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Copper(II) Compounds with the Potentially Quinquedentate Ligand N,N′-Bissalicylidene-1,5-diimino-3-azapentane, Including an X-ray Structure Analysis of $[Cu_2(C_{18}H_{19}N_3O_2)_2]\cdot 2C_3H_6O$

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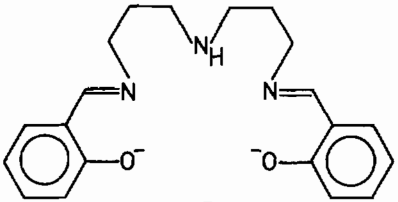
Abstract

The reaction of copper(II) acetate with the Schiff base ligand of the title gives mixed green polymeric materials. 'Recrystallisation' of these from various solvents gives crystalline solvates of a green dimeric copper(II) compound, the structure of which has been determined by a three-dimensional X-ray analysis of one crystalline form of the acetone solvate. Crystals of the title compound are monoclinic: a = 12.86(1), b = 16.74(2), c = 9.86(1) Å, β = 105.1(1)°, space group $P2_1/c$. Using 3555 independent reflections, obtained on a 2-circle diffractometer, the structure was solved by conventional Patterson and Fourier methods, and refined by block-diagonal least squares to R = 0.043. The two multidentate ligands bridge two five-coordinate copper atoms in a centrosymmetric molecule. The salicylaldiminato moieties from the different ligands are bidentate to each copper [Cu–O(1) = 1.936(3); Cu–O(2) = 1.975(3); Cu–N(1) = 1.962(3); and Cu–N(3) = 1.984(3) Å] and the fifth ligand for each copper is the secondary amine nitrogen at a longer distance of 2.405(3) Å.

Introduction

The ligand I is unable, without gross strain, to act in a monomeric species as a quinquedentate ligand to metal atoms which have metal → donor-atom distances near 2.0 Å.

For larger metal acceptor atoms, as in uranyl compounds, it was clear that planar quinquedentate function was possible, and this has been proven [1] by an X-ray structural analysis of one of our compounds [2].



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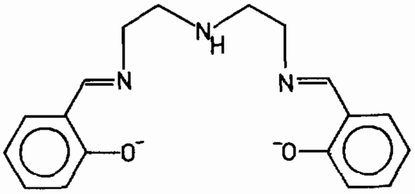

II

However, for the first row Group VIII metals, simple monomeric quinquedentate species of the type [3] formed by the more flexible ligand **II** were seen to be most unlikely. Hence, we were interested in the nature of the compounds already described [4, 5] for ligand **I**. They seemed to offer further possible examples of the addition of water or alcohols to azomethine groups [6]. Such reactions, with change in geometry at one or both nitrogens of ligand **I**, would give the modified ligand sufficient flexibility for it to act as a simple quinquedentate.

For this study we concentrated on an intensive study of the copper(II) system: this metal shows the greatest variability in its stereochemistry, and the greatest tendency to form five co-ordinate species. Also Augustin *et al.* [4] had apparently described two different copper(II) compounds of **I**: a *green* species precipitated from ethanol, and *blue* crystals of 'the same compound', which were said to result from 'recrystallisation' from chloroform.

Our study has concentrated on the nature of the initial green products from ethanol, and the results of 'recrystallising' these from a range of

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solvents A preliminary report of this work has already appeared [7]

Experimental

Preparation of Compounds

Green 'Cu($C_{18}H_{19}N_3O_2$)'

As previously reported [4], solid bissalicylaldehydatocopper(II) was suspended in ethanol (95% or absolute), the amine (approx equiv amount) was added, the mixture was refluxed (~3 h), and then usually was set aside overnight The green crude product was isolated, washed with ethanol and dried in the air If approx equivalent amounts of copper compound and amine were used, yields varied between 60 and 80%, if, however, an excess of amine was used, yields decreased markedly, and were as low as 3% in several cases where the Cu amine ratio approached 1 1 4 Several of the products slowly deliquesced over several weeks, but the majority were stable for years Similar reactions in methanol or acetone also gave similar green products 'Recrystallisations' from a range of solvents (Table I and IA) generally gave green crystalline solids

Blue species, as described by Augustin *et al* [4], were sometimes obtained from wet chloroform For example, 1 g of the above green product, when refluxed in 100 ml lab reagent $CHCl_3$, gave a green solution After filtration, this hot solution was divided into two portions The first, on cooling, gave a mixture of green $[Cu_2(C_{18}H_{19}N_3O_2)_2]\cdot 2CHCl_3$, and blue crystals of another reaction product, the other, when diluted with an equal vol of $CHCl_3$, and set aside, gave only the blue crystals Other halocarbon solvents and dioxan also gave similar (IR spectra) blue species (Table I)

Physical Measurements

Instruments used were a Perkin-Elmer PE457 for the IR spectra, Unicam SP700 + SP735 for the electronic spectra, Phillips 11 46 cm Debye-Scherrer powder camera for the X-ray diffraction patterns (Cu Kα radiation)

Table I The Products of the Various 'Recrystallisations'

Solvent[a]	Product[b]	Crystalline form[c]
MeOH	Green $[Cu_2L_2]nMeOH$	
EtOH	Green $[Cu_2L_2]2EtOH$	X
n-BuOH	Green $[Cu_2L_2]nBuOH$	X
Benzene[a]	Green $[Cu_2L_2]\cdot 2C_6H_6$	X
Toluene	Green $[Cu_2L_2]nC_7H_8$	
Acetone[a]	Green $[Cu_2L_2]\cdot 2C_3H_6O$[d]	α β
2-Butanone[a]	Green $[Cu_2L_2]\cdot 2C_4H_8O$[d]	α β
3-Methylpentan-2-one	Green $[Cu_2L_2]nC_6H_{12}O$	X
Dioxan	Green $[Cu_2L_2]nC_4H_8O_2$	
	Blue $[Cu_2(OH)_2(C_{11}H_{16}N_3O)_2]nC_4H_8O_2$	D
$CHCl_3$	Green $[Cu_2L_2]\cdot 2CHCl_3$	C
	Blue $[Cu_2(OH)_2(C_{11}H_{16}N_3O)_2]\cdot 2CHCl_3$	D
CCl_4	Green $[Cu_2L_2]\cdot 2CCl_4$	C
1,1-$C_2H_4Cl_2$[a]	Green $[Cu_2L_2]\cdot nC_2H_4Cl_2$	
1,2-$C_2H_4Cl_2$	Green $[Cu_2L_2]\cdot C_2H_4Cl_2$	E
	Blue $[Cu_2(OH)_2(C_{11}H_{16}N_3O)_2]nC_2H_4Cl_2$	
C_2HCl_3[a]	Green $[Cu_2L_2]C_2HCl_3$	E
C_2Cl_4	Green $[Cu_2L_2]nC_2Cl_4$	E
$C_2H_2Br_2$	Green $[Cu_2L_2]nC_2H_2Br_2$	
	Blue $[Cu_2(OH)_2(C_{11}H_{16}N_3O)_2]nC_2H_2Br_2$	

[a] This designates the solvents that give good yields of the green compounds [b] Where the number of solvent molecules is denoted by an *n*, elemental analyses were not obtained These species were characterised only by their colours and IR spectra The solvent molecules are generally held firmly in the crystals, neither the acetone nor the benzene solvates lost weight at 100 °C *in vacuo* By contrast, the blue crystals readily lost solvent, turning opaque often within hours of isolation Where blue crystals also were obtained, these were formed most readily from more dilute solutions and in wet solvents [c] This column refers to the X-ray powder diffraction patterns X simply denotes that a well-defined crystalline form was characterised in this way [d] The α and β forms of the ketone solvates were very closely related, *i e* the two α forms are isomorphous, as are the β forms, C, D and E denote isomorphous sets Products from the ketone recrystallisations were often mixtures of the α and β forms

TABLE 1A The Analytical Data

Compound	Analyses					
	Found			Calc		
	C	H	N	C	H	N
$[Cu_2L_2]\cdot 2EtOH$	52.0	5.5	10.2	51.3	6.0	10.0
$[Cu_2L_2]\cdot$2Acetone	58.8	6.0	9.5	58.5	5.8	9.7
$[Cu_2L_2]\cdot$2Acetone	60.0	6.1	9.6			
*$[Cu_2L_2]\cdot$2Butane-2-one	54.2	6.3	9.3	54.4	6.1	9.4
$[Cu_2L_2]\cdot$2Benzene	64.0	5.8	9.4	63.9	5.6	9.3
$[Cu_2L_2]\cdot 2CHCl_3$	46.0	4.3	8.6	46.4	4.1	8.5
$[Cu_2L_2]\cdot 2CCl_4$	43.8	3.7	8.1	43.3	3.6	8.0
$[Cu_2L_2]\cdot C_2H_4Cl_2(1,2)$	53.7	4.8	9.9	54.0	5.0	9.9
$[Cu_2L_2]\cdot C_2HCl_3$	51.6	4.7	9.5	52.0	4.5	9.6

The X-ray Analysis

Green diamond shaped plates from acetone were used. Crystals were selected from a sample shown by its powder pattern to be the α-form. Sampling was by microscopic inspection of the sample. The data crystal had dimensions 0.4 × 0.3 × 0.15 mm.

Crystal Data

$C_{36}H_{36}N_6O_4Cu_2\cdot 2C_3H_6O$, M = 862.0, monoclinic, a = 12.86(1), b = 16.74(2), c = 9.86(1) Å, β = 105.1(1), U = 2049 Å^3, D_m = 1.39 g cm^{-3}, Z = 2, D_c = 1.397 g cm^{-3}, $F(000)$ = 900. Space group $P2_1/c$ (No. 14) from symmetry and systematic absences. Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 10.91 cm^{-1}.

X-ray data with $6.5 < 2\theta < 50°$ were collected on a Stoe Stadi-2 automatic diffractometer, using graphite monochromated Mo Kα radiation. Angular step-scan ranges were systematically varied to allow for variations in peak-width of the different reflections, and a counting time of 1.0 s was used for each 0.01° increment of scan. Background counts were accumulated for 30 s at each extremity of the scan.

Reflections with intensity $I < 3\sigma(I)$ were ignored, as were those with background difference $\Delta > 3\sigma$. Corrections were applied for Lorentz and polarisation factors, but not for absorption. The final data set consisted of 3555 planes.

The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares, using finally anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms, being observed in a difference Fourier synthesis, were included but not refined. The calculated positions were set at C–H and N–H = 0.98 Å, and no account was taken of the methyl hydrogens of the acetone. Fixed isotropic temperature factors were assigned to the hydrogen atoms at values 2.0 greater than the latest-refined isotropic values for the atoms to which they are attached.

Anomalous dispersion corrections (both Δf′ and Δf″) were applied for all atoms. The final R was 0.043. Final atomic parameters are listed in Table II.

Scattering factors and correction parameters were taken from International Tables [8]. Programmes used are part of the Sheffield X-Ray system. Calculations were performed on the Sheffield University ICL 1907 computer. Observed and calculated structure factors are listed in a Table available from the Editor.

The observed molecular geometry and the atom numbering are in Fig. 1. Hydrogen atoms attached to carbon atoms are given the same numbers as those carbons.

Results and Discussion

The Structural Analysis

This revealed a dimeric molecular species (Fig. 1), in which two molecules of the dianionic ligand I bridge two copper atoms. The molecule is centrosymmetric, and is accompanied in the crystal by two molecules of acetone per dimer.

The coordination geometry about the copper (Fig. 1 and Tables III and IV) is one of those common distorted copper(II) species that can be described in various ways. We previously chose [7] a trigonal bipyramidal description. Equally one can see each half of the molecule as an essentially tetrahedral $[Cu(N_2O_2)]$ bissalicylaldiminatocopper(II) species with an extra, longer bond to a fifth donor atom [N(2) at 2.405(3) Å].

For this latter description, we note that plane 1 of Table IV puts the salicylaldiminate N and O donors equally 0.33–0.34 Å above or below the plane (*cf.* ±0.57 Å for a regular tetrahedron with these bond lengths), and that the metal is 0.27 Å from the centre of this $[N_2O_2]$ tetrahedron towards atom N(2).

TABLE II Atomic Positions and Thermal Vibrational Parameters with e s d s in Parentheses

Atom	x/a	y/b	z/c	B
(a) Atomic position (×10^4) of the non-hydrogen atoms				
Cu	-989 2(0 3)	6152 9(0 2)	2848 6(0 4)	
O(1)	-2343(2)	5839(2)	1574(3)	
O(2)	370(2)	6734(1)	2977(3)	
O(3)	7056(6)	5516(3)	5434(7)	
N(1)	-1650(2)	7116(2)	3396(3)	
N(2)	-573(2)	6042(2)	5365(3)	
N(3)	-352(2)	5141(2)	2393(3)	
C(1)	-3160(3)	6311(2)	1037(4)	
C(2)	-3978(3)	6032(3)	-130(4)	
C(3)	-4858(3)	6500(3)	-727(5)	
C(4)	-5000(4)	7250(3)	-206(5)	
C(5)	-4220(3)	7527(3)	918(5)	
C(6)	-3303(3)	7074(2)	1560(4)	
C(7)	-2569(3)	7406(2)	2795(4)	
C(8)	-1017(3)	7449(2)	4741(4)	
C(9)	-963(3)	6809(2)	5839(4)	
C(10)	-597(3)	4099(2)	4043(3)	
C(11)	-888(3)	4382(2)	2507(3)	
C(12)	472(3)	5116(2)	1885(3)	
C(13)	1181(3)	5764(2)	1769(3)	
C(14)	2018(3)	5604(2)	1120(4)	
C(15)	2771(4)	6172(3)	1037(5)	
C(16)	2726(3)	6908(3)	1647(5)	
C(17)	1929(3)	7093(2)	2308(4)	
C(18)	1114(3)	6533(2)	2368(3)	
C(19)	5598(6)	5460(5)	3420(8)	
C(20)	6491(5)	5097(4)	4554(6)	
C(21)	6628(6)	4230(4)	4580(8)	
(b) Calculated hydrogen atom positions (×10^3) and B's				
H(2)	-389	550	-50	6 83
H(3)	-541	629	-154	7 77
H(4)	-563	757	-65	8 00
H(5)	-430	806	130	7 17
H(7)	-280	789	319	5 83
H(8a)	-137	793	499	5 65
H(8b)	-29	759	468	5 65
H(9a)	-47	697	673	5 66
H(9b)	-168	672	598	5 66
H(10a)	-110	375	427	5 32
H(10b)	8	383	432	5 32
H(11a)	-66	398	192	5 49
H(11b)	-167	445	219	5 49
H(12)	64	460	153	5 48
H(14)	205	508	69	6 76
H(15)	333	605	57	7 54
H(16)	327	732	161	7 20
H(17)	190	762	273	6 39

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
(c) Anisotropic thermal vibration parameters (×10^5)[a]						
Cu	533(0)	243(0)	904(1)	-16(1)	235(1)	75(1)
O(1)	662(3)	399(2)	1512(6)	-454(5)	-207(7)	214(4)
O(2)	623(3)	295(1)	1238(5)	-24(4)	651(6)	4(3)
O(3)	2492(13)	853(5)	3841(19)	-81(15)	-1085(26)	-1245(13)
N(1)	596(3)	273(2)	873(5)	25(4)	332(6)	102(3)

(continued on facing page)

TABLE II *(continued)*

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
N(2)	624(3)	241(2)	827(4)	−151(4)	193(6)	83(3)
N(3)	592(3)	259(2)	756(4)	−1(4)	176(6)	49(3)
C(1)	543(4)	405(2)	1064(6)	26(6)	386(8)	38(5)
C(2)	599(4)	557(3)	1268(8)	−237(8)	161(9)	−9(6)
C(3)	591(4)	691(4)	1268(8)	12(9)	61(10)	70(7)
C(4)	639(4)	658(4)	1509(9)	227(10)	93(11)	310(7)
C(5)	625(4)	493(3)	1411(8)	234(8)	296(10)	273(6)
C(6)	534(3)	366(2)	1015(6)	173(6)	471(8)	112(4)
C(7)	633(4)	304(2)	1087(6)	139(6)	565(8)	140(5)
C(8)	702(4)	244(2)	1017(6)	−167(5)	313(8)	85(4)
C(9)	774(4)	282(2)	946(6)	−245(5)	374(8)	150(5)
C(10)	558(3)	266(2)	916(6)	−39(5)	213(7)	−17(4)
C(11)	689(4)	245(2)	814(5)	−74(5)	109(8)	−32(4)
C(12)	658(4)	297(2)	758(5)	−45(5)	274(7)	129(4)
C(13)	567(3)	336(2)	830(5)	101(5)	319(7)	83(4)
C(14)	754(5)	491(3)	1109(7)	−59(7)	699(10)	95(6)
C(15)	713(5)	633(3)	1471(9)	28(9)	901(11)	−24(7)
C(16)	644(5)	531(3)	1612(9)	359(9)	560(11)	−119(6)
C(17)	601(4)	373(2)	1422(8)	206(7)	401(9)	−36(5)
C(18)	523(4)	332(2)	847(6)	221(5)	204(7)	121(4)
C(19)	1435(10)	882(6)	2464(17)	1239(17)	1116(23)	307(13)
C(20)	1087(7)	805(5)	1861(12)	238(13)	579(16)	−771(11)
C(21)	1229(9)	607(5)	2729(18)	65(15)	−269(20)	120(11)

[a]The expression for the temperature factor is: $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

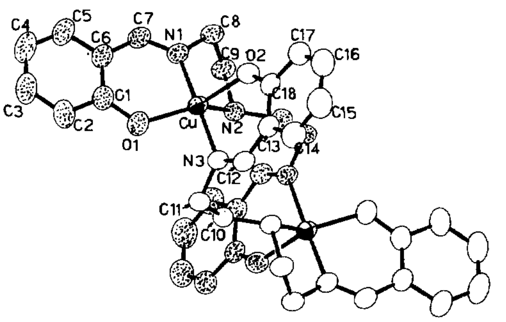


Fig. 1. The observed molecular structure and the atom labelling scheme. The shaded atoms are those of a complete ligand.

In these and all other aspects, the molecule is an unexceptionable copper(II) species. Bond lengths and angles (Table III) are within previously observed limits, as are the molecular planes (Table IV).

One view of the packing of the molecules in the crystal, together with the free acetone molecules, is shown in Fig. 2, which is a projection on to the *ab* plane. No significantly short inter- or intramolecular contacts were observed.

The Preparations and 'Recrystallisations'

(*A*) All green products from the various 'recrystallisations' (Table I) are almost certainly different

TABLE III. Bond Lengths and Angles with e.s.d.s in Parentheses.

Bond lengths (Å)		Bond angles (°)			
Copper molecule:					
Cu–O(1)	1.936(3)	O(1)–Cu–O(2)	143.7(1)	O(2)–Cu–N(1)	91.0(1)
Cu–O(2)	1.975(3)	O(1)–Cu–N(1)	91.2(1)	O(2)–Cu–N(3)	91.4(1)
Cu–N(1)	1.962(3)	O(1)–Cu–N(3)	88.6(1)	O(2)–Cu–N(2)	90.9(1)
Cu–N(3)	1.984(3)	O(1)–Cu–N(2)	124.8(1)	N(1)–Cu–N(3)	176.2(1)
Cu–N(2)	2.405(3)	N(2)–Cu–N(3)	100.0(1)	N(1)–Cu–N(2)	77.1(1)
O(1)–C(1)	1.311(5)	Cu–O(1)–C(1)	126.1(3)	O(1)–C(1)–C(6)	124.5(3)
C(1)–C(2)	1.420(6)	O(1)–C(1)–C(2)	118.4(4)	C(2)–C(1)–C(6)	117.1(4)
C(2)–C(3)	1.376(7)	C(1)–C(2)–C(3)	120.9(4)		

(continued overleaf)

TABLE III *(continued)*

Bond lengths (Å)		Bond angles (°)			
C(3)–C(4)	1 386(7)	C(2)–C(3)–C(4)	121 9(5)		
C(4)–C(5)	1 368(7)	C(3)–C(4)–C(5)	118 0(5)		
C(5)–C(6)	1 407(6)	C(4)–C(5)–C(6)	122 2(4)		
C(6)–C(1)	1 407(5)	C(1)–C(6)–C(5)	119 9(4)	C(1)–C(6)–C(7)	122 6(3)
C(6)–C(7)	1 443(5)	C(5)–C(6)–C(7)	117 4(3)		
C(7)–N(1)	1 273(5)	N(1)–C(7)–C(6)	124 8(3)	Cu–N(1)–C(7)	126 9(3)
N(1)–C(8)	1 473(5)	C(7)–N(1)–C(8)	120 3(3)	Cu–N(1)–C(8)	112 4(2)
C(8)–C(9)	1 512(5)	N(1)–C(8)–C(9)	106 7(3)		
C(9)–N(2)	1 497(5)	N(2)–C(9)–C(8)	110 0(3)		
N(2)–C(10′)[a]	1 485(4)	C(9)–N(2)–C(10′)	113 6(3)		
C(10)–C(11)	1 537(5)	N(2′)–C(10)–C(11)	113 4(3)		
C(11)–N(3)	1 463(4)	N(3)–C(11)–C(10)	110 2(3)	C(11)–N(3)–C(12)	117 0(3)
N(3)–C(12)	1 286(4)	Cu–N(3)–C(11)	119 6(2)	Cu–N(3)–C(12)	123 1(2)
C(12)–C(13)	1 441(5)	N(3)–C(12)–C(13)	127 6(3)	C(12)–C(13)–C(14)	117 7(3)
C(13)–C(14)	1 413(6)	C(12)–C(13)–C(18)	122 6(3)	C(14)–C(13)–C(18)	119 6(3)
C(14)–C(15)	1 375(7)	C(13)–C(14)–C(15)	121 8(4)		
C(15)–C(16)	1 380(7)	C(14)–C(15)–C(16)	118 8(4)		
C(16)–C(17)	1 385(6)	C(15)–C(16)–C(17)	121 6(4)		
C(17)–C(18)	1 419(5)	C(16)–C(17)–C(18)	121 2(4)	C(13)–C(18)–C(17)	116 9(3)
C(18)–C(13)	1 428(5)	C(13)–C(18)–O(2)	123 7(3)	O(2)–C(18)–C(17)	119 3(3)
Acetone					
O(3)–C(20)	1 20(1)	O(3)–C(20)–C(19)	120 2(6)		
C(19)–C(20)	1 51(1)	O(3)–C(20)–C(21)	121 3(6)		
C(20)–C(21)	1 45(1)	C(19)–C(20)–C(21)	118 5(6)		

[a] The primed atoms are at $-x, 1-y, 1-z$

TABLE IV Equations to some Least-Squares Planes These are given in the form $lX + mY + nZ = d$ (where X, Y and Z are coordinates in Å referred to a, b and c^*) The deviations (Å) of various atoms from these planes are given in square brackets Angles between some of the planes are given at the end of the Table

	l	m	n	d
Plane (1) O(1), O(2), N(1), N(3)				
	−0 1996	−0 3782	0 9039	−1 3184
[O(1) −0 34, O(2) −0 33, N(1) 0 33, N(2) 0 34, Cu 0 27]				
Plane (2) O(1), O(2), N(2)				
	−0 4588	0 8847	0 0824	10 3380
[Cu −0 08, N(1) 1 84, N(3) −2 05]				
Plane (3) C(1)–C(6)				
	0 6730	0 4055	−0 6186	0 7567
[C(1)–C(6) ≯ 0 006, O(1) −0 02, C(7) −0 08, N(1) 0 06, C(8) −0 19, Cu 0 40]				
Plane (4) C(13)–C(18)				
	−0 3652	0 3328	−0 8694	1 3624
[C(13) −0 00, C(14) −0 01, C(15) 0 01, C(6) −0 00, C(17) −0 01, C(18) 0 02, O(2) 0 03, C(12) −0 12, N(3) −0 09, C(11) −0 35, Cu 0 44]				
Plane (5) C(1)–C(7), N(1), O(1)				
	0 6717	0 4080	−0 6184	0 7875
[Cu 0 39]				

TABLE IV *(continued)*

	l	m	n	d
Plane (6) C(12)–C(18), N(3), O(2)				
	0 3741	−0 3084	0 8746	−1 0724
[Cu −0 48]				

Angles between planes (°)

(1)–(2)	99 7	(5)–(6)	114 5
(1)–(5)	147 9	(2)–(5)	89 9
(1)–(6)	33 6	(2)–(6)	111 9

solvates of the same dimeric species [Cu_2L_2] (where L is the ligand I)

The IR spectra are consistent, showing no unexpected features, and, apart from the bands expected for the different solvent molecules, showed only the variations in the 'fingerprint' region expected for different crystalline species The colours of all green products showed no detectable differences, nor did the electronic spectra, both for solutions and for solid state diffuse reflectance Further, there were some useful correlations in the X-ray powder patterns (Table I)

The X-ray powder diffraction patterns of the green $CHCl_3$ and CCl_4 solvates were almost identical,

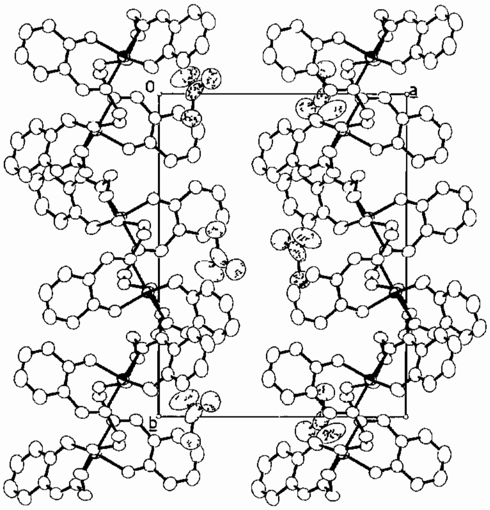


Fig 2 The packing of the copper(II) dimers and the acetone molecules in the crystal This view is down *c* The atoms of the acetone molecules are shaded

as were those of at least the 1,2-$C_2H_4Cl_2$ and C_2HCl_3 solvates Two crystalline forms from acetone were obtained (α and β), but their diffraction patterns appeared similar except for the line spacings it seems that in the β-form the atom positions are not very different from those in the α-form used for the three-dimensional analysis, but the cell is somewhat larger The two crystalline forms containing butan-2-one correlate closely with the two containing acetone

(*B*) Blue crystals are obtainable [4] by 'recrystallising' from $CHCl_3$, and other solvents (Table I), but, despite the comments in ref [4], they do not represent copper(II) compounds of the ligand **I**

The IR spectra of these blue species clearly showed the presence of -NH_2 groups, they formed only in wet halocarbon solvents or in dioxan (Table I and Experimental), and the analytical data on the compound from $CHCl_3$ confirmed a formulation $[Cu_2(OH)_2(C_{11}H_{16}N_3O)_2]\cdot 2CHCl_3$ (*Anal* Found C, 36 0, H, 4 3, N, 10 4 Calc for $C_{12}H_{18}N_3O_2Cl_3Cu$ C, 35 5, H, 4 5, N, 10 3%) That is, they are hydrolytic products, in which the ligand **I** has lost one of its salicylidene groups They are probably hydroxy-bridged species—a common feature of copper chemistry—as implied in the above formulation, but of no further interest here

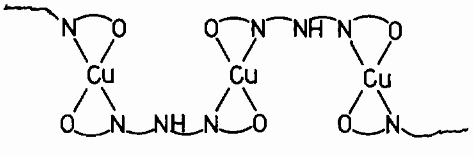
(*C*) The preparative method (from [Cu sal$_2$] and amine in ethanol) generally gave robust green powders, the X-ray powder patterns of which generally showed indifferent crystallinity (only low angle diffraction), and the number of equally intense low angle lines suggested mixtures

By contrast, the products from the low yield reactions gave diffraction patterns that were dominated by the independently characterised crystalline species $[Cu_2(L)_2]2EtOH$

However, the IR spectra, and the colours and electronic spectra of these crude reaction products were not significantly different from those of the various cystalline solvates of $[Cu_2L_2]$

Their behaviour on 'recrystallising' suggested chemical reaction rather than simple physical dissolution fast initial solution of part only of the material, followed by some slow dissolution of the bulk of the material, and usually some residue even after several hours of refluxing All gave the same green $[Cu_2L_2]\cdot n$solvent species as the only recoverable crystalline product The same solubility effects were noted with the yellow preparations of the nickel(II) 'compound' of ligand **I**

We interpret these observations as indicating that the initial products, formed by the reaction of the amine with what is largely a suspension of [Cu sal$_2$], as being mixtures of oligomers/polymers of type **III**, that these oligomers react to form $[Cu_2L_2]$ in solution, and that the dimeric species



III

observed in the X-ray structural analysis is the primary, and probably only molecular species obtainable in this system

In adopting this dimeric (or polymeric) structure, the system obviates the various strains that would be inherent in a monomeric copper compound of the ligand **I**

References

1 M N Akhtar, E D McKenzie, R E Paine and A J Smith, *Inorg Nucl Chem Lett*, *5*, 673 (1969), M N Akhtar and A J Smith, *Acta Crystallogr Sect B*, *29*, 275 (1973)
2 E D McKenzie, R E Paine and S J Selvey, *Inorg Chim Acta*, *10*, 41 (1974)
3 L Sacconi and I Bertini, *J Am Chem Soc*, *88*, 5182 (1966), P L Orioli, M Di Vaira and L Sacconi, *Inorg Chem*, *10*, 553 (1971), R H Niswander and L T Taylor, *Inorg Chem*, *15*, 2361 (1976)
4 M Augustin, H-J Kerrinnes and W Langenbeck, *J Prakt Chem*, *26*, 130 (1964)
5 L W Lane and L T Taylor, *J Coord Chem*, *2*, 295 (1973)
6 C M Harris and E D McKenzie, *Nature (London)*, *196*, 670 (1962), C M Harris and E D McKenzie, *J Chem Soc A*, 746 (1969), M Cressy, E D McKenzie and S Yates, *J Chem Soc A*, 2677 (1971), Z P Haque, M McPartlin and P A Tasker, *Inorg Chem*, *18*, 2920 (1979)
7 E D McKenzie and S J Selvey, *Inorg Chim Acta*, *18*, L1 (1976)
8 'International Tables for X-ray Crystallography, Vol IV', Kynoch Press, Birmingham, 1974