Crystal Structure of [*NN′*-Ethylenebis-(2-amino-5-chlorobenzylideneiminato)]cobalt(II)

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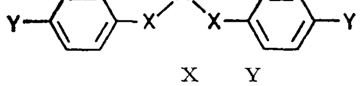
The crystal structure of the title compound (III) has been solved from single-crystal *X*-ray diffractometer data by direct methods and refined to *R* 0·07 for 707 data. Crystals are orthorhombic, space group *Pnam*, with $Z = 4$ in a unit cell of dimensions $a = 7{\cdot}097(4)$, $b = 7{\cdot}658(4)$, and $c = 28{\cdot}37(2)$ Å. In contrast to [*NN′*-ethylenebis-(salicylideneiminato)]cobalt(II) and -copper(II), there is no co-ordination by the metal normal to the plane of the complex.

THE compound [*NN′*-ethylenebis(salicylaldehydeiminato)]cobalt(II), Co(salen), (I), like many analogues of vitamin B_{12r}, readily bonds at its axial position; it co-ordinates with pyridine,[1] it reacts with molecular oxygen in solution,[2] and forms Co–C σ bonds.[3] It also forms a dimer in the solid state.[4] In contrast, [*NN′*-ethylene-bis-(*o*-aminobenzylideneiminato)]cobalt(II), Co(amben), (II), does not co-ordinate with pyridine,[5] reacts with oxygen only in polar solvents,[6,7] and forms only a very unstable methyl derivative if any at all.[6] The present structure investigation was undertaken to determine whether Co(5-Cl-amben), (III), (which forms better crystals than Co(amben) itself), forms dimeric units in the



	X	Y
(I)	O	H
(II)	NH	H
(III)	NH	Cl

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solid, and whether there are any significant conformational differences between it and Co(salen).

EXPERIMENTAL

(III) was crystallised from dimethylformamide. Preliminary cell dimensions were obtained from Weissenberg and rotation photographs and refined from diffractometer data.

Crystal Data.—$C_{16}H_{14}Cl_2CoN_2$, $M = 293{\cdot}16$, Orthorhombic, $a = 7{\cdot}097(4)$, $b = 7{\cdot}658(4)$, $c = 28{\cdot}37(2)$ Å, $U = 1541{\cdot}9$ Å^3, $D_m = 1{\cdot}60$ (by flotation), $Z = 4$, $D_c = 1{\cdot}69$. Space group Pnam, a nonstandard setting of space group no. 62.

Crystals of (II) and (III) have the same space groups and closely similar intensity patterns. The cell dimensions of (II), obtained from Weissenberg photographs are: $a = 6{\cdot}94$, $b = 7{\cdot}53$, and $c = 26{\cdot}20$ Å.

The 707 independent intensities were measured within a θ limit of 22° on a Hilger and Watts four-circle diffractometer with a θ—2θ scan technique and MoK_α radiation. The crystal dimensions were $0{\cdot}3 \times 0{\cdot}1 \times 0{\cdot}1$ mm^3. The scan interval was 0·70° taken in steps of 0·01°, each peak being measured for 210 s, with a stationary background on each side for half that time. Data were corrected for the Lorentz polarisation factor but not for absorption.

The structure was solved by direct methods with the aid of the program, MULTAN.[8] A Fourier map based on the most consistent sign combination among the 125 strongest E-values revealed all the atoms other than hydrogen. Except for those attached to C(8), all the hydrogen atoms were found in different Fourier maps, but their positions could not be determined very accurately. They were therefore inserted at calculated positions (Table 1) with the isotropic thermal parameters of their attached carbon or nitrogen atoms. Only the position for H(1) was taken from the difference-Fourier map. 615 reflections having $\sigma(I)/(I) < 0{\cdot}40$ were each given unit weight, and the structure refined anisotropically (keeping the hydrogen atoms fixed) by full-matrix least-squares method to R 0·05 (R 0·07 for all reflections).

TABLE 1

Final co-ordinates ($\times 10^4$) with standard deviations in parentheses

	x	y	z
Co	−196(2)	4601(2)	2500(0)
Cl	−2294(6)	6146(5)	4951(1)
C(1)	−1934(12)	4387(12)	3419(3)
C(2)	−3539(14)	4048(14)	3714(3)
C(3)	−3611(15)	4510(16)	4175(4)
C(4)	−2111(18)	5400(15)	4376(3)
C(5)	−534(16)	5774(15)	4123(4)
C(6)	−405(14)	5294(12)	3642(4)
C(7)	1254(15)	5699(14)	3392(4)
C(8)	3367(14)	5970(18)	2748(3)
N(1)	−1875(10)	3988(10)	2957(3)
N(2)	1513(9)	5397(10)	2941(3)
H(1) *	−3100	4000	2850
H(2)	−4700	3300	3570
H(3)	−4900	4300	4370
H(5)	600	6400	4280
H(7)	2400	6300	3580

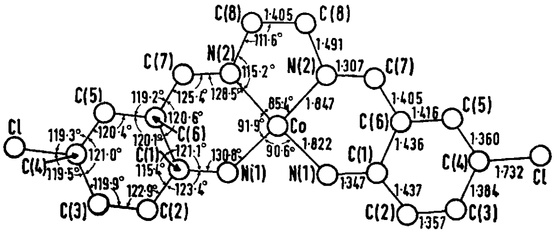
* Hydrogen atoms are numbered according to the C or N atom to which they are attached.

Final parameters are given in Tables 1 and 2. Bond distances and angles are given in the Figure, which shows the molecule projected on to its least-squares plane, inclined at 66° to the b axis. Despite the successful refinement there is a strong possibility that the space group is $Pna2_1$ instead of $Pnam$. This is suggested by the high anisotropic thermal vibration of atom C(8) out of the plane of the five-membered ring (Table 2) and by its apparently short (1·405 Å) single bond to its mirror-related atom. The choice of space group $Pnam$ thus implies the assumption of a slight disorder about the ethylene bridge.*

TABLE 2

Vibration tensor components (Å^2 $\times$ 10^3) for the temperature factor expression $\exp\left(-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{23}b^*c^*kl\right)$ with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	33(1)	31(1)	77(1)	−3(1)		
Cl	99(3)	107(4)	63(3)	8(3)	−5(2)	−18(2)
C(1)	47(6)	30(5)	73(8)	−20(5)	−14(6)	14(6)
C(2)	60(7)	69(8)	69(8)	−11(6)	−10(6)	12(6)
C(3)	61(8)	84(8)	66(9)	−7(7)	0(7)	20(7)
C(4)	79(8)	70(8)	66(7)	1(8)	−11(7)	3(6)
C(5)	68(9)	62(8)	83(9)	−5(7)	−7(7)	5(7)
C(6)	56(7)	44(6)	74(8)	−1(6)	−12(6)	15(6)
C(7)	58(7)	47(6)	88(9)	−8(6)	−27(7)	10(7)
C(8)	44(6)	161(13)	102(8)	−44(8)	−13(6)	56(8)
N(1)	54(5)	44(5)	61(5)	−13(4)	−11(4)	2(4)
N(2)	42(5)	40(5)	84(6)	−6(4)	−5(4)	7(5)



A drawing of the molecule. Mean estimated standard deviations are: C–C 0·016, C–N 0·016, and Co–N 0·008 Å; N–Co–N 0·4 and other angles 0·9°

DISCUSSION

In the present analysis, no co-ordination occurs between the different molecular units, the shortest intermolecular Co–N distance being 3·84 Å. Two structure investigations [4,9,10] of (I) have been made. The form which will be represented, $[Co(salen)]_2$, is dimeric[4] with Co-O bonding links of 2·25 Å between its halves [Cu(salen), which is isomorphous, has a similar structure].[11] In Co(salen)$CHCl_3$ there is no axial co-ordination,[9] the nearest intermolecular atom to one cobalt being a second at 3·45 Å. Solid $[Co(salen)]_2$ does not react with oxygen,[4] but Co(salen)$CHCl_3$ does.[9] Reaction with oxygen occurs

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20504 (5 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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in solution[2] where Co(salen) is monomeric. Activity towards oxygen may depend on monomeric character in Co(salen) but our results show that the same cannot be true for (II).

In spite of the lack of axial co-ordination, (III) does not have a perfectly planar geometry. The CoN_4 unit is a very squat pyramid, the cobalt atom lying 0·14 Å above the N_4 plane. The benzene rings are tilted below this plane, their planes lying at an angle of 31° to each other, which contrasts with that of 22° in $[Co(salen)]_2$,[4] and with $Co(salen)CHCl_3$ in which the overall skeleton of the molecule is nearly planar.[9] On the basis of a steric argument the greater displacement of cobalt in (III) from the bulk of the molecule, compared with the salen systems, would be expected to enhance activity towards addition of another ligand, which is clearly not correct.

Recently it has been shown[12] that in its cobalt(III) state, amben forms five-co-ordinate complexes which are probably square pyramidal in shape, *e.g.* Co(amben)Cl, and which can coexist with more normal six-co-ordinate species, *e.g.* Co(amben)Cl(pyridine). The existence of these five-co-ordinate species could be related to the rather large interplanar angle of 31° in (III).

The Co–N bond distances in (III) [1·822(8) and 1·847(8) Å, see Figure] are shorter than the analogous bonds in $[Co(salen)]_2$ (Co–N 1·88, Co–O 1·88 and 1·95 Å),[4] but roughly comparable with those in $Co(salen)CHCl_3$ [Co–N 1·864(5) and 1·829(5), Co–O 1·835(4) and 1·869(5) Å].[9] The latter is probably better for comparison because of its monomeric nature, and its mean Co–N and Co–O distances (1·848 and 1·853 Å) are more nearly equal than corresponding bonds in (III). In the esr spectrum of Co(amben) in pyridine there is a small lifting of the degeneracy of the $g_\perp$ absorption, which Co(salen) does not show under comparable conditions.[13]

In attempting to explain the differences in chemical behaviour between Co(amben) and Co(salen), one can now eliminate structural arguments based on dimer formation or lack of planarity of the complexes. Moreover it is unlikely that the slight variations in bond lengths in the CoN_4 unit compared with the CoN_2O_2 could be important in a spatial sense. It seems more probable that the differences in gross chemical properties arise for electronic reasons,[6,13] Co(amben) having a ground state of B_2 symmetry compared with that of A_1 in Co(salen).

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