The Molecular Structure of Δ-*cis*-α-[(*S*)-*N*,*N*′-Bis(2-pyridylmethyl)-propylenediamine]dichlorochromium(III) Chloride

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Synopsis. The molecular structure of Δ-*cis*-α-[$CrCl_2$-(*S*-picpn)]$^+$ (*S*-picpn=(*S*)-*N*,*N*′-bis(2-pyridylmethyl)propylenediamine) was determined by X-ray analysis, the absolute configuration being confirmed to coincide with that assigned from the circular dichroism spectrum.

Two diastereomers, $(+)^{CD}_{600}$ and $(-)^{CD}_{600}$ ones of *cis*-α-[$CrCl_2$(*S*-picpn)]$^+$ complex (*S*-picpn=(*S*)-*N*,*N*′-bis(2-pyridylmethyl)propylenediamine), were isolated and their absolute configurations assigned from the circular dichroism (CD) spectra.[1] The present note deals with the X-ray structure analysis of a chloride of the more stable isomer, $(+)^{CD}_{600}$ one, which has been assigned to a Δ configuration from its CD spectrum.

Experimental

Ruby-red needle-like single crystals suitable for X-ray analysis were prepared by slow evaporation of an aqueous solution of the complex $(+)^{CD}_{600}$-[$CrCl_2$(*S*-picpn)]Cl at room temperature. Systematic absence indicated the monoclinic space group $P2_1$. Unit cell dimensions obtained by least-squares refinement of the setting angles of 11 reflections measured on a diffractometer were a=8.46 (2), b=15.68 (1), c=7.20 (1) Å and β=103.6 (1) °. The observed density 1.48 g cm^{-3} (by flotation in benzene-carbon tetrachloride) coincides with the calculated value 1.48 g cm^{-3} for Z=2. A crystal of the dimension 0.36×0.15×0.11 mm was used for the intensity measurement. Intensities were measured on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). The θ—2θ scan mode with a scan speed of 4 °min^{-1} in 2θ was employed. The scan range was calculated to be (1.0+0.35 tanθ)°. Intensities of 1704 independent reflections were collected in the range $1.0 \leq 2\theta \leq 50.0°$. Of these reflections 209 were measured as $|F_o|=0.0$. The intensities were corrected for Lorentz and polarization factors. No absorption correction was made [μ(Mo $K\alpha$)=1.072 mm^{-1}].

The structure was solved by the heavy atom method. The positions of chromium and two coordinated chlorine atoms were determined from a Patterson map. An electron density map based on the phases calculated from these atomic parameters revealed all the non-hydrogen atoms. The parameters were refined by the block-diagonal least-squares program HBLS-5,[2] with anisotropic thermal factors. The reliability factors $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $Rw=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0.077 and 0.088, respectively, for 1495 non-zero reflections. The final weighting scheme for minimization of $\sum w(|F_o|-|F_c|)^2$ was $w=[\sigma^2(F_o)+0.00022|F_o|+0.00357|F_o|^2]^{-1/2}$. The positions of the hydrogenes were not determined.

Results and Discussion

Final atomic parameters, bond distances and angles are given in Tables 1, 2, and 3, respectively. The F_o-F_c data and final thermal parameters are deposited as Document No. 8119 at the Office of the Chemical Society of Japan. The quadridentate ligand takes an α configuration, the two chloro ligands occupying *cis* positions. There is no significant difference between the distances of chromium to amine nitrogens and chromium to pyridine nitrogens. Angles N(1)–Cr–N(2) of the central chelate ring and Cl(1)–Cr–Cl(2) are 83.9° and 95.1°, respectively, the coordination geometry being slightly distorted from a regular octahedron.

A stereoscopic view of the complex cation drawn by PLUTO[4] is shown in Fig. 1. The absolute configuration of the complex was determined during the course of synthesis from the fact that the asymmetric carbon atom C(8) adopts the (*S*)-configuration,[1] without using the anomalous dispersion technique. The Δ configuration coincides with that assigned from the CD data.[1]

The least-squares planes and the dihedral angles between the planes are given in Table 4. The two

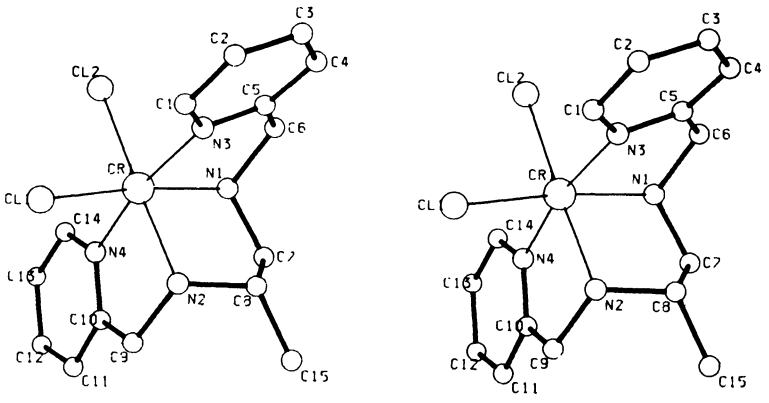

Fig. 1. Stereoview of the complex cation Δ-*cis*-α-[$CrCl_2$(*S*-picpn)]$^+$ and the numbering scheme of the atoms.

Table 1. Final positional parameters and their standard deviations (in parentheses)

	x	y	z	B_{eq}[a)]/Å^2
Cr	0.1947(2)	0	0.4004(2)	1.60
Cl(1)	0.1647(4)	0.0850(2)	0.1363(4)	2.82
Cl(2)	0.4313(3)	−0.0645(2)	0.3632(5)	2.93
Cl(3)	−0.1864(6)	0.2333(2)	0.3428(7)	6.21
N(1)	0.1980(11)	−0.0676(7)	0.6457(13)	2.85
N(2)	−0.0217(10)	0.0481(15)	0.4433(12)	1.70
N(3)	0.3300(10)	0.0837(6)	0.5937(14)	2.82
N(4)	0.0400(11)	−0.0916(6)	0.2499(13)	2.27
C(1)	0.3756(17)	0.1631(8)	0.5510(20)	4.00
C(2)	0.4783(17)	0.2090(10)	0.6928(22)	4.66
C(3)	0.5314(17)	0.1773(11)	0.8762(22)	4.96
C(4)	0.4811(15)	0.0980(10)	0.9181(20)	4.23
C(5)	0.3862(13)	0.0497(8)	0.7721(17)	2.79
C(6)	0.3415(15)	−0.0407(9)	0.8040(16)	3.09
C(7)	0.0371(15)	−0.0578(8)	0.6997(18)	3.06
C(8)	−0.0258(13)	0.0328(7)	0.6473(15)	2.30
C(9)	−0.1619(12)	0.0139(7)	0.2928(15)	2.29
C(10)	−0.1181(12)	−0.0722(7)	0.2224(15)	2.15
C(11)	−0.2387(16)	−0.1261(9)	0.1180(19)	3.53
C(12)	−0.1951(17)	−0.2015(10)	0.0404(23)	4.85
C(13)	−0.0275(17)	−0.2201(8)	0.0687(21)	3.92
C(14)	0.0854(16)	−0.1649(8)	0.1794(17)	3.03
C(15)	−0.1933(15)	0.0475(10)	0.6921(17)	3.60

a) B_{eq} is calculated by the method of Hamilton.[3)]

Table 2. Bond distances (Å) and their standard deviations (in parentheses)

Cr–Cl(1)	2.286(3)	C(6)–N(1)	1.52(2)
Cr–Cl(2)	2.314(4)	N(1)–C(7)	1.51(2)
Cr–N(1)	2.06(1)	C(7)–C(8)	1.53(2)
Cr–N(2)	2.07(1)	C(8)–C(15)	1.54(2)
Cr–N(3)	2.06(1)	C(8)–N(2)	1.50(1)
Cr–N(4)	2.07(1)	N(2)–C(9)	1.51(1)
N(3)–C(1)	1.36(2)	C(9)–C(10)	1.53(2)
C(1)–C(2)	1.38(2)	C(10)–C(11)	1.40(2)
C(2)–C(3)	1.38(2)	C(11)–C(12)	1.39(2)
C(3)–C(4)	1.37(2)	C(12)–C(13)	1.42(2)
C(4)–C(5)	1.39(2)	C(13)–C(14)	1.39(2)
C(5)–N(3)	1.37(2)	C(14)–N(4)	1.35(2)
C(5)–C(6)	1.50(2)	N(4)–C(10)	1.34(1)

terminal chelate rings take distorted λ envelope conformations. The two pyridine rings are nearly planar within error and make an angle 75.9° with each other. The two planes P1 and P3 are nearly perpendicular to plane P2. The central chelate ring CrN(1)C(7)C(8)N(2) has a distorted δ conformation with an equatorial methyl carbon C(15), carbon C(8) being more deviated than C(7) from plane P2.

Table 3. Bond angles (in degrees) and their standard deviations (in parentheses)

Cl(1)–Cr–Cl(2)	95.1(1)	N(3)–C(1)–C(2)	118.2(13)
Cl(1)–Cr–N(1)	172.7(3)	C(1)–C(2)–C(3)	121.8(15)
Cl(1)–Cr–N(2)	89.0(3)	C(2)–C(3)–C(4)	119.1(15)
Cl(1)–Cr–N(3)	97.3(3)	C(3)–C(4)–C(5)	119.0(14)
Cl(1)–Cr–N(4)	92.1(3)	C(4)–C(5)–N(3)	120.6(12)
Cl(2)–Cr–N(1)	92.1(3)	C(5)–N(3)–C(1)	121.0(11)
Cl(2)–Cr–N(2)	175.2(3)	C(4)–C(5)–C(6)	121.5(12)
Cl(2)–Cr–N(3)	89.9(3)	N(3)–C(5)–C(6)	117.9(11)
Cl(2)–Cr–N(4)	95.4(3)	C(5)–C(6)–N(1)	109.5(11)
N(1)–Cr–N(2)	83.9(4)	C(6)–N(1)–C(7)	113.0(10)
N(1)–Cr–N(3)	81.7(4)	N(1)–C(7)–C(8)	108.3(10)
N(1)–Cr–N(4)	88.3(4)	C(7)–C(8)–C(15)	111.7(11)
N(2)–Cr–N(3)	92.2(4)	C(7)–C(8)–N(2)	107.6(9)
N(2)–Cr–N(4)	81.8(4)	C(15)–C(8)–N(2)	114.5(10)
N(3)–Cr–N(4)	168.8(4)	C(8)–N(2)–C(9)	117.0(8)
Cr–N(1)–C(6)	110.4(8)	N(2)–C(9)–C(10)	110.1(9)
Cr–N(1)–C(7)	109.7(8)	C(9)–C(10)–C(11)	120.8(11)
Cr–N(2)–C(8)	108.2(6)	C(10)–C(11)–C(12)	120.0(13)
Cr–N(2)–C(9)	109.8(6)	C(11)–C(12)–C(13)	117.9(14)
Cr–N(3)–C(1)	125.0(9)	C(12)–C(13)–C(14)	119.0(13)
Cr–N(3)–C(5)	113.7(8)	C(13)–C(14)–N(4)	121.8(12)
Cr–N(4)–C(10)	114.0(7)	C(14)–N(4)–C(10)	120.0(10)
Cr–N(4)–C(14)	126.0(8)	N(4)–C(10)–C(11)	121.3(11)
		N(4)–C(10)–C(9)	117.7(10)

Table 4. The least-squares planes with displacements of atoms from the planes (Å)
$X=ax+cz\cos\beta$, $Y=by$, and $Z=cz\sin\beta$.

Plane P1					
$-0.8830X+0.4615Y+0.0863Z=-0.6157$					
Cr	0	N(1)	0	N(3)	0
C(5)	−0.2925	C(6)	−0.5461		
Plane P2					
$0.3815X+0.7455Y+0.5465Z=1.9013$					
Cr	0	N(1)	0	N(2)	0
C(7)	0.2326	C(15)	−0.2301	C(8)	−0.4572
Plane P3					
$0.0855X+0.5475Y-0.8324Z=-2.2486$					
Cr	0	N(2)	0	N(4)	0
C(9)	0.5033	C(10)	0.2160		
Plane P4 (Pyridine Ring)					
$0.8815X-0.3913Y-0.2644Z=-0.0408$					
C(1)	0.0020	C(2)	0.0131	C(3)	−0.0092
C(4)	−0.0373	C(5)	0.0387	N(3)	0.0062
Plane P5 (Pyridine Ring)					
$0.2433X+0.4896Y-0.8373Z=-2.1955$					
C(10)	0.0040	C(11)	−0.0042	C(12)	−0.0066
C(13)	0.0181	C(14)	−0.0193	N(4)	0.0083
Dihedral angles between planes (°)					
P1 ∧ P2	93.11	P2 ∧ P4	84.27		
P1 ∧ P3	83.96	P2 ∧ P5	90.01		
P1 ∧ P4	169.01	P3 ∧ P4	85.34		
P1 ∧ P5	93.50	P3 ∧ P5	9.64		
P2 ∧ P3	89.19	P4 ∧ P5	75.87		

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