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Metal Complexes of EDTA and Its Related Compounds. I. Geometric Isomers of [Co(X)(*N*-methyl-trimethylenediamine-*N*, *N'*, *N'*-triacetate)] Complexes with X=H_2O, NH_3, Cl^- or CN^-

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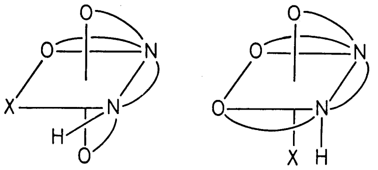
Two isomers of the complexes of the type, [Co(X)(*N*-Me-trdtra)] (*N*-Me-trdtra=*N*-methyl-trimethylenediamine-*N*,*N'*,*N'*-triacetate) have been isolated for each X=H_2O, NH_3, and Cl^-. The structures have been assigned from their PMR and absorption spectra and from the results of kinetic studies. The isomers have equatorial-skew and polar-chair structures and no indication of the formation of polar-skew isomer was observed. Isomerization reaction of the aqua complex in an aqueous solution indicated that the polar-chair isomer is more stable than the equatorial-skew isomer. Only the polar-chair isomer of H[Co(CN)(*N*-Me-trdtra)] has been obtained.

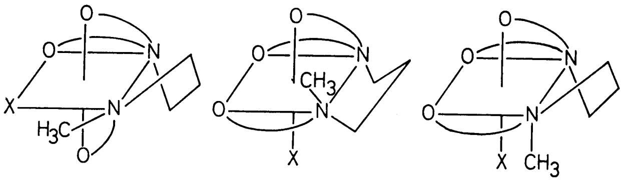
When a quinquedentate ligand such as ethylenediaminetriacetate ($edtra^{3-}$) forms a cobalt(III) complex together with a unidentate ligand, there are two possible geometric isomers as shown in Fig. 1. A similar situation arises in ethylenediaminetetraacetate ($edta^{4-}$) complexes when one acetate group remains uncoordinated. Recent PMR studies,[1] however, have disclosed that all these complexes exist only in the equatorial form. Most recently Bell and Blackmer[2] confirmed this form for K[Co(NO_2)(edtra)]·1.5H_2O by the X-ray analysis. The acetate arm in the plane involving the two amino nitrogen atoms seems to be more strained as compared with that axial to the plane; the Co–O bond length in the plane is 1.919 Å, while that out of the plane, 1.883 Å. A similar difference in the Co–O bond lengths was found in $[Co(edta)]^-$.[3] The differences in the Co–O bond lengths in these complexes may be closely related to the conformation of the ethylenediamine moiety and the valence bond angles of the amino nitrogen atoms. It is, therefore, interesting to examine the geometrical isomerism in cobalt(III) complexes of trimethylenediaminetriacetate, since the trimethylenediamine moiety forms a six-membered chelate ring with conformations different from those of the ethylenediamine moiety of $edtra^{3-}$ ligand.



equatorial isomer polar isomer

Fig. 1. Two geometric isomers of [Co(X)(edtra)].

As a first step of studying such an isomerism, we have attempted to prepare cobalt(III) complexes of *N*-methyl-trimethylenediamine-*N*,*N'*,*N'*-triacetate, [Co(X)(*N*-Me-trdtra)] (X=unidentate ligand). The complexes of this type have three possible geometric isomers as shown in Fig. 2. They are designated as equatorial-skew, polar-skew or polar-chair, depending on the position of the unidentate ligand and on the conformation of the six-membered trimethylenediamine chelate. Other forms involving equatorial-chair or boat conformations of the diamine may not be yielded owing to steric conditions.[4] In the present study, we have obtained two geometric isomers for each [Co(X)(*N*-Me-trdtra)] (X=H_2O, NH_3, and Cl^-) and one isomer of $[Co(CN)(N\text{-Me-trdtra})]^-$. This paper deals with the preparation and isolation of these complexes and their geometric structures as determined by PMR and ultraviolet absorption spectroscopy. A kinetic study of the isomerization reaction of [Co(H_2O)(*N*-Me-trdtra)] has also been carried out to give support to the assignment of structures.



equatorial-skew polar-chair polar-skew

Fig. 2. Three geometric isomers of [Co(X)(*N*-Me-trdtra)].

Experimental

Preparation of sodium N-*methyl-trimethylenediamine*-N,N',N'-*triacetate* (Na_3N-*Me-trdtra*). Na_3*N*-Me-trdtra was prepared by a method similar to that for *N*-methyl-ethylenediamine-*N*,*N'*,*N'*-triacetate by Van Saun and Douglas.[5] To a cold solution of monochloroacetic acid (37.8 g) in water (100 ml) was added dropwise a cold solution of sodium hydroxide (28 g) in water (70 ml) with steady stirring to keep temperature of the reacting solution below 15 °C. *N*-Methyl-trimethylenediamine (8.8 g) (Tokyo Kasei Co.) was then added. The solution was heated at 80 °C for 40 min, concentrated under reduced pressure at 70 °C and filtered to remove sodium chloride. The filtrate was used directly for the preparation of each cobalt(III) complex without isolating the free ligand. This procedure was justified by analyses of the complexes obtained.

Preparation of Complexes. [*Co*(H_2O)(N-*Me-trdtra*)]·H_2O. An aqueous solution (50 ml) of $Co(NO_3)_2\cdot 6H_2O$ (29.1 g) was added to the previously prepared *N*-Me-trdtra solution which had been diluted to 500 ml and acidified to pH 6 with conc. hydrochloric acid. Activated charcoal (5 g) and 30% hydrogen peroxide (6 ml) were added and a stream of air was

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bubbled through the mixture for 3 days to complete the oxidation of the cobalt(II). After removal of the charcoal, the solution was diluted to about 20 l and the pH adjusted to about 5 with conc. hydrochloric acid. The solution was passed through a column of Dowex 50 WX8 cation exchange resin in H^+ form (700 ml) and then through a column of Dowex 1X8 anion exchange resin in Cl^- form (700 ml) to remove electrolytes and to obtain hydrochloric acid solution of the chargeless complex $[Co(H_2O)(N\text{-Me-trdtra})]$. The blue violet solution was evaporated to almost dryness under reduced pressure at 50 °C. The residue was again dissolved in 100 ml of water and treated with silver oxide to remove chloride ions. The product was filtered, evaporated to a small volume, and poured carefully on a column ($\phi 3 \times 60$ cm) of Dowex 50 WX8 cation exchange resin in H^+ form. Elution with water gave two separate bands, blue and violet, the former being eluted faster. Blue and violet crystals were obtained by evaporating each eluate to dryness under reduced pressure below 40 °C. The blue complex was highly soluble, but the violet one moderately soluble in water. The latter gave higher yield than the former.

Found: Blue complex, C, 33.43; H, 5.38; N, 7.67%. Violet complex, C, 33.51; H, 5.34; N, 7.95%. Calcd for $[Co(H_2O)(N\text{-Me-trdtra})]\cdot H_2O$, $(C_{10}H_{19}N_2O_8Co)$: C, 33.91; H, 5.41; N, 7.91%.

$[Co(NH_3)(N\text{-Me-trdtra})]\cdot 2H_2O$. Violet and red isomers of the complex were obtained by the same method as that for the aqua complexes except that 28% aqueous ammonia (100 ml) was added to the solution containing cobalt(II) ions and the ligand. On the separation of two isomers by column chromatography (column, $\phi 3 \times 60$ cm), the violet isomer was eluted faster and followed by the red isomer. The former was much more soluble in water than the latter.

Found: Violet complex, C, 32.35; H, 5.71; N, 10.95%. Red complex, C, 32.81; H, 5.80; N, 11.40%. Calcd for $[Co(NH_3)(N\text{-Me-trdtra})]\cdot 2H_2O$, $(C_{10}H_{22}N_3O_8Co)$: C, 32.35; H, 5.97; N, 11.32%.

$H[Co(Cl)(N\text{-Me-trdtra})]\cdot nH_2O$. Greenish blue and bluish green isomers of the complex were prepared from the blue and the violet aqua complex, respectively, by treating with hydrochloric acid. A solution of each aqua complex in a small amount of conc. hydrochloric acid was warmed at 50 °C for 1 hr, and then evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of water and poured on a column of Dowex 1X8 anion exchange resin in Cl^- form. The column was washed with water, and eluted with 0.5 M hydrochloric acid. The eluate was evaporated to a small volume under reduced pressure and stored in a vacuum desiccator over phosphorus pentoxide and sodium hydroxide. Both chloro complexes were very soluble in water.

Found: Greenish blue complex, C, 29.79; H, 5.65; N, 6.32%. Calcd for $H[Co(Cl)(N\text{-Me-trdtra})]\cdot 3H_2O$, $(C_{10}H_{22}N_2O_9ClCo)$: C, 29.39; H, 5.43; N, 6.86%.

Found: Bluish green complex, C, 30.60; H, 4.72; N, 6.77%. Calcd for $H[Co(Cl)(N\text{-Me-trdtra})]\cdot 2H_2O$, $(C_{10}H_{20}N_2O_8ClCo)$: C, 30.74; H, 5.16; N, 7.17%.

$H[Co(CN)(N\text{-Me-trdtra})]\cdot 2H_2O$. A dimethylsulfoxide (DMSO) (30 ml) solution containing the violet aqua complex (1×10^{-3} mol) and potassium cyanide (1.5×10^{-3} mol) was warmed at 70 °C for 3 hr. The solution was passed through a column of Dowex 1X8 anion exchange resin in Cl^- form. The column was washed with water and the adsorbed red band was eluted with 0.3 M hydrochloric acid. Red crystals were obtained by evaporating the eluate under reduced pressure. The same cyano complex was obtained by the reaction of the blue aqua complex with potassium cyanide.

Found: C, 34.59; H, 5.17; N, 10.58%. Calcd for $H[Co(CN)(N\text{-Me-trdtra})]\cdot 2H_2O$, $(C_{11}H_{20}N_3O_8Co)$: C, 34.65; H, 5.29; N, 11.02%.

Measurements. Visible and ultraviolet absorption spectra were recorded with a Hitachi 323 recording spectrophotometer. PMR spectra were recorded with Varian A-60 and Varian HA-100 spectrometers in a deuterium oxide solution containing sodium 3-(trimethylsilyl)-1-propanesulfonate (TMS*) as the internal standard. All the measurements were made at room temperature.

Results and Discussion

Blue and violet complexes which gave correct analytical values as $[Co(H_2O)(N\text{-Me-trdtra})]\cdot H_2O$ were obtained as shown in the Experimental part. Since each complex was confirmed to consist of a single species as described later, these complexes will be two of the three possible geometric isomers shown in Fig. 2. As Fig. 3 and Table 1 show, their absorption spectra differ notably from each other in the first absorption band region. However, no structural assignment can be made from the spectra at present, because both complexes belong to the same *cis*-$[CoN_2O_4]$ type. On the other hand, the spectrum of the violet isomer in an aqueous solution was found to change on heating. Figure 4 shows an example of such spectral changes. Two isosbestic points are observed at 520 and 468 nm. Spectrum E in the figure agrees satisfactorily with that of the blue isomer. The spectrum of the blue isomer in water remained unchanged over a prolonged heating of the aqueous solution. These results indicate that the violet isomer isomerizes to the blue isomer and that the reverse reaction can be neglected. The isomerization between the equatorial-skew and the polar-chair isomer will occur by interchanging the coordination sites of one acetate arm and the aqua ligand. On

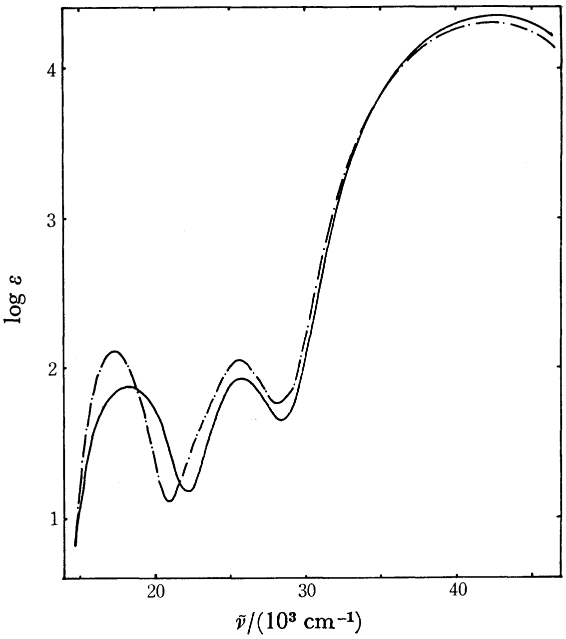

Fig. 3. Absorption spectra of violet (equatorial-skew) (——) and blue (polar-chair) (—·—) isomers of $[Co(H_2O)(N\text{-Me-trdtra})]$ in water.

TABLE 1. ABSORPTION DATA OF [Co(X)(*N*-Me-trdtra)] COMPLEXES $\tilde{\nu}/10^3\ \mathrm{cm}^{-1}$ (log ε)

equatorial-skew isomer			
[Co(H_2O)(*N*-Me-trdtra)]·H_2O(violet)	18.27(1.85)	25.81(1.90)	42.56(4.34)
[Co(NH_3)(*N*-Me-trdtra)]·2H_2O(violet)	18.27(1.98)	26.30(2.12)	42.74(4.30)
H[Co(Cl)(*N*-Me-trdtra)]·2H_2O (bluish green)	18.27(1.71) 16.29sh(1.85)	24.51(1.90)	40.83(4.27)
polar-chair isomer			
[Co(H_2O)(*N*-Me-trdtra)]·H_2O(blue)	17.39(2.11)	25.64(2.04)	42.40(4.28)
[Co(NH_3)(*N*-Me-trdtra)]·2H_2O(red)	18.80(2.02)	26.46(1.97)	43.10(4.37)
H[Co(Cl)(*N*-Me-trdtra)]·3H_2O(greenish blue)	16.78(2.04)	24.88(2.01)	41.67(4.25)
H[Co(CN)(*N*-Me-trdtra)]·2H_2O(red)	20.16(2.07)	27.33(1.90)	42.56(4.29)

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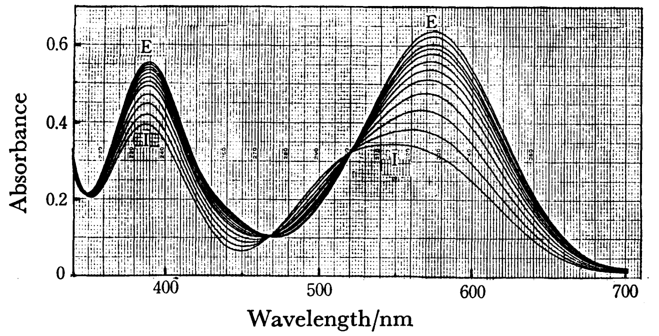

Fig. 4. Spectral change of violet-[Co(H_2O)(*N*-Me-trdtra)] in aqueous solution at 70 °C, pH=1.22 ($HClO_4$) and I=0.10 ($NaClO_4$–$HClO_4$). (I); t=0, (E); $t=\infty$.

the other hand, the isomerization reactions between the equatorial-skew and the polar-skew, and between the polar-chair and the polar-skew isomer will require less feasible change; *i.e.* interchange between the coordination sites of two acetate arms, or the inversion of configuration of the methyl and the acetate groups at the nitrogen atom. The first isomerization would take place more easily than do those of the latter two. Thus, the spectral changes described above may correspond to the isomerization reaction of the equatorial-skew into the polar-chair isomer or *vice versa* and the two isolated isomers can be concluded to have the equatorial-skew and the polar-chair structure.

Kinetic investigation for the isomerization reaction was carried out at an ionic strength (I) of 0.10 ($NaClO_4$–$HClO_4$). The reaction rate was independent of the hydrogen ion concentration over the range from 7×10^{-3} to 0.1 M. The acid independent rate constant was $2.08\times10^{-4}\ \mathrm{s}^{-1}$ at 70 °C, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were 35.0 kcal/mol and +26.5 e.u., respectively.

In order to determine which isomer corresponds to the equatorial-skew or the polar-chair, we have utilized PMR spectroscopy in D_2O. The 100 MHz PMR spectrum of the blue isomer exhibits three AB patterns due to the acetate protons with coupling constants, 16.0, 16.2, and 19.0 Hz (Fig. 5 and Table 2). The grouping of these AB patterns was confirmed by comparison with the spectrum in 60 MHz. In [Co(edta)]$^-$ and its related complexes, it is known that the magnitude of the geminal coupling constant for the in-plane acetate protons is about 16 Hz, while that for the out-of-plane acetate protons about 18 Hz.[1] Therefore, the blue isomer should have two in-plane and one out-of-plane acetate arms and can be assigned to the polar-chair structure. The violet isomer, on the other hand, shows PMR signals corresponding to two out-of-plane acetate arms (J=17.5 and 18.5 Hz) and one in-plane acetate arm (J=16.5 Hz) as shown in Fig. 5 and Table 2, and thus, the violet isomer is assigned to the equatorial-skew structure in agreement with the previous discussion.

Two isomers, violet and red [Co(NH_3)(*N*-Me-trdtra)]·2H_2O were obtained similarly in the present study. Although neither of them isomerized without decomposition under a condition similar to that for the aqua complex, they could be assigned to the equatorial-skew and the polar-chair isomers as in the case of the aqua complexes. Figure 6 shows the absorption

TABLE 2. CHEMICAL SHIFTS (ν_A, ν_B in ppm) AND COUPLING CONSTANTS (J_{AB} IN Hz) FOR ACETATE PROTONS OF [Co(X)(*N*-Me-trdtra)] IN D_2O (100 MHz)

	out-of-plane			in-plane		
	J_{AB}	ν_A	ν_B	J_{AB}	ν_A	ν_B
equatorial-skew isomer						
[Co(H_2O)(*N*-Me-trdtra)]·H_2O(violet)	18.5	4.26	3.59	16.5	4.27	3.26
	17.5	4.07	3.71			
[Co(NH_3)(*N*-Me-trdtra)]·2H_2O(violet)	17.5	3.68	3.35	16.0	3.99	3.67
	19.0	4.00	3.72			
polar-chair isomer						
[Co(H_2O)(*N*-Me-trdtra)]·H_2O(blue)	19.0	3.67		16.0	3.87	3.09
				16.2	3.87	3.37
H[Co(CN)(*N*-Me-trdtra)]·2H_2O(red)	18.5	4.12	3.35	16.0	3.77	3.49
				16.5	3.88	3.16

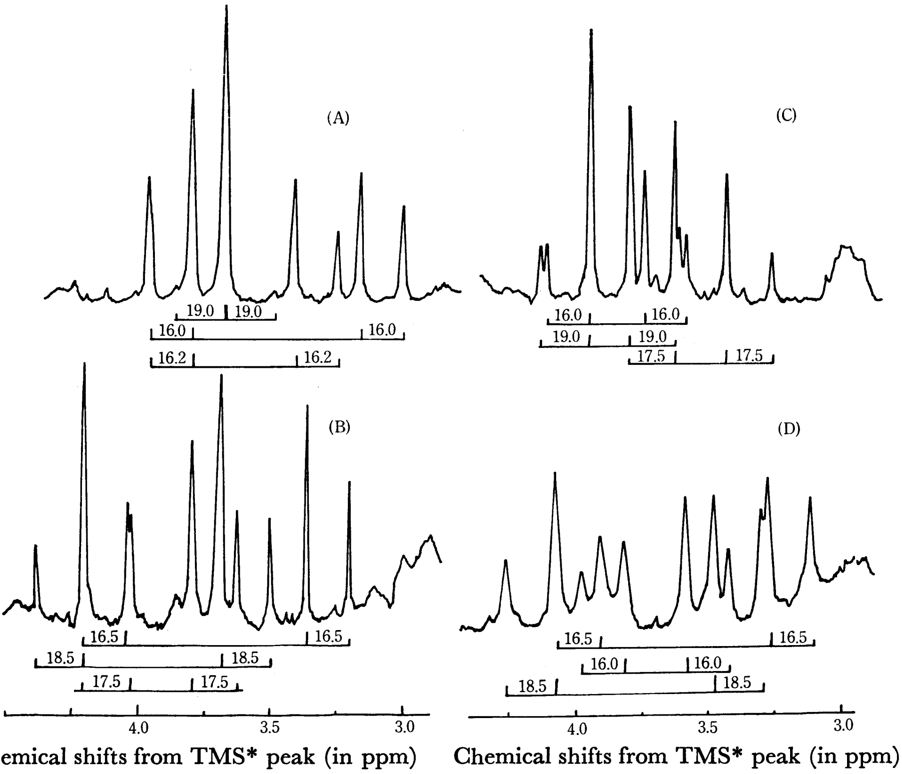

Fig. 5. PMR spectra (100 MHz) of blue (polar-chair) [Co(H_2O)(*N*-Me-trdtra)] (A), violet (equatorial-skew) [Co(H_2O)(*N*-Me-trdtra)] (B), violet (equatorial-skew) [Co(NH_3)(*N*-Me-trdtra)] (C), and [Co(CN)(*N*-Me-trdtra)] (D) in D_2O. Numerical values given in the figure indicate coupling constants in Hz for acetate protons.

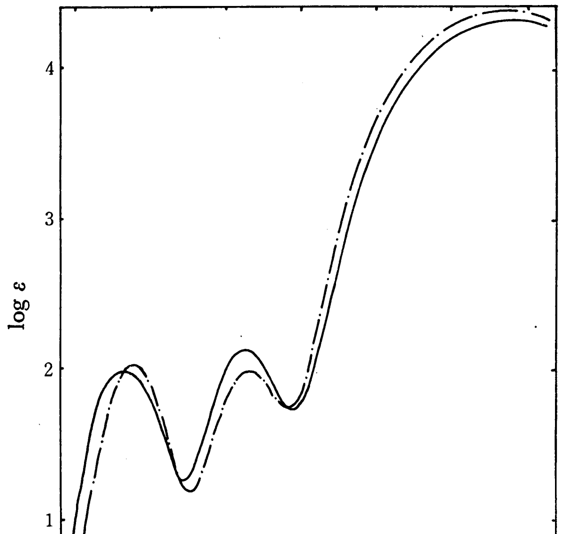

Fig. 6. Absorption spectra of violet (equatorial-skew) (——) and red (polar-chair) (-·-·-) isomers of [Co(NH_3)(*N*-Me-trdtra)] in water.

spectra of these ammine complexes. The first absorption band of the red isomer is narrower than that of the violet isomer. The polar-chair and the equatorial-skew [Co(NH_3)(*N*-Me-trdtra)] belong to *fac*- and *mer*-[CoN_3O_3] type, respectively, with respect to the configuration of the nitrogen and the oxygen atoms around the metal ion. A *fac*-[CoN_3O_3] complex exhibits a narrow and symmetrical first absorption band as compared with a *mer*-[CoN_3O_3] complexes.[6] Therefore, the red and the violet isomer may be assigned to *fac*-(polar-chair) and *mer*-(equatorial-skew) structure, respectively. This assignment will be supported by the PMR spectra. The PMR spectrum of the highly soluble violet isomer shows three AB patterns with coupling constants, 16.0, 17.5, and 19.0 Hz (Fig. 5 and Table 2). The AB pattern with 16.0 Hz is attributed to the in-plane acetate protons and those with 17.5 and 19.0 Hz to the out-of-plane acetate protons. Thus, the violet isomer is assigned safely to the equatorial-skew structure in agreement with the conclusion obtained from the absorption spectra. The red isomer was not soluble enough in D_2O to obtain PMR spectrum.

Greenish blue and bluish green isomers of H[Co(Cl)(*N*-Me-trdtra)] have been obtained from the blue and the violet aqua complex, respectively, by warming with hydrochloric acid. The reactions should proceed without isomerization under the given condition, since each chloro complex liberates the chloride ion gradually in a neutral aqueous solution to give the corresponding original aqua complex. Therefore, the greenish blue and bluish green isomer are assigned to the polar-chair and the equatorial-skew structure, respectively. This assignment will be supported by the fact that the shape of the first absorption band of the greenish blue isomer is very similar to that of [Co(Cl)(*R*,*S*-2,4-

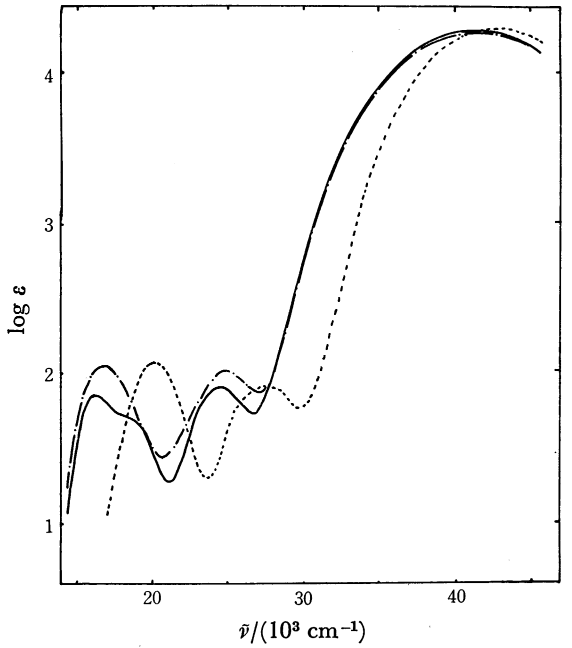

Fig. 7. Absorption spectra of bluish green (equatorial-skew) (——) and greenish blue (polar-chair) (—·—) isomers of [Co(Cl)(*N*-Me-trdtra)]$^-$ in 0.1 M HCl and [Co(CN)(*N*-Me-trdtra)]$^-$ (-----) in water.

ptnta)]$^-$ (*R*,*S*-2,4-ptnta=*R*,*S*-2,4-pentanediaminetetraacetate ion) which takes the polar-chair structure stereospecifically.[4] These polar-chair complexes do not show any splitting in the first absorption band in contrast to the distinct splitting observed for the bluish green, equatorial-skew isomer (Fig. 7). There seems to be a relation between the absorption spectra and the structure of the *N*-Me-trdtra complexes as discussed later.

Only one red complex, H[Co(CN)(*N*-Me-trdtra)]·2H_2O was obtained by the reaction of the violet and the blue aqua complex with potassium cyanide in DMSO. Its PMR spectrum shows three AB patterns due to the acetate protons. The coupling constants are 16.0, 16.5, and 18.5 Hz, and the complex may be assigned to the polar-chair structure (Fig. 5 and Table 2). The complex shows a sharp and symmetrical first absorption band, being identified as the polar-chair structure (Fig. 7). The polar-skew isomer is not likely to be yielded by analogy with other *N*-Me-trdtra complexes.

For each aqua, ammine and chloro complex, no indication for the presence of more than two isomers was found in the present syntheses. The reason why the polar-skew isomers are not produced is not clear at present. The methyl group in the polar-skew structure takes an axial orientation to the chelate ring formed by the diamine moiety in a skew conformation, while that in the equatorial-skew structure an equatorial orientation to the same ring. However, such a difference will not be important in the present complexes, becasue the polar-chair isomer has an axially oriented methyl group to the diamine chelate ring. Further, the equatorial-skew isomer of [Co(H_2O)(*N*-Me-trdtra)] (violet) isomerizes in water into the polar-chair isomer (blue) by heating, and the reverse reaction does not take place under the same condition. This indicates that the polar-chair isomer is more stable thermodynamically than the equatorial-skew isomer. As stated in the Experimental part, the fact that the latter is produced much more than the former, may owe to a kinetically prefered route to form the equatorial-skew isomer favorably. The absence of the polar-skew isomer may also be related to such a prefered route in the complex formation. On the other hand, it should be noted that in the skew isomers the in-plane acetate arm seems to be still more strained than the out-of-plane acetate arm as seen in the [Co(edta)]$^-$ and [Co(X)(edtra)] (*vide ante*). It was deduced that the six-membered diamine chelate ring in K[Co(trdta)]·2H_2O (trdta=trimethylenediamine-tetraacetate ion) takes a skew conformation.[7] According to the X-ray analysis, the Co–O distances in the plane and axial to the plane are 1.904 and 1.861 Å, respectively.[8] The difference in these two bond distances is smaller than that reported for [Co(edta)]$^-$ (1.912 and 1.833 Å), but it may still be big enough to prevent the formation of the polar-skew isomer.

The absorption spectra of all the complexes we prepared are shown in Figs. 3, 6, and 7. The maximum frequencies of the first and the second absorption bands depend on the kind of the unidentate ligand, and shift in accordance with the spectrochemical series.[9] On the other hand, the first absorption bands of the equatorial-skew isomers are broader than those of the polar-chair isomers. The equatorial-skew isomer of the chloro complex shows the first absorption band split apparently into two components. The origin of the difference in the band shape between the two geometric isomers is not clear at present. Yamatera's theory[6] on the band splitting for a cobalt(III) complex will not be applicable to the present complexes. The first absorption bands of both isomers of the aqua complex differ considerably from each other, although the isomers belong to the same *cis*-[CoN_2O_4] configuration, as stated previously.

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