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THE NOVEL TYPE STRUCTURE OF Δ-*CIS*-α-[(1R,2R)-N,N'-BIS(2-PYRIDYLMETHYL)-1,2-CYCLOHEXANEDIAMINE]DICHLOROCHROMIUM(III) CATION

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The molecular structure of Δ-*cis*-α-[$CrCl_2$(RR-picchxn)]$^+$ was determined by the X-ray structure analysis (RR-picchxn = (1R,2R)-N,N'-bis(2-pyridylmethyl)-1,2-cyclohexanediamine). The terminal chelate ring formed by the coordination of *equatorially-oriented* substituent on the secondary nitrogen atom is of novel type.

The ruby-red crystals of Δ-*cis*-α-[$CrCl_2$(RR-picchxn)]ClO_4[1] were grown from a mixture of acetone and ethanol. They crystalize in space group $P2_12_12_1$, with a = 15.13(1), b = 14.62(2), and c = 11.55(1)Å, Z = 4. The structure was determined by X-ray structure analysis with MULTAN78,[2] μ[MoKα] = 0.818 mm^{-1}.

Bond distances and angles are given in Tables 1 and 2, respectively. The stereoview of the complex cation is shown in Fig. 1. The complex takes Δ-*cis*-α configuration. The absolute configuration was determined during the course of synthesis from the fact that the two asymmetric carbon atoms adopt the (R)-configuration, without using the anomalous dispersion technique. The configuration coincides with that assigned from the CD data.[1] The two terminal chelate rings take the very rare type structure in which the *equatorially-oriented* substituents on the secondary nitrogen atoms are coordinated at the apical positions. In this structure, the steric repulsion between the methylene proton of terminal chelate ring and the hydrogen atom adjacent to the asymmetric carbon atom of cyclohexanediamine ring is less than that in the corresponding Λ-*cis*-α structure. The isomer of Λ-*cis*-α structure was obtained for R-picpn (Δ for S-picpn)[3] but not for the present RR-picchxn ligand[1] (S-picpn = (S)-N,N'-bis(2-pyridylmethyl)propylenediamine).

In Fig. 2 are shown the Newmann projections of the present complex and those of Δ-*cis*-α-[$CrCl_2$(S-picpn)]$^+$. The methylene carbon atoms in the terminal chelate rings, C(6) and C(9), take larger angle from the apical nitrogen atoms than in the Δ-*cis*-α-[$CrCl_2$(S-picpn)]$^+$ complex. The difference shows the novelty of the present Δ-*cis*-α-RR (Λ-*cis*-α-SS) complex clearly.

Table 1. Bond distances (Å) and their standard deviations (in parenthesis).

Cr-Cl(1) 2.32(1)	N(3)-C(1) 1.36(3)	C(5)-C(6) 1.54(3)	C(9)-C(10) 1.49(3)	C(14)-N(4) 1.27(3)
Cr-Cl(2) 2.33(1)	C(1)-C(2) 1.38(3)	C(6)-N(1) 1.52(3)	C(10)-N(4) 1.33(3)	C(8)-C(15) 1.59(4)
Cr-N(1) 2.11(2)	C(2)-C(3) 1.43(3)	N(1)-C(7) 1.54(2)	C(10)-C(11) 1.51(3)	C(15)-C(16) 1.51(5)
Cr-N(2) 2.12(3)	C(3)-C(4) 1.37(3)	C(7)-C(8) 1.51(3)	C(11)-C(12) 1.28(4)	C(16)-C(17) 1.51(5)
Cr-N(3) 2.06(2)	C(4)-C(5) 1.42(3)	C(8)-N(2) 1.47(3)	C(12)-C(13) 1.49(4)	C(17)-C(18) 1.62(4)
Cr-N(4) 2.12(2)	C(5)-N(3) 1.35(2)	N(2)-C(9) 1.47(3)	C(13)-C(14) 1.42(3)	C(18)-C(7) 1.53(3)

Table 2 Several bond angles (in degree) and their standard deviations (in parenthesis).

Cl(1)-Cr-Cl(2) 95.6(2)	N(1)-Cr-N(2) 81.8(6)	Cr-N(2)-C(8) 109.3(11)
Cl(1)-Cr-N(1) 170.1(5)	N(1)-Cr-N(3) 97.8(6)	Cr-N(2)-C(9) 105.8(14)
Cl(1)-Cr-N(2) 81.8(6)	N(1)-Cr-N(4) 98.2(6)	Cr-N(3)-C(1) 128.9(13)
Cl(1)-Cr-N(3) 92.8(5)	N(2)-Cr-N(3) 97.8(6)	Cr-N(3)-C(5) 114.2(12)
Cl(1)-Cr-N(4) 89.3(5)	N(2)-Cr-N(4) 78.3(6)	Cr-N(4)-C(10) 111.1(13)
Cl(2)-Cr-N(1) 90.5(5)	N(3)-Cr-N(4) 175.7(6)	Cr-N(4)-C(14) 125.1(14)
Cl(2)-Cr-N(2) 167.2(5)	Cr-N(1)-C(6) 106.8(11)	C(6)-N(1)-C(7) 110.2(14)
Cl(2)-Cr-N(3) 90.8(5)	Cr-N(1)-C(7) 109.3(12)	C(8)-N(2)-C(9) 113.7(17)
Cl(2)-Cr-N(4) 92.8(5)		

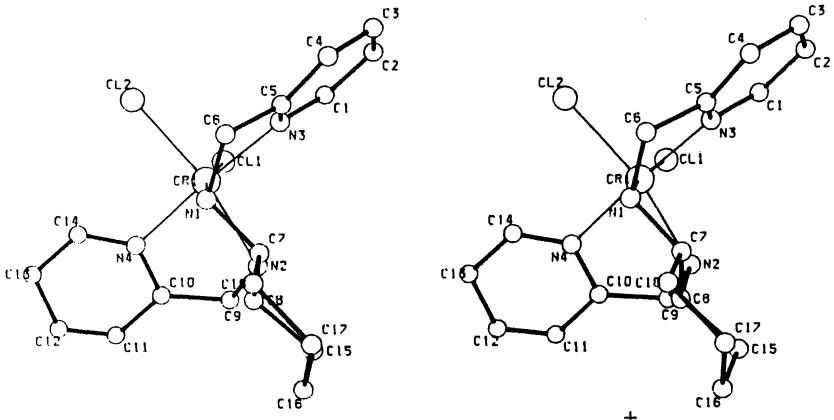
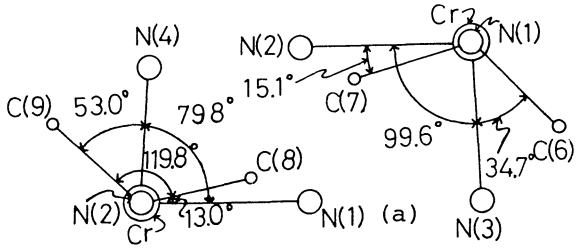


Fig. 1 Stereoview of Λ-*cis*-α-$[CrCl_2(SS\text{-picchxn})]^+$ and the numberings of the atoms drawn by PLUTO.[4] The absolute configuration is reversed for comparison to the structure of Δ-*cis*-α-$[CrCl_2(S\text{-picpn})]^+$.[3]



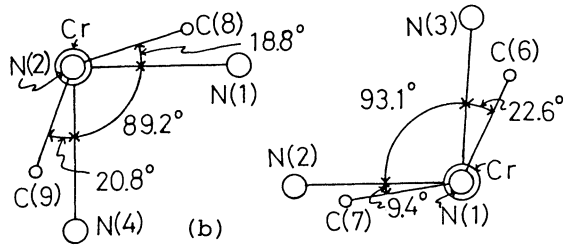


Fig. 2 The Newmann projections of a) Λ-*cis*-α-$[CrCl_2(SS\text{-picchxn})]^+$ and b) Δ-*cis*-α-$[CrCl_2(S\text{-picpn})]^+$.[3]

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