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Structure of [4-Methoxymethyl-6-methyl-2-(salicylideneamino)-3-(salicylideneaminomethyl)pyridinato(2−)-*N*,*N*′,*O*,*O*′]copper 1·5 Hydrate, $C_{23}H_{21}CuN_3O_3.1{\cdot}5H_2O$

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Abstract. $M_r = 478{\cdot}01$, monoclinic, $P2_1/c$, $a = 13{\cdot}788$ (4), $b = 7{\cdot}881$ (1), $c = 19{\cdot}899$ (6) Å, $\beta = 100{\cdot}74$ (3)°, $V = 2124$ (1) Å^3, $Z = 4$, $D_m = 1{\cdot}49$, $D_x = 1{\cdot}494$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 1{\cdot}73$ mm^{-1}, $F(000) = 992$, $T = 293$ K. Final $R = 0{\cdot}074$ for 2857 observed reflections. The ligand is quadridentate, forming three six-membered chelate rings with the metal atom. The coordination sphere of Cu is partially tetrahedral, the dihedral angle CuON-CuO′N′ being 33·8 (2)°. Both Cu—O bond lengths are nearly the same, 1·900 (5) and 1·906 (5) Å, while both Cu—N bond lengths are different, 1·972 (5) and 1·931 (5) Å, the longer one involving the N adjacent to the pyridine ring. The crystal water molecules are statistically disposed in cavities along the twofold screw axes. Elemental analysis and mass spectrometric data are in agreement with the determined structure.

Introduction. Comprehensive data have already been published about the metal complexes of Schiff bases (Maslen & Waters, 1975; Casellato, Vigato & Vidali, 1977; references cited in both reviews), but the interest in further studies still exists stimulated by numerous reasons. Among them the use as biological models, the diverse properties and the general ease of preparation have been highlighted (Maslen & Waters, 1975).

The manifold applicability of Schiff bases as analytical reagents for metals represents another significant reason encouraging the investigations of the corresponding complexes (Jungreis & Thabet, 1969; Morishige, 1980; Okafor, 1980). The same reason was the motive for our work with the ligand of the Schiff base type obtained by condensation of 2-amino-3-aminomethyl-4-methoxymethyl-6-methylpyridine with salicylaldehyde (Cimerman, Deljac & Štefanac, 1980). The study of the suitability of this ligand as an extractant for transition-metal ions included also the structure determination of isolated crude complexes. As far as copper complexes were concerned a species of unexpected elemental composition was isolated under certain experimental conditions.

Experimental. Slow evaporation of a methanolic solution containing equimolar amounts of 2-amino-4-methoxymethyl-6-methyl-3-(salicylideneaminomethyl)pyridine and copper(II) sulphate resulted in the formation of white crystals of dibasic tetrasubstituted pyridine sulphate along with green crystals of the copper(II) complex. The crystals were filtered off and washed with large amounts of water. The water-insoluble copper(II) complex, separated in this way from the very soluble amine salt, was recrystallized several times from the chloroform/methanol system, m.p. 533–538 K (decomp.). After drying *in vacuo*, the colour of the isolated complex changed from green to dark brown. Elemental analysis, found: C 61·13, H 4·69, Cu 14·32, N 9·32; calc. for $C_{23}H_{21}CuN_3O_3$: C 61·26, H 4·69, Cu 14·08, N 9·32%. Exposure to air causes absorption of water as was evidenced by repeated elemental analyses, thermogravimetric analyses and the crystal-structure determination. This water can be easily removed by drying *in vacuo*.

Dark-brown prismatic crystals. Density determined by flotation in a mixture of CCl_4 and petroleum ether. Philips PW 1100 four-circle diffractometer, ω–2θ scanning technique, scan range 2·40°, scan rate 0·08° s^{-1}. Unit-cell dimensions refined from measurements on 14 reflections. Absent reflections $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ confirmed $P2_1/c$ space group. Of 3082 unique reflections measured within quadrant $\pm h,k,l$ ($h \pm 16$, k 9, l 24) up to $\sin\theta/\lambda = 0{\cdot}61$ Å^{-1} (80 of symmetry-related pairs averaged), 225 with $I < 3\sigma(I)$ classified as unobserved. Three standard reflections ($\bar{6}00$, 302, $0\bar{2}2$) measured after each group of about 60 measurements showed an averaged variation of 4(2)%, but no systematic change could be noticed. Corrections

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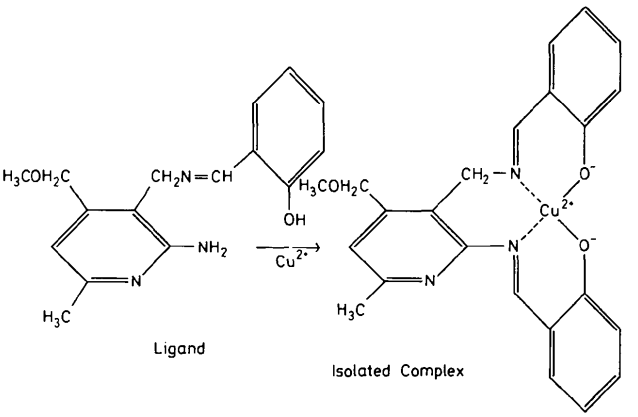
applied for Lorentz and polarization effects, not for absorption. Cu atom located by heavy-atom method, all other non-H ligand atoms from a subsequent Fourier map. Most H atoms located in difference map; only H(192) and H(232) from terminal methyl groups placed at calculated positions (with C–H = 1·09 Å).

The difference map also revealed three undefined atoms, represented by three maxima approximately half the height of a C and twice that of the strongest H maximum, repeated infinitely along the twofold screw axis; their mutual distances and angles of 1·37 (2), 1·55 (2), 1·52 (2) Å and 146 (1), 151 (1), 131 (1)°, respectively, showed no reasonable compound bonding scheme but their positions in cavities with a cross-section of nearly 6 Å in diameter (Fig. 2), at distances within O···O hydrogen bonds from salicylidene O atoms, indicated that they are statistically disposed O atoms. The possibility of the peaks belonging to water or methanol O atoms, assuming that peaks of methanol C atoms are not recognizable, was considered. Thermogravimetric (TG) analysis, performed on a Cahn RG Electrobalance, showed a weight loss of 5·8 (5)% between 315 and 323 K, *i.e.* 1·54 (14) molecule of water or 0·86 (8) molecule of methanol. The least-squares refinement of their population parameters converging to values of 0·56 (1), 0·55 (1) and 0·56 (1) was comparable to the result of TG analysis interpreted for water O atoms. Density measurements agreed better with the presumption for water than for methanol O atoms. The very low temperature of their liberation determined by TG analysis indicated that no strict content of the crystal water could be predicted. From crystal-structure analysis, density and TG measurements it was assumed that the number of water of crystallization molecules was 1·5.

In block-diagonal least-squares refinement on F, H atoms were included with fixed isotropic temperature factors of their carrier atoms increased by 0·015 Å^2; y,z and x,y coordinates of H(192) and H(232) respectively were kept fixed on account of their unrealistic shifts during refinement. Crystal water atoms were refined with isotropic thermal parameters, kept fixed in the last cycles of refinement. Refinement with anisotropic thermal parameters for all other non-H atoms gave $R = 0{\cdot}074$, $R_w = 0{\cdot}089$; weighting scheme used $w^{-1} = 1{\cdot}0 + \sigma^2(F_o) + 0{\cdot}00025\,F_o^2$; corresponding $S = 1{\cdot}51$, that using unit weights 1·97. $(\Delta/\sigma)_{max} = 0{\cdot}3$, $(\Delta/\sigma)_{mean} = 0{\cdot}1$. Final difference map revealed no residuals greater than 0·55 e Å^{-3}, except three irregular maxima up to 1·40 e Å^{-3} near Cu. Scattering factors of Cromer & Mann (1968) used for non-H and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Calculations performed mainly with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a Univac 1110 computer at the University Computing Centre of Zagreb.

Discussion. Final atomic coordinates (based on the unit-weights refinement) are listed in Table 1.*

Repeatedly undertaken condensations of 2-amino-3-aminomethyl-4-methoxymethyl-6-methylpyridine with salicylaldehyde afforded a product identical with the structure given in the scheme that was confirmed by elemental analyses as well as by UV/visible, IR, ^{1}H NMR and mass spectrometric data.



Complementary to the study concerning the applicability of this ligand as a reagent for the extraction of copper(II), the isolation of crude complex species was accomplished (Cimerman *et al.*, 1980). Essentially different species were obtained as dependent on polarity of the solvent used and on lipophilic character of the anion moiety of the cupric salt added. The working conditions described also in this paper afforded repeatedly a copper complex of reproducible elemental composition. Elemental analyses and mass spectrometric data conform to the copper complex having an as yet undescribed quadridentate ligand bearing not only the salicylaldimine moiety involving the 3-aminomethyl substituent but also an additional one formed at the 2-amino group on the pyridine ring (see scheme). The unexpected formation of such a ligand unobtainable without the presence of copper called for conclusive evidence.

The following crystallographic structure is based on the preliminary X-ray investigations already reported (Galešić, 1980). Fig. 1 shows a perspective view of the molecule with the atomic numbering. Intramolecular bond lengths and relevant angles are listed in Table 2.

The coordination sphere of Cu can be described as partially tetrahedral (Waters, 1982) consisting of two N and two O atoms from two salicylaldimine moieties. No other approaches of non-H atoms to the Cu atom are

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, mean planes, additional bond angles and puckering parameters and a projection of the structure along **a** have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38800 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

less than 3·5 Å. The ligand thus forms three six-membered chelate rings with the metal atom (*D*, *E* and *F*, Fig. 1). The fourfold coordination of the Cu atom accompanied by the brown colour of the crystals is in agreement with the observations of Waters & Hall (1959). The deviations of Cu, O(1), O(1*A*), N(1) and N(1*A*) from their mean plane are 0·003 (1), 0·431 (5), −0·379 (5), −0·422 (5) and 0·413 (6) Å, respectively. The dihedral angle θ adopted as a measure of tetrahedrality (Holm & O'Connor, 1971) and defined as the angle between planes through Cu, O(1), N(1) and Cu, O(1*A*), N(1*A*) is 33·9 (2)°. The complex might be considered as slightly stepped with half-steps τ_A and τ_B (the distances of Cu from the mean planes of the benzene rings *A* and *B*) of 0·074 (1) and −0·088 (1) Å respectively. These values are comparable with the analogous values of 0·01 and −0·12 Å for the *p*-nitrophenol adduct of *N,N'*-ethylenebis(salicylaldiminato)copper(II) (Baker, Hall & Waters, 1970). The distance of Cu from the mean plane of the pyridine ring is considerably larger amounting to −0·970 (1) Å (τ_C). Bites of the salicylaldimine rings (Lingafelter & Braun, 1966), O(1*A*)···N(1*A*) and O(1)···N(1), are 2·797 (7) and 2·847 (7) Å respectively.

Table 1. *Fractional positional parameters of non-*H *atoms* (×10⁴; ×10⁵ *for* Cu), *isotropic temperature factors* (×10²) *for crystal water* O *atoms and equivalent isotropic factors* (×10²) *for other non-*H *atoms*

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

	x	*y*	*z*	U_{eq}/U(Å²)
Cu	16408 (7)	39009 (13)	58343 (5)	5·48 (3)
O(1)	1802 (3)	4858 (7)	6725 (2)	7·1 (2)
O(1*A*)	526 (3)	2707 (6)	6032 (2)	6·1 (2)
O(3)	3203 (4)	3808 (9)	2744 (2)	9·2 (2)
O*w*(1)†	132 (9)	2599 (16)	7409 (6)	11·3 (5)
O*w*(2)†	−147 (8)	4194 (15)	7182 (5)	10·1 (5)
O*w*(3)†	57 (8)	6125 (16)	7137 (6)	10·7 (5)
N(1)	3034 (4)	4202 (7)	5754 (2)	5·0 (2)
N(1*A*)	1163 (4)	3864 (7)	4859 (3)	5·7 (2)
N(3)	4284 (4)	2999 (7)	5239 (3)	5·2 (2)
C(1)	3561 (5)	5225 (9)	6924 (3)	5·7 (2)
C(2)	2622 (5)	5305 (9)	7117 (3)	5·9 (3)
C(3)	2587 (6)	5965 (11)	7773 (4)	7·7 (3)
C(4)	3410 (6)	6437 (12)	8211 (4)	8·5 (3)
C(5)	4342 (6)	6316 (12)	8029 (4)	8·2 (4)
C(6)	4399 (5)	5719 (11)	7399 (4)	7·4 (3)
C(7)	3690 (5)	4673 (9)	6264 (3)	5·5 (2)
C(1*A*)	−314 (4)	2254 (8)	4889 (3)	5·3 (2)
C(2*A*)	−190 (5)	2042 (8)	5597 (3)	5·4 (2)
C(3*A*)	−909 (5)	1052 (9)	5849 (4)	6·3 (3)
C(4*A*)	−1704 (5)	375 (8)	5420 (4)	6·7 (3)
C(5*A*)	−1841 (5)	595 (9)	4726 (4)	6·8 (3)
C(6*A*)	−1136 (5)	1528 (9)	4464 (4)	6·5 (3)
C(7*A*)	363 (4)	3173 (8)	4556 (3)	5·1 (2)
C(15)	1768 (4)	4784 (9)	4451 (3)	5·4 (2)
C(16)	2783 (4)	3972 (8)	4514 (3)	4·7 (2)
C(17)	3372 (4)	3698 (8)	5140 (3)	4·7 (2)
C(18)	4627 (4)	2570 (8)	4665 (3)	5·3 (2)
C(19)	5659 (5)	1849 (10)	4790 (4)	6·9 (3)
C(20)	4102 (5)	2800 (9)	4030 (3)	5·5 (2)
C(21)	3155 (4)	3535(8)	3925 (3)	5·0 (2)
C(22)	2592 (5)	3855 (11)	3225 (3)	6·7 (3)
C(23)	2761 (6)	4372 (13)	2090 (4)	9·1 (4)

† Population parameters of O*w*(1), O*w*(2) and O*w*(3) are 0·56 (1), 0·55 (1) and 0·56 (1), respectively, and their temperature factors were kept fixed in the last cycles of the refinement.

Table 2. *Bond lengths* (Å) *and relevant bond angles* (°) *of non-*H *atoms, and* O···O *hydrogen-bond lengths* (Å)

Cu–O(1)	1·900 (5)	C(3)–C(4)	1·348 (11)
Cu–O(1*A*)	1·906 (5)	C(4)–C(5)	1·402 (13)
Cu–N(1)	1·972 (5)	C(5)–C(6)	1·355 (11)
Cu–N(1*A*)	1·931 (5)	C(1*A*)–C(2*A*)	1·397 (9)
O(1)–C(2)	1·297 (8)	C(1*A*)–C(6*A*)	1·404 (9)
O(1*A*)–C(2*A*)	1·297 (7)	C(1*A*)–C(7*A*)	1·437 (9)
O(3)–C(22)	1·388 (9)	C(2*A*)–C(3*A*)	1·425 (10)
O(3)–C(23)	1·402 (9)	C(3*A*)–C(4*A*)	1·366 (9)
N(1)–C(7)	1·281 (7)	C(4*A*)–C(5*A*)	1·370 (11)
N(1)–C(17)	1·443 (8)	C(5*A*)–C(6*A*)	1·395 (11)
N(1*A*)–C(7*A*)	1·277 (8)	C(15)–C(16)	1·523 (9)
N(1*A*)–C(15)	1·460 (9)	C(16)–C(17)	1·372 (8)
N(3)–C(17)	1·353 (8)	C(16)–C(21)	1·405 (9)
N(3)–C(18)	1·357 (9)	C(18)–C(19)	1·509 (9)
C(1)–C(2)	1·418 (10)	C(18)–C(20)	1·346 (9)
C(1)–C(6)	1·404 (9)	C(20)–C(21)	1·408 (9)
C(1)–C(7)	1·427 (10)	C(21)–C(22)	1·486 (8)
C(2)–C(3)	1·414 (10)		

O(1)–Cu–O(1*A*)	87·8 (2)	Cu–N(1)–C(17)	120·6 (4)
O(1)–Cu–N(1)	94·6 (2)	C(7)–N(1)–C(17)	117·3 (5)
O(1)–Cu–N(1*A*)	154·5 (2)	Cu–N(1*A*)–C(7*A*)	125·8 (5)
O(1*A*)–Cu–N(1)	155·8 (2)	Cu–N(1*A*)–C(15)	115·3 (4)
O(1*A*)–Cu–N(1*A*)	93·6 (2)	C(7*A*)–N(1*A*)–C(15)	118·9 (5)
N(1)–Cu–N(1*A*)	94·4 (2)	N(1)–C(7)–C(1)	128·8 (6)
Cu–O(1)–C(2)	127·3 (5)	N(1*A*)–C(7*A*)–C(1*A*)	125·1 (6)
Cu–O(1*A*)–C(2*A*)	127·2 (4)	N(1*A*)–C(15)–C(16)	111·0 (5)
C(22)–O(3)–C(23)	114·6 (6)	O(3)–C(22)–C(21)	111·3 (5)
Cu–N(1)–C(7)	121·7 (5)		

O(1)···O*w*(3)	2·862 (13)	O(1*A*)···O*w*(2)	2·874 (13)
O(1)···O*w*(2)*	3·040 (13)	O*w*(1)···O*w*(3)	2·829 (18)
O(1*A*)···O*w*(1)	2·892 (14)	O*w*(1)···O*w*(2^{I})	2·803 (17)
		O*w*(2)···O*w*(3^{II})	2·764 (17)

Symmetry operations: (i) $-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$.

* Hydrogen contact.

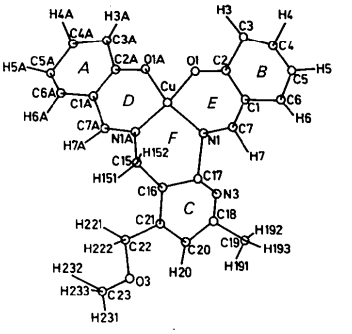


Fig. 1. A perspective view of the complex molecule along **b** showing the atomic numbering.

The salicylaldimine chelate rings *D* and *E* moderately deviate from planarity within ±0·039 (5) and ±0·070 (5) Å respectively, while ring *F* adjacent to the pyridine ring is strongly non-planar, with deviations from the mean plane within ±0·493 (7) Å. In accordance with a recent proposal for a quantitative characterization of the conformation of six-membered chelate rings (Herak & Simon, 1982), we calculated the puckering parameters (Cremer & Pople, 1975; Boeyens, 1978) of the three chelate rings. The results are quoted in a deposited table along with analogous

parameters published for two other unsubstituted four-coordinated (salicylaldiminato)copper(II) complexes (Baker, Hall & Waters, 1966, 1970). The salicylaldiminato chelate rings are slightly puckered with total puckering amplitudes of 0·057 (5) and 0·095 (5) Å.

Bond lengths and angles involving both O donor atoms are nearly the same contrary to the situation at N donor sites. Both Cu–N–C angles at N(1), adjacent to the pyridine ring, are close to the ideal sp^2 hybridization angle of 120° while the angles at N(1*A*) are 115·3 (4) and 125·8 (5)°. The Cu–N bond lengths are also different, 1·931 (5) and 1·972 (5) Å, the N donor farther from the pyridine ring being involved in the shorter bond length.

There are three hydrogen bonds ranging from 2·76 (2) to 2·83 (2) Å in length between statistically disposed crystal water O atoms in cavities along the twofold screw axes, and another three hydrogen bonds with lengths 2·86 (1) to 2·89 (1) Å, and one hydrogen contact of 3·04 (1) Å between the water and salicylidene O atoms (Table 2, Fig. 2). Thus, water O atoms may occupy, in any cavity, either only the sites designated in Fig. 2 by full circles, or only those designated by open circles. The most suitable content is probably 1·5 water molecules which, upon entering the complex, stabilize the three-dimensional network. The cavities in which the water molecules are trapped in a disordered fashion communicate in some way with the outside of the crystal, their exchange being possible, as was shown by chemical analysis.

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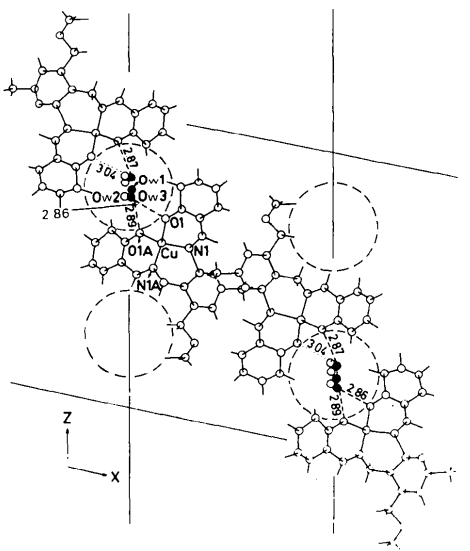

Fig. 2. Projection of the structure showing O···O hydrogen bonds (Å) viewed along **b** (the dashed circles, drawn in cavities, illustrating magnitude of their cross-sections, have a radius of 3 Å with centres at $0,0,\frac{1}{4}$ and $0,0,\frac{3}{4}$). The water O atoms are distributed in a disordered fashion between the sites indicated by full and open circles.

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