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Absorption Spectra of Geometrical Isomers of Hexacoordinated Complexes

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The application of the crystal field theory to complexes makes it possible to distinguish between geometrical isomers by a comparison of their absorption spectra. In order to test the theoretical treatment several cobalt(III) complexes of known structure were prepared and their spectra determined. The experimental results were generally found to be in good agreement with the theoretical predictions. Applying this method to α and β-tris(glycine)cobalt(III), it was possible to show that the α-form is the *trans* isomer.

Much of the apparent confusion in the literature with regard to an interpretation of the absorption spectra of *cis* and *trans* complexes of cobalt(III) and chromium(III) appears to have resulted from a failure to recognize the significance of the value of the molar extinction coefficient, ε. It has been shown [1–4] that "the transition group spectra" with an $\varepsilon \lesssim 10^2$ can be explained by applying the crystal field theory to the complex, while the "electron transfer bands" with $\varepsilon \gtrsim 10^3$ can be accounted for by means of Mulliken's LCAO methods [5].

On the basis of crystal field theory nothing can be said about the "third band" of Tsuchida [6] which is reported to occur in all *trans* complexes. The value of the molar extinction coefficient of this "third band" suggests that it is an electron transfer band. It would therefore appear to be accidental if such a band were only to be found in *trans* complexes [7]. On the other hand, all the "low" bands occurring in the visible and near ultraviolet region of the spectra of *cis* and *trans* complexes can be readily treated by means of the crystal field theory.

It is thus somewhat curious that some bands ($\varepsilon \lesssim 10^2$) can be treated as if the complex were "ionic", whereas other bands in the same complex require the assumption that the complex is "covalent" ($\varepsilon \gtrsim 10^3$). It would appear

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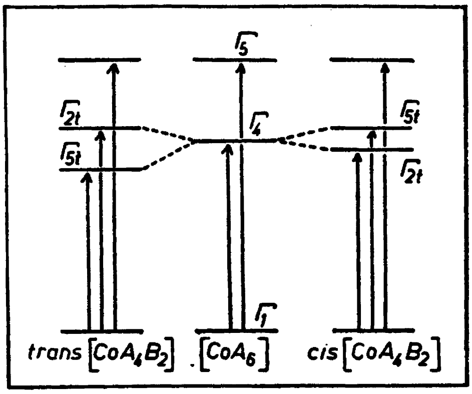

Fig. 1. Transitions responsible for the absorption bands of cobalt(III) complexes with cubic [CoA_6] and with tetragonal [CoA_4B_2] crystal fields.[3]

that such a difficulty arises from the fact that both points of view are merely approximations. Furthermore, it should be made clear that the considerations of the crystal-field theory do not support the distinction made between "ionic" and "covalent" complexes in terms of their magnetic susceptibilities [1]. The magnetic criterion as a guide to actual bond type in complexes is therefore somewhat limited.

Ballhausen and Klixbüll Jørgensen [3] have treated the *cis* and *trans* isomers of hexacoordinated complexes from the point of view of the crystal field. It was shown that if the absorption bands of a cubic complex [MA_6] were split up by superimposing a crystal field of lower symmetry upon the metal ion, then the splitting of a *trans* complex [MA_4B_2] would be twice the splitting of the same *cis* isomer. That this is approximately what has been observed can be seen from the spectra given by Linhard and Weigel [8] as well as from the curves in this paper.

The complexes investigated and discussed here are cobalt(III) complexes. This choice was made merely because several of these complexes of known structure can easily be prepared and their spectra determined. Orgel [4] has shown that the two absorption bands of luteo cobalt(III) complexes [CoA_6] are due to $\Gamma_1 \rightarrow \Gamma_4$ and $\Gamma_1 \rightarrow \Gamma_5$. Further that to a first approximation whenever the cubic crystal field of the luteo complex is altered to a tetragonal field only the first band is split (Fig. 1). These splittings are determined by the sum of the contributions along each axis. However, the splittings are apparent only when an appreciable difference exists between these contributions.

A qualitative estimate of this difference is furnished by the spectrochemical series originally developed by Fajans [9] and Tsuchida [6],

$$I^- < Br^- < Cl^- \lesssim OH^- < RCOO^- < NO_3^- < F^- \lesssim H_2O \lesssim SCN^- < NH_3 < en$$
$$\lesssim NO_2^- < o\text{-phen} << CN^-.$$

Orgel[4] has shown that if in a complex of the type CoA_4B_2, the substituent B is placed to the left of A in the above series, then for the split band of the *trans*

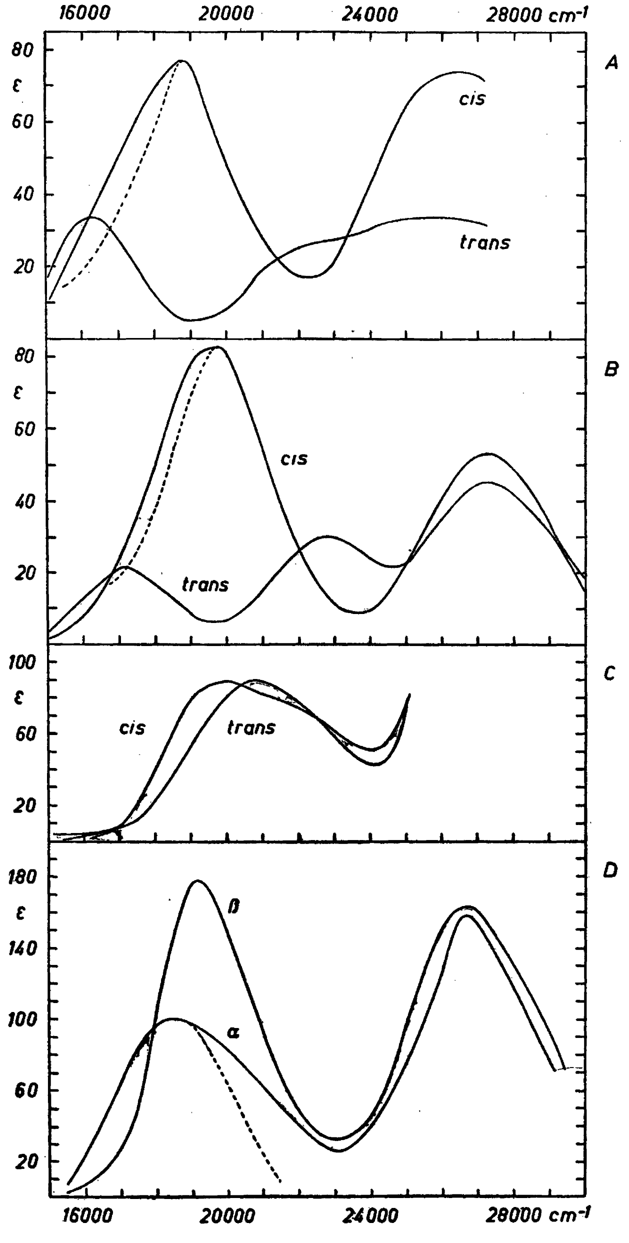

Fig. 2. Molar extinction coefficient ε vs *wavenumber in cm*$^{-1}$.

A: *cis*-[Co en$_2$Cl$_2$]Cl 0.02015 *M*
tr.-[Co en$_2$Cl$_2$]Cl 0.01672 *M*
B: *cis*-[Co en$_2$F$_2$]NO$_3$ 0.0177 *M*
tr.-[Co en$_2$F$_2$]NO$_3$ 0.0184 *M*

C: *cis*-[Co en$_2$(NO$_2$)Cl]Cl 0.01617 *M*
tr.-[Co en$_2$(NO$_2$)Cl]NO$_3$ 0.00771 *M*
D: α-[Co(NH$_2$CH$_2$COO)$_3$], 2H$_2$O 0.00188 *M*
β-[Co(NH$_2$CH$_2$COO)$_3$], H$_2$O 0.000511 *M*

complex the long wavelength component will be twice as intense as the short wavelength component. If B is placed to the right of A then it is the short wavelength component of the band which is going to be twice the long wavelength component. For a *cis* complex of this type, the reverse of the above arguments applies.

Further, it can be shown that when the complex under discussion has a center of symmetry as $[MA_6]$ and *trans*-$[MA_4B_2]$, the total area under the bands, which gives a measure of the intensity of the absorption, is smaller than if there is no center of symmetry (*cis*-$[MA_4B_2]$). It follows that the intensity of a *cis*-compound MA_4B_2 should be greater than that of the *trans* compound. For complexes in which neither geometrical isomer possesses a center of symmetry ($[MA_4BC]$ and $[MA_3B_3]$), both *cis* and *trans* compounds will have approximately the same area under the absorption curves. That this is the case can be seen in the plots shown in this paper.

EXPERIMENTAL

Preparation of compounds. The compounds investigated were prepared by methods described in the literature as previously reported [7].

The tris(glycine)cobalt(III) was prepared in two forms by Ley and Winkler [10]; a violet soluble form (α) with two molecules of water, and a red nearly insoluble form (β) with one water of crystallization. They are supposed to be *cis* and *trans* isomers of the type $[MA_3B_3]$, but it has not been definitely established as to which has the *cis* and which the *trans* structure.

The *cis* and *trans* isomers of $[Co\ en_2F_2]NO_3$ were kindly supplied by W. R. Matoush, who will soon publish the method of synthesis and properties of these complexes in the Journal of the American Chemical Society.

Measurements. All measurements were made with a Cary spectrophotometer using 1 cm corex cells, and 10 cm cells for the most dilute solutions. The solvent was water and dilute nitric acid solution in case of aquo complexes. The cobalt concentrations of the solutions were between $\sim 10^{-2}$ and $\sim 10^{-3}$ *M*. Measurements were made at room temperature and a total operation time of less than ten minutes was required, starting from the time the water was added to the solid salt. Only in the case of *trans*-$[Co\ en_2(NO_2)Cl]^+$, which aquates fairly rapidly [11], was it necessary to determine the spectrum at three different times and extrapolate back to zero time in order to get the spectrum of the chloro complex.

DISCUSSION OF RESULTS

Some examples which show that the absorption spectra found are in good agreement with the predictions, are given in Fig. 2. Plots A and B ($[Co\ en_2Cl_2]^+$ and $[Co\ en_2F_2]^+$, respectively) demonstrate (1) that the displacements of the bands follow the spectrochemical series, and (2) that the splitting of *trans* isomers of this type is approximately twice that for the same *cis* isomer. It is further observed (3) that the areas under the curves are less for the *trans* isomers, which have a center of symmetry, than for the same *cis* isomers which do not have this property.

Considering that F^- and H_2O are very close together in the spectrochemical series, it was expected that the spectra of the diaquo complexes should resemble the spectra of the difluoro complexes. That this is the case has been demonstrated by Bjerrum and Rasmussen [12]. On the other hand we cannot understand why the first band of the hydroxo complexes [12] does not show any splittings.

Plot C gives the absorption spectra for isomers of the type [MA_4BC]. The available data show that too much emphasis must not be placed on the "absolute" positions of the ligands in the spectrochemical series in complexes with increasing number of different ligands. For the complex considered [Co $en_2(NO_2)Cl]^+$, a splitting of the band is observed with the *cis*, but not with the *trans* isomer. According to the theory the splitting is determined by differences in the sum of the crystal field contributions along each axis [3].

Because of the fact that the contribution of the chloride ion is much less than that of $\frac{1}{2}$en and NO_2^- the configuration of the *cis* isomer is approximately tetragonal. Since in the *trans* isomer the tetragonal axis is more similar to the other axis than in the *cis* isomer, splitting should be expected to occur in the *cis* rather than in the *trans* complex.

Since neither of these isomers has a center of symmetry, the areas under their curves are approximately equal.

Geometrical isomers of [Co $en_2(NO_2)_2]^+$, [Co $en_2(NCS)_2]^+$, [Co $en_2NO_2NCS]^+$ and [Co $en_2(H_2O)NO_2]^{++}$ were also investigated. Neither the *cis* nor the *trans* isomers of the dinitro, dithiocyanato or the nitrothiocyanato complexes showed any splitting. This is attributed to the fact that these ligands are not too "different", therefore the sum of the contributions along each axis in the complexes are approximately the same. However, the absorption spectrum of *cis*-[Co $en_2(H_2O)NO_2]^{++}$ shows a slight splitting contrary to that of the *trans* isomer; these results are similar to the chloronitro complex.

Finally on the basis of the curves in Fig. 2 D, it is believed that the *trans* configuration can be assigned to the α-tris(glycine)cobalt(III) complex. The absorption band of this isomer is clearly split in accord with a rhombic crystal field, whereas that for the β-form is not split as expected for a cubic crystal field.

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