Structure and Spectroscopic Properties of Bis(*N*-cyclohexyl-3-methoxysalicylideneiminato)copper(II)

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The structure of the title complex (2) has been determined from three-dimensional *X*-ray counter data. The material crystallizes in the monoclinic space group $P2_1/c$ with two monomeric units in a cell of dimensions a = 11.793(5), b = 18.043(14), c = 6.484(3) Å, and β = 67.12(2)°. Least-squares refinement of 1 190 independent data has led to final values of R and R' of 0.047 and 0.046, respectively. The monomeric units are crystallographically constrained to be square planar. The green solid yields reddish solutions in various solvents. Electronic and e.s.r. spectroscopic data support the presence of pseudo-tetrahedrally distorted species in solutions. Spectroscopic data for planar (2) are compared with data for pseudo-tetrahedral bis(*N*-cyclohexylsalicylideneiminato)copper(II), (1). Structure-spectra correlations applicable to the solid state cannot necessarily be straightforwardly applied to solution species.

SCHIFF-BASE complexes of transition metals have been extensively investigated for many years.[1] Their ready syntheses and myriad properties have contributed greatly to their popularity and to the development of inorganic chemistry. The spectral and magnetic properties of copper(II) Schiff-base species have been, and continue to be, of considerable interest.[1-6] Copper(II) Schiff-base complexes have been suggested as models for enzymes

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[1] A. E. Martell and M. Calvin, 'Chemistry of the Metal Chelate Compounds,' Prentice-Hall, Englewood Cliffs, New Jersey, 1952.

[2] W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, 1969, **5**, 47.

[3] R. H. Holm, G. E. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

[4] L. Sacconi, *Co-ordination Chem. Rev.*, 1966, **1**, 126.

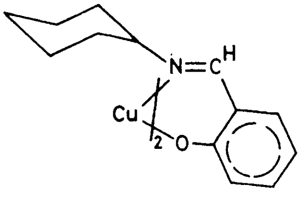
[5] H. S. Maslen and T. N. Waters, *Co-ordination Chem. Rev.*, 1975, **17**, 137.

[6] R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, 1971, **14**, 241.

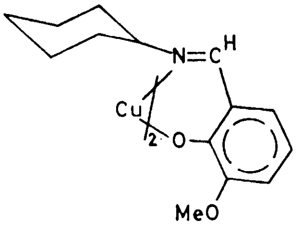
such as galactose oxidase [7,8] and the 'blue' copper proteins.[9,10]

A rather notable feature of the chemistry of copper(II) Schiff base,[5,6] diantipyrylmethane,[11] and other complexes [12,13] is the existence of distortion isomerism,[11-13] *i.e.* isomerism involving two or more equilibrium arrangements of ligands differing in the distortions of the co-ordination polyhedron of the metal. The tetrachlorocuprate(II) anion, for which several structures have been found,[14,15] is probably the best documented example of a species exhibiting distortion isomerism. The Jahn–Teller or pseudo-Jahn–Teller origin of distortion isomerism has been reviewed.[13] Notably, external factors stabilizing a particular configuration can be any weak low-symmetry perturbation, *e.g.* hydrogen bonding, van der Waals interactions, *etc.*, or co-operative interactions. Since energy levels and total energies of various configurations of a given species differ little, the properties, *e.g.* electronic spectra, of distortion isomers are not radically different.[11-13]

Closely related to the distortion isomerism of copper(II) complexes is the variation of spectroscopic properties on going from the solid state to solution. Here, only solvational forces, and not necessarily solvent co-ordination to the metal, are considered to be responsible for minor structural variations in the solid and liquid phases. Crystal-structure data for pseudo-tetrahedral copper(II) Schiff-base complexes, summarized by Wei,[16] show that bis(*N*-isopropylsalicylideneiminato)copper(II), [Cu(*N*-Pr^i-sal)$_2$], is more tetrahedral than bis(*N*-t-butylsalicylideneiminato)copper(II), [Cu(*N*-Bu^t-sal)$_2$]. Electronic spectral band maxima and oscillator strengths, as well as isotropic nuclear hyperfine coupling constants from e.s.r. spectra, demonstrate [17] that in solution [Cu(*N*-Bu^t-sal)$_2$] is more tetrahedrally distorted than [Cu(*N*-Pr^i-sal)$_2$]. In the course of a study of the electronic structure of pseudo-tetrahedral copper(II) Schiff-base complexes [17] it was noticed that bis(*N*-cyclohexylsalicylideneiminato)copper(II), [Cu(*N*-C$_6$H$_{11}$-sal)$_2$] (1), is reddish brown and gives similarly coloured solutions in a wide variety of solvents. In contrast, bis(*N*-cyclohexyl-3-methoxysalicylideneiminato)copper(II), [Cu(*N*-C$_6$H$_{11}$-3MeO-sal)$_2$] (2), is a green solid which yields red-brown solutions very similar to those obtained with (1). The electronic and e.s.r. spectra [17] of (1) and (2) show that both species are pseudo-tetrahedral in solution. In view of the green colour of solid (2), suggestive of four- or four-plus-two co-ordination, and the solution spectral behaviour supporting a pseudo-tetrahedral geometry in solution, it was decided to determine the structure of solid (2) and further characterize its solution behaviour.



(1)



(2)

EXPERIMENTAL

3-Methoxysalicylaldehyde (*o*-vanillin) and cyclohexylamine were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, and used without further purification. Copper was determined by titration with ethylenediaminetetra-acetate. Complexes (1) and (2), described previously,[17] were prepared by adding a stoicheiometric amount of copper(II) acetate monohydrate to a hot ethanol solution containing equimolar amounts of the appropriate salicylaldehyde and cyclohexylamine. The powdered product was isolated by filtration after partially evaporating the solvent. Crystals of (2) were obtained by recrystallizing the powdered material from acetone, chloroform, nitromethane, or dichloromethane.

Electronic spectra were obtained with a Cary model 17 recording spectrometer using matched 1.0-cm quartz cells. E.s.r. spectra were recorded with a Varian E-3 spectrometer at room temperature or at 77 K. Quartz sample tubes were employed for powders and solutions. Spectra were calibrated using diphenylpicrylhydrazyl (dpph, *g* 2.003 6) as a field marker. A sample of polycrystalline dpph taped to a tube containing oxobis(pentane-2,4-dionato)vanadium(IV) in benzene served as a double standard for checking field strength, frequency, and sweep-rate settings.[18]

On the basis of Weissenberg and precession photographs, the green hexagonal prismatic crystals of the title complex were assigned to the monoclinic system; the observed systematic absences of $h0l$ for l odd and $0k0$ for k odd are consistent only with the space group $P2_1/c$ (no. 14). The cell constants were obtained by least-squares methods from the 2θ, χ, and φ values of 12 accurately centred reflections using Mo-K_{α_1} radiation (λ 0.709 3 Å).

Crystal Data.—$C_{28}H_{36}CuN_2O_4$, $M = 528.15$, Monoclinic, $a = 11.793(5)$, $b = 18.043(14)$, $c = 6.484(3)$ Å, $\beta = 67.12(2)°$, $U = 1\ 270.9$ Å^3, $D_m = 1.39(4)$ g cm^{-3} (flotation in benzene–$CHBr_3$), $Z = 2$, $D_c = 1.380$ g cm^{-3}, μ(Mo-K_α) = 12.3 cm^{-1}, space group $P2_1/c$.

Data Collection.—Intensity data were collected from a prismatic crystal bounded by faces of the forms [010], [100], and [011]; the separations between these opposite faces

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[7] R. S. Giordano and R. D. Bereman, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 203; *J. Amer. Chem. Soc.*, 1974, **96**, 1017.

[8] R. S. Giordano and R. D. Bereman, *J. Amer. Chem. Soc.*, 1974, **96**, 1023.

[9] R. C. Rosenberg, C. A. Root, P. K. Bernstein, and H. B. Gray, *J. Amer. Chem. Soc.*, 1975, **97**, 2092.

[10] J. A. Fee, *Structure and Bonding*, 1975, **23**, 1.

[11] G. L. Seebach, D. K. Johnson, H. J. Stoklosa, and J. R. Wasson, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 295; D. K. Johnson, H. J. Stoklosa, J. R. Wasson, and G. L. Seebach, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1397.

[12] J. Gazo, *Pure Appl. Chem.*, 1974, **38**, 279.

[13] J. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Co-ordination Chem. Rev.*, 1976, **19**, 253.

[14] D. W. Smith, *Co-ordination Chem. Rev.*, 1976, **21**, 93.

[15] J. R. Wasson, J. W. Hall, H. W. Richardson, and W. E. Hatfield, *Inorg. Chem.*, 1977, **16**, 458.

[16] C. H. Wei, *Inorg. Chem.*, 1972, **11**, 2315.

[17] J. R. Wasson, H. W. Richardson, and W. E. Hatfield, *Z. Naturforsch.*, 1977, **B32**, 551.

[18] I. Bernal and P. H. Rieger, *Inorg. Chem.*, 1963, **2**, 256; D. H. Chen and G. R. Luckhurst, *Trans. Faraday Soc.*, 1969, **65**, 656.

were 0.31, 0.041, and 0.39 mm, respectively. The crystal was mounted roughly parallel to [010], and at this orientation intensity data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator and using Mo-K_α radiation, as previously described.[19] A unique data set of 3 537 reflections with $2 \leqslant 2\theta \leqslant 50°$ was collected. There was no noticeable decline in the intensities of three standard reflections (measured after every 100 reflections) with exposure time.

Data processing was carried out as described by Corfield *et al.*[20] After correction for background, the intensities were assigned standard deviations according to formula [20] (1), and the value of p was selected as 0.04. The values of I

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{\frac{1}{2}} \qquad (1)$$

and $\sigma(I)$ were corrected for Lorentz-polarization effects; since the sample chosen was small and the absorption coefficient for this complex was only 8.95 cm^{-1}, no correction for absorption was made. Of the 3 537 data collected, only 1 190 having intensities greater than three times their estimated standard deviations were used in the subsequent structure analysis and refinement.[21]

Solution and Refinement of the Structure.—All the least-squares refinements in this analysis were carried out on F, minimizing $\Sigma w(|F_o| - |F_c|)^2$; the weights, w, were defined as $4F_o^2/\sigma^2(F_o)^2$. In all calculations of F_c the atomic scattering factors for non-hydrogen atoms were from International Tables,[22] and those for hydrogen were from Stewart *et al.*[23] The effect of the anomalous dispersion of Cu was included in the calculation of F_c; the values of $\Delta f'$ and $\Delta f''$ were from Cromer and Liberman.[24]

With two formula units in $P2_1/c$, the copper atom is constrained to lie on a crystallographic inversion centre. The remaining non-hydrogen atoms were located in several least-squares iterations and difference-Fourier summations. Isotropic least-squares refinement of these atoms gave values of the conventional agreement factors $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$ of 0.101 and 0.112, respectively. Anisotropic refinement reduced these values to 0.070 and 0.081, respectively. The hydrogen atoms were located in a subsequent difference-Fourier map. The final least-squares cycles involved anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydrogen atoms, with 1 190 observations and 232 variables. The final values of R and R' were 0.047 and 0.046, respectively.

In the final cycle of least squares no atomic parameter exhibited a shift greater than 0.4σ, which is taken as evidence of convergence. Examination of the values of $|F_o|$ and $|F_c|$ suggested that no correction for secondary extinction was necessary, and none was applied. A final difference-Fourier map was featureless, with no peak higher than 0.064 e Å^{-3}. The value of R' showed no unusual dependence on sinθ or on $|F_c|$, which suggests that the weighting scheme is appropriate. The atomic positional parameters, together with their standard deviations as estimated from the inverse matrix, are listed in Table 1. Observed and calculated structure amplitudes and thermal parameters are listed in Supplementary Publication No. 22255 (11 pp.).*

TABLE 1

Positional parameters ($\times 10^4$, $\times 10^3$ for H) for complex (2)

Atom	*x*	*y*	*z*
Cu	0	0	0
O(1)	332(3)	635(2)	2 446(7)
O(2)	201(4)	1 439(2)	5 669(7)
N	1 773(3)	43(3)	298(7)
C(1)	2 434(5)	965(3)	3 310(10)
C(2)	1 318(5)	997(3)	3 641(10)
C(3)	1 298(5)	1 452(3)	5 444(10)
C(4)	2 292(6)	1 851(3)	6 708(12)
C(5)	3 383(6)	1 824(3)	6 325(12)
C(6)	3 449(5)	1 387(3)	4 682(11)
C(7)	2 563(5)	485(3)	1 665(10)
C(8)	2 188(5)	−446(3)	−1 129(10)
C(9)	2 474(8)	−1 208(4)	−103(15)
C(10)	2 773(10)	−1 734(5)	−1 676(21)
C(11)	3 797(7)	−1 448(5)	−2 323(15)
C(12)	3 506(6)	−677(4)	−3 274(12)
C(13)	3 276(6)	−168(3)	−1 620(12)
C(14)	96(9)	1 877(5)	7 430(17)
H(1)	155(4)	−45(3)	−251(8)
H(2)	329(5)	−117(3)	147(10)
H(3)	184(6)	−136(3)	20(11)
H(4)	213(7)	−183(4)	−287(15)
H(5)	307(6)	−214(4)	−87(12)
H(6)	395(5)	−176(3)	−328(10)
H(7)	456(5)	−142(3)	−106(9)
H(8)	281(5)	−67(3)	−459(9)
H(9)	414(5)	−53(3)	−372(9)
H(10)	319(5)	33(4)	−214(11)
H(11)	408(5)	−14(3)	−13(10)
H(12)	−69(6)	179(3)	726(11)
H(13)	17(6)	239(4)	714(12)
H(14)	73(7)	173(4)	874(12)
C(4H)	231(5)	213(3)	802(9)
C(5H)	409(4)	211(3)	731(8)
C(6H)	413(5)	134(3)	445(8)
C(7H)	337(5)	51(3)	160(8)

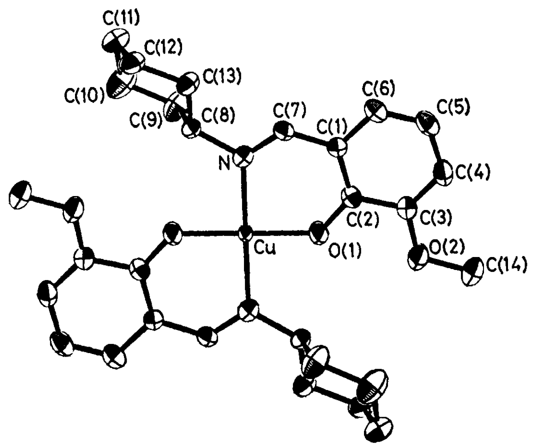

FIGURE 1 View of the square-planar monomeric unit in (2)

RESULTS AND DISCUSSION

Description of the Structure.—The structure of complex (2) consists of monomeric units, with the exactly square-planar configuration around Cu being dictated by the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[19] E. S. Estes, W. E. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 106.

[20] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[21] For a description of the programs used, see R. P. Scaringe, P. Singh, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 1127.

[22] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. 4, 1974.

[23] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[24] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

crystallographic inversion centre; a view of the unit is shown in Figure 1. The bond lengths and angles are similar to those observed in bis(*N*-phenylsalicylideneiminato)copper(II)[25] and bis(*N*-methylsalicylideneiminato)copper(II);[26] the bond lengths and angles are listed in Tables 2 and 3, respectively. The Cu–N bond [2.025(4) Å] is slightly larger than that [1.993(4) Å] found in the *N*-phenyl complex. Moreover, the hypothesis that the Cu–N bond distance is lengthened by steric interference between the nitrogen substituent and the opposite ligand[27] is supported by the significantly shorter Cu–N bond length observed in bis(salicylideneiminato)copper(II) (1.90 Å).[28]

TABLE 2

Interatomic distances (Å) in (2)

Cu–O(1)	1.869(4)	O(2)–C(14)	1.417(9)
Cu–N	2.025(4)	C(4)–C(4H)	0.98(5)
O(1)–C(2)	1.295(6)	C(5)–C(5H)	0.97(5)
C(2)–C(1)	1.415(7)	C(6)–C(6H)	0.87(5)
C(2)–C(3)	1.436(8)	C(7)–C(7H)	0.97(5)
C(3)–C(4)	1.349(8)	C(8)–H(1)	0.92(5)
C(4)–C(5)	1.403(9)	C(9)–H(2)	1.10(6)
C(5)–C(6)	1.352(8)	C(9)–H(3)	0.88(6)
C(6)–C(1)	1.406(8)	C(10)–H(4)	0.87(8)
C(1)–C(7)	1.427(8)	C(10)–H(5)	0.88(7)
C(7)–N	1.284(7)	C(11)–H(6)	0.91(6)
N–C(8)	1.493(7)	C(11)–H(7)	0.95(5)
C(8)–C(9)	1.507(9)	C(12)–H(8)	0.92(5)
C(9)–C(10)	1.531(11)	C(12)–H(9)	0.94(5)
C(10)–C(11)	1.514(11)	C(13)–H(10)	0.95(6)
C(11)–C(12)	1.506(10)	C(13)–H(11)	1.06(5)
C(12)–C(13)	1.514(9)	C(14)–H(12)	0.91(6)
C(13)–C(8)	1.522(7)	C(14)–H(13)	0.93(7)
C(3)–O(2)	1.366(7)	C(14)–H(14)	0.95(7)

TABLE 3

Bond angles (°) in (2)

O(1)–Cu–N	91.6(2)	C(6)–C(1)–C(7)	119.3(5)
O(1)–Cu–N′	88.4(2)	C(6)–C(1)–C(2)	119.7(6)
Cu–O(1)–C(2)	131.3(4)	C(1)–C(7)–N	129.3(5)
O(1)–C(2)–C(1)	124.1(5)	C(7)–N–Cu	122.3(4)
O(1)–C(2)–C(3)	118.7(5)	Cu–N–C(8)	119.6(3)
C(2)–C(3)–O(2)	113.9(5)	C(8)–N–C(7)	118.1(4)
C(4)–C(3)–O(2)	125.2(6)	N–C(8)–C(9)	109.7(5)
C(3)–O(2)–C(14)	117.7(5)	N–C(8)–C(13)	116.2(5)
C(1)–C(2)–C(3)	117.2(5)	C(9)–C(8)–C(13)	109.3(5)
C(2)–C(3)–C(4)	121.0(6)	C(8)–C(9)–C(10)	109.9(7)
C(3)–C(4)–C(5)	121.0(6)	C(9)–C(10)–C(11)	112.9(8)
C(4)–C(5)–C(6)	119.8(6)	C(10)–C(11)–C(12)	110.4(6)
C(5)–C(6)–C(1)	121.3(6)	C(11)–C(12)–C(13)	110.2(6)
C(2)–C(1)–C(7)	120.9(5)	C(12)–C(13)–C(8)	110.2(5)

The whole molecule is essentially planar. The deviations of each atom from the plane were calculated using both the molecule as a whole and the phenyl ring as the defining plane; the results are shown in Table 4. Only the nitrogen atom is significantly out of the plane (<0.13 Å), indicating that the molecule has a slightly stepped configuration.

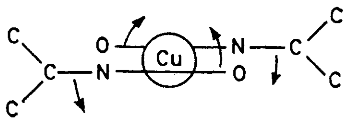
The square-planar configuration at copper cannot be caused by 'crystal-packing forces'; the packing diagram in Figure 2 illustrates that the cyclohexyl substituent (in the chair form) on nitrogen atom effectively blocks the approach of the monomeric units. It has been postulated on ligand-field grounds[5] that increased electron density on the chelate ring (especially at N) increases the tendency towards a tetrahedral configuration around Cu. The ability of the nitrogen substituent to donate electrons will be enhanced by its ability to stabilize a positive charge,[5] but a cyclohexyl group is not able to redistribute this positive charge through a hyperconjugative mechanism as well as a substituent with methyl groups on the α carbon.[29,30] This inability to stabilize a positive charge leads to low electron density on nitrogen and consequently to a square-planar configuration in this case.

TABLE 4

Displacements (Å) of atoms from the best mean plane defined by (*a*) the molecule and (*b*) a phenyl ring

	(*a*)	(*b*)
Cu	0.082 4	0.067 5
O(1)	0.039 0	0.029 6
O(2)	−0.030 7	−0.027 6
N	−0.101 3	−0.131 4
C(1)	0.020 1	−0.005 2
C(2)	0.026 9	0.012 8
C(3)	−0.002 6	−0.010 2
C(4)	0.011 7	−0.000 5
C(5)	0.032 2	0.008 8
C(6)	0.024 0	−0.005 7
C(7)	−0.050 5	−0.082 9
C(14)	−0.051 2	−0.041 0

Complex (2) is both substituent-*cis* and substituent-*trans* [terms from ref. 5, illustrated in (3)], and it has been suggested that for complexes of this type any deviation from square planar will be resisted by C–H ··· O attractive forces.[5] In this case, there are two possible hydrogen bonds, involving C(8)–H(1) ··· O(1′) and C(9)–H(3) ··· O(1′) with H ··· O distances of 2.26(5) and 2.79(6) Å, respectively; the C ··· O distances are 2.776(6) and 3.228(10) Å, respectively, and the C–H ··· O angles are 115(4) and 112(5)°, respectively. Sutor[31] has suggested that a C–H group directly attached to a more electronegative atom has the activated hydrogen atom necessary for a C–H ··· O hydrogen bond;[31] C(8) is attached directly to the nitrogen atom and could have an activated hydrogen atom. C–H ··· O interactions have been postulated in organic molecules such as caffeine, ethylene carbonate, and 1,3,7,9-tetramethyluric acid.[31] For these molecules, C ··· O and H ··· O contact distances and C–H ··· O bond angles were found in the ranges 3.00—



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[25] L. Wei, R. M. Stogsdill, and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1058.

[26] E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, 1961, **14**, 1222.

[27] A. J. McKinnon, T. N. Waters, and D. Hall, *J. Chem. Soc.*, 1964, 3290.

[28] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1966, 680.

[29] J. W. Baker, 'Hyperconjugation,' Oxford University Press, Fair Laven, New Jersey, 1952.

[30] M. J. S. Dewar, 'Hyperconjugation,' Ronald Press, New York, 1962.

[31] D. J. Sutor, *Nature*, 1962, **195**, 68 and refs. therein.

3.24, 2.26—2.76 Å, and 103—121°,[31] respectively. The C · · · O, H · · · O, and C–H · · · O values found in this complex are within the ranges cited for this type of interaction. Donohue,[32] however, disputes the existence of hydrogen bonds of this nature, proposing that the H · · · O contact distances would have to be less than 2.2 Å. In the present case, therefore, any interaction of this type would surely be weak, if it existed at all, and could not be responsible for the observed square-planar configuration around Cu.

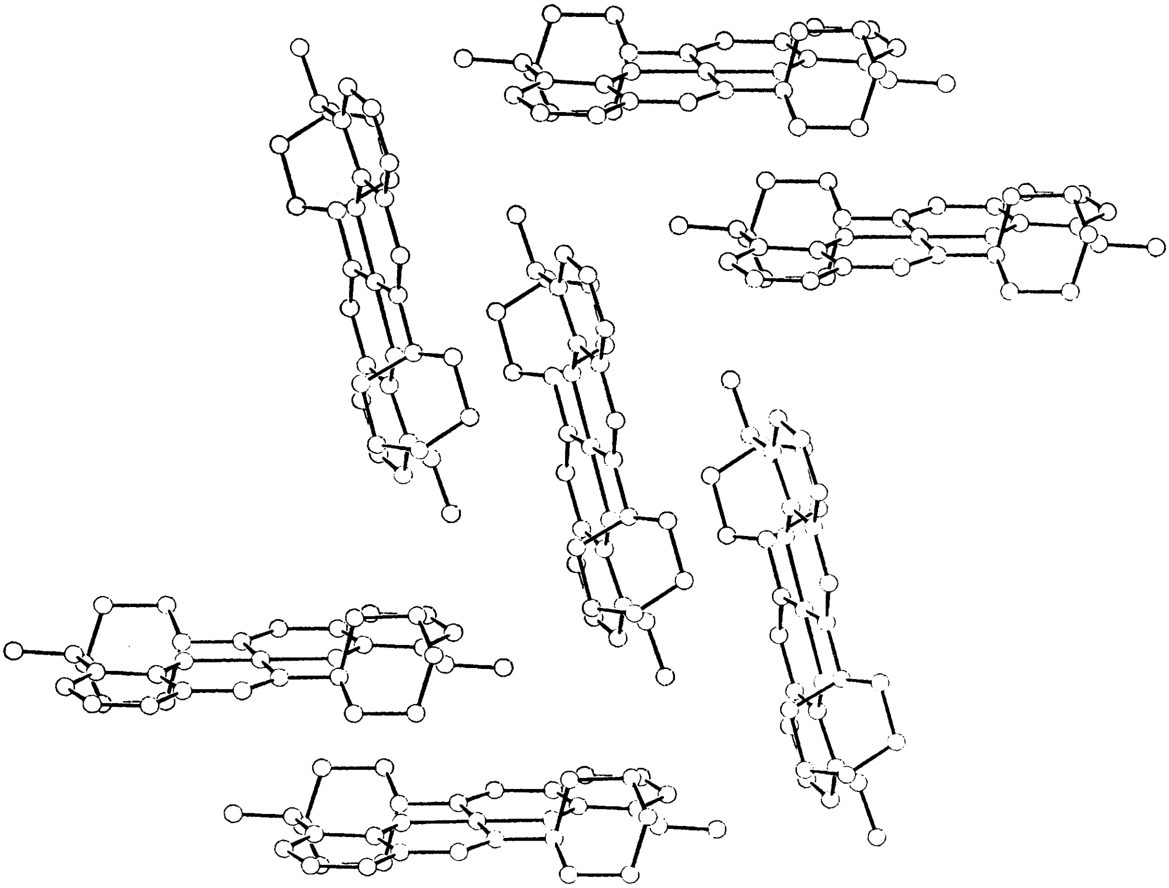

FIGURE 2 Packing diagram of (2) showing the cyclohexyl ring blocking the approach of the monomeric units

The differences in the carbon–carbon bond distances in the phenyl ring vary over a range of 1.349(8)—1.436(8) Å. The longest distances are between C(6) and C(1), C(1) and C(2), and C(2) and C(3). Such lengthening of bonds adjacent to the extra-annular substituents is commonly observed; salicylic acid,[33] salicylamide,[34] and bis(*N*-ethylsalicylideneiminato)copper(II) (both the monoclinic [35] and orthorhombic [36] forms) all exhibit this trend. In bis(*N*-n-propylsalicylideneiminato)copper(II) two of these bonds are also long, although C(2)–C(3) is reported to be short (1.36 Å).[37]

The short C(1)–C(2) (1.295 Å) and the short N–C(7) (1.284 Å) bonds observed in this and similar structures [25–28,38] are indicative of considerable double-bond character in both the O–C and the N–C bonds. The Cu–O(1)–C(2) angle in this complex is 131.3(4)°, illustrating that the oxygen atom is in an approximately sp^2 hybridized state with its p_z orbital as a part of the π system;[5] this value of the Cu–O–C angle is comparable

TABLE 5

Electronic spectral data

Complex	Solvent	$\tilde{\nu}/\mu m^{-1}$	$\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$
(1)	Nujol mull	1.65	
	Chloroform	1.62	157
	Chlorobenzene	1.54	100
	Nitromethane	1.52	122
(2)	Nujol mull	1.69	
	Chloroform	1.56	188
	Chlorobenzene	1.59	133
	Nitromethane	1.56	64

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[32] J. Donohue, 'Selected Topics in Hydrogen Bonding,' in 'Structural Chemistry and Molecular Biology,' eds. A. Rich and N. Davidson, W. H. Freeman, San Francisco, 1968.

[33] M. Sundaralinggam and L. H. Jensen, *Acta Cryst.*, 1965, **18**, 1053.

[34] Y. Sasada, T. Takano, and M. Kakudo, *Bull. Chem. Soc. Japan*, 1964, **37**, 940.

[35] C. Panattoni, G. Bombieri, and R. Graziani, *Acta Cryst.*, 1967, **23**, 537.

[36] G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc. (A)*, 1969, 2808.

[37] G. Bombieri, C. Panattoni, E. Forsellini, and R. Graziani, *Acta Cryst.*, 1969, **B25**, 1208.

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

to the results obtained in other square-planar structures of this type.[28,38,39]

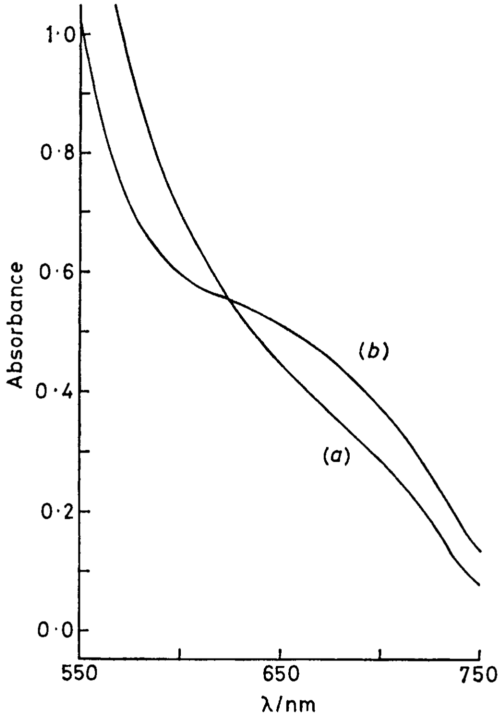

FIGURE 3 Electronic spectra of *ca.* 10^{-3} mol dm^{-3} solutions of (*a*) (1) and (*b*) (2) in chlorobenzene

Electronic Spectra.—Typical electronic spectra are shown in Figure 3 and pertinent data are summarized in Table 5. In the solid state the band maximum of planar (2) is at a shorter wavelength than that of pseudo-tetrahedral (1). This is in accord with expectations[40,41] for the structural differences between the complexes. In chloroform and chlorobenzene both complexes exhibit rather similar broad spectral maxima with molar absorption coefficients commensurate with the presence of pseudo-tetrahedral solution species.[17,40,41] In nitromethane, a better donor solvent than chloroform or chlorobenzene, the molar absorption coefficient and band maximum for (2) suggests the presence of a five-co-ordinate or pseudo-octahedral species with solvent molecules co-ordinated to the metal ion. In general, the shifts in the band maxima to lower energies demonstrated that the solution species are more tetrahedrally distorted than the complexes in the solid state.

E.S.R. Spectra.—The e.s.r. spectra of pure polycrystalline (1) and (2) are shown in Figure 4. The regions where g values were obtained are indicated. It is noted that the low-field part of the spectrum of (1) had to be recorded at a higher gain in order to clearly resolve the perpendicular part of the spectrum. The three g values for (2) are just barely resolved for the powdered material. The data are summarized in Table 6 and show that there is a noticeable solvent effect on the spectra. In general, as a complex becomes more tetrahedral, the g value and isotropic g value increase and the A_0 and $A_{\parallel}$ values decrease[17] relative to corresponding values for the planar distortion isomer.[11-13,17] The data in Table 6 show that (1) is more tetrahedral in the solid state than (2). This is in agreement with the more tenuous conclusion based on electronic spectra. The differences between A_0 and $\langle A\rangle$ values and g_0 and $\langle g\rangle$ values in Table 6 indicate that the room-temperature and frozen-solution species may not be identical since otherwise the values would be very close. Using A_0 and $A_{\parallel}$

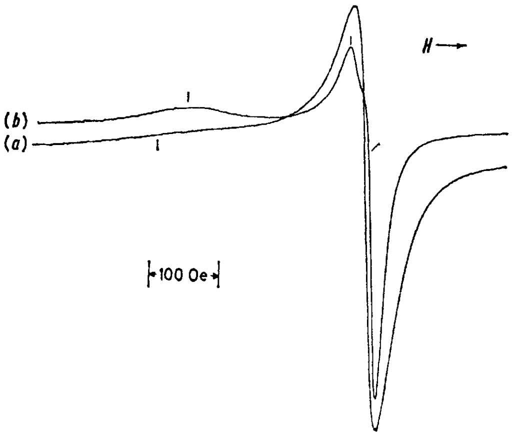

FIGURE 4 X-Band e.s.r. spectra of polycrystalline (1) (*a*) and (2) (*b*). The short dark lines indicate where the g values were taken. 1 Oe = 10^{-4} T

TABLE 6

E.s.r. data

Complex	Host lattice	g_0 [a]	$\langle g\rangle$ [b]	$g_{\parallel}$	$g_{\perp}$	A_0	$\langle A\rangle$	$A_{\parallel}$	$A_{\perp}$
						10^4 cm^{-1}			
(2)	Powder		2.104	2.205	2.044 2.062				
(1)	Powder		2.113	2.233	2.053				
(2)	Nitromethane	2.119	2.118	2.241	2.057	68.0	63.8	173.3	9.0
(1)	Nitromethane	2.114	2.118	2.238	2.059	8.17	73.7	195.0	13.0
(2)	Chlorobenzene [c]	2.117	2.146	2.248	2.095	68.0	74.7	180.4	21.9
(1)	Chlorobenzene [d]	2.114	2.145	2.242	2.096	72.5	78.9	191.4	22.9

[a] g_0 = Isotropic value (room-temperature solution system); similarly for A_0. [b] $\langle g\rangle = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$; similarly for $\langle A\rangle$. Anisotropic g and A values were obtained from e.s.r. spectra of frozen solutions (77 K). [c] $A_{\perp} = 4.6 \times 10^{-4}$ cm^{-1} observed in frozen-solution spectrum. [d] $A_0 = 4.6 \times 10^{-4}$ cm^{-1} in room-temperature spectrum and $A_{\perp} = 9.2 \times 10^{-4}$ cm^{-1} in frozen-solution spectrum.

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[39] G. Marongiu and E. C. Lingafelter, *Acta Cryst.*, 1971, **B27**, 1195.

[40] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, New York, 1966, pp. 357—359.

[41] R. L. Belford and W. A. Yeranos, *Mol. Phys.*, 1963, **6**, 121.

values as a measure of the distortion from planarity, (2) is more distorted than (1) in both nitromethane and chlorobenzene, with (1) being more planar in both solvents. Nitrogen-14 superhyperfine splitting, which is best resolved at low temperatures and tends to disappear with distortion from planarity,[42] is observed in the frozen-solution spectrum of (2) (Figure 5) in chlorobenzene and in the chlorobenzene solution spectra of (1). The presence of ^{14}N superhyperfine splitting demonstrates the electron delocalization in the complexes. At this juncture, the magnitude of the superhyperfine splitting is little more than an indication that large distortions from planarity are absent. The difficulty in unequivocal structural assignments on the basis of spectroscopic information can be traced to the ' plasticity of the co-ordination spheres '[12,13] of copper(II) complexes. The e.s.r. and electronic-spectral data in Tables 5 and 6 and the structure of (2) demonstrate that spectra–structure correlations apply rather well to the solid state but are severely limited when applied to solutions. For copper(II) Schiff-base complexes in solution the possibilities of association [43] and scrambling with other species that might also be present [44] can also add complications to the problem of elucidating gross structural features on the basis of spectra–structure correlations.

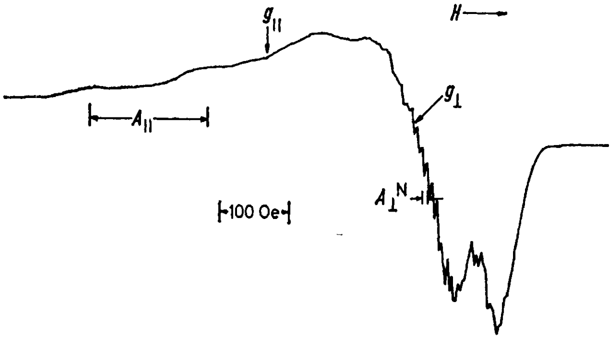

FIGURE 5 Frozen-solution e.s.r. spectrum of (2) in chlorobenzene (77 K)

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[42] Y. Nonaka, T. Tokii, and S. Kida, *Bull. Chem. Soc. Japan*, 1974, **47**, 312.

[43] D. J. Cookson, T. D. Smith, and J. R. Pilbrow, *Bull. Chem. Soc. Japan*, 1975, **48**, 2832.

[44] H. Yokoi and M. Chikira, *J. Amer. Chem. Soc.*, 1975, **97**, 3975.