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The Raman Spectra of Cobalt(III) Complexes. V.[1] Differentiation between Two *cis*(a) Isomers of $[Coa_2(NH_3)_2(en)]$ Type Complexes ($a=NO_2^-$ and CN^-)

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Three geometrical isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$ were newly prepared. Two *cis*(NO_2) isomers (*trans*-(NH_3) and *cis,cis*) were clearly differentiated on the basis of the polarizabilities of the Raman bands due to Co-N(NH_3 and en) stretching vibrations. The Raman polarization measurement was also applied successfully to the determination of the geometrical configurations of two $[Co(CN)_2(NH_3)_2(en)]^+$ isomers. The structural assignments were substantiated by optical resolution of the *cis,cis* isomers of $[Coa_2(NH_3)_2(en)]^+$ ($a=NO_2^-$ and CN^-).

Three geometrical isomers (*trans*(a), *trans*(NH_3), and *cis,cis*) of $[Coa_2(NH_3)_2(en)]$ type complex were first prepared by Bailar and Peppard[2] for $a=Cl^-$. In general, it is difficult to distinguish the two *cis*(a) isomers (*trans*(NH_3) and *cis,cis*) of $[Coa_2(NH_3)_2(en)]$ type complexes on the basis of their electronic absorption spectra, since no definite difference could be expected between the spectra of the two *cis*(a) isomers because of the similarity in the ligand field strengths of NH_3 and ethylenediamine. Bailar and Peppard[2] distinguished the two *cis*(Cl) isomers of $[CoCl_2(NH_3)_2(en)]^+$ on the basis of their preparative method. Their assignment was confirmed later by optical resolution of the *cis,cis* isomer by Hawkins *et al.*[3] It is of interest to find a reliable spectroscopic method for differentiating the two *cis*(a) isomers of $[Coa_2(NH_3)_2(en)]$ type complexes.

Raman spectra in the skeletal vibration region have been applied successfully to the differentiation of geometrical isomers of cobalt(III) complexes.[1,4,5] The Raman criteria established for the cobalt(III) complexes are expected to be profitably applied to the determination of the geometry of other metal analogs, whereas NMR method, although widely used in the stereochemistry of cobalt(III) complexes, would incur some difficulties in application to paramagnetic complexes such as chromium(III) complexes. In this paper, we report the preparation of three geometrical isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$ complex for the first time and the Raman method for differentiation between the two *cis*(a) isomers of $[Coa_2(NH_3)_2(en)]$ type complexes.

Experimental

Three Geometrical Isomers of $[Co(NO_2)_2(NH_3)_2(en)]ClO_4$. *Method I*: To a green solution of 0.9 g (3.5 mmol) of *trans*-(Cl)-$[CoCl_2(NH_3)_2(en)]Cl$[2] in 20 cm^3 of water containing a few drops of glacial acetic acid was added a solution of 0.9 g (13 mmol) of $NaNO_2$ in 10 cm^3 of water. After being stirred for 12 h, the color of the solution changed to yellowish brown. The solution was diluted to 2 dm^3 with water and poured onto a cation-exchange column (SP-Sephadex, C-25, Na^+ form; 3×50 cm). By eluting with 0.03 M $NaClO_4$ (1 M=1 mol dm^{-3}), two colored bands, both yellowish brown, descended. Each eluate was concentrated to a small volume in a rotary evaporator and ethanol was added to induce a precipitation of a yellowish brown powder. This powder was recrystallized from a small amount of warm water by adding ethanol. From the electronic absorption and Raman spectra the complex which was obtained from the first eluate was identified to be the *trans*(NO_2) isomer and that from the second eluate the *cis,cis* isomer. Yield: 0.3 g for the *trans*(NO_2) isomer and 0.2 g for the *cis,cis* one. Absorp. max. $\sigma/10^3\,cm^{-1}$ (log $\varepsilon/mol^{-1}\,dm^3\,cm^{-1}$): 22.8 (2.28), 29.1 (3.54), 39.8 (4.22) for the *trans*(NO_2) isomer; 22.8 (2.24), 31.2 (3.65), 42.2 (4.30) for the *cis,cis* isomer. Found: C, 6.96; H, 4.16; N, 24.23% for the *trans*(NO_2) isomer. C, 6.96; H, 4.05; N, 24.42% for the *cis,cis* isomer. Calcd for $[Co(NO_2)_2(NH_3)_2(en)]ClO_4=CoC_2ClH_{14}N_6O_8$: C, 6.97; H, 4.10; N, 24.39%.

Method II: The *cis,cis* isomer was also prepared in a high yield by this method. To a solution of 3 g (10 mmol) of *cis*-$[Co(CO_3)(NH_3)_2(en)]ClO_4$[2] in 100 cm^3 of 3% $HClO_4$ was added 6.0 g (100 mmol) of $NaNO_2$. The mixture was kept at 60 °C for half an hour, then cooled in a refrigerator. The yellowish brown crystals which deposited were collected by filtration and recrystallized from a small amount of warm water. Yield: 2.0 g.

Method III: The remaining isomer, *trans*(NH_3), was obtained by this method. To a bluish violet solution of 1.5 g (6 mmol) of *trans*(NH_3)-$[CoCl_2(NH_3)_2(en)]Cl$[2] in 20 cm^3 of water was added a solution of 1.5 g (22 mmol) of $NaNO_2$ in 10 cm^3 of water. The mixture was stirred at 25 °C for 12 h, whereupon the color of the solution turned to yellowish brown. Addition of a large amount of solid $NaClO_4$ to this solution induced the precipitation of a yellowish brown solid. This solid was recrystallized from a small amount of warm water. Yield: 1.2 g. Absorp. max. $\sigma/10^3\,cm^{-1}$ (log $\varepsilon/mol^{-1}\,dm^3\,cm^{-1}$): 23.0 (2.22), 31.0 (3.71), 41.9 (4.49). Found: C, 6.93; H, 4.09; N, 24.42%. Calcd for $[Co(NO_2)_2(NH_3)_2(en)]ClO_4=CoC_2ClH_{14}N_6O_8$: C, 6.97; H, 4.10; N, 24.39%.

trans(*CN*)- *and* cis,cis-$[Co(CN)_2(NH_3)_2(en)]ClO_4$. These had been obtained by Maki and Sakuraba.[6] The complexes were obtained more conveniently, however, by the following methods. Powdered *trans*(Cl)-$[CoCl_2(NH_3)_2(en)]Cl$ (4 g; 15 mmol) was added to a solution of KCN (2 g; 30 mmol) in 300 cm³ of dimethyl sulfoxide (DMSO). After being stirred continuously at 80 °C for 3 h, the reaction mixture consisted of an orange yellow solution and a small amount of orange precipitate. The mixture was diluted to 2 dm³ with water and poured onto a cation-exchanger column (SP-Sephadex, C-25, Na^+ form; 3×60 cm). By eluting with 0.03 M $NaClO_4$, two colored bands, orange and yellow, descended in that order. Each eluate was concentrated to dryness by a rotary evaporator and the residue washed with ethanol to remove the contaminated $NaClO_4$. The crude compound thus obtained was recrystallized from warm water. The electronic absorption spectra of the orange and yellow isomers coincide respectively with those of *trans*(CN)- and *cis*(CN)-$[Co(CN)_2(NH_3)_2(en)]^+$ reported by Maki and Sakuraba.[6] The *cis*(CN) isomer was identified to be *cis,cis* from the Raman spectrum. Yield: 1.7 g for the *trans*(CN) isomer and 0.2 g for the *cis,cis* one.

The *cis,cis* isomer was also prepared in a high yield by the following method.

To a solution of *trans*(Cl)-$[CoCl_2(NH_3)_2(en)]Cl$ (2.6 g; 10 mmol) in 60 cm³ of DMSO was added a solution of $AgNO_3$ (1.7 g; 10 mmol) in a small amount of DMSO. The silver chloride deposited was filtered off. To the filtrate was added 5.4 g (40 mmol) of AgCN and the resulting suspension was stirred continuously at 80 °C for 5 h. During this time, the color of the liquid phase changed from bluish violet to brownish yellow. To the suspension 1 dm³ of water was added and the insoluble product filtered off. The filtrate was chromatographed in a similar manner as above. In this case, only one band, *cis,cis*, descended. Yield: 1.1 g. Absorp. max. $\sigma/10^3\,cm^{-1}$ ($\log \varepsilon/mol^{-1}\,dm^3\,cm^{-1}$): 21.5 sh (1.48), 24.2 (1.76), 31.9 (1.88), 47.4 (4.61) for the *trans*(CN) isomer; 23.5 sh (1.84), 25.1 (1.87), 32.2 (1.94), 47.7 (4.32) for the *cis,cis* one. Found: C, 15.72; H, 4.64; N, 27.63% for the *trans*(CN) isomer. C, 15.72; H, 4.67; N, 27.57% for the *cis,cis* one. Calcd for $[Co(CN)_2(NH_3)_2(en)]ClO_4$=$CoC_4ClH_{14}N_6O_4$: C, 15.77; H, 4.63; N, 27.59%.

Attempts to obtain the *trans*(NH_3) isomer from *trans*(NH_3)-$[CoCl_2(NH_3)_2(en)]Cl$ were not successful; the reaction with AgCN yielded only the *cis,cis* isomer and with KCN only the *trans*(CN) and *cis,cis* ones.

Optical Resolution of cis,cis *Isomers of* $[Coa_2(NH_3)_2(en)]^+$ *(a=*NO_2^- *and* CN^-*).* $(+)^{CD}_{450}$-cis, cis-$[Co(NO_2)_2(NH_3)_2(en)]Cl$: A solution of racemic *cis,cis*-$[Co(NO_2)_2(NH_3)_2(en)]ClO_4$ was passed through an anion-exchange resin column (Dowex 1×8, Cl^- form) and the eluate was evaporated to dryness. The crude product was recrystallized from a minimun amount of hot water and dried in air. Found: C, 8.27; H, 5.01; N, 29.76%. Calcd for $[Co(NO_2)_2(NH_3)_2(en)]Cl$=$CoC_2ClH_{14}N_6O_4$: C, 8.56; H, 5.01; N, 29.96%.

The chloride of the *cis,cis* isomer (0.5 g; 1.8 mmol) was dissolved in 10 cm³ of water and to the solution was added solid $(+)_{546}$-$K[Co(edta)]\cdot 2H_2O$[7] (0.7 g; 1.8 mmol) at 40 °C with stirring. The resulting reddish violet solution was evaporated to half the initial volume below 20 °C and kept standing in a refrigerator overnight. The reddish violet crystals which deposited were collected by filtration and recrystallized from a small amount of warm water (at *ca.* 40 °C) to give crystals of the less-soluble diastereomer with a needle-like shape. Found: C, 23.54; H, 4.62; N, 18.36%. Calcd for $[Co(NO_2)_2(NH_3)_2(en)][Co(edta)]\cdot H_2O$=$Co_2C_{12}H_{28}N_8O_{13}$: C, 23.61; H, 4.63; N, 18.36%.

The less-soluble diastereomer was converted into the chloride salt by passing a solution through an anion-exchange resin (Dowex 1×8, Cl^- form) and evaporating the eluate to dryness. CD $\sigma_{ext}/10^3\,cm^{-1}$ ($\Delta\varepsilon/mol^{-1}\,dm^3\,cm^{-1}$): 21.6 (+0.34), 24.4 (−0.18), 29.7 (−1.49), 35 sh (+1.80), 38.6 (+2.56), 43.2 (−14.6). Found: C, 8.30; H, 5.10; N, 29.76%. Calcd for $[Co(NO_2)_2(NH_3)_2(en)]Cl$=$CoC_2ClH_{14}N_6O_4$: C, 8.56; H, 5.01; N, 29.96%.

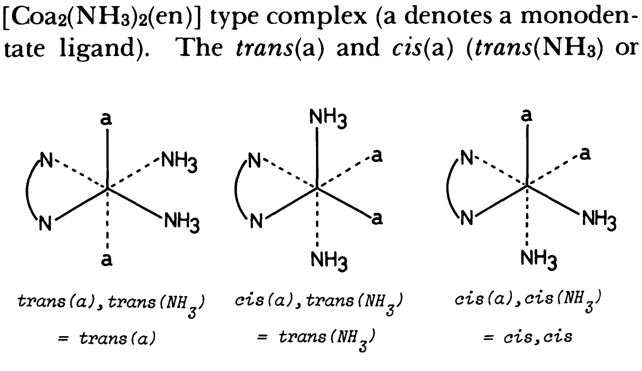
$(+)^{CD}_{450}$-*cis,cis*-$[Co(CN)_2(NH_3)_2(en)]ClO_4$: A solution of racemic *cis,cis*-$[Co(CN)_2(NH_3)_2(en)]ClO_4$ (0.46 g; 1.5 mmol) in 20 cm³ of warm water was passed through a Cl^- form ion-exchange resin. To the filtrate was added $(-)_{546}$-$Ag[Co(edta)]$[8] (0.69 g; 1.5 mmol) with stirring and the silver chloride deposited was filtered off. The filtrate was evaporated to dryness and a small amount of methanol was added to the residue. The crude brownish violet powder of the less-soluble diastereomer was recrystallized from warm water; the dark reddish violet crystals which deposited were recrystallized from a minimum amount of warm water. Found: C, 27.72; H, 5.31; N, 18.35%. Calcd for $[Co(CN)_2(NH_3)_2(en)][Co(edta)]\cdot 3H_2O$=$Co_2C_{14}H_{32}N_8O_{11}$: C, 27.73; H, 5.33; N, 18.48%.

The less-soluble diastereomer was converted to the perchlorate salt by adding $NaClO_4$ to a chloride solution obtained by means of a chromatographic method. CD $\sigma_{ext}/10^3\,cm^{-1}$ ($\Delta\varepsilon/mol^{-1}\,dm^3\,cm^{-1}$): 20.5 (−0.01), 23.2 (+0.22), 26.6 (−0.22), 32.0 (+0.06), 35.5 sh (−0.01), 41.1 (−1.7), 45.4 (+9.7). Found: C, 15.62; H, 4.64; N, 26.98%. Calcd for $[Co(CN)_2(NH_3)_2(en)]ClO_4$=$CoC_4ClH_{14}N_6O_4$: 15.77; H, 4.64; N, 27.59%.

Measurements. Electronic absorption spectra were recorded on a Hitachi 220 spectrophotometer. Raman spectra were recorded in water on a JASCO R-800 Laser Raman spectrophotometer, using a He-Ne laser (632.8 nm; 50 mW) as an excitation source. A spinning sample cell was employed to avoid decomposition of the sample induced by laser illumination. Polarization measurements were carried out by employing a half-wave plate for incident light and a polarization analyzer for scattered light. Infrared spectra were recorded on a JASCO IRA-3 as Nujol mulls. Circular dichroism (CD) spectra were recorded on a JASCO MOE-1 spectropolarimeter in aqueous solution.

Results and Discussion

Electronic Absorption Spectra. Figure 1 shows the configurations of geometrical isomers of $[Coa_2(NH_3)_2(en)]$ type complex (a denotes a monodentate ligand). The *trans*(a) and *cis*(a) (*trans*(NH_3) or



trans(a), *trans*(NH_3) = *trans*(a) *cis*(a), *trans*(NH_3) = *trans*(NH_3) *cis*(a), *cis*(NH_3) = *cis,cis*

Fig. 1. Three geometrical isomers of $[Coa_2(NH_3)_2(en)]$ type complex (a denotes a monodentate ligand).

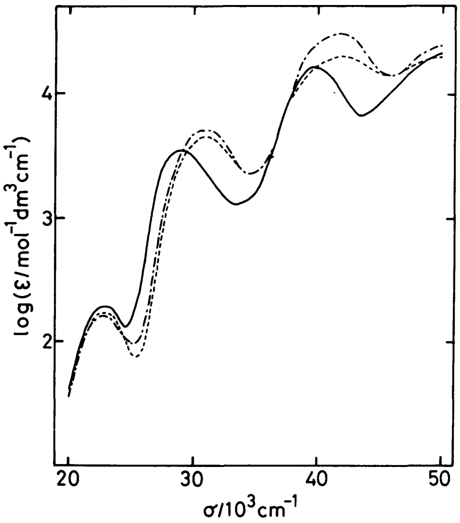


Fig. 2. Electronic absorption spectra of the three geometrical isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$ (——); *trans*(NO_2), (----); *trans*(NH_3), and (– – –); *cis,cis*.

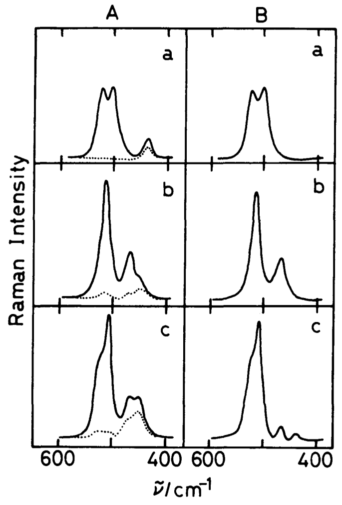


Fig. 3. Polarized Raman spectra (A) [(——), ∥; (----), ⊥] and difference Raman spectra (B) [$I_{\parallel} - I_{\perp} \times 4/3$] of the three isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$: a; *trans*($NO_2$), b; *trans*($NH_3$), and c; *cis,cis*.

cis,cis) isomers can be differentiated on the basis of their electronic absorption spectra in a similar manner as for the corresponding isomers of $[Coa_2(en)_2]$ or $[Coa_2(NH_3)_4]$ type complexes. Figure 2 shows the electronic absorption spectra of the three isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$. It has been shown for dinitro cobalt(III) complexes that the "nitro-specific" band of the *trans* isomer is always more bathochromic than the band of the *cis* isomer.[9] Therefore, the isomer which exhibits the "nitro-specific" band in the lower energy region (29100 cm^{-1}) than those of the other two isomers (31000 and 31200 cm^{-1}) can be unambiguously assigned to the *trans*(NO_2) isomer. It is difficult to differentiate the two *cis*(NO_2) isomers by their electronic absorption spectra, since their absorption bands are similar.

Maki and Sakuraba[6] obtained the two (orange and yellow) of the three geometrical isomers of $[Co(CN)_2(NH_3)_2(en)]^+$ complex. By comparing their absorption curves with those of the *trans* and *cis* isomers of $[Co(CN)_2(en)_2]^+$ and $[Co(CN)_2(NH_3)_4]^+$ complexes in the first d-d absorption band region, the orange isomer was assigned to the *trans*(CN) one and the yellow *cis*(CN). However, they did not mentioned further assignment for the *cis*(CN) isomer (*trans*(NH_3) or *cis,cis*). Also in this case, it is difficult to determine which *cis*(CN) isomer was obtained only from its absorption spectrum.

Raman Spectra. We examined what difference exists between the Raman spectra of the two *cis*(NO_2) isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$. The most striking difference was found in the polarizabilities of the Raman bands due to Co–N(NH_3 and en) stretching vibrations. Figure 3-A shows the polarized Raman spectra of the three isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$ in the 400—600 cm^{-1} region, where Co–N(NH_3 and en) stretching vibrations are expected.[4] If it is assumed that the molecular symmetry of the *trans*(a) isomer of $[Coa_2(NH_3)_2(en)]$ type complex is C_{2v}, that of the *trans*(NH_3) is C_{2v}, and that of the *cis,cis* is C_1, the Co–N(NH_3 and en) stretching vibrations are reduced to ($2A_1+2B_1$), ($2A_1+B_1+B_2$), and (4A), respectively. Although the apparent difference can be recognized in the number of the observed Raman bands between the two *cis*(NO_2) isomers (Fig. 3-A-b and -c), no explicit differences could be expected in the number of Raman bands, because of all the modes being Raman active. However, some differences would be expected in the polarizabilities of the Raman bands. Thus, a Raman band due to a totally symmetric vibration (A_1 or A mode) should be observed as a polarized band ($I_{\perp}/I_{\parallel}<3/4$), whereas that due to a non-totally symmetric vibration (B_1 or B_2 mode) as a depolarized band ($I_{\perp}/I_{\parallel}=3/4$). Therefore, the *trans*(a) and *trans*(NH_3) isomers should have one or more depolarized bands in their Raman spectra, while all the Raman bands should be observed as polarized bands for the *cis,cis* isomer. Unfortunately, the accurate depolarization ratio, $\rho=I_{\perp}/I_{\parallel}$, can not be obtained directly from the Raman spectra of the three isomers of $[Co(NO_2)_2(NH_3)_2(en)]^+$, since the observed bands are partially overlapped (Fig. 3-A). Therefore, we calculated the difference spectra ($I_{\parallel}-I_{\perp}\times4/3$) as shown in Fig. 3-B. The depolarized band would vanish completely in the difference spectra since $I_{\perp}=I_{\parallel}\times3/4$. On the other hand, the polarized band would leave some trace in the difference spectra. A weak band at *ca.* 450 cm^{-1} completely disappeared in each of the difference spectra of the *trans*(NO_2) (Fig. 3-a) and one of the *cis*(NO_2) isomer (Fig. 3-b), *i.e.*, these bands can be regarded as depolarized. On the other hand, all the bands leave some traces in the difference

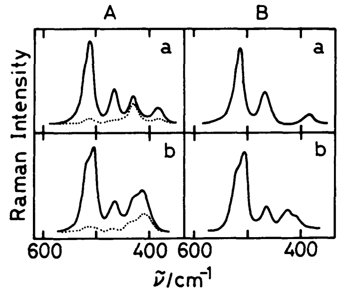


Fig. 4. Polarized Raman spectra (A) [(——), ∥; (----), ⊥] and difference Raman spectra (B) [$I_{\parallel} - I_{\perp} \times 4/3$] of the two isomers of $[Co(CN)_2(NH_3)_2(en)]^+$: a; *trans*(CN) and b; *cis,cis*.

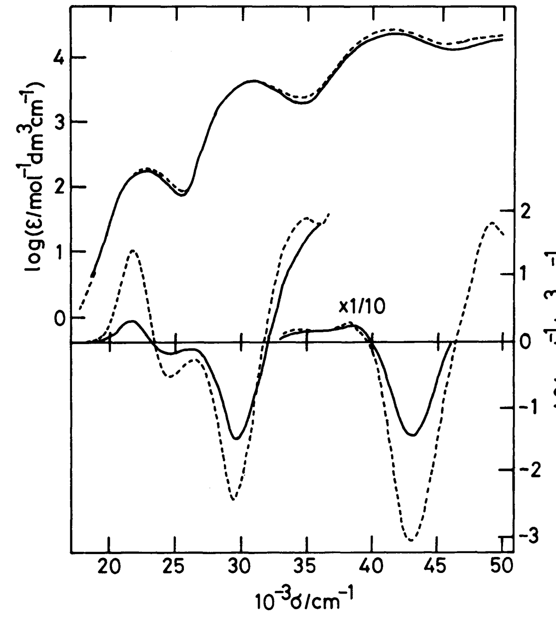


Fig. 5. Electronic absorption and CD spectra of $(+)^{CD}_{450}$-*cis-cis*-$[Co(NO_2)_2(NH_3)_2(en)]Cl$ (——) and Λ-$[Co(NO_2)_2(en)_2]Cl$ (----).

spectrum of another *cis*(NO_2) isomer (Fig. 3-c), *i.e.*, all can be regarded as polarized. It is concluded, therefore, that the *cis*(NO_2) isomer which has a depolarized band in its Raman spectrum has a *trans*(NH_3) configuration and that another *cis*(NO_2) isomer whose Raman bands are all polarized has a *cis,cis* configuration. The other Raman active depolarized bands of the *trans*(NO_2) and *trans*(NH_3) isomers would be very weak, and hidden by the strong polarized bands. An infrared band was observed at 491 cm^{-1} for the *trans*(NO_2) isomer and also at 496 cm^{-1} for the *trans*(NH_3) isomer, they being counterparts of the hidden Raman bands.

Figure 4 shows the polarized Raman spectra (A) and the difference spectra (B) of the two isomers of $[Co(CN)_2(NH_3)_2(en)]^+$. The bands around 400 cm^{-1} can be assignable to the Co–CN stretching vibrations. By a similar argument as above, it is concluded that the present *cis*(CN) isomer has the *cis,cis* configuration, since all the Raman bands are polarized.

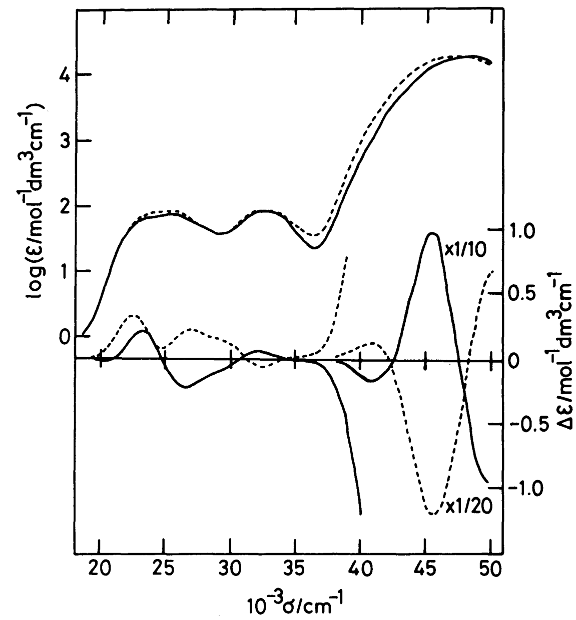
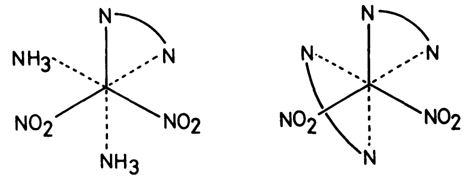
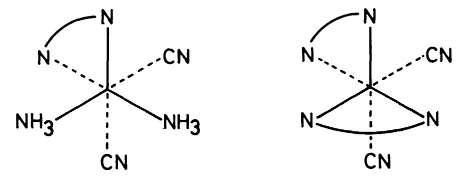


Fig. 6. Electronic absorption and CD spectra of $(+)^{CD}_{450}$-*cis,cis*-$[Co(CN)_2(NH_3)_2(en)]ClO_4$ (——) and Λ-$[Co(CN)_2(en)_2]Cl$ (----).



(a) *(R)* (b) Λ

Fig. 7. Absolute configurations of $(+)^{CD}_{450}$-*cis,cis*-$[Co(NO_2)_2(NH_3)_2(en)]^+$ (a) and Λ-$[Co(NO_2)_2(en)_2]^+$ (b).



(a) *(S)* (b) Δ

Fig. 8. Absolute configurations of $(+)^{CD}_{450}$-*cis,cis*-$[Co(CN)_2(NH_3)_2(en)]^+$ (a) and Δ-$[Co(CN)_2(en)_2]^+$ (b).

Optical Resolution. The differentiation among the geometrical isomers of $[Coa_2(NH_3)_2(en)]$ type complexes (a=NO_2^- and CN^-) based upon the Raman spectra was confirmed by the optical resolution of the *cis,cis* isomers. Figure 5 shows the absorption and CD spectra of $(+)^{CD}_{450}$-*cis,cis*-$[Co(NO_2)_2(NH_3)_2(en)]^+$ complex which was obtained from the less-soluble diastereomer with $\Delta(+)_{546}$-$[Co(edta)]^-$ and Fig. 6 those of $(+)^{CD}_{450}$-*cis,cis*-$[Co(CN)_2(NH_3)_2(en)]^+$ which was obtained from the less-soluble diastereomer with $\Lambda(-)_{546}$-$[Co(edta)]^-$. These figures also show the absorption and CD spectra of Λ-[Co(NO$_2$)$_2$(en)$_2$]$^+$ and Λ-[Co(CN)$_2$(en)$_2$]$^+$, respectively, for comparison. The absolute configurations of these bis(ethylenediamine) complexes have been determined by previous CD[10] and X-ray[11,12] studies. The CD spectral pattern of $(+)^{CD}_{450}$-[Co(NO$_2$)$_2$(NH$_3$)$_2$(en)]$^+$ is similar to that of Λ-[Co(NO$_2$)$_2$(en)$_2$]$^+$ not only in the visible but also in the ultraviolet region, though the CD intensity of the former complex is about half that of the latter. Therefore, the absolute configuration of $(+)^{CD}_{450}$-[Co(NO$_2$)$_2$(NH$_3$)$_2$(en)]$^+$ corresponds to the Λ configuration of bis(chelate) complexes, being assigned to the (*R*) configuration by Cahn, Ingold, and Prelog's Nomenclature[13] (Fig. 7). Since the $(+)^{CD}_{450}$-[Co(CN)$_2$(NH$_3$)$_2$(en)]$^+$ isomer shows a reversed CD pattern with respect to Λ-[Co(CN)$_2$(en)$_2$]$^+$ except for the lowest energy region, the absolute configuration corresponds to the Δ configuration as is shown in Fig. 8 and can be assigned to the (*S*) configuration.

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