CHEMISTRY LETTERS, pp. 423-426, 1974. Published by the Chemical Society of Japan

THE PREPARATION OF CIS,CIS-DICYANOCARBONATODIAMMINECOBALTATE(III) AND CIS,CIS-OXALATODIAQUODIAMMINECOBALT(III) COMPLEXES[1]

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Two new complexes having cis,cis-geometry with respect to unidentate ligands, $Na[Co(CN)_2CO_3(NH_3)_2]\cdot 2H_2O$ and $[Co(C_2O_4)(H_2O)_2(NH_3)_2]NO_3$, have been prepared and their resolutions have also been achieved.

The resolution of a cobalt(III) complex consisting of three kinds of unidentate ligands has not yet been reported.[2] As for similar complex containing a symmetrical bidentate ligand in place of two identical unidentates, the complete resolution of cis-dichloro-cis-diammine-ethylenediaminecobalt(III) complex, cis,cis-$[CoCl_2(NH_3)_2en]^+$, has been reported by Hawkins et al.[3,4] We now succeeded in preparing two new complexes, cis-dicyano-carbonato-cis-diammine complex and oxalato-cis-diaquo-cis-diammine complex, using tricarbonatocobaltate(III) complex as their starting materials. We were also successful in the resolution of these complexes.

Sodium cis,cis-Dicyanocarbonatodiamminecobaltate(III) Dihydrate To a cold, green solution of tricarbonatocobaltate(III) ($Co(NO_3)_2\cdot 6H_2O$ 15 g (0.05 mol) scale), was added potassium cyanide (7.5 g, 0.12 mol) and the mixture was stirred at room temperature for an hour, whereby a deep red solution of the cis-$[Co(CN)_2(CO_3)_2]^{3-}$ complex was obtained.[5] After this solution had been neutralized with aqueous perchloric acid, ammonium perchlorate (15 g, 0.12 mol) and concentrated aqueous ammonia (50 mℓ) were added to it. The mixture was then stirred at room temperature for several hours. The solution once filtered was concentrated to a half of original volume. The concentrated solution was again neutralized and filtered. The filtrate was diluted to treble volume with water and then charged on an ion-exchange column containing Dowex 1 X 8 resin in Cl-form (5 X 20 cm). By elution with 0.3 M sodium chloride, an orange band came out before the others. The effluent was evaporated to dryness under reduced pressure at ca. 30°C. The solid material obtained was extracted with methanol, and the methanol solution was evaporated to dryness. The residue was dissolved in a minimum amount of water. In keeping the solution in a refrigerator after addition of ethanol, yellow crystals deposited. These were recrystallized three times from water. The yield was about 0.3 g.

Found: C, 13.98; H, 4.23; N, 20.91%. Calcd for $Na[Co(CN)_2CO_3(NH_3)_2]\cdot 2H_2O$: C, 13.64; H, 3.82; N, 21.22%.

Reaction of the $[CoCO_3(NH_3)_4]^+$ complex with potassium cyanide also gave the same complex, but the yield was poorer.

For the resolution of this complex, organic agents such as brucine and strychinine were tried without success, but the $(-)_{589}$-$[Co(C_2O_4)(en)_2]^+$ complex gave a crystalline diastereoisomer; the racemate (2.4 g, 0.01 mol) dissolved in water (10 mℓ) was added to an aqueous solution of the resolving agent (2 g (0.005 mol)/40 mℓ H_2O) prepared as the acetate salt by the literature method.6) After the removal of the precipitated material, the solution was kept in a refrigerator, whereupon orange crystals deposited. Recrystallization was repeated until the CD peak at 24.1 kK reached to a constant value. The yield was about 0.3 g.

Found: C, 21.31; H, 5.25; N, 21.78%. Calcd for $[Co(C_2O_4)(C_2H_8N_2)_2][Co(CN)_2CO_3(NH_3)_2]\cdot 2H_2O$: C, 21.44; H, 5.16; N, 22.05%.

This diastereoisomer could be broken by passing it down a cation-exchange column (Dowex 50W X 8, Na-form), and the resulting species preserved its optical activity for a day at room temperature.

cis,cis-Oxalatodiaquodiamminecobalt(III) Nitrate To a solution of potassium carbonatooxalatodiamminecobaltate(III) monohydrate (5.8 g (0.02 mol)/60 mℓ H_2O), which had been prepared by the reaction of potassium tricarbonatocobaltate(III) and ammonium oxalate,7) aqueous nitric acid (3 N) was added until the evolution of carbon dioxide ceased. After the solution was filtered, a small amount of aqueous nitric acid was added to the filtrate, and it was then kept in a refrigerator overnight. Red-purple crystals thus obtained were recrystallized by dissolving in water (~40°C) and adding aqueous nitric acid in the cold. The yield was about 4.0 g.

Found: C, 8.84; H, 3.89; N, 14.78%. Calcd for $[Co(C_2O_4)(H_2O)_2(NH_3)_2]NO_3$: C, 8.61; H, 3.62; N, 15.06%.

The corresponding sulfate could be obtained by dissolving the carbonato complex in aqueous sulfuric acid.

The resolution of this complex was carried out with $Na(+)_{546}$-$[Co(edta)]$.8,9) A proper amount of the above complex was dissolved in water slightly acidified with acetic acid, and the solution was passed into a Dowex 1 X 8 resin column (Cl-form). To the effluent was added a half-equimolar amount of the resolving agent, and the mixture was concentrated to a small volume under reduced pressure and then kept in a refrigerator. The crystals deposited were dissolved in a minimum amount of cold water previously acidified with acetic acid (~pH 3). After the solution was filtered, a small amount of ethanol was added to the filtrate with scratching under iced condition, whereupon red-violet precipitate of the diastereoisomer formed. This was recrystallized several times from water containing acetic acid.

Found: C, 23.97; H, 4.27; N, 9.36%. Calcd for $[Co(C_2O_4)(H_2O)_2(NH_3)_2][Co(C_{10}H_{12}O_8)]\cdot 2H_2O$: C, 24.01; H, 4.37; N, 9.33%.

In general, the $[Co(chelate)A_2B_2]$-type complexes have three possible geometrical isomers concerning with the arrangements of the unidentate ligands A and B. However, it is obvious from the successful resolutions that the present dicyanodiammine and diaquodiammine complexes have cis,cis-arrangements with respect to the unidentate ligands. Figure 1 shows the absorption spectrum of the racemic $[Co(CN)_2CO_3(NH_3)_2]^-$ complex and the CD spectrum of the resolved species; there are two absorption maxima at 20.7 (log ε=1.96) and 23.5 kK (log ε=2.02) in the first absorption band region. The CD spectrum shows three peaks at 20.9 ($\Delta\varepsilon$=+0.980), 24.1 ($\Delta\varepsilon$=-1.11) and 29.7 kK ($\Delta\varepsilon$=+0.245). The first two CD peaks relate closely to the two maxima of the first absorption band. The second absorption band is considerably covered by the so-called third absorption band, but the maximum position is assumed from the third peak of the CD spectrum.

After a solution containing this resolved complex species had been acidified with aqueous perchloric acid, the resulting solution was submitted to spectrum measurements. The results are shown in Fig. 2. It was ascertained that the diaquo complex species thus formed was chromatographically pure. In both the absorption and CD spectra, their features are similar to those of the parent carbonato complex. The second absorption band reveals its maximum in this case. Furthermore, it was found that these absorption and CD spectra of the diaquo complex were completely reformed into those of the carbonato complex, when excess sodium carbonate was added to the acid solution. These facts indicate that acid-hydrolysis of the resolved dicyanocarbonatodiammine complex takes place with full retention of configuration. Attempt to isolate the active $[Co(CN)_2(H_2O)_2(NH_3)_2]^+$ complex as crystals has not yet been succeeded.

Figure 3 shows the absorption spectra of the $[Co(C_2O_4)(H_2O)_2(NH_3)_2]^+$ (racemate) and $[Co(CO_3)(C_2O_4)(NH_3)_2]^-$ (racemate) complexes. The CD spectrum of the resolved diaquo complex is also shown in Fig. 3; the diaquo complex shows the first absorption maximum at 18.2 kK (log ε=1.84) and the second maximum at 26.2 kK (log ε=2.02). The CD spectrum shows two peaks at 17.0 (Δε=-0.23) and 19.6 kK (Δε=+0.20) in the first absorption band region.

When a solution of the resolved complex prepared in form of the chloride was alkalized with potas-

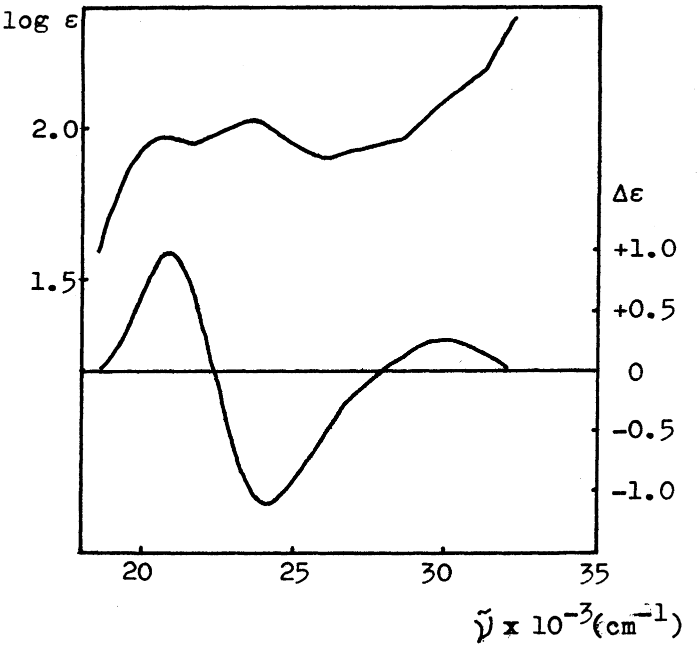

Fig.1 Absorption and CD spectra of the $[Co(CN)_2CO_3(NH_3)_2]^-$ complex

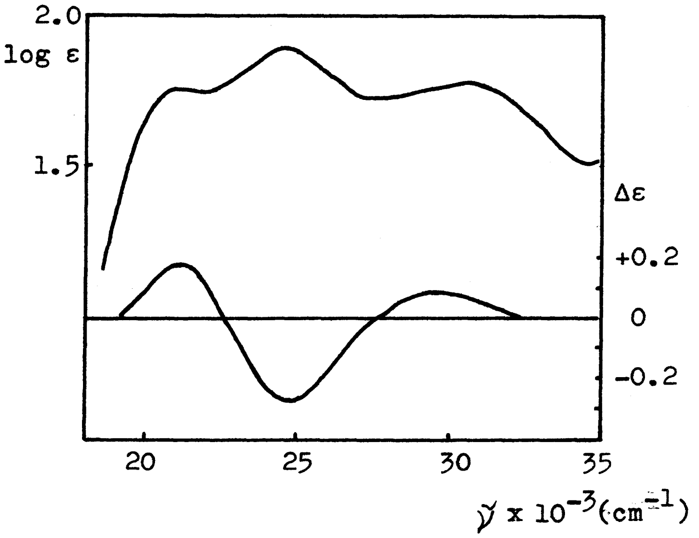

Fig.2 Absorption and CD spectra of the $[Co(CN)_2(H_2O)_2(NH_3)_2]^+$ complex

sium bicarbonate, the resulting solution exhibited the same absorption spectrum as that of the cis-$[Co(CO_3)(C_2O_4)(NH_3)_2]^-$ complex. And the CD spectrum of the solution showed a dominant positive peak at 17.6 kK (Fig. 3). When this alkaline solution was acidified with a mineral acid, the resulting solution exhibited the same CD spectrum as that of the original diaquo complex except for a little decrease in Δε value. These facts suggest that the conversion between the resolved $[Co(C_2O_4)(H_2O)_2(NH_3)_2]^+$ species and the active $[Co(CO_3)(C_2O_4)(NH_3)_2]^-$ species takes place with retension of configuration. By the way, the resolution of the $[Co(CO_3)(C_2O_4)(NH_3)_2]^-$ complex is in progress.

In comparison with the before-mentioned dicyanodiammine complex, this diaquodiammine complex was rather unstable to racemization; the resolved complex species, in neutral aqueous solution, lost its optical activity within 30 minutes at room temperature. When the solution was acidified and cooled, the racemization was considerably controlled.

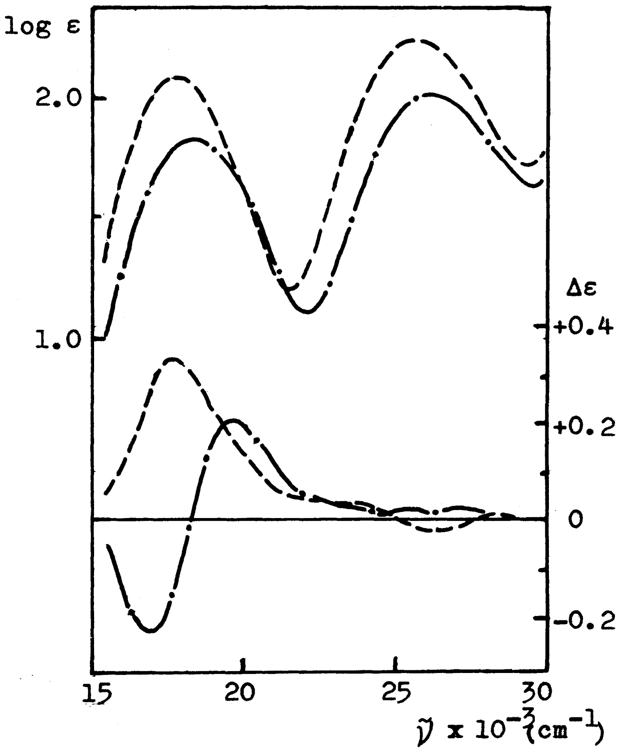

Fig.3 Absorption and CD spectra of the $[Co(C_2O_4)(H_2O)_2(NH_3)_2]^+$ (—•—) and $[Co(CO_3)(C_2O_4)$-$(NH_3)_2]^-$ (-----) complexes

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(Received March 11, 1974)