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Solid-Phase Thermal Reactions of Chromium(III) and Copper(II) Complexes Containing Pentadentate Ethylenediaminetetraacetate and 1,2-Propanediaminetetraacetate Ions

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Synopsis. Thermal reactions of the solid complexes [Cr{Hedta or (*RS*)-Hpdta}(H_2O)] and [Cu{H_2edta or (*RS*)-H_2pdta(H_2O)] were investigated under quasi-isothermal and -isobaric conditions (Q-conditions) and under open dynamic conditions (D-conditions), where Hedta and H_2edta, and Hpdta and H_2pdta denote mono- and diprotonated ethylenediaminetetraacetate and 1,2-propanediaminetetraacetate ions, respectively.

We previously reported the thermal deaquation of the chromium(III) complex [Cr{Hedta or (*RS*)-Hpdta}(H_2O)][1] and thermal dehydrohalogenation of the cobalt(III) complex Na[CoX{Hedta or (*RS*)-Hpdta}] (X=Cl or Br) under D-conditions, where Hedta and Hpdta are monoprotonated ethylenediaminetetraacetate and 1,2-propanediaminetetraacetate ions, respectively.[2] In the latter case, pentadentate edta or pdta changed to hexadentate ligand after dehydrohalogenation, but in the former case we failed to isolate hexadentate edta and pdta chromium(III) complexes by deaquation because the reaction was accompanied by a subsequent decomposition. Quasi-isothermal and -isobaric conditions (Q-conditions) are fundamentally different from D-conditions.[3] The present study was therefore undertaken to investigate the thermal reactions of [Cr{Hedta or (*RS*)-Hpdta}(H_2O)]·$n$$H_2O$ (n is 0 for the Hedta and 1 for the Hpdta complexes) under Q-conditions. Thermal reactions of [Cu{(*RS*)-H_2pdta}(H_2O)]·1/2H_2O and their optical antipodes are not yet known. The optical pairs (+)$_D$- and (−)$_D$-[Cu{(*S*)- and (*R*)-H_2pdta}]·1/2H_2O were newly prepared in this study, of which thermal reactions were also investigated.

Experimental

Preparation of Complexes. [Cr(Hedta)(H_2O)] (**1**),[4] [Cr{(*RS*)-Hpdta}(H_2O)]·H_2O (**2**),[4] [Cu(H_2edta)(H_2O)] (**3**),[5] and [Cu(*RS*)-H_2pdta(H_2O)]·1/2H_2O (**4**)[6] were prepared according to the respective methods of literatures.

(+)$_D$-[Cu{(*S*)-H_2pdta}]·1/2H_2O (**5**) was prepared from (−)$_D$-Ba[Cu{(*S*)-pdta}(H_2O)]·2H_2O.[6] The barium salt (2.78 g) in hot water (45 cm^3) was treated with exactly one equivalent of sulfuric acid (10 cm^3, 0.5 mol dm^{-3}), and the mixture was heated to boiling. The $BaSO_4$ thus formed was removed by filtration, the filtrate was evaporated to 10 cm^3 and cooled in refrigerator. The light blue colored compound was collected by filtration and washed with ethanol and then ether. Found: C, 34.94; H, 4.53; N, 7.60%. Calcd for $C_{11}H_{17}N_2O_{8.5}Cu$: C, 35.05; H, 4.51; N, 7.43%.

(−)$_D$-[Cu{(*R*)-H_2pdta}]·1/2H_2O (**6**) was prepared by the same method as that described for complex **5** except that (+)$_D$-Ba[Cu{(*R*)-pdta}(H_2O)]·2H_2O was used as the starting material. Found: C, 34.86; H, 4.40; N, 7.10%. Calcd for $C_{11}H_{17}N_2O_{8.5}Cu$: C, 35.05; H, 4.51; N, 7.43%.

Thermal Measurements. The thermal reactions of the complexes were carried out under Q-conditions and D-conditions by using Q-derivatograph[3,7] and a Seiko SSC/580 TG/DTA-30 thermal analyzer, respectively. The measurements under D-conditions were carried out under a constant flow of nitrogen at the heating rate of 2 °C min^{-1}.

Spectral Measurements. The electronic spectra of the samples in aqueous solution were monitored on a Jasco UVIDEC-505 UV/VIS recording digital spectrophotometer, and those in powder state on a Hitachi EPU-2A spectrophotometer equipped with a standard Hitachi reflection attachment (Type R-3). IR spectra of the samples were measured by a KBr-disk method with a Jasco A-3 infrared spectrophotometer.

Specific Rotation Measurement. All rotations were measured in 1 dm tube in aqueous solution at 15 °C by a Jasco DIP—181 digital polarimeter. An 18.0 mg sample in 10 cm^3 of water was used for each measurement.

Results and Discussion

Figure 1 shows the TG curves of complexes **1** and **2** measured under Q-conditions. The TG curve of [Cr(Hedta)(H_2O)] (**1**) is essentially similar to that of D-derivatogram reported earlier[1] except that the deaquation temperature under Q-conditions is higher (302 °C) than that under D-conditions (280 °C), and it suggests a slim possibility of synthesizing the deaquated hexadentate complex H[Cr(edta)]. Thermal behavior of [Cr{(*RS*)-Hpdta}(H_2O)]·H_2O (**2**) under Q-conditions is different from that under D-conditions. Under Q-conditions, the complex starts to lose water molecule slowly at 171 °C, then a sharp mass loss can be seen at 235—247 °C and a clear plateau is obtained. The weight loss (9.0%) is close to that (9.2%) calculated for 2 mol of water. The product isolated at 250 °C under Q-conditions is pure H[Cr{(*RS*)-pdta}], where pdta functions as hexadent-

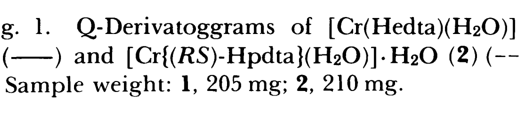

Fig. 1. Q-Derivatoggrams of [Cr(Hedta)(H_2O)] (**1**) (——) and [Cr{(*RS*)-Hpdta}(H_2O)]·H_2O (**2**) (----). Sample weight: **1**, 205 mg; **2**, 210 mg.

ate ligand. It is interesting to note that the lattice and coordinated waters are evolved simultaneously. The complex before heating shows two IR bands at 1738 and 1610 cm^{-1} which are due to free -COOH and coordinated -COO$^-$ groups, respectively. The product, however, does not give the band due to free -COOH group. It is thus clear that the non-coordinated -COOH group comes into coordination toward chromium(III) ion after the elimination of the coordinated water molecule.

The crystal structure of [Cu(H$_2$edta)(H$_2$O)] (**3**) is known.[8] The potentially hexadentate edta ligand acts as pentadentate with a water molecule taking up the sixth position, giving rise to a six-coordinated environment about copper(II) ion. The IR (in the carbonyl region) and electronic reflectance spectra of complex **3** and [Cu{(*RS*)-H$_2$pdta}(H$_2$O)]·1/2H$_2$O (**4**) are essentially similar to each other. These results suggest that the stereochemistry around the copper(II) ion in complex **4** must be the same as that of complex **3**.

Figure 2 shows the TG and DTA curves (D-conditions) and TG curve of complex **4** under Q-conditions. Under D-conditions, the complex loses its lattice water (Found: 2.23%, Calcd: 2.28%) and coordinated water (Found: 4.57%; Calcd: 4.56%) in the temperature range of 75—90 °C and 150—175 °C respectively, and then a clear plateau is obtained. The corresponding DTA curve shows initially an endothermic peak due to the elimination of lattice water then two overlapping endothermic peaks for the evolution of coordinated water molecule. The elimination of the coordinated water takes place in two steps, but details thereof are still unknown.

$$\underset{\text{light blue}}{[\mathrm{Cu}\{(RS)\text{-}\mathrm{H_2pdta}\}(\mathrm{H_2O})]\cdot 1/2\mathrm{H_2O}} \xrightarrow[\Delta]{-1/2\mathrm{H_2O}}$$

$$\underset{\text{light greenish blue}}{[\mathrm{Cu}\{(RS)\text{-}\mathrm{H_2pdta}\}(\mathrm{H_2O})]} \xrightarrow[\Delta]{-\mathrm{H_2O}} \underset{\text{deep blue}}{[\mathrm{Cu}\{(RS)\text{-}\mathrm{H_2pdta}\}]}$$

The IR spectrum of complex **4** shows a medium strong band at 1740 cm^{-1} due to free -COOH group and a very strong broad peak at 1590 cm^{-1} due to coordinated COO$^-$ group. As the dehydrated complex has a tendency to absorb water molecule, the IR spectrum of **4** has been recorded at 125 and 190 °C in nitrogen atmosphere. The peak due to free -COOH group was always observed. This suggests that the non-coordinated -COOH group remains free even after the elimination of the coordinated water molecule, and pdta still functions as pentadentate ligand. Consequently, Cu^{II} ion is penta-coordinated in the dehydrated complex. The solid state reflectance spectra (350—850 nm) of complex **4** and its dehydrated form show bands at about 740 and about 710 nm. The shifting of the absorption band toward the shorter wavelength region also suggests the formation of penta-coordinated Cu^{II} complex.[9] The dehydrated complex may be either trigonal bipyramidal or square pyramidal in structure, but the decision could not be made.

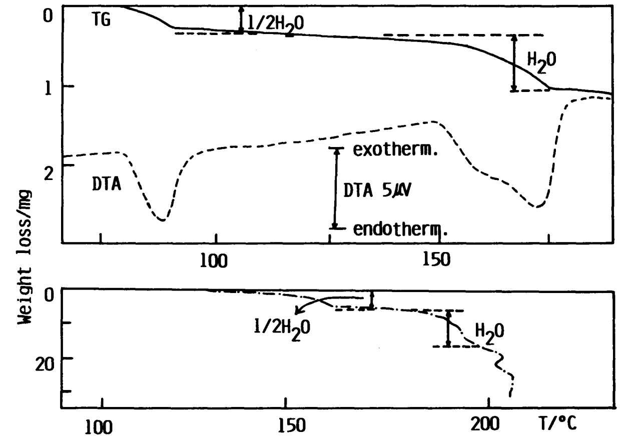

Fig. 2. TG (——) and DTA (----) curves (D-conditions), and TG (—·—) curve (Q-conditions) of [Cu{(*RS*)-H$_2$pdta}(H$_2$O)]·1/2H$_2$O (**4**). Sample weight: for TG-DTA (D-conditions), 15.6 mg; for TG (Q-conditions), 199 mg.

Under Q-conditions, the thermal reaction of complex **4** is unusual. The complex evolves its lattice water in the temperature range of 124—163 °C, and above 163 °C evolution of coordinated water molecule takes place upto 195 °C. The product isolated in this stage is violet in color. The product shows a broad absorption band at 561 nm and its analytical composition nicely fits with [Cu(H$_2$pdta)] (Found: C, 35.10; H, 4.39; N, 7.46%. Calcd for C$_{11}$H$_{16}$N$_2$O$_8$Cu: C, 35.19; H, 4.35; N, 7.61%). The IR spectrum of the product shows two peaks of comparable intensity at 1733 and 1718 cm^{-1} due to free -COOH group and a broad peak at 1610 cm^{-1} due to coordinated carboxylato groups. The two peaks at 1733 and 1718 cm^{-1} indicate the presence of two free -COOH groups in the product.[10] From the spectral and analytical data, it is conceivable that pdta functions as tetradentate ligand toward Cu^{II} ion.

We attempted to get a pair of optical antipodes of complex **4** from(−)$_D$-Ba[Cu{(*S*)-pdta}(H$_2$O)]·2H$_2$O ([α]$_D$: −126°) and (+)$_D$-Ba[Cu{(*R*)-pdta}(H$_2$O)]·2H$_2$O ([α]$_D$: +128°)[6]. However, complexes **5** and **6** were always isolated which do not contain any coordinated water molecule. The specific rotations of complexes **5** and **6** are [α]$_D$=+136.4° and −133.7°, respectively. It is interesting to note that pure complexes **5** and **6** can be obtained from the respective barium complexes. Appearance of a medium strong band at 1738 cm^{-1} in the IR spectra of complexes **5** and **6** does not support the full coordination of pdta. Therefore, Cu^{II} ion is probably pentacoordinated in the isomers. The electronic spectra of complex **6** in water and in the solid state (reflectance) were not identical, suggesting that the structure in water is different from that in the solid state. The electronic spectra of the racemic complex **4** and optical pairs **5** and **6** in water were identical. Thus, in water the optical pairs possess similar structure to that of the racemic complex **4**.

TGA runs of the optical isomers (under both Q- and D-conditions) show that dehydration occurs soom after heating is begun (30—35 °C). Anhydrous weight levels are attained at 140—190 °C (amounting to 2.4% of the total weight). As the temperature is raised further, there is a slow loss of weight resulting from the decomposition of the complexes. The dehydrated complexes **5** and **6** show $[\alpha]_D=+138.3°$ and $-137.3°$, respectively. The increase of rotations are due to the loss of molecular weight resulting from the elimination of lattice water.

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