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The Raman Spectra of Cobalt(III) Complexes. IV. Differentiation between *cis* and *trans* Isomers of Bis(trimethylenediamine)cobalt(III) Complexes

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Synopsis. The Raman and the infrared spectra of bis(trimethylenediamine)cobalt(III) complexes have been studied to establish a definite distinction between the *cis* and *trans* isomers. A differentiation between the isomers can be made on the bases of the number of the Raman bands in the region of 480—550 cm^{-1} and of the mutual exclusion in the region of 400—500 cm^{-1}.

In the previous paper,[1] the Raman criterion has been established for differentiating *cis* and *trans* isomers of bis(ethylenediamine)cobalt(III) complexes. Many infrared studies[2–6] have been done on the stereochemistry of bis(ethylenediamine)cobalt(III) complexes, but few vibrational studies of bis(trimethylenediamine)cobalt(III) complexes have been reported. Kawaguchi and Kawaguchi[7–9] have applied Baldwin's criteria[5] and Hughes and McWhinnie's criteria[6] for bis(ethylenediamine)cobalt(III) complexes to isomeric pairs of bis(trimethylenediamine)cobalt(III) complexes. They have noted that the former criteria have not been useful for $[Co(NCS)_2(tn)_2]Cl$ and $[Co(N_3)_2(tn)_2]NO_3$, and the latter were not useful for $[Co(CN)(SO_3)(tn)_2]$.

In the present work, we tried to establish vibrational criteria for differentiating *cis* and *trans* isomers of bis(trimethylenediamine)cobalt(III) complexes on the basis of the Raman and the infrared spectra. The established criteria were then applied to the isomeric pair of $[Co(NH_3)_2(tn)_2]Cl_3$ obtained in the present work.

Experimental

Preparation. *Isomeric Pair of* $[Co(NH_3)_2(tn)_2]Cl_3$: This complex has been obtained by Ogino[10] through the reaction of $[Co(NH_3)_5(H_2O)]^{3+}$ with trimethylenediamine, but he did not refer to its geometrical configuration. We have prepared the isomeric pair by two methods.

Method I. Powdered *trans*-$[CoCl_2(tn)_2]Cl$ (5 g) was dissolved in 100 cm^3 of liquid ammonia. The ammonia was then allowed to evaporated spontaneously, leaving behind an orange powder. This powder was washed with a large amount of ethanol and dissolved in a minimum amount of warm water, then the solution was cooled in a refrigerator. The reddish orange precipitate (isomer I) was filtered and dried. The other isomer was obtained by adding a large amount of ethanol to the filtrate as an orange powder (isomer II). Yields: isomer I: 1.5 g; isomer II: 0.3 g.

Method II. Powdered *trans*-$[CoCl_2(tn_2)]Cl$ (5 g) was dissolved in 200 cm^3 of methanol which was saturated with ammonia. The solution was warmed on a water bath for 5 min. The orange powder which deposited was filtered and washed with ethanol. The same compounds as those obtained by method I were isolated by a fractional crystallization, but the ratio of the yields was reversed. Yields: isomer I: 0.7 g; isomer II: 2.5 g. Found: C, 19.16; H, 8.15; N, 22.45% for isomer I. C, 19.18; H, 8.07; N, 22.46% for isomer II. Calcd for $[CoC_6H_{26}N_6]Cl_3\cdot 1.5H_2O$: C, 19.24; H, 7.81; N, 22.45%.

Isomeric Pair of $[Co(NO_2)_2(tn)_2]Cl$: This isomeric pair was first obtained by Kawaguchi and Kawaguchi.[7,8] Later, Celap *et al.*[11] have prepared it by different methods; they have shown that the property of the *cis* isomer is different from that obtained by Kawaguchi and Kawaguchi.[8] We have prepared the isomeric pair from the reaction mixture obtained by Kawaguchi's method[7] for the *trans* isomer by using an ion-exchange column chromatography (SP-Sephadex, C-25; ϕ 30 mm × 500 mm; eluent-0.04 mol/dm^3 KCl solution). The electronic spectrum of each isomer obtained by this method is identical with that of respective isomer observed by Celap *et al.*[11]

Other Complexes. All the other complexes were obtained by the method of Kawaguchi and Kawaguchi.[7–9]

Measurements. The Raman spectra were recorded on a JASCO R-800 Laser Raman spectrometer, using a He–Ne (632.8 nm) or an Ar$^+$ ion (514.5 nm) laser as an excitation source. The infrared spectra were recorded on a JASCO A-3 spectrometer. The observed frequencies were calibrated by the 533.8 cm^{-1} band of indene for the Raman spectra and the 618.0 cm^{-1} band of polystylene film for the infrared spectra. The observed frequencies are accurate within ±2 cm^{-1}.

Results and Discussion

The most consistent variation between the vibrational spectra of *cis* and *trans* isomers has been found in the region of 400—550 cm^{-1}. The Raman and the infrared spectra in this region for the *cis* and *trans* isomeric pair of bis(trimethylenediamine)cobalt(III) complexes are shown in Fig. 1 and those of other *trans* isomers are in Fig. 2. The very strong Raman bands at *ca.* 450 cm^{-1} can be confidently assigned to the Co–N(tn) stretching mode, ν(Co–N(tn)), by comparison with the Raman

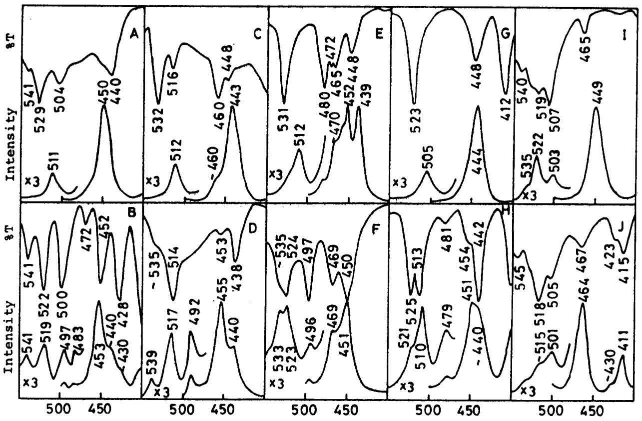

Fig. 1. The Raman and the infrared spectra of the isomeric pair of $[Coab(tn)_2]X$-type complexes. A(*trans*) and B(*cis*); a=b=CN$^-$, X=Cl$^-$. C(*trans*) and D(*cis*); a=b=NO$_2^-$, X=Cl$^-$. E(*trans*); a=b=NCS$^-$, X=Br$^-$. F(*cis*); a=b=NCS$^-$, X=Cl$^-$. G(*trans*) and H(*cis*); a=b=N$_3^-$, X=NO$_3^-$. I(*trans*) and J(*cis*); a=CN$^-$, b=SO$_3^{2-}$.

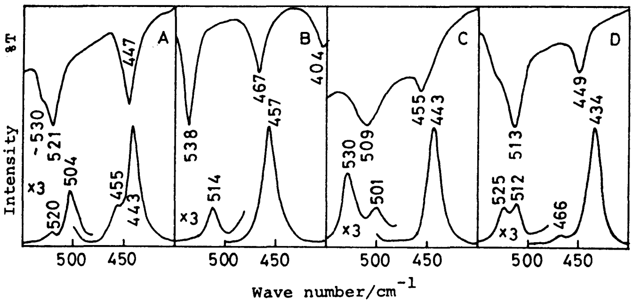

Fig. 2. The Raman and the infrared spectra of *trans*-[Coab(tn)$_2$]X-type or M[Coab(tn)$_2$]-type complexes. A; a=b=Cl$^-$, X=Cl$^-$. B; a=b=NO$_3$$^-$, X=NO$_3$$^-$, C; a=b=SO$_3$$^{2-}$, M=Na$^+$. D; a=Cl$^-$, b=SO$_3$$^{2-}$.

spectra of bis(ethylenediamine)cobalt(III) complexes.[1] Therefore, the infrared bands in the vicinity of 450 cm^{-1} may be assigned to the ν(Co–N(tn)), though Kawaguchi and Kawaguchi[8,9] have regarded the infrared bands in the region of 500—550 cm^{-1} as the ν(Co–N(tn)). The bands in the region of 480—550 cm^{-1} are assignable to the deformation vibration of the chelate ring, δ(CCN), by considering the assignment for ethylenediamine complexes based on the normal coordinate analysis.[12]

It can be seen from Figs. 1 and 2 that the *trans* isomers generally show one band due to δ(CCN) in the 480—550 cm^{-1} region of the Raman spectra and also in the infrared region. Further, the mutual exclusion between the Raman and the infrared spectra occurs, as expected from the approximate symmetry (D_{2h}) of the *trans* isomers. All the *cis* isomers have at least two bands in the 480—550 cm^{-1} region of the Raman spectra and most bands have their counterparts in the infrared spectra. Thus a complex which has one band in the Raman spectra and/or in the infrared spectra of 480—550 cm^{-1} region can be unambiguously assigned to the *trans* isomer. In the sulfito-containing complexes, the band due to the degenerate bending of the sulfito group, $\delta_d(SO_3)$, obscured the band due to the δ(CCN), so this region is not helpful for structural diagnosis. Forbidden vibrations under the assumption of a D_{2h} symmetry appear as a very weak band in the infrared spectrum of the *trans*-dinitro complex and in the Raman spectrum of the *trans*-dichloro complex, but the mutual exclusion approximately holds between the strongest band of the Raman spectrum in the 480—550 cm^{-1} region and that of the infrared one in the same region, in contrast to the *cis* isomers. The bands in the region of 460—480 cm^{-1} for the bis(isothiocyanato)complexes can be assigned to the δ(NCS).

The mutual exclusion generally holds also in the region of the ν(Co–N(tn)) of the *trans* isomers (see Figs. 1 and 2). This criterion can be used even for the sulfito-containing complexes. But in the *trans*-dinitro and the *trans*-diazido complexes, the mutual exclusion does not hold. This may be interpreted as a symmetry lowering in the solid state or as an accidental degeneracy.

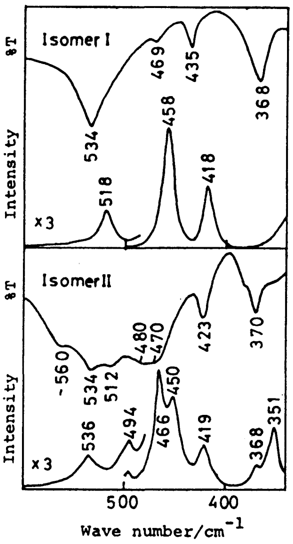

Fig. 3. The Raman and the infrared spectra of the isomeric pair of [Co(NH$_3$)$_2$(tn)$_2$]Cl$_3$.

In conclusion, three criteria for differentiating the geometrical isomers of bis(trimethylenediamine)cobalt(III) complexes are established: the first is based on the number of bands in the region of 480—550 cm^{-1}, the second on the mutual exclusion in the same region, and the last on the mutual exclusion in the ν(Co–N(tn)) region. But each criterion has some exceptions, so only a combination of the three criteria would provide reliable diagnosis.

These criteria were applied to the isomeric pair of [Co(NH$_3$)$_2$(tn)$_2$]Cl$_3$. The Raman and the infrared spectra of the isomers are shown in Fig. 3. It is clear that isomer I has a *trans* configuration and isomer II has a *cis* configuration.

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