Crystal and Molecular Structure of Dichloro[(−)-spartein]cobalt(II)

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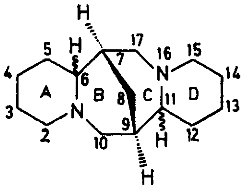
The structure of the title compound has been determined by single-crystal *X*-ray analysis and refined by least-squares methods based on diffractometer data (968 counter intensities, *R* 0.040). Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 4$, and $a = 11.192(7)$, $b = 11.897(6)$, $c = 12.438(9)$ Å. The cobalt(II) ion has a distorted tetrahedral co-ordination geometry with N–Co–N 90.4 and Cl–Co–Cl 114.1°.

THE chiral transition-metal complexes which have been investigated in the most detail, from either a structural[1] or a spectroscopic[2] viewpoint, are six-co-ordinate with D_3 or lower symmetry. The quantitative analysis of the *d*-electron optical activity of the D_3 tris-diamine complexes of cobalt(III) by the dynamic-coupling ligand polarisation model[3] is dependent upon the wide range of detailed structural information available[1] for these complexes.



(I): 6*R*, 11*S*
(II): 6*R*, 11*R*
(III): 6*S*, 11*S*

Recently the synthesis of a series of neutral four-co-ordinate complexes from the chiral bidentate ligand (−)-spartein (sp)(I) was reported,[4] $[M(sp)X_2]$, where X is a halide ion and the metal M is cobalt(II), nickel(II), copper(II), or zinc(II). The diastereoisomeric ligands, (−)-α-isospartein (II) and (−)-β-isospartein (III) form analogous complexes with copper(II) chloride.[5] The electronic spectra of the complexes[4] $[M(sp)X_2]$ and of their diastereoisomeric $CuCl_2$ analogues[5] indicate a quasi-tetrahedral co-ordination of the metal ion, and the c.d. spectrum of $[Ni(sp)Cl_2]$ shows[4] that each *d*-electron transition over the frequency range 6—25 kK has a substantial optical activity.

In order to establish the precise co-ordination geometry of the metal ion and to obtain the structural information required for a dynamic-coupling analysis of the *d*-electron optical activity, the crystal structure of the complex $[Co(sp)Cl_2]$ has been determined. The absolute configuration of (−)-spartein is known[6,7] (6*R*, 7*S*, 9*S*, 11*S*), and a crystal structure has been reported for spartein N(16)-oxide sesquiperchlorate,[8] α-isospartein monohydrate,[9] 7-hydroxy-β-isospartein perchlorate,[10] and dichloro(β-isospartein)copper(II).[11]

EXPERIMENTAL

The blue complex[4] $[Co\{(-)\text{-spartein}\}Cl_2]$ was recrystallised from ethanol and a crystal of dimensions 0.34 × 0.30 × 0.22 mm was selected for a structure analysis. Unit-cell dimensions were determined from Weissenberg photographs and were subsequently refined on a diffractometer.

Crystal Data.—$C_{15}H_{26}N_2CoCl_2$, $M = 364.2$, Orthorhombic, $a = 11.192(7)$, $b = 11.897(6)$, $c = 12.438(9)$ Å, $U = 1\,656.1$ Å^3, $D_c = 1.461$, $Z = 4$, $D_m = 1.46$ g cm^{-3} (by flotation), $F(000) = 764$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) $= 12.8$ cm^{-1}. Space group $P2_12_12_1$.

Intensities were measured with Mo-K_α radiation on a Nonius CAD 4 automatic diffractometer operated in the θ—2θ scan mode, up to 2θ 46°. Of 1 336 measured reflections, 969 with $|F_o| \geqslant 3\sigma$ were used for the refinement.

Structure Determination.—The structure was solved by the heavy-atom method. A three-dimensional Patterson function afforded the positions of the Co and the two Cl atoms. Subsequent Fourier syntheses with least-squares refinements gave the positions of all atoms other than the hydrogen atoms. Full-matrix least-squares refinement, with anisotropic temperature factors, produced convergence with *R* 0.063. The positional parameters obtained were used to calculate idealised hydrogen positions and a difference synthesis at this stage confirmed the positions computed.

Further refinements with anisotropic temperature factors for all the non-hydrogen atoms and with isotropic temperature factors for the hydrogen atoms, which were maintained at their idealised bonded positions, decreased *R* to 0.053. The strongest lower-order reflection (0,2,0) showed a significant discrepancy between $|F_o|$ and $|F_c|$ ($|F_o| < |F_c|$), presumably on account of the extinction effect. Removal of this reflection substantially improved

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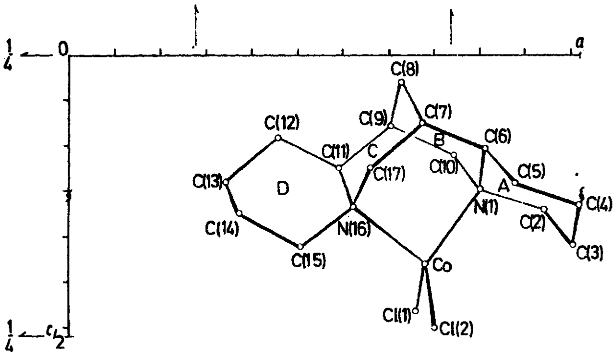
the structure, reducing the standard deviations as well as the R factor. By considering the anomalous scattering due to the cobalt and chlorine atoms, R was ultimately reduced to 0.040. Equal weight was assigned to each of the reflections, and atomic scattering factors were taken from ref. 12. Calculations were carried out with the University of London CDC 7600 computer, by use of the programme SHELX written by Dr. G. Sheldrick. Final atomic positional parameters are listed in Table 1. Equations of mean planes, observed and calculated structure amplitudes, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21908 (9 pp., 1 microfiche).*

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

	X	*Y*	*Z*
Co	6 953(1)	2 350(1)	3 698(1)
Cl(1)	6 775(4)	680(2)	4 528(2)
Cl(2)	7 137(3)	3 813(2)	4 825(2)
N(1)	8 080(8)	2 092(6)	2 404(6)
C(2)	9 270(10)	1 766(9)	2 751(9)
C(3)	9 879(10)	2 692(10)	3 365(8)
C(4)	9 970(12)	3 768(9)	2 667(10)
C(5)	8 728(11)	4 087(8)	2 267(9)
C(6)	8 123(10)	3 123(8)	1 681(7)
C(7)	6 920(11)	3 383(7)	1 193(8)
C(8)	6 514(10)	2 380(10)	487(8)
C(9)	6 330(10)	1 395(8)	1 251(9)
C(10)	7 541(10)	1 126(9)	1 785(9)
C(11)	5 296(10)	1 626(8)	2 027(8)
C(12)	4 096(9)	1 644(9)	1 478(8)
C(13)	3 081(11)	1 908(9)	2 240(8)
C(14)	3 332(10)	3 018(9)	2 814(9)
C(15)	4 528(9)	2 963(9)	3 372(8)
N(16)	5 569(7)	2 675(6)	2 677(6)
C(17)	5 912(10)	3 665(8)	1 986(9)



FIGURE

Perspective view from the crystal *b* axis

DISCUSSION

A perspective view from the crystal *b* axis of the molecular structure is shown in the Figure. The co-ordination of the ligand atoms to the cobalt(II) ion is substantially distorted from the tetrahedral, as expected from the magnetic moment and electronic spectrum of the complex.[4] The distortion arises not only from the different pairs of ligands but also from the inequivalence of the two tertiary nitrogen atoms, owing to the *trans*- and the *cis*-ring junction of the A–B and the C–D rings, respectively. The nuclear configuration of the $[CoN_2Cl_2]$ chromophore is reduced to pseudo-C_2 symmetry, with an angle of 84° between the N, Co, N and Cl, Co, Cl planes, compared with the approximate C_{2v} symmetry found in the β-isospartein complex,[11] $[Cu(\beta\text{-isp})Cl_2]$, where both the corresponding ring-junctions are *trans*.

Bond distances and bond angles are listed in Table 2.

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances			
Co–Cl(1)	2.246(3)	C(7)–C(17)	1.54(2)
Co–N(16)	2.040(7)	C(9)–C(11)	1.53(1)
N(1)–C(10)	1.51(1)	C(12)–C(13)	1.51(2)
C(4)–C(5)	1.53(2)	C(15)–N(16)	1.49(1)
C(7)–C(8)	1.55(1)	Co–N(1)	2.068(8)
C(9)–C(10)	1.54(2)	N(1)–C(6)	1.52(1)
C(11)–C(12)	1.51(1)	C(3)–C(4)	1.55(2)
C(14)–C(15)	1.51(1)	C(6)–C(7)	1.51(2)
Co–Cl(2)	2.244(3)	C(8)–C(9)	1.52(1)
N(1)–C(2)	1.45(1)	C(11)–N(16)	1.52(1)
C(2)–C(3)	1.50(2)	C(13)–C(14)	1.53(1)
C(5)–C(6)	1.52(1)	N(16)–C(17)	1.51(1)
(*b*) Angles			
N(1)–Co–N(16)	90.4(3)	N(1)–Co–Cl(1)	106.2(2)
Cl(1)–Co–Cl(2)	114.1(1)	N(1)–Co–Cl(2)	123.1(2)
N(16)–Co–Cl(1)	112.7(2)	N(16)–Co–Cl(2)	108.1(2)
Co–N(1)–C(2)	111.6(6)	Co–N(1)–C(6)	111.0(6)
Co–N(1)–C(10)	105.4(6)	Co–N(16)–C(11)	109.2(6)
Co–N(16)–C(15)	106.0(5)	Co–N(16)–C(17)	108.0(6)
C(2)–N(1)–C(6)	111.2(8)	C(6)–N(1)–C(10)	109.0(7)
C(2)–N(1)–C(10)	108.3(7)	N(1)–C(2)–C(3)	111.8(8)
C(2)–C(3)–C(4)	109.2(6)	C(3)–C(4)–C(5)	109.1(1.0)
C(4)–C(5)–C(6)	112.1(9)	C(5)–C(6)–N(1)	109.8(8)
N(1)–C(6)–C(7)	112.0(8)	C(5)–C(6)–C(7)	115.9(8)
C(6)–C(7)–C(8)	109.4(8)	C(8)–C(7)–C(17)	108.5(9)
C(6)–C(7)–C(17)	116.2(9)	C(7)–C(8)–C(9)	106.2(8)
C(8)–C(9)–C(10)	108.0(9)	C(8)–C(9)–C(11)	110.9(9)
C(10)–C(9)–C(11)	115.4(9)	N(1)–C(10)–C(9)	114.4(8)
C(9)–C(11)–N(16)	109.3(8)	C(9)–C(11)–C(12)	113.0(8)
N(16)–C(11)–C(12)	114.2(8)	C(11)–C(12)–C(13)	112.9(9)
C(12)–C(13)–C(14)	109.5(1.0)	C(13)–C(14)–C(15)	109.9(9)
C(14)–C(15)–N(16)	115.9(9)	C(15)–N(16)–C(11)	109.9(8)
C(15)–N(16)–C(17)	110.5(7)	C(11)–N(16)–C(17)	113.0(7)
N(16)–C(17)–C(7)	112.5(8)		

The N–Co–N angle is 90.4(3)° and the two Co–N bond lengths differ significantly [2.068(8) and 2.040(7) Å]. The longer bond, Co–N(1), links the metal ion to ring A, which is folded in towards the $CoCl_2$ group, whereas the shorter bond, Co–N(16), connects the metal ion to ring D, which folds away from that group. The folding of ring A towards the $CoCl_2$ group also accounts for the difference between the two N–Co–Cl angles [123.1(2) and 112.7(2)°]. The larger of these two angles, N(1)–Co–Cl(2), refers to the chlorine ion which is situated closer to the hydrogen atoms of ring A [Cl(2) · · · H(C3) 2.89, Cl(2) · · · H(C5) 2.70 Å]. The same steric factor gives the Co–N(1)–C(2) angle a larger value [111.6(6)°] than that of the corresponding Co–N(16)–C(15) angle [106.0(5)°].

The bond angles and distances of the (−)-spartein ligand observed in the complex with $CoCl_2$ agree with the corresponding values found in spartein N(16)-oxide sesquiperchlorate[8] except for the bonds around the N(1) atom, which are the most sterically perturbed by co-ordination to the cobalt(II) ion. All four rings of the (−)-spartein ligand have the chair conformation. The angle

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

[12] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1968.

between the mean planes of each pair of rings is listed in Table 3, together with the corresponding values for the β-isospartein ligand in the complex [Cu(β-isp)Cl_2], calculated from the atomic co-ordinates reported for the latter complex.[11] A comparison of corresponding interplanar angles in the two complexes shows (Table 3) that the steric constraints imposed upon the terminal ring A of the [Co{(−)-sp}Cl_2] complex do not affect the mutual disposition of the mean planes of rings B, C, and D.

TABLE 3

Angles (°) between average planes of the ligand ring in (*a*) the (−)-spartein complex with $CoCl_2$, and (*b*) the (−)-β-isospartein complex with $CuCl_2$

	B	C	D
(*a*) [Co{(−)-sp}Cl_2]			
A	7.4	85.1	65.9
B		78.0	68.4
C			61.2
(*b*) [Cu(β-isp)Cl_2]			
A	60.0	69.8	84.4
B		77.1	68.5
C			62.5

In the unit cell of the crystal, each complex [Co{(−)-sp}Cl_2] molecule is oriented with the pseudo-C_2 axis approximately parallel to the crystallographic *c* axis. This orientation is favourable for single-crystal spectroscopic studies which are in progress, together with calculations of the energy-levels and the rotational and dipole strengths of the *d*-electron transitions in the [Co{(−)-sp}Cl_2] complex, based upon the atomic co-ordinates determined in the present work.

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