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# The Raman Spectra of Cobalt(III) Complexes. III. Differentiation between *cis* and *trans* Isomers of Tetraamminecobalt(III) Complexes

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The Raman and the infrared spectra of tetraamminecobalt(III) complexes have been measured to find the vibrational criteria for differentiating between the *cis* and *trans* configurations. Conspicuous differences between the isomers were found in the $\nu$(Co–NH$_3$) region. Thus, generally the *trans* isomers have two bands at ca. 480 and *ca.* 450 cm$^{-1}$ in the Raman spectra and one band at *ca.* 510 cm$^{-1}$ in the infrared spectra, and the mutual exclusion rule virtually holds. On the other hand, the *cis* isomers have more than three bands in the region of both the Raman and the infrared spectra.

In our previous paper,[1)] we identified the Raman criterion for differentiating the geometrical isomers of bis(ethylenediamine)cobalt(III) complexes. Many infrared criteria[2—6)] have been also used for these complexes. However little vibrational work has been done to study the stereochemistry of tetraamminecobalt(III) complexes. Faust and Quagliano[7)] first applied infrared measurements in the NaCl region to *cis*- and *trans*-tetraamminedinitrocobalt(III) ions and found that the spectrum of the *cis* isomer reveals a slightly more complicated feature than that of the *trans* isomer in the NO$_2$ stretching region. Conspicuous differences between the geometrical isomers have been found in the skeletal vibration region (200—600 cm$^{-1}$) in both the infrared[8)] and the Raman[9)] spectra.

The present study was undertaken to find definite vibrational criteria for differentiating the geometrical isomers of tetraamminecobalt(III) complexes. For this purpose, the Raman and the infrared spectra of a large number of tetraamminecobalt(III) complexes were examined in the $\nu$(Co–NH$_3$) region (350—550 cm$^{-1}$). The established criteria were then applied to $[\mathrm{Co(NCS)_2(NH_3)_4}]^+$, $[\mathrm{CoCl(NCS)(NH_3)_4}]^+$ and $[\mathrm{CoX(NO_2)(NH_3)_4}]$-type complexes prepared in the present work (X=Cl$^-$, H$_2$O, CN$^-$).

## Experimental

*Preparation.* *[Co(NCS)$_2$(NH$_3$)$_4$]Cl*: One of the isomers has been obtained by Werner.[10)] We prepared the isomeric pair by the following method. A solution containing 24 g of cobalt(II) chloride hexahydrate and 76 g of ammonium thiocyanate in 200 cm$^3$ of 10% aqueous ammonia was oxidized by bubbling air for 6 h at 40 °C, whereupon a red powder separated. The red powder was filtered and washed with a large amount of ethanol. The yield of the crude product was about 13 g. One gram of the crude product was dissolved in 1000 cm$^3$ of water and the solution was passed through Sephadex cation-exchange resin (SP, C-25; 30 mm × 600 mm). By elution with a 0.05 M LiCl solution, two bands, pinkish red one and brick red one, descended in that order. Each eluate was concentrated to a small volume below 40 °C and mixed with ethanol. Each compound thus obtained was recrystallized from water by adding a saturated solution of lithium chloride. Yield 0.3 g for the pinkish red isomer. 0.2 g for the brick red isomer. The infrared spectrum of the brick red isomer is identical with that of the complex obtained by Werner's method.[3)] Absorp. max. $10^{-3}\,\sigma$/cm$^{-1}$ (log $\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$): 19.5(2.24), 31.75(3.38) for the pinkish red isomer; 20.3 (2.54), 32.3 (3.58) for the brick red isomer. Found: C, 8.66; H, 4.60; N, 30.27% for the former isomer. C, 8.60; H, 4.43; N, 29.72% for the latter isomer. Calcd for $[\mathrm{CoC_2H_{12}N_6S_2}]$Cl: C, 8.62; H, 4.34; N, 30.16%.

*[CoCl(NCS)(NH$_3$)$_4$]Cl*: The *trans* isomer was obtained according to the method of Poon.[11)] The *cis* isomer was obtained by the following method. A solution of 6 g of *trans*-$[\mathrm{CoCl_2(NH_3)_4}]$SCN in 80 cm$^3$ of water was stirred at 50 °C for half an hour. The resulting reddish violet solution was cooled to room temperature and 80 cm$^3$ of concd HCl was added. Then a reddish violet precipitate was deposited. The precipitate was added to 400 cm$^3$ of 6 mol dm$^{-3}$ HCl and the mixture was warmed on a water bath for a few minutes and then filtered. The filtrate was cooled to room temperature and ethanol was added to it. The complex thus precipitated was filtered, washed with methanol and dried in air. The complex was recrystallized from cold water by adding concd HCl. Yield 4 g. Found: C, 4.51; H, 4.96; N, 26.70%. Calcd for $[\mathrm{CoCClH_{12}N_5S}]\mathrm{Cl}\cdot 0.5\mathrm{H_2O}$: C, 4.53; H, 4.76; N, 26.43%.

*[CoCl(NO$_2$)(NH$_3$)$_4$]Cl*: The *trans* isomer was obtained by the method of Werner.[12)] Meyer and Rampoldt[13)] have shown the scheme for the preparation of the *cis* isomer through a reaction of tetraamminecarbonatocobalt(III) salt with nitrosyl chloride but the detailed procedure has not been described. So, the *cis* isomer was obtained by the following method. A solution of 2.8 g of sodium nitrite in 30 cm$^3$ of water was added to a solution of 10.8 g of *cis*-$[\mathrm{CoCl(NH_3)_4(H_2O)}]\mathrm{Cl_2}$ in 400 cm$^3$ of water and the mixture was stirred at 40 °C for 10 min. The resulting brown solution was evaporated to a small volume below 40 °C under reduced pressure, and a large amount of ethanol was added to it. The precipitate thus obtained was added to 400 cm$^3$ of 6 mol dm$^{-3}$ HCl and the mixture was stirred for half an hour and then filtered. To the filtrate, 400 cm$^3$ of methanol was added and the solution was cooled in a refrigerator for 12 h. The desired complex was deposited as brownish red needle-like crystals. Yield 5 g. Found: H, 5.00; N, 28.64%. Calcd for $[\mathrm{CoClH_{12}N_5O_2}]$Cl: H, 4.96; N, 28.71%.

*[Co(NO$_2$)(NH$_3$)$_4$(H$_2$O)](NO$_3$)$_2$*: The *trans* isomer was obtained by the method of Jörgensen.[14)] The *cis* isomer has been prepared from $[\mathrm{Co(SO_4)(NH_3)_4(H_2O)}]\mathrm{NO_2}$ by King and Mistry[15)] and from $[\mathrm{Co(ONO)(NH_3)_4(H_2O)}](\mathrm{NO_3})_2$ by Yalman and Kuwana.[16)] However, the isomer was obtained more easily from *cis*-$[\mathrm{CoCl(NO_2)(NH_3)_4}]$Cl by the following method. A solution of 3.4 g of silver nitrate in 20 cm$^3$ of water was added to a solution of 2.6 g of *cis*-$[\mathrm{CoCl(NO_2)(NH_3)_4}]$Cl in 20 cm$^3$ of water and the mixture was stirred at 50 °C. The silver chloride deposited was filtered off and 20 cm$^3$ of concd HNO$_3$ and then methanol was added to the filtrate. The crude orange powder was recrystallized from hot water by adding concd HNO$_3$. Yield 1.5 g. Found: H, 4.51; N, 30.99%. Calcd for $[\mathrm{CoH_{14}N_5}$-

$O_3](NO_3)_2$: H, 4.48; N, 31.12%.

*[Co(CN)(NO$_2$)(NH$_3$)$_4$]Cl*: The *trans* isomer was obtained from $[CoCl(CN)(NH_3)_4]Cl$.[17] To a suspension of 1.2 g of $[CoCl(CN)(NH_3)_4]Cl$ in 30 cm$^3$ of water, 0.35 g of solid sodium nitrite was added and the mixture was stirred at 50 °C for 2 h, then a brownish yellow solution was obtained. Ethanol was added to the solution and the yellow crystals deposited were filtered and recrystallized from hot water by adding ethanol. Yield 0.7 g. Found: C, 4.79; H, 5.59; N, 32.70%. Calcd for $[CoCH_{12}N_6O_2]Cl\cdot H_2O$: C, 4.76; H, 5.59; N, 33.28%.

The *cis* isomer was obtained from *cis*-$[CoCl(NO_2)(NH_3)_4]Cl$. A solution of 1.7 g of silver nitrate in 30 cm$^3$ of dimethylsulfoxide (DMSO) was added to a solution of 2.6 g of *cis*-$[CoCl(NO_2)(NH_3)_4]Cl$ in 150 cm$^3$ of DMSO and the silver chloride deposited was filtered off. Then, 2 g of silver cyanide was added to the filtrate. The suspension was stirred at 60 °C for 5 h; the color of the liquid phase was changed from brownish red to orange yellow. To the suspension, 500 cm$^3$ of water was added and the insoluble product was filtered off. The filtrate was poured onto Sephadex ion-exchange resin (SP, C-25; 30 mm × 700 mm). By elution with a 0.05 M LiCl solution, three bands colored brownish yellow descended. The desired complex was obtained from the second eluate. This eluate was concentrated to a small volume. A brownish yellow precipitate was obtained by the addition of ethanol and recrystallized from warm water. Yield 0.5 g. It was found from absorption measurements that the first eluate contains *trans*-$[Co(CN)(NO_2)(NH_3)_4]^+$ and the third one contains *cis*-$[Co(NO_2)_2(NH_3)_4]^+$. Found: C, 5.00; H, 5.36; N, 33.94%. Calcd for $[CoCH_{12}N_6O_2]Cl\cdot 0.5H_2O$: C, 4.93; H, 5.35; N, 34.51%.

*Other Complexes*: *trans*-$Na[Co(SO_3)_2(NH_3)_4]$ was prepared by the method of Akamatsu *et al.*[18] All the other complexes are well known and were prepared by standard means.

*Measurements.* The Raman spectra were recorded on a JASCO R-800 Laser Raman spectrometer with a data processor, 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 one. The observed frequencies are accurate within ±2 cm$^{-1}$.

## Results and Discussion

If it is assumed that a *trans* isomer of $[Coa_2(NH_3)_4]$-type complexes (a represents a unidentate ligand) possesses a $D_{4h}$ symmetry, the cobalt-ammonia stretching vibrations transform as $(A_{1g}+B_{1g}+E_u)$, the g modes being Raman allowed and the u mode infrared allowed. Therefore mutual exclusion will be expected. Supposing a $C_{4v}$ symmetry for *trans*-$[Coab(NH_3)_4]$-type complexes (a and b represent an unidentate ligand), the cobalt-ammonia stretching vibrations transform as $(A_1+B_1+E)$, all of which are formally Raman active, and $A_1+E$ modes are formally infrared active. However, the $A_1$ and the E modes are closely correlated with the $A_{1g}$ and the $E_u$ modes of $D_{4h}$ symmetry, respectively. So we expect that the E mode will be hardly detectable in the Raman spectra of $[Coab(NH_3)_4]$-type complexes. In the same way, the infrared intensity of the $A_1$ mode will be very weak. Thus, the mutual exclusion will virtually hold for this type of complex. If the *cis* isomers of $[Coa_2(NH_3)_4]$-type and $[Coab(NH_3)_4]$-type complexes have a $C_{2v}$ and a $C_s$ symmetry, respectively, the cobalt-ammonia stretching vibrations transform as $(2A_1+B_1+B_2)$ and $(3A'+A'')$, respectively, and all of the modes are active in both the Raman and the infrared spectra.

Figures 1 and 2 show the Raman and the infrared spectra of 350—550 cm$^{-1}$ region, where the cobalt-ammonia stretching vibrations, $\nu(Co–NH_3)$, are expected. As shown in Fig. 1, the Raman spectra of the *trans* isomers have a similar spectral feature. Thus, each spectrum shows a very strong band at *ca.* 480 cm$^{-1}$ and a medium or a weak one at *ca.* 450 cm$^{-1}$, except for that of the dinitro complex in which the two bands are situated at about 10 cm$^{-1}$ higher. The bands at *ca.* 480 and *ca.* 450 cm$^{-1}$ are assigned to the $A_{1g}$ (or $A_1$) mode and the $B_{1g}$ (or $B_1$) mode of $\nu(Co–NH_3)$, respectively, by polarization measurements. The resemblance in the Raman frequencies of $\nu(Co–NH_3)$ among the trans isomers may be interpreted in terms of mechanical couplings among normal modes. The $A_{1g}$ species of $D_{4h}$ symmetry contain $\nu(Co–NH_3)$ and $\nu$(Co–a), but the displacement vector of these vibrations are perpendicular to each other. So mechanical coupling between these vibrations will be virtually absent. The $B_{1g}$ species contains only one mode, $\nu(Co–NH_3)$. Therefore, the Raman active $\nu(Co–NH_3)$ modes of *trans*-tetraamminecobalt(III) complexes are expected to be mechanically free from the other modes. The very weak bands at *ca.* 510 cm$^{-1}$

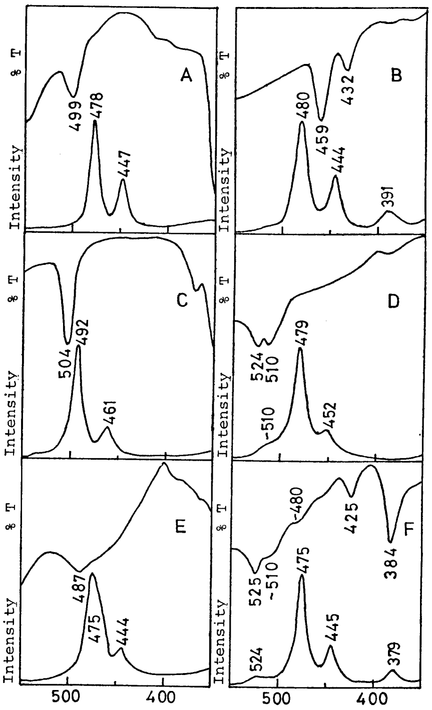

Fig. 1. Raman and infrared spectra of *trans*-$[Coab(NH_3)_4]X$- or *trans*-$M[Coab(NH_3)_4]$-type complexes.
A: a=b=$Cl^-$; X=$Cl^-$, B: a=b=$CN^-$; X=$Cl^-$, C: a=b=$NO_2^-$; X=$Cl^-$, D: a=b=$SO_3^{2-}$; M=$Na^+$, E: a=b=$Br^-$; X=$ClO_4^-$, F: a=$CN^-$; b=$SO_3^{2-}$.

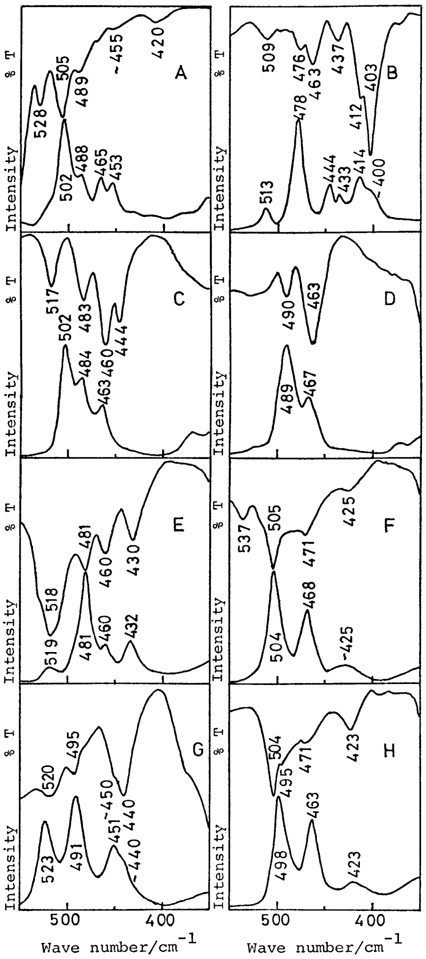

Fig. 2. Raman and infrared spectra of *cis*-[Coab$(NH_3)_4$]X- or *cis*-M[Coab$(NH_3)_4$]-type complexes.

A: a=b=$Cl^-$; X=$Cl^-$, B: a=b=$CN^-$; X=$Cl^-$, C: a=b=$NO_2^-$; X=$Cl^-$, D: a=b=$NO_2^-$; X=$NO_3^-$, E: a=b=$SO_3^{2-}$; M=$NH_4^+$, F: a=b=$F^-$; X=$Cl^-$, G: a=b=$H_2O$; X=$(NO_3^-)_3$, H: a=$Cl^-$; b=$H_2O$; X=$(Cl^-)_2$.

(Fig. 1-D) and at 524 cm$^{-1}$ (Fig. 1-F) are assigned to the degenerate bending of the coordinated sulfito group, $\delta_d(SO_3)$. The bands at 391 cm$^{-1}$ (Fig. 1-B) and at 379 cm$^{-1}$ (Fig. 1-F) are assigned to the $\nu$(Co–CN) by measurements of the deuterated compounds.

The infrared spectra of *trans*-tetraamminecobalt(III) complexes show one band due to the $E_u$ (or E) mode of $\nu(Co–NH_3)$ in the region of 490—510 cm$^{-1}$, except for that of the dicyano complex, in which the $\nu(Co–NH_3)$ is observed at 459 cm$^{-1}$ (see Fig. 1). The bands at 524 cm$^{-1}$ (Fig. 1-D) and at 525 cm$^{-1}$ (Fig. 1-F) are assigned to the $\delta_d(SO_3)$ and the bands at 432 cm$^{-1}$ (Fig. 1-B) and at 425 and 384 cm$^{-1}$ (Fig. 1-F) to the $\nu$(Co–CN) or $\delta$(Co–CN). The mutual exclusion with respect to the $\nu(Co–NH_3)$ virtually holds in all of the spectra in Fig. 1.

On the other hand, both the Raman and the infrared spectra of the *cis* isomers generally show at least three bands in the region of 400—550 cm$^{-1}$ and many coincidences are found in the frequency between the Raman and the infrared bands (see Fig. 2). Although the Raman spectrum of *cis*-[Co$(NO_2)_2$$(NH_3)_4$]$NO_3$ (Fig. 2-D) show two bands similar to that of the *trans* isomer, the Raman bands have counterparts in the infrared spectrum incontrast to that of the *trans* isomer.

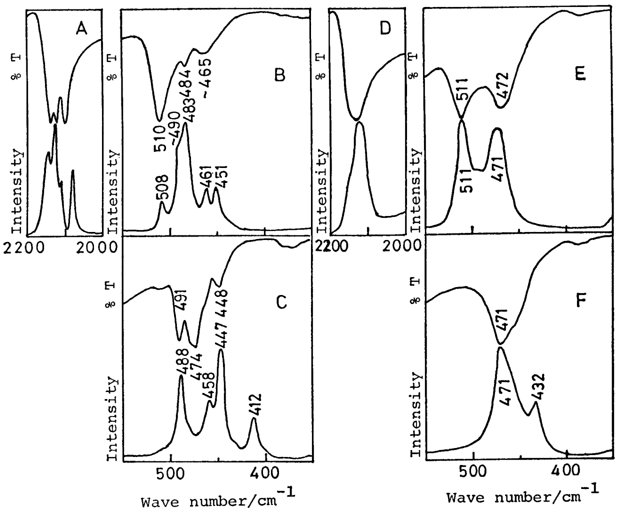


Fig. 3. Raman and infrared spectra of [Co$(NCS)_2$$(NH_3)_4$]Cl.

A and B: Pinkish red isomer, C: *N*-deuterated pinkish red isomer, D and E: brick red isomer, F: *N*-deuterated brick red isomer.

In conclusion, two criteria will be established for differentiating the geometrical isomers of tetraamminecobalt(III) complexes. The first is based on the number of bands due to $\nu(Co–NH_3)$ and their frequencies; *trans* isomer of tetraamminecobalt(III) complexes shows two Raman bands (generally at *ca.* 480 cm$^{-1}$ and at *ca.* 450 cm$^{-1}$) and one infrared band (generally at 490—510 cm$^{-1}$), while the *cis* isomer generally shows more than three bands in both the infrared and the Raman spectra. Another is based on mutual exclusion; this mutual exclusion virtually holds in the *trans* isomers and not in the *cis* isomers. It is clear that only a combination of both these two criteria would provide reliable structural diagnosis.

It is obviously of interest to apply these vibrational criteria to tetraamminecobalt(III) complexes of unknown or doubtful configurations. Werner[10] has obtained one of the isomers of [Co$(NCS)_2(NH_3)_4$]$^+$ and the infrared spectrum of this complex has been studied for the C–N and the C–S stretching region by Chamberlain and Bailar.[3] They have regarded this complex as the *trans* isomer. We obtained the other isomer in this work. The Raman and the infrared spectra of the isomeric pair in the region of 350—550 cm$^{-1}$ are shown in Fig. 3, together with the $\nu$(CN) region. The pinkish red isomer (see Experimental section) has three or four bands in the $\nu$(CN) region, while the brick red one shows only one broad band. The splitting of $\nu$(CN) was frequently identified with a *cis* configuration for the related complexes. Also in the region of 400—550 cm$^{-1}$, the spectra of the pinkish red isomer (Fig. 3-B) are apparently more complicated than those of the brick red one (Fig. 3-E), though more than two bands seem

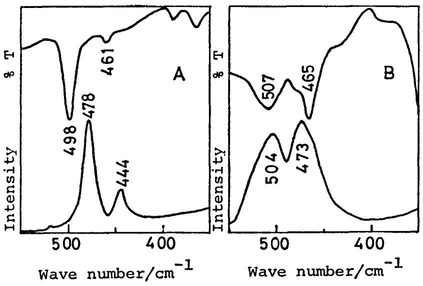

Fig. 4. Raman and infrared spectra of $[CoCl(NCS)(NH_3)_4]Cl$.
A: The isomer obtained by Poon's method,11) B: the isomer obtained in this work.

to be overlapped in the spectra of the latter isomer. In these complexes, the bands due to $\delta$(NCS) will appear in the same region as the $\nu$(Co–NH$_3$). In order to eliminate the bands due to $\delta$(NCS), the spectra of the *N*-deuterated complexes have been measured (Figs. 3-C,F). By the comparison of the spectra of normal complexes with those of the deuterated ones, the bands at *ca.* 490 cm$^{-1}$ and *ca.* 460 cm$^{-1}$ of the pinkish red isomer and a part of the band at *ca.* 470 cm$^{-1}$ of the brick red isomer can be assigned to the $\delta$(NCS). Then the bands at 510 cm$^{-1}$ (very weak in the Raman but very strong in the infrared spectrum), at 483 cm$^{-1}$ (very strong in the Raman but very weak in the infrared spectrum) and at 451 cm$^{-1}$ (which does not appear in the infrared spectrum) are assigned to the $\nu$(Co–NH$_3$) for the pinkish red isomer. This spectral feature is a characteristic of a *trans* configuration, except for the appearance of the very weak bands. The Raman and the infrared spectra of the brick red isomer show apparently two bands. However, the facts that the intensity of the Raman band at 511 cm$^{-1}$ is very strong and the Raman spectrum has no band at about 450 cm$^{-1}$ suggest that the isomer has not a *trans* configuration but a *cis* configuration. In the *trans* isomer, the appearance of the band at 510 cm$^{-1}$ ($E_u$ mode) in the Raman spectrum and the band at 483 cm$^{-1}$ ($A_{1g}$ mode) in the infrared spectrum, and the complicated feature in the $\nu$(CN) region may be due to the symmetry lowering in the solid state. This assignment of the geometrical configurations is compatible with that on the basis of the relative positions of the absorption maxima in the first d-d absorption band or the "specific band" of thiocyanato groups, and also with the elution order of the column chromatography.

The Raman and the infrared spectra of the isomeric pair of $[CoCl(NCS)(NH_3)_4]Cl$ are shown in Fig. 4. On the basis of the observed band positions in the Raman and the infrared spectra and the comparison between the two spectra, the isomer which was obtained by Poon's method11) is assigned to the *trans* structure and the isomer obtained in this work to the *cis* structure.

The Raman and the infrared spectra of $[CoX(NO_2)(NH_3)_4]$-type ($X=NCS^-$, $Cl^-$, $H_2O$, $CN^-$) complexes are shown in Fig. 5. The Raman spectra (Figs. 5-A,C,E, and G) of the complexes, whose geometrical configurations are assumed to be *trans*, show the characteristic feature of a *trans* configuration. The band at 417 cm$^{-1}$, which was observed for *trans*-$[Co(CN)(NO_2)(NH_3)_4]Cl$ is assigned to the $\nu$(Co–CN). The Raman spectra of the others (Figs. 5-B,D,F, and H) have more than three bands due to $\nu$(Co–NH$_3$) and most of the bands have counterparts in the infrared spectra, so *cis* configurations are confirmed for these complexes. It is seen from Fig. 5 that the assignments of the geometrical configurations by the infrared spectra alone are not conclusive for these complexes.

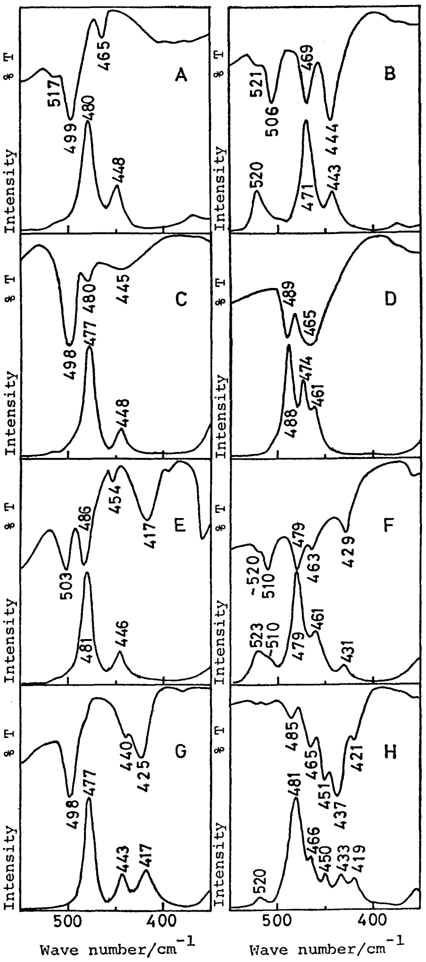

Fig. 5. Raman and infrared spectra of $[Coa(NO_2)(NH_3)_4]X$-type complexes.
A (*trans*) and B (*cis*): a=$NCS^-$; X=$Cl^-$, C(*trans*) and D(*cis*): a=$Cl^-$; X=$Cl^-$, E(*trans*) and F(*cis*): a=$H_2O$; X=$(NO_3^-)_2$, G(*trans*) and H(*cis*): a=$CN^-$; X=$Cl^-$.

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