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Trimethylenediamine Complexes. VII.[1] Optically Active Mixed-Ligand Cobalt(III) and Chromium(III) Complexes Containing Trimethylenediamine and the Acetylacetonate Anion

Mamoru Nakano, Shinichi Kawaguchi,* and Hiroshi Kawaguchi[2]

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558

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The $[\mathrm{M(acac)(tn)_2}]^{2+}$ and $[\mathrm{M(acac)_2(tn)}]^{+}$ complexes (M=Co and Cr) have been prepared and resolved by (*R*,*R*)-tartratoarsenate(III) and hydrogen-(*R*,*R*)-di-*O*-benzoyltartrate, respectively. On the basis of the CD-spectral studies in comparison with the corresponding ethylenediamine complexes, the absolute configurations of $(+)_{589}$-$[\mathrm{Co(acac)(tn)_2}]^{2+}$, $(-)_{589}$-$[\mathrm{Co(acac)_2(tn)}]^{+}$, $(+)_{589}$-$[\mathrm{Cr(acac)(tn)_2}]^{2+}$, and $(-)_{589}$-$[\mathrm{Cr(acac)_2(tn)}]^{+}$ were all assigned to Λ. Electronic spectra of these complexes and proton NMR spectra of the cobalt(III) complexes are also reported.

There have been published many papers dealing with the interrelation between the Cotton effect and the absolute configuration of dissymmetric metal complexes.[3] The absolute configurations of $(+)_{589}$-$\mathrm{Co(en)_3}^{3+}$[4] and $(-)_{589}$-$\mathrm{Co(tn)_3}^{3+}$[5] were determined by X-ray analysis both to be Λ. By comparison of the CD spectrum with that of Λ-$\mathrm{Co(en)_3}^{3+}$, absolute configurations of a number of dissymmetric $\mathrm{D_3}$ and $\mathrm{D_2}$ complexes have been assigned. Although the CD-spectral feature in the first d-d band region of Λ-$\mathrm{Co(tn)_3}^{3+}$[6] is remarkably different from that of Λ-$\mathrm{Co(en)_3}^{3+}$,[7] the empirical criterion of McCaffery *et al.*[8] seems to be applicable also to the six-membered chelate compounds.[9] However, the assignment of the E and $\mathrm{A_2}$ components of the CD band in the first absorption region is not unambiguous for $\mathrm{Co(tn)_3}^{3+}$,[10] whereas Δ-$[\mathrm{Co}(R,R\text{-ptn})_3]\mathrm{Cl_3{\cdot}2H_2O}$ (ptn=2,4-pentanediamine) was confirmed to have negative E and positive $\mathrm{A_2}$ components in the solid-state CD spectrum[11] in accordance with the informations from the solution spectra.[12]

Thus synthesis and examination of the absolute configuration of still more dissymmetric trimethylenediamine complexes especially of metal ions other than cobalt(III) are desired. The present paper is concerned with the optically active $\mathrm{Cr(acac)}_x\mathrm{(tn)}_{3-x}$ complexes (x=1 or 2), which are compared with the $\mathrm{Cr(acac)}_x\mathrm{(en)}_{3-x}$ complexes and also with the corresponding cobalt(III) complexes.

Experimental

Preparation and Resolution of Complexes. The starting compounds, *trans*-$[\mathrm{CoCl_2(tn)_2}]\mathrm{Cl}$,[13] $\mathrm{Na[Co(NO_2)_2(acac)_2]}$,[14] *trans*-$[\mathrm{CrCl_2(tn)_2}]\mathrm{Cl}$,[15] and *cis*-$[\mathrm{CrCl_2(tn)_2}]\mathrm{Cl{\cdot}H_2O}$[15] were prepared according to the literatures. The resolving agents, sodium (*R*,*R*)-tartratoarsenate(III) and (*R*,*R*)-di-*O*-benzoyltartaric acid were prepared by the reaction of sodium hydrogen-(*R*,*R*)-tartrate with arsenic(III) oxide[16] and that of (*R*,*R*)-tartaric acid with benzoyl chloride,[17] respectively.

$(-)_{589}$-Acetylacetonatobis(trimethylenediamine)cobalt(III) Iodide, $(-)_{589}$-$[Co(acac)(tn)_2]I_2$: Preparation and optical resolution of this compound were performed in a similar way as that for the corresponding ethylenediamine complex.[18] To a 1 M sodium hydroxide solution (60 ml) containing acetylacetone (8 g) was added *trans*-$[\mathrm{CoCl_2(tn)_2}]\mathrm{Cl}$ (12.5 g), and the solution was heated at about 70 °C until it turned red. The solution was then cooled to room temperature and an excess amount (37.5 g) of potassium iodide was added to the solution kept in ice to deposit a red precipitate, which was filtered, washed with cold water followed by cold methanol, and air-dried. The yield was 20.0 g (89.6%) and recrystallization from hot water gave red prisms. Found: C, 23.54; H, 4.94; N, 9.90%. Calcd for $\mathrm{C_{11}H_{27}O_2N_4I_2Co}$: C, 23.59; H, 4.86; N, 10.00%.

A mixture of the racemic complex (8 g) and silver acetate (5 g) was stirred in water (25 ml) for 30 min. Silver iodide and unreacted silver acetate were filtered and washed with water (10 ml). To the filtrate was added slowly a solution (8 ml) of sodium (*R*,*R*)-tartratoarsenate(III) hydrate (3.75 g) and the mixture was kept in a desiccator to precipitate red orange crystals. The yield was 1.5 g (13.4%). Found: C, 29.10; H, 4.50; N, 7.14%. Calcd for $\mathrm{C_{19}H_{35}O_{16}N_4As_2Co}$: C, 29.75; H, 4.39; N, 6.98%.

A mixture of the diastereomer (1.5 g) and potassium iodide (1.0 g) was stirred in an 0.1 M sodium hydroxide solution (10 ml) for 10 min to separate out white and red precipitates. When washed with methanol, the red precipitate was dissolved to leave the white one. A red precipitate was recovered on addition of diethyl ether to the washings. The yield was 0.6 g (56.0%). Found: C, 23.49; H, 4.92; N, 9.60%. In order to assure the optical purity, the resolution process was repeated and the final product showed the following molar rotation in aqueous solution at room temperature: $[M]_{589}=-430°$, $[M]_{546}=-1180°$, $[M]_{436}=+6970°$.

$(-)_{589}$-Bis(acetylacetonato)(trimethylenediamine)cobalt(III) Iodide Hydrate, $(-)_{589}$-$[Co(acac)_2(tn)]I{\cdot}H_2O$: A method of preparation analogous to that for $[\mathrm{Co(acac)_2(en)}]\mathrm{ClO_4}$[19] was employed. Trimethylenediamine (1.2 g) and active charcoal (1.0 g) were added to a solution (100 ml) of $\mathrm{Na[Co(NO_2)_2(acac)_2]}$ (6.2 g). After stirring for 15 min at room temperature, the charcoal was filtered and washed with water (30 ml). The filtrate and washings were combined and concentrated to *ca.* 50 ml by evaporation at 50 °C. The concentrate was then filtered and potassium iodide (30 g) was added to the filtrate to precipitate deep red needles on cooling. The yield was 6.5 g (81.9%), and recrystallization from hot water gave deep red needles. Found: C, 32.99; H, 5.52; N, 5.88%. Calcd for $\mathrm{C_{13}H_{26}O_5N_2ICo}$: C, 32.79; H, 5.50; N, 5.88%.

After a mixture of the racemic complex (4.5 g) and silver acetate (4.0 g) was stirred in water (20 ml) for 10 min, silver iodide and remaining silver acetate were separated by filtration and washed with water (10 ml). A solution (50 ml) of sodium hydrogen-(*R*,*R*)-di-*O*-benzoyltartrate (3.6 g) was added slowly to the filtrate and the solution was kept in a desiccator to deposit a deep violet precipitate. The yield was 1.5 g (23.1%). Found: C, 54.13; H, 5.44; N, 3.95%. Calcd for $\mathrm{C_{31}H_{37}O_{12}N_2Co}$: C, 54.07; H, 5.42; N, 4.07%.

A mixture of the diastereomer (1.0 g) and silver acetate (1.0 g) was stirred in methanol (20 ml). A precipitate was filtered and washed with methanol (20 ml). The washings was combined with the filtrate and the solvent was evaporated to dryness. The residue was dissolved in water (5 ml) and the solution was filtered. Solid potassium iodide was added to the filtrate to separate out a deep red precipitate. The yield was 0.3 g (43.4%). Found: C, 32.80; H, 5.50; N, 5.85 %. The specimen was dissolved in a minimum amount of water and the solution was cooled to deposit a precipitate. After filtration, potassium iodide was added to the filtrate to obtain a precipitate which showed an improved optical activity. This procedure was repeated to attain the following constant molar rotation in aqueous solution at room temperature: $[M]_{589}=-1810°$, $[M]_{546}=+9140°$, $[M]_{436}=-15610°$.

$(+)_{589}$-Acetylacetonatobis(trimethylenediamine)chromium(III) Iodide Hemihydrate, $(+)_{589}$-$[Cr(acac)(tn)_2]I_2\cdot 0.5H_2O$: To an aqueous solution (25 ml) of acetylacetone (1.0 g) and sodium hydroxide (0.4 g) was added *cis*-$[CrCl_2(tn)_2]Cl\cdot H_2O$ (3.3 g), and the mixture was stirred at 70 °C to become a clear orange solution. After cooling to room temperature, solid potassium iodide (10 g) was dissolved in the solution, which was then kept in an ice bath to separate out an orange precipitate. The crude product was filtered, washed with small portions of water and acetone successively and air-dried. The yield was 2.0 g (35.0%) and recrystallization from hot water gave orange plates. Found: C, 23.61; H, 5.01; N, 9.94; I, 45.09 %. Calcd for $C_{11}H_{28}O_{2.5}N_4I_2Cr$: C, 23.50; H, 5.02; N, 9.96; I, 45.14%.

In a similar manner to the corresponding cobalt(III) complex, the racemic compound (2.0 g) was converted to the acetate and resolved by the (*R*,*R*)-tartratoarsenate(III). The diastereomer (0.9 g) was then treated with potassium iodide to give $(+)_{589}$-$[Cr(acac)(tn)_2]I_2\cdot 0.5H_2O$ (0.3 g). Found: C, 23.58; H, 4.98; N, 9.73%. After repeated resolution the final specimen showed the following molar rotation in aqueous solution at room temperature: $[M]_{589}=+310°$, $[M]_{546}=+630°$, $[M]_{436}=-5020°$.

$(-)_{589}$-Bis(acetylacetonato)(trimethylenediamine)chromium(III) Iodide Hydrate, $(-)_{589}$-$[Cr(acac)_2(tn)]I\cdot H_2O$: To an aqueous solution (50 ml) of acetylacetone (2.0 g) and sodium hydroxide (0.8 g) was added *trans*-$[CrCl_2(tn)_2]Cl$ (3.1 g), and the mixture was heated at 70 °C to result in a red solution. After cooling solid potassium iodide (10 g) was added and the solution was kept in ice to form a red precipitate, which was filtered and extracted with acetone. The solvent was evaporated and the residue was recrystallized from hot water to obtain red needles. The yield was 1.5 g (32.2%). Found: C, 33.67; H, 5.59; N, 6.09; I, 27.45%. Calcd for $C_{13}H_{26}O_5N_2ICr$: C, 33.27; H, 5.58; N, 5.97; I, 27.04%.

The racemic iodide (1.5 g) was converted to the acetate and resolved by the (*R*,*R*)-di-*O*-benzoyltartrate. The diastereomer (2.7 g) was treated in a similar manner as the case of $[Co(acac)_2(tn)]^+$ to obtain $(-)_{589}$-$[Cr(acac)_2(tn)]I\cdot H_2O$ (1.4 g). Found: C, 34.18; H, 5.40; N, 5.98%. The resolution procedure was repeated until the following constant molar rotation was observed in aqueous solution at room temperature: $[M]_{589}=-420°$, $[M]_{546}=+5000°$, $[M]_{436}=-5750°$.

Measurements. The electronic absorption spectra were measured by a Hitachi EPS-3T spectrophotometer. The optical rotations were determined with a Yanagimoto OR-50 polarimeter, and the CD spectra with JASCO J-20 recording spectrometer. The proton NMR spectra were recorded on a JEOL-C 60HL spectrometer with TMS as an external reference.

Results and Discussion

The mixed ligand complexes $[Co(acac)(en)_2]I_2\cdot H_2O$,[18] $[Co(acac)_2(en)]I$,[20] $[Cr(acac)(en)_2]Cl_2\cdot H_2O$,[21] and $[Cr(acac)_2(en)]Cl\cdot 1.5H_2O$[21] were prepared and resolved by $Na_2[(R,R)As_2(C_4H_2O_6)_2]\cdot 2H_2O$ according to previously reported procedures. The same resolving agent was successfully applied to the acetylacetonatobis(trimethylenediamine) complexes. The enantiomer of $[Co(acac)(tn)_2]^{2+}$ forming a less-soluble diastereomer with the resolving agent shows an opposite CD pattern as compared with that of the corresponding diastereomer of $[Co(acac)(en)_2]^{2+}$ as is seen in Fig. 1. It is worth noting that the solubility criterion for relative configuration does not hold even in this couple of quite similar complexes. In the case of bis(acetylacetonato)(trimethylenediamine) complexes, on the other hand, the tartratoarsenate was not suitable and the di-*O*-benzoyltartrate was used as a resolving agent. Brennan, Igi, and Douglas resolved $[Co(acac)_2(tn)]^+$ as the (*R*,*R*)-tartrate.[22]

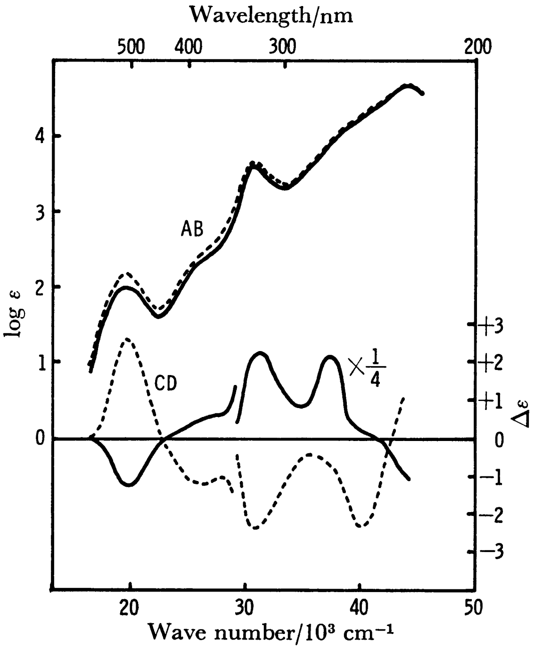

Fig. 1. Absorption (AB) and circular dichroism (CD) spectra of $(-)_{589}$-$[Co(acac)(tn)_2]I_2$ (——) and $(+)_{589}$-$[Co(acac)(en)_2]I_2\cdot H_2O$ (----) in water.

The cobalt(III) complexes $(-)_{589}$-$[Co(acac)(tn)_2]^{2+}$ and $(-)_{589}$-$[Co(acac)_2(tn)]^+$ are quite stable and the aqueous solutions showed no change in the optical rotation at room temperature over one month. On the contrary, the corresponding chromium(III) complexes are not so stable. The optical rotations of $(+)_{589}$-$[Cr(acac)(tn)_2]^{2+}$ and $(-)_{589}$-$[Cr(acac)_2(tn)]^+$ in aqueous solutions diminished gradually on standing at room temperature to one-half after six days. The absorption spectra also changed, indicating that reactions other than racemization proceeded.

Electronic Spectra. The electronic absorption spectra of the complexes obtained are displayed in

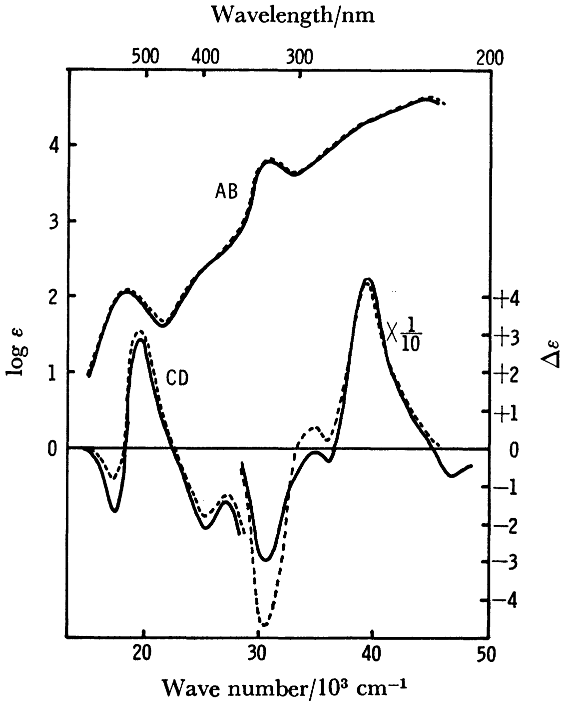

Fig. 2. Absorption (AB) and circular dichroism (CD) spectra of $(-)_{589}$-$[Co(acac)_2(tn)]I \cdot H_2O$ (——) and $(-)_{589}$-$[Co(acac)_2(en)]I$ (----) in water.

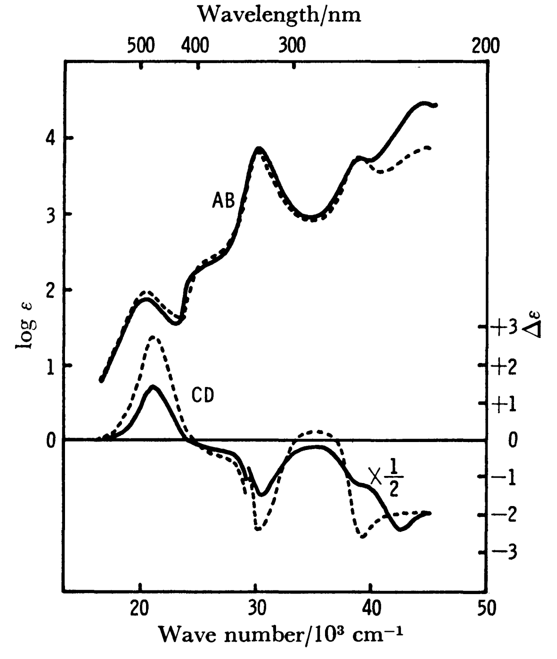

Fig. 3. Absorption (AB) and circular dichroism (CD) spectra of $(+)_{589}$-$[Cr(acac)(tn)_2]I_2 \cdot 0.5H_2O$ (——) and $(+)_{546}$-$[Cr(acac)(en)_2]Cl_2 \cdot H_2O$ (----) in water.

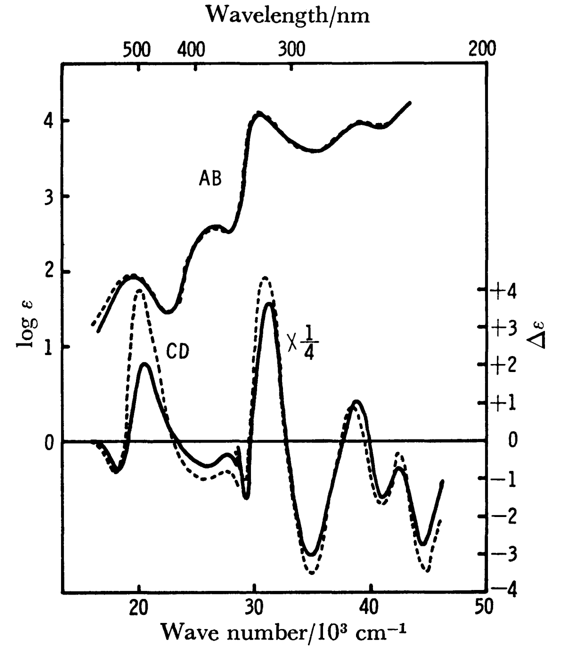

Fig. 4. Absorption (AB) and circular dichroism (CD) spectra of $(-)_{589}$-$[Cr(acac)_2(tn)]I \cdot H_2O$ (——) and $(+)_{546}$-$[Cr(acac)_2(en)]Cl \cdot 1.5H_2O$ (----) in water.

Figs. 1—4 together with those of the corresponding ethylenediamine complexes for the sake of comparison. In the earlier papers of this series,[23–25] several dianionobis(trimethylenediamine)cobalt(III) complexes have been reported, of which the first absorption maxima all located in the lower energy region than those of the corresponding ethylenediamine complexes, indicating that the ligand field of trimethylenediamine is a little weaker than that of ethylenediamine. In the present case, however, the first bands of $[Co(acac)(tn)_2]^{2+}$ (19800 cm^{-1}) and $[Co(acac)_2(tn)]^+$ (18500 cm^{-1}) nearly coincide with the data for $[Co(acac)(en)_2]^{2+}$ (19800 cm^{-1})[26] and $[Co(acac)_2(en)]^+$ (18600 cm^{-1}),[20] respectively, and those of $[Cr(acac)(tn)_2]^{2+}$ (20300 cm^{-1}) and $[Cr(acac)_2(tn)]^+$ (19200 cm^{-1}) are even higher in frequency than $[Cr(acac)(en)_2]^{2+}$ (20200 cm^{-1}) and $[Cr(acac)_2(en)]^+$ (19000 cm^{-1}).[21] In either of cobalt(III) and chromium(III) complexes, participation of acetylacetone as ligand diminishes the frequency of the absorption maximum due to its lower field as compared with ethylenediamine and trimethylenediamine. As to the assignment of the UV absorption bands, Boucher[20] discussed on $[Co(acac)_2(en)]^+$ and Kaizaki *et al.*[21] on $[Cr(acac)_2(en)]^+$.

CD Spectra and Absolute Configuration. Figures 1—4 show the CD spectra of the $[Co(acac)_x(tn)_{3-x}]$ and $[Cr(acac)_x(tn)_{3-x}]$ complexes ($x=1$ or 2) together with those of the corresponding ethylenediamine complexes. The CD pattern of $(-)_{589}$-$[Co(acac)(tn)_2]^{2+}$ in aqueous solution is just opposite in sign as compared with that of $(+)_{589}$-$[Co(acac)(en)_2]^{2+}$ which was reported to have the Λ configuration.[26] Thus a Δ configuration is assigned to $(-)_{589}$-$[Co(acac)(tn)_2]^{2+}$ and has in fact been confirmed by X-ray analysis.[27] The CD spectra of $(-)_{589}$-$[Co(acac)_2(en)]^+$ and $(-)_{589}$-$[Co(acac)_2(tn)]^+$ show a striking resemblance to each other (Fig. 2). Boucher assigned the Λ configuration to the ethylenediamine complex on the basis of the positive sign of the dominant CD band (A_2+B_2) in the first absorption region.[20] Then the Λ configuration of $(-)_{589}$-$[Co(acac)_2(tn)]^+$ is quite obvious and the same conclusion was drawn already by Brennan *et al.*[22]

Kaizaki *et al.* prepared and characterized $(+)_{546}$-$[Cr(acac)(en)_2]Cl_2$ and $(+)_{546}$-$[Cr(acac)_2(en)]Cl$ by the absorption and CD spectra in both the visible and ultraviolet region, assigning the Λ configuration to both of the mixed-ligand complexes.[21] As is seen in Figs. 3 and 4, the CD spectra of $(+)_{589}$-$[Cr(acac)(tn)_2]^{2+}$ and $(-)_{589}$-$[Cr(acac)_2(tn)]^+$ are quite similar to those of $(+)_{546}$-$[Cr(acac)(en)_2]^{2+}$ and $(+)_{546}$-$[Cr(acac)_2(en)]^+$, respectively, except that the rotational strength of each CD band is smaller for the tn complex than for the corresponding en complex. Thus the two (acetylacetonato)(trimethylenediamine)chromium(III) complexes may be concluded to have the Λ configuration. The X-ray analysis of a red prism of $(-)_{589}$-$[Cr(acac)_2(tn)]I \cdot H_2O$ now in progress confirms the Λ configuration with a tn chelate ring of chair form.[28]

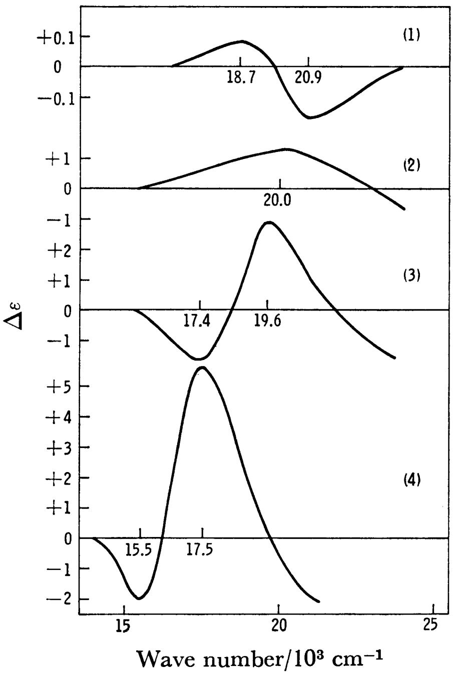

Fig. 5. Circular dichroism spectra in the first d-d absorption region of Λ-$[Co(tn)_3]^{3+}$ (1),[6] Λ-$[Co(acac)(tn)_2]^{2+}$ (2), and Λ-$[Co(acac)_2(tn)]^+$ (3) in water and of Λ-$[Co(acac)_3]$ (4)[29] in ethanol.

Figure 5 compares the CD patterns of the $[Co(acac)_x(tn)_{3-x}]$ complexes (x=0—3) in the first absorption region. The absolute configuration of $(-)_{546}$-$[Co(acac)_3]$ was determined as Λ by X-ray analysis.[29] The predominant positive CD band at 17500 cm^{-1} was assigned to the E component on the basis of the polarized crystal spectrum[30] in accordance with the empirical spectroscopic rule that for the Λ isomer the CD component with E symmetry has positive rotational strength.[8] The CD spectral pattern of Λ-$[Co(acac)_2(tn)]^+$ is quite similar to that of $[Co(acac)_3]$ except that the peak positions are shifted to the higher energy region due to the higher ligand field of tn than that of acac. Thus the positive CD band at 19600 cm^{-1} of Λ-$[Co(acac)_2(tn)]^+$ may be assigned to the E component.

The positive CD band of $[Co(tn)_3]^{3+}$ was attributed to the E component based on the ion-pairing effect.[31,9] It should be noted that the E component lies at lower energy side of the A_2 component for $[Co(tn)_3]^{3+}$ on the contrary to the $[Co(acac)_3]$ case where the E component lies at higher energy side of the A_2 component. Λ-$[Co(acac)(tn)_2]^{2+}$ exhibits a single positive CD band which is drawn as a reverse of the band observed for Δ-$[Co(acac)(tn)_2]^{2+}$ (Fig. 1). The E-A_2 split seems small and cancellation of the two components with each other is extensive, leaving residue of the predominant E component.

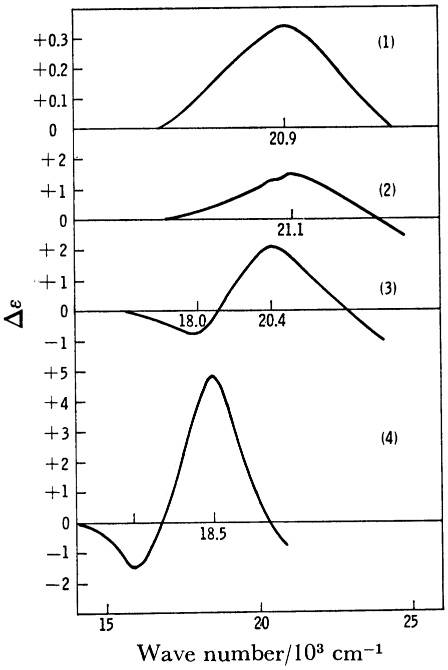

Fig. 6. Circular dichroism spectra in the first d-d absorption region of Λ-$[Cr(tn)_3]^{3+}$ (1),[35] Λ-$[Cr(acac)(tn)_2]^{2+}$ (2), and Λ-$[Cr(acac)_2(tn)]^+$ (3) in water and of Λ-$[Cr(acac)_3]$ (4)[32] in ethanol.

In a similar fashion Fig. 6 shows the CD spectra of the $[Cr(acac)_x(tn)_{3-x}]$ complexes in the first d-d absorption region. Mason *et al.*[32] prepared optically pure $(-)_{589}$-$[Cr(acac)_3]$ and assigned the absolute configuration to Δ based on comparison of the CD spectrum with those of four isomers of tris((+)-3-acetylcamphorato)chromium(III)[33] of which $\Lambda(+)$-*trans*-$[Cr((+)\text{-atc})_3]$ had been confirmed to be Λ by X-ray analysis.[34] The curve (4) in Fig. 6 is drawn as a reverse of the CD spectrum reported by Mason *et al.* for Δ-$[Cr(acac)_3]$,[32] showing the CD spectrum of Λ-$[Cr(acac)_3]$. Thus the positive major band at 18500 cm^{-1} can be assigned to the E component. The CD spectrum of $\Lambda(-)_{589}$-$[Cr(acac)_2(tn)]^+$ is also similar in the pattern to that of Λ-$[Cr(acac)_3]$ and the positive major band is assigned to the E component.

The CD spectrum of $(+)_{546}$-$[Cr(tn)_3]^{3+}$ reproduced in Fig. 6 was reported by Kaizaki *et al.*[35] On addition of sodium selenite to the solution, intensity of the positive CD band at 477 nm was diminished and a new negative CD band appeared at 435 nm. Thus the positive band was assigned to the ^4E component and the absolute configuration of $(+)_{546}$-$[Cr(tn)_3]^{3+}$ was concluded to be Λ.[35] The CD pattern of $(+)_{589}$-$[Cr(acac)(tn)_2]^{2+}$ (curve 2 in Fig. 6) is similar to that of $(+)_{546}$-$[Cr(tn)_3]^{3+}$

and the positive CD band is considered to be a residue of the predominant ^4E component after cancellation with a negative ^4A component.

The ligand-metal-ligand bond angle θ exceeds 90° in the six-membered chelate ring formed by trimethylenediamine with cobalt(III), whereas θ is generally less than 90° in the five-membered ethylenediamine cobalt(III) chelates. The empirical criterion relating the positive E component of the lowest-energy d-d absorption band to the Λ isomer of the cobalt(III) ethylenediamine chelate[8] has been shown to apply to the cobalt(III) trimethylenediamine complexes in spite of the larger angle θ.[31] In contrast with the N–Co–N angle of 96(1)° in $(-)_{589}$-$[Co(acac)(tn)_2]^{2+}$,[27] the N–Cr–N angle in $(-)_{589}$-$[Cr(acac)_2(tn)]^+$ was found to be 88.8(4)°.[28] The striking resemblance of the CD patterns depicted in Fig. 6 to those in Fig. 5 indicates that the same generalization as established for the cobalt(III) complexes applies to the chromium(III) complexes, too.

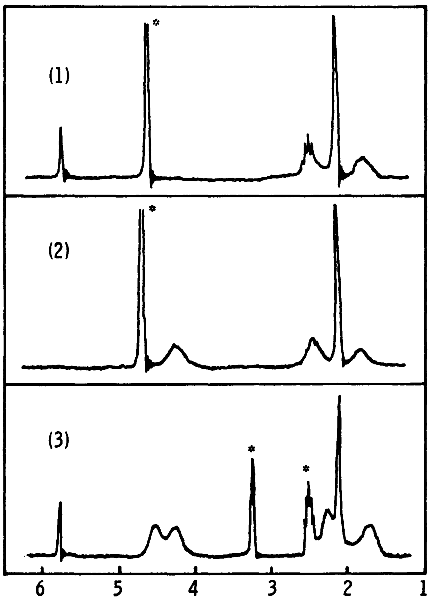

Fig. 7. Proton NMR spectra of $[Co(acac)(tn)_2]I_2$ in D_2O (1), *ca.* 0.1 M DCl–D_2O (2), and dimethylsulfoxide-d_6 (3). The asterisks denote the peaks due to solvent impurities.

Proton NMR Spectra. Figure 7 shows the proton NMR spectra of $[Co(acac)(tn)_2]I_2$ in D_2O, DCl–D_2O and DMSO-d_6. Two sharp signals observed at 5.75 and 2.16 ppm in D_2O with the area ratio of *ca.* 1 : 6 are assigned to the methine and methyl protons of the acetylacetonate ligand. The methine signal is lost in acidic solution due to the exchange reaction. Three broad signals observed at 4.24, 2.51, and 1.84 ppm in 0.1 M DCl–D_2O solution with the relative intensity of 2 : 2 : 1 are assigned to the NH_2, α-CH_2 and β-CH_2 protons of trimethylenediamine, NH_2–$CH_2(\alpha)$–$CH_2(\beta)$–$CH_2(\alpha)$–NH_2. In neutral D_2O the amine protons are deuterated and the methylene signals become sharper.

In DMSO-d_6 solution the methylene protons resonate at a little higher field (2.28 and 1.70 ppm) and the amine protons exhibit two signals at 4.55 and 4.27 ppm with equal intensities. Clifton and Pratt found that the chemical shifts of ammine or amine protons trans to halide or oxygen-donor ligand in $[CoX(NH_3)_5]^{(3-n)+}$ and *cis*-$[CoCl_2(en)_2]^+$ are appreciably smaller than those of the cis amine protons.[36] The same situation is realized in $[Co(acac)(tn)_2]^{2+}$ and the 4.27 ppm signal is assigned to the amine groups trans to the acetylacetonate oxygen and the 4.55 ppm signal to the mutually trans amine groups.

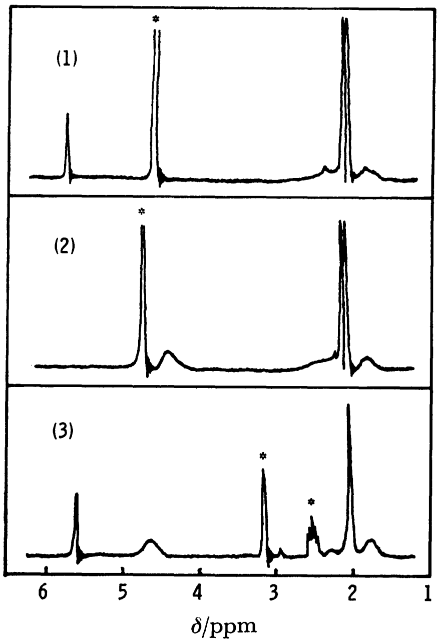

Fig. 8. Proton NMR spectra of $[Co(acac)_2(tn)]I \cdot H_2O$ in D_2O (1), *ca.* 0.1 M DCl–D_2O (2), and dimethylsulfoxide-d_6 (3). The asterisks denote the peaks due to solvent impurities.

As is seen in Fig. 8 the spectrum of $[Co(acac)_2(tn)]^+$ in D_2O shows two methyl signals at 2.11 and 2.15 ppm together with a methine signal at 4.28 ppm in accord with expectations. In DCl–D_2O solution three signals due to trimethylenediamine are observed at 4.47, 2.43, and 1.88 ppm with the relative intensity of 2 : 2 : 1 and assigned to the NH_2, α-CH_2 and β-CH_2, respectively. In DMSO-d_6, however, the relative intensities of the two methylene signals are reversed, the higher-field signal at 1.80 ppm being twice as large in area as the lower-field one at 2.27 ppm. It is not conceivable that the α-CH_2 protons resonate at a higher field than the β-CH_2 in this case, but nonequivalence of the geminal α-CH_2 protons may be responsible for this phenomenon. The complex *cis*-$[Co(CN)_2(tn)_2]^+$ shows three methylene signals of equal intensity in D_2O.[25] The two protons in each methylene group of $NH_2CH_2CHXCH_2NH_2$ (X=OH or Cl) coordinated to platinum(II) are not equivalent, the axial proton resonating at higher field than the equatorial one.[37] In the spectrum of $[Co(acac)_2(tn)]^+$, the signal at 2.27 ppm may be attributed to the equatorial protons of the two α-CH_2 groups and the chemical shift of the axial α-CH_2 protons may be assumed to coincide with that of β-CH_2 by chance. The trimethylenediamine molecule coordinated to cobalt(III) has the chair conformation in crystals of $(-)_{589}$-$[Co(tn)_3]Br\cdot H_2O$,[5] $(+)_{589}$-$[Co(en)_2(tn)]Br_3$,[38] $(-)_{589}$-$[Co(acac)(tn)_2][As\text{-}(+)\text{-}tart]_2\cdot H_2O$,[27] $(-)_{589}$-*cis*-$[Co(NCS)_2(tn)_2][Sb\text{-}(+)\text{-}tart]\cdot 2H_2O$,[39] *trans*-$[Co(NO_3)_2(tn)_2]NO_3$,[40] and $[Co(CO_3)(tn)_2]ClO_4$.[41] However, the chair conformation of the six-membered chelate ring seems only slightly more stable than the skew-boat conformation,[42] and the CD spectra of $[Co(tn)_3]^{3+}$ ions in solutions were interpreted to indicate the equilibrium between these two conformers.[43] The remarkable difference now observed in the NMR spectra in D_2O and DMSO-d_6 may reflect the change of the equilibrium among conformers with solvent.

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