The Crystal Structure of $(-)_{589}$-Dinitrobis(ethylenediamine)cobalt(III) $(+)_{589}$-Bis(malonato)ethylenediaminecobaltate(III)

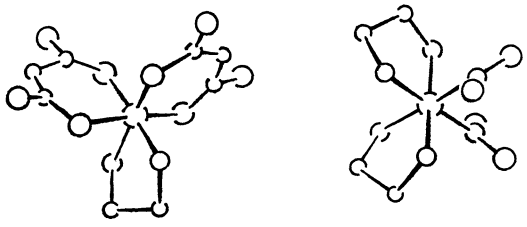
Keiji MATSUMOTO and Hisao KUROYA

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

(Received September 10, 1971)

The CD and ORD spectra of $(+)_{589}$-[Co mal_2en]$^-$ (mal=malonate ion) were studied by Douglas and his co-workers.[1] They identified the lowest-frequency CD peak with a negative sign as the *A* component and gave it the *Δ* configuration by making use of Mason's empirical rule.[2] Recently, Judkins and Royer[3] confirmed experimentally Piper's prediction[4] that the sign of the Cotton effect is reversed as the coordination angle(θ) in the chelate ring goes from less than to greater than 90°. This was, however, not taken into account by Douglas *et al.* in applying Mason's rule to $(+)_{589}$-[Co mal_2en]$^-$. In order to reexamine directly the absolute configuration of the complex anion, we have carried out a crystal-structure analysis of $(-)_{589}$-[Co$(NO_2)_2en_2$] $(+)_{589}$-[Co mal_2en].[5,6]

The crystal structure has been determined from the three-dimensional photographic data. The structure was refined by a least-squares method to an *R* factor of 0.101 for 1442 reflections. The absolute configurations of the complex anion as well as of the cation were determined by means of the anomalous dispersion effect of the cobalt atoms for Cu$K\alpha$ radiation. Crystal data: triclinic, space group $P\bar{1}$; a=10.58(2), b=7.98(1), c=7.99(1) Å, α=122.8(2), β=105.3(2), γ=74.6(2)°; Z=1 (D_m=1.81, D_c=1.82 g·cm^{-3}); μ=35.9 cm^{-1} for Ni$K\alpha$.



$(+)_{589}$-[Co mal_2en]$^-$ $(-)_{589}$-[Co$(NO_2)_2en_2$]$^+$

Fig. 1. The absolute configurations of the complex ions

The perspective drawings of $(-)_{589}$-[Co$(NO_2)_2en_2$]$^+$ and $(+)_{589}$-[Co mal_2en]$^-$ are presented in Fig. 1. Each of the complex ions has an approximate two-fold axis. The ethylenediamine ligands in both complexes are of the *ob*-conformation. The two six-membered malonate chelate rings are nearly planar, the O–Co–O angle being 96° and greater than the N–Co–N angle in the cobalt(III)-trimethylenediamine chelate ring.[7]

The absolute configuration of $(-)_{589}$-[Co$(NO_2)_2en_2$]$^+$ can be denoted as *Δ* in accordance with the assignment made by those investigating ORD[8] and CD.[2,9,10] It is notable that an empirical rule connecting the absolute configuration of a metal complex and the sign of the Cotton effect of the $^1A_1 \rightarrow A$ electronic transition holds for this complex.

The absolute configuration of $(+)_{589}$-[Co mal_2en]$^-$ has been determined as of *Δ* and is in agreement with the assignment made by Douglas *et al.* Their assignment of the *A* component seems to be correct. However, if Piper's prediction still holds in the case of the trismalonatocobalt(III) complex, the E_a component of $\Delta(+)_{589}$-[Co ox_3]$^{3+}$(θ<90°) and that of *Δ* trismalonatocobalt(III) (θ>90°, possibly) will be opposite in sign. The *A* component of the bismalonatocobalt(III) complex derives mainly from the E_a component of the trismalonatocobalt(III) complex.[2] Consequently, the sign of the *A* component of $\Delta(+)_{589}$-[Co mal_2en]$^-$ should be the reverse of that of the E_a component of $\Delta(+)_{589}$-[Co ox_3]$^{3-}$, though these two complexes have the same configuration. Therefore, the assignment of the *A* component by Douglas *et al.* is not entirely satisfactory.

1) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

2) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, **1965**, 5094.

3) R. R. Judkins and D. J. Royer, *Inorg. Nucl. Chem. Lett.*, **6**, 305 (1970).

4) T. S. Piper and A. Karipides, *Mol. Phys.*, **5**, 475 (1962).

5) F. P. Dwyer, I. K. Reid, and F. L. Garvan, *J. Amer. Chem. Soc.*, **83**, 1285 (1961).

6) Recently, the *Δ* configuration of $(+)_{589}$-[Co mal_2en]$^-$ has been worked out for Na$(+)_{546}$-[Co mal_2en]·2H_2O by K. R. Butler and M. R. Show [*Chem. Commun.*, **1971**, 550]. However, we became aware of it after we had submitted the present paper to the Chemical Society of Japan.

7) Y. Saito, T. Nomura, and F. Marumo, This Bulletin, **41**, 530 (1968).

8) T. E. McDermott and A. M. Sargeson, *Aust. J. Chem.*, **16**, 334 (1963).

9) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, **1964**, 1368.

10) G. A. Barclay, E. Goldschmied, N. E. Stephenson, and A. M. Sargeson, *Chem. Commun.*, **1966**, 540.