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

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The Raman spectra of bis(ethylenediamine)cobalt(III) complexes have been studied with a view toward differentiating between the *cis* and *trans* configurations. It is shown that a correlation can be made between the configurations of the complexes and the intensity of the band due to the chelate-ring-deformation vibration, δ(cycle). Thus, *trans* isomers exhibit a strong and sharp band near 270 cm^{-1} due to this mode, while *cis* isomers exhibit no intense band at this frequency.

Several attempts have been made, with varying degrees of success, to correlate the configurations of bis(ethylenediamine)cobalt(III) complexes with the infrared spectra. Merritt and Wiberley[1)] have suggested that a differentiation between *cis* and *trans* isomers of bis(ethylenediamine)cobalt(III) complexes may be made on the basis of the shift of the band in the 1500—1600 cm^{-1} region to lower frequencies from a *cis* to a *trans* configuration. Chamberlain and Bailar[2)] have proposed a means for differentiating the *cis* and *trans* isomers by the number of bands in the 1120—1150 cm^{-1} region. Morris and Busch[3)] and Baldwin[4)] have attempted to correlate the splitting of the 1600 cm^{-1} and the 870—900 cm^{-1} bands respectively with the *cis* configuration. Hughes and McWhinnie[5)] have suggested that a differentiation between the *cis* and *trans* isomers may be made on the basis of the complexity of the spectra in the 500—600 cm^{-1} region.

The present study was undertaken to correlate the configuration of the bis(ethylenediamine)cobalt(III) complex with the Raman spectrum. All the previous infrared studies, with the exception of the one by Hughes and McWhinnie,[5)] have been concerned with the intra-ligand vibrations. The difference between the symmetries of the *cis* and *trans* isomers of bis(ethylenediamine)cobalt(III) complexes should, however, be reflected more sensitively in the skeletal vibrations than in the intra-ligand vibrations. It was thought worthwhile to study the metal-ligand vibrations of the *cis* and *trans* isomers, and Raman spectroscopy is suitable for this purpose. The Raman spectra were measured for the complexes whose geometrical configurations has already been determined, and on the basis of the observed Raman spectral difference between the *cis* and *trans* isomers, the Raman spectral criterion for differentiating the isomers was established. This criterion was then applied to the [CoX(SO$_3$)(en)$_2$]-type complexes (X=N$_3^-$, NCS$^-$, NH$_3$) obtained in the present work.

Experimental

Preparation. cis-*[Co(NCS)(SO$_3$)(en)$_2$]·0.5H$_2$O*: *trans*-[CoCl(SO$_3$)(en)$_2$] (6 g) and NaSCN (1.7 g) were dissolved in 50 cm^3 of water, and the mixture was heated on a water bath for 3 h. The resulting mixture was cooled to room temperature. Then pale brown needles (*trans*-[Co(NCS)(SO$_3$)(en)$_2$]) were filtered off, and the filtrate was left standing overnight at room temperature. Orange-yellow leaflet crystals were deposited; they were then filtered off and recrystallized from hot water. Absorp. max. $10^{-3}\sigma$/cm^{-1} (log ε): 21.5 (2.44), *ca.* 29 sh (2.9), 35.0 (4.12). Found: C, 18.22; H, 5.29; N, 21.44%. Calcd for [Co(NCS)(SO$_3$)(C$_2$H$_8$N$_2$)$_2$]·0.5H$_2$O: C, 18.41; H, 5.25; N, 21.46%.

trans-*[Co(N$_3$)(SO$_3$)(en)$_2$]·0.5H$_2$O*: *trans*-[Co(SO$_3$)(en)$_2$(H$_2$O)]ClO$_4$ (6 g) was dissolved in 100 cm^3 of water, and then NaN$_3$ (5 g) was added. On occasional heating at 40 °C, the mixture was stirred for 1 h. On cooling and the addition of ethanol, a reddish-brown powder appeared; this was filtered off and dried. Absorp. max. $10^{-3}\sigma$/cm^{-1} (log ε): 21.2 (2.55), *ca.* 30 sh (3.5), 36.5 (4.68). Found: C, 15.40; H, 5.54; N, 31.04%. Calcd for [Co(N$_3$)(SO$_3$)(C$_2$H$_8$N$_2$)$_2$]·0.5H$_2$O: C, 15.49; H, 5.52; N, 31.61%.

trans-*[Co(SO$_3$)(NH$_3$)(en)$_2$]Cl·H$_2$O*: *trans*-[CoCl(SO$_3$)(en)$_2$] (6 g) was dissolved in 50 cm^3 of liquid ammonia. The ammonia was then allowed to evaporate spontaneously, leaving behind a brown solid, which was recrystallized from hot water. Absorp. max. $10^{-3}\sigma$/cm^{-1} (log ε): 21.6 (2.22), *ca.* 28 sh (2.3), 36.4 (4.15). Found: C, 14.58; H, 6.40; N, 21.18%. Calcd for [Co(SO$_3$)(NH$_3$)(C$_2$H$_8$N$_2$)$_2$]·H$_2$O: C, 14.57; H, 6.42; N, 21.24%.

Other Complexes: *cis*-[Co(CN)(SO$_3$)(en)$_2$] and *cis*-[CoBr(CN)(en)$_2$]Br were prepared according to the method of Ohkawa, Hidaka, and Shimura.[6)] *trans*-[Co(CN)(SO$_3$)(en)$_2$] was prepared according to the method of Chan and Tobe.[7)] *trans*-[CoBr(CN)(en)$_2$]Br was prepared by the method of Chan.[8)] *cis*-[Co(CN)(NO$_2$)(en)$_2$]Br and *trans*-[Co(CN)(NO$_2$)(en)$_2$]ClO$_4$ were prepared by the method of Ohkawa, Hidaka, and Shimura.[9)] *trans*-[Co(NCS)(SO$_3$)(en)$_2$] and *cis*-[Co(SO$_3$)(NH$_3$)(en)$_2$]Cl were prepared by the method of Baldwin.[10)] *cis*-[Co(N$_3$)(SO$_3$)(en)$_2$] was prepared by the method of Hughes and McWhinnie.[5)] *cis*-Li[Co(S$_2$O$_3$)$_2$(en)$_2$] was prepared by the method of Akamatsu, Hidaka, and Shimura.[11)] All the other complexes are well known and were prepared by standard means. All the complexes were identified by means of the visible and ultra-violet spectra.

Measurements. The Raman spectra were recorded on a JASCO Laser Raman spectrometer (model R-800), using a He–Ne laser (632.8 nm) or an Ar$^+$ ion laser (514.5 or 457.9 nm) as the excitation source. Generally, the spectra were measured in aqueous solutions in order to avoid the appearance of lattice modes and the band splitting due to a crystal field.

Results and Discussion

The Raman spectra in the skeletal vibration region of *trans*- and *cis*-bis(ethylenediamine)cobalt(III) complexes whose geometrical configurations have previously been determined are shown in Fig. 1 and 2. The isomeric pair of complexes reveals a quite different Raman spectrum in this region. In general, the spectra of the *cis* isomers reveal more complicated

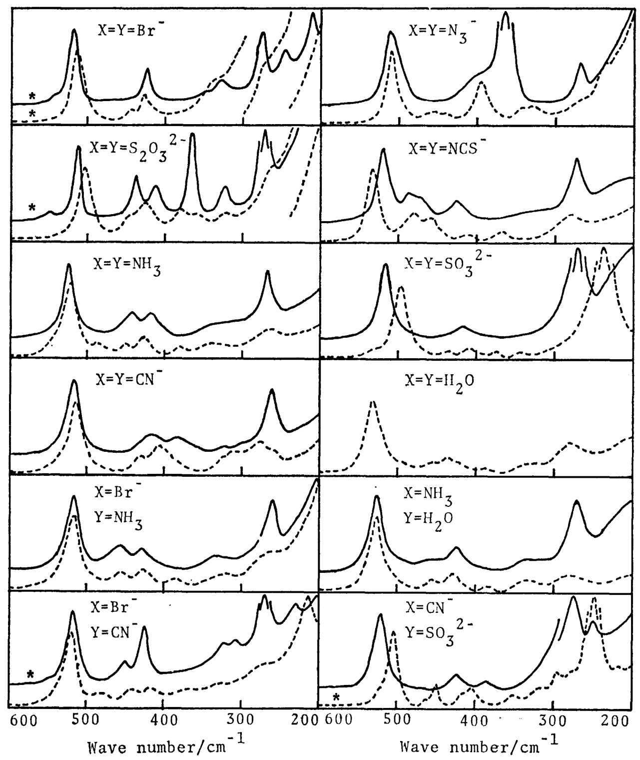

Fig. 1. Raman spectra of [CoXY(en)$_2$]-type complexes. *trans* isomer (——) and *cis* isomer (----). (* Denotes a solid-state spectrum.)

features than those of the *trans* isomers. The most striking difference is found near 270 cm^{-1}. That is, the Raman spectra of the *trans* isomers have a strong and sharp band near 270 cm^{-1}, while those of the *cis* isomers have no intense band at that frequency.

Two different assignments for the *ca.* 270 cm^{-1} band have been proposed. Gouteron-Vaissermann[12)] has assigned the *ca.* 270 cm^{-1} band of [Co(en)$_3$]$^{3+}$ to the bending vibration of the N–Co–N angle, which does not include the chelate ring. On the other hand, Krishnan and Plane[13)] have assigned the corresponding band to the chelate-ring-deformation vibration, δ(cycle), in their Raman study of complexes of ethylenediamine with zinc(II), cadmium(II), and mercury(II). The latter assignment is regarded as reasonable because the band at *ca.* 270 cm^{-1} in the Raman spectrum of *trans*-[CoX$_2$(en)$_2$]-type complexes is polarized and only the symmetric chelate-ring deformation of the nine skeletal deformation modes belongs to a totally symmetric species. Therefore, the strong band obserbed near 270 cm^{-1} in the Raman spectrum of *trans*-bis(ethylenediamine)cobalt(III) complexes may confidently be assigned to δ(cycle).

In the case of complexes containing a nitro or chloro group (see Fig. 2), careful measurements are required in estimating the intensity of δ(cycle) because ν(Co–NO$_2$) or ν(Co–Cl) appears as a intense band in the vicinity of δ(cycle). For example, the low-resolution Raman spectra of *cis*- and *trans*-[Co(NO$_2$)$_2$(en)$_2$]$^+$ are similar to each other in the *ca.* 270 cm^{-1} region; *i.e.*, the aqueous Raman spectrum of each isomer apparently shows a strong band in the region because of the band overlapping of δ(cycle) with ν(Co–NO$_2$). The differentiation between δ(cycle) and ν(Co–NO$_2$) or ν(Co–Cl) is performed by means of the Raman measurement of *N*-deuterated complexes. The band due to δ(cycle) shows a shift to a lower frequency (about 5 cm^{-1}) following a deuteration of the amino protons of the ethylenediamine group, while the band due to ν(Co–NO$_2$) or ν(Co–Cl) is not affected.

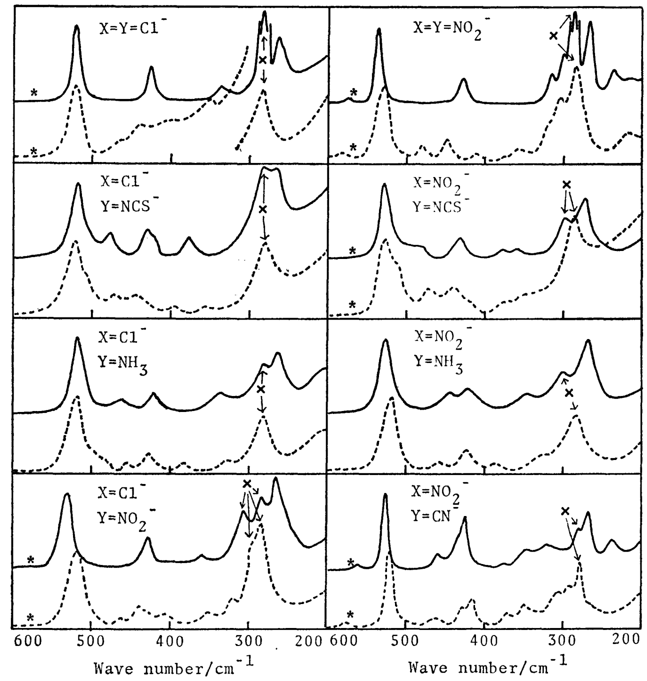

Fig. 2. Raman spectra of [CoXY(en)$_2$]-type complexes, where X or Y is a chloro or nitro group. *trans* isomer (——) and *cis* isomer (----). (* Denotes a solid-state spectrum; × denotes ν(Co–Cl) or ν(Co–NO$_2$).)

In conclusion, *cis-trans* isomeric pairs of [CoX$_2$(en)$_2$]-type and [CoXY(en)$_2$]-type complexes were successfully differentiated on the basis of the examination of the Raman intensity of the band due to δ(cycle) near 270 cm^{-1}.

It is obviously of interest to apply the present results to complexes of unknown or doubtful geometrical configurations. For the geometrical configuration of [Co(NO$_3$)$_2$(en)$_2$]NO$_3$, two different assignments have been proposed. Shimura and Tsuchida[14)] have proposed that the complex has a *trans* configuration because the electronic absorption spectrum in the visible region shows the splitting of the first d-d absorption band. On the other hand, Krebs and Diewald[15)] have regarded the complex as a *cis* isomer on the basis of the optical resolution by starch chromatography. Figure 3 shows the Raman spectrum of solid [Co(NO$_3$)$_2$(en)$_2$]NO$_3$. This complex is very unstable in water, and the Raman spectrum in an aqueous solution could not be obtained. The presence of the strong band at 276 cm^{-1} due to the δ(cycle) and the simple features of the spectrum reveal that the complex has a *trans* configuration. It can, therefore, be presumed that the complex which was optically resolved by Krebs and Diewald[15)] might be an aquation-and-

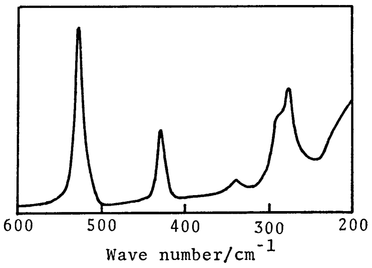

Fig. 3. Raman spectrum of solid $[Co(NO_3)_2(en)_2]NO_3$.

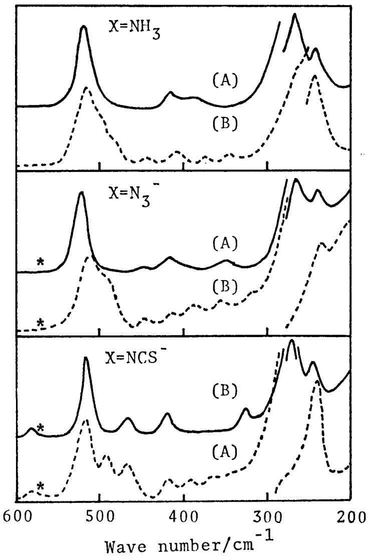

Fig. 4. Raman spectra of $[CoX(SO_3)(en)_2]$-type complexes.
trans isomer (——) and *cis* isomer (----). (* Denotes a solid-state spectrum; (A) refers to the spectra of the complexes which were prepared in the present work, and (B), to those of the complexes which were prepared by the methods in the Refs. 5 and 10.)

isomerisation product of the complex. The Raman spectrum of the aquation product of the complex does not show an intense band near 270 cm^{-1}.

Baldwin[10)] has obtained a geometrical isomer of $[CoX(SO_3)(en)_2]$-type complexes ($X{=}H_2O$, NCS^-, NH_3) by means of substitution reactions of $[CoCl(SO_3)(en)_2]$. Hughes and McWhinnie[5)] have also obtained a geometrical isomer of $[Co(N_3)(SO_3)(en)_2]$ by a similar method. These complexes have been assumed to have a *cis* configuration on the basis of the infrared spectra. However, the X-ray studies of $[Co(SO_3)(en_2)(H_2O)]ClO_4 \cdot H_2O$[16)] and $[Co(NCS)(SO_3)(en)_2] \cdot 2H_2O$[17)] show that these complexes have a *trans* configuration.

We have applied the Raman intensity criterion for δ(cycle) to the ammine and the azido complexes and have also prepared another isomer of the $[CoX(SO_3)(en)_2]$-type complexes ($X{=}NH_3$, N_3^-, NCS^-). The Raman spectra of the isomeric pairs of the complexes are shown in Fig. 4, where the (A) spectra refer to the isomers which have been prepared in the present work, and the (B) spectra, to the isomers which have been obtained by the methods in the literature. The Raman criterion indicates that the ammine and the azido complexes prepared by the present method have a *trans* configuration, while the complexes prepared by the methods in Refs. 5 and 10 have a *cis* configuration, consistent with the prediction made on the basis of the infrared spectra. It is also confirmed that the isothiocyanato complex obtained in the present work has a *cis* configuration.

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