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Preparation and Circular Dichroism Spectrum of a (Triazacyclononane)(tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecene)cobalt(III) Complex

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Synopsis. A new $[Co(tacn)(tri)]^{3+}$ complex has been prepared and optically resolved (TACN represents 1,4,7-triazacyclononane, and TRI, tribenzo[*b*,*f*,*j*][1,5,9]triazacyclo dodecene). From the CD spectral similarity of $(+)^{CD}_{500}$-$[Co(tacn)(tri)]^{3+}$ with $(+)_{546}[Co(tri)_2]^{3+}$, it has been concluded that the metal-centered optical activity of the two tri complexes is derived from a chiral arrangement of (benzene ring)–C=N– moieties.

Cummings and Busch[1] have reported the formation of a macrocyclic terdentate ligand, tribenzo[*b*,*f*,*j*][1,5,9]triazacyclododecene (abb. as TRI), by the condensation of three molecules of *o*-aminobenzaldehyde in the presence of metal ions. There are two geometrical isomers in a bis(tri)cobalt(III) complex; one is chiral form and the other meso form. The former has been prepared and resolved by Cummings and Busch.[1] The absolute configuration of the $(+)_{546}[Co(tri)_2]^{3+}$ complex has been determined by Wing and Eiss[2] by means of X-ray analysis. The $(+)_{546}$ isomer exhibits a similar CD spectrum to that of the $(+)_{546}$-$[Co(en)_3]^{3+}$ complex in the first absorption band region; the arrangement of the donor atoms in the $(+)_{546}$-$[Co(tri)_2]^{3+}$ isomer also resembles that in the $(+)_{546}$-$[Co(en)_3]^{3+}$ complex to give a left-handed helix about the threefold symmetry axis. On these bases, Wing and Eiss regarded the bis(tri) complex as strong evidence for the metal-centered optical activity arising from the twisted crystal field. On the other hand, Mason and Seal[3] have explained the optical activity of the $[Co(en)_3]^{3+}$ complex in terms of a dynamic coupling model. Therefore, it is necessary to reinvestigate the source of the optical activity in the $[Co(tri)_2]^{3+}$ complex.

In this report, the preparation and optical resolution of a complex containing a symmetric cyclic-terdentate TACN ligand and a dissymmetric TRI ligand, $[Co(tacn)(tri)]^{3+}$, will be reported (TACN represents 1,4,7-triazacyclononane). The CD spectrum of the resolved complex will be compared with that of the $[Co(tri)_2]^{3+}$ complex in order to determine the sources of the metal-centered optical activity.

Experimental

Preparation and Optical Resolution of $[Co(tacn)(tri)]^{3+}$. The $[Co(NO_2)_3(tacn)]$ complex[4] (2.5 g, 7.7 mmol) was suspended in a mixture of ethanol (275 cm^3) and 64% $HClO_4$ (25 cm^3). The whole system was stirred at 60 °C for 3—4 h, whereupon the color of the solution turned from yellow to deep red-brown. After cooling of the resulting solution to room temperature and removal of some precipitated material by filtration, the filtrate was adjusted to pH 3 by a 2 mol/dm^3 ethanolic KOH solution, and then the precipitated $KClO_4$ was filtered off. To the filtrate was added freshly prepared *o*-aminobenzaldehyde[5] (5 g, 41 mmol), and the mixture was refluxed at 80 °C for 8—9 h. The resulting solution was cooled to room temperature, and the precipitated material was filtered and washed with small amounts of ethanol and acetone in turn. The product was dissolved in a large amount of water (*ca.* 2000 cm^3) which had been adjusted to pH 4 by diluted HCl (all adjustments of pH were carried out with diluted HCl, unless otherwise noted). The solution was charged on a column of SP-Sephadex C-25 (2.5×30 cm). The column was rinsed with water (pH 3), and then the adsorbed band was eluted with a 0.3 mol/dm^3 NaCl solution adjusted to pH 3. A yellow band of tervalent cation was collected in a fraction. The effluent was diluted with a large amount of water (*ca.* 2000 cm^3, pH 4), and then poured onto a column of SP-Sephadex C-25 (2×20 cm). The adsorbed band was eluted with a 0.3 mol/dm^3 $NaClO_4$ solution adjusted to pH 3 with diluted $HClO_4$, whereupon one species was eluted and the other remained. The former was identified to be the known $[Co(tacn)_2]^{3+}$ species.[6] The remaining band was then eluted with a 0.3 mol/dm^3 NaCl solution (pH 3). The effluent was concentrated by a rotary evaporator at *ca.* 35 °C, with simultaneous removal of the eluent. To the final filtrate was added small amounts of 64% $HClO_4$ and solid $NaClO_4$, and the whole was kept in a refrigerator for a few days. The yellow crystals which deposited were collected and washed with water (pH 3). The crystals were dried *in vacuo*. The yield was *ca.* 30 mg. Found: C, 40.75; H, 3.80; N, 10.56%. Calcd for $[Co(tacn)(tri)](ClO_4)_3=CoC_{27}H_{30}N_6O_{12}Cl_3$: C, 40.39; H, 3.75; N, 11.02%. The product is explosive on heating.

A partial optical resolution was attained by means of a column chromatography (SP-Sephadex C-25, 2 cm×110 cm) by use of a 0.3 mol/dm^3 $Na_2[Sb_2(d\text{-tart})_2]$ solution as eluent.[7] The earlier eluted species was $(+)^{CD}_{500}[Co(tacn)(tri)]^{3+}$ isomer.

Measurements. The absorption and CD spectra were measured with a Hitachi 323 spectrophotometer and a JASCO J-40CS automatic recording spectropolarimeter, respectively.

Results and Discussion

The absorption and CD spectra of the $(+)^{CD}_{500}[Co(tacn)(tri)]^{3+}$ complex are shown in Fig. 1, with those of the related $(+)_{546}[Co(tri)_2]^{3+}$ and $(+)_{546}[Ni(tri)(H_2O)_3]^{2+}$ complexes. The absorption spectrum of the $[Co(tacn)(tri)]^{3+}$ exhibits a shoulder at *ca.* 21000 cm^{-1} ($\log\varepsilon\simeq2.5$), which is assignable to the first absorption band. The band is observed at a frequency higher by 1000 cm^{-1} than the corresponding band for the $[Co(tri)_2]^{3+}$ complex, indicating that the ligand field strength of TRI is weaker than that of TACN. An absorption band observed at 34000 cm^{-1} is assigned intra-ligand transition.[2] Both $(+)^{CD}_{500}[Co(tacn)(tri)]^{3+}$ and $(+)_{546}[Co(tri)_2]^{3+}$ exhibit a positive CD peak at the lowest frequency in the d-d absorption band region, in contrast to $(+)_{546}[Ni(tri)(H_2O)_3]^{2+}$ which shows no apparent CD peak. In the region of 33000—37000 cm^{-1}, the three complexes exhibit one or two intense CD peaks with negative sign. These bands

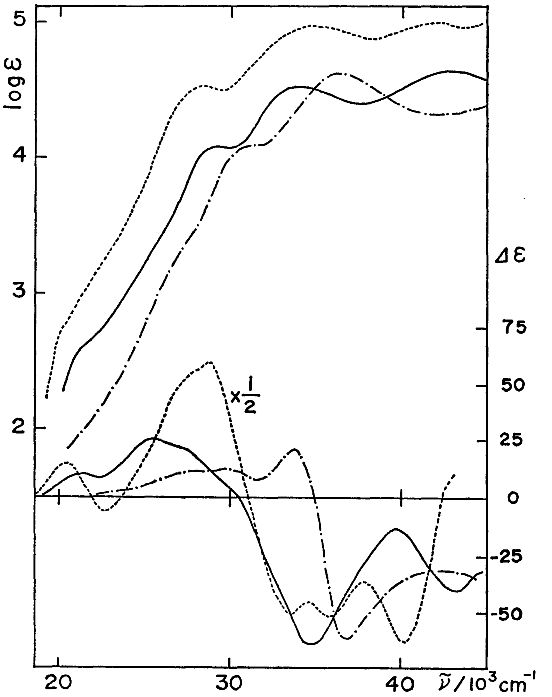

Fig. 1. Absorption and CD spectra.
——: $(+)^{\rm CD}_{500}$[Co(tacn)(tri)]$^{3+}$, ----: $(+)_{546}$[Co(tri)$_2$]$^{3+}$, —·—·—: $(+)_{546}$[Ni(tri)(H$_2$O)$_3$]$^{2+}$.

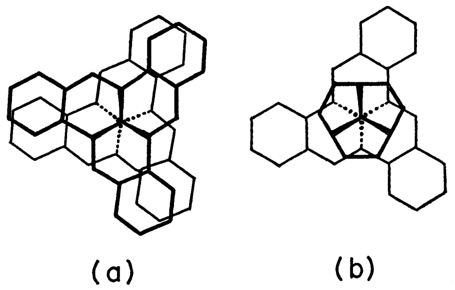

Fig. 2. Absolute configurations.
a): $(+)_{546}$[Co(tri)$_2$]$^{3+}$, b): $(+)^{\rm CD}_{500}$[Co(tacn)(tri)]$^{3+}$.

are considered to be associated with a benzene ring inclining against a –C=N– bond, as is seen in a styrene chromophore.[8] Therefore, it is concluded that these complexes have the same absolute configuration with respect to the TRI ligand, namely, the pitch of the benzene rings has the sense of a left-handed screw.[2] The absolute configuration of $(+)^{\rm CD}_{500}$[Co(tacn)(tri)]$^{3+}$ is predicted as shown in Fig. 2.

According to the X-ray analysis of $(+)_{546}$[Co(tri)$_2$]$^{3+}$,[2] there is a distortion around a threefold axis to give a twisted trigonal prism having the sense of a left-handed screw, due to a strong attractive interaction between two aromatic ligands. Wing and Eiss[2] have considered two sources of the metal-centered optical activity in the $(+)_{546}$[Co(tri)$_2$]$^{3+}$ complex; one is the arrangement of donor atoms distorted from octahedron, and another is structural features inherent in the TRI ligand such as a pitch of the benzene rings or a chiral arrangement of (benzene ring)–C=N– moieties. On the basis of the CD spectrum of $(+)_{546}$-[Ni(tri)(H$_2$O)$_3$]$^{2+}$, they have concluded that one TRI ligand is ineffective in generating dissymmetric environment around a metal ion and that the former source is the principal one in $(+)_{546}$[Co(tri)$_2$]$^{3+}$.

On the other hand, the present [Co(tacn)(tri)]$^{3+}$ complex exhibits a clear CD peak in the d-d absorption band region, like $(+)_{546}$[Co(tri)$_2$]$^{3+}$ does. Furthermore, the distortion around the threefold symmetry axis seems to be small in $(+)^{\rm CD}_{500}$[Co(tacn)-(tri)]$^{3+}$, on account of a weak interaction between the TACN and TRI ligands, which is considered to be repulsive rather than attractive. Consequently, the crystal field distortion is not regarded as the principal source for the metal-centered optical activity in the $(+)^{\rm CD}_{500}$[Co(tacn)(tri)]$^{3+}$ and $(+)_{546}$[Co(tri)$_2$]$^{3+}$ complexes. It is known[7] that the TACN chelate rings in [Co(tacn)$_2$]$^{3+}$ and [Co(gly)(NH$_3$)(tacn)]$^{2+}$ are flexible and the conformations are not fixed in an aqueous solution. Stereo models suggest that there is no preferential conformation of TACN in the [Co-(tacn)(tri)]$^{3+}$ complex. Therefore, the optical activity due to conformations of TACN is considered to be small. It is reasonable to consider that the TRI complexes gain some activity from the chiral sequence of the (benzene ring)–C=N– moieties through the dynamic coupling mechanism.[3] A helical arrangement of the six benzene rings in $(+)_{546}$[Co(tri)$_2$]$^{3+}$ (in a sense of a left-handed helix, Λ) is also ineffective in raising the apparent metal-centered optical activity.

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