

The Absolute Configuration of $(-)_589$ -*trans,trans*-Dichlorobis- (*N*-methylethylenediamine)cobalt(III) Perchlorate Hemihydrate

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Summary The absolute configuration of the complex $(-)_589$ -*trans,trans*-[Co meen₂Cl₂]ClO₄·½H₂O has been determined and its solution circular dichroism compared with that for $(+)_589$ -*trans*-[Co trien Cl₂]ClO₄.

THE preparation of $(-)_589$ -*trans,trans*-dichlorobis(*N*-methylethylenediamine)cobalt(III) perchlorate, [Co meen₂Cl₂]ClO₄ has been described, along with its visible and u.v. absorption and c.d. spectra.¹ An analysis of the c.d. curve in the region of the first ligand-field band compared with that for the $(+)_589$ -*trans*-dichlorotriethylenetetraminecobalt(III) ion of known configuration,² allowed a tentative assignment for the configuration of the *N*-methylethylenediamine complex. To establish the absolute configuration of the asymmetric nitrogen-centres, the crystal structure of $(-)_589$ -*trans,trans*-[Co meen₂Cl₂]ClO₄·½H₂O has been determined using three-dimensional data collected at room temperature using a Nonius integrating Weissenberg camera and Cu-*K*_α X-radiation. This isomer crystallizes in space group *D*₂³-*P*2₁2₁2 of the orthorhombic system, with *a* = 10·72,

b = 15·02, *c* = 9·29 Å, and *Z* = 4. The intensities of 691 independent reflections, including more than 100 Bijvoet pairs, have been included in least-squares refinements leading to a conventional *R*-factor of 9·8%. When the signs of all positional parameters were reversed the resulting antimeric configuration would not refine beyond an *R*-factor of 14·4%. This difference is significant and results from the rigorous application³ of corrections for the anomalous scattering of Cu-*K*_α X-radiation by cobalt and chlorine atoms. For many Bijvoet pairs pronounced intensity differences were observed and, in every case, were confirmed by the calculations. Consistent differences of this magnitude cannot be compromised by adsorption effects and, for the small crystal used in the experiments, calculations have shown this effect to be negligible. The absolute configuration was deduced by relating the calculated result to the geometry of the recording camera following Bijvoet,⁴ and is given in Figure 1.

Beside the cation, which exhibits no crystallographic symmetry, there are two perchlorate anions and one water

molecule, all centred on two-fold rotation axes, in the crystal chemical unit. The perchlorate oxygen atoms exhibit disorder.⁵

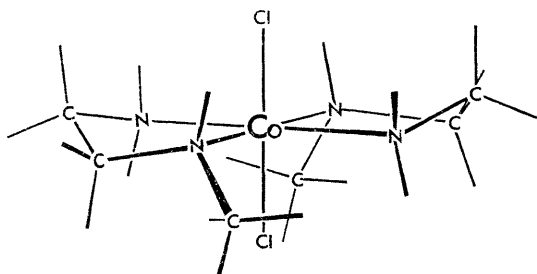


FIGURE 1. Absolute configuration of the $(-)$ ₅₈₉-*trans,trans*-[Co meen₂Cl₂]⁺ ion.

The structural analysis confirms the previous assignment of geometrical configuration to the ion.¹ The Cl⁻ ions are *trans* to each other and so are the methyl groups. However, the absolute configuration is the mirror image of that deduced by the previous analysis of the c.d. curves¹ where it was assumed the "effective" C₂ axis did not coincide with the real C₂ axis. Figure 2 gives c.d. spectra for the two complexes having the same absolute configuration about the nitrogen centres. The striking dissimilarity between the curves points to the hazards in the interpretation of c.d. spectra, even for complexes which have similar visible absorption spectra and chromophores which have effectively D_{4h} symmetry. A difference between the $(+)$ ₅₈₉-*trans*-[Co trien Cl₂]⁺ and $(-)$ ₅₈₉-*trans,trans*-[Co meen₂Cl₂]⁺ ions resides in different orientations of their C₂ axes and if the transition A → A(C₂) in both instances gives a negative c.d. band then the analysis of the observed dichroism could be consistent with the known configurations. Although we can be sure for $(-)$ ₅₈₉-*trans,trans*-[Co meen₂Cl₂]⁺ that the A → A transition is negative (*ca.*

465 nm.) it is not certain which is the A and which the B symmetry transition [corresponding to E(D_{4h})] in the c.d. curve for the $(+)$ ₅₈₉-*trans*-[Co trien Cl₂]⁺ ion, so that this proposal cannot be tested.

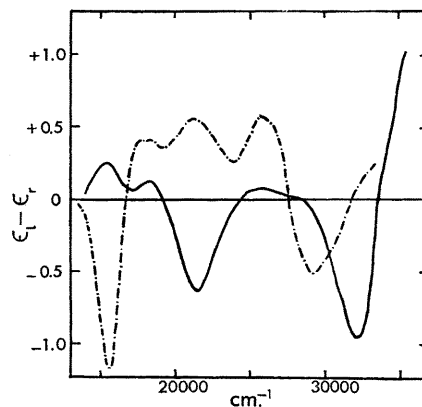


FIGURE 2. C.d. spectra for $(-)$ ₅₈₉-*trans,trans*-RR-[Co meen₂Cl₂]-ClO₄ (—) and $(+)$ ₅₈₉-*trans*-RR-[Co trien Cl₂]-ClO₄ (-----), in 10⁻³M-HClO₄.

The conformation of the chelate rings in the lattice orientate the methyl groups in the "equatorial" condition as opposed to the mirror image conformation which requires the methyl group "axial." This is consistent with the conformational analysis of ions of this type.¹ In addition, the method of preparation requires $(+)$ ₅₈₉-*trans,trans*-[Co meen₂(NO₂)₂]⁺ to have at least the same absolute configuration about the asymmetric nitrogen-centres as the $(-)$ ₅₈₉-*trans*-dichloro-complex.

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¹ D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1968, 7, 915.

² D. A. Buckingham, P. A. Marzilli, A. M. Sargeson, S. F. Mason, and P. G. Beddoe, *Chem. Comm.*, 1967, 433.

³ J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, 17, 781.

⁴ A. F. Peerdman and J. M. Bijvoet, *Acta Cryst.*, 1956, 9, 1012.

⁵ D. A. Buckingham and W. T. Robinson, to be published.