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

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The structure of the title complex has been determined by single-crystal *X*-ray analysis and refined by least-squares methods based on diffractometer data (1 366 counter intensities, *R* 0.033). The crystals are tetragonal, space group $P4_32_12$, with $Z = 4$, $a = 8.034(1)$, and $c = 25.295(2)$ Å. The cobalt(II) ion has a distorted tetrahedral co-ordination geometry with N–Co–N 89.0 and Cl–Co–Cl 109.0°. The observed distortions are compared with those reported for analogous (−)-spartein and (−)-β-isospartein metal complexes.

THE present work reports an *X*-ray diffraction study of the crystal and molecular structure, including a determination of the absolute stereochemical configuration, of the quasi-tetrahedral complex formed by (−)-α-isospartein(L^1) with cobalt(II) chloride. The principal aims of the study are, first, the determination of the unit-cell structure and the site symmetry of the complex, required for an analysis of the polarized electronic spectrum of the complex orientated in a single crystal, and, secondly, the determination of the atomic co-ordinates within the molecular frame of the complex, required for the application of the angular-overlap model[1] and of the ligand-polarization model[2] to the calculation of the *d*-electron transition energies and of the corresponding transition probabilities, respectively.

A set of transition probabilities unique to chiral molecules comprises the rotational strengths, governing the optical activity, for an estimate of which knowledge is required of the absolute stereochemical configuration of the enantiomer studied. While the absolute configurations of L^1, (−)-spartein (L^2), and (+)-β-isospartein (L^3) are well established by chemical and other correlations with standards of known configuration,[3] these relations are extended, and an additional potentially chiral centre at the metal ion is introduced on co-ordination of each of the ligands L^1—L^3 to a transition-metal dihalide or other metal salt. Accordingly, a determination of the absolute configuration of the chiral centres in the $[CoCl_2L^1]$ complex was undertaken by the anomalous-scattering *X*-ray method.

The stereoisomeric ligands L^1—L^3 and their metal complexes are important for their biological activity,[4] and as enantioselective catalysts.[5,6] With the bivalent transition-metal halides[4,7] and pseudohalides[8] of the first long period, ligands L^1—L^3 form neutral four-co-ordinate complexes soluble in a range of common solvents. In water the copper(II) chloride complexes of L^1—L^3 hydrolyze with a half-life of 3—5 h at 25 °C,[4,9] but in chloroform solution these complexes and their analogues are stable indefinitely, and their e.s.r.[10] and electronic-absorption spectra[4,7,10] indicate tetrahedral co-ordination in each case.

Since the conformational lability of the ligands is suppressed on co-ordination to a metal ion, the solid-state structure of the complex is expected to provide a reliable guide to the stereochemistry of the complex in non-co-ordinating solvents. The *X*-ray analyses of the crystal and molecular structure of dichloro[(−)-β-isospartein]copper(II)[11] and $[CoCl_2L^2]$[12] have been described previously. The present work completes a set of representative structures for the quasi-tetrahedral complexes formed by the ligands L^1—L^3 with the transition-metal dichlorides and it allows, through a comparison of the three structures with each other, an analysis of the stereochemical modifications of the complex imposed by a change in the configuration of the chiral centres in the ligand.

EXPERIMENTAL

The blue complex $[CoCl_2L^1]$ was synthesized by the method described[7] for the preparation of the corresponding (−)-spartein (L^2) analogue. The ligand (−)-α-isospartein (L^1) was obtained from commercial L^2 by the method of Winterfeld and Rauch.[13] The crystal studied (dimensions 0.33 × 0.32 × 0.30 mm) was obtained from a chloroform solution of the complex. Cell parameters were determined from Weisenberg photographs and subsequently refined on a diffractometer.

Crystal Data.—$C_{15}H_{26}Cl_2CoN_2$, $M = 364.2$, Tetragonal, $a = 8.034(1)$, $c = 25.295(2)$ Å, $U = 1\,632.6$ Å^3, $D_m = 1.48$ g cm^{-3}, $Z = 4$, $D_c = 1.482$, $F(000) = 764$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 12.9 cm^{-1}, space group $P4_32_12$.

Intensities were measured with Mo-K_α radiation on a Nonius CAD4 automatic diffractometer operated in the θ—2θ scan mode up to $2\theta = 60°$. Of the 1 595 unique reflections for the 422 point group, 1 366 with $|F_o| \geqslant 3\sigma$ were used for the refinement.

Structure Determination.—The structure was solved by the heavy-atom method using the program SHELX. The number of formula units per unit cell requires the location of the cobalt atoms at special positions with two-fold symmetry. These positions and those of the chlorine atoms were determined from a three-dimensional Patterson map, which showed that the cobalt atoms are located close to the two-fold screw axes perpendicular to the two-fold pure-rotation axes. Pseudo-symmetry appeared in the initial stage of the structure analysis owing to the particular location of the cobalt atoms.

Subsequent Fourier syntheses with least-squares refinements gave the positions of all the atoms heavier than hydrogen. Full-matrix least-squares refinement with anisotropic temperature factors improved *R* to 0.055. The positional parameters obtained were used to calculate the idealized hydrogen-atom locations and a difference synthesis at this stage confirmed the positions computed. Further refinements with isotropic thermal factors for the hydrogen atoms, which were maintained at their idealized positions, and with anisotropic thermal factors for the heavier atoms, reduced *R* to 0.033. An equal weight was assigned to each of the reflections, and corrections were made for the anomalous scattering due to the cobalt and the chlorine atoms. The atomic scattering factors were taken from ref. 14, and the calculations carried out by means of the University of London CDC 7600 computer. The final set of atomic co-ordinates is listed in Table 1. Observed and calculated structure amplitudes and anisotropic thermal factors are listed in Supplementary Publication No. SUP 22419 (8 pp).*

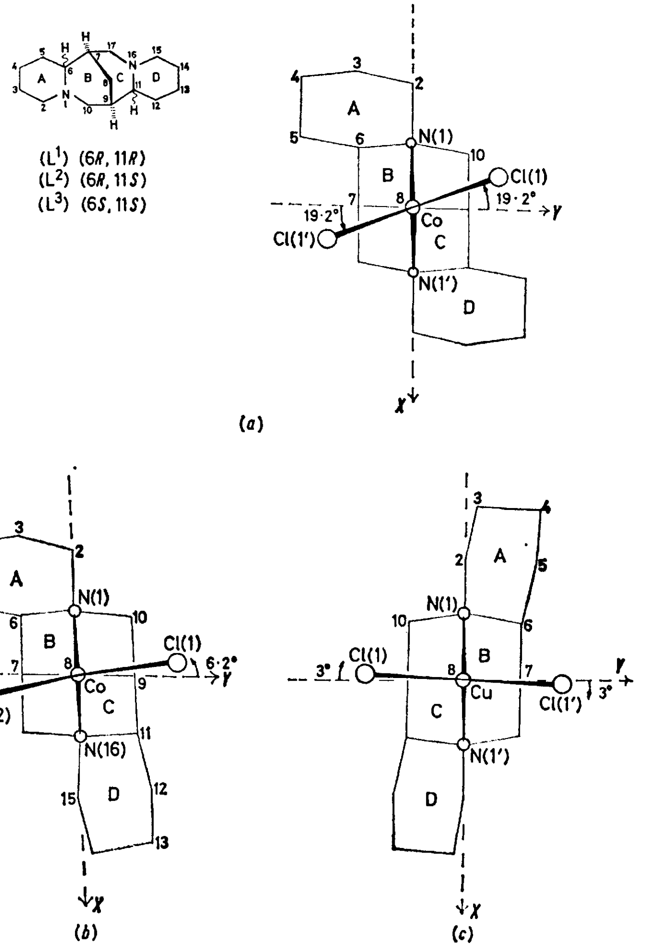

FIGURE 1 Projection of the molecular structure on the *XY* plane perpendicular to the $C_2(Z)$ axis, or pseudo-C_2 axis, of (*a*) [CoCl$_2$L^1], (*b*) [CoCl$_2$L^2], and (*c*) dichloro[(—)-β-isospartein]copper(II)

TABLE 1

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations

Atom	*x*	*y*	*z*
Co	4 961(1)	5 039(1)	7 500
Cl(1)	4 975(2)	2 756(1)	8 014(0)
N(1)	2 505(4)	5 188(4)	7 253(1)
C(2)	1 914(6)	3 548(5)	7 048(2)
C(3)	2 909(7)	3 031(5)	6 562(2)
C(4)	2 784(7)	4 330(6)	6 132(2)
C(5)	3 246(6)	6 048(5)	6 339(2)
C(6)	2 258(5)	6 487(5)	6 835(2)
C(7)	2 628(6)	8 212(5)	7 065(2)
C(8)	1 387(5)	8 613(5)	7 500
C(10)	1 512(5)	5 616(5)	7 741(2)

Absolute Configuration.—Equi-inclination Weissenberg photographs were taken around the crystal *c* axis with Cu-K_α radiation. The relations between $|F(hkl)|^2$ and $|F(\bar{h}kl)|^2$ observed and calculated for the (1*R*,6*R*,7*S*,9*S*,11*R*,16*R*) configuration of the (—)-α-isospartein ligand (L^1) are compared in Table 2. The previously assigned [3] configuration of ligand (L^1) is confirmed, and the additional chiral centre of the cobalt atom in the complex studied is found to have the configuration in which the line joining the two chloride ligands, and the line joining the two nitrogen atoms of ligand L^1, form a segment of a right-handed helix [Figure 1(*a*)]. The nomenclature proposed for chiral co-ordination compounds,[15] when extended from six- to four-co-ordinate

TABLE 2

Determination of the absolute configuration. Relations between $|F_c(hkl)|^2$ and $|F_c(\bar{h}kl)|^2$ observed and calculated for the (1*R*,6*R*,7*S*,9*S*,11*R*,16*R*) configuration of L^1

h	*k*	*l*	$\|F_c(hkl)\|^2$	Relation observed	$\|F_c(\bar{h}kl)\|^2$
1	3	1	1 296	<	1 600
1	2	2	900	>	144
3	6	2	144	<	361
1	6	2	1 089	>	729
2	4	4	2 025	<	2 500
1	5	4	2 401	>	1 764
1	2	6	7 225	>	5 776

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

complexes, suggests the term δ configuration for the chirality of the CoN_2Cl_2 chromophore in [$CoCl_2L^1$] [Figures 1(*a*) and 2(*a*)] and in the related complex [12] [$CoCl_2L^2$] [Figures 1(*b*) and 2(*b*)]. On the same basis, the CuN_2Cl_2 chromophore of dichloro[(−)-β-isospartein]copper(II) has the λ configuration [Figure 1(*c*)], the tetracyclic ligand in this complex [4,11] being the enantiomer of ligand L^3 which shares a common (1*R*,7*S*,9*S*,16*R*) configuration with ligands L^1 and L^2.

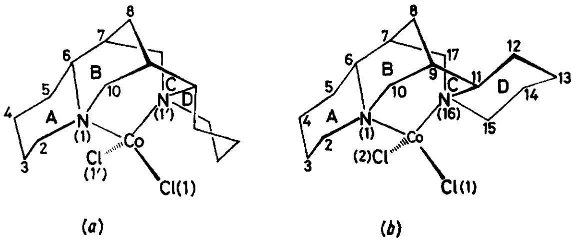

FIGURE 2 Perspective view of the molecular structure of (*a*) [$CoCl_2L^1$] and (*b*) [$CoCl_2L^2$]

DISCUSSION

A perspective view and the numbering scheme of the complex [$CoCl_2L^1$] are illustrated [Figure 2(*a*)], together with those of the corresponding (−)-spartein complex [12] [Figure 2(*b*)]. As required crystallographically, the α-isospartein complex has strict C_2 symmetry. The bond distances and bond angles of this complex are listed in Table 3.

TABLE 3

Bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses. Primed atoms are related to the corresponding unprimed atoms by two-fold rotational symmetry

Co–Cl(1)	2.248(1)
Co–N(1)	2.073(3)
N(1)–C(2)	1.493(5)
C(2)–C(3)	1.524(6)
C(3)–C(4)	1.511(6)
C(4)–C(5)	1.523(6)
C(5)–C(6)	1.526(6)
N(1)–C(6)	1.498(5)
C(6)–C(7)	1.524(6)
C(7)–C(8)	1.536(5)
N(1)–C(10)	1.511(5)
C(7′)–C(10)	1.518(6)

N(1)–Co–N(1′)	89.0(2)	C(2)–C(3)–C(4)	111.0(4)
Cl(1)–Co–Cl(1′)	109.0(1)	C(3)–C(4)–C(5)	111.2(3)
Cl(1)–Co–N(1)	103.1(1)	C(4)–C(5)–C(6)	111.5(4)
Cl(1′)–Co–N(1)	127.0(1)	C(5)–C(6)–N(1)	110.5(3)
Co–N(1)–C(2)	110.9(2)	N(1)–C(6)–C(7)	110.5(3)
Co–N(1)–C(6)	112.3(2)	C(5)–C(6)–C(7)	113.9(3)
Co–N(1)–C(10)	105.6(2)	C(6)–C(7)–C(8)	109.6(3)
C(2)–N(1)–C(6)	109.2(3)	C(8)–C(7)–C(10′)	109.0(3)
C(2)–N(1)–C(10)	108.4(3)	C(6)–C(7)–C(10′)	115.9(4)
C(6)–N(1)–C(10)	110.4(3)	C(7)–C(8)–C(7′)	105.2(5)
N(1)–C(2)–C(3)	110.7(3)	N(1)–C(10)–C(7′)	114.3(8)

In the series of dichlorometal(II) complexes of the ligands L^1—L^3, significant changes in the co-ordination geometry of the metal ion derive from the different steric foldings of the terminal A and D rings of the tetracyclic ligand. The projection of the co-ordination geometry of the metal ion on a plane perpendicular to the C_2 (or pseudo-C_2) rotation axis of the complex shows (Figure 1) that the torsional distortion of the Cl–Co–Cl and the N–Co–N planes from orthogonality is large for the (−)-α-isospartein complex where both the A–B and the C–D ring pairs have *trans* junctions. The smaller angle between the two planes is 70.8° in this case, compared with the angle of 87° between the Cl–Cu–Cl and N–Cu–N planes of the (−)-β-isospartein complex [11] where both the corresponding ring junctions of the tetracyclic ligand are *cis*.

With a *trans* junction of both the A–B and the C–D ring pairs in the (−)-α-isospartein complex, the terminal rings of ligand L^1 fold inwards towards the $CoCl_2$ group [Figure 2(*a*)]. The atoms of the terminal rings lie predominantly in positive quadrants of the *XY* projection plane perpendicular to the $C_2(Z)$ axis, and the chloride ligands are sterically constrained to the negative quadrants of the *XY* plane [Figure 1(*a*)]. Even with the torsional distortion of the N_2CoCl_2 co-ordination tetrahedron by 19.2° around the C_2 axis, the contact between the chloride ligands and the axial C–H groups at the 5 and 5′ position of ligand L^1 is close (2.70 Å). The Co–N bond in the (−)-α-isospartein complex is of comparable length to that (2.068 Å) of the Co–N(1) bond in the corresponding (−)-spartein complex [12] linking the metal ion to the nitrogen atom at the *trans* A–B ring junction, but significantly longer than the Co–N(16) bond (2.040 Å) to the nitrogen atom at the *cis* C–D ring junction.

With a *cis* junction of both the A–B and the C–D ring pairs, the terminal rings of ligand (L^3), or its enantiomer in the dichloro[(−)-β-isospartein]copper(II) complex, fold outwards away from the $CuCl_2$ group and the torsional distortion [11] of the plane of that group is only 3° [Figure 1(*c*)]. In the case of [$CoCl_2L^2$], with a *trans* A–B and *cis* C–D ring junction [12] [Figure 2(*b*)], the respective

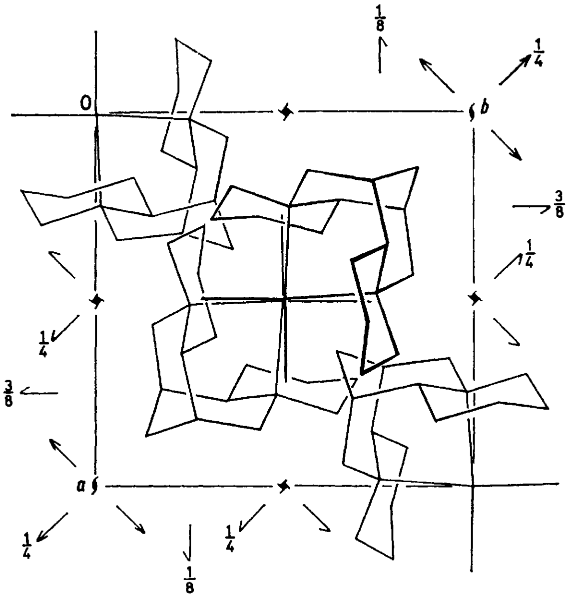

FIGURE 3 Projection of the crystal structure of [$CoCl_2L^1$] on a plane perpendicular to the crystal *c* axis

major and minor steric constraints are mutually accommodated to a degree, giving the projected Co–Cl bonds torsional distortions of 10.0 and 6.2°, respectively [Figure 1(*b*)].

All the four rings of ligand (L^1) have the chair conformation in the complex [$CoCl_2L^1$] [Figure 2(*a*)]. The angles between the average planes of the A–B, A–C, B–C, and A–D rings are 7.1, 84.8, 77.7, and 88.1°, respectively, the first three values being similar to the comparable angles (7.4, 85.1, and 78.0°, respectively) in the [$CoCl_2L^2$] complex.[12]

The packing mode of [$CoCl_2L^1$] in the crystal is shown (Figure 3) in projection on a plane perpendicular to the crystal *c* axis. These planes are parallel to the main crystal faces of the thin square plates which form the dominant crystal habit. Since the crystal is optically isotropic in this plane, it is suitable for single-crystal circular dichroism studies with the radiation propagated along the crystal *c* axis. Measurements of the polarized single-crystal spectra are in progress, together with calculations of the energy levels and the rotational and dipole strengths of the *d*-electron transitions in the [$CoCl_2L^1$] complex, based on the atomic co-ordinates determined in the present work.

We thank Mr. S. J. Hirst for samples of [$CoCl_2L^1$], Dr. M. B. Hursthouse for the use of the diffractometer at Queen Mary College, the Biophysics Department of King's College for the use of photographic *X*-ray facilities, and the S.R.C. for support.

[8/1256 *Received*, 6*th July*, 1978]

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