O_{40}]$-type ($M=Cu^{II}$, Fe^{III}, Co^{II}) with Dodecatungstate as Tetrahedral Ligand

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Tetrabutylammonium salts of 12-heteropolytungstates with central transition metal ions in a tetrahedral oxygen environment, $MW_{12}O_{40}$ ($M=Cu^{II}$, Fe^{III}, Co^{II}), have been prepared and their spectroscopic data (infrared (IR), near-infrared, UV-vis, and magnetic circular dichroism (MCD)) presented.

12-Tungstometallate, $MW_{12}O_{40}$, is a typical 12-heteropolytungstate with the central transition metal in a tetrahedral oxygen environment. The compound is also considered as a transition metal complex with quadridentate dodecatungstate "ligand," $W_{12}O_{40}$, having tetrahedral cavity. Therefore, the formula can be rewritten as $MO_4W_{12}O_{36}$.

12-Tungstocuprate(II) anion, first reported by Brown and Mair,1) is not easily prepared because of the extremely low yield and the difficulty of controling experimental conditions, pH and temperature, into the very narrow range allowed. Subsequently, except for the polarographic study by Wexell and Pope,2) no precedent has been reported. On the contrary, 12-tungstocobaltate(II) and 12-tungstoferrate(III) anions, although purification takes time and yields are not so high, are not so difficult to prepare,3–6) and many investigations have been reported.7–14) Nevertheless, little spectroscopic data, especially IR data, of these heteropoly compounds have been reported.

Heteropoly compounds have contained different numbers of solvated water molecules (18 to 1), because the degree of hydration of K^+, Na^+, and Cs^+ salts of the anion varies according to the temperature of crystallization and the humidity at which the crystals are stored. Furthermore, most of the studies have been limited to aqueous systems. However, these compounds sometimes undergo hydrolytic decomposition in aqueous solution, the electronic spectra being influenced by the pH of the aqueous solvent because of the protonation of the dodecatungstate framework. We isolated these anions as tetrabutylammonium salts and measured the optical spectra in nonaqueous solution.

In this work, from a structural point of view, IR spectra of tetrabutylammonium salts of heteropolyanions with $M=Cu^{II}$ **1**, Fe^{III} **2**, and Co^{II} **3**, as heteroatom have been studied both in the solid and in the solution. On the basis of the results, the near-infrared and UV-vis spectra have been interpreted; MCD spectra have been measured to aid the resolution of the overlapping visible spectra.

Experimental

Near-infrared and UV-vis absorption spectra were measured on a Hitachi 340-spectrophotometer with an attached computer key-board. MCD spectra were recorded by a JASCO J-40AS spectropolarimeter mounted with 10.0 kG electromagnet. The MCD intensity is expressed in terms of $\Delta\varepsilon=\varepsilon_1-\varepsilon_r$. Measurements were made at room temperature. IR spectra in acetonitrile were measured using a KBr cell with 0.1 mm optical path.

Preparation. $H_2[(C_4H_9)_4N]_4[CuW_{12}O_{40}]$,*(1)*: Preparation of 12-tungstocuprate(II) is mainly performed according to the Brown-Mair's method.1) Instead of using copper(II) nitrate solution, we modified as follows: the pH of sodium tungstate solution ($Na_2WO_4\cdot 2H_2O$ 56.2 g, 0.170 mol, in 300 cm^3 water) was adjusted within 4.5—5.0 by 1 mol dm^{-3} nitric acid and the temperature was maintained at 68—70°C. To this solution, the dropwise addition throughout 6 h of copper(II) sulfate solution ($CuSO_4\cdot 5H_2O$ 6.2 g, 2.48×10^{-2} mol, in 300 cm^3 water) was made with continuous stirring. During the process of purification, the metatungstate by-product should be removed. The product was dried on a steam bath followed by extraction with water; the separation of 12-tungstocuprate(II) and metatungstate was monitored by the near-infrared spectrum at *ca.* 1340 nm, until the spectra of its aqueous solution become unchanged.

The aqueous solution, acidified with nitric acid, of excess tetrabutylammonium bromide was added to the aqueous solution of purified 12-tungstocupric acid. The precipitate formed was filtered, washed thoroughly with water, dried *in vacuo* and recrystallized twice from acetonitrile (yield 1%, yellow). Found: C, 19.41; H, 3.83; N, 1.48%. Calcd for $H_2[(C_4H_9)_4N]_4[CuW_{12}O_{40}]$: C, 19.79; H, 3.76; N, 1.44%.

$H[(C_4H_9)N]_4[FeW_{12}O_{40}]$ *(2)*: The 12-tungstoferrate(III) is prepared by a modification of the method reported by Pope and Varga,4) and purified by Mair's method.3) The compound structure is confirmed by the absorption spectrum of an aqueous solution as reported by Brown.8) The aqueous solution, acidified with nitric acid, of excess tetrabutylammonium bromide was added into the aqueous solution of the purified 12-tungstoferric acid. The precipitate was washed thoroughly with water and recrystallized three times from acetonitrile (yield 1%, pale yellow). Found: C, 19.87; H, 3.95; N, 1.52%. Calcd for $H[(C_4H_9)_4N]_4[FeW_{12}O_{40}]$: C, 19.84; H, 3.74; N, 1.45%.

$K_2[(C_4H_9)_4N]_4[CoW_{12}O_{40}]\cdot CH_3CN$*(3)*: Potassium 12-tungstocobaltate(II) is prepared and purified by the method of Baker and McCutcheon.5,6) The structure of the potassium compound is confirmed by the absorption spectrum of the aqueous solution as reported by Rollins.11) This compound is converted to tetrabutylammonium salts (yield 1%, blue-green). Found: C, 19.58; H, 3.87; N, 1.49%. Calcd for $K_2[(C_4H_9)_4N]_4[CoW_{12}O_{40}]\cdot CH_3CN$: C, 19.83; H, 3.68; N, 1.75%.

$Na_2[(C_4H_9)_4N]_4[H_2W_{12}O_{40}]$*(4)*: Tungsten(VI) oxide monohydrate, $WO_3\cdot H_2O$ (yellow), obtained by acidic decomposition of $Na_2WO_4\cdot 2H_2O$, is converted to the sodium metatungstate (white) by Freedman's method.15) This compound is converted to tetrabutylammonium salts as described above. Found: C, 20.18; H, 3.94; N, 1.46%. Calcd for $Na_2[(C_4H_9)_4N]_4[H_2W_{12}O_{40}]$: C, 20.12; H, 3.83; H, 1.47%. $[(C_4H_9)_4N]_4[SiW_{12}O_{40}]$ (**5**) and $[(C_4H_9)_4N]_3[PW_{12}O_{40}]$, (**6**) were prepared by the usual manner.16)

Table 1. The IR data of tetrabutylammonium salts of $MW_{12}O_{40}$ anions in the solid[a)]

M						Assignment
Cu^{II}	Fe^{III}	Co^{II}	H_2	Si	P	
					1072 s	$\nu_3(F_2)$; ν(P–O)
1024 w	1025 w	1017 w		1010 m		
			956 s			ν(O–H, tetrahedral)
943 s	952 s	940 s	947 s	966 vs	969 s	ν(W–O, terminal)
				920 vs		$\nu_3(F_2)$; ν(Si–O)
875 vs	875 vs	870 vs	880 vs	882 m	887 s	ν(W–O–W, O_h edge-sharing)
			800 vs	805 vs	804 vs	ν(W–O–W, O_h corner-sharing)
765 vs	775 vs	760 vs				ν(W–O–W, O_h corner-sharing) and $\nu_3(F_2)$; ν(M–O)
					584 w	
				528 m		$\nu_4(F_2)$; δ(O–Si–O)
540—580 w	500—580 w	520—580 w	520—580 w			
					505 m	$\nu_4(F_2)$; δ(O–P–O)
				477 w	460 w	
437 m	440 m	441 m				$\nu_4(F_2)$; δ(O–M–O)
			410 s			ν(O–H, tetrahedral)

a) KBr disk, cm^{-1}.

Results and Discussion

IR Spectra. The IR spectra of heteropolycompounds of M=Cu^{II}, Fe^{III}, and Co^{II} and metatungstate, recorded in KBr disks, in the metal-oxygen stretching region are shown in Fig. 1. The vibrational frequencies are presented in Table 1, together with the data of the M=Si and P compounds.

Fig. 1. IR spectra of tetrabutylammonium salts of $MW_{12}O_{40}$ heteropolyanions in 1000—400 cm^{-1} region measured in KBr disk; semi-dashed line (-·-·) for M=Cu^{II}, dashed line (------) for M=Fe^{III}, full line (——) for M=Co^{II} and dotted line (······) for metatungstate.

Three prominent bands in the tungstate spectra of **1**—**3** were assigned by comparison with the spectra of tetrabutylammonium salts of metatungstate $H_2W_{12}O_{40}{}^{6-}$ **4**, which is considered to be metal-free ligand, α-$SiW_{12}O_{40}{}^{4-}$ **5** and $PW_{12}O_{40}{}^{3-}$ **6**; ≈940 cm^{-1}, ν(W–O, terminal); ≈870 cm^{-1}, ν(W–O–W, octahedral edge-sharing); ≈770 cm^{-1}, ν(W–O–W, octahedral corner-sharing).[17)] The characteristics of **1**—**3** compounds are as follows; (1) new bands appear at *ca.* 440 cm^{-1} and (2) the corner-sharing bands at *ca.* 770 cm^{-1} are more asymmetric and broader than that of **4**, and have some shoulder peaks.

In general, for an undistorted tetrahedron (T_d symmetry) of the $MO_4{}^{n-}$ type ion there are four fundamental vibrational modes (A_1+E+2F_2), only triply degenerated F_2 modes of which are IR active; one of the F_2 is predominantly the M–O stretching motion, $\nu_3(F_2)$ and the other F_2 is the deformation by O–M–O angle bending motion, $\nu_4(F_2)$. The asymmetric stretch ν_3 is normally very strong in the IR and $\nu_3 > \nu_4$.[18)] In the heteropolyanions **1**—**3**, by analogy with ν_3 and ν_4 of **4**, **5**, and **6** compounds, the new bands at *ca.* 440 cm^{-1} may be assigned to $\nu_4(F_2)$, and $\nu_3(F_2)$ band to be overlapped with the W–O–W octahedral corner-sharing band at *ca.* 770 cm^{-1}.

Table 2. Numerical data of the vibrational mode $\nu_4(F_2)$ of tetrabutylammonium salts of $MW_{12}O_{40}$ anions

M	In the solid (KBr disk) Max. cm^{-1}	In the solution (in CH_3CN)	
		Max. cm^{-1}	Half-width cm^{-1}
Cu^{II}	437[a)]	444[a)]	68±4
Fe^{III}	440	447	18±4
Co^{II}	441	450	39±4
Si	528[a)]	530[a)]	34±13
P	505	513[b)]	46±4

a) Asymmetric triplet. b) Center of doublet.

The expected splitting of ν_3 and ν_4 for different site symmetries has been described.[19] When the effects of crystal packing and/or environment upon ν_3 and ν_4 are eliminated, the spectral envelopes of both bands will show whether the central site symmetry is regularly tetrahedral or distorted. Accordingly, we have examined the variation in the frequencies and the widths of these vibrational modes, especially ν_4, in acetonitrile solution. The results are presented in Table 2. It was observed that the positions of the ν_4 band are essentially insensitive to the crystalline state and the apparent features of the envelopes are not significantly varied, except for the P compound.

The very symmetrical envelope and small width of the ν_4 for the $\mathrm{Fe^{III}}$ compound may be indicative of the regular tetrahedron of the $\mathrm{FeO_4}$ moiety of this compound. The envelope for the $\mathrm{Co^{II}}$ compound is also very symmetrical, although the width is rather broad. This compound can be expected to retain excellent tetrahedral symmetry. On the contrary, the envelopes for the $\mathrm{Cu^{II}}$ and Si compounds are asymmetric; there are actually splittings into three bands and significant broadenings, indicating that the $\mathrm{MO_4}$ moieties of these compounds possess far from perfect tetrahedral site symmetry. Since these bands are also asymmetric and broadened in the solid state (KBr disk), the features will not be caused by the effect of crystal packing, but mainly by the intrinsic structure of the tetrahedral complexes surrounded by dodecatungstate ligand. The significant distortion of the $\mathrm{SiO_4}$ moiety in α-$\mathrm{Ba_2[SiW_{12}O_{40}]}$ has been established by X-ray structural analysis.[20] The $\mathrm{Cu^{II}}$ compound is considered to have an intrinsic distortion on account of the Jahn-Teller effect of the $\mathrm{d^9}$ configuration. It may be anticipated that the distortion reflects plausibly on the spectral envelope of ν_4 band. In the case of the P compound, the envelope of ν_4 band is very sharp and symmetric in the solid, whereas there is a splitting to two bands and the width is more broadened in the solution. If the above-mentioned hypothesis is true, the data indicate some departure from regular tetrahedral symmetry in the $\mathrm{PO_4}$ moiety occurs.

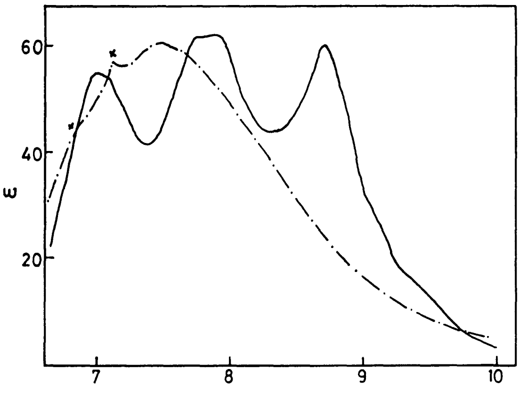

Fig. 2. Near-infrared spectra of tetrabutylammonium salts of $\mathrm{[Cu^{II}W_{12}O_{40}]^{6-}}$ (–·–·) and $\mathrm{[Co^{II}W_{12}O_{40}]^{6-}}$ (——) in acetonitrile solution. The cross mark stands for the absorption of contaminated water.

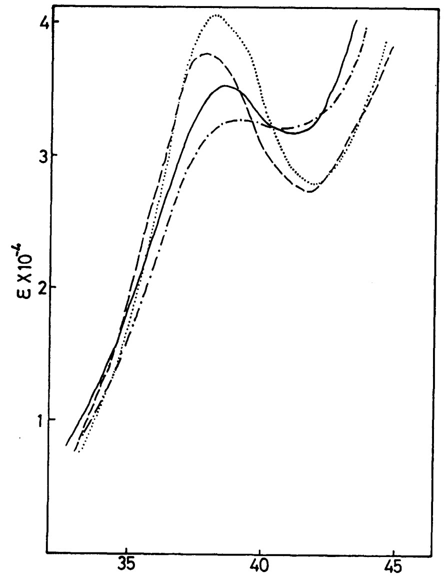

Fig. 3. UV spectra of tetrabutylammonium salts of $\mathrm{MW_{12}O_{40}}$ heteropolyanions in acetonitrile solution; semidashed line (–·–·) for M=$\mathrm{Cu^{II}}$, dashed line (------) for M=$\mathrm{Fe^{III}}$, full line (——) for M=$\mathrm{Co^{II}}$ and dotted line (······) for metatungstate.

Regarding the two W–O–W stretchings of **4**, there are two cases as follows; where the heteroatom is a non-transition metal, those two bands are relatively unchanged or only slightly shifted to a higher frequency region, whereas if the heteroatom is a transition metal, the bands are shifted considerably to a low frequency region. Thus, the central transition metals may give rise to the strong electronic interaction with the dodecatungstate lattice.

Near-infrared, UV-vis, and MCD Spectra. The near-infrared and UV-vis spectra (Figs. 2 and 3) of an acetonitrile solution of 12-tungstocuprate(II) **1** shows a broad band at 7490 cm^{-1} (ε 60.1) and another at 39000 cm^{-1} (ε 32400). The former is slightly higher than that in water reported by Brown and Mair.[1] The former band is due to the d-d transition of $\mathrm{Cu^{II}}$ ($\mathrm{d^9}$) displaced to this position in the tetrahedral oxygen lattice and is broadened by some components based on a Jahn-Teller effect in the ground state. Since the expected value should be around 4/9 of 12500 cm^{-1} (the value of 10 Dq for $\mathrm{Cu(H_2O)_6{}^{2+}}$), *i.e.* around 5560 cm^{-1}, the ligand field strength by $\mathrm{W_{12}O_{40}}$ "ligand" may be greater than the corresponding hypothetical four hydrate. A band at 39000 cm^{-1} is due to the charge transfer transition within the oxotungstate lattice and is observed in the spectra of other dodecatungstates of central nonmetals and transition metals.

The electronic and MCD spectra of 12-tungstoferrate(III) **2** in acetonitrile are shown in Figs. 3 and 4. This anion has perfect $\mathrm{T_d}$ symmetry; no distortion of the central $\mathrm{FeO_4}$ tetrahedra would occur in solution. The three absorption bands observed at 20900 (ε 0.7), 24210 (ε 10.9) and 37590 cm^{-1} (ε 38400) are in good agreement with the results in aqueous solution, although the intensities of the visible absorptions are less than the halves of the previous data.[8] These have been assigned

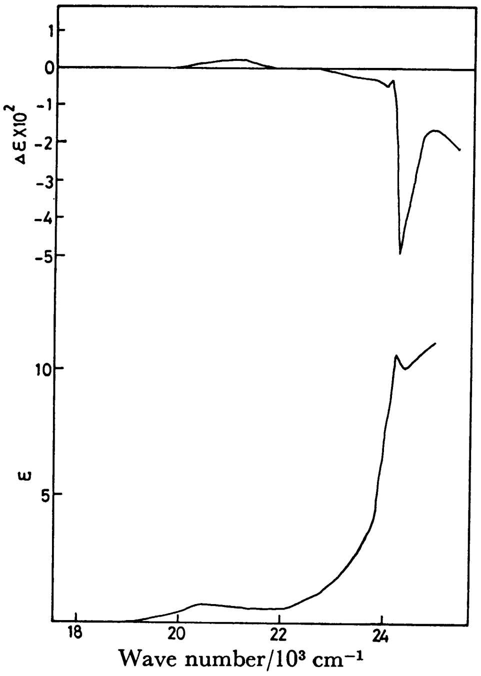

Fig. 4. Vis and MCD spectra of tetrabutylammonium salt of $[Fe^{III}W_{12}O_{40}]^{5-}$ in acetonitrile solution.

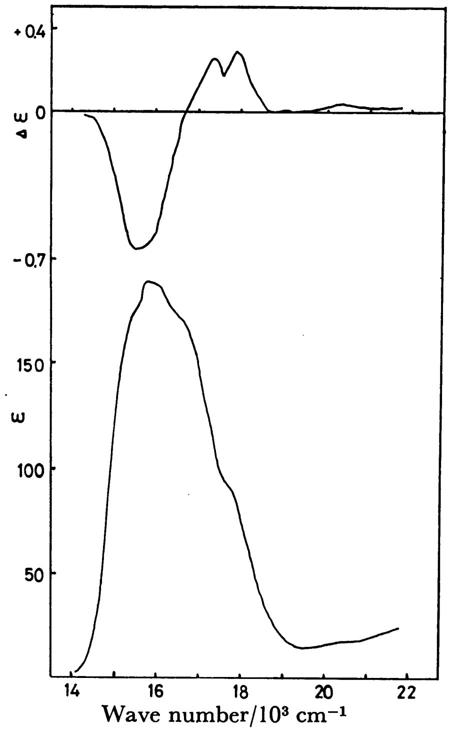

Fig. 5. Vis and MCD spectra of tetrabutylammonium salt of $[Co^{II}W_{12}O_{40}]^{6-}$ in acetonitrile solution.

to $^4T_1(G) \leftarrow {}^6A_1(S)$, $^4A_1(G)+{}^4E(G) \leftarrow {}^6A_1(S)$ and the charge transfer band, respectively. A very sharp band at 24210 cm^{-1} corresponds to a sharp band observed commonly in other high-spin d^5 ions such as $Mn(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, being on account of the independence of *Dq*. The negative MCD peak corresponding to this absorption is also very sharp. The very weak shoulder about 24×10³ cm^{-1} which has been suggested as $^4T_2(G) \leftarrow {}^6A_1(S)$ from the spectral shape in the aqueous solution,[8] is obscure in this visible spectrum. However, the MCD spectrum shows such a band explicitly at 23950 cm^{-1}. The higher peaks due to d-d transitions of Fe(III) ion are swamped by the tail of the charge transfer band in both the electronic and the MCD spectra. These spectral data give us a 10 *Dq* value of 6200 cm^{-1} and a *B* value of 740 cm^{-1}, where the previously reported values are 6000 and 810 cm^{-1}, respectively. The 10 *Dq* value is in good agreement with the expected value, 4/9 of a 10 *Dq* value, 14200 cm^{-1}, for $Fe(H_2O)_6^{3+}$, *i.e.* about 6300 cm^{-1}.

The near-infrared, UV-vis absorption spectra, and the MCD spectrum in visible region of 12-tungstocobaltate(II) **3** are shown in Figs. 2, 3, and 5. The absorption spectrum shows the typical pattern of many common tetrahedral Co(II) complexes;[21] in the near-infrared region the spin-allowed transition to the excited quartet state, $^4T_1(F) \leftarrow {}^4A_2(F)$, at *ca.* 7.8×10³ cm^{-1} and in the visible region $^4T_1(P) \leftarrow {}^4A_2(F)$ at *ca.* 16×10³ cm^{-1}. In the UV region, there is a strong band at 38460 cm^{-1} (ε 35200) due to the charge transfer transition of the lattice. The near-infrared band exhibits much fine structure. Since many more peaks are observed than predicted by spin-orbit coupling, another causes must be sought; one may be a Jahn-Teller effect in the excited state.[21] The peak ($^4T_1(F) \leftarrow {}^4A_2$, 7.8×10³ cm^{-1}) suggests a 10 *Dq* value of about 4100 cm^{-1}. This is estimated by using the energy level diagram for tetrahedrally coordinated Co(II), presented by Cotton and his coworkers.[21] The value is in good agreement with the expected values, 4/9 of 9200 cm^{-1} (the 10 *Dq* value of $Co(H_2O)_6^{2+}$), *i.e.* about 4090 cm^{-1} and the 10 *Dq* value of 4230 cm^{-1} for $Co(OH)_4^{2-}$.

The visible band is complicated because of a number of transitions to doublet excited states which occur in the same region, and these gain some of their intensity by means of spin-orbit coupling.[22] However, the corresponding MCD spectrum is much more resolved and suggests at least four different transitions; (1) intense and broad band with negative sign centered at *ca.* 15.6×10³ cm^{-1}, (2) positive band at *ca.* 17.3×10³ cm^{-1}, (3) positive band at *ca.* 17.9×10³ cm^{-1}, and (4) weak and broad band with positive sign at *ca.* 20.4×10³ cm^{-1}. There are further complications because each of (1), (2), and (3) includes some components. However, as suggested from the sign and the intensity of MCD, the band (1) will be mainly dominated by spin-allowed transition to a quartet excited state and the others (2)—(4) by transitions to doublet excited ones.

This type of heteropolyanions studied here is a real tetrahedral complex and stable even in dilute nonaqueous solution. These compounds lie in high-spin state, or paramagnetic state because of small 10 *Dq*. The crystal field theory and ligand field theory, which have been applied to the traditional octahedral coordination complexes, are acceptable to explain the spectral and magnetic properties.

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