any W atoms. He concluded that exchange rates were faster than predicted for diffusion control and postulated some sort of charge-transfer complex formation between the anions in the nonaqueous solvents.

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New Type of Atropisomerism in Metal Complexes. Preparation and Resolution of (3,4-Diacetyl-2,5-hexanedionato)-bis[(2,2′,2″-triaminotriethylamine)cobalt(III)] Ion[1,2]

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Abstract: A metal complex, (3,4-diacetyl-2,5-hexanedionato)bis[(2,2′,2″triaminotriethylamine)cobalt(III)] ion, was prepared and optically resolved. The optical resolution of the complex confirmed the expected novel twin structure and presented a new type of atropisomer in coordination chemistry. The optical absorption and circular dichroism are discussed in connection with the absorption spectrum of the related complex, (2,4-pentanedionato)(2,2′,2″-triaminotriethylamine)cobalt(III) ion, which corresponds to half of the above twin structure.

Recently, several metal complexes having a new type of chiral source (restricted rotation) have been reported that possess chirality different from those of traditional types which are confined mostly to the class of centrodissymmetry.[3] Utsuno reported a propeller-like, fixed chiral conformation of pyridine rings in the *trans*-dichlorotetrakis(pyridine)cobalt(III) ion.[4] We have reported the optical isomerism of a series of Co^{III}(tren) complexes of 3-aryl-2,4-pentanedione, the chirality of which comes from restricted rotation of an aryl group.[5] Figure 1 shows a typical example. In the present study, a new type of atropisomerism is reported. The twin complex $[\{Co(tren)\}_2tae]^{4+}$ (Figure 2) is the first example of an atropisomer in binuclear metal complexes.[6] Although this complex may be only an extension of this series, since a different ligand is introduced into the $[Co(acac)tren]^{2+}$ system instead of the aryl group in the above series, it is unique because it contains no unnecessary moiety and therefore shows genuine electronic transitions of the $[Co(acac)tren]^{2+}$ chromophore. Thus, the title complex gives important information about the electronic states of $[Co(acac)tren]^{2+}$.

Experimental Section

Instruments. Circular dichroism, IR, UV-visible, ^1H NMR, and ^{13}C NMR spectra were measured with JASCO Model J-500, Hitachi 295, Hitachi 200-10, Hitachi R-20, and JEOL JNM-FX60 spectrometers, respectively. Elemental analyses were carried out with a YANACO MT02 CHN-order.

Preparations. (a) (2,4-Pentanedionato)(2,2′,2″-triaminotriethylamine)cobalt(III). A mixture of $[Co(CO_3)tren]ClO_4{\cdot}1.5H_2O$ (5.5 g, 14 mmol)[7] and 2 N hydrochloric acid solution (20 mL) was stirred for one-half hour. To this solution were added acetylacetone (4 mL) and 1 N sodium hydroxide solution (30 mL). The mixture was kept at 60–80 °C for 2 h under stirring. After the mixture cooled, potassium iodide (18.4 g, 0.11 mol) was added to give a red precipitate, yield 7.6 g (87%). A small amount of the complex was purified by means of cation-exchange chromatography using an SP-Sephadex column and 0.5 N sodium chloride solution as the eluent. After most of the sodium chloride was removed from the eluted solution of $[Co(acac)tren]^{2+}$, excess sodium bromide was added to the resulting solution. The precipitate was recrystallized from water: IR 1520 and 1570 cm^{-1}; ^1H NMR δ 2.12, 2.20 (two kinds of methyl protons of the acetylacetonate ring), and 5.73 (methine proton of the acetylacetonate ring). Anal. Calcd for $C_{11}H_{25}N_4O_2CoBr_2{\cdot}3H_2O$: C, 25.50; H, 6.03; N, 10.81. Found: C, 25.79; H, 6.28; N, 11.10.

(b) (3,4-Diacetyl-2,5-hexanedionato)bis[(2,2′,2″-triaminotriethylamine)cobalt(III)]. A reaction of $[Co(CO_3)tren]^{2+}$ (1.0 equiv) with H_2tae (0.5 equiv)[8] similar to the preparation of $[Co(acac)tren]^{2+}$ described above gave a solution of crude $[\{Co(tren)\}_2tae]^{4+}$. Sodium perchlorate (6–8 equiv) was added to the solution. The precipitate was filtered and recrystallized from water, yield 34%. The complex was often contaminated with brown impurities and therefore purified by means of ion-exchange chromatography. IR 1560 cm^{-1}; ^1H NMR δ 2.10, 2.17 (CH_3 of the acac ring), and 2.5–3.8 (CH_2 of the tren chain). Anal. Calcd for $C_{22}H_{48}Cl_4Co_2N_8O_{20}{\cdot}2H_2O$: C, 25.40; H, 5.40; N, 10.77. Found: C, 25.10; H, 5.10; N, 10.50.

Optical Resolution of $[\{Co(tren)\}_2tae]^{4+}$. A previous communication reported the partial resolution of the complex by means of ion-exchange chromatography using a sodium D-tartrate solution as the eluent.[6] A better result is obtained when the complex is recycled 7 times through an SP-Sephadex column (4.5 cm in diameter and 90 cm in length) using a 0.275 M solution of sodium D-tartratoantimonate(III) as the eluent. Although the eluted fraction does not separate as two bands, we were able to obtain the enantiomeric isomers from the head and tail fractions which show a constant ratio of circular dichroism intensity to absorption coefficient. The head fractions show a negative sign at the lowest energy region ($\Delta\epsilon = -0.57$ at 18.42×10^3 cm^{-1}), and tail fractions show a positive sign ($\Delta\epsilon = +0.55$ at the same position). The concentration of the aqueous solution for the measurement of CD spectra was obtained from the calibration curve of the purified racemate.

Results and Discussion

Characterization of $[Co(acac)tren]^{2+}$. The infrared spectrum of the complex showed two strong peaks at 1520 and 1570 cm^{-1}

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(1) The following abbreviations were used throughout this paper; tren for 2,2′,2″-triaminotriethylamine, acacH for acetylacetone, en for ethylenediamine, tae for tetraacetylethane.

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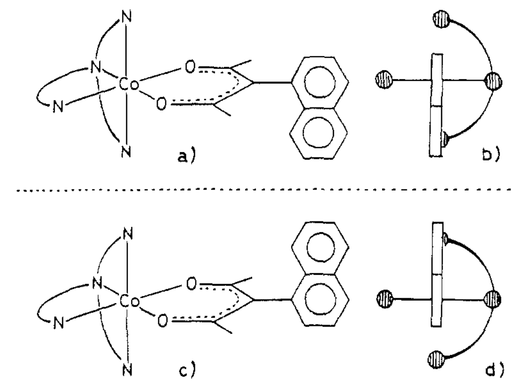

Figure 1. Representative aryl-substituted (β-diketonato)cobalt(III) complex. The absolute configurations are denoted by the CIP notation: (a) the *R* configuration and (b) the right-hand side view of the tren and aryl groups; (c) the *S* configuration and (d) right-hand side view of the tren and aryl groups.

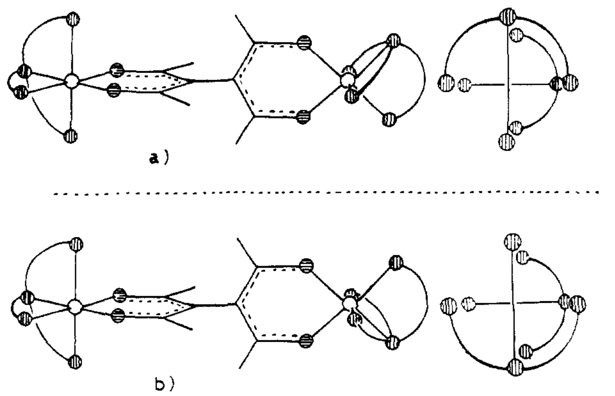

Figure 2. Structural model and absolute configuration of $[\{Co(tren)\}_2tae]^{4+}$. The absolute configurations of (a) and (b) are *S* and *R*, respectively.

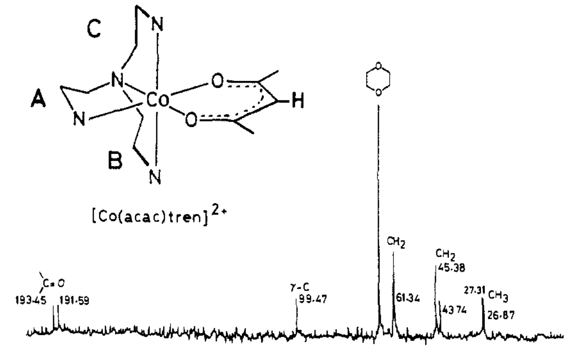

Figure 3. ^{13}C NMR spectrum of $[Co(acac)tren]^{2+}$.

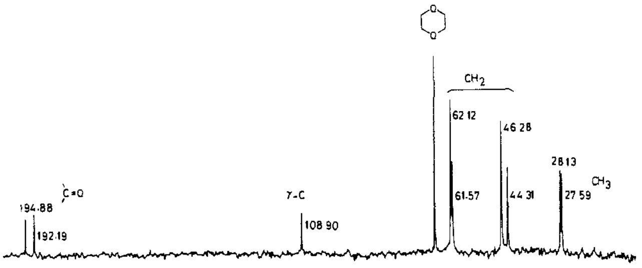

Figure 4. ^{13}C NMR spectrum of $[\{Co(tren)\}_2tae]^{4+}$.

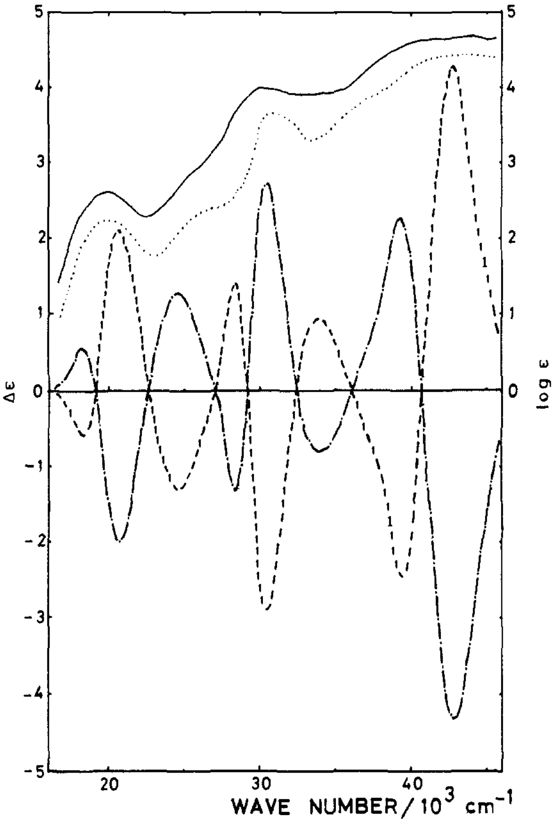

Figure 5. Absorption spectrum of $[Co(acac)tren]^{2+}$ (···) and absorption (—) and circular dichroism spectra of $[\{Co(tren)\}_2tae]^{4+}$ in aqueous solution, head fractions (- - -), and tail fractions (–·–·–).

that are characteristic of a chelated β-diketone[9] and are assigned to $\nu_{C=C}$ and $\nu_{C=O}$. The methine and methyl proton signals were observed in the ^1H NMR spectrum. Thus, these findings indicate that acetylacetonate ligand coordinates to Co(III) ion to form a usual six-membered chelate.

While the methylene proton signals of tren in ^1H NMR overlapped each other and resulted in broad peaks of a complicated multiplet, ^{13}C NMR signals of the tren carbon atoms appeared as well-defined, sharp peaks, and they were separated into two groups of signals as shown in Figure 3. One group (61.34 and 61.73 ppm from Me_4Si, 2:1 intensity ratio) contains signals from three carbon atoms adjacent to the tertiary amino nitrogen, and another group (43.74 and 45.38 ppm, 2:1 intensity) contains those of the three carbon atoms adjacent to the primary amino nitrogen. The former group appeared at a lower magnetic field side than the latter group due to β-substituents effect.[10] Apparently, the 2-fold intense signals are those for the B and C rings of the tren moiety (A, B, and C rings denote three chains of the tren moiety as shown in Figure 3). Since these methylene signals are sharp and the A ring tends to adopt a flexible conformation, the B and C rings of the tren moiety are sterically almost equivalent and the A ring undergoes a rapid conversion between the δ and λ conformations. The crystal structures of other Co^{III}(tren) complexes[11] substantiate the above description of the stereochemistry of the A, B, and C rings. Thus, the cobalt(III) complex ion $[Co(acac)tren]^{2+}$ has virtually a symmetry plane which is coplanar with the acac ring.

Characterization of $[\{Co(tren)\}_2tae]^{4+}$. When the complex was subjected to ion-exchange chromatography on an SP-Sephadex column, its elution rate was found to be very slow when compared to the complex bearing a charge of +2. The slow elution rate is consistent with the higher charge and stronger interaction with the cation-exchange resin. In the infrared spectrum a strong band characteristic of the β-substituted acetylacetone ring was observed at 1560 cm^{-1}. Figure 4 shows the ^{13}C NMR spectrum. The

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methylene carbon signal patterns of the two tren chains gave the same conclusion as in the case of $[Co(acac)tren]^{2+}$. Thus, the complex consists of two units of $[Co(acac)tren]^{2+}$, and each of them has a symmetry plane, even considering the rapid conformational changes of the A ring of tren chain.

Electronic Absorption of $[Co(acac)tren]^{2+}$. The absorption spectrum is shown in Figure 5, together with the absorption and CD spectra of the binuclear tae complex. A splitting of the first absorption band of d–d transition into two components is expected from the holohedralized symmetry (D_{4h}) of this complex (*cis*-CoO_2N_4). However, only one broad band is observed at 19 800 cm^{-1} in aqueous solution. It is considered that the splitting is not large, and thus apparently one absorption band forms as seen in analogous cobalt(III) complexes. The strong absorption at about 30×10^3 cm^{-1} is assigned to a charge-transfer band. The second absorption band of d–d transition was observed as a shoulder of the charge-transfer band. Although the electronic absorption of π–π^* transition of the acetylacetone ring is too obscure to assign the transition at this stage, the CD spectrum of the twin complex described below clarified the uncertainty and revealed the $\pi \rightarrow \pi^*$ transition of the acetylacetonate ring. Extensive studies summarized in ref 12 suggest that one of the transition positions at 34–35 $\times 10^3$ cm^{-1} is in accordance with the value obtained from the CD spectrum of the twin complex.

Electronic Absorption of $[\{Co(tren)\}_2tae]^{4+}$. The absorption coefficient of the complex was approximataely twice that of $[Co(acac)tren]^{2+}$. It is in accordance with the fact that the complex consists of two units of $[Co(acac)tren]^{2+}$. Since no shift in the absorption peaks as compared to those of the $[Co(acac)tren]^{2+}$ was observed, the two units were assumed to be electronically almost independent.

Enantiomerism and Circular Dichroism Spectrum of $[\{Co(tren)\}_2tae]^{4+}$. The enantiomerism of $[\{Co(tren)\}_2tae]^{4+}$ comes from a combination of the two bow parts of the tren chain of the two units. Considering the relative configuration of two pairs of the B and C rings (bow parts) of tren chain, the absolute configuration of the twin complex may be denoted similarly to chiral biphenyls (CIP notation) and are shown in Figure 2.[13] The molecular model of the twin complex further shows that the tae moiety has four chiral conformations with a $H_3CCCCCH_3$ skelton, but the four conformers are likely to compensate for each other. Thus, the conformational contribution of the tae moiety is not assumed to be significant. The circular dichroism intensities in the first absorption band region are not large compared to those of usual complexes with configurational chirality, e.g., $[Co(acac)(en)_2](ClO_4)_2$,[14] probably because the chirality source of the tae complex is out of the coordination sphere and because the chirality source of the tae complex is out of the coordination sphere and far from the cobalt ion. Two CD peaks with opposite signs in the first absorption band region are observed, as is predicted on the basis of the holohedralized symmetry of the $[Co(acac)tren]^{2+}$ unit. It is worthwhile to note that the CD strength in the second absorption band at 24 700 cm^{-1}, which is both electric and magnetic dipole forbidden, is comparable to those in the first absorption band region. The bands at 28 450 and 30 500 cm^{-1} are assigned to charge-transer bands (transfer of d electrons of the cobalt(III) ion to the lowest vacant π molecular orbital of β-diketonate ring). Those at 34 000 and 39 400 cm^{-1} are assigned to $\pi \rightarrow \pi^*$ transitions of the β-diketonate ring.[15] The intensities of the last four peaks are very weak compared to the corresponding CD peaks of $[Co(acac)(en)_2]^{2+}$. It seems reasonable on a qualitative basis that the CD intensities of the four peaks are small, since the major chirality source is the relative configuration of tren chains and since the β-diketone rings are not involved directly with the chirality.

If tren is changed to other (tripod) quadridentate as well as mixed ligands (L_4), we expect to be able to obtain important knowledge which we cannot obtain from complexes such as $[Co(acac)L_4]$, which possess only C_s symmetry.

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Registry No. $[Co(acac)tren]Br_2$, 104716-24-7; $[\{Co(tren)\}_2tae]Cl_4$, 104716-25-8; (*S*)-$[\{Co(tren)\}_2toe]^{4+}$, 104759-84-4; (*R*)-$[\{Co(tren)\}_2tae]^{4+}$, 104759-85-5; $[Co(CO_3)tren]ClO_4$, 41593-06-0.

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