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PREPARATION AND OPTICAL RESOLUTION OF A NOVEL TRIAMMINEGLYCINATONITROCOBALT(III) COMPLEX

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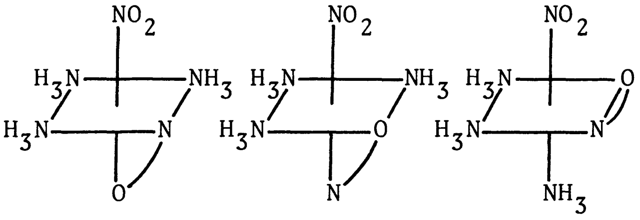
Three isomers of a new complex $[Co(NO_2)(gly)(NH_3)_3]Cl$ have been prepared and characterized from the ultra-violet absorption spectra in terms of the angular overlap model. A fac(NH_3) isomer, which exhibits a novel optical isomerism due to the arrangement of the donor atoms, has been resolved by means of a column chromatography, and the CD spectra of the resolved isomers have been measured.

There are three possible geometrical isomers in a triammineglycinatonitrocobalt(III) complex. As is seen in Fig. 1, two isomers in which three ammonia molecules occupy meridional position in an octahedron are designated as mer(NH_3)-trans(NO_2,O) and mer(NH_3)-trans(NO_2,N), and remaining isomer as fac(NH_3). The two mer(NH_3) isomers are achiral, but the fac(NH_3) isomer has a chirality which is mainly due to the arrangement of donor atoms around a central metal ion. There have been a few works on such a kind of chiral complexes compared with the accumulated works on the optically active complexes containing two or three bidentate ligands.[1-6] It is necessary to establish the relationship between the CD spectra and the absolute configurations of this type of chiral complexes. In this communication, the preparation of three geometrical isomers of the $[Co(NO_2)(gly)(NH_3)_3]^+$ complex and optical resolution of the fac(NH_3) isomer will be reported.



mer(NH_3)-trans(NO_2,O) mer(NH_3)-trans(NO_2,N) fac(NH_3)

Fig. 1. Three geometrical isomers of $[Co(NO_2)(gly)(NH_3)_3]^+$.

To an aqueous solution of $[Co(NO_2)(NH_3)_5]Cl_2$ (2 g in 20 cm^3 H_2O) were added Hgly (0.5 g), Na_2CO_3

(0.3 g) and activated charcoal (0.3 g), and the mixed solution was stirred for a day at room temperature. After filtering off the activated charcoal, the filtrate was adjusted to pH 7 and chromatographed with a column of Dowex 50W-X8 (Na^+ form, 100-200 mesh, 4 x 30 cm). By elution with a 0.1 mole/dm^3 NaCl solution, three bands of univalent cation were descended and labelled A, B and C in the order of elution. Each fraction was rechromatographed with a long column of the same resin (2 x 70 cm); When elutions were performed with a 0.05 mole/dm^3 $K_2[Sb_2(d\text{-}tart)_2]$ solution, the adsorbed bands were separated into two, three and three bands for the fraction A, B and C, respectively. The bands were labelled as A1, A2, B1-B3 and C1-C3 according to the elution orders. The labels are also used to designate the complex species in each band. When each frontal band descended in the neighborhood of the outlet of the column, the bands were washed sufficiently with water, and then eluted with a 0.1 mole/dm^3 NaCl solution. Each fraction was concentrated by means of a rotary evaporator with simultaneous removal of precipitated eluent. To the final filtrate was added a small amount of ethanol, and the whole was kept in a refrigerator. The crude product precipitated was recrystallized from a minimum amount of warm water. A1 was identified to be $[Co(NO_2)_2(NH_3)_4]^+$, and B1, B2, C1 and C2 to be the isomers of a known complex, $[Co(gly)_2(NH_3)_2]^+$.7) A2, B3 and C3 were orange in color. Elemental analyses, absorption and IR spectra of the orange crystals proved the formula $[Co(NO_2)(gly)(NH_3)_3]Cl$. The B3 band was partially resolved into optical antipodes during the elution. Found for A2: C, 8.81; H, 5.19; N, 26.22%. Found for B3: C, 9.10; H, 5.12; N, 26.19%. Found for C3: C, 9.02; H, 4.97; N, 26.51%. Calcd for $[Co(NO_2)(gly)(NH_3)_3]Cl$: C, 9.05; H, 4.94; N, 26.39%.

Absorption spectral data of the isomers are listed in Table 1. Absorption maxima in the d-d absorption band region are not so different each other, hence it was difficult to assign the isomers from the spectral data of the d-d absorption bands. As to the absorption bands in the ultra-violet region, the maxima in A2 are

Table 1. Absorption Spectral Data of the $[Co(NO_2)(gly)(NH_3)_3]^+$ Complex

		$\tilde{\nu}/10^3cm^{-1}$ (log ε)		
	isomer	I	II	III
A2	mer(NH_3)-trans(NO_2,O)	21.4 (2.15)	29.6 (3.29)	40.6 (4.26)
B3	fac(NH_3)	20.9 (2.02)	30.4 (3.18)	41.5 (4.19)
C3	mer(NH_3)-trans(NO_2,N)	21.2 (2.02)	30.3 (3.33)	41.5 (4.21)

observed at a lower frequency to the extent of 700-900 cm^{-1} than those in the other isomers. Miskowski and Gray[8)] have assigned the absorption band observed at 42000 cm^{-1} in $[Co(NO_2)(NH_3)_5]^{2+}$ to the CT band from the ligand $\sigma(NO_2)$ to the metal $d(z^2)$ orbital. If an assumption that the ligand $\sigma(NO_2)$ orbitals in the three isomers lie at the same energy level, the observation suggests that the metal $d(z^2)$ orbital in A2 lies lower than those in B3 and C3 to the extent of 900 cm^{-1}. According to the angular overlap model,[9)] the $d(z^2)$ orbital in the trans(NO_2,O) isomer is predicted to lie lower than those in the trans(NO_2,N) and fac(NH_3) isomers. Since the ligand field strength of NH_3 is almost equal to that of N donor of glycinato ligand, the energy difference between the $d(z^2)$ orbital in the trans(NO_2,O) and that in either the trans(NO_2,N) or the fac(NH_3) is expressed by $3(e_\sigma(N)-e_\sigma(O))/4$, and roughly estimated to be ca. 1000 cm^{-1}, where $e_\sigma(N)$ is a σ-antibonding parameter for N donor of NH_3 or glycinato ligand, and $e_\sigma(O)$ for O donor of glycinato ligand. Consequently, A2 is assignable to the trans(NO_2,O) isomer. As B3 is optically resolved by the elution with a $K_2[Sb_2(d\text{-}tart)_2]$ solution, B3 is assigned to the fac(NH_3) isomer, C3 being trans(NO_2,N) isomer.

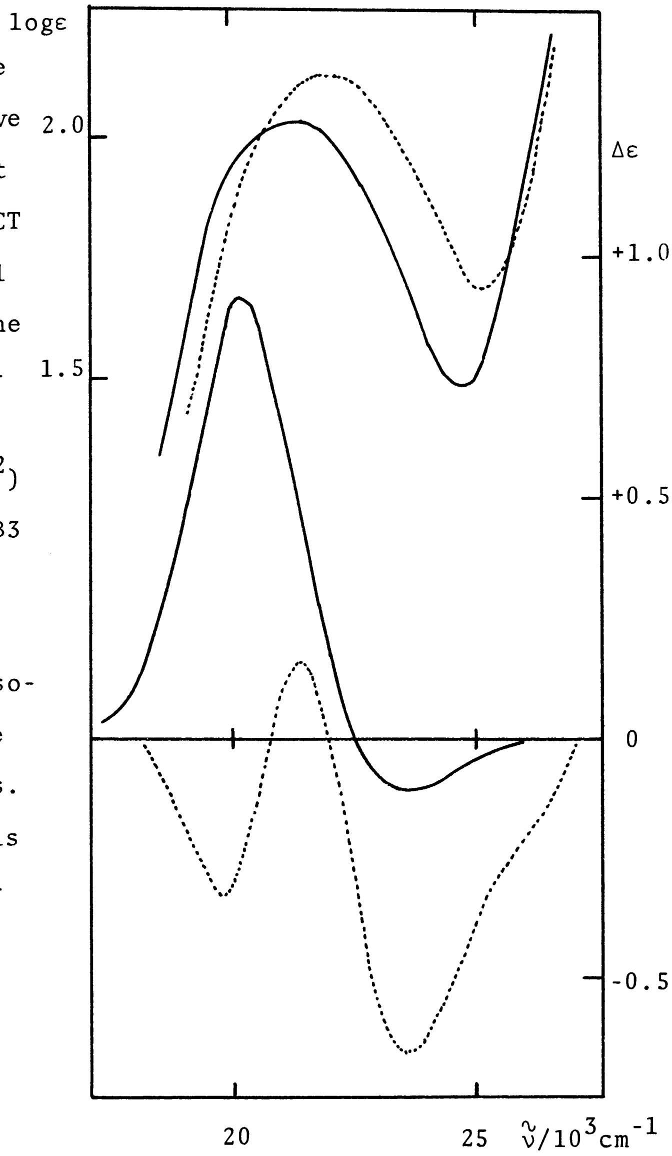


Fig. 2. Absorption and CD spectra of; fac(NH_3)-$[Co(NO_2)(gly)(NH_3)_3]^+$ (——), and $[Co(NO_2)(gly)(tacn)]^+$ (· · · ·).

It is notable that total optical resolution of the fac(NH_3) complex was attained by use of 200-400 mesh resin in stead of 100-200 mesh one. An enantiomer exhibits two Cotton peaks in the first absorption band region, as shown in Fig. 2; 20200 cm^{-1} ($\Delta\varepsilon$=+0.92) and 23500 cm^{-1} ($\Delta\varepsilon$=-0.09) for the earlier eluate in a column chromatography. In the previous paper,5) we reported the CD spectrum of a $[Co(NO_2)(gly)(tacn)]^+$ complex whose chromophore resembles the $fac(NH_3)$ isomer (tacn represents triazacyclononane). As is seen in Fig. 2, the CD spectrum of the earlier eluate in a column chromatography for the tacn complex exhibits -,+,- Cotton peaks from a lower frequency in the first absorption band region, being different from that of the $fac(NH_3)$ isomer in both shape and net rotatory strength. It indicates that the tacn chelate affects the rotatory strength to some extent, in spite of cancellation of Λ and Δ herical configurations consisting of the tacn and gly chelate rings. Judging from the order of elution in a column chromatography, the absolute configuration of the earlier eluted isomer in the $fac(NH_3)$ complex is predicted as shown in Fig. 1, on the basis of the results in the tacn complex.5) In order to confirm the prediction, an X-ray analysis of the optically active $fac(NH_3)$ complex is in progress. It is also found that the $fac(NH_3)$ complex is acid-hydrolyzed by concd HBr at ca. 50°C, retaining the optical activity.

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