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An Improved Preparation and Characterization of Tetrahedral Co^{II} and Co^{III} Complexes with Dodecatungstate as the Tetrahedral Ligand

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Tetrabutylammonium salt of the 12-tungstoheteropolyanion with central Co^{II} as the heteroatom in a tetrahedral oxygen environment, $[Co^{II}W_{12}O_{40}]^{6-}$, has been prepared by an improved manner. This manner remarkably shortens the total time needed for preparation, especially the time for purification, and gives a compound of a high purity. The corresponding Co^{III} compound has been obtained by oxidation with potassium peroxodisulfate from the potassium salt of the Co^{II} compound; its spectroscopic data (IR, near-infrared, UV-vis, and MCD) are presented.

Recently we have reported on the syntheses and the spectroscopic properties of tetrahedral transition-metal complexes of the $[MW_{12}O_{40}]$ type ($M=Cu^{II}$, Fe^{III}, Co^{II}), with dodecatungstate as the tetrahedral ligand.[1] In this paper, we wish to report on an improved method for the preparation of the cobaltate(II) ion and its subsequent conversion to the cobaltate(III) ion. The purities and absorption coefficients of the compounds obtained here were superior to those previously reported.[1–3] The cobaltate(III) ion is a d^6 high-spin complex in a tetrahedral field of the $W_{12}O_{40}$ ligand and is one of the spectrophotometrically interesting compounds. From the point of view of a reaction, the Co^{III} compound has been known to promote the oxidation of alkyl-substituted aromatic hydrocarbons[4] and to exchange an electron with the parent Co^{II} compound *via* an outer-sphere mechanism.[5] In this paper, we wish also to report the spectroscopic data (IR spectra both on a solid and in a solution and the near-infrared and UV-vis spectra and the MCD spectra in the UV-vis region) of the tetrabutylammonium cobaltate(III).

Experimental

The near-infrared and vis-UV absorption spectra were measured by means of a Hitachi 340-spectrophotometer with a computer keyboard attached. The intensity is expressed in terms of the molar absorptivity, ε, which has units of $mol^{-1}\ dm^3\ cm^{-1}$. The MCD spectra were recorded by means of a JASCO J-40AS spectropolarimeter with a 10.0-kG† electromagnet mounted on it. The MCD intensity is expressed in terms of $\Delta\varepsilon=\varepsilon_l-\varepsilon_r$, which has units of $mol^{-1}\ dm^3\ m^{-1}\ G^{-1}$. Measurements were made at room temperature. The IR spectra in acetonitrile were measured by using a KBr cell with a 0.1-mm optical path.

Preparation. $K_6[Co^{II}W_{12}O_{40}]\cdot nH_2O$: The pH of a sodium tungstate solution ($Na_2WO_4\cdot 2H_2O$ 79.2 g (0.24 mol) in 160 cm^3 water) was adjusted within 6.5—7.0 by the use of glacial acetic acid. The solution was then boiled over an open flame. $Co(CH_3COO)_2\cdot 4H_2O$ 10.0 g (0.04 mol) was dissolved in 50 cm^3 hot water, whereinto some drops of glacial acetic acid were added. This solution was then added, with continuous stirring, into a boiling sodium tungstate solution. After this addition, the solution was boiled further for about 10 min. The hot solution was then filtered, and a hot, aqueous solution saturated with KCl (52 g) was added to the boiling filtrate. The dark green solution thus obtained was allowed to stand overnight at room temperature. The green crystals of the dicobalt species, $K_8[CoCoW_{11}O_{40}H_2]$, obtained were recrystallized twice from an acid solution with the ratio of 2 cm^3 of glacial acetic acid to 400 cm^3 of water. The green compound obtained in this step was not yet pure. The crude sample was dissolved in about 150 cm^3 of water, whereinto ether was added. Into this solution, 400 cm^3 of 6 M-sulfuric acid ($1\ M=1\ mol\ dm^{-3}$) was continuously stirred, drop by drop. The system separated into three layers; the highest was an ether, and the second was an aqueous layer, while the lowest layer contained the ether adduct of 12-tungstocobaltic acid and metatungstic acid as impurities. The lowest layer was collected, diluted with a small amount of water, and evaporated to dryness on a steam-bath. During the process, metatungstic acid (white) was decomposed to tungsten oxide (yellow), which was insoluble in water. The residue was extracted with water and again heated on a steam-bath. This procedure was repeated until no yellow compound was formed. During the ether-extraction and the purification, the intermediate dicobalt species was changed to the monocobalt species. Free acid, $H_6[Co^{II}W_{12}O_{40}]$, obtained as blue-green crystals, was converted to the potassium salt from a concentrated aqueous solution of potassium chloride. The potassium salt was coarsely ground and thoroughly dried at 110 °C; in this procedure, the hydrogen chloride as an adduct was lost. When the compound was analyzed, it was found to be potassium tetrabutylammonium salt. Found: C, 19.91; H, 3.79; N, 1.66%. Calcd for $K_2[(C_4H_9)_4N]_4[Co^{II}W_{12}O_{40}]$: C, 19.84; H, 3.72; N, 1.75%.

$K[(C_4H_9)_4N]_4[Co^{III}W_{12}O_{40}]$: Using the potassium salt of the Co^{II} compound, the potassium salt of the Co^{III} compound was prepared by oxidation with potassium peroxodisulfate according to the method of Baker and his co-workers.[2,3] It should be noted that the free acid of the Co^{II} compound could not be directly converted into that of the Co^{III} compound because of the decomposition of the peroxodisulfate by the very strong acidity of the cobaltate(II) and/or cobaltate(III). The aqueous solution, acidified with nitric acid, with an excess of tetrabutylammonium bromide was added to the aqueous solution of potassium cobaltate(III). The precipitate thus formed was filtered, washed thoroughly with water, dried *in vacuo*, and recrystallized from acetonitrile (yield, 7.2%; golden yellow). Found: C, 19.64; H, 3.71; N, 1.43%. Calcd for $K[(C_4H_9)_4N]_4[Co^{III}W_{12}O_{40}]$: C, 19.53; H, 3.74; N, 1.48%.

Results and Discussion

The cobalt(II) compound has been obtained as potassium salt by the acid-decomposition of the intermediate dicobalt species, $K_8[Co^{II}Co^{II}W_{11}O_{40}H_2]$, which is itself formed by adding a sodium tungstate solution

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† $1\ G=10^{-4}\ T$.

TABLE 1. NEAR-INFRARED AND UV-VIS SPECTRA OF $K_2[(C_4H_9)_4N]_4[Co^{II}W_{12}O_{40}]$ IN AN ACETONITRILE SOLUTION

Transition	Absorption maximum 10^3 cm^{-1}	Molar absorptivity This work	Molar absorptivity Recrystallization method[1]
$^4T_1(F) \longleftarrow {}^4A_2$	6.99	59	55
	7.72	67	61
	7.87	68	62
	8.70	67	61
	9.39[a]	17	17
$^4T_1(P) \longleftarrow {}^4A_2$	15.43[a]	194	172
	15.92	209	187
	16.56[a]	186	172
	17.73[a]	102	93
Charge transfer	38.76	3.33×10^4	3.51×10^4

a) Shoulder.

TABLE 2. IR DATA OF TETRABUTYLAMMONIUM SALTS OF $MW_{12}O_{40}$ ANIONS IN A SOLID[a]

M: Co^{II}	M: Co^{III}	Assignment
1017 w	1024 w	
940 s	950 s	ν(W–O, terminal)
870 vs	876 s	ν(W–O–W, octahedral edge-sharing)
760 vs	780 vs	ν(W–O–W, octahedral corner-sharing) and ν(M–O, tetrahedral); $\nu_3(F_2)$
520—580 w(br)	490—560 w(br)	
441 m	436 m	δ(O–M–O); $\nu_4(F_2)$

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

to an acidic solution of cobalt(II) acetate at 80 °C.[2] The dicobalt compound has been purified by repeated recrystallizations from an acidic aqueous solution. This process takes more than one month, however, we tried the extraction with ether and 6 M-sulfuric acid for the purification of the dicobalt compound, for such extraction has been a traditional work-up for the preparation of many other analogous tetrahedral complexes $[MW_{12}O_{40}]$ (M=Cu^{II}, Fe^{III}, Al^{III}, Zn^{II}, and so on), as has been described by Brown and Mair.[6–8] In this manner, free acid of the monocobalt compound, $H_6[Co^{II}W_{12}O_{40}]$, could be obtained without the procedure of acid-decomposition, although metatungstic acid is present as an impurity. The cobaltate(II) acid can be easily separated by repeatedly heating the mixture on a steam-bath, followed by extraction with water, because the metatungstic acid (white) is readily decomposed to tungsten oxide (yellow), which is insoluble in water. After the isolated free acid is converted into the potassium salt, the potassium salt of the cobalt(III) compound, $K_5[Co^{III}W_{12}O_{40}]$, is obtained by oxidation with potassium peroxodisulfate. By the use of this modified manner, the total time for preparation is shortened to within two weeks.

The analytical values of two tetrabutylammonium compounds, $K_2[(C_4H_9)_4N]_4[Co^{II}W_{12}O_{40}]$, which have been obtained with both the previous recrystallization method[1] and the present ether-extraction method agree within the allowed range (0.3%). However, the intensities of the absorption bands in the near-infrared and visible regions of the previous compound are about 10% smaller than those of the present compound, whereas the intensity in the UV region is about 10% larger. Since metatungstate has only an absorption band in the UV region, it seems that the previous compound contains metatungstate as an impurity. This cannot be completely removed only by recrystallization. A contaminating metatungstate of about 10% may not influence the analytical value because of the relatively large molecular weight of the cobalt(II) compound. This shows the essential disadvantage of the recrystallization method, for such contamination significantly influences the purity of the final product, the cobalt(III) compound. The absorption maxima and molar absorptivities of the cobalt(II) compounds obtained by two methods are presented in Table 1.

IR Spectra. The frequencies of the cobalt(III) anion in the metal-oxygen vibrational region, recorded in a KBr disk, are presented in Table 2, together with the data on the parent cobalt(II) anion. The listed bands correspond to the Keggin-structure with a $W_{12}O_{40}$ skeleton and a central tetrahedral CoO_4 moiety, as has been previously in the case of the $[MW_{12}O_{40}]$ anions (M=Cu^{II}, Fe^{III}, Si, P).[1,9] In the undistorted tetrahedron (T_d symmetry) of an MO_4^{n-}-type ion, there are two IR active F_2 modes: $\nu_3(F_2)$ and $\nu_4(F_2)$, both triply degenerated. The former is the mode by the M–O stretching motion, and the latter, the deformation mode by the O–M–O angle bending motion. The spectral envelopes of these bands are diagnostic, whether the central-site symmetry is a regular tetrahedron or distorted, if the effects of the crystal packing and/or the environment upon these bands are eliminated. Since the ν_3 band is overlapped with the W–O–W octahedral

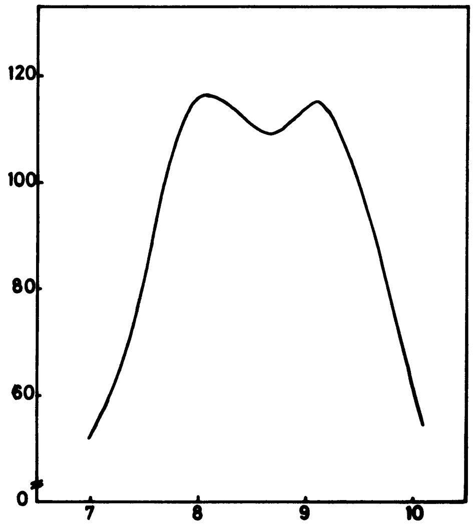

Fig. 1. Near-infrared spectrum of tetrabutylammonium salt of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ in acetonitrile solution.

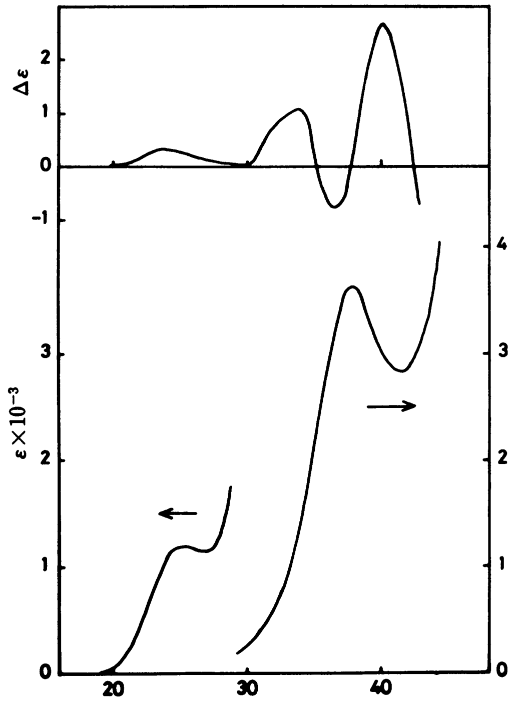

Fig. 2. Absorption and MCD spectra in UV-vis region of tetrabutylammonium salt of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ in acetonitrile solution.

corner-sharing band at *ca.* 780 cm^{-1}, the variations in the frequency and the half-width about the ν_4 band were examined in the acetonitrile solution. No splitting of the ν_4 band has been observed; a relatively symmetrical and sharp band appeared at 440 cm^{-1}, with a half-width of 25±0 cm^{-1}. This fact suggests that this compound may retain an excellent T_d symmetry in the ground state, like the parent cobalt(II) compound. This is in good agreement with the crystallographical feature of $K_5[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]\cdot 20H_2O$ found by Baker and his co-workers.[10]

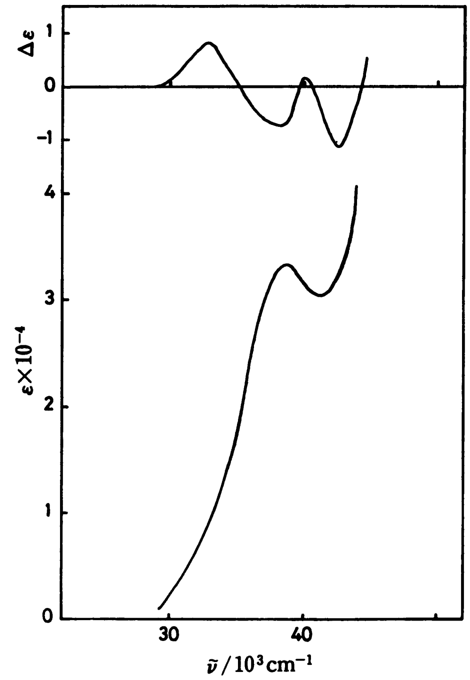

Fig. 3. UV and MCD spectra of tetrabutylammonium salt of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ in acetonitrile solution.

Absorption and MCD Spectra. The electronic spectra of the cobalt(III) compound, the absorption in the near-infrared region and the absorption and MCD in the UV-vis region, are shown in Figs. 1 and 2, respectively. The absorption in the near-infrared region with a double structure (8.06×10^3 and 9.09×10^3 cm^{-1}; ε 116 and 115 respectively; a splitting of 1.03×10^3 cm^{-1}) is due to the d-d transition. The compound is a d^6 high-spin system in a tetrahedral field. Thus, only one absorption band due to the excitation of the d shell electrons ($^5T_2\leftarrow{}^5E$) is to be expected if no account is taken of (1) the spin-orbit coupling, (2) the static and permanent distortion of the tetrahedron in the ground state, and (3) the Jahn-Teller effect in the electronically excited state.[11] In this system, the spin-orbit coupling may be discounted, for the observed splitting is 10 times the magnitude of the spin-orbit coupling constant for cobalt(III) ion. Furthermore, IR studies have indicated that there is little distortion around the CoO_4 moiety in the ground state. It must, then, be concluded that the Jahn-Teller effect in the electronically excited state may occur.

The large band at 37.9×10^3 cm^{-1} (ε 3.62×10^4) is due to the charge-transfer transition within the dodecatungstate lattice, such as is commonly observed in the spectra of other dodecatungstates of both central nonmetals and transition metals, and even of metatungstate. The MCD spectrum in the region clearly shows two positive and one negative components; the negative one appears near the position of the absorption maximum and exists between the two positive ones. This is characteristic of the compounds with a $W_{12}O_{40}$ skeleton, but not of the compounds with a $Mo_{12}O_{40}$ skeleton; the intensity of each component changes with the central transition metal. In Fig. 3, the absorption and MCD in the UV region of the parent cobalt(II) compound are shown. Thus, the W–O charge-transfer band, observed as one absorption, has been found to be composed of several transitions and to be strongly influenced by the central metal.

The broad maximum at 25.4×10^3 cm^{-1} (ε 1.18×10^3) is a band unique to the cobalt(III) compound, having been first observed by Shimura and Tsuchida.[12] The MCD spectrum shows a comparably small and broad band with a positive sign. The absorption has been previously attributed to a charge transfer of the O atom, which occupies the corner of the central tetrahedral cavity, to the central Co^{III} ion.[13]

References

1) K. Nomiya, M. Miwa, R. Kobayashi, and M. Aiso, *Bull. Chem. Soc. Jpn.*, **54**, 2983 (1981).

2) L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956).

3) L. C. W. Baker and V. E. Simmons, *J. Am. Chem. Soc.*, **81**, 4744 (1959).

4) A. W. Chester, *J. Org. Chem.*, **35**, 1797 (1970).

5) P. G. Rasmussen and C. H. Brubaker, *Inorg. Chem.*, **3**, 977 (1964).

6) J. A. Mair and J. L. T. Waugh, *J. Chem. Soc.*, **1950**, 2372.

7) D. H. Brown and J. A. Mair, *J. Chem. Soc.*, **1958**, 2597.

8) D. H. Brown, *J. Chem. Soc.*, **1962**, 3281.

9) D. H. Brown, *Spectrochim. Acta*, **19**, 585 (1963).

10) K. Eriks, N. F. Yannoni, U. C. Agarwala, V. E. Simmons, and L. C. W. Baker, *Acta Crystallogr.*, **13**, 1139 (1960).

11) F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

12) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **30**, 502 (1957).

13) V. E. Simmons, Ph. D. Thesis, Boston University, 1963.