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Chirality of Waugh-type Enneamolybdomanganate(IV) Heteropolyanion. Observation of a Pfeiffer Effect

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Synopsis. Enneamolybdomanganate(IV), $[Mn^{IV}Mo_9O_{32}]^{6-}$, so-called Waugh-type heteropolyanion, has a chirality based on the D_3 symmetry around an MnO_6 octahedron. Attempts to resolve the racemic polyanion have been unsuccessful. A Pfeiffer effect was observed for the tetrabutylammonium salt in organic media containing *l*-brucine sulfate as an environment substance. This is the third example of heteropolyanions which show an optical activity.

Waugh-type enneamolybdomanganate(IV) formulated as $[Mn^{IV}Mo_9O_{32}]^{6-}$ is an octahedral manganese (IV) complex with the Mo_9O_{32} ligand, which was prepared first as potassium and barium salts by Hall.[1] Absorption spectrum of the ammonium salt was measured first in aqueous solution by Shimura and Tsuchida,[2,3] and the absorption bands were assigned to d^3 ions by Baker and Weakley.[4] A structure determination of the ammonium salt, $(NH_4)_6[MnMo_9O_{32}]\cdot 8H_2O$, by the single-crystal X-ray diffraction technique has shown that an MnO_6 octahedron has the D_3 symmetry.[5] Thus, this complex should be chiral. However, all attempts to resolve the racemic complex have failed.[4] There may be several reasons: (1) relatively rapid racemization, (2) the potassium and ammonium salts dissolve only in water, and (3) all resolving agents tested sofar form insoluble diastereomers in water. In this work we prepared the quaternary ammonium salt of the complex which is soluble in organic solvents and observed the Pfeiffer effect in the presence of *l*-brucine sulfate as an environment substance. This is the third example of heteropolyanions which show an optical activity; the first is $(NH_4)_6[Co_2Mo_{10}O_{34}(OH)_4]\cdot 7H_2O$, which was resolved by Shimura and his co-workers,[6] and the second is $[(C_4H_9)_4N]_5H[P_2Mo_{18}O_{62}]$, chirality of which is shown by observing the Pfeiffer effect by Garvey and Pope.[7]

Experimental

Electronic absorption and CD spectra were measured on a Hitachi 340-spectrophotometer with computer key-board and on a JASCO J-40AS spectropolarimeter, respectively. IR spectra were recorded with a JASCO IR-G spectrophotometer. Measurements were made at room temperature. For IR spectra measurement in acetonitrile a KBr cell with 0.1 mm optical path was used.

Preparation. The orange-red complex was prepared according to the literature,[4] analyzed and formulated as $(NH_4)_6[MnMo_9O_{32}]\cdot 6H_2O$ (Found: H, 2.11; N, 5.05%. Calcd: H, 2.20; N, 5.10%). This complex salt was converted to the free acid by passing the aqueous solution through a cation-exchange resin (Dowex-50W, H form) column. The acid form of the complex is readily soluble in aqueous solution and stable except when it is left standing for a long time. An aqueous solution containing an equimolar amount of tetrabutylammonium bromide (9.75 g) and potassium chloride (2.25 g) was added to the free acid solution obtained from the starting ammonium salt (5 g). Pale brick-red precipitate was collected, washed several times with a small amount of water, and dried *in vacuo*. The complex is readily soluble in water and various organic solvents except for ethyl ether, and cannot be easily recrystallized. The complex is contaminated with yellow $Mo_6O_{19}^{2-}$ as an impurity, which shows chracteristic IR bands at 800 and 950 cm^{-1}. The impurity crystallizes out of the acetonitrile solution and is removed by filtration. The complex can be reprecipitated by adding excess isobutyl methyl ketone to the filtrate, although the yield is remarkably low. The complex thus obtained was formulated as $K_2[(C_4H_9)_4N]_4[MnMo_9O_{32}]\cdot 13H_2O$ (Found: C, 28.32; H, 5.63; N, 2.02%. Calcd: C, 28.34; H, 5.35; N, 2.07%). The potassium tetrabutylammonium salt is sufficiently stable in the solid state, while it decomposes in organic media after a long time.

Results and Discussion

Absorption spectra of the complex in the acetonitrile solutions (6.6×10^{-4} mol dm^{-3}), which contain various molar ratios of *l*-brucine sulfate as an environment substance, are shown in Fig. 1, together with that of the solution without *l*-brucine sulfate. The form

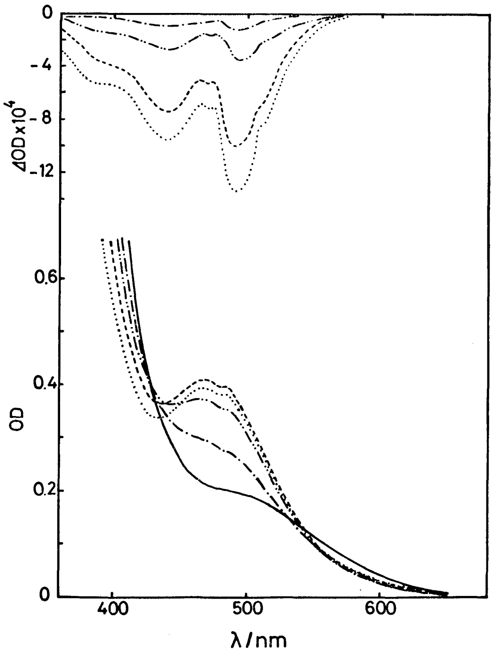

Fig. 1. Absorption and CD spectra of the tetrabutylammonium salt of $[MnMo_9O_{32}]^{6-}$ anion (6.6×10^{-4} mol dm^{-3}) in acetonitrile containing various moles of *l*-brucine sulfate. Molar ratios of brucine: complex are 2:1 (—·—·—), 4:1 (—··—··—), 6:1 (----) and 8:1 (······). A full line shows the spectrum of the complex alone.

of the spectrum of the parent ammonium salt in an aqueous solution has been known to depend markedly on the pH.[4] The spectrum of the tetrabutylammonium salt in acetonitrile is similar to that of the ammonium salt at pH 2.9. As the molar ratio of brucine to the complex increases, the absorbance at 480 nm increases, with a double peak appearing at 468 and 484 nm. For the solution with the molar ratio of brucine higher than 4 the spectral change becomes very small. The double peak coincides with that of the ammonium salt observed in the aqueous solution of pH 3.5—4.9. The splitting is due to a trigonal distortion of the first spin-allowed transition ($^4T_{2g} \leftarrow {}^4A_{2g}$) in the d^3 octahedral MnO_6 ion.[4,8] Thus, the effect of *l*-brucine for the complex in acetonitrile resembles the pH-raising effect for the ammonium salt in an aqueous solution.

The circular dichroism (CD) spectra were observed for mixtures of the complex and *l*-brucine, the optical activity of which appeared only after the addition of *l*-brucine. They are also shown in Fig. 1. A remarkable change in the CD spectra is found for solutions with the molar ratio of brucine to the complex, 4:1, 6:1, and 8:1, whereas their absorption spectral change is very small. This is attributed neither to the induced CD accompanied with outer-sphere association, nor to the chemical reaction between the complex and *l*-brucine since the experiments were performed in a relatively low concentration ($\approx 10^{-3}$ mol dm^{-3}) of the latter. Conclusively, this is attributed to a shift of the equilibrium between two enantiomers of the racemic complex, *viz.* the Pfeiffer effect.

IR spectra have shown that the structure of polyanion-moiety depends significantly on the cation, and the bands of the tetrabutylammonium salt in 700—500 cm^{-1} were less split than those of the parent ammonium salt. This shows that a site symmetry of the tetrabutylammonium salt may be higher than that of the parent ammonium salt. IR spectrum of the acetonitrile solution of the tetrabutylammonium salt was also measured with and without *l*-brucine sulfate. When the molar ratio of brucine:complex is 4:1, the IR spectrum is close to that of the solid ammonium salt which has the D_3 symmetry around the MnO_6 octahedron. The IR spectrum in the absence of *l*-brucine is substantially unchanged from that of the solid tetrabutylammonium salt except for the sharpening of bands. These results indicate that the site symmetry of the complex ion is lowered to D_3 by the addition of *l*-brucine.

Further, DMF and *l*-strychnine sulfate were used as the solvent and the environment substance, respectively to demonstrate the Pfeiffer effect and the shift of the equilibrium toward the (+)-enantiomer of the complex. Unfortunately the equilibrium shift was not observed; only the shift toward the (−)-enantiomer by the Pfeiffer effect was shown. Besides, the observed CD was much reduced than that observed in the brucine-complex system in acetonitrile.

The CD spectrum of the brucine-complex system in acetonitrile, in which the (−)-enantiomer predominates, shows peaks at 510, 490, 470, 440, and 390 nm. The selection rule for the first and the second magnetic dipole transitions of the d^3 ion under the D_3 symmetry indicates that two transitions ($^4E \leftarrow {}^4A_2$ and $^4A_1 \leftarrow {}^4A_2$) for the first electronic transition, and only one transition ($^4E \leftarrow {}^4A_2$) for the second transition are allowed. Even if a contribution from spin-forbidden transitions is taken into account, the number of the CD peaks is too many. This may indicate that the electronic transitions are not pure d-d ones. Further investigation on the origin of the CD peaks is required.

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