

Krebs, 1968) and $\text{Re}(\text{bpy})\text{ClO}_3$ (Sergiyenko, Khodashova, Porai-Koshits & Butman, 1977).

The shift from Re to Re(i) (0.60 Å) is essentially a shift away from O(1) and toward Cl(2). Other distances remain more or less the same. In fact, the Re(i)—Cl(2) distance is almost equal to the Re—O(1) distance, and *vice versa*. It might thus be suggested that the molecule is disordered by 'reflexion' in the plane of O(2), O(3), H_2O , and Cl(1). Alternatively, it could be said that the molecule occupies two alternative sites, in which the positions of these four atoms are more or less constant.

The phenanthroline cations have the normal structure. All interatomic distances and angles are similar to those found in $\text{C}_{12}\text{H}_8\text{N}_2 \cdot 2\text{HClO}_4 \cdot \text{H}_2\text{O}$ (Thevenet, Rodier & Khodadad, 1978), where the phenanthroline groups also exist as diprotonated cations.

The packing of the Cl^- ions in the unit cell is shown in Fig. 1. The shortest contacts for Cl^- anions are with N(1) and N(10) [H(1) and H(10)] and two with H_2O molecules from two different complex anions. The values of these distances (2.99–3.08 Å) suggest that these are hydrogen bonds.

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Structure of Bis[μ -bis(salicylaldehyde)ethylenediimine]-dicobalt(III) Dichloride Chloroform Solvate*

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Abstract. $[\text{Co}_2(\text{C}_{32}\text{H}_{28}\text{N}_4\text{O}_4)]^{2+} \cdot 2\text{Cl}^- \cdot 4\text{CHCl}_3$, FW 1198.89, *Pbca*, $a = 24.588$ (9), $b = 11.124$ (2), $c = 17.034$ (2) Å, $Z = 4$, $\rho_c = 1.71$, $\rho_o = 1.61$ Mg m^{-3} , $F(000) = 2400$, $\lambda(\text{Co } K\alpha_1) = 1.78892$ Å, $\lambda(\text{Co } K\alpha_2) = 1.79278$ Å. The oxygen-carrying compound bis(salicylaldehyde)ethylenediiminedicobalt(II) [Co(salen)] is oxidized by O_2 in chloroform solution to give a Co^{III} (salen) chloride dimer. Refinement by least squares of all 1845 data gave a final *R* index of 0.126. The dimers are formed across a center of symmetry by

the Co atom coordinating to a salen O atom of the other half of the dimer. The Co—O bond is short [1.99 (1) Å] and the tricoordinated salen O atom causes the salen group to be slightly distorted.

Introduction. In the course of trying to obtain crystals of an oxygen adduct of bis(salicylaldehyde)ethylenediiminedicobalt(II) [Co(salen)], we obtained brown crystals of a material which was inactive toward oxygen. An X-ray structural determination showed that the compound was an irreversibly oxidized Co(salen) dimer similar to those found for Co^{II} (salen) (Delasi, Holt & Post, 1971), for Cu(salen) (Hall & Waters, 1960; Pachler & von Stackelberg, 1960) and for Fe(salen) chloride (Gerloch & Mabbs, 1967). It seemed useful to report our structure for comparison with these compounds, as well as to provide some bonding parameters for an unambiguous Co^{III} complex.

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The compound was prepared by dissolving Co(salen) in boiling chloroform to obtain a saturated solution, and cooling to 275 K. The red crystals of the oxygen-active Co(salen)·CHCl₃ which form were filtered (Schaefer & Marsh, 1969) and the solution was left to stand at 275 K in contact with air. After some weeks brown boat-shaped crystals appeared; these were removed, washed, and used for the structural determination.

Oscillation and Weissenberg photographs gave preliminary cell dimensions and showed *mmm* symmetry. Systematic absences indicated the orthorhombic space group *Pbca* (No. 61). Cell dimensions were measured and data collected using Co *Kα* radiation on a GE quarter-circle diffractometer automated by Datex. A θ - 2θ scan was used at a scan speed of 2° min⁻¹, with 20 s background counts taken at each end of the scan. The variances in the intensities, $\sigma^2(I)$ (used to derive the weights for the least-squares refinement), were obtained from counting statistics plus an additional term: $(0.02 \times \text{scan counts})^2$.

The coordinates of the Co atom were determined from a Patterson map and the remaining non-hydrogen atoms were located by the usual structure factor/Fourier techniques. H atoms were added as fixed contributions at calculated positions ($d_{\text{C-H}} = 0.95 \text{ \AA}$, $B = 5 \text{ \AA}^2$) and the structure was refined with anisotropic thermal parameters for Co and Cl. The refinement converged with R_1 (for all 1845 reflections) = 0.126 [$R_1 = (\sum |F_o - F_c| / \sum F_o) / \sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4$]^{1/2} and $R_2 = 0.130$. The goodness-of-fit, $[\sum w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, is 1.65. Final positional parameters are given in Table 1.* The relatively high values of the *R* indices reflect that (1) all the non-negative structure factors were used in the refinement and in calculating these indices, and (2) the molecules of solvent chloroform in the structure exhibit very high anisotropic thermal motion which is not well fit by the model. This latter aspect of the high *R* indices is also reflected in the goodness of fit which is larger than we would expect. The high apparent thermal motion may be just that, it may represent a disorder of the chloroform molecules, it may arise from partial occupancy of the solvent molecule sites, or it may result from some combination of all these factors. The resulting CHCl₃ molecules are somewhat distorted (Cl-C-Cl angles range from 106.2 to 113.2°), but the pattern of the thermal motion is not simple. The Co dimer, however, is not affected by these difficulties and it shows no unusual thermal motion. This portion of the structure is better determined than are the chloroform molecules.

* Lists of structure factors, thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34239 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters ($\times 10^4$, for $C \times 10^3$) of the non-hydrogen atoms

	x	y	z
Co	360 (-8)	117 (2)	4287 (1)
Cl(1)	495 (1)	894 (3)	3170 (2)
O(1)	-179 (3)	969 (7)	4717 (4)
O(2)	903 (3)	842 (7)	4758 (4)
N(1)	859 (4)	-1289 (9)	3944 (5)
N(2)	-181 (4)	-1056 (9)	3774 (6)
Cl(2)	1764 (2)	1820 (6)	1901 (3)
Cl(3)	2426 (2)	1689 (5)	3239 (3)
Cl(4)	2156 (3)	-388 (4)	2464 (3)
Cl(5)	261 (2)	4370 (4)	3435 (2)
Cl(6)	724 (2)	4328 (4)	4996 (2)
Cl(7)	1388 (2)	3876 (5)	3661 (3)
C(1)	61 (1)	-217 (1)	339 (1)
C(2)	1 (1)	-228 (1)	363 (1)
C(3)	-64 (1)	-66 (1)	354 (1)
C(4)	-84 (1)	53 (1)	369 (1)
C(5)	-130 (1)	89 (1)	327 (1)
C(6)	-149 (1)	203 (1)	337 (1)
C(7)	-126 (1)	283 (1)	388 (1)
C(8)	-82 (1)	246 (1)	431 (1)
C(9)	-59 (1)	132 (1)	423 (1)
C(10)	138 (1)	-135 (1)	413 (1)
C(11)	165 (1)	-49 (1)	456 (1)
C(12)	222 (1)	-71 (1)	472 (1)
C(13)	252 (1)	-8 (1)	513 (1)
C(14)	230 (1)	113 (1)	539 (1)
C(15)	175 (1)	140 (1)	524 (1)
C(16)	141 (1)	57 (1)	485 (1)
C(17)	192 (1)	98 (1)	269 (1)
C(18)	76 (1)	369 (1)	405 (1)

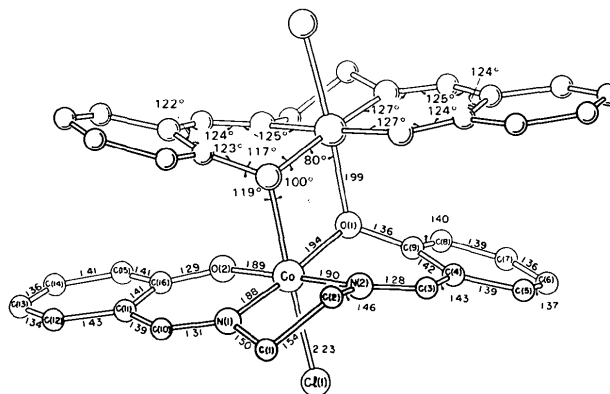


Fig. 1. View of the dimer showing the numbering system, distances (Å) and some angles (°). Standard deviations are: Co-Cl, Co-O and O-C 0.01 Å; N-C and C-C 0.02 Å; and for angles 1°.

Discussion. The structure of the dimer, the numbering scheme, bond distances and bond angles are shown in Fig. 1. Angles about the Co atom are given in Table 2. The Co achieves near-octahedral geometry by coordinating to a salen O atom of a centrosymmetrically related monomer and a chloride ion. The in-plane Co-O(1) distance of 1.94 (1) Å is longer than that observed in other Co(salen) complexes (1.90 Å; Calligaris, Nardin & Randaccio, 1972), because of the additional coordination of the O. The C(9)-O(1) bond, 1.36 (1) Å, is also lengthened, and the geometry about

Table 2. *Angles around Co (°)*

Cl(1)—Co—O(1')	175.5 (3)	O(1')—Co—N(2)	88.5 (4)
Cl(1)—Co—O(1)	96.3 (2)	O(1)—Co—O(2)	88.3 (3)
Cl(1)—Co—O(2)	88.4 (3)	O(1)—Co—N(1)	174.2 (4)
Cl(1)—Co—N(1)	89.3 (3)	O(1)—Co—N(2)	92.2 (4)
Cl(1)—Co—N(2)	89.4 (3)	O(2)—Co—N(1)	93.5 (4)
O(1')—Co—O(1)	79.8 (3)	O(2)—Co—N(2)	177.8 (4)
O(1')—Co—O(2)	93.7 (3)	N(1)—Co—N(2)	86.2 (4)
O(1')—Co—N(1)	94.6 (4)		

O(1) implies that its hybridization is more nearly tetrahedral (*sp*³) than trigonal (*sp*²). A similar lengthening of the Co—O bond was observed by Brückner, Calligaris, Nardin & Randaccio (1969) in the structure of a dimer of Co^{II}(salen). In that structure, the bonding about the tricoordinated O atom is not so obviously tetrahedral but the C—O bond length (1.34 Å) is slightly longer than normal (1.32 Å).

Because of the nature of the chloride ligand (unambiguously Cl⁻), the Co atom is definitely present as Co^{III}. Thus the bonding parameters, especially the axial Co—O(1') distance of 1.99 Å, can be considered as characteristic of Co^{III}. This can be contrasted with the comparable distance of 2.25 Å observed by Bruckner *et al.* in [Co^{II}(salen)]₂. It is interesting that O(1) has moved out of the plane of the Co(salen) group in order to achieve a shorter *axial* Co^{III}—O distance, whereas the in-plane Co—O and Co—N distances seem to be unaffected by the oxidation state of the Co. The in-plane Co—O distance here is also much shorter than the comparable distances in the previously reported Fe (2.18 Å) and Cu (2.41 Å) complexes. Only in the present case does this bonding lead to an 18-electron complex; in the Cu case it leads to a 19-electron complex while in the Fe^{III} and Co^{II} cases it leads to 17-electron complexes. In all of these compounds the metal—metal distances of more than 3 Å preclude any bonding interaction.

The crystal contains two molecules of chloroform per monomer, both of which appear to be involved in weak hydrogen bonding. Distances and angles within these molecules, as shown in Table 3, are reasonable. H(17) forms a weak hydrogen bond to Cl(1) while H(18) forms weak bifurcated hydrogen bonds to Cl(1) and O(2). Distances and angles of these interactions are detailed in Table 4. Similar interactions were observed in the structure of Co(salen).CHCl₃ (Schaefer & Marsh, 1969). Because these interactions are weak it is not unreasonable to suspect that the solvent sites may

Table 3. *Distances (Å) and angles (°) in the chloroform molecules*

C(17)—Cl(2)	1.68 (1)	C(18)—Cl(5)	1.77 (1)
C(17)—Cl(3)	1.75 (1)	C(18)—Cl(6)	1.76 (1)
C(17)—Cl(4)	1.68 (1)	C(18)—Cl(7)	1.70 (1)
C(17)—H(17)	0.96	C(18)—H(18)	0.94
Cl(2)—C(17)—Cl(3)	109 (1)	Cl(5)—C(18)—Cl(6)	110 (1)
Cl(2)—C(17)—Cl(4)	113 (1)	Cl(5)—C(18)—Cl(7)	111 (1)
Cl(3)—C(17)—Cl(4)	106 (1)	Cl(6)—C(18)—Cl(7)	111 (1)
H(17)—C(17)—Cl(2)	103	H(18)—C(18)—Cl(5)	106
H(17)—C(17)—Cl(3)	117	H(18)—C(18)—Cl(6)	109
H(17)—C(17)—Cl(4)	108	H(18)—C(18)—Cl(7)	110

Table 4. *Distances (Å) and angles (°) for the hydrogen bonding*

C(17)···Cl(1)	3.59 (2)	C(17)—H(17)—Cl(1)	160
H(17)···Cl(1)	2.67	C(18)—H(18)—Cl(1)	143
C(18)···Cl(1)	3.52 (2)	C(18)—H(18)—O(2)	145
H(18)···Cl(1)	2.72	Cl(1)—H(18)—O(2)	66
C(18)···O(2)	3.41 (2)	H(17)—Cl(1)—Co	105
H(18)···O(2)	2.61	H(18)—Cl(1)—Co	87
		H(17)—Cl(1)—H(18)	86
		H(18)—O(2)—Co	98
		H(18)—O(2)—C(16)	118

be only partially occupied, possibly explaining the low observed density, which is consistent with a formulation containing 1.7 CHCl₃ instead of 2 CHCl₃.

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