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PREPARATION OF $[Co(TeO_6H_4)(en)_2]^+$ AND ITS CONDENSED COMPLEXES

Yutaka HOSOKAWA and Yoichi SHIMURA
Department of Chemistry, Faculty of Science, Osaka University
Toyonaka, Osaka 560

Three new complexes, $[Co(TeO_6H_4)(en)_2]^+$, $[Co(en)_2(Te_2O_{10}H_4)\text{-}Co(en)_2]^{2+}$, and $[\{Co(en)_2\}_2(Te_2O_{10})\{Co(en)_2\}_2]^{4+}$, have been isolated as their chlorides from the reaction solutions of cis-$[CoCl_2(en)_2]^+$ and $Te(OH)_6$, and their optical resolutions have been achieved.

Orthotellurate anion $[TeO_6H_{6-n}]^{n-}$, which is capable of coordinating with a cobalt(III) center as was exemplified by the isolation of $K_3[Co(TeO_6H_3)_2(OH_2)_2]$1), has a marked tendency to condense into polynuclear species such as $[Te_2O_{10}H_4]^{4-}$.2) Thus the anion is a promising ligand for the synthesis of new polynuclear compounds of a hybrid type between so-called Werner complex and heteropoly oxoanion; a few examples of such compounds with periodate3) or niobate4) ligand have already been reported from our laboratory. The present paper deals with the preparation of the corresponding polynuclear tellurato cobalt(III) complexes and of their starting mononuclear complex, $[Co(TeO_6H_4)(en)_2]^+$.

A solution of 1.15g (5 mmol) of $Te(OH)_6$ in 15 cm^3 of water was added to a solution of 1.43g (5 mmol) of cis-$[CoCl_2(en)_2]Cl$ in 10 cm^3 of water, and to the mixture was added 0.24g (10 mmol) of LiOH. After stirring mechanically at about 35°C for an hour, the solution was cooled to room temperature and an appropriate amount of ethanol was gradually added to it. After the solution had been kept in a refrigerator overnight, the light red precipitate deposited was separated by a centrifuge. This was dissolved in a small amount of water and the solution was poured into a column (3 cm × 60 cm) of strong acid cation exchanger (SP Sephadex C-25, Li^+ form). The adsorbed band was eluted with 0.25M LiCl solution, which was adjusted in advance to pH 10 by 1M LiOH solution. During the elution the column was cooled by flushing ice-water. Two red bands, F_1 and F_2, were eluted in this order.

The earlier eluate (F_1) was concentrated by freeze-drying method. The product obtained was recrystallized from water (pH 10 by LiOH) at 0°C by adding ethanol, and washed repeatedly with methanol and acetone. The later eluate (F_2) was concentrated at 15°C in a rotary evaporator, and a large volume of ethanol was added to the concentrated solution. After the solution had been kept in a refrigerator overnight, the product deposited was collected by a centrifuge. The product was recrystallized from an aqueous LiOH solution of pH 10 at 0°C by adding acetone-methanol mixture and washed repeatedly with ethanol and acetone. Found (F_1): C,9.49; H,4.76; N, 11.26%. Calcd for $[Co(TeO_6H_4)(en)_2]Cl\cdot 3H_2O$: C,9.68; H,5.29; N,11.29%. Found (F_2): C,11.28; H,4.74; N,11.55%; Co/Te (molar ratio)=1.1. Calcd for $[Co(en)_2(Te_2O_{10}H_4)Co(en)_2]Cl_2\cdot CH_3OH\cdot 4H_2O$: C,11.34; H,5.09; N,11.77%; Co/Te (molar ratio)= 1.0. Cobalt and tellurium were determined for the eluates from the column; the former was weighed as Co_3O_4, and the latter as the metal. The F_2 complex was obtained predominantly by raising the reaction temperature to ca. 60°C, and F_1 complex predominantly by using DMSO as solvent at ca. 35°C.

To obtain another condensed complex, the similar procedure to that of F_1 and F_2 complexes was adopted using 1.15g (5 mmol) of $Te(OH)_6$, 2.86g (10 mmol) of cis-$[CoCl_2(en)_2]Cl$, and 0.48g (20 mmol) of LiOH. The reaction was carried out at 60°C, and the reaction solution was poured into a column directly. The products separated on the column consisted of two red bands, F_2 and a new F_3 in this order, when eluted with 0.35M LiCl solution (pH 10 1M LiOH). The F_3 complex was purified by the same method as that of F_2 complex. Found (F_3): C,13.58; H,6.07; N,14.55%; Co/Te (molar ratio)=2.1. Calcd for $[\{Co(en)_2\}_2(Te_2O_{10})\{Co(en)_2\}_2]Cl_4\cdot CH_3OH\cdot 12H_2O$: C, 13.42; H,6.10; N,14.73%; Co/Te (molar ratio)=2.0.

Thus F_1, F_2, and F_3 complexes having molar ratio Co/Te = 1, 1, and 2, respectively, were prepared from the reaction solutions of cis-$[CoCl_2(en)_2]Cl$, $Te(OH)_6$, and LiOH. Other highly condensed complexes were observed in trace amounts on the column, but they were too unstable to be isolated. Because the pure F_1 - F_3 complexes showed slow reequilibrium reactions in solution at room temperature, their solutions were always handled carefully below 5°C. In particular, F_1 complex converted rapidly into F_2 in aqueous solution at room temperature. This rapid conversion corresponds to the dehydration condensation of the monomeric complex $[Co(TeO_6H_4)(en)_2]^+$ into the "dimer" complex $[Co(en)_2(Te_2O_{10}H_4)Co(en)_2]^{2+}$.

As is seen in the Figure, the absorption spectrum of F_1 complex shows a characteristic feature of the cis-CoN_2O_4 type complex and is similar to that of

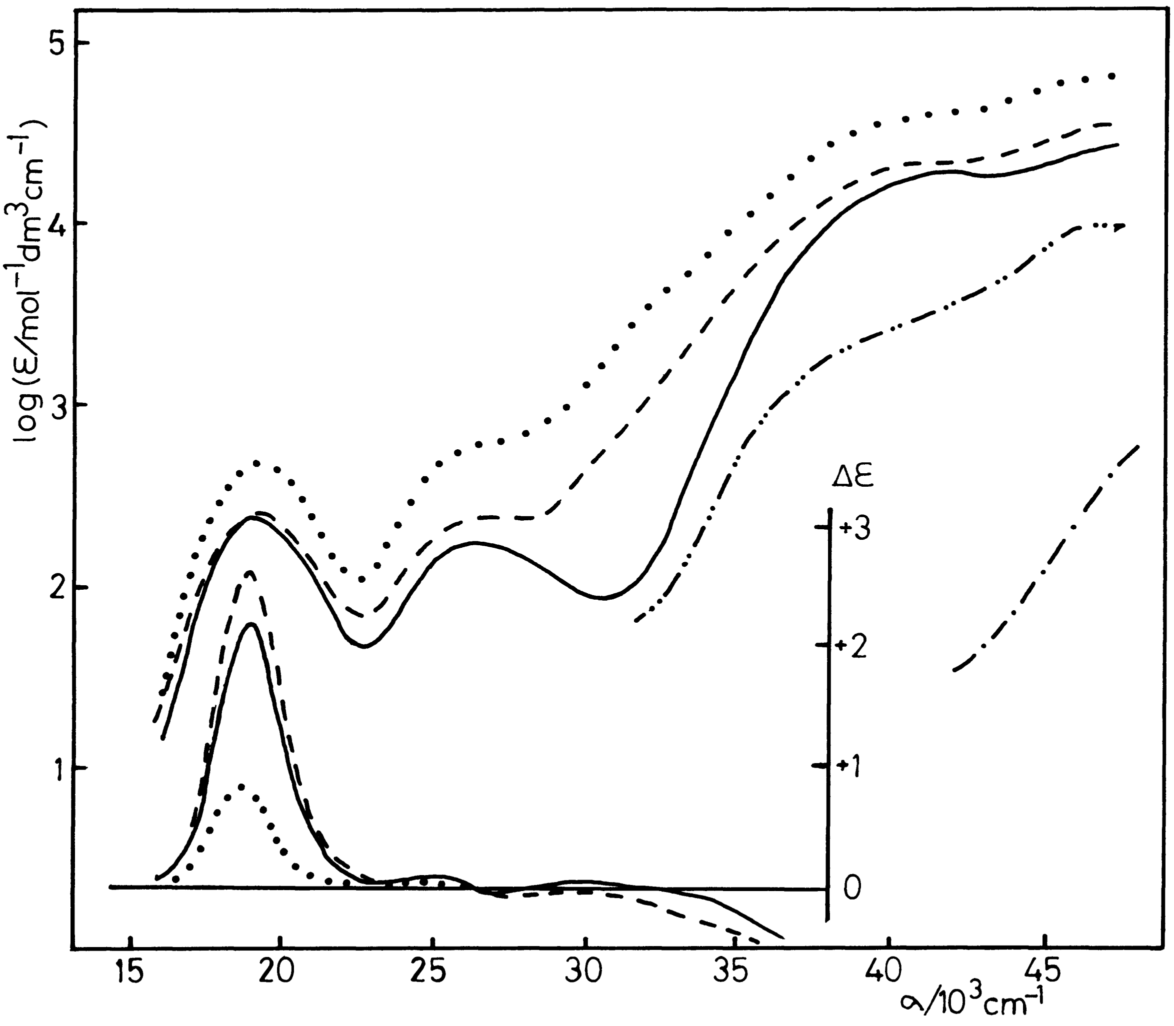

Figure. Absorption and CD spectra of F_1 complex $[Co(TeO_6H_4)(en)_2]^+$ (———), F_2 complex $[Co(en)_2(Te_2O_{10}H_4)Co(en)_2]^{2+}$ (– – – –), and F_3 complex $[\{Co(en)_2\}_2(Te_2O_{10})\{Co(en)_2\}_2]^{4+}$ (•••••). Absorption spectra of $[TeO_6H_{6-n}]^{n-}$ (—•—•—) and $[Te_2O_{10}H_{8-n}]^{n-}$ (—••—••—) are shown for comparison (pH = 10 - 11).

$[Co(CO_3)(en)_2]^+$ 5) in the first and second absorption band region. The first absorption bands of F_1, F_2, and F_3 complexes are located at 19200 cm^{-1}, having log $(\varepsilon/mol^{-1}dm^3cm^{-1})$ = 2.37, 2.41, and 2.67, respectively. The second absorption bands of F_2 and F_3 complexes appear as a shoulder because of overlapping with an absorption band at 30000 - 35000 cm^{-1}. The latter band is assigned to the ditellurate band modified by coordination; the free ditellurate ion has its longest wavelength absorption band at about 38000 cm^{-1} as a shoulder in contrast to the free orthotellurate ion which scarcely absorbs in the region of 35000 - 42000 cm^{-1} (see Figure). The occurrence of the ditellurate band and the F_1 → F_2 conversion in solution support that F_2 complex, $[Co(en)_2(Te_2O_{10}H_4)Co(en)_2]^{2+}$, corresponds to the condensation product of F_1 complex, $[Co(TeO_6H_4)(en)_2]^+$. Similarly, it is supposed that F_3 complex, $[\{Co(en)_2\}_2(Te_2O_{10})\{Co(en)_2\}_2]^{4+}$, is a condensation product of $[Co(en)_2(TeO_6H_2)Co(en)_2]^{2+}$, which has not been isolated in this work.

Optically active F_1 and F_2 complexes were obtained by the preparation starting from $(+)_{589}$-$[CoCl_2(en)_2]^+$.6) The $(+)^{CD}_{589}$-F_1 and $(+)^{CD}_{589}$-F_2 complexes have $\Delta\varepsilon = +0.39$ and $+0.44$, respectively, at the Na D line. The optical resolution of F_3 complex was made by the solubility difference between diastereomers. A solution of 0.015g of $K_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 3H_2O$ in 5 cm^3 of water was gradually added with stirring to a solution of 0.07g of F_3 complex in 10 cm^3 of LiOH solution of pH 10 on an ice bath. To the mixture was added an appropriate amount of acetone, and the solution was kept in a refrigerator overnight. The light red diastereomer deposited was isolated by a centrifuge and washed with methanol a few times. This less soluble diastereomer was stirred at 0°C in LiOH solution of pH 10 containing anion-exchange Sephadex (QAE A-25, Cl^- form). The solution was filtered to remove Sephadex, and CD of the filtrate was measured. The $(+)^{CD}_{589}$-F_3 complex has $\Delta\varepsilon = +0.18$ at Na D line.

CD patterns of the optically active complexes are similar to that of Λ-$[Co(CO_3)(en)_2]^+$ ($\Delta\varepsilon = +3.7$ at 18900 cm^{-1})5) in the first and second absorption band region, and show only one CD band in the first band region (Figure). Thus, the absolute configuration of $(+)^{CD}_{589}$-F_1 complex ($\Delta\varepsilon = +2.24$ at 19000 cm^{-1}) is assigned to be Λ. This corresponds well to the fact that the optically active F_1 complex has been derived from $(+)_{589}$-$[CoCl_2(en)_2]^+$ (Λ configuration).5,7) In the case of $(+)^{CD}_{589}$-F_2 complex ($\Delta\varepsilon = +2.63$ at 19000 cm^{-1}), the skew pair of two ethylenediamine chelates about each local Co(III) center is also supposed to have Λ configuration. However, further details of the structures of F_2 and F_3 complexes are not clear at the present stage.

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