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PREPARATION AND RESOLUTION OF THE *fac*-TRIS(2-AMINOETHYLDIMETHYLPHOSPHINE)COBALT(III) COMPLEX AND THE ABSOLUTE CONFIGURATION OF ITS $(+)_{589}$-ISOMER DETERMINED BY X-RAY ANALYSIS

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A new lemon-yellow *fac*-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]Br_3\cdot 3H_2O$ complex was prepared and resolved into enantiomers by SP-Sephadex column chromatography. The absolute configuration of the $(+)_{589}$-isomer was determined by the X-ray method to be Δ-configuration.

Little work has been reported on optically active cobalt(III) complexes containing phosphine ligands.[1] The title complex, $[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ will be one of the most useful complexes for comparing spectral properties of cobalt(III)-phosphines with those of cobalt(III)-ammines studied extensively. This letter deals with its preparation, resolution, and absorption and circular dichroism (CD) spectra and also with the absolute configuration of the $(+)_{589}$-isomer determined by the X-ray method.

2-Aminoethyldimethylphosphine was prepared from tetramethyldiphosphine[2] and aminoethylchloride. To liquid ammonia containing two equivalent moles of metallic sodium was added tetramethyldiphosphine with stirring in an atmosphere of nitrogen, followed by addition of one equivalent mole of aminoethylchloride hydrochloride. The liquid ammonia was evaporated off. From the residue the aminophosphine was obtained as colorless liquid by extracting with $CHCl_3$ and by removing the solvent *in vacuo*. The ligand was extremely air-sensitive, so that it was immediately used to prepare the complex without further purification.

To an N,N-dimethylformamide solution of *cis*-$[CoCl_2(en)_2]Cl$ (en=ethylenediamine) was added three equivalent moles of the ligand with stirring in an atmosphere of nitrogen. After 3 h the solution was diluted with a large amount of water and poured into a column of an SP-Sephadex C-25 ion exchanger. The adsorbed band was eluted with 0.4 mol/dm^3 NaBr and the eluate of the first yellow band was concentrated under reduced pressure to give lemon-yellow crystals of the complex. (yield: 34%) Optical resolution was achieved by SP-Sephadex C-25 column chromatography using 0.2 mol/dm^3 sodium $(+)_{589}$-tartratoantimonate(III) as an eluent. From the fast and the slowly eluted fractions $(-)_{589}$- and $(+)_{589}$-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]Br_3\cdot 3H_2O$ were obtained, respectively. Analytical data of the racemic and optically active complexes are in good accord with the calculated values as the composition given. The complex is very stable in both the solid and solution states.

The crystal data of the $(+)_{589}$-isomer are as follows: orthorhombic, $P2_12_12_1$, a = 26.501(8), b = 9.573(4), c = 10.081(5)Å, Z = 4, D_c = 1.73, D_m = 1.73 gcm^{-3}. Intensity data were collected on a diffractometer with MoKα radiation. 1924 independent reflections with $I > 2\sigma(I)$ were selected. The structure was solved by the heavy-atom method and refined by a least-squares method to R = 6.6%. Figure 1 shows the structure of the complex ion. The three phosphorus atoms are arranged in the facial manner and the absolute configuration of the $(+)_{589}$-isomer is Δ. The chelate rings are of the λ-gauche conformation and hence the complex ion can be designated as the lel_3 structure, although the NCCP torsion angles (44.3 ~ 53.3°) are smaller than those of 1,2-diamine chelate complexes of cobalt(III) (~ 55°).

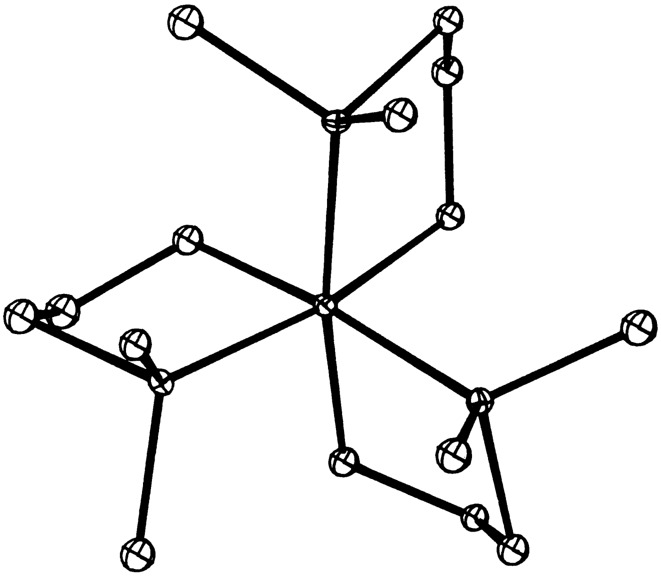

Figure 1. View of the $(+)_{589}$-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ ion.

Figure 2 compares the absorption and CD spectra of the $(-)_{589}$-Λ-isomer with those of Λ-$[Co(en)_3]^{3+}$.$^{3)}$ The aminophosphine complex shows two absorption bands at 23700 cm^{-1} (ε = 474) and 30200 cm^{-1} (ε = 229) which can be assigned to the first and the second absorption bands, respectively. Both bands are located at high wavenumbers and have fairly strong intensity compared with the corresponding bands of the en complex. The energy difference between the first and the second absorption maxima is considerably smaller than that of the en complex. The B (Racah's parameter of interelectronic repulsion) values obtained from the spectra ($\tilde{\nu}_{II} - \tilde{\nu}_{I} = 16B$) are 406 and 506 cm^{-1} for the aminophosphine and en complexes, respectively. The value of 406 cm^{-1} is as small as that of $[Co(CN)_6]^{3-}$ (416 cm^{-1}).$^{4)}$ Thus, it is concluded that 2-aminoethyldimethylphosphine coordinates to a cobalt(III) ion with strong covalent character.

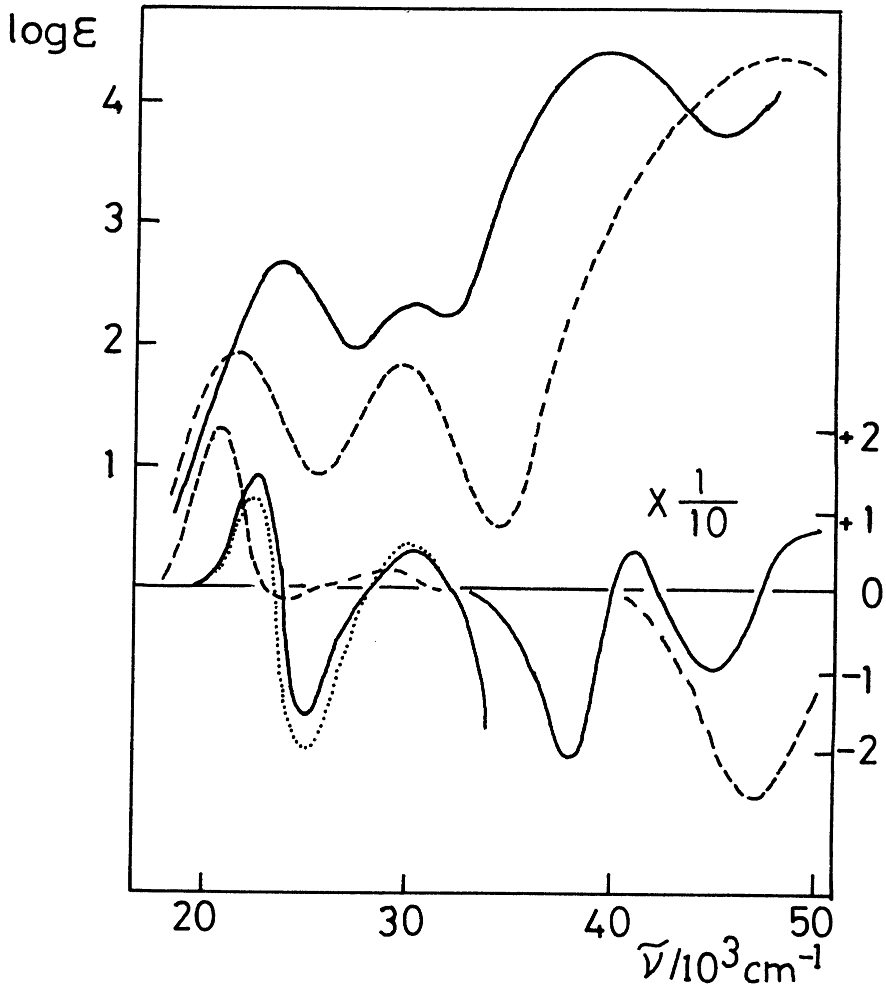

Figure 2. Absorption and CD spectra of $(-)_{589}$-Λ-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ in water (———) and in 0.1 mol/dm^3 PO_4^{3-} (·····), and $(+)_{589}$-Λ-$[Co(en)_3]^{3+}$ in water (-----).

The CD spectrum of $(-)_{589}$-Λ-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ in an aqueous solution shows a positive ($\Delta\varepsilon$ = +1.45, 22300 cm^{-1}) and a negative ($\Delta\varepsilon$ = -1.56, 24800 cm^{-1}) CD band of almost equal strength in the region of the first absorption band as seen in Figure 2. This pattern is similar to that of the Λ-$[Co(en)_3]^{3+}$ ion, although the strength of the negative CD band is considerably stronger than that of the corresponding CD band of the en complex. The positive CD component at lower wavenumbers of the aminophosphine complex diminishes its strength on addition of phosphate ions, while the negative CD component at higher wavenumbers enhances. The same effect of oxoanions on the CD strength is well known to occur in the positive(E) and the negative(A_2) CD components of the Λ-$[Co(en)_3]^{3+}$ ion.$^{5)}$ Therefore, the positive and the negative CD components of the Λ-aminophosphine complex can be assigned to E and A_2 symmetry (D_3 approximation), respectively. This result agrees with that a Λ-tris(diamine)cobalt(III) complex shows a positive CD component with E symmetry in the region of the first absorption band.

The aminophosphine complex gives a strong absorption band at 39800 cm^{-1} (ε = 26400) which can be assigned to the charge transfer transition from the ligand to the Co(III). Corresponding to this band, the Λ-complex exhibits three CD bands; $\Delta\varepsilon$ = -20.4 (38000 cm^{-1}), +4.72 (41000 cm^{-1}), and -9.09 (44500 cm^{-1}). Of those bands, the one at the lowest wavenumbers has the negative sign. The $[Co(en)_3]^{3+}$ and other tris(diamine)cobalt(III) complexes in the Λ-configuration are known to show a negative CD band at the lowest wavenumbers in the charge transfer region.[3,6] The CD spectrum of the $[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]^{3+}$ complex exhibits similar characteristics to those of diamine complexes.

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