The Crystal Structure of Dichloro(diethyl pyridine-2,6-dicarboxylato)cobalt(II), a Chlorine-bridged Dimer

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Crystals of the 1 : 1 complex between cobalt(II) chloride and diethyl pyridine-2,6-dicarboxylate are triclinic, with $a = 9.33(1)$, $b = 10.26(1)$, $c = 8.16(1)$ Å, $\alpha = 104.23(1)$, $\beta = 105.36(1)$, and $\gamma = 92.94(1)^\circ$, space group $P\bar{1}$, Z = 2. The atomic positions have been determined by Patterson and Fourier methods from diffractometer *X*-ray intensity data and refined by full-matrix least-squares to *R* 4.17% for 2 325 reflexions. The compound lies on a crystallographic centre and has a dimeric structure with distorted octahedral co-ordination about each metal atom. The two cobalt atoms are linked by a double chlorine bridge with Co–Cl distances of 2.311(1) and 2.553(1) Å while the distance to the third, non-bridging, chlorine atom is 2.348(1) Å. Slight distortion of the ligand occurs on co-ordination but with the exception of the ethoxy-group it is nearly planar.

DIETHYL pyridine-2,6-dicarboxylate (depc) forms 1 : 1 complexes with Co^{II}, Ni^{II}, Mn^{II}, and Cu^{II} chlorides.[1] I.r. spectra of these complexes indicate that depc behaves as a tridentate ligand, co-ordinating through the nitrogen of the pyridine ring and the two carboxylate oxygen atoms. On the basis of their colour, magnetic properties, reflectance spectra, and molar conductance, the complexes may be formulated as either five-co-ordinate monomers or chlorine-bridged six-co-ordinate dimers. The cobalt complex $CoCl_2$·depc for instance is blue, has a room-temperature magnetic moment (4.9 B.M.†) within the range reported for both five- and six-co-ordinate Co^{II} complexes, and is non-conducting in common solvents. An unambiguous formulation of this complex, therefore, necessitated the determination of its crystal structure.

EXPERIMENTAL

Suitable crystals of the compound were obtained by slow crystallization from an equimolar solution of anhydrous cobalt(II) chloride and depc in tetrahydrofuran.

Crystal Data.—$C_{11}H_{13}Cl_2CoNO_4$, $M = 352.9$, Triclinic, $a = 9.33(1)$, $b = 10.26(1)$, $c = 8.16(1)$ Å, $\alpha = 104.23(1)$, $\beta = 105.36(1)$, $\gamma = 92.94(1)$,° $U = 724.8$ Å^3, $D_c = 1.62$ g cm^{-1}, $Z = 2$, $F(000) = 358$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 16.03 cm^{-1}, space group $P\bar{1}$.

The unit-cell dimensions originally obtained from oscillation and Weissenberg photographs were refined on a Hilger and Watts four-circle diffractometer using Mo-K_α radiation. Diffractometer data were obtained for 2 325 observed reflections with intensities $>3\sigma$ in the range $0 < \theta < 25^\circ$. The intensities were corrected for Lorentz and polarization effects but not for absorption or secondary extinction. Data reduction and subsequent crystallographic calculations used the CRYSTALS programs;[2]

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† 1 B.M. = 9.27×10^{-24} A m^2.

[1] G. Singh, unpublished results.

[2] J. R. Carruthers, ' The Oxford Crystallographic Package—CRYSTALS.'

atomic scattering factors were taken from ref. 3. A three-dimensional Patterson synthesis showed four major peaks of which the second most intense was associated with the Co–Co vector. The most intense peak was the result of the fortuitous superposition of two Co–Cl vectors. Possible positions were then calculated for the metal and the two chlorine atoms from these Patterson peaks and a Fourier synthesis phased on these atoms revealed the positions of the carbon, nitrogen, and oxygen atoms. Two cycles of full-matrix refinement with isotropic thermal parameters led to a reduction of the R value to 12.0%, and after two further cycles using anisotropic thermal parameters R was reduced to 5.3%. Appropriate positions for the 13 hydrogen atoms were then calculated but in the next two cycles of anisotropic refinement which caused convergence at R 4.42% their positions were not refined. Analysis of the reflection data pointed to a weighting scheme which assigned unit weights to those reflections with $F_0 < 50$ but weights of $(50/F_0)^2$ for those of higher intensity. Two further cycles of refinement gave final convergence at R 4.17%; a difference Fourier at this stage showed no peaks with intensity > 0.3 eÅ^{-3}.

TABLE 1

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	x/a	y/b	z/c
Co(1)	4 208.9(5)	1 485.5(4)	784.4(5)
Cl(1)	2 783(1)	3 167(1)	−25(1)
Cl(2)	4 049(1)	115(1)	−1 983(1)
O(1)	2 397(3)	526(2)	1 551(3)
O(2)	6 313(3)	2 929(3)	1 545(3)
O(3)	1 446(3)	664(3)	3 829(3)
O(4)	7 946(3)	4 350(3)	3 885(4)
N(1)	4 592(3)	2 431(2)	3 440(3)
C(1)	2 420(3)	1 018(3)	3 079(4)
C(2)	6 715(4)	3 515(4)	3 088(6)
C(3)	330(4)	−532(4)	2 790(5)
C(4)	983(6)	−1 775(5)	3 052(8)
C(5)	8 893(5)	4 479(5)	2 677(7)
C(6)	9 677(6)	3 244(7)	2 299(8)
C(7)	3 632(3)	2 106(3)	4 274(4)
C(8)	3 829(4)	2 693(3)	6 045(4)
C(9)	5 079(5)	3 642(4)	6 955(4)
C(10)	6 081(4)	3 967(3)	6 089(4)
C(11)	5 791(3)	3 333(3)	4 311(4)

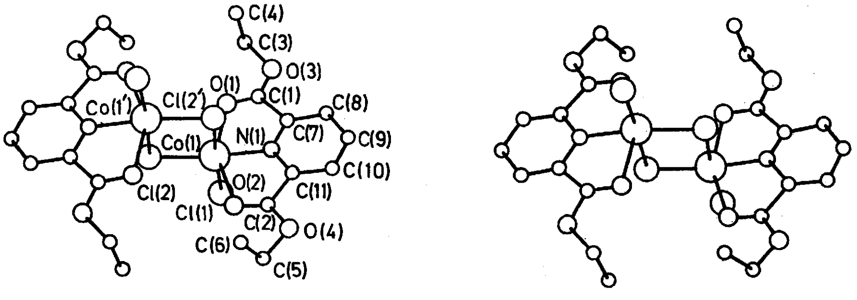

FIGURE 1 Stereoscopic view of the molecule and numbering of the atoms. The primed atoms are related to the corresponding unprimed atom by inversion through the molecular centre

Observed and calculated structure factors, anisotropic thermal parameters, and the calculated hydrogen atom positions are listed in Supplementary Publication No. SUP 21922 (23 pp., 1 microfiche).† Atomic co-ordinates for the non-hydrogen atoms are listed in Table 1, while bond-distance and -angle data are given in Table 2. A stereoscopic diagram of the molecule is shown in Figure 1 which also gives the atom numbering scheme and a view of the unit cell projected down the c axis is shown in Figure 2.

TABLE 2

Intramolecular distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Co(1)–Cl(1)	2.348(1)	Co(1)–O(1)	2.216(2)
Co(1)–Cl(2)	2.311(1)	Co(1)–O(2)	2.244(3)
Co(1)–Cl(2′)	2.553(1)	Co(1)–N(1)	2.071(2)
O(1)–C(1)	1.219(4)	O(2)–C(2)	1.201(5)
C(1)–O(3)	1.304(4)	C(2)–O(4)	1.307(4)
O(3)–C(3)	1.483(4)	O(4)–C(5)	1.511(5)
C(3)–C(4)	1.480(7)	C(5)–C(6)	1.503(7)
C(1)–C(7)	1.493(4)	C(2)–C(11)	1.518(5)
C(7)–N(1)	1.334(4)	C(11)–N(1)	1.328(4)
C(7)–C(8)	1.381(4)	C(11)–C(10)	1.383(5)
C(8)–C(9)	1.389(5)	C(10)–C(9)	1.385(5)

(*b*) Angles

Cl(1)–Co(1)–Cl(2)	99.66(3)	Cl(2)–Co(1)–Cl(2′)	86.12(3)
Cl(1)–Co(1)–Cl(2′)	173.06(3)	Cl(2)–Co(1)–O(1)	103.81(7)
Cl(1)–Co(1)–O(1)	93.13(7)	Cl(2)–Co(1)–O(2)	105.55(7)
Cl(1)–Co(1)–O(2)	89.99(8)	Cl(2)–Co(1)–N(1)	168.75(7)
Cl(1)–Co(1)–N(1)	91.59(7)		
O(1)–Co(1)–Cl(2′)	89.19(7)	O(2)–Co(1)–Cl(2′)	84.72(8)
O(1)–Co(1)–O(2)	149.49(9)	O(2)–Co(1)–N(1)	74.57(9)
O(1)–Co(1)–N(1)	75.01(9)	N(1)–Co(1)–Cl(2′)	82.68(7)
Co(1)–O(1)–C(1)	113.4(2)	Co(1)–O(2)–C(2)	113.0(2)
O(1)–C(1)–O(3)	125.2(3)	O(2)–C(2)–O(4)	125.2(4)
C(1)–O(3)–C(3)	116.7(3)	C(2)–O(4)–C(5)	113.1(3)
O(3)–C(3)–C(4)	109.0(3)	O(4)–C(5)–C(6)	110.7(4)
O(1)–C(1)–C(7)	120.7(3)	O(4)–C(2)–C(11)	113.4(3)
O(3)–C(1)–C(7)	114.0(3)	O(2)–C(2)–C(11)	121.5(3)
N(1)–C(7)–C(8)	122.0(3)	N(1)–C(11)–C(10)	121.6(3)
N(1)–C(7)–C(1)	111.5(3)	N(1)–C(11)–C(2)	110.4(3)
C(1)–C(7)–C(8)	126.4(3)	C(2)–C(11)–C(10)	128.0(3)
C(7)–C(8)–C(9)	117.7(3)	C(11)–C(10)–C(9)	118.3(3)
C(8)–C(9)–C(10)	120.1(3)		
Co(1)–N(1)–C(7)	119.2(2)	Co(1)–N(1)–C(11)	120.5(2)
C(7)–N(1)–C(11)	120.3(3)		
Co(1)–Cl(2)–Co(1′)	93.88(3)		

DISCUSSION

As shown in Figure 1 the compound has a dimeric structure with a double chlorine bridge between two cobalt atoms rather than the alternative five-co-ordinate monomeric structure. The dimer lies on a crystallographic centre of symmetry with bridging Co–Cl distances of 2.311(1) and 2.553(1) Å. The former distance is

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† For details see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[3] 'International Tables for X-ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

surprisingly shorter than that for the second non-bridging chlorine atom [Co–Cl(1), 2.348 Å] which occupies a position *cis* to Cl(2). These distances, however, are close to those observed in previous structure determinations.[4] The remaining three co-ordination positions are occupied by the nitrogen and carboxylate oxygens of the ligand as was suggested by i.r. spectroscopy; the cobalt atoms are therefore in a distorted octahedral environment.

Equations for the best planes through each of the sets of four atoms of the octahedron are given in Table 3 which also lists the distances of relevant atoms from the planes. While the mean deviations are 0.05 Å for the atoms in planes (1) and (2), the corresponding deviation is 0.23 Å for the four atoms constituting plane (3). The large value here is a result of the distortion of O(1) and O(2) toward the nitrogen atom of the ligand so that the angle O(1)–Co(1)–O(2) is 149.5° rather than the ideal of 180°. Further, Cl(2′) being part of the bridge system is constrained so that the angle Cl(2)–Co(1)–Cl(2′) is 86.1° and also contributes to the larger observed deviations from plane (3). The angles between the three planes are close to 90°, *i.e.* plane (1)–plane (2) 90.4, plane (1)–plane (3) 91.8, and plane (2)–plane (3) 89.4°, but as expected the difference is greatest when plane (3) is involved.

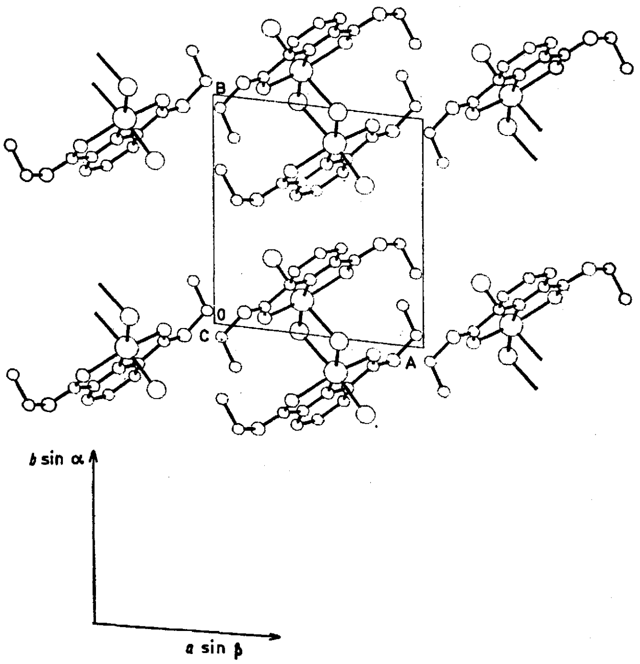

FIGURE 2 Projection of the unit cell down the *c* axis

Because of the ligand stereochemistry the three donor groups must occupy meridional positions in the octahedral co-ordination sphere, but there is slight asymmetry in the co-ordination and the symmetry (a two-fold axis or a mirror plane) that might have been present in the co-ordinated ligand is not found. The asymmetry in co-ordination is shown by (*a*) the small but significant difference in the Co(1)–O(1) and Co(1)–O(2) distances, (*b*) the differences in the angles at Co(1) between Cl(1), Cl(2), and Cl(2′), and N(1) and respectively O(1) and O(2), and (*c*) the differences in the C(1)–O(1) and C(2)–O(2) distances. In spite of this, the three ring systems associated with the co-ordinated ligand are individually close to planarity [see Table 3, planes (4), (5), and (6)], and further the mean deviation from the best plane through the atoms of all three rings [plane (7)] is 0.026 Å.

TABLE 3

Equations of mean planes [distances (Å) of relevant atoms from the plane are in parentheses]

Plane (1): O(1), O(2), N(1), Cl(2)

$$5.026x - 8.179y + 3.052z = 1.301$$

[O(1) −0.052, O(2) −0.051, N(1) 0.069, Cl(2) 0.035, Co(1) −0.161]

Plane (2): N(1), Cl(1), Cl(2), Cl(2′)

$$7.637x + 5.453y - 3.113z = 3.815$$

[N(1) −0.053, Cl(1) 0.046, Cl(2) −0.043, Cl(2′) 0.050, Co(1) −0.035]

Plane (3): O(1), Cl(1), O(2), Cl(2′)

$$1.626x - 2.730y - 7.036z = -0.624$$

[O(1) −0.221, Cl(1) 0.230, O(2) −0.236, Cl(2′) 0.228, Co(1) 0.351]

Plane (4): N(1), C(7), C(8), C(9), C(10), C(11)

$$4.885x - 8.694y + 2.321z = 0.932$$

[N(1) −0.004, C(7) 0.004, C(8) 0.000, C(9) −0.003, C(10) 0.003, C(11) 0.001]

Plane (5): Co(1), N(1), C(1), C(7), O(1)

$$5.226x - 8.382y + 2.373x = 1.158$$

[Co(1) −0.017, N(1) 0.021, C(1) −0.016, C(7) −0.010, O(1) 0.022]

Plane (6): Co(1), N(1), C(2), C(11), O(2)

$$-4.949x + 8.660y - 2.278z = -0.962$$

[Co(1) −0.013, N(1) 0.011, C(2) −0.021, C(11) 0.000, O(2) 0.022]

Plane (7): Co(1), O(1), C(1), O(2), C(2), N(1), C(7), C(8), C(9), C(10), C(11)

$$-5.039x + 8.562y - 2.335z = -1.061$$

[Co(1) 0.029, O(1) −0.059, C(1) −0.006, O(2) 0.027, C(2) −0.034, N(1) 0.025, C(7) 0.035, C(8) 0.026, C(9) −0.004, C(10) −0.029, C(11) −0.011]

The consequences of the presence of a strongly asymmetric bridging system in the solid-state dimer are being investigated, for example to determine the stability of the bridge system when the solid is dissolved in donor solvents.

From preliminary powder diffraction measurement it seems probable that the Mn^{II} and Ni^{II} complexes are isostructural with the Co^{II} compound but the data point to a different structure for the Cu^{II} complex.

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[4] M. Laing and E. Horsfield, *Chem. Comm.*, 1969, 902; C. Kowala and J. A. Wunderlich, *Inorg. Chim. Acta*, 1973, **7**, 331.