Crystal Structure of a Sodium Complex, Bis-[*NN'*-ethylenebis(salicylideneiminato)copper(II)]perchloratosodium–*p*-Xylene

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A purple compound is formed between sodium perchlorate and two molecules of the copper complex of the Schiff's base *NN'*-ethylenebis(salicylideneimine) (salen); the *p*-xylene solvate has been subjected to three-dimensional *X*-ray crystal structure analysis. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to R 0·070 for 1083 diffractometer observations. $Z = 4$ in a monoclinic unit cell having $a = 24{\cdot}44 \pm 0{\cdot}01$, $b = 11{\cdot}283 \pm 0{\cdot}006$, $c = 14{\cdot}766 \pm 0{\cdot}004$ Å, $\beta = 101{\cdot}22 \pm 0{\cdot}03°$, space group $C2/c$. The sodium ion lies on a two-fold axis and is co-ordinated approximately octahedrally by oxygen atoms; two, at 2·55 Å, from a perchlorate ion also situated on the two-fold axis, and four from the two salen molecules, so that the sodium ion shares these oxygen atoms with a copper atom, Na–O 2·36, Cu–O 1·90 Å. The copper is four-co-ordinated, Cu–N 1·94 Å, and the salen ligand as a whole is nearly planar apart from the carbon atoms of the ethylenediamine entity which correspond to a gauche conformation about the C–C bond. Axial contacts to copper are to an oxygen in the other salen ligand (3·43 Å) and to a copper atom in another molecule (3·42 Å). The *p*-xylene molecule occupies a centre of symmetry and fills a space in a loosely packed structure; its nearest carbon atom neighbour is at 3·93 Å.

SCHIFF bases have been studied extensively as models for enzyme reactions.[1] One feature of their behaviour is that their metal complexes can themselves act as ligands. A series of such interactions had been described[2] in which a bivalent metal (M^1) chelated by a tetradentate Schiff base (tsb) formed binuclear $M^1(tsb)M^2X_2$ with M^2X_2 (X is a co-ordinating ligand), and trinuclear complexes $[\{M^1(tsb)\}_2M^2]Y^2$ with M^2Y_2 (Y is a non-co-ordinating ligand). In the first reported complexes M^1 and M^2 were transition metals. Later[3-5] a variety of complexes of metal perchlorates $(M^1)^{n+}(ClO_4)_n$ their syntheses, and magnetic moments were described. Among these was the complex of sodium perchlorate with two molecules of Cu(salen), the copper complex of *NN*-ethylenebis(salicylideneimine); it was obtained as a chloroform solvate.[3] A characteristic of the compounds is that they may crystallise with different molecules of solvent.[6] We obtained suitable crystals for crystal structure analysis from chloroform–*p*-xylene; these contain *p*-xylene of crystallisation. In our preliminary report[7] we showed that the sodium ion was in a discrete and unequivocally complex environment. We now describe the structure in detail.

Description of the Structure.—There are four formula units $NaClO_4[Cu(salen)]_2$*p*-xylene in a unit cell having the monoclinic space group $C2/c$ so that the positions of the sodium, chlorine, and the centre of the xylene ring have crystallographic symmetry imposed. As shown in Figure 1, where the designations of the atoms are given, the sodium and chlorine atoms lie along a two-fold axis which relates two Cu(salen) groups and pairs of oxygen atoms of the perchlorate ion. Figure 2 shows the structure as a whole projected down the two-fold axis.

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[1] See, *e.g.*, D. L. Leussing and C. K. Stanfield, *J. Amer. Chem. Soc.*, 1966, **88**, 5726.

[2] S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 495; 1968, **4**, 107; *Inorg. Chem.*, 1968, **7**, 268; *J. Chem. Phys.*, 1968, **49**, 2183.

[3] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.

[4] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 391.

[5] M. D. Hobday and T. D. Smith, *Co-ordination Chem. Rev.*, 1973, **9**, 311.

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[7] G. H. W. Milburn, M. R. Truter, and B. L. Vickery, *Chem. Comm.*, 1968, 1188.

Discrete $Na^+ClO_4^-$ ion pairs have the sodium co-ordinated by two oxygen atoms of the perchlorate ion and by four oxygen atoms from two Cu(salen) complexes. The centre of the *p*-xylene molecule is on a crystallographic centre of symmetry at $\frac{1}{4},\frac{1}{4},0$. In bulk the crystals look the same colour as potassium permanganate, but under the microscope they appear magenta and are pleochroic; absorption is greatest when the light is vibrating normal to the needle axis, *c*, and the reason for this is clear from Figure 2, even though the plane of the xylene molecules is not parallel to that of the Cu(salen) entities.

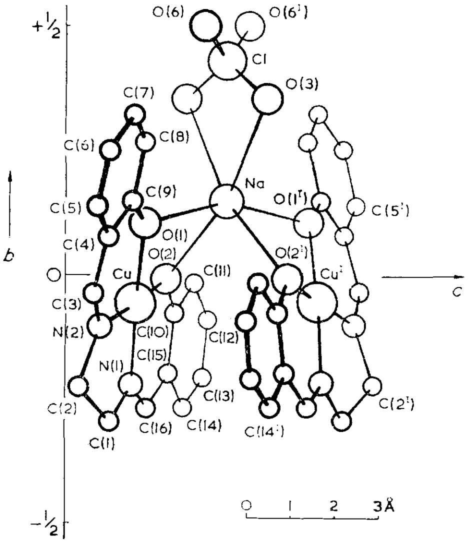

FIGURE 1 One $Na^+ClO_4^-$ ion pair and the two chelating [*NN*-ethylenebis(salicylideneiminato)]copper(II) molecules as seen along the crystallographic *a* axis. The directions of the two-fold axis, *b*, and of the *c* axis are indicated. The designations of the atoms in the asymmetric unit are given; those with the Roman numeral superscript I are at $-x, y, \frac{1}{2} - z$, *i.e.* related by a two-fold axis

Atomic co-ordinates and vibration parameters are given in Table 1, bond lengths and angles in Figure 3 and Table 2, inter- and intra-molecular contacts in Table 3, and planes through various groups of atoms in Table 4. Because the intensities showed a rapid fall-off as sin θ/λ increased, the vibration parameters and the standard deviations in co-ordinates are large.

Packing.—The structure is not closely packed, as suggested by large vibrations at room temperature, but the m.p. is high (265—267 °C). The xylene is necessary for crystallisation: if it is lost the crystals become opaque but remain purple. Other isomers of xylene may occupy the same position in a disordered way, crystallisation from a mixture of isomers resulting in diffuse spots on the *X*-ray photographs. The nearest neighbour to xylene along the normal to the plane is C(2) at 3·93 Å (Figure 2) and there are no atoms within 3·5 Å.

Packing distances are given in Table 3. Those from the O(6) of the perchlorate ion to the molecule in the next cell up the *b* axis, *i.e.* to $C(16^{IV})$ and $C(16^{VI})$, can be visualised with the aid of Figure 1. Relations across the centre of symmetry at the origin, *i.e.* to atoms superscript III, can be seen in Figure 2 as between atoms of superscripts I and II (the centre of symmetry being at $0,0,\frac{1}{2}$); this type of contact, *ca.* 3·4 Å, between average Cu(salen) planes is the closest in the structure.

Of particular interest in view of the possibility of antiferromagnetic interactions are the Cu $\cdots$ Cu separations. Within a molecule, *i.e.* from Cu $\cdots$ Cu^I, this is 4·52 Å consistent with lack of magnetic interaction.[3] Across the centre of symmetry at 0,0,0 the Cu $\cdots$ Cu^{III}

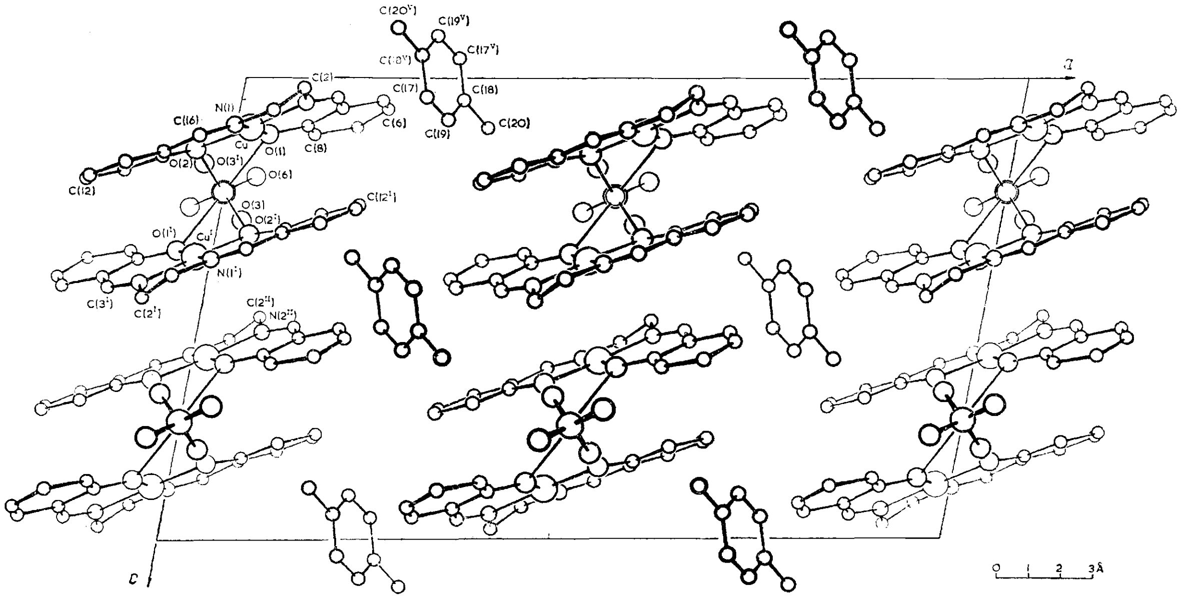

FIGURE 2 The structure as a whole projected down the *b* axis. The numbering of the atoms of the xylene molecule is shown. Roman numeral superscripts are defined in Table 3

TABLE 1

Fractional atomic co-ordinates and vibration parameters ($Å^2$), with standard deviations in parentheses

	x/a	y/b	z/c	B_{iso}
Cu	0·01939(7)	0·05429(18)	0·10965(12)	[4·5]
Cl	0	−0·4304(6)	0·25	[8·1]
Na	0	−0·1488(7)	0·25	[4·6]
O(1)	0·0441(4)	−0·1055(9)	0·1239(6)	5·5(2)
O(2)	−0·0439(4)	0·0056(9)	0·1566(7)	5·2(2)
O(3)	0 0302(7)	−0·3554(18)	0·3115(12)	[11·1]
O(6)	0·0379(9)	−0·5040(16)	0·2161(16)	[12·2]
N(1)	−0·0017(6)	0·2181(14)	0·1027(9)	6·7(3)
N(2)	0·0828(6)	0·1023(13)	0·0542(9)	6·5(3)
C(1)	0·0440(10)	0·2943(22)	0·0701(16)	9·5(7)
C(2)	0·0768(10)	0·2236(22)	0·0214(16)	9·6(7)
C(3)	0·1225(6)	0·0357(15)	0·0441(11)	5·7(3)
C(4)	0·1304(6)	−0·0773(14)	0·0666(10)	5·6(3)
C(5)	0·1804(7)	−0·1376(17)	0·0501(12)	6·7(4)
C(6)	0·1892(9)	−0·2482(21)	0·0695(14)	8·5(5)
C(7)	0·1540(9)	−0·3226(23)	0·1077(16)	9·5(5)
C(8)	0·1023(8)	−0·2671(19)	0·1242(13)	7·8(5)
C(9)	0·0913(6)	−0·1491(14)	0·1053(10)	5·3(3)
C(10)	−0·0853(6)	0·0756(13)	0·1713(9)	5·0(3)
C(11)	−0·1302(7)	0·0171(15)	0·2005(11)	6·1(4)
C(12)	−0·1764(8)	0·0900(18)	0·2204(13)	7·5(4)
C(13)	−0·1729(8)	0·2079(19)	0·2123(13)	7·8(5)
C(14)	−0·1309(8)	0·2671(20)	0·1829(14)	8·2(5)
C(15)	−0·0843(6)	0·1985(14)	0·1610(10)	5·5(3)
C(16)	−0·0435(7)	0·2685(16)	0·1248(11)	6·2(4)
C(17)	0·2345(9)	0·3504(20)	0·0420(14)	8·2(5)
C(18)	0·2824(8)	0·1643(20)	0·0495(13)	7·9(5)
C(19)	0·2679(8)	0·2623(20)	0·0925(13)	8·0(5)
C(20)	0·3196(13)	0·0716(30)	0·1089(22)	12·9(8)

For atoms shown with B_{iso} in square brackets the final anisotropic vibration parameters, 10^{-3} $Å^2$, were:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu	57(1)	68(1)	57(1)	−9(1)	0(1)	20(1)
Cl	158(7)	62(4)	120(5)	0	0	67(5)
Na	58(5)	63(5)	68(5)	0	0	30(4)
O(3)	144(14)	168(16)	134(12)	15(12)	−44(12)	13(10)
O(6)	229(21)	97(11)	231(21)	7(13)	−48(13)	119(17)

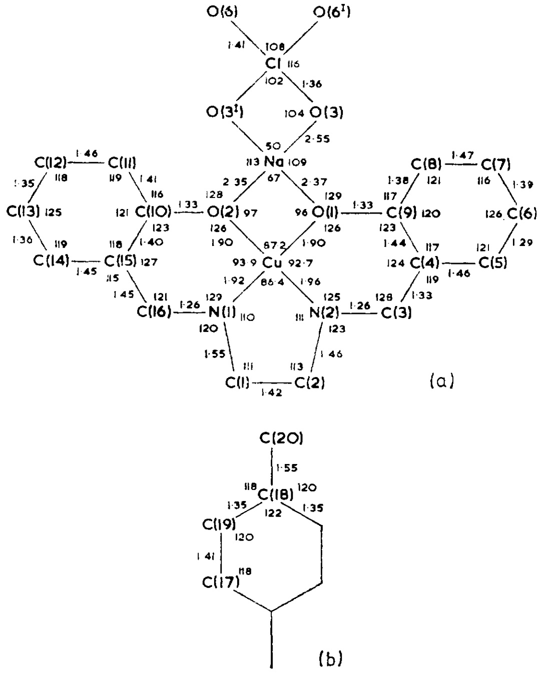

FIGURE 3 Bond lengths and angles in (a) Cu(salen)$Na^+ClO_4^-$, and (b) the *p*-xylene molecule. Standard deviations and additional angles are given in Table 2

distance is 3·42 Å, the shortest contact from copper to a 'fifth' atom.

Cu(salen) *Ligand*.—In a series of copper–salen derivatives it has been found that Cu(salen) itself is dimeric with the copper five-co-ordinate, the 'fifth' bond (2·41 Å) being to an oxygen atom in the other half of the dimer,[8] leading to a Cu · · · Cu distance of 3·2 Å and spin–spin coupling.[9] If one co-ordinated oxygen atom takes part in hydrogen bonding as in Cu(salen)($CHCl_3$) [10] or Cu(salen)(*p*-nitrophenol),[11] the length of the O · · · Cu-(dimer) bond from the other oxygen atom increases: the stronger the hydrogen bonding the weaker the dimerisation. The change in colour from the green of the free dimeric molecule to red in various adducts is associated [10] with the weakening of the dimer bond,

TABLE 2

(*a*) Bond angles (°) not shown in Figure 3, and those with standard deviations of less than 1°

Cu–O(1)–C(9)	126·5(5)	O(1)–Cu–N(1)	176·1(3)
Cu–O(1)–Na	95·7(3)	O(2)–Cu–N(2)	176·8(3)
Na–O(1)–C(9)	129·4(3)		
Cu–N(2)–C(2)	111·4(6)	O(1)–Cu–O(2)	87·2(1)
Cu–N(2)–C(3)	125·3(6)	O(1)–Cu–N(2)	92·7(2)
C(2)–N(2)–C(3)	123·2(9)	O(2)–Cu–N(1)	93·9(1)
		N(1)–Cu–N(2)	86·4(2)
Cu–O(2)–C(10)	126·1(5)		
Cu–O(2)–Na	96·5(3)	O(1)–Na–O(1^I)	156(1)
Na–O(2)–C(10)	128·1(3)	O(1)–Na–O(2^I)	95(1)
Cu–N(1)–C(1)	110·1(6)	O(1)–Na–O(3^I)	93(1)
Cu–N(1)–C(16)	129·5(6)	O(2)–Na–O(2^I)	84(1)
C(1)–N(1)–C(16)	120·3(9)	O(2)–Na–O(3)	162(1)
		O(3)–Cl–O(6)	107(1)

(*b*) Standard deviations (Å) in bond lengths:

0·01	Cu–O, Na–O(1), and Na–O(2)
0·02	Cu–N, Na–O(3), Cl–O
0·025	C–O, C–N, and C–C in salen ligand except C(1)–C(2)
0·03	C(17)–C(19), C(18)–C(19), C(18)–C(17^V)
0·04	C(18)–C(20), C(1)–C(2)

(*c*) Standard deviations (°) in bond angles:

1	at Cl and Na [except O(3)–Na–O(3^I) 2°]
1—2	in the salen ligand
2	in the xylene molecule

TABLE 3

Intermolecular distances $<3·5$ Å. Each distance is given once, *e.g.* O(2) · · · N(3^{III}) but not N(3) · · · O(2^{III})

(*a*) From one Cu(salen) ligand to the other, molecule (I)			
Cu · · · C(10^I)	3·33	Cu · · · O(2^I)	3·43
O(1) · · · O(2^I)	3·47	O(1) · · · C(11^I)	3·31
O(2) · · · O(2^I)	3·16	C(9) · · · C(11^I)	3·41
(*b*) Between complexes			
Cu · · · Cu^{III}	3·419	O(6) · · · C(16^{IV})	3·37
O(2) · · · N(2^{III})	3·31	O(6) · · · C(16^{VI})	3·48
O(2) · · · C(3^{III})	3·24	C(4) · · · C(10^{III})	3·47
O(3) · · · C(2^{II})	3·42	N(1) · · · C(9^{III})	3·49
O(6) · · · C(1^{IV})	3·16	C(3) · · · C(10^{III})	3·38

Roman numeral superscripts corresponding to the following equivalent positions relative to an atom at x, y, z in Table 1:

I	$-x, y, \frac{1}{2} - z$	IV	$x, y - 1, z$
II	$x, -y, \frac{1}{2} + z$	V	$\frac{1}{2} - x, \frac{1}{2} - y, -z$
III	$-x, -y, -z$	VI	$-x, y - 1, \frac{1}{2} - z$

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[8] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.

[9] W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 216.

[10] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. (A)*, 1970, 406.

[11] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc. (A)*, 1970, 400.

i.e. a change from five- to four-co-ordination for the copper. Similar effects have been found for other metal–salen complexes and their adducts.[12] The effect on the M–O and M–N bond length is subtle; the increase in ligand field from five- to four-co-ordination should correlate with shorter bonds but the M–O distance to the hydrogen-bonded oxygen may be longer than the other M–O distance, as in cobalt [12] and one copper compound,[11] or shorter as in the chloroform adduct of Cu(salen).[10] The bond lengths we have found (Cu–O 1·90, Cu–N 1·94 Å) are within the usual range.[12] The direction of the Cu · · · Cu contact in the ' fifth ' position is 11° to the normal to the co-ordination plane of the copper [plane (*A*), Table 4]. While for a ' sixth ' position the nearest atom is $C(10^{\mathrm{I}})$ and the nearest potential donor atom $O(2^{\mathrm{I}})$ at 3·43 Å is too far to be bonded, the directions of these atoms are at 11 and 32° to the normal to the co-ordination plane.

TABLE 4

(*a*) Planes through various atoms. Direction cosines refer to orthogonal axes parallel to the crystallographic *a*, *b*, and *c** axes. Deviations (Å) of relevant atoms are given in square brackets; atoms not included in the calculation of the plane are italicised

Plane (*A*): $-0{\cdot}3493x - 0{\cdot}1925y - 0{\cdot}9170z + 1{\cdot}6810 = 0$

[Cu 0, N(1) −0·088, N(2) 0·074, O(1) −0·045, O(2) 0·037, *Na −0·807*]

Plane (*B*): $-0{\cdot}4311x - 0{\cdot}1643y - 0{\cdot}8872z + 1{\cdot}6711 = 0$

[N(1) 0·033, N(2) −0·035, C(1) −0·183, C(2) 0·203, *Cu 0·031*]

Plane (*C*): $-0{\cdot}3186x - 0{\cdot}2574y - 0{\cdot}9122z + 1{\cdot}6147 = 0$

[O(1) 0, N(2) −0·004, C(3) 0·011, C(4) −0·009, C(9) 0·003, *Cu −0·089*]

Plane (*D*): $-0{\cdot}3461x - 0{\cdot}1360y - 0{\cdot}9283z + 1{\cdot}6597 = 0$

[O(2) −0·011, N(1) 0·012, C(16) −0·004, C(15) −0·027, C(10) 0·036, *Cu −0·003*]

Plane (*E*): $-0{\cdot}3128x - 0{\cdot}0843y - 0{\cdot}9461z + 1{\cdot}6957 = 0$

[C(10) −0·006, C(11) −0·001, C(12) 0·014, C(13) −0·016, C(14) 0·002, C(15) 0·007, *O(2) −0·055, C(16) 0·114*]

Plane (*F*): $-0{\cdot}3129x - 0{\cdot}2531y - 0{\cdot}9154z + 1{\cdot}6109 = 0$

[C(4) −0·002, C(5) 0·003, C(6) 0·002, C(7) −0·011, C(8) 0·008, C(9) −0·001, *O(1) −0·010, C(3) 0·023*]

Plane (*G*): $0{\cdot}8710x + 0{\cdot}4746y - 0{\cdot}1273z - 6{\cdot}6600 = 0$

[C(17) −0·028, C(18) −0·041, C(19) 0·040, C(20) 0·054]

(*b*) Angles (°) between normals to planes

	(*B*)	(*C*)	(*D*)	(*E*)	(*F*)	(*G*)
(*A*)	5	4	3	7	4	106
(*B*)		9	6	9	9	110
(*C*)			7	10	0	106
(*D*)				4	7	104
(*E*)					10	103
(*F*)						106
(*G*)						

The bond lengths and angles (Figure 3 and Table 2) show that corresponding values for the halves of the Schiff-base molecule do not differ by $>2{\cdot}4\sigma$ [N(1)–C(1) compared with N(2)–C(2)]. This would not be regarded as chemically significant and all the bond lengths and angles are within the mean range for sixteen salen complexes.[12] The greatest difference (0·09 Å, *i.e.* $2{\cdot}5\sigma$) is for C(1)–C(2) of the ethylenediamine ring; there is the usual gauche configuration about this bond and its apparent shortness may be due to disorder with most molecules having C(1) and C(2) respectively ' below ' and ' above ' the plane [(*B*), Table 4], but some with C(1) above and C(2) below, a suggestion supported by the small deviation from plane (*B*) and by the relatively high vibration parameters for C(1) and C(2) compared with those for C(3) and C(16) which are also bonded to nitrogen atoms. A feature of the sixteen values quoted in ref. 12 is that the smaller the deviation of the carbon atoms from the M–N–N plane the shorter is the corresponding C–C bond, consistent with disorder. Usually the five-membered ring is described as being more planar, and no explanation is offered for the shortening of the C–C bond length. Recently a copper complex of a Schiff's-base analogue in which all the ligand atoms are nitrogen has been subjected to crystal structure analysis,[13] and disorder of the propylenediamine bridge demonstrated.

The configuration of the molecule as a whole is ' umbrella-shaped,' the angle between the six-membered chelate rings C and D being 7·2°. This shape can be seen in Figure 2, which also shows qualitatively the effect given quantitatively in Table 4, that the phenyl rings E and F are planar and the substituents O(2) and C(16) are significantly out-of-plane, while O(1) and C(3) are not. The relatively weak packing forces seems unlikely to account for this difference. An umbrella shape with a gauche configuration about the C–C bond has been found previously only in the dimeric iron complex $[\mathrm{ClFe(salen)}]_2$.[14]

The present compound differs from the hydrogen-bonded Cu(salen) adducts in that both oxygen atoms make an additional contact, one of 2·35 and one of 2·37 Å to sodium. The angles subtended at the oxygen atoms O(1) and O(2), within the six-membered chelate ring, are greater than 120°, as is usually found, compensating for the approximately 90° angle at the metal. Because the sodium does not lie in the plane of the Cu(salen) molecule as a whole, the other angles subtended at the oxygens are not consistent with a planar arrangement about the oxygen atoms, and it is not possible to deduce where any lone pairs of electrons on these atoms may be situated.

Environment of the Sodium Ion.—The sodium ion is surrounded by six oxygen atoms in an environment which approximates to octahedral rather than to any of the other possible polyhedra.[15] The relative orientation of a pair of opposite faces O(1), $O(2^{\mathrm{I}})$, O(3) and $O(1^{\mathrm{I}})$, O(2), $O(3^{\mathrm{I}})$, chosen because there are no restraints due to attachment to another atom, is 40°. Ideally it would be 0° for a trigonal prism and 60° for an octahedron.

Six-co-ordination is frequently found for sodium and the observed Na–O distances are within the normal range. Application of the empirical relation [16] between interatomic distances and bond strength gives 0·20 and 0·21 for Na–O(salen) and 0·13 for the Na–O(ClO_4), a

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[12] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

[13] D. Hall, T. N. Waters, and P. E. Wright, *J.C.S. Dalton*, 1973, 1508.

[14] M. Gerloch and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1967, 1900.

[15] D. Britton and J. D. Dunitz, *Acta Cryst.*, 1973, **A29**, 362.

[16] I. D. Brown and R. D. Shannon, *Acta Cryst.*, 1973, **A29**, 266.

paradoxical result because intuitively one would expect the ion-pair interaction to be stronger, and hence shorter. However, this is not unique, *e.g.* Ca–O in the $Ca^{2+}CO_3{}^{2-}$ ion pair of the hexahydrate is the second shortest, the shortest being to a water molecule.[17] In general sodium–oxygen distances do not vary systematically with the formal charge on the oxygen. The oxygen parameters in sodium perchlorate could not be measured accurately [18] but the minimum Na · · · Cl distance is (3·25 Å) comparable with the value (3·17 Å) in the present compound.

In the present compound the presence of three chelating ligands must give a *cis*-arrangement of the copper–salen ligands. A *cis*-arrangement for an octahedrally co-ordinated central atom in a trinuclear complex was originally postulated [3,4] because it allows this metal, M^2, to be nearly in the plane of the M^1(tsb) ligands. This postulate has just been confirmed [19] for sodium co-ordinated by two cobalt–salen molecules and two molecules of tetrahydrofuran (thf) in $[Co(salen)_2Na(thf)_2]^+[Ph_4B]^-$.

Although no strictly analogous compounds have been isolated from natural systems, the green fungal pigment Ferroverdin was found [20] to be a complex of iron(II) with sodium in an irregular octahedral environment of oxygen atoms, some shared with the transition metal.

Perchlorate Ion.—Although the anion has been much used in co-ordination chemistry because of its poor complex-forming properties, there is evidence for its forming in solution [21] ion pairs just as stable as those of other univalent anions. Direct unidentate co-ordination to transition metals has been established by crystal-structure analysis [22-24] and also by i.r. spectroscopy [25-27] which for at least one compound [26] is consistent with the presence of a chelate perchlorate ion as found here. Amma and co-workers have studied complexes of silver perchlorate with several aromatic systems. The perchlorate ion may be uni- (Ag–O 2·68 Å) [28] or bi-dentate, bridging two silver ions with Ag–O in the range 2·48—2·63 Å.[29] A bridging perchlorate ion has been found in dimethyl(1,10-phenanthroline)thallium(III) perchlorate [30] with Tl–O 2·87(4) Å. The bond lengths in the bridging perchlorate anion (Cl–O 1·41—1·46),[29,30] do not show any significant difference whether the oxygen is co-ordinated or not.

Our bond lengths for the co-ordinated and unco-ordinated oxygen are not significantly different [1·36(2) and 1·41(2) Å]. Neither have been corrected for systematic errors due to libration of the perchlorate ion, so that they appear shorter than accurate values obtained in low-temperature studies, *e.g.* 1·45(1) (ref. **31**) and 1·437(4) Å.[32]

EXPERIMENTAL

The compound was made [33] after the method of ref. 3 which yields the chloroform solvate. Recrystallisation from *p*-xylene–absolute ethanol (1 : 1) gave *purple crystals* (m.p. 265—267 °C) which were dried at 110 °C (P_2O_5) and 1 mmHg (Found: C, 54·9; H, 4·1; Cl, 3·9; Cu, 14·0; N, 6·2; Na, 2·6. $C_{40}H_{33}ClCu_2N_4NaO_8$ requires C, 54·1; H, 4·3; Cl, 4·0; Cu, 14·3; N, 6·3; Na, 2·6%). Sodium was determined with a flame photometer, copper volumetrically with edta, and other elements by combustion.

Examination of preliminary *X*-ray photographs showed that the crystals were monoclinic with space group *Cc* or *C2/c*, containing four formula units. Accurate unit-cell dimensions were obtained by use of a Picker diffractometer.

Crystal Data.—$C_{40}H_{33}ClCu_2N_4NaO_8$, M = 888·4, Monoclinic, a = 24·44 ± 0·01, b = 11·283 ± 0·006, c = 14·766 ± 0·004 Å, β = 101·22 ± 0·03°, U = 3993 Å^3, D_m = 1·56 (by flotation), Z = 4, D_c = 1·47, F(000) = 1824. Space group *C2/c* or *Cc* from systematic absences: hkl when $h + k = 2n + 1$, and $h0l$ when $l = 2n + 1$; shown by structure analysis to be *C2/c* (C_{2h}). Mo-K_α radiation, $\lambda(K_{\alpha1})$ = 0·7093, $\lambda(K_{\alpha2})$ = 0·7135 Å (1 Å = 10^{-10} m)]; μ(Mo-K_α) = 12·4 cm^{-1}; diffractometer intensity measurement.

The discrepancy between D_m and D_c may be due to replacement of xylene by the more dense liquid used for flotation. Although the crystals immediately sank in trichloroethylene and seemed unaffected by immersion in a mixture of this and tetrabromoethane, they were found to have become opaque when viewed under a microscope. Their behaviour on heating also indicated that removal of xylene led to opacity. On a hot-stage microscope bubbles appeared at 248 °C (the boiling point of *p*-xylene is only 138°) and the crystals retained their form but became opaque; at 265—267 °C they melted, giving a magenta liquid which on cooling solidified without changing colour. As $[Cu(salen)]_2$ is green it is probable that the association with the sodium perchlorate persists despite melting.

Observations of intensities and *inter alia* unit-cell dimensions were made on a crystal which was a six-sided prism showing the forms {110} and {100} with maximum and minimum dimensions 0·165 and 0·095 mm; it was 0·281 mm parallel to c and bounded by (001) and (00$\bar{1}$). The crystal was mounted with the c axis approximately coincident with the ϕ axis of the diffractometer.

Intensity measurements were made by Dr. J. A. J. Jarvis on the Picker single-crystal four-circle diffractometer in the Petrochemical and Polymer Laboratory (now the Corporate Laboratory) of Imperial Chemical Industries

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Ltd., by their usual θ—2θ scan procedure.[34] Three standard reflections were measured at intervals and showed no intensity reduction with time, indicating that the crystal was stable in the *X*-ray beam. High intensities were obtained at low values of θ but there was a rapid fall with increasing θ, and by 2θ 40° no more were acceptable by the criterion that the measured value must be five times the standard deviation. Test calculations showed that application of an absorption correction produced maximum and minimum factors of 1·091 and 1·056 for the structure factors so these were not applied. Further evidence that an absorption correction was not necessary came from the $0kl$ and $0k\bar{l}$ observations. Both were collected and found to agree to 1·5% of the mean. Lorentz and polarisation corrections had been applied[35] to give 1084 independent reflections.

The structure was solved from a three-dimensional Patterson synthesis.[36] Systematic absences corresponded to the space groups $C2/c$ or Cc. With $Z = 4$, the latter space group would have one formula unit as the asymmetric unit and there would be two independent copper atoms. In the centrosymmetric space group $C2/c$ the sodium ion would have to occupy a special position, either on a two-fold axis or a centre of symmetry. The same restriction applies to the centre of the xylene molecule, while the Cl of a perchlorate ion must be situated on a two-fold axis. The eight copper atoms in the unit cell could occupy general positions and this was the situation found; Cu · · · Cu peaks were identified at $2x,2y,2z$, and $0,2y,\frac{1}{2}$. Structure factors were calculated for the copper atom at $x/a = 0{\cdot}02$, $y/b = 0{\cdot}05$, $z/c = 0{\cdot}1$ and an isotropic temperature factor B 4·5 Å^2; R was 0·41. Least-squares refinement suggested very small changes, and a three-dimensional electron-density synthesis then enabled location of all the atoms, other than hydrogen, revealing the structure shown in Figure 2.

Isotropic refinement[36] reduced R to 0·095; full-matrix refinement,[37] allowing anisotropic vibration for Cu, Cl, Na, and the perchlorate oxygen atoms, reduced R to 0·070. A final difference-Fourier synthesis showed no peaks $>0{\cdot}6$ eÅ^3. Some of these were at the positions calculated for hydrogen atoms, assuming C–H 1·0 Å and the completion of trigonal or tetrahedral geometry about the carbon atoms. However, equally large peaks appeared in positions which could not be attributed to hydrogen atoms, while some calculated sites corresponded to negative areas in the difference synthesis. It seemed unlikely that the hydrogen atoms had been located and no attempt was made to add their parameters to the already large number in the refinement.

In the least-squares refinement the function minimised was $R' = \Sigma w|(|F_o| - |F_c|)|^2$ where the weight w was inversely proportional to the standard deviation measured experimentally. The final R' was 0·089. One plane, (002) was omitted from refinement because $|F_o| \ll |F_o|$, a discrepancy which we attributed to multiple reflection. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20908 (8 pp., 1 microfiche).* Scattering factors were taken from ref. 38 for neutral atoms, Cu, Cl, Na, O, N, and C.

Bond lengths and angles and their standard deviations,[39] and intermolecular distances[40] $<3{\cdot}5$ Å, and planes through groups of atoms[36] were calculated on our IBM 1130 computer.

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