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Metal Complexes of EDTA and Its Related Compounds. II.[1)] Geometric Isomers of [Co(X)(trimethylenediamine-*N*,*N*,*N*′-triacetate)] Complexes with X=H_2O, NH_3, Cl^-, and CN^-

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Three geometric isomers, equatorial-skew, polar-chair and polar-skew, of [Co(X)(trdtra)] ($trdtra^{3-}$=trimethylenediamine-*N*,*N*,*N*′-triacetate) have been prepared for each X=H_2O, NH_3 and Cl^-, and the structures assigned mainly by comparing their electronic spectra with those of the equatorial-skew and the polar-chair isomers of *N*-methyl-trdtra complexes reported previously. The cyano complex gives only the polar-chair isomer.

Cobalt(III) complexes containing a quinquedentate trimethylenediamine-*N*,*N*,*N*′-triacetate($trdtra^{3-}$) or its *N*-substituted derivatives can have three probable geometric isomers as shown in Fig. 1.1) Of these, the equatorial-skew and the polar-chair isomers were found for aqua, ammine and chloro complexes of *N*-methyl-trimethylenediamine-*N*,*N*′,*N*′-triacetate(*N*-Me-$trdtra^{3-}$).1) In the present study, all the three isomers have been obtained for the aqua, ammine and chloro complexes with trdtra in place of *N*-Me-trdtra.

Experimental

*Preparation of Sodium Trimethylenediamine-*N,N,N′*-triacetate (Na_3trdtra).* This ligand was prepared by a method similar to that for Na_3*N*-Me-trdtra.1) An aqueous solution containing 0.3 mol of chloroacetic acid, 0.1 mol of trimethylenediamine and 0.7 mol of sodium hydroxide was heated at 80 °C for 40 min, concentrated under a reduced pressure at 70 °C and filtered to remove sodium chloride. The filtrate was used for the preparation of cobalt(III) complexes without isolating the free ligand.

Preparation of Complexes. [Co(H_2O)(trdtra)]: The aqua complex was prepared from cobalt(II) nitrate and the aqueous Na_3trdtra solution and separated into geometric isomers by a method similar to that for [Co(H_2O)(*N*-Me-trdtra)]·H_2O.1) On the separation of three isomers by column chromatography, the order of elution was bluish violet(polar-chair), reddish violet(polar-skew) and violet(equatorial-skew) isomer. Each eluate was evaporated to dryness under a reduced pressure below 40 °C. Pure isomers were obtained by dissolving the residues in a small amount of water and by adding ethanol. The solubility in water increases in the order of the bluish violet, the reddish violet and the violet isomer. Total yield of the three isomers based on trimethylenediamine was about 20% and the ratio of the bluish violet, the reddish violet and the violet isomer was 1 : 1 : 8.

[(Co(NH_3)(trdra)]: Violet(equatorial-skew), reddish violet(polar-skew) and red(polar-chair) isomers of the complex were obtained by a similar method to that for [Co(NH_3)(*N*-Me-trdra]·$2H_2O$.1) The isomers were eluted from the column in the order given above. The solubility in water increases in the order of the red, the reddish violet and the violet isomer.

H[(Co(Cl)(trdra)]: The violet(equatorial-skew), reddish violet(polar-skew) and bluish violet(polar-chair) isomers of [Co(H_2O)(trdtra)] were converted to bluish green(A)(equatorial-skew), bluish green(B)(polar-skew) and greenish blue (polar-chair) isomers, respectively, by a method similar to that for H[Co(Cl)(*N*-Me-trdtra)].1) The greenish blue isomer includes one mole of crystalline ethanol which can hardly be removed by usual methods.

H[Co(CN)(trdra)]·$2H_2O$: The complex was prepared from the violet aqua complex by a method similar to that for H[Co(CN)(*N*-Me-trdtra)]·$2H_2O$.1) The reactions with the other isomers of aqua complex gave also the same red cyano complex(polar-chair).

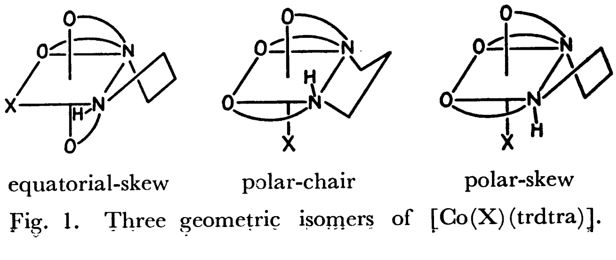
The analytical data for the complexes prepared in this work are summarized in Table 1.

Measurements. Visible and ultraviolet absorption spectra were recorded on a Hitachi 323 recording spectrophotometer. PMR spectra were obtained on a Varian HA-100 spectrometer in a D_2O solution containing sodium 3-trimethylsilyl-1-propanesulfonate(TMS*) as the internal standard. All the measurements were made at room temperature.

Results and Discussion

Figure 1 shows three geometric isomers of the complex [Co(X)(trdtra)]. This complex could have further possible geometric isomers than the three. They have two acetate groups on the tertiary nitrogen coordinated *trans* to each other. Such a form was found in [Co(NO_2)((*R*)-pdtra)]$^-$ 2) ((*R*)-pdtra=(*R*)-1,2-propanediaminetriacetate) and [Co(en)((*R*)-H_2pdta)]$^+$ 3) (en = ethylenediamine, (*R*)-pdta = *R*-1,2-propanediaminetetraacetate). However, this form is expected to be stable only for complexes of diamine-tri- or -tetraacetate with bulky groups on carbon atoms of the diamine moiety.2) In fact, no indication for the presence of more than three isomers was found in the present syntheses of trdtra complexes. Thus, the three isomers for each aqua, ammine and chloro trdtra complex obtained here may have all the *cis* form in which two acetate groups on the tertiary nitrogen are coordinated *cis* to each other as shown in Fig. 1.

Both violet and bluish violet isomers of the aqua complex isomerize to each other in an acid aqueous



equatorial-skew polar-chair polar-skew

Fig. 1. Three geometric isomers of [Co(X)(trdtra)].

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Table 1. Summary of analytical data for the complexes prepared in this work

Complex	C/%		H/%		N/%	
	Calcd	Found	Calcd	Found	Calcd	Found
Equatorial-skew isomer						
$[Co(H_2O)(trdtra)]\cdot 2H_2O$ (violet)	30.18	30.50	5.35	5.32	7.82	7.87
$[Co(NH_3)(trdtra)]$ (violet)	33.65	33.91	5.02	5.06	13.09	12.98
$H[Co(Cl)(trdtra)]\cdot 3H_2O$ (bluish green(A))	27.39	27.06	5.11	4.61	7.10	7.10
Polar-chair isomer						
$[Co(H_2O)(trdtra)]\cdot H_2O$ (bluish violet)	31.77	31.82	5.04	5.36	8.24	7.89
$[Co(NH_3)(trdtra)]$ (red)	33.65	33.35	5.02	5.00	13.09	12.94
$H[Co(Cl)(trdtra)]\cdot C_2H_5OH\cdot H_2O$ (greenish blue)	32.64	32.47	5.48	5.28	6.92	7.13
$H[Co(CN)(trdtra)]\cdot 2H_2O$ (red)	32.71	33.09	4.94	4.95	11.45	11.64
Polar-skew isomer						
$[Co(H_2O)(trdtra)]\cdot 2H_2O$ (reddish violet)	30.18	29.97	5.35	5.37	7.82	8.02
$[Co(NH_3)(trdtra)]\cdot 2H_2O$ (reddish violet)	30.26	30.82	5.64	5.49	11.77	11.30
$H[Co(Cl)(trdtra)]\cdot 3H_2O$ (bluish green(B))	27.39	27.53	5.11	4.78	7.10	7.55

Table 2. Visible and ultraviolet absorption data of $[Co(X)(trdtra)]$ complexes, $\tilde{\nu}/10^3\ cm^{-1}(\log \varepsilon)$

Equatorial-skew isomer			
$[Co(H_2O)(trdtra)]\cdot 2H_2O$ (violet)	19.53(1.82) 17.70 sh(1.80)	26.32(1.88)	43.86(4.30)
$[Co(NH_3)(trdtra)]$ (violet)	18.18(2.03)	26.82(2.19)	44.64(4.37)
$H[Co(Cl)(trdtra)]\cdot 3H_2O$ (bluish green)	19.31(1.75) 16.18 sh(1.92)	25.26(1.94)	40.81(4.30)
Polar-chair isomer			
$[Co(H_2O)(trdtra)]\cdot H_2O$ (bluish violet)	18.02(2.02)	26.18(2.02)	43.86(4.26)
$[Co(NH_3)(trdtra)]$ (red)	19.23(2.08)	27.40(1.93)	44.25(4.34)
$H[Co(Cl)(trdtra)]\cdot C_2H_5OH\cdot H_2O$ (greenish blue)	17.18(2.03)	25.12(2.06)	41.67(4.29)
$H[Co(CN)(trdtra)]\cdot 2H_2O$ (red)	20.41(2.15)	28.41(1.97)	43.64(4.33)
Polar-skew isomer			
$[Co(H_2O)(trdtra)]\cdot 2H_2O$ (reddish violet)	18.52(1.91)	26.46(2.01)	44.25(4.27)
$[Co(NH_3)(trdtra)]\cdot 2H_2O$ (reddish violet)	18.58(2.01)	26.98(2.16)	44.25(4.38)
$H[Co(Cl)(trdtra)]\cdot 3H_2O$ (bluish green)	17.12(1.93)	25.44(2.03)	41.32(4.30)

sh: shoulder band.

solution on warming. The equilibrium constant between the two isomers was 0.12 at 63 °C and pH 3, the violet isomer being predominant. On the other hand, the reddish violet isomer shows no spectral change under a similar condition. We reported that the isomerization between the equatorial-skew and the polar-chair isomer takes place more easily than do those between the polar-skew and the other two isomers.[1] Therefore, the violet and the bluish violet isomer can be assigned to either the equatorial-skew or the polar-chair, and the reddish violet isomer to the polar-skew. The assignment for the first two isomers was made by comparing the absorption spectra with those of the corresponding *N*-Me-trdtra complexes. As Fig. 2 and the Table 2 show, the bluish violet isomer exhibits a sharp first absorption band at longer wave length and an intense second absorption band as compared with those of the violet isomer. Such spectral differences resemble those between the two isomers of the aqua *N*-Me-trdtra complex, and the bluish violet isomer can be assigned to the polar-chair, and the violet isomer to the equatorial-skew.

Tanaka *et al.*[4] obtained the violet isomer by thermal decomposition of $K[Co(trdta)]\cdot 2H_2O$ ($trdta^{4-}$=trimethylenediaminetetraacetate) at 250 °C, but they did not describe its structure.

The absorption spectra of three isomers of the ammine complex are shown in Fig. 2. The equatorial and the polar structure correspond to *mer*- and *fac*-$[CoN_3O_3]$ type, respectively.

The red isomer shows a sharp first absorption band and can be assigned to *fac* type.[5] On the other hand, the violet and the reddish violet isomers give broad first absorption bands, indicating *mer* type, although only one *mer* type is expected. To assign the structure of these two isomers, PMR spectrum of the violet isomer was measured in deuterium oxide. The spectrum shows three AB patterns with coupling constants, 16.0, 18.3 and 18.5 Hz (Fig. 3). The AB pattern with 16.0 Hz is attributed to the in-plane acetate protons and those with 18.3 and 18.5 Hz to the out-of-plane acetate protons.[6] Thus, the violet isomer can be assigned to the equatorial-skew (*mer*) and hence, the reddish violet isomer to the *fac*. Of the two *fac* isomers, the red isomer can be assigned to the polar-chair structure, since its absorption spec-

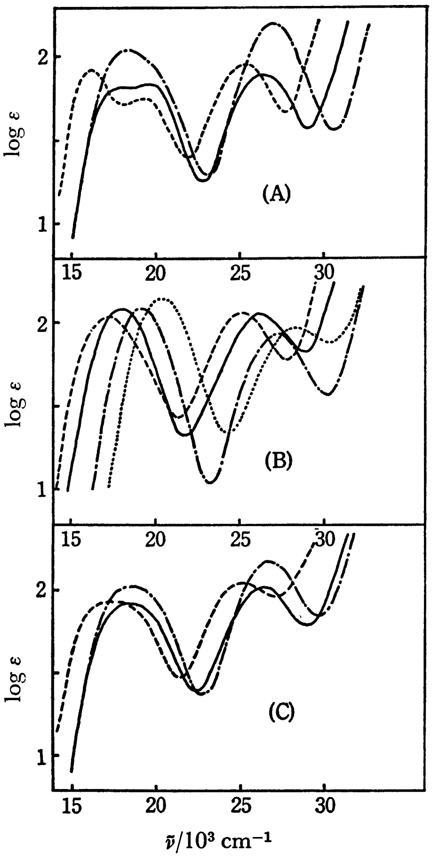

Fig. 2. Absorption spectra of (A): equatorial-skew, (B): polar-chair and (C): polar-skew isomers of [Co(X)(trdtra)] in water except chloro complexes (in 1 M HCl). ——: aqua, — —: ammine, ----: chloro, and ······: cyano complexes.

trum resembles very closely that of the corresponding *N*-Me-trdtra complex. The remaining reddish violet isomer, therefore should have the polar-skew structure, although it gives a broad first absorption band. The broadening of the first absorption band seems to be characteristic of trdtra and its related complexes with a skew conformation in the trimethylenediamine moiety. The [Cotrdta]$^-$ in which the trimethylenediamine moiety takes a skew conformation[7] shows also a broad first absorption band.[8]

The chloro complexes were prepared from the aqua complexes by treating with hydrochloric acid. Since the substitution reactions would be configuration retention[1] under the present experimental condition, the bluish green(A), the bluish green(B) and the greenish blue isomer would have the structure of the equatorial-skew, the polar-skew and the polar-chair, respectively. The absorption spectra of these isomers are shown in Fig. 2. The first absorption bands of the two skew isomers are broader than that of the chair isomer, as seen in the aqua and ammine complexes. The equatorial-skew isomer shows the first absorption band split apparently into two components.

The cyano complex gives always only one red isomer on the reactions of any isomer of aqua complex with potassium cyanide. It exhibits a sharp and symmetrical first absorption band which is almost identical with that of the corresponding *N*-Me-trdtra complex (Fig. 2). Thus, the complex would have the same structure as that of the *N*-Me-trdtra complex, the polar-chair.

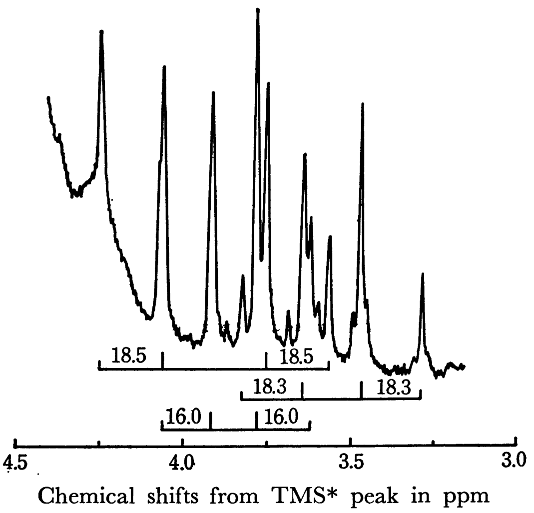

Fig. 3. PMR spectrum of violet (equatorial-skew) [Co(NH$_3$)(trdtra)] in D$_2$O (100 MHz). Numerical values in the figure indicate coupling constants in Hz for acetate protons.

The absorption spectra of all the complexes obtained in the present study are compared in Fig. 2. As stated previously, the first absorption bands of the skew isomers are broader than those of the chair isomers. The equatorial-skew isomers of the aqua and the chloro complex give the first absorption band split into two components. When the kind of unidentate ligand is changed, the lower frequency components shift to a greater extent than do the higher frequency components, although all the bands shift in accordance with the spectrochemical series.

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