Absorption Spectra of Heteropolyanions. II[1] *The Heteropolytungstates Containing Co(II), Co(III) or Mn(IV) as Central Ions*

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Introduction

In the former paper of this series[1], the absorption spectra were reported for the heteropolymolybdates containing Co(III), Cr(III), Fe(III), Al(III), Mn(IV) or Ni(IV) as central ions. X-ray investigations[2,3], magnetic measurements[4] and other physico-chemical studies[5] by many authors have revealed that the central ion M is at the center of MO_6 octahedron. The absorption spectra of these heteropolymolybdates were therefore regarded as the absorption spectra of $[M(O^=)_6]$-complexes.

In the present paper, absorption spectra of the heteropolytungstates containing some transition metals as central ions have been measured. Of special interest are the heteropolyanions containing Co (II) or Co(III), which were very recently discovered and thoroughly investigated by Baker and McCutcheon[6]. Our spectral studies have clearly established the fact that the Co(II) or Co(III) ion is at the center of a tetrahedron, in contrast to the conclusion of Baker et al., who offered some octahedral structures.

The present paper is probably the first one that describes the absorption spectra of $[Co^{II}(O^=)_4]$- and $[Co^{III}(O^=)_4]$-complexes.

Experimental

The absorption measurements were made in aqueous solutions by a Beckman DU spectrophotometer at room temperature. The concentration of the solutions varied from 0.5×10^{-2} to 0.2×10^{-4} F/l. The formula weights were calculated from the formulae listed in Table I, on which are also tabulated the literature for preparation and the tentative structural formulae which are proposed for the anions from our spectral studies.

Results and Discussion

(1) $3Na_2O \cdot 5WO_3 \cdot Mn^{IV}O_2 \cdot 18H_2O$—The absorption spectrum of this compound is shown in Fig. 1, in which the spectrum[1] of $[Mn^{IV}O_6Mo_9O_{26}]^{6-}$ is also plotted for comparison. The structure of the latter ion was well established by an X-ray analysis[2]. Therefore, a broad band at 64.1×10^{13}/sec. ($\log \varepsilon_{max}=2.42$) and a narrow band at 42.9 (0.55), are equally due to the complex $[Mn^{IV}(O^=)_6]$. Recently, from the viewpoint of crystal field theory, Jørgensen[8] suggested that the narrow band is due to a spin-forbidden transition $^4\Gamma_2-^2\Gamma_3$ and the broad band to a spin-allowed transition $^4\Gamma_2-^4\Gamma_5(F)$.

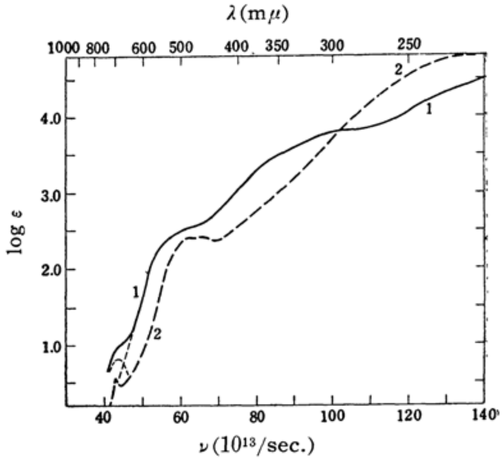

Fig. 1. Absorption spectra of:
1, $3Na_2O \cdot 5WO_3 \cdot Mn^{IV}O_2 \cdot 18H_2O$;
2, $(NH_4)_6[Mn^{IV}O_6Mo_9O_{26}] \cdot 6H_2O$[1].

As to the heteropolytungstate presently studied, the narrow band is observed as an inflation of the absorption curve. A curve analysis shown in Fig. 1 as dotted lines, gives the maximum intensity log ε=ca. 0.8 at frequency ca. 43.5. The broad band is similar to that of the correspond-

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1) Part I of this series: Y. Shimura, H. Ito and R. Tsuchida, *J. Chem. Soc. Japan*, **75**, 560 (1954).

2) J. L. T. Waugh, D. P. Shomaker and L. Pauling, *Acta Cryst.*, **7**,438 (1954).

3) C. W. Wolfe, M. L. Block and L. C. W. Baker, *J. Am. Chem. Soc.*, **77**, 2200 (1955).

4) P. Rây, A. Bhaduri and B. Sarma, *J. Indian Chem. Soc.*, **25**, 51 (1948).

5) L. C. W. Baker, G. Foster, W. Tan, F. Scholnick and T. P. McCutcheon, *J. Am. Chem. Soc.*, **77**, 2136 (1955).

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

7) A. Just, *Ber.*, **36**, 3619 (1903).

8) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

TABLE I

FORMULAE OF THE HETEROPOLYTUNGSTATES

Formula previously used	Formula Weight	Color	Literature for preparation	Tentative structural formulae for the heteropoly-anions
$3Na_2O\cdot 5WO_3\cdot Mn^{IV}O_2\cdot 18H_2O$	1756.5	orange red	7)	$[(Mn^{IV}O_6W_5O_{14})_n]^{6n-}$
$K_5H_5[Co^{II}(W_2O_7)_6]\cdot 16H_2O$	3426.1	bluish green	6)	$[Co^{III}O_4W_{12}O_{38}]^{10-}$ or $[Co^{III}O_4W_{12}O_{36}]^{6-}$
$K_4H_5[Co^{III}(W_2O_7)_6]\cdot 18H_2O$	3423.0	golden yellow	6)	$[Co^{III}O_4W_{12}O_{38}]^{9-}$ or $[Co^{III}O_4W_{12}O_{36}]^{5-}$
$(NH_4)_8[Co^{II}Co^{II}(W_{12}O_{42})]\cdot 20H_2O$	3501.3	emerald green	6)	$[Co^{II}O_4(W_{12}O_{32})O_6Co^{II}]^{8-}$
$K_7[Co^{II}Co^{III}(W_{12}O_{42})]\cdot 16H_2O$	3558.2	dark brown	6)	$[Co^{III}O_4(W_{12}O_{32})O_6Co^{II}]^{7-}$

ing molybdenum compound, i.e., maximum at about 63 with intensity log ε_{max}=ca. 2.5.

Another very broad band is situated at the frequency region of 70–100. This is probably due to a polynuclear structure, i.e., a structure having two or more central manganese(IV) atoms with a linkage of Mn-O-Mn in the anion. A similar conclusion was previously obtained by the present authors[1] in connection with a heteropolymolybdate, $2(NH_4)_2O\cdot Co^{III}{}_2O_3\cdot 10MoO_3\cdot 12H_2O$, in which the ratio of central hetero-atom to molybdenum atom is 1 : 5. Likewise in the heteropoly tungstate concerned, the ratio of Mn : W is 1 : 5.

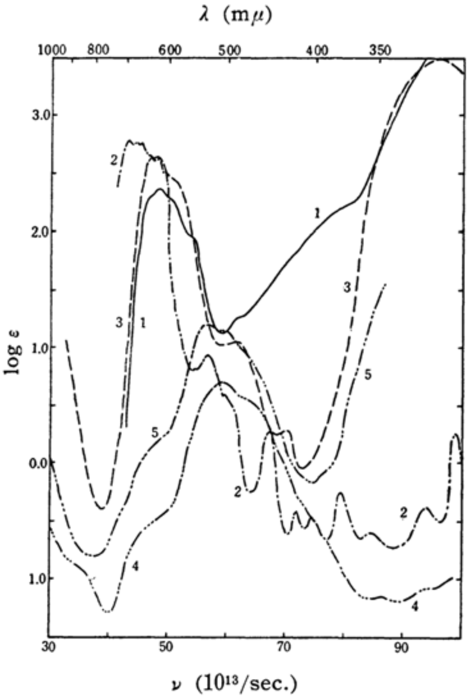

Fig. 2. Absorption spectra of:
1, $K_5H_5[Co^{II}(W_2O_7)_6]\cdot 16H_2O$;
2, $[Co\ Cl_4]^{2-}$ [11];
3, $[Co\ (NCS)_4]^{2-}$ [12];
4, $[Co\ (OH_2)_6]^{2+}$ [13];
5, $[Co\ (ox)_2\ (OH_2)_2]^{2-}$ [14].

In conclusion, a tentative structural formula $[(Mn^{IV}O_6W_5O_{14})_n]^{6n-}$ may be assigned to the anion of this salt.

(2) $K_5H_5[Co^{II}(W_2O_7)_6]\cdot 16H_2O$—In Fig. 2, the absorption spectrum of this compound is compared with those of some cobalt (II) complexes, the structure of which was well established. $[CoCl_4]^{2-}$ and $[Co\ (NCS)_4]^{2-}$ are tetrahedral and have very different spectra in visible region as compared with those of octahedrally co-ordinated cobalt (II) complexes such as $[Co(OH_2)_6]^{2+}$ etc.[12,15,16] From the figure, it is evident that the heteropolytungstate has a tetrahedrally co-ordinated cobalt (II) ion. The spectrochemical series for ligands of tetrahedrally co-ordinated cobalt (II) complexes have now been determined as follows:

$O^{=}$ (heteropolytungstate)*, NCS^-, Cl^-, Br^- [17], I^- [17].

The order coincides very well with that of cobalt (III) complexes[9,10]. Baker et al.[6] assigned to this heteropolyanion a structural formula $[Co^{II}O_6W_{12}O_{36}]^{10-}$. But some modifications seem necessary on the basis of the above spectral data. The anion is probably represented by the formula $[Co^{II}O_4W_{12}O_{38}]^{10-}$ or $[Co^{II}O_4W_{12}O_{36}]^{6-}$.

(3) $K_4H_5[Co^{III}(W_2O_7)_6]\cdot 18H_2O$—This is a cobalt (III) analogue of the cobalt (II)

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[9] R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).

[10] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

[11] A. Kiss and M. Gerendás, *Z. Physik. Chem.*, **A180**, 117 (1937).

[12] S. Yamada and R. Tsuchida, This Bulletin, **27**, 436 (1954).

[13] H. Ito, *J. Chem. Soc. Japan*, **77**, 1383 (1956).

[14] H. Ito, unpublished data.

* Maximum values: $\nu_{max}=48.4\times 10^{13}$/sec., log ε_{max}= 2.36.

[15] C. J. Ballhausen and C. K. Jϕrgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

[16] L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

[17] W. R. Brode, *J. Am. Chem. Soc.*, **53**, 2457 (1931).

compound above mentioned. The two species can be reversibly converted into each other by oxidation and reduction6). This fact suggests that the central cobalt (III) atom in the oxidized species is also surrounded by four oxigen atoms. As was expected from this, the spectrum of this compound has a very unique feature and is entirely different from the spectra of hexa-coordinated Co (III) complexes (Fig. 3). A broad maximum is observed at frequency of about 77.0 with intensity $\log \varepsilon = 3.10$. This is the first example of such a tetrahedrally co-ordinated cobalt (III) complex, of which the spectrum was measured. A heteropolymolybdate containing a hexa-coordinated Co (III) atom shows in this region two absorption bands with lower intensities1).

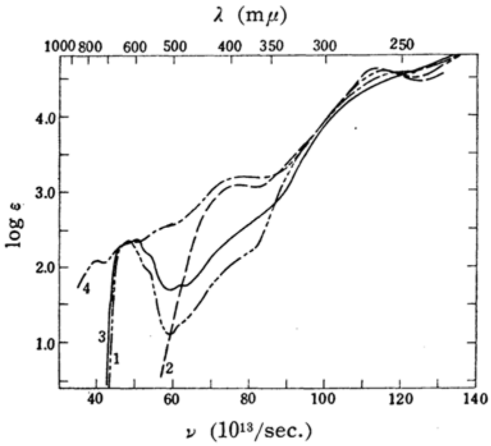

Fig. 3. Absorption spectra of:
1, $K_5H_5[Co^{II}(W_2O_7)_6]\cdot 16H_2O$;
2, $K_4H_5[Co^{III}(W_2O_7)_6]\cdot 18H_2O$;
3, $(NH_4)_8[Co^{II}Co^{II}(W_{12}O_{42})]\cdot 20H_2O$;
4, $K_7[Co^{II}Co^{III}(W_{12}O_{42})]\cdot 16H_2O$.

(4) $(NH_4)_8[Co^{II}Co^{II}(W_{12}O_{42})]\cdot 20H_2O$ — The absorption spectrum of this compound (Fig. 3) reveals that it contains at least one cobalt(II) atom in tetrahedrally co-ordinated state. The intensity of the band characteristic of the tetrahedral cobalt(II) ion is of the same order of the uninuclear cobalt(II) heteropolytungstate above mentioned. Thus it is perhaps certain that the other cobalt(II) atom in this compound has an octahedrally co-ordinated structure. Since such an octahedrally co-ordinated cobalt(II) ion is expected to have less intense absorption than a tetrahedral cobalt(II) ion, the presence of the octahedral cobalt(II) ion has little contribution to the total form of the absorption curve. A tentative structural formula $[Co^{II}O_4(W_{12}O_{32})O_6Co^{II}]^{8-}$ seems adequate for the anion. This is in good agreement with the chemical evidence reported by Baker et al.6) who concluded that the two cobalt atoms are structurally non-equivalent.

(5) $K_7[Co^{II}Co^{III}(W_{12}O_{42})]\cdot 16H_2O$ — This dark brown compound can be reversibly converted into the above mentioned $Co^{II}Co^{II}$ compound. The absorption curve of the compound has a complicated structure as is seen in Figs. 3 and 4. The occurrence of a broad band at about 78.0 ($\log \varepsilon_{max} = 3.20$) proves that the cobalt atom which was oxidized is the tetrahedrally co-ordinated one. Therefore the formula of this anion becomes $[Co^{III}O_4(W_{12}O_{32})O_6Co^{II}]^{7-}$.

The complicated bands in the visible region suggest the interactions between the

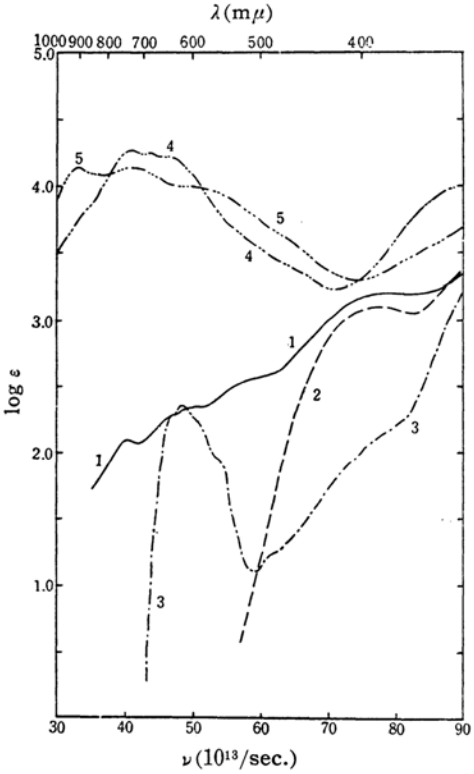

Fig. 4. Absorption spectra of:
1, $[Co^{III}O_4(W_{12}O_{32})O_6Co^{II}]^{7-}$;
2, $[Co^{III}O_4(W_{12}O_{38})]^{9-}$ or $[Co^{III}O_4(W_{12}O_{36})]^{5-}$;
3, $[Co^{II}O_4(W_{12}O_{38})]^{10-}$ or $[Co^{II}O_4(W_{12}O_{36})]^{6-}$;
4, $+4e^-$ reduction product of $H_4[SiO_4Mo_{12}O_{36}]$18);
5, $+5e^-$ reduction product of $H_4[SiO_4Mo_{12}O_{36}]$18).

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18) J. D. H. Strickland, *J. Am Chem. Soc.*, **74**, 862 (1952).

cobalt atoms in different oxidation states. For this anion, Baker et al.[6] assigned the structure wherein given WO_6 octahedra are simultaneously attached to two central cobalt atoms. If this is the case, the interactions between the two cobalt atoms must occur through the bridged —O—W—O— group. If an electron-transfer-process is considered, this interaction will be represented as follows:

$$\begin{aligned} &Co^{3+}-O-W^{6+}-O-Co^{2+} \\ &\rightleftharpoons Co^{3+}-O-W^{5+}-O-Co^{3+} \\ &\rightleftharpoons Co^{2+}-O-W^{6+}-O-Co^{3+} . \end{aligned}$$

It is well known that the reduction products of tungstates or molybdates are colored intense deep blue. The absorption spectra of such reduction products of $H_4[SiO_4Mo_{12}O_{36}]$, which were thoroughly studied by Strickland[18], are reproduced in Fig. 4. The resemblance of these spectra with the visible spectrum of the $Co^{II}Co^{III}$ heterotungstate anion, except that the intensity of the latter compound is lower by a factor of about 10^2, will be regarded as a proof for the interaction of the above mentioned type.

(6) Absorption band originating in tungstate skeleton.—All of the heteropolytungstates herein studied have very broad and intense absorption bands in ultraviolet region. This is certainly the absorption due to the tungstate skeleton. Similar but more diffuse molybdate bands have been observed by the present authors[1] for the heteropolymolybdates previously reported.

Summary

The visible and ultraviolet absorption spectra have been measured for some heteropolytungstates containing cobalt(II), cobalt(III) or manganese(IV) as central ions.

It has been shown that some cobalt(II) or cobalt (III) ions in the heteropolytungstates have tetrahedral co-ordination. This is the first case of the absorption spectra of $[Co^{II}(O^{=})_4]$- and $[Co^{III}(O^{=})_4]$-complexes being measured.

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