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THE ABSOLUTE CONFIGURATION OF THE $(-)_{589}$-ACETYLACETONATO-BIS(TRIMETHYLENEDIAMINE)COBALT(III) ION

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The crystal structure of $(-)_{589}$-[Co acac tn_2][As-(+)-tart]$_2$ H_2O has been determined by the X-ray method. The absolute configuration of the complex cation can be nenoted as Δ . A simple empirical rule, proposed by Mason et al., relating the sign of the Cotton effect of a particular electronic transition to the absolute configuration of the metal complex seems to hold in this case.

The $(-)_{589}$-$[Co(NCS)_2tn_2]^+$ complex has already been determined to be of the Λ configuration by means of the X-ray diffraction method. 1) As a part of our structural investigations on the bis(trimethylenediamine)cobalt(III) complexes, we will report here the absolute configuration of the $(-)_{589}$-[Co acac $tn_2]^{2+}$ complex.

[Co acac tn_2]I_2 was prepared by the reaction of trans-$[CoCl_2tn_2]Cl$ with acetylacetone in 1 N aqueous solution of NaOH. Just as in the case of [Co acac $en_2]^{2+}$, 2) the arsenic(III) (+)-tartrate anion was used as the resolving agent and the crystals of $(-)_{589}$-[Co acac tn_2][As-(+)-tart]$_2$ H_2O suitable for the X-ray work were obtained. Crystal data: monoclinic, space group $P2_1$; a = 12.02(1)Å, b = 13.73(2)Å, c = 9.02(1)Å, β = 107.4(3)°; Z = 2. Multiple-film, equi-inclination Weissenberg photographs were taken with NiKα radiation (λ = 1.6591Å) from h0l to h7l and from 0kl to 6kl. The intensities of 2241 reflections were estimated visually and the usual corrections were applied. The structure was determined by the conventional Fourier technique and refined by a least-squares method to an R factor of 0.100. The assignment of the absolute configuration for the complex cation was made on the basis of the known configuration of the (+)-tartrate ion.

The perspective view of the complex cation is presented in Fig. 1. The type of its configuration can be denoted as Δ. According to Mason et al., the rotational strengths of the E_a transitions of $\Lambda(+)_{589}$-[Co $en_3]^{3+}$ 3) and $\Lambda(-)_{589}$-[Co $tn_3]^{3+}$ 4) are positive. Therefore, the $(+)_{589}$-[Co acac $en_2]^{2+}$ complex was concluded to have the Λ configuration, 5) since the complex shows a single CD band of the positive sign in the visible region and this can be regarded as derived mainly from the E_a component of the first absorption band of $\Lambda(+)_{589}$-[Co $en_3]^{3+}$. 5) On the contrary, the Cotton effect of the $(-)_{589}$[Co acac $tn_2]^{2+}$ cation in this region is negative and indicative of the Δ configuration, as can be seen in Fig. 2. This spectral assignment is quite compatible with the result in the present X-ray study. Recently, however, Judkins and Royer 6) identified the negative CD band of $\Lambda(-)_{589}$-[Co $tn_3]^{3+}$ in the region of the octahedral T_{1g} transition as due to the E_a component. If their assignment of the CD band is correct, the Λ configuration should be given to $(-)_{589}$-[Co acac $tn_2]^{2+}$, and this is inconsistent with the result of the present X-ray work. Furthermore, Piper's model for optical activity 7) is not supported in this case.

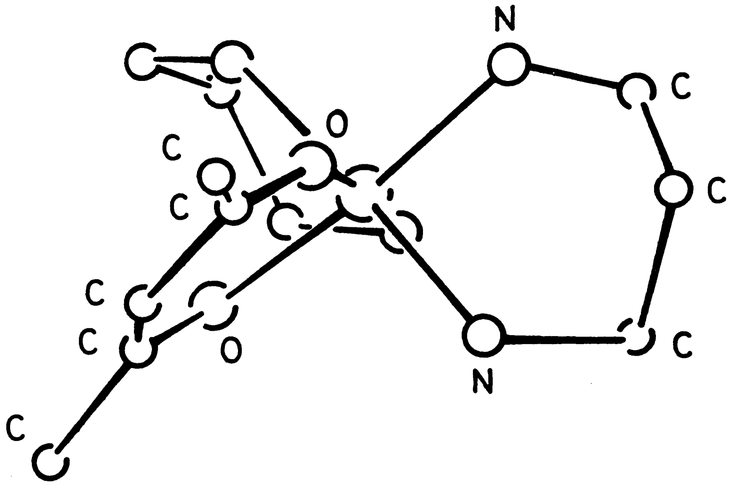

Fig. 1. The absolute configuration of $(-)_{589}$-[Co acac $tn_2]^{2+}$.

The two diamine chelate rings are of the chair form. The average distance of Co-N (1.98Å) compares well with those found in $(-)_{589}$-[Co tn_3] Br_3 H_2O (2.00Å) 8) and trans-[Co$(NO_3)_2tn_2]NO_3$ (1.99Å). 9) The N-Co-N angle is 96°, slightly larger than that (94°) observed in $(-)_{589}$-[Co $tn_3]Br_3$ H_2O. 8) The Co-acac chelate ring is almost planar and the maximum deviation of the atom from the mean plane is 0.08Å. The Co-O bond is 1.89Å, and the O-Co-O angle in the chelate ring is 96°.

The geometry of [As-(+)-tart]$_2^{2-}$ is identical with that of [Sb-(+)-tart]$_2^{2-}$.$^{1)}$ The dimeric structure is built up of the two tetradentate tartrate ions and the two arsenic atoms. The two kinds of As-O distances are found as in the case of [Sb-(+)-tart]$_2^{2-}$, being equal to 1.81Å in the one (alcohol group) and to 2.04Å in the other (carboxyl group).

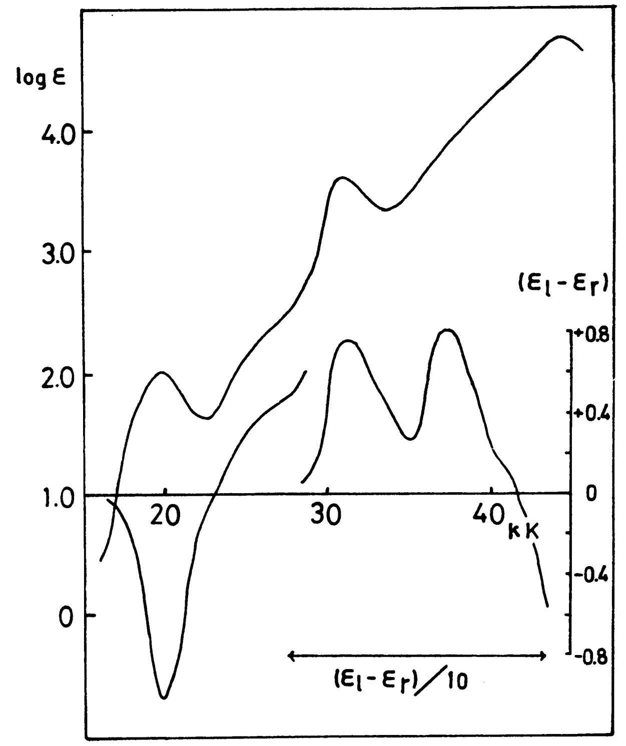

Fig. 2. Circular dichloism, and absorption spectrum of $(-)_{589}$-[Co acac tn_2]I_2.

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