Optical Resolution of a Heteropolymolybdate Anion

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Shimura(1) studied the electronic absorption spectrum of a dark olive green heteropolymolybdate containing cobalt(III) in a ratio of Co : Mo= 1 : 5, and concluded that the heteropoly anion contains two or more central cobalt(III) atoms with a linkage of $\mathrm{Co^{III}\text{-}O\text{-}Co^{III}}$. Recently, Evans and Showell(2) determined the crystal structure of the ammonium salt of this anion and proved the dimeric structure of the anion, $[\mathrm{H_4Co_2Mo_{10}O_{38}}]^{6-}$ with the two $\mathrm{CoO_6}$ octahedra sharing two oxygens. They showed that the dicobalt(III)-decamolybdate(VI) anion has a point group symmetry D_2, and that it might be possible to resolve the complex ion into the optical antipodes.

We have succeeded in the optical resolution as follows. To a solution of $(\mathrm{NH_4})_6[\mathrm{Co_2Mo_{10}O_{34}(OH)_4}]\cdot 7\mathrm{H_2O}$ (1.0 g, 0.5 mmol, in 1000 m*l* of water) was added a solution of $(+)_{589}$-[Co $\mathrm{en_3}$]$\mathrm{Br_3\cdot H_2O}$ (0.25 g, 0.5 mmol, in 200 m*l* of water). After the solution had been kept at 55°C for 4 hr, the less soluble dark yellowish green diastereomer deposited was collected by filtration.

Found: C, 6.20; H, 3.03; N, 7.19%. Calcd for $(+)_{589}$-[Co $\mathrm{en_3}]_2\cdot(+)_{589}$-$[\mathrm{Co_2Mo_{10}O_{34}(OH)_4}]\cdot 9\mathrm{H_2O}$: C, 6.18; H, 3.00; N, 7.21%. The diastereomer was stirred with the cation-exchange resin (Dowex 50 W×8, 200—400 mesh, $\mathrm{NH_4^+}$ form) in water. After the resin had been filtered off, ammonium chloride was dissolved in the green filtrate. The solution was kept in a refrigerator overnight in order to complete the crystallization of the optically active isomer. $[\alpha]^{25}_{589}=+100°$.

Found: H, 1.99; N, 4.42%. Calcd for $(+)_{589}$-$(\mathrm{NH_4})_6[\mathrm{Co_2Mo_{10}O_{34}(OH)_4}]\cdot 5\mathrm{H_2O}$: H, 2.03; N, 4.45%.

The electronic absorption and circular dichroism (CD) spectra are shown in Fig. 1. Four CD bands, (−), (+), (−) and (−) listing from the longer wavelength side, are observed in the region of d-d absorption bands of the $(+)_{589}$ isomer. The isomer shows two rather strong CD bands in the region of near ultraviolet absorption band, which may be assigned to a charge-transfer band characteristic to the bridging oxygen ligands in the linkage of $\mathrm{Co^{III}}{<}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}{>}\mathrm{Co^{III}}$. Similar CD bands have also been reported for some tetranuclear Co(III) complexes containing OH-bridges.(3)

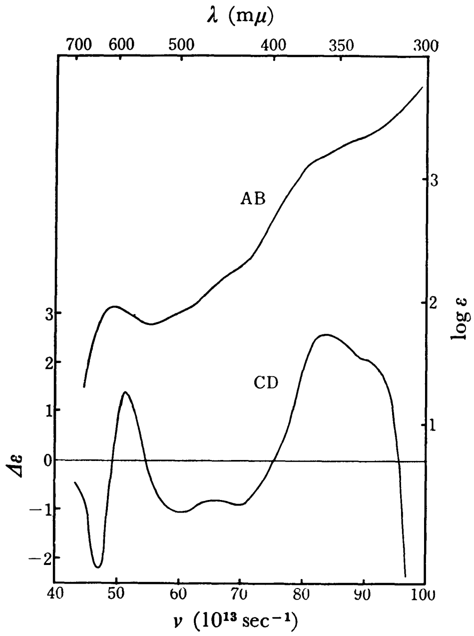

Fig. 1. Absorption AB and CD curves of $(+)_{589}$-$(\mathrm{NH_4})_6[\mathrm{Co_2Mo_{10}O_{34}(OH)_4}]\cdot 5\mathrm{H_2O}$.

This heteropolymolybdate anion appears to be the first heteropoly complex which has been optically resolved.

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1) Y. Shimura, H. Ito and R. Tsuchida, *Nippon Kagaku Zasshi*, **75**, 560 (1954).

2) H. T. Evans, Jr., and J. S. Showell, *J. Amer. Chem. Soc.*, **91**, 6881 (1969).

3) S. F. Mason and J. W. Wood, *Chem. Commun.*, **1967**, 209.