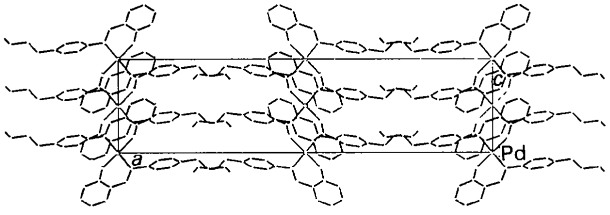

Fig. 2. Projection of the structure along **b**.

plane-to-plane stacks involving the metal complexes and/or the organic portions. Stacks of these two types have been found in [2-(4-methoxyphenylazo-N^2)-5-methoxyphenyl](8-quinolinolato)palladium(II) (Manotti Lanfredi, Ugozzoli, Ghedini & Licoccia, 1984).

The stepped molecules are connected by centrosymmetric Pd···H interactions involving palladium and hydrogen atoms from adjacent complexes [Pd···H(7)(x, $-\frac{1}{2}-y$, $\frac{1}{2}+z$) and Pd···H(7)($1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) = 2·86 (6) Å] in slices parallel to (100) at $x = 0$ and $x = \frac{1}{2}$ (Fig. 2).

Packing of the slices is determined by van der Waals contacts involving hydrogen atoms of the n-butyl groups.

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Structure of Copper(II) Distrontium(II) Formate Octahydrate, $CuSr_2(HCOO)_6.8H_2O$

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Abstract. $M_r = 652{\cdot}5$, triclinic, $P\bar{1}$, $a = 6{\cdot}61\ (1)$, $b = 8{\cdot}84\ (2)$, $c = 8{\cdot}90\ (2)$ Å, $\alpha = 104{\cdot}5\ (1)$, $\beta = 96{\cdot}0\ (1)$, $\gamma = 88{\cdot}5\ (1)°$, $U = 500{\cdot}7\ (7)$ Å^3, $Z = 1$, $D_m = 2{\cdot}19$ (pycnometric), $D_x = 2{\cdot}17$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 100$ cm^{-1}, $\mu(\mathrm{Mo}\ K\alpha) = 70$ cm^{-1}, $F(000) = 323$, final $R = 0{\cdot}092$ for 1458 independent reflexions. The structure consists of layers parallel to (010), linked to each other by only one type of H bond. Coordination around the heavy atoms is normal.

Introduction. During a survey on possible ferroelectric materials related to the well known ferroelectric $Cu(HCOO)_2.4H_2O$, we came across the mixed salt $CuSr_2(HCOO)_6.8H_2O$, which we tested for its electrical properties.

Although ferroelectricity tests proved negative in the range of stability of the compound, some intriguing features were observed regarding the dehydration of single crystals (a shape-preserving process, with the appearance of new, single-crystal-like diffraction spots). This fact encouraged further work on the subject and, as part of this more general work, we report here the crystal structure of the hydrated species $CuSr_2(HCOO)_6.8H_2O$.

Experimental. Crystals obtained at room temperature by slow evaporation of a 20% formic acid solution of $CuCO_3$ and $SrCO_3$ in 1:2 molar ratio. Predominant habit: light-blue (010) plates. Some batches showed ⟨100⟩ and ⟨001⟩ needles as well. Typical well developed faces: {010}, {100}, {001}, {110}. Cell

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parameters measured from *h*0*l* and 0*kl* precession photographs (Mo *K*α). Axial ratios in fair agreement with previously reported optical data (Winchell, 1954). Two crystals used throughout data collection; typical dimensions of cross sections: $d = 0{\cdot}12$, $l = 0{\cdot}30$ mm; μr (Cu *K*α) = 0·60, μr (Mo *K*α) = 0·42. Weissenberg data: levels 0*kl* to 5*kl* (Cu *K*α). Precession data: levels *h*0*l* to *h*2*l* (Mo *K*α). Although crystals became black on irradiation, periodic checks of the zero levels showed no detectable variation in the intensities. Intensity measurement: by visual comparison with appropriate calibrated scales. Corrections performed: spot size and Lp (no absorption correction). Solution of the structure: a three-dimensional Patterson synthesis showed the heavy atoms, suggesting $P\bar{1}$ as the correct space group. Remaining non-H atoms were found in subsequent ΔF synthesis. Refinement: full-matrix least squares using *SHELX*76 (Sheldrick, 1976). Atomic scattering factors: as provided in the computer program; Sr^{2+} and Cu^{2+} from *International Tables for X-ray Crystallography* (1974). Full-matrix least squares on $|F|$, anisotropic vibration tensors for the heavy atoms, and isotropic temperature factors for the rest (H atoms excluded), $w = 10{\cdot}3/[\sigma^2(F) + 0{\cdot}00036F^2]$. Final $R = 0{\cdot}092$, $R_w = 0{\cdot}096$ for 1458 reflexions (omitted: 400 unobserved plus the three strong reflexions 010, 020, 030, which could not be accurately measured owing to saturation). Refinement ended when $\Delta/\sigma < 0{\cdot}2$. No significant single peak in final ΔF synthesis.

Discussion. The final atomic positions are shown in Table 1, and the interatomic distances and angles are in Table 2.*

The Cu atom is situated at a centre of symmetry, surrounded by six different formate anions, each contributing one O atom to the Cu coordination polyhedron (c.p.). This is a typical Jahn–Teller-deformed octahedron, with four short equatorial [1·95 (1) and 2·00 (1) Å] and two long axial [2·45 (1) Å] bonds. The resulting bipyramid has the base stretched out of the ideal square shape owing to strong interaction with the Sr c.p., with a basal angle of 82 (1)° and the apical bond 5 (1)° out of the normal to the basal plane.

The Sr atom is coordinated to nine nearest neighbours. Three are independent O atoms [O(11), O(21) and O(31)] from three different formate groups, while the other six come from three pairs of centrosymmetrically related atoms [O(22), O(22′), *W*(1), *W*(1)′, *W*(2), *W*(2′)].† The Sr—O lengths range from 2·54 (1) to 2·81 (1) Å, with a mean value of 2·65 (1) Å. The distribution of ligands in this sphere of coordination is quite regular. Favas & Kepert (1981) have discussed in detail the expected configuration for a ninefold-coordinated cation, when repulsion between electron clouds prevails over directional chemical bonding in determining the stereochemistry. Their discussion led to two energetically almost equivalent ideal configurations: a tricapped trigonal prism (t.t.p.), with C_{3v} symmetry, and a monocapped square antiprism (m.s.a.), with C_{4v} symmetry. Both can be described by the set of angles *CMA*, *BMA*, and *DMA* (Fig. 1). Table 3 gives the expected values for a t.t.p. and an m.s.a. as well as mean values for this structure. The rather similar (though high) values of the angles *CMA* and *DMA* suggest some m.s.a. character for the O-atoms' distribution, with loose, overall C_{4v} symmetry. Departures from the ideal configuration are to be expected from the far-from-free character of the ligands involved. As an example, the Cu and Sr sharing of O(31) and

Table 1. *Fractional atomic coordinates and thermal parameters* (× 10⁴), *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq} or U(Å²)
Cu	0	0	0	110
Sr	2486 (2)	248 (1)	3831 (1)	62
Formate (I)				
C(1)	2532 (26)	3181 (21)	2072 (20)	241 (35)
O(11)	2370 (20)	2987 (16)	3408 (15)	328 (30)
O(12)	2477 (19)	2136 (15)	823 (15)	304 (28)
Formate (II)				
C(2)	2848 (21)	−410 (16)	7802 (16)	95 (26)
O(21)	983 (15)	−306 (11)	7948 (11)	99 (19)
O(22)	3665 (17)	−319 (13)	6608 (13)	189 (23)
Formate (III)				
C(3)	−2487 (26)	2726 (20)	9766 (20)	234 (35)
O(31)	−2090 (16)	1314 (12)	9120 (12)	160 (21)
O(32)	−2003 (21)	3453 (17)	1078 (17)	371 (32)
Water molecules				
W(1)	5124 (17)	2289 (13)	6069 (13)	200 (23)
W(2)	−21 (17)	1857 (13)	5723 (13)	192 (23)
W(3)	2492 (18)	3363 (14)	8277 (14)	262 (26)
W(4)	−2397 (19)	4020 (15)	4551 (15)	308 (29)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cu—O(12)	2·45 (1)	Sr—*W*(2)	2·63 (1)
Cu—O(21)	1·95 (1)	Sr—*W*(2^{ii})	2·62 (1)
Cu—O(31)	2·00 (1)	Sr···Sr^{i}	3·80 (1)
Cu···Sr	3·58 (1)	Sr···Sr^{ii}	4·15 (1)
Sr—O(11)	2·54 (1)	C(1)—O(11)	1·26 (1)
Sr—O(22)	2·67 (1)	C(1)—O(12)	1·25 (1)
Sr—O(22^{i})	2·62 (1)	C(2)—O(21)	1·25 (1)
Sr—O(31^{ii})	2·63 (1)	C(2)—O(22)	1·26 (1)
Sr—O(21^{ii})	2·65 (1)	C(3)—O(31)	1·27 (1)
Sr—*W*(1)	2·81 (1)	C(3)—O(32)	1·20 (1)
Sr—*W*(1^{i})	2·72 (1)		
O(12)—Cu—O(21)	85·1 (11)	O(11)—C(1)—O(12)	126·4 (17)
O(12)—Cu—O(31)	93·0 (12)	O(21)—C(2)—O(22)	125·7 (13)
O(21)—Cu—O(31)	82·4 (12)	O(31)—C(3)—O(32)	128·7 (17)

Symmetry code: (i) $1 - x, -y, -z$; (ii) $-x, -y, -z$.

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* Lists of structure factors and anisotropic temperature factors, and an indexed powder diagram (up to $2\theta = 50°$, Cu *K*α) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39634 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Throughout this paper, the symbol *W* stands for the O atom of a water molecule.

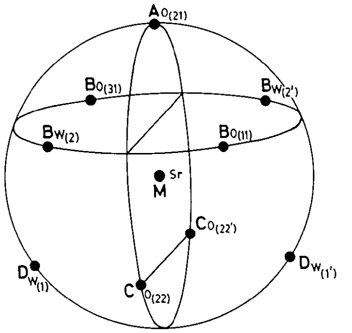

Fig. 1. Schematic drawing showing the general stereochemistry for ninefold coordination as well as the atom label of each site in $CuSr_2(HCOO)_6.8H_2O$.

Table 3. *Selected angles (°) describing different ninefold coordination arrays*

	t.t.p.(C_{3v})	m.s.a.(C_{4v})	Mean values for this structure*
B–M–A	70·5	70·1	70·0 (32)
C–M–A	131·8	125·7	135·9 (6)
D–M–A	120·0	125·7	133·4 (9)

* For the occupancy of different sites, refer to Fig. 1.

O(21) forces the latter 7° out of the apical site *A*. As a result, both O(31)–Cu–O(21) and O(31)–Sr–O(21) angles are smaller than the average in each c.p., and the O(31)···O(21) distance [2·60 (1) Å] becomes the shortest non-bonded O···O distance in the structure.

These two different types of c.p. are strongly linked to each other to form a tightly woven two-dimensional network parallel to (010). This is achieved through multiple edge sharing as well as by the bridging of formate groups. As a result of these strong interactions one of the Sr···Sr distances [3·80 (1) Å] equals the sum of the corresponding covalent radii. Although rather short for this type of 'open' structure, similar values are found in many 'perovskite-like' compounds: Sr_2MnO_4, Sr_2MoO_4, Sr_2WO_4 {Sr···Sr 3·72 Å through 3·92 Å [*Structure Reports* (1955), **19**, 323–324]}; TiO_3Sr {Sr···Sr 3·90 Å [*Structure Reports* (1952), **16**, 251]}. Even shorter values can be found in compounds with strong ionic character {SrO (Sr···Sr 3·62 Å) [*Structure Reports* (1954), **18**, 576–577]; SrO_2 (Sr···Sr 3·56 Å) [*Structure Reports* (1956), **20**, 452–453]; Sr_2Sb (Sr···Sr 3·54 Å) (Martinez-Ripoll, Haase & Brauer, 1973)}.

H atoms were not found in the *F* synthesis, but it was still possible to derive a reasonable H-bonding scheme from the analysis of bond lengths and angles. The result is shown in Fig. 2(*b*) and summarized in Table 4. All of the H bonds proposed contribute to the intralayer cohesion except for *W*(3)–H···O(32), which is the only link between layers. This anisotropy in bonding strength fully explains the neat cleavage found in (010). A distinction between two different types of water

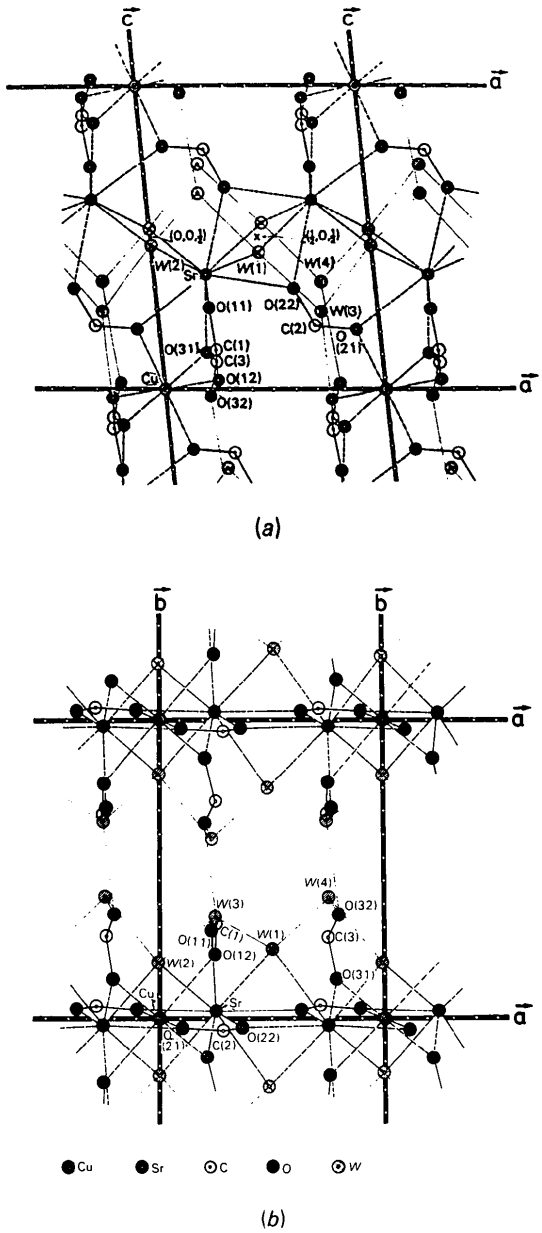

Fig. 2. Projections of the structure (*a*) along **b***, showing (010) layers, and (*b*) along **c**, showing weak interconnexion between layers. H bonds are marked by fine dotted lines.

Table 4. *H-bonding-scheme summary (general bond: Z–H···X–H···Y)*

X	*Y*	*X*···*Y* (Å)	*Z*	*X*···*Z* (Å)
W(1)	*W*(3)	2·73		
	W(4)	2·90		
W(2)	*W*(3)	2·74		
	W(4)	2·77		
W(3)	O(32)	2·75	*W*(1)	2·73
	O(12)	2·74	*W*(2)	2·74
W(4)	O(32)	3·03	*W*(1)	2·90
			W(2)	2·77

molecules can readily be made on the grounds of their interactions with the rest of the structure: those with their O atom directly bonded to the heavy atoms [$W(1)$ and $W(2)$], presumably more strongly attached, and those which only interact through H bonds. This correlates nicely with TGA data, which show a two-step dehydration process in the ranges 338–345 K, and 349–375 K, with weight losses of 11 and 12% (expected values, 11% each).

Formate groups are very active in coordinating the structure. Both formate (I) and formate (II) ions have a rather symmetrical coordination pattern, and the sharing of the acidic character between both O atoms is evidenced by the very similar C—O distances [C(1)—O(11) 1·26 (1), C(1)—O(12) 1·25 (1), C(2)—O(21) 1·25 (1), C(2)—O(22) 1·26 (1) Å]. Formate (III), instead, has only one O atom involved in direct coordination to a heavy ion [Sr—O(31) 2·63 (1) Å]. The other O atom is a double acceptor of H bonds and, through this, the only link between layers. This asymmetrical nature is clearly revealed in the C—O distances [C(3)—O(31) 1·27 (1), C(3)—O(32) 1·20 (1) Å].

Thermal parameters show relative values in fair agreement with the vibrational behaviour expected from coordination considerations. Thus, there is a clear distinction between doubly coordinated water molecules and H-bonded ones, as well as between formate O atoms shared by two heavy-atom c.p. and those involved only once.

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Structure of the 2/1 Complex Dibenzotetrathiafulvalenium Hexachlorocuprate(II),* $2C_{14}H_8S_4{}^+.Cu_2Cl_6{}^{2-}$

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Abstract. $M_r = 948\cdot54$, monoclinic, $C2/m$, $a = 9\cdot224\,(1)$, $b = 24\cdot976\,(3)$, $c = 7\cdot317\,(2)$ Å, $\beta = 108\cdot28\,(1)°$, $V = 1600\cdot7\,(6)$ Å^3, $Z = 2$, $D_m = 1\cdot96$, $D_x = 1\cdot97$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 109\cdot54$ cm^{-1}, $F(000) = 944$, $T = 293$ K, $R = 0\cdot053$ for 1337 observed reflections. The central C=C bond in the cation is longer than that found in the neutral compound, but agrees with that of other dibenzotetrathiafulvalenium cations. The structure contains stacking columns of the dibenzotetrathiafulvalenium cation along the c axis. The $Cu_2Cl_6^{2-}$ anion has normal bond lengths and angles.

Introduction. Organic charge-transfer radical salts consisting of the electron donor TTF (tetrathiafulvalene) and an electron acceptor such as TCNQ (tetracyano-*p*-quinodimethane) display high electric conductivities (Cohen, Coleman, Garito & Heeger, 1974). The crystal structures of the organic conductors are composed of characteristic columns in which the donor cation and acceptor anion radicals are stacked separately. Electrons and holes are delocalized in the respective columns. This causes high anisotropy in the solid-state properties of the organic conductors, such as electric, optical and magnetic ones. Many compounds analogous to TTF have been synthesized to obtain radical salts with high electric conductivity. Dibenzotetrathiafulvalene (DBTTF) is one of them and the direct oxidation of DBTTF by halogens and metal

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* Alternative nomenclature: bis(2,2′-bi-1,3-benzodithiolyl-denium) hexachlorodicuprate.

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