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Oxygen-Carrying Cobalt Compounds. I. Bis(salicylaldehyde)ethylenediiminecobalt(II) Monochloroformate

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The structure of bis(salicylaldehyde)ethylenediiminecobalt(II) monochloroformate, $CoO_2N_2C_{16}H_{14}.CHCl_3$ has been determined by Patterson and Fourier techniques and refined by three-dimensional least squares, using 1938 reflections, to an R index of 0·086. The substance crystallizes in space group $P2_1/n$ with $a=13·92$, $b=7·69$, $c=17·46$ Å, and $\beta=98·4°$. The crystal contains pairs of nearly planar bis(salicylaldehyde)ethylenediiminecobalt(II) molecules at van der Waals distances (3·5 Å) apart and related by a center of symmetry. The chloroform molecules occupy passageways parallel to the b axis and are weakly hydrogen-bonded to the metal complexes. The passageways provide an explanation for the ease of oxygen uptake of this substance. Bond distances and angles in both the metal complex and the chloroform molecule are normal.

Introduction

A number of complexes of cobalt (II) have the interesting ability to absorb and desorb oxygen reversibly. These complexes were originally reported by Pfeiffer, Breith, Lubbe & Tsumaki (1933) and were studied in detail by Calvin and collaborators (Martell & Calvin, 1952*a*). A part of these latter studies included the X-ray examination by E. W. Hughes of many such compounds (Martell & Calvin, 1952*b*). Hughes found a monoclinic cell for the compound bis(salicylaldehyde)-ethylenediiminecobalt(II) with dimensions $a=14·07$, $b_0=7·06$, and $c_0=26·25$ Å; $\beta=97·7°$. The space group was $A2/a$, with 8 molecules in the unit cell. From the assumed size and shape of the molecule and from packing considerations, he was able to deduce a structure which fitted the available data for the compound. However, since he did not have complete three-dimensional data, he could not determine the molecular structure with any accuracy.

We are trying to learn the way in which the oxygen molecule is bound when this chelate absorbs oxygen, and as part of the preliminary studies we wanted to determine the structure of the unoxygenated form of the complex. We prepared the substance in a nitrogen atmosphere after the method of Tsumaki (1938) and crystallized it from several solvents. We obtained well-formed, cherry-red crystals from chloroform which, upon being exposed to air, turned a shiny black. This paper reports the structure of this active but unoxygenated compound, bis(salicylaldehyde)ethylenediiminecobalt(II)monochloroformate.

Experimental

The compound was prepared as directed by Tsumaki (1938); most of the operations were done in a nitrogen-filled glove bag. The first product was dissolved in boiling chloroform and the hot saturated solution filtered into a Dewar flask. This was stoppered and left overnight to cool. Short, red needles formed which were removed by filtration and stored in a nitrogen-filled desiccator. The crystal used for the collection of the X-ray data was removed from the nitrogen atmosphere and mounted, using an epoxy cement, in contact with the air; it was then completely covered with the mounting cement to prevent loss of $CHCl_3$ or addition of O_2. Crystals which were not so covered deteriorated on standing overnight; they appeared to be shiny black and crystalline, but their diffraction pattern was that of a powder. The coated crystal showed no powder lines on a rotation photograph taken six days after it had been mounted. The crystal was placed on a Picker four-circle diffractometer, centered, and unit cell dimensions were measured. Because of a blunder, a triclinic cell was chosen with half the volume of the correct cell, and a complete set of data was collected. A cursory inspection of the Patterson map calculated from these data revealed a symmetry higher than triclinic, so a new cell was chosen and its dimensions measured with the use of the 2θ values of both Co $K\alpha$ and $K\beta$ peaks for nine reflections. A complete set of new data was collected with this cell, and prior to any further calculations the two sets of data were each

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indexed to refer to a cell in space group $P2_1/n$. The resulting cell dimensions are given, along with other crystal data, in Table 1. Our density measurement is very imprecise. It was made by flotation in an aqueous cadmium nitrate solution, but the crystals appeared to increase in density rapidly, as soon as they were immersed in the solution, so only a rough value could be obtained. These were old crystals, and the fact that the measured density is so low implies that there had been a spontaneous loss of chloroform of crystallization; such a loss has been noted earlier (Tsumaki, 1938).

Table 1. *Crystal data for bis(salicylaldehyde)-ethylenediiminecobalt(II) monochloroformate*

$a_0=13{\cdot}92$ (1) Å	$CoO_2N_2C_{16}H_{14}.CHCl_3$
$b_0=7{\cdot}69$ (1)	M.W. $=444{\cdot}6$
$c_0=17{\cdot}46$ (2)	Space group $P2_1/n$
$\beta=98{\cdot}4$ (2)°	$z=4$
	$F(000)=900$
$D_m=1{\cdot}5$ g.cm^{-3}	$D_x=1{\cdot}60$ g.cm^{-3}
λCo $K\alpha=1{\cdot}7902$ Å	λCo $K\beta=1{\cdot}62075$ Å

The intensity data were collected on an automated Picker diffractometer using cobalt radiation, an iron metal filter (0·0008″), and a θ–2θ scan. No attenuators were required for any reflection. The scan range included both $K\alpha_1$ and $K\alpha_2$ peaks. The crystal used was a fragment $0{\cdot}24\times0{\cdot}18\times0{\cdot}11$ mm^3, cut from a needle and mounted with the 0·24 mm direction (the b axis) roughly parallel to the φ axis of the diffractometer.

The first data set was collected in about one week of continuous operation. During this time a single reflection (262) was monitored; it showed no appreciable variations greater than those expected from counting statistics. Because of the choice of the small triclinic cell, this data set comprized only half of the reflections available below $2\theta=133°$ (those with $h+k+l=2n$), but each one was measured twice. The second data set included all the reflections available below 2θ–$133°$. It required about ten days to collect, and a different reflection ($\bar{2}22$) was followed during this time. Its intensity decreased substantially during this period, from about 116,000 counts to about 100,000 counts. The decrease was approximately linear, and therefore a correction linear with time was applied to all the reflections of the second data set. For all reflections, a standard deviation $\sigma(I)$ was assigned from the formula

$$\sigma^2I=\sigma_1^2+(\sigma_2^2+\sigma_3^2)\,(t/80)^2\,.$$

Here $\sigma_1=\sqrt{S}+dS$, $\sigma_2=\sqrt{B_1}+dB_1$, and $\sigma_3=\sqrt{B_2}+dB_2$; S is counts in scan, B_1 and B_2 are counts in the background, t is the time for the scan (each background was counted 40 sec), and the constant d, which takes account of errors not attributable to counting statistics, was chosen to be 0·02 (Busing & Levy, 1957).

All of the reflections for which I was greater than zero were treated as observed, but for those reflections for which I was less than $3\sigma(I)$, the value of $\sigma(I)$ was increased by the factor $(F_{obs}+2)/(F_{obs}+1)$. The purpose of this was to downweight the very weak reflections; our experience has been that standard deviations computed from counting statistics alone seem to be too small for very weak reflections. A total of 4372 reflections were measured, of which 2730 were more than 3σ above background. These resulted, when merged, in a total of 2042 independent reflections, of which 1938 were non-zero and were used in the solution and refinement of the structure. In general, those reflections with $h+k+l$ even were measured three times and those with $h+k+l$ odd only once. Therefore, the even reflections received higher weights in the refinement.

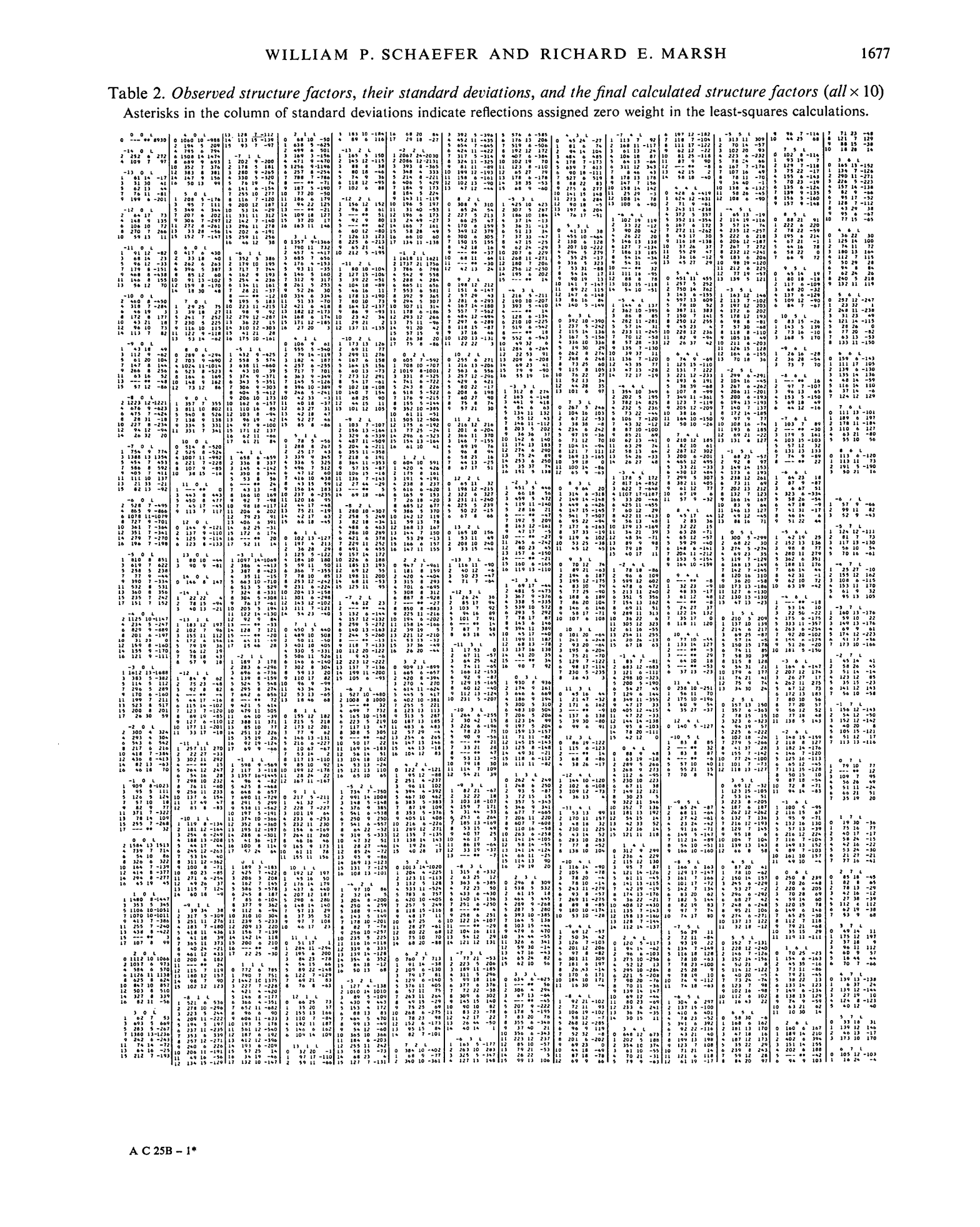
Both sets of data were corrected for Lorentz and polarization factors, and were then merged by a least-squares calculation of the inter-group scaling factor. No absorption corrections were applied; μ for this compound is 51·6 cm^{-1}, and μr_{max} is thus 0·82. Neglect of this correction could have led to errors in the relative values of the structure factors of about 10% in the extreme case.

Solution and refinement of the structure

The complete data set was used to calculate a three-dimensional sharpened Patterson map, and from this map the coordinates of the cobalt atoms were easily obtained. At this point, we looked for a vector set due to the three chlorine atoms in the chloroform molecule, but did not find it. The measured density had been low, and so we were not sure that our material contained chloroform. Because we did not find a clear indication of it in the Patterson map we concluded that it was absent and calculated an electron density map based only on the cobalt atoms. This map revealed about half the light atoms (and the three chlorine atoms, although they were not noticed); a second map phased on the new light atoms plus the cobalt showed the rest of the bis(salicylaldehyde)ethylenediiminecobalt(II) molecule. These atoms were carefully located and a least-squares refinement was initiated; however, the refinement diverged quickly. A check of the second electron density map showed that the chloroform molecule was indeed present; when the carbon atom and the three chlorine atoms were included in a structure factor calculation, the R index (defined as $\Sigma\,||F_o|-|F_c||/\,\Sigma\,|F_o|$) was 0·27. Three cycles of full-matrix least-squares, varying the scale factor, positional parameters for all the non-hydrogen atoms, anisotropic thermal parameters for the four heavy atoms, and isotropic thermal parameters for the light atoms, reduced R to 0·14. The hydrogen atoms were then introduced at their calculated positions and four more cycles of refinement, including the hydrogen positional parameters (their thermal parameters were fixed at $B=5{\cdot}0$ Å^2) and anisotropic thermal parameters for all the non-hydrogen atoms, completed the refinement. The final cycles included 272 parameters in two

Table 2. *Observed structure factors, their standard deviations, and the final calculated structure factors* (*all* × 10)

Asterisks in the column of standard deviations indicate reflections assigned zero weight in the least-squares calculations.



full matrices: the positional parameters of all of the atoms in one (120 parameters) and a scale factor, a secondary extinction factor (Larson, 1967), and anisotropic thermal parameters for all the non-hydrogen atoms in the other (152 parameters). The final R index is 0·086, and the 'goodness of fit' is 2·02; during the last cycle, the maximum shift of any parameter was less than one-half its standard deviation. The quantity minimized in the least-squares calculations was $\Sigma\, w(F_o^2-F_c^{*2})^2$, where $w=[\sigma(F_o^2)]^{-2}$ and F_c^* is as defined by Larson (1967), equation 3.

Calculations of cell dimensions, calculations for the operation of the diffractometer, and preliminary data processing were done on an IBM 7044 machine using programs written by Professor Håkon Hope and Dr A.T.Christensen; the rest of the calculations were carried out on an IBM 7094 computer using subprograms operating under the CRYRM system (Duchamp, 1964). Atomic form factors for Co, Cl, O, N, and C were taken from *International Tables for X-ray Crystallography* (1962), the values for cobalt being reduced by 2·19 electrons to take account of anomalous dispersion (Cromer, 1965). $\Delta f'$ was obtained by interpolation, $\Delta f''$ was ignored. Form factors for hydrogen were taken from Stewart, Davidson, & Simpson, (1965).

The observed structure factors, their estimated standard deviations and the calculated structure factors are given in Table 2. The final parameters and their standard deviations are given in Table 3. Because the final refinement was by block matrix, the derived e.s.d.'s are slightly underestimated. A difference map calculated from the final parameters showed one excursion of +0·64 e.Å^{-3}, about 1 Å from the cobalt atom; no others greater than 0·5 e.Å^{-3} were found. A final electron-density map calculated in the plane of the molecule is shown in Fig. 1.

Description of the structure

(*A*) *The bis(salicylaldehyde)ethylenediiminecobalt(II) molecule*

The molecule is essentially planar. Fig. 2 shows the bond distances (2*a*) and bond angles (2*b*). The standard deviations given for the distances and angles were calculated from the e.s.d.'s in the positional parameters; the agreement found among equivalent distances is in general not as good as these e.s.d.'s would predict. The coordination about the cobalt atom is very nearly square planar; the Co–N and Co–O distances are essentially the same and the angles differ from 90° by very little. In many cobalt complexes, Co–N distances are about 1·96 Å and Co–O distances 1·90 Å (Sutton, 1958, 1965). Thus the Co–O and Co–N distances in the bis(salicylaldehyde)ethylenediimine complex are both rather short; this is probably because the cobalt atom forms only four bonds, so each of these can be stronger than normal. The complex molecules are stacked in pairs related by a center of symmetry, with about 3·5 Å between complexes (see Fig. 3): a given Co atom is 3·45 Å from the Co atom in the nearest other complex, and this neighbor is in a direction roughly perpendicular to the O–O–N–N plane of the complex. (The nearest neighbor on the other side of the plane is a carbon atom, C(3), 4·12 Å away.) The only close approaches to cobalt in a direction perpendicular to the plane of the molecule are of hydrogen atoms connected to the ethylene bridging group. The Co...Co distance is 1 Å longer than that found for a direct Co–Co bond

Table 3(*a*). The final heavy atom parameters

Values in parentheses are standard deviations. Anisotropic temperature factors are of the form

$$\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]\,.$$

All values have been multiplied by 10^3.

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co	615(1)	1853(1)	4802(1)	40(1)	183(3)	40(1)	3(2)	3(1)	11(2)
O(1)	1301(3)	2251(6)	5789(3)	40(3)	259(12)	39(2)	32(10)	-1(4)	-13(8)
O(2)	1748(3)	885(5)	4580(2)	40(3)	255(11)	33(2)	-6(8)	9(3)	-3(7)
N(1)	-40(3)	1492(7)	3805(3)	44(4)	204(14)	40(3)	-2(11)	-18(5)	10(9)
N(2)	-520(3)	2753(7)	5038(3)	31(3)	254(16)	47(3)	3(11)	2(5)	36(11)
C(1)	-1051(6)	2133(12)	3694(6)	58(6)	254(22)	83(5)	11(17)	-44(8)	-20(17)
C(2)	-1371(6)	2677(12)	4406(5)	55(5)	388(25)	50(4)	84(18)	12(7)	126(15)
C(3)	-690(5)	3428(9)	5679(5)	52(5)	220(18)	62(4)	25(15)	28(7)	37(14)
C(4)	14(5)	3542(8)	6367(4)	62(5)	137(15)	53(4)	2(13)	59(7)	-4(11)
C(5)	-270(5)	4228(10)	7040(5)	62(5)	284(21)	62(4)	34(15)	51(7)	19(14)
C(6)	341(7)	4305(11)	7714(5)	105(7)	373(29)	58(4)	18(21)	82(8)	-50(15)
C(7)	1284(7)	3646(11)	7741(4)	101(7)	363(25)	40(3)	6(20)	30(8)	-25(14)
C(8)	1588(5)	2954(11)	7096(4)	61(5)	287(21)	45(3)	26(16)	19(6)	13(14)
C(9)	955(5)	2893(10)	6385(4)	47(5)	228(18)	43(3)	5(15)	35(6)	-16(13)
C(10)	301(5)	794(9)	3236(4)	78(5)	210(17)	31(3)	-44(14)	-15(6)	0(11)
C(11)	1239(4)	98(12)	3250(3)	55(4)	196(14)	43(3)	-14(21)	11(6)	15(17)
C(12)	1485(6)	-716(10)	2584(4)	85(6)	274(22)	38(3)	-46(16)	9(7)	1(12)
C(13)	2362(6)	-1501(11)	2581(5)	82(6)	257(21)	42(3)	-15(18)	37(7)	-46(14)
C(14)	3003(5)	-1482(10)	3246(4)	69(5)	274(21)	50(4)	18(16)	42(7)	-19(13)
C(15)	2796(5)	-700(9)	3899(4)	60(5)	270(21)	38(3)	-3(14)	13(6)	-7(11)
C(16)	1918(3)	147(11)	3943(3)	38(3)	198(14)	41(3)	-18(18)	21(5)	13(15)
C(17)	-1492(5)	1722(11)	360(4)	59(5)	296(19)	45(3)	0(16)	-7(6)	-1(14)
Cl(1)	-1298(1)	352(4)	1162(1)	96(2)	608(9)	53(1)	-19(8)	-23(2)	120(6)
Cl(2)	-1656(1)	455(3)	-473(1)	104(2)	484(9)	52(1)	30(6)	2(2)	-131(4)
Cl(3)	-516(2)	3096(4)	352(2)	102(2)	409(7)	122(2)	-155(6)	-73(3)	97(6)

(*b*). The hydrogen positional parameters

Values in parentheses are standard deviations. All values have been multiplied by 10^3. All hydrogen atoms were assigned isotropic temperature factors, $B=5{\cdot}0$ Å^2.

Atom	x	y	z
H(1)	-139(4)	139(7)	355(3)
H(2)	-108(4)	315(8)	335(3)
H(3)	-161(4)	379(7)	441(3)
H(4)	-175(4)	144(7)	461(3)
H(5)	-134(4)	395(6)	571(3)
H(6)	-88(3)	452(7)	704(3)
H(7)	10(3)	465(8)	815(3)
H(8)	162(4)	370(7)	822(3)
H(9)	221(4)	253(7)	713(3)
H(10)	.1(4)	80(7)	280(3)
H(11)	109(3)	-67(7)	219(3)
H(12)	249(4)	194(8)	215(3)
H(13)	359(4)	-198(7)	321(3)
H(14)	311(4)	-70(7)	432(3)
H(15)	-203(4)	239(7)	45(3)

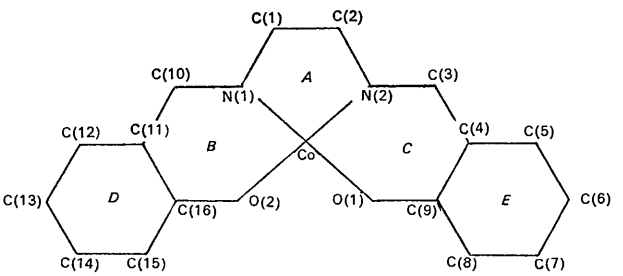
(Pauling, 1960) so that there is no significant metal—metal interaction in these complexes; the spacing between the complexes is determined by van der Waals forces.

The planarity of the molecule is illustrated in Fig. 4. This is a projection parallel to the least-squares plane through the two oxygen and two nitrogen atoms. It can be seen that the central portion of the molecule is very nearly flat and that the major departures from planarity are found in the carbon atoms of the ethylenediimine bridging group and in the two benzene rings. Least-squares planes were calculated for various parts of the molecule and the deviations of selected atoms from these planes are given in Table 4. A plane was calculated for the entire molecule (weighting Co 2·6 times as heavily as the lighter atoms) and the average deviation of an atom from this plane was found to be 0·058 Å. It may be noted from Table 4 that the two benzene rings (*D* and *E*) are planar within the experimental error and the two other six-rings (*B* and *C*) are very nearly so. The overall deviations, however, result in the molecule having the slightly bowed shape shown in Fig. 4.

The positional parameters of all the hydrogen atoms in this structure were refined and the hydrogen atoms, in general, ended up in reasonable positions. The average C–H distance turned out to be 0·91 Å with an e.s.d. of 0·09 Å; this is about twice the e.s.d. calculated for an individual C–H distance. The average deviation of a C–C–H angle in the metal complex from 120° is 3·0°, except, of course, in the ethylenediimine bridge; the angles involving these hydrogen atoms have an average deviation of 5·7° from 109·5°.

The crystal structures of two other bis(salicylaldehyde)ethylenediimine complexes have been studied: the copper compound (Cu salen) (Hall & Waters,

Table 4. *Some deviations of atoms from their least-squares planes*



Plane through:	Deviations from the plane, Å:
N(1), N(2), O(1), O(2)	Co −0·003; N(1) −0·026; N(2) +0·025; O(1) −0·026; O(2) +0·026; C(1) −0·073; C(2) +0·104
A	Co +0·004; N(1) +0·029; N(2) −0·035; C(1) −0·055; C(2) +0·057
B	Co +0·009; N(1) +0·009; O(2) −0·027; C(10) −0·014; C(11) −0·001; C(16) +0·025
C	Co −0·001; O(1) −0·020; N(2) +0·016; C(3) −0·011; C(4) −0·013; C(9) +0·029
D	C(11) +0·008; C(12) −0·001; C(13) −0·005; C(14) +0·003; C(15) +0·004; C(16) −0·009
E	C(4) −0·001; C(5) +0·006; C(6) −0·006; C(7) +0·001; C(8) +0·003; C(9) −0·004
N(1), Co, N(2)	C(1) −0·062; C(2) +0·086

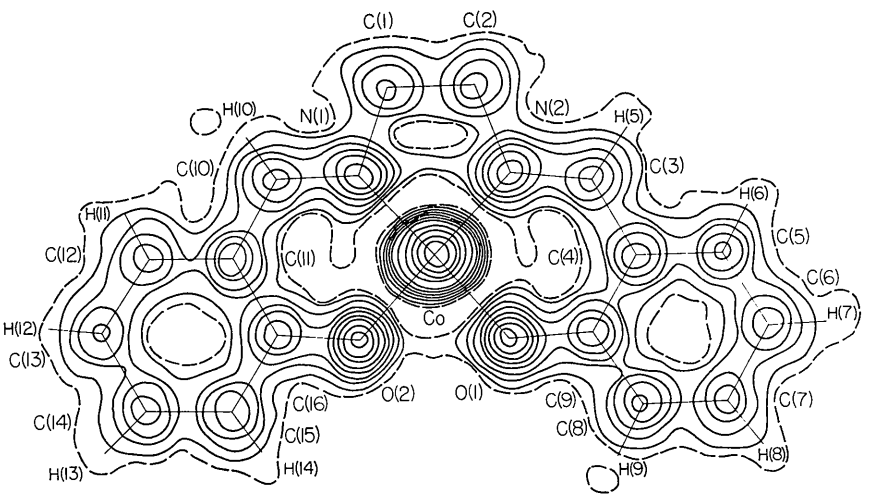


Fig. 1. Electron density map in the plane of the molecule, calculated after the final refinement. Contours are at 0·5, 1,2,3...8, 11,15,20...e.Å^{-3}.

1960; Pachler & v. Stackelberg, 1960) and the iron compound (Fe salen Cl) (Gerloch & Mabbs, 1967). Unlike the cobalt compound, both the copper and iron compounds form bridged dimeric units, one oxygen atom of the salicylaldehyde groups being coordinated to the neighboring metal atom. As a result of this oxygen atom being three-coordinate, the individual complexes are non-planar and the bond distances are not directly comparable to those in Co salen. Nevertheless, there is good agreement between the values we find in Co salen and those reported by Gerloch & Mabbs (1967) for Fe salen Cl (Table 5); no comparison with the copper compound is appropriate since its structure was studied only in projection.

In Table 5 we also list the average bond distances for several salicylaldehyde complexes, as reported by Lingafelter & Braun (1966). The overall pattern of agreement is very reasonable, confirming Lingafelter's statement that this portion of the molecule is relatively insensitive to the nature of the metal ion.

The thermal parameters listed in Table 3 imply, for the Co, N, and O atoms, a moderately anisotropic motion with the principal axes of the thermal ellipsoids oriented rather randomly. The value of B_{max} for these atoms ranges from 5·1 Å^2(Co) to 6·8 Å^2 [N(2)]. The carbon atoms are vibrating more anisotropically with B_{max} for C(1), C(2), and C(10) between 10·2 Å^2 and 12·0 Å^2; for the other carbon atoms, the highest value of B_{max} is 8·7 Å^2. The pattern of thermal motion is best understood by looking at Fig. 5.

(*B*) *The chloroform molecule*

There have been many determinations of the dimensions of the chloroform molecule (Sutton, 1958, 1965). Fig. 6 shows the chloroform molecule with the bond distances and angles we found. The C–Cl distance is apparently short in our molecule, but the effects of thermal motion must be accounted for. The chlorine atoms are, in fact, vibrating very anisotropically, with B_{max} for Cl(3) equal to 19·9 Å^2. This vibration is in a direction nearly perpendicular (the angle is 78·8°) to the C(17)–Cl(3) bond, and it implies a root mean square amplitude of vibration of about 16°, which is very large. The principal motions of the other two chlorine atoms are again approximately perpendicular to the C–Cl bonds (see Fig. 7), and still substantial [14° for Cl(1), 13° for Cl(2)]. Thus, all three C–Cl distances must be corrected for the effects of this vibration. If we use the equation $d_{corr}=[d^2+(B_{max}-\overline{B_{C(17)}})/8\pi^2]^{1/2}$ the average C–Cl distance becomes 1·772 Å, compared to 1·767 Å measured in the vapor phase (Sutton, 1958). In view of the relatively high uncertainty in the corrected bond length, the agreement appears to be satisfactory.

The C(17)–H(15) distance is somewhat short (as in fact are all the C–H distances) but it seemed a bit surprising that the hydrogen atom could be located at all, considering how much the chlorine atoms are vibrating.

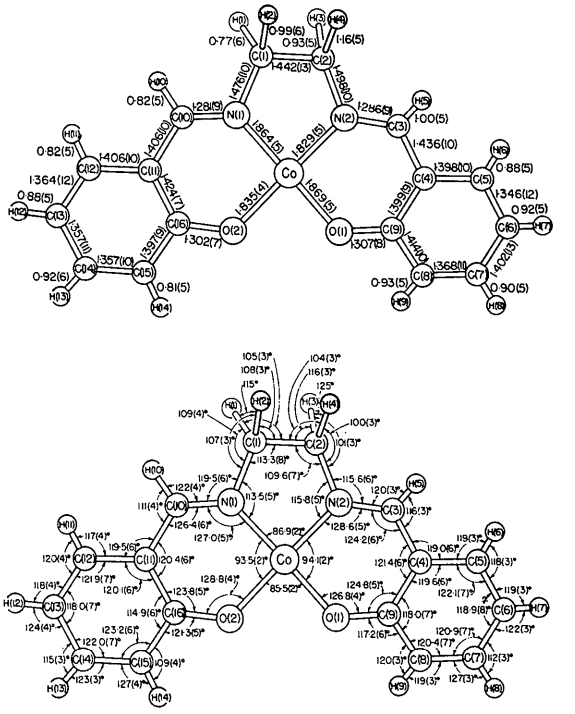


Fig. 2. Bond distances (*a*) and angles (*b*) in the bis(salicylaldehyde)ethylenediiminecobalt(II) molecule.

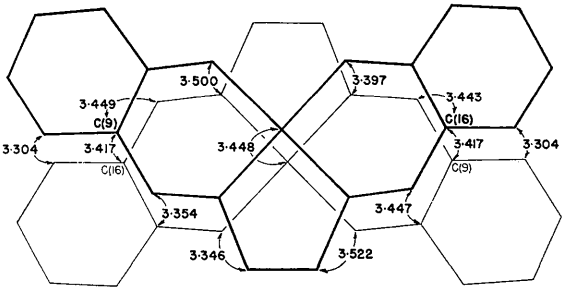


Fig. 3. A pair of bis(salicylaldehyde)ethylenediiminecobalt(II) molecules viewed perpendicular to the planes of the molecules showing close intermolecular contacts.

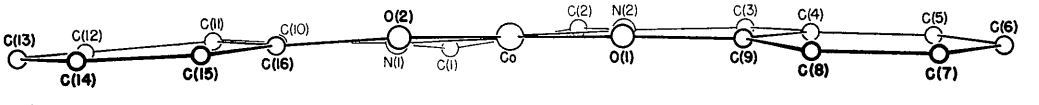


Fig. 4. A side view of the bis(salicylaldehyde)ethylenediiminecobalt(II) molecule showing the deviations of the atoms from a plane.

The explanation probably is that the chloroform molecule is weakly hydrogen bonded to the two oxygen atoms of the bis(salicylaldehyde)ethylenediimine complex. The C(17)–H(15)...O(1) and O(2) distances are 3·362 and 3·205 Å; the two H...O distances are both 2·492 Å. Thus, although the interaction is weak, it serves to fix the position of the hydrogen atom. The chlorine atoms have no such bonding to hold them in place and may, in fact, be randomly oriented, rather than vibrating over such large amplitudes: the two situations would be hard to distinguish. In either case, because the C and H atoms are relatively fixed, the result will appear to be a libration of r.m.s. amplitude 15° about the C–H bond.

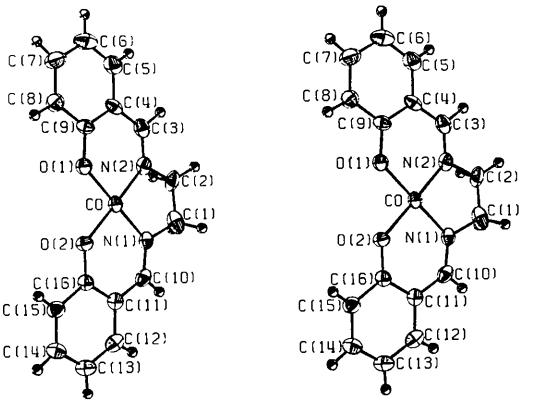


Fig. 5. A representation of the thermal motion in the bis(salicylaldehyde)ethylenediiminecobalt(II) molecule, drawn with *ORTEP* (Johnson, 1965).

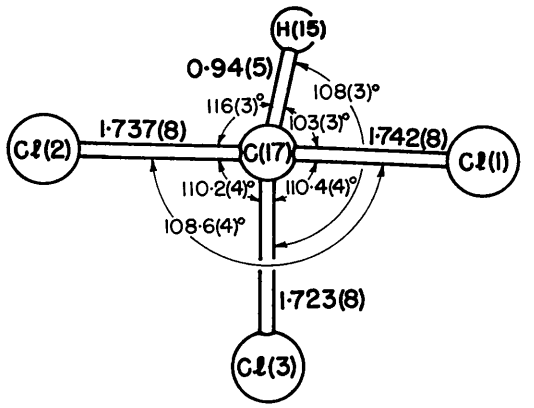


Fig. 6. Bond distances and angles in the chloroform molecule. The thermal motion of the atoms in this molecule is so great that the individual distances and angles are not too reliable. The average corrected C–Cl distance of 1·772±0·008 Å is probably more nearly right (see text).

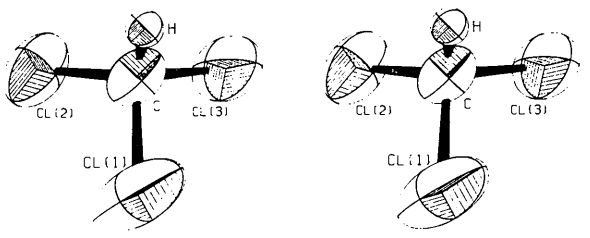


Fig. 7. A representation of the thermal motion in the chloroform molecule. (Johnson, 1965).

(C) *The arrangement of the molecules*

The overall structure of this crystal is of particular interest because of the fact that it is capable of reversibly absorbing oxygen (Tsumaki, 1938). The chloroform can be driven off easily at 100°C (even at room temperature it will come off slowly) and the resulting compound absorbs not quite a stoichiometric amount of oxygen. Tsumaki recorded a weight increase of 3·5%, while one mole of oxygen per two moles of complex corresponds to a 4·9% increase in weight. The easy loss of chloroform is explained by the existence of passageways parallel to **b** which extend through the entire crystal. These passageways contain the chloroform molecules, loosely bound to the complexes, and afford a means by which the chloroform molecules can diffuse out of the crystal. Other molecules then can diffuse in through these same holes. The replacement of chloroform by oxygen, however, must involve more than just this, for the entire structure of the crystal changes; there may be a general reorientation of the cobalt complexes upon oxygenation. It is pertinent to note that some other crystalline modifications of bis(salicylaldehyde)ethylenediiminecobalt(II) are completely inactive and do not absorb or react with oxygen in any way (Martell & Calvin, 1952*c*).

Fig. 8 shows a projection of the contents of the unit cell down the *b* axis, showing how the complex ions are associated in pairs and showing the chloroform molecule that is attached to each complex. The pairs of molecules seem to be the same as the pairs of molecules Hughes found in the unsolvated complex (Martell & Calvin, 1952*b*) but, of course, the overall arrangement is different because of the different composition and space group.

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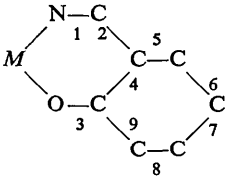
Table 5. *Comparison of bond distances in salicylaldimine chelates*



Avg. of 9	1	2	3	4	5	6	7	8	9
determinations*	1·295 (5)	1·430 (6)	1·312 (3)	1·415 (6)	1·423 (4)	1·367 (3)	1·384 (5)	1·388 (3)	1·415 (5)
This work	1·283	1·413	1·322	1·422	1·410	1·344	1·391	1·383	1·404
Gerloch & Mabbs, 1967	1·283	1·443	1·352 1·337	1·404	1·419	1·377	1·392	1·388	1·393

* Lingafelter & Braun, 1966.

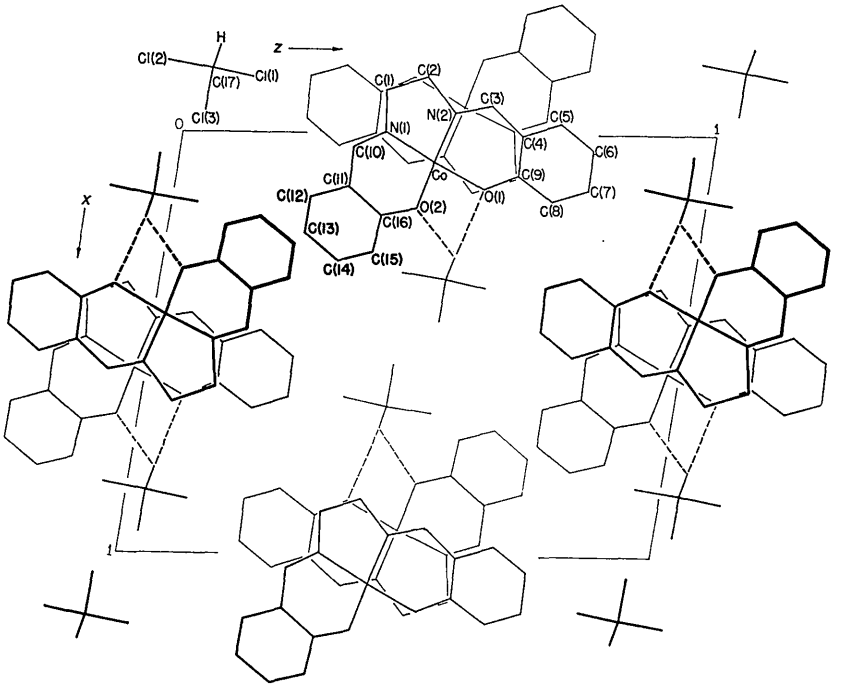


Fig. 8. A projection of the contents of a unit cell down the *b* axis.

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