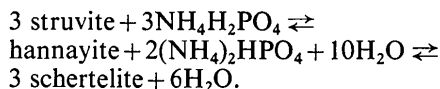presence of aqueous ammonium phosphate solutions. Particularly, struvite is reported to react with a saturated solution of ammonium dihydrogen phosphate to form hannayite, which is then slowly replaced by schertelite; these reactions can be summarized as follows:

3 struvite + 3NH₄H₂PO₄ ⇄
hannayite + 2(NH₄)₂HPO₄ + 10H₂O ⇄
3 schertelite + 6H₂O.

Inversely, schertelite and hannayite undergo hydrolytic reactions dissolving incongruently in water:

schertelite + 2H₂O ⇄
struvite + NH₄H₂PO₄, hannayite + 4H₂O ⇄
struvite + 2 newberyite + NH₄H₂PO₄.
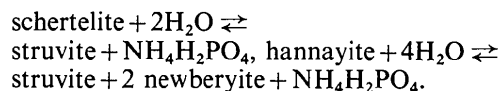
Such transformations also probably occur in human renal liquids under pathological conditions. They can be explained by the strong tendency of systems with this chemical composition to give crystals characterized by a layered structure, where the amount of NH_4^+ ions between layers and the degree of condensation of coordination polyhedra inside the layers vary according to the concentrations of the different chemical species. When hannayite transforms into schertelite, for instance, the condensation of polyhedra decreases strongly, with the formation of isolated $Mg(H_2O)_4(OPO_2OH)_2$ groups. The first bonds which break in hannayite are likely to be Mg(2)–O(3) and Mg(2)–O(7) (Fig. 2), since they involve the most underbonded O atoms in the structure ($\sum s_i = 1.83$ v.u.); this should be true both for complete solubilization of crystals and for incomplete solubilization with partial solid-state reaction. The latter mechanism would agree with the fact that, by breaking Mg(2)–O(3), isolated

groups of $Mg(H_2O)_4(OPO_2OH)_2$ are formed, which could build up the schertelite crystal framework.

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Crystallographic Studies of Bis-(N-p-tolylsalicylaldiminato)copper(II)

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The structure of bis-(N-p-tolylsalicylaldiminato)copper(II) has been determined by the photographic method and refined to $R = 0.09$. The crystals are monoclinic needles, $a = 13.584$, $b = 7.546$, $c = 12.221$ Å, $\beta = 110.8°$, $Z = 2$. The structure consists of discrete molecules in which the metal atom exhibits trans-planar fourfold coordination and has Cu–O 1.899 and Cu–N 2.010 Å. The p-tolyl group is inclined by 124° to the salicylaldimine plane.

Introduction

In order to gather more information on the structural features and their dependence on various steric and electronic effects in the presence of different types of substituents on the N of the salicylaldimine (designated hereafter sim) moiety, considerable attention has been given to the study of solid-state properties. Holm,

Everett & Chakravorty (1966) have reported (p-tolyl-sim)$_2$Cu to be diamagnetic in the solid state. We have now determined its crystal structure by X-ray diffraction. A preliminary account of the crystal data has appeared (Bhatia, Bindlish & Jain, 1975).

Experimental

The sample was prepared by the method of Holm, Everett & Chakravorty (1966). Oscillation and Weissenberg photographs showed the crystals to be monoclinic.

Crystal data

$C_{28}H_{24}N_2O_2Cu$, $M=483.5$; $a=13.584$ (7), $b=7.546$ (10), $c=12.221$ (9) Å, $\beta=110.8$ (8)°, $U=1170$ Å^3; space group $P2_1/a$; $D_c=1.37$, $D_m=1.41$ g cm^{-3} for $Z=2$; μ(Cu $K\alpha)=15.90$ cm^{-1}, $\lambda=1.5418$ Å.

A crystal, $0.50 \times 0.35 \times 0.10$ mm, was mounted along **b** (needle direction). Integrated intensities for the $h0l \rightarrow h4l$ layers were collected by the equi-inclination Weissenberg method with a four-film pack and an exposure of 80 h for each layer. Intensities for the $0kl \rightarrow 2kl$ layers were also collected with another crystal of nearly the same size. The estimation of intensity was carried out by the visual method with a calibrated strip. Out of 1165 independent reflexions 94 were termed unobserved. Each reflexion was corrected for Lorentz and polarization effects, but not for absorption. In the final stages of refinement secondary extinction corrections were applied.

Structure solution and refinement

With $Z=2$, Cu should occupy the special positions 000 and $\frac{1}{2}\frac{1}{2}0$. Initial structure factor calculations with Cu gave $R=0.51$. A series of Fourier syntheses led to the location of all non-hydrogen atoms. Further refinement of the positional and isotropic thermal parameters reduced R to 0.13. Least-squares refinement with an-

isotropic temperature factors gave $R=0.105$. A difference map at this stage revealed the positions of all H atoms. The observed positions were in good agreement with those calculated. The positions of the H atoms and their isotropic temperature factor ($B=4.0$ Å^2) were not refined but were included in the subsequent refinement.

Finally, refinement was carried out with weights $\sqrt{w}=1/(1.62-0.027F_o)$ for $F_o \leq 15.5$, $\sqrt{w}=1/(0.64+0.037F_o)$ for $F_o>15.5$; giving $R=0.09$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

All calculations were performed on CDC 3600 and ICL 1905E computers. Programs employed included the Fourier summation program of Blount (1965), the least-squares program of Busing, Martin & Levy (1962), the NRC programs of Ahmed, Hall, Pippy & Huber (1970), the *CALCAT* program for hydrogen of Watenpaugh (1972) and *ORTEP* (Johnson, 1970).

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

Values for the chelate ring are included in Table 4.

C(1)—C(2)	1.424 (16)	O——C(1)—C(2)	117.4 (19)
C(2)—C(3)	1.423 (15)	C(2)—C(1)—C(6)	117.4 (10)
C(3)—C(4)	1.374 (20)	C(1)—C(2)—C(3)	119.8 (17)
C(4)—C(5)	1.368 (17)	C(2)—C(3)—C(4)	121.4 (13)
C(5)—C(6)	1.416 (14)	C(3)—C(4)—C(5)	119.9 (10)
C(8)—C(9)	1.387 (7)	C(4)—C(5)—C(6)	121.4 (10)
C(9)—C(10)	1.403 (17)	C(5)—C(6)—C(1)	120.0 (12)
C(10)—C(11)	1.415 (14)	C(5)—C(6)—C(7)	119.3 (10)
C(11)—C(14)	1.545 (20)	C(7)—N——C(8)	115.3 (11)
C(11)–C(12)	1.361 (8)	C(8)—N——Cu	121.8 (6)
C(12)–C(13)	1.393 (18)	C(9)—C(8)—N	122.3 (8)
C(13)–C(8)	1.402 (14)	C(8)—C(9)—C(10)	119.5 (10)
		C(9)—C(10)–C(11)	121.4 (10)
		C(10)–C(11)–C(12)	117.4 (9)
		C(10)–C(11)–C(14)	121.0 (10)
		C(12)–C(11)–C(14)	121.5 (10)
		C(11)–C(12)–C(13)	122.6 (10)
		C(12)–C(13)–C(8)	119.6 (10)
		C(13)–C(8)—N	118.3 (9)
		C(13)–C(8)—C(9)	119.0 (13)

Table 1. *Atomic parameters* ($\times 10^4$) *of non-hydrogen atoms with their e.s.d.'s in parentheses*

The thermal parameters are of the form exp $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	0	67 (1)	162 (5)	80 (1)	22 (2)	14 (1)	−6 (2)
O	1144 (5)	753 (10)	1336 (5)	49 (4)	203 (18)	83 (6)	25 (7)	10 (4)	−42 (8)
N	−922 (5)	1973 (10)	184 (6)	54 (4)	74 (17)	60 (6)	5 (7)	10 (4)	−9 (8)
C(1)	1117 (7)	1744 (14)	2200 (8)	53 (6)	142 (26)	84 (8)	−17 (10)	19 (6)	8 (12)
C(2)	2042 (7)	1812 (15)	3221 (8)	57 (6)	184 (27)	84 (9)	−5 (10)	7 (6)	−9 (12)
C(3)	2033 (8)	2773 (16)	4220 (9)	75 (8)	238 (32)	74 (8)	−24 (12)	1 (6)	−10 (13)
C(4)	1155 (8)	3679 (15)	4214 (8)	81 (8)	162 (30)	77 (8)	−13 (12)	20 (7)	−27 (12)
C(5)	255 (7)	3626 (14)	3245 (8)	70 (7)	134 (28)	85 (9)	9 (10)	18 (6)	−42 (12)
C(6)	205 (7)	2658 (12)	2234 (8)	66 (6)	76 (23)	66 (8)	9 (9)	15 (6)	1 (10)
C(7)	−742 (7)	2757 (14)	1192 (8)	61 (6)	119 (26)	74 (8)	6 (9)	24 (6)	14 (11)
C(8)	−1937 (6)	2359 (12)	−711 (8)	50 (5)	61 (24)	80 (8)	6 (8)	24 (5)	−3 (10)
C(9)	−2879 (7)	2067 (14)	−538 (7)	56 (6)	138 (26)	64 (7)	1 (10)	22 (6)	−14 (11)
C(10)	−3833 (7)	2470 (16)	−1437 (8)	62 (6)	148 (28)	89 (9)	10 (10)	33 (7)	−23 (12)
C(11)	−3855 (7)	3178 (13)	−2517 (8)	60 (7)	84 (23)	82 (8)	32 (9)	12 (6)	−10 (11)
C(12)	−2914 (7)	3497 (15)	−2640 (8)	63 (6)	216 (31)	75 (8)	8 (10)	15 (6)	36 (12)
C(13)	−1953 (7)	3100 (15)	−1769 (8)	49 (6)	230 (27)	78 (8)	5 (10)	23 (6)	41 (13)
C(14)	−4909 (8)	3537 (16)	−3523 (9)	64 (7)	181 (32)	95 (9)	47 (11)	1 (6)	−2 (13)

Atomic parameters are given in Table 1. A view of the packing along **a** is shown in Fig. 1. Fig. 2 shows the thermal ellipsoid plot at the 50% level and also the numbering scheme. Bond distances and angles are listed in Table 2. The deviations of atoms from various mean planes are given in Table 3. Table 4 contains the geometrical parameters of the chelate ring of some related sim–Cu molecules.*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31838 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Coefficients of the least-squares planes equations and distances (Å) of atoms from these planes*

$lx + my + nz - p = 0$, where x, y, z are orthogonal ångström space coordinates referred to crystallographic a, b and c^* axes.

Plane		l	m	n	p
(I)	Coordination	0·715	0·304	0·629	0·250
(II)	Benzene	−0·454	−0·817	0·356	0·428
(III)	*p*-Tolyl group	0·120	−0·924	−0·364	1·654
(IV)	Chelate ring	−0·499	−0·801	0·331	0·452
(V)	Salicylaldimine	0·487	0·802	−0·345	−0·442

Plane (I):   Cu 0·250, O 2·080, N −0·117
Plane (II): C(1) −0·008, C(2) −0·004, C(3) 0·013, C(4) −0·007, C(5) −0·005, C(6) 0·012
Plane (III): C(8) 0·026, C(9) −0·004, C(10) −0·020, C(11) −0·012, C(12) −0·024, C(13) 0·001, C(14) 0·036
Plane (IV): Cu 0·452, O 0·015, N −0·007, C(1) −0·053, C(6) 0·033, C(7) −0·003
Plane (V):   Cu −0·442, O −0·038, N 0·031, C(1) 0·022, C(2) 0·057, C(3) 0·028, C(4) −0·001, C(5) −0·042, C(6) −0·049, C(7) 0·014

Dihedral angles (°)

(I)–(II)	110·4	(II)–(IV)	2·8
(I)–(III)	115·1	(II)–(V)	177·6
(I)–(IV)	113·1	(III)–(IV)	56·1
(I)–(V)	68·1	(III)–(V)	123·9
(II)–(III)	55·2	(IV)–(V)	178·2

Discussion

The molecules lie practically in the *xz* plane. Cu has a *trans*-planar configuration. The benzene ring of the salicylaldimine group has a mean bond length of 1·40 Å and an interbond angle of 120°, whilst in the *p*-tolyl group it has mean values of 1·39 Å and 119·9°. C(11)–C(14), 1·54 Å, is normal taking into account the high anisotropy for C(14). C(6)–C(7)–N, 128°, seems to be a little large (Table 4) but agrees well with the values
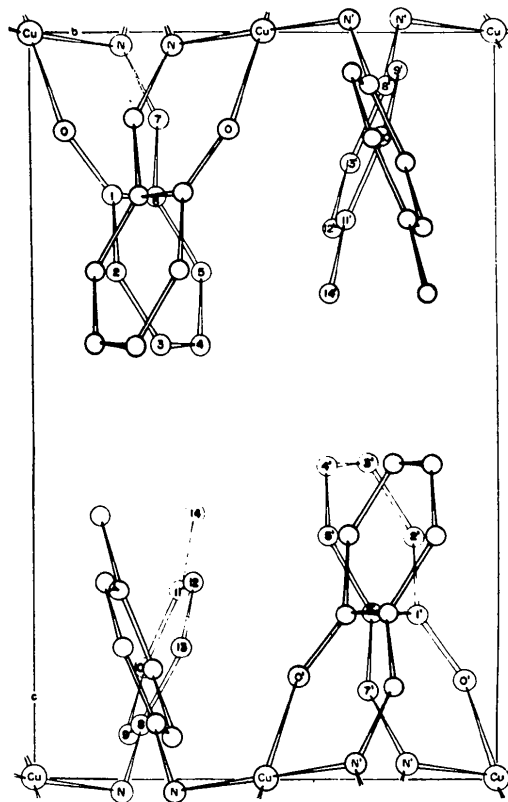

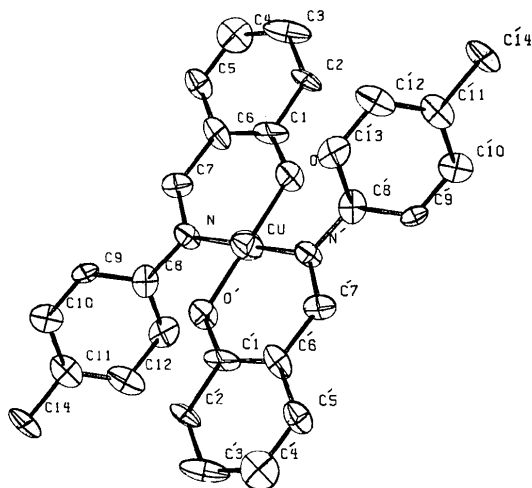Fig. 1. Bis-(*N*-*p*-tolylsalicylaldiminato)copper(II) projected on to the [100] plane.

Table 4. *Bond distances (Å) and interbond angles (°) of the chelate ring in some related sim–Cu molecules*

	Present work	(*N*-Phenyl-sim)₂Cu (Wei, Stogsdill & Lingafelter, 1964)	Pyridine solvate of (*N*-phenylsim)₂Cu (Hall, Sheat-Rumball & Waters, 1968)		(*N*-α-Phenyl-ethylsim)₂Cu (Starikova, 1966)		(*N*-2-Pyridyl-sim)₂Cu (Drummond & Wood, 1972)
Cu—O	1·899 (7)	1·878 (3)	1·888 (6)	1·889 (7)	1·93	1·89	1·965 (6)
Cu—N	2·010 (10)	1·993 (4)	2·002 (6)	2·008 (6)	1·97	2·01	1·975 (8)
O——C(1)	1·306 (12)	1·313 (4)	1·28 (1)	1·28 (1)	1·36	1·31	1·335 (11)
N——C(7)	1·310 (12)	1·302 (5)	1·29 (1)	1·29 (1)	1·30	1·30	1·338 (13)
C(1)–C(6)	1·432 (12)	1·399 (6)	1·39 (1)	1·38 (1)	—		1·437 (15)
C(6)–C(7)	1·457 (15)	1·436 (6)	1·42 (1)	1·43 (1)	1·43	1·45	1·431 (16)
N——C(8)	1·454 (15)	1·438 (6)	1·45 (1)	1·46 (1)	1·56	1·51	1·484 (14)
N——Cu——O	92·0 (4)	91·0	87·7	86·7			90·2
Cu—N——C(7)	121·7 (8)	123·0	124·2	124·5			122·6
Cu—O——C(1)	128·2 (16)	128·0	130·2	130·5			125·0
O——C(1)–C(6)	125·0 (12)	124·0	122·0	124·9			
N——C(7)–C(6)	127·7 (18)	126·0	125·2	125·7			124·6
C(1)–C(6)–C(7)	120·3 (9)	123·0	125·4	123·7			125·7

Fig. 2. Thermal ellipsoid plot of bis-(*N*-*p*-tolylsalicylaldimi-nato)copper(II) at 50% probability.

The benzene ring retains its planarity. C(3) has the maximum deviation of 0·013 Å which is due to its in-plane high thermal vibrations (Table 1). The benzene ring and the chelate ring are nearly coplanar with an angle of tilt of 3°. Omitting C(14), the deviations of other atoms of the *p*-tolyl group range from −0·02 to 0·04 Å. The Cu atom is farther out (−0·41) and the N atom is out (0·12 Å) in the opposite direction from the mean benzene plane.

C–H lengths and bond angles involving H atoms are normal. Most of the bond lengths fall within the range 0·90–1·10 Å. There are no unusual contacts of H atoms with other atoms of the molecule.

found in (ethylsim)₂Cu (Clark, Hall & Waters, 1969) and (isopropylsim)₂Cu (Orioli & Sacconi, 1966). Cu–N, 2·01, and Cu–O, 1·90 Å, fall within the range reported for 21 sim–Cu molecules (Jain & Syal, 1973). Although there is a slight increase in both the Cu–O and Cu–N lengths compared to (phenylsim)₂Cu (Wei, Stogsdill & Lingafelter, 1964), the difference of 0·11 Å is in excel-lent agreement. The CH₃ group of the *p*-tolyl group is quite far away from the chelate ring. The inclination of the *p*-tolyl group of 124° to the remaining part of the asymmetric unit (Table 3) has resulted in some close contacts, namely C(8)···C(7) 2·32, C(8)···C(9) 2·97 and C(8)···Cu 3·30 Å, which affect the geomet-rical conformation of the chelate ring, especially in the neighbourhood of N. The result is that the bond lengths and interbond angles of the chelate ring are slightly different in the present case from the values found in (phenylsim)₂Cu (Wei, Stogsdill & Lingafelter, 1964) and in the pyridine solvate of (phenylsim)₂Cu (Hall, Sheat-Rumball & Waters, 1968). N–C(8), 1·45 Å, is similar to the value observed in other sim–Cu molecules having an aromatic ring substituent on N. A study of N–C(8) lengths in different types of N-substituted sim–Cu mol-ecules shows that molecules having a simple phenyl group or *p*-tolyl group as substituent (Table 4) have, in gen-eral, a length of about 1·45 Å whereas those having a linear chain (Jain, Bindlish & Kashyap, 1976), cyclo-hexyl ring, or ethylenediamine as substituent normally have a value above 1·47 Å. Thus N shows greater dona-tion to the multibonding system in the presence of aromaticity around it.

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