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THREE ISOMERS OF DINITROOXALATODIAMMINECOBALTATE(III) COMPLEX

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Three isomers of the dinitrooxalatodiamminecobaltate(III) complex have been isolated; the cis-cis- and trans(NO_2)-isomers have been obtained from the reaction mixture of the cis-cis-$[Coox(H_2O)_2(NH_3)_2]^+$ complex and KNO_2, the remaining trans(NH_3)-isomer from that of the $[Co(NO_2)_4(NH_3)_2]^-$ complex and oxalic acid.

Several researches[1-4] intended to determine the geometrical structure of Erdmann's salt, ammonium tetranitrodiamminecobaltate(III), resulted in the contradictory statements regarding the resolvability of the oxalato-derivative, dinitrooxalatodiamminecobaltate(III) complex. Later, the X-ray studies showed that the two ammonia groups were in the trans-position in each one of the silver,[5,6] potassium[7] and ammonium[8] salts. On the other hand, it was claimed that in aqueous solution of Erdmann's salt, the trans and cis isomers exist as an equilibrium mixture,[9] and this problem remains unresolved. Furthermore, the definite information regarding the synthesis of the oxalato complex resolvable into optical antipodes has not been reported.

We now succeeded in obtaining three isomers of the oxalato complex, to say, trans-dinitro, cis-dinitro-cis-diammine and trans-diammine isomers; the former two were given by the reaction between cis-cis-oxalatodiaquodiamminecobalt(III) complex and potassium nitrite and the latter one by the action of oxalic acid on the potassium salt of tetranitrodiamminecobaltate(III). In this connection, the preparation of three isomers of the same complex has been reported,[10] but there is doubt concerning actual isomeric forms.

To a solution of cis-cis-$[Coox(H_2O)_2(NH_3)_2]NO_3$[11] (11.2 g (0.04 mol)/150 ml H_2O), KNO_2 (8.5 g, 0.1 mol) was added, and it was then made acidic (pH ~5) with 6 N acetic acid (10 ml). The mixture was stirred for an hour at room temperature, and filtered. The filtrate was charged on an ion-exchange column containing Dowex 1 X 8 resin in the Cl-form (100~200 mesh, 4 X 20 cm). After the column was washed with water, the elution was continued with 0.1 M KCl solution; a minor orange-brown band descended, followed by a major band with the same color. These were collected in fractions. Each fraction was concentrated to a small volume, and after filtering, kept in a refrigerator. Each product obtained was recrystallized from a minimum amount of warm water (~40°C). The yields were 0.1 g for the product obtained from the first fraction (Complex I) and 2.5 g for that from the second fraction (Complex II).

Found for Complex I: C, 7.65; H, 2.73; N, 17.03%. Calcd for $K[Co(NO_2)_2C_2O_4(NH_3)_2]\cdot H_2O$: C, 7.28; H, 2.44; N, 16.97%.

Found for Complex II: C, 7.69; H, 2.29; N, 17.42%. Calcd for $K[Co(NO_2)_2C_2O_4(NH_3)_2]\cdot 0.5H_2O$: C, 7.48; H, 2.20; N, 17.45%.

An aqueous solution of $K[Co(NO_2)_4(NH_3)_2]$12) was treated with oxalic acid according to the way described in a literature.12) The product obtained was recrystallized from warm water (~40°C) (Complex III).

Found: C, 7.39; H, 2.78; N, 16.81%. Calcd for $K[Co(NO_2)_2C_2O_4(NH_3)_2]\cdot H_2O$: C, 7.28; H, 2.44; N, 16.97%.

It was ascertained by chromatography that this product consisted of a single isomeric species and no other isomeric species existed in the mother liquor.

To a hot solution of Complex II (5 g (0.017 mol)/60 ml H_2O) was added an aqueous solution of the resolving agent prepared from ℓ-$[Co(NO_2)_2(en)_2]I$13) (3.1 g (0.008 mol)/20 ml H_2O) and silver acetate (1.3 g, 0.008 mol), and the mixture was allowed to stand for a while at room temperature. The orange-yellow needle-like diastereoisomer precipitated was recrystallized from water until $\Delta\varepsilon$ of the CD peak at 22300 cm^{-1} reached to a constant value. The final yield was 2 g.

Found: C, 13.00; H, 4.48; N, 24.82%. Calcd for $[Co(NO_2)_2(C_2H_8N_2)_2][Co(NO_2)_2C_2O_4(NH_3)_2]\cdot H_2O$: C, 12.81; H, 4.30; N, 24.91%.

This less soluble diastereoisomer was broken by means of a cation-exchange column (Dowex 50W X 8, K-form) and the effluent was submitted to the CD spectrum and polarimetric measurements. $[\alpha]_{589}^{23} = -92.8^{\circ}$.

The same procedure was carried out with Complex III. In this case, too, orange-yellow needle-like product was precipitated and its recrystallization was repeated several times.

Found: C, 13.27; H, 4.31; N, 25.13%. Calcd for $[Co(NO_2)_2(C_2H_8N_2)_2][Co(NO_2)_2C_2O_4(NH_3)_2]\cdot 0.5H_2O$: C, 13.03; H, 4.19; N, 25.32%.

The CD spectrum measurement with potassium salt provided from this compound gave no evidence for its resolution.

Because of the successful resolution it is obvious that Complex II has the cis-cis structure. Figure 1 exhibits the CD spectrum of the resolved species. The spectrum gives three peaks at 19500 ($\Delta\varepsilon$=-0.89), 22300 (+1.47) and 26500 cm^{-1} (-0.37). The resolved species preserved its activity for a day under iced condition, in contrast to the suggestion for fast racemization by earlier authors.1,10)

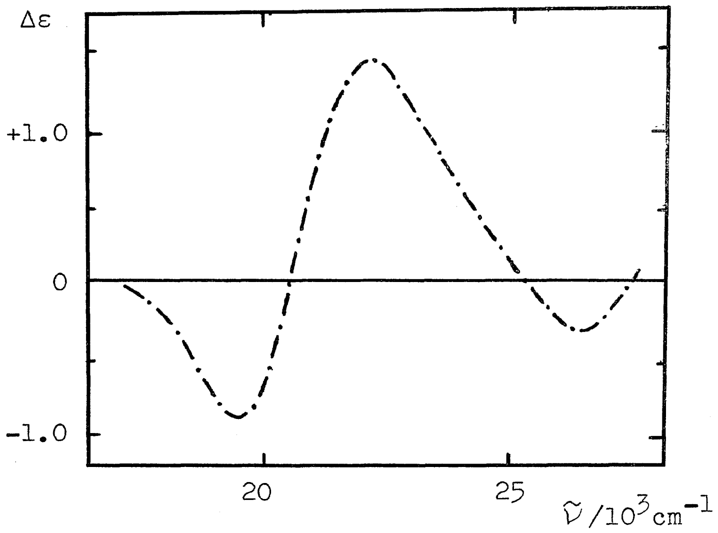

Fig.1 CD spectrum of the $(-)_{589}$-$[Co(NO_2)_2ox(NH_3)_2]^-$ complex

The facts that the action of oxalic acid on the $[Co(NO_2)_4(NH_3)_2]^-$

complex gave only one isomeric complex and that the isomeric complex could not be resolved suggest that Complex III is the trans-diammine isomer. If aqueous solution of the $[Co(NO_2)_4(NH_3)_2]^-$ complex consist of an equilibrium mixture of cis and trans isomeric species, two or more species should be formed in the reaction mixture with oxalic acid. Accordingly, the remaining isomer, Complex I, will be assigned to the trans-dinitro one.

Figure 2 shows the absorption spectra of the three isomers. The observed maxima (cm^{-1}) and intensities (log ε) are as follows;

Complex I (trans-NO_2^-) : 21030 (2.28), 28370 (3.70), 38670 (4.30).
Complex II (cis-cis) : 20920 (2.21), 29800 (3.63), 39920 (4.35).
Complex III (trans-NH_3): 20900 (2.27), 29560 (3.66), 40290 (4.44).

Yamatera's treatment[14] predicts that the separation of the components of the first absorption band for the trans-dinitro isomer is much larger than that for the trans-diammine one; calculated values were 2720 and 380 cm^{-1} for the trans-dinitro and trans-diammine isomers, respectively. In fact observed half-widths were 5100 cm^{-1} for Complex I and 3600 cm^{-1} for Complex III. These support the foregoing assignments of the two trans-isomers.

The far-infrared spectra of the three isomers are shown in Figure 3. The NO_2 wagging vibration is observed at ca. 620 cm^{-1} in common with all isomers. Complex I has two peaks due to ν(Co-O)+ ν(CC) at 560 and 544 cm^{-1}, whereas Complex III has a shoulder at ca. 560 cm^{-1} and two peaks at 550 and 530 cm^{-1}. Complex I and Complex III exhibit a peak assignable ν(Co-N(NH_3)) at 493 and 475 cm^{-1}, respectively. In Complex II, the corresponding absorption splits into a shoulder at 508 cm^{-1} and a peak at 490 cm^{-1}.[15-18]

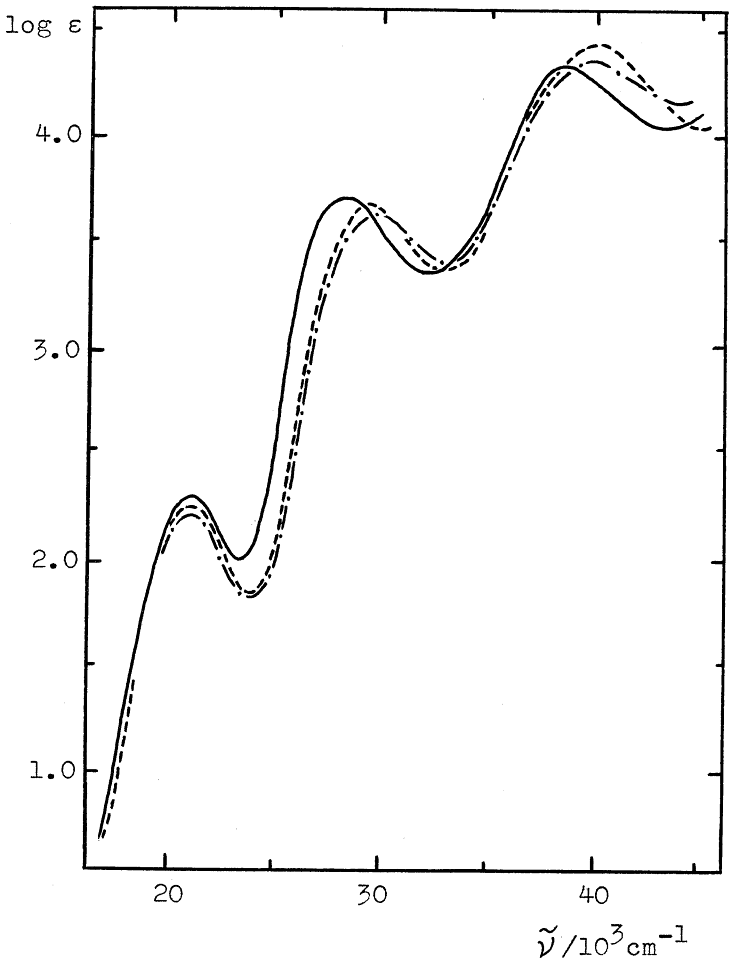

Fig.2 Absorption spectra of the three isomers:
Complex I ———
Complex II -·-·-
Complex III -----

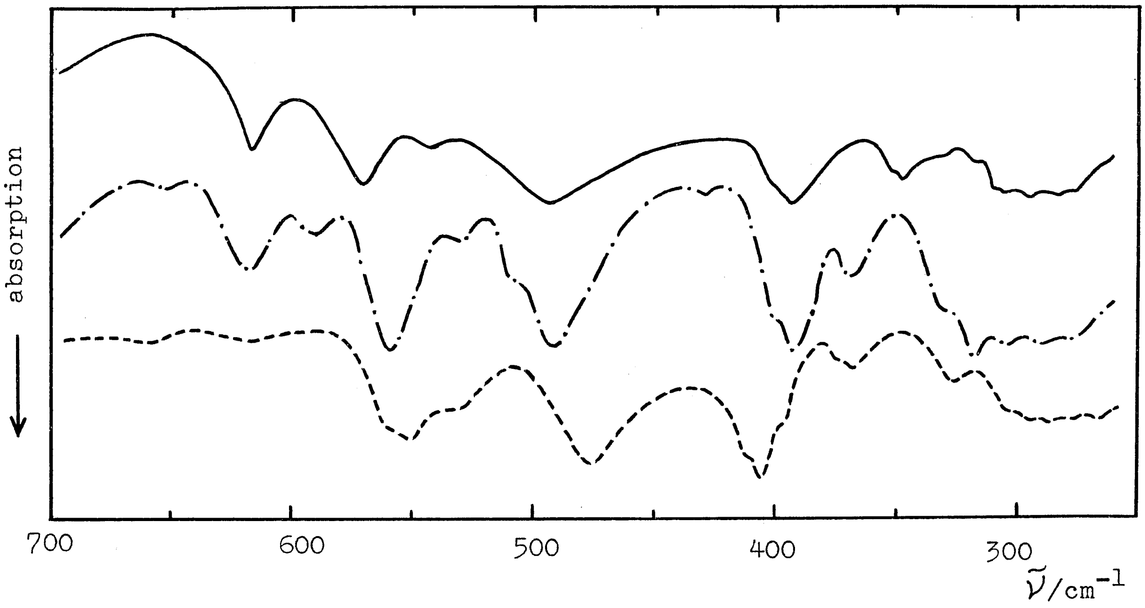

Fig.3 Far-infrared spectra of the three isomers:
Complex I ———, Complex II -·-·-, Complex III -----

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