Preparation and Optical Resolution of μ-Amido-μ-superoxo and μ-Amido-μ-peroxo Tetrakis(α-di-imine) Dicobalt(III) Ions

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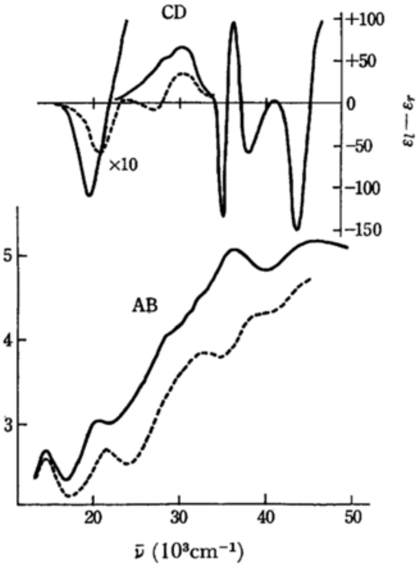
New binuclear cobalt(III) complexes of the type, $[L_2Co(\mu\text{-}NH_2,O_2)CoL_2](ClO_4)_n$, where L is 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bip), and $n=3$ and $n=4$ correspond to the so-called μ-peroxo and μ-superoxo form, respectively, were prepared and resolved into their optical isomers. These are first examples of binuclear cobalt(III) complexes involving conjugated aromatic ligands, and their circular dichroism (CD) spectra will provide useful information in elucidating the electronic state of binuclear complexes. The μ-peroxo complexes were precipitated by warming a mixture of $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4](ClO_4)_4$ and phen or bip (molar ratio 1 : 4) in methanol at 60°C for 10 hr, and recrystallized from hot water. The μ-superoxo complexes were obtained by adding solid sodium perchlorate to 7N nitric acid solutions of the corresponding μ-peroxo complexes. Found: C, 47.75; H, 2.72; N, 10.29%. Calcd for $C_{48}H_{36}N_9O_{15}Co_2Cl_3=[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_3\cdot H_2O$: C, 47.76; H, 3.01; N, 10.44%. Found: C, 43.60; H, 2.94; N, 9.34%. Calcd for $C_{48}H_{38}N_9O_{20}Co_2Cl_4=[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_4\cdot 2H_2O$: C, 43.66; H, 2.90; N, 9.55%. Found: C, 42.99; H, 3.31; N, 11.45%. Calcd for $C_{40}H_{38}N_9O_{16}Co_2Cl_3=[(bip)_2Co(\mu\text{-}NH_2,O_2)Co(bip)_2](ClO_4)_3\cdot 2H_2O$: C, 42.71; H, 3.41; N, 11.21%. Found: C, 39.69; H, 3.11; N, 10.50%. Calcd for $C_{40}H_{36}N_9O_{19}Co_2Cl_4=[(bip)_2Co(\mu\text{-}NH_2,O_2)Co(bip)_2](ClO_4)_4\cdot H_2O$: C, 39.82; H, 3.01; N, 10.45%. The racemic μ-peroxo complexes were converted into chloride and treated with silver *d*-antimonyltartrate to be resolved into optical isomers. The optically active μ-superoxo complexes were prepared from the corresponding active μ-peroxo complexes.



Fig, 1. The absorption (AB) and CD spectra of $(+)_D\text{-}[(phen)_2Co(\mu\text{-}NH_2,O_2)Co(phen)_2](ClO_4)_4$ in 60% perchloric acid (——) and $\Lambda\Lambda\text{-}[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2](NO_3)_4$ in water (------).

As the figure shows, the CD spectrum of $(+)_D$-μ-superoxo-phen complex is similar to that of $(-)_D\text{-}\Lambda\Lambda\text{-}[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$ (en= ethylenediamine)[1] in the visible region. Furthermore, the phen complex gives a strong negative and a positive CD component from longer to shorter wavelength corresponding to the π-π^* transition of chelated phen (34000—37000 cm^{-1}). These results lead to the conclusion that the $(+)_D$-μ-superoxo-phen complex has $\Lambda\Lambda$ absolute configuration.[2,3] The enantiomers, $(+)_D$-μ-peroxo-phen, $(+)_D$-μ-superoxo-bip and $(+)_D$-μ-peroxo-bip have also $\Lambda\Lambda$ configuration.

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[1] Y. Sasaki, J. Fujita and K. Saito, This Bulletin, **42**, 146 (1969).

[2] S. F. Mason and J. W. Wood, *Chem. Commun.*, **1968**, 1512.

[3] B. Bosnich, *Inorg. Chem.*, **7**, 178 (1968).