Conformational Influences in Copper Co-ordination Compounds. Part V.[1] Crystal and Molecular Structure of {1,2-bis-[(2-aminobenzylidene)-amino]propanato(2−)}copper(II)

By **David Hall, T. Neil Waters,*** and **Peter E. Wright,** Chemistry Department, University of Auckland, New Zealand

Crystals of the title compound are orthorhombic, space group $P2_12_12_1$ with $a = 9{\cdot}096(2)$, $b = 24{\cdot}551(9)$, and $c = 7{\cdot}159(3)$ Å, $Z = 4$. The molecular structure was solved by the heavy-atom method and refined to an R 0·076 for 1068 diffractometer data. There is an ' umbrella-shaped ' molecule with a disordered 1,2-propane bridge. It is argued that this result is unexpected and indicative of electronic, rather than steric, demands. The Cu atom is four-co-ordinate, mean Cu–N 1·91 Å.

An attribute of many supposedly planar complexes of copper(II) is the additional co-ordination they achieve by dimerisation,[2] polymerisation,[3] or through the binding of solvent molecules.[4] This feature has been linked with the ligand-field strength of the donor atoms,[1,5] in order to explain, *e.g.* the five- or six-co-ordinate nature of isomers of bis-(*N*-methylsalicylaldiminato)copper(II) [2,3] in which the copper–nitrogen bond length is *ca.* 1·99 Å and the four-co-ordination found in bis(salicylaldiminato)copper-(II) [6] (Cu–N 1·90 Å). In a separate demonstration of the phenomenon the degree of dimerisation of [*NN'*-ethylenebis(salicylaldiminato)]copper(II) has been correlated with the changing ligand-field strength of the oxygen donors consequent upon their involvement in hydrogen bonding.[1,7] A feature of this particular change and of similar situations in other molecules is the increase in overall molecular planarity accompanying the decrease in co-ordination. In the methylammonium perchlorate adduct of [*NN'*-ethylenebis(acetylacetoneiminato)]copper(II) [8] the ultimate situation is reached in which the whole molecule, including the ethylene bridging group which normally has a *gauche* conformation, adopts mirror symmetry.

This assumption of complete planarity has been taken as testifying to the forces involved since such a conformation is not generally expected. As already noted, ethylene bridges normally take the staggered arrangement seen in simple chelates of ethylenediamine and it also found, especially in copper(II) complexes, that molecular distortions are present within the salicylaldiminato-moieties. These can be summarised by noting that the molecules are generally bent about a line through the donors so as to give rise to ' stepped ' or ' umbrella-shaped ' complexes. It is also noticed in copper(II) complexes that the dihedral angle of bending is rarely equal for the two chelating residues,[9] nor is the staggering of carbon atoms in the ethylene bridge symmetrical in the sense of displacing the carbon atoms equally from the plane through the copper and nitrogen donor atoms.[10] Also, in a quadridentate ligand of the bridged salicylaldimine type there is a link between the bending at the donor atoms and the staggered positioning of the ethylene carbons, since the trigonally bonded nitrogen atoms are common to both situations. As a consequence, stepped complexes favour a *gauche* bridge whereas an umbrella-shaped molecule requires the unfavourable *cis* or eclipsed arrangement of ethylene atoms. Thus the umbrella-shaped complex aquo-[*NN'*-ethylenebis(acetylacetoneiminato)]copper(II) has a *cis*-ethylene bridge [10] but many compounds appear to have the ' stepped and *gauche* ' geometry. An exception is found in the dimeric isomer of the iron complex chloro-[*NN'*-ethylenebis(salicylaldiminato)]iron(III), [ClFe(salen)]$_2$, in which a *gauche* bridge and an umbrella-shape is present at the expense of a tetrahedral displacement of nitrogen donor atoms from planar co-ordination.[11]

Since nitrogen generally has a stronger ligand-field than oxygen, experience, as briefly summarised, suggests that a salicylaldimine-type complex containing four nitrogen donor atoms is likely to be more clearly four-co-ordinate and more nearly planar than are true salicylaldimine compounds where extra co-ordination and stepped distortions linked to *gauche* carbon–carbon bridges can be expected. Recently we have prepared the complex {1,2-bis[(2-aminobenzylidene)amino]propanato(2−)}copper(II) which has four nitrogen donors and report the result of an *X*-ray structure determination undertaken to confirm the general stereochemistry of this class of compound for correlation of spectra with those of salicylaldimines, and to compare its detailed geometry with that expected.

EXPERIMENTAL

Crystal Data.—$C_{17}H_{18}CuN_4$, *M*, 341·9, Orthorhombic, $a = 9{\cdot}096(2)$, $b = 24{\cdot}551(9)$, $c = 7{\cdot}159(3)$ Å (from least-

---

[1] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

[2] D. Hall, Sylvia V. Sheat, and T. N. Waters, *J. Chem. Soc.* (*A*), 1968, 460.

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

[4] D. Hall, Sylvia V. Sheat-Rumball, and T. N. Waters, *J. Chem. Soc.* (*A*), 1968, 2721.

[5] H. C. Freeman, ' The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York, 1966, p. 105.

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

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

[8] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 396.

[9] T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1966, 685.

[10] G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1969, 823.

[11] M. Gerloch and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1967, 1900.

squares fit to diffractometer co-ordinates of 12 reflexions), D_m = 1·37 (by flotation), Z = 4, D_c = 1·42. Space group = $P2_12_12_1$. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 19·7 cm^{-1}.

Intensity data were collected by four-circle diffractometry (Hilger–Watts Y 290) by use of θ/ω scan. 1068 Intensities $>2\sigma(I)$ were classed as observed. The crystal dimensions in the a, b, and c directions were 0·10 × 0·25 × 0·30 mm. No absorption corrections were applied.

Structure solution was by the conventional heavy-atom method, all nonhydrogen atoms being placed from the second electron-density map but with those in the propane bridge proving difficult to locate accurately. Isotropic refinement was by block-diagonal least-squares, a real dispersion correction of −2·1 being applied to copper(0) scattering factors.[12] The weighting scheme, based on observed standard deviations, was of the form $w = 4F_o^2/\sigma^2(F^2)$. Refinement converged at R 0·112, bond lengths and angles being reasonable except for those in the propane bridge. Hydrogen atoms, apart from those associated with the bridge, were then included in the refinement model at computed positions after they had been approximately located by a difference-Fourier synthesis; their isotropic temperature factors were set at 5·0 Å^2. Refinement was then continued with all non-hydrogen atoms except those in the bridge assigned anisotropic thermal parameters, convergence occurring this time at R 0·095. Since bond lengths and angles in the propane group were still unsatisfactory these three atoms were omitted from a structure-factor calculation (R 0·141) and a difference-Fourier synthesis. It was immediately apparent that all three atoms were defining long arcs of electron density (see Figure 1) and that there were no small maxima indicative of disorder over a number of discrete sites within these regions. It was thus clear that a model for the bridge could not be deduced but would have to be imposed. The atoms were therefore placed centrally and refined anisotropically in the hope of achieving the best possible fit with the data. Convergence was reached with this scheme at R 0·076, bond lengths within the bridge still being unsatisfactory. This last stage of the refinement was repeated with only isotropic temperature factors assumed for the three bridge atoms, when R was reduced to 0·078. Since the extra parameters involved in the fully anisotropic refinement did not give a significantly better result,[13] final output from the more restrictive scheme was used in the subsequent calculation of the molecular geometry.

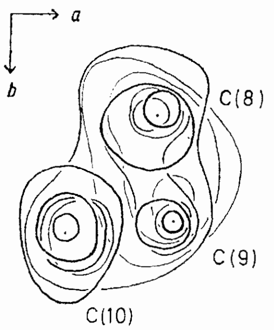

FIGURE 1 Electron-density arcs in the region of C(8)—(10). Contours are at arbitrary intervals drawn on sections perpendicular to c from $z = \overline{0·04}$ through 0·36 (*ca.* 2·9 Å)

Atom co-ordinates, temperature parameters, bond lengths,

TABLE 1

Atom co-ordinates with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	0·22353(20)	0·15306(7)	0·11599(25)
N(1)	0·2582(14)	0·2029(4)	0·3197(15)
N(2)	0·0801(15)	0·1994(5)	0·0133(18)
N(3)	0·1673(13)	0·1068(4)	−0·0925(18)
N(4)	0·3822(13)	0·1060(4)	0·1770(15)
C(1)	0·1936(14)	0·2524(5)	0·3483(18)
C(2)	0·2400(18)	0·2851(5)	0·5071(19)
C(3)	0·1817(17)	0·3355(6)	0·5310(20)
C(4)	0·0816(15)	0·3595(5)	0·4079(22)
C(5)	0·0329(17)	0·3280(5)	0·2649(22)
C(6)	0·0904(15)	0·2760(1)	0·2260(20)
C(7)	0·0353(20)	0·2475(7)	0·0652(21)
C(8)	0·0091(27)	0·1816(9)	−0·1775(34)
C(9)	0·0429(22)	0·1271(8)	−0·1945(29)
C(10)	−0·1126(23)	0·1151(8)	−0·0617(33)
C(11)	0·2363(17)	0·0644(5)	−0·1553(19)
C(12)	0·3640(15)	0·0415(5)	−0·0772(20)
C(13)	0·4254(18)	−0·0051(6)	−0·1671(21)
C(14)	0·5496(16)	−0·0292(6)	−0·1015(23)
C(15)	0·6232(17)	−0·0093(6)	0·0561(23)
C(16)	0·5622(15)	0·0349(5)	0·1449(22)
C(17)	0·4370(14)	0·0621(5)	0·0902(19)
H(1)	0·328	0·185	0·398
H(4)	0·420	0·121	0·291
H(21)	0·319	0·268	0·603
H(31)	0·217	0·359	0·651
H(41)	0·039	0·400	0·428
H(51)	−0·047	0·346	0·174
H(71)	−0·051	0·267	0·013
H(111)	0·194	0·045	−0·278
H(131)	0·373	−0·022	−0·289
H(141)	0·594	−0·064	−0·172
H(151)	0·721	−0·028	0·107
H(161)	0·616	0·050	0·269

TABLE 2

(*a*) Thermal parameters * (×10^4) with estimated standard deviations in parentheses

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu	173·0(2)	18·5(2)	187·3(4)	4·3(2)	−6·7(7)	−11·4(2)
N(1)	237(2)	18(2)	222(3)	26(1)	−165(4)	−13(1)
N(2)	261(3)	25(3)	265(3)	25(1)	−165(5)	−56(2)
N(3)	213(2)	22(2)	291(3)	23(1)	−185(5)	−52(2)
N(4)	208(2)	19(2)	187(3)	10(1)	−78(4)	−53(1)
C(1)	150(2)	19(2)	189(3)	9(1)	29(4)	−15(2)
C(2)	217(3)	21(3)	201(3)	11(2)	−32(6)	−14(2)
C(3)	210(3)	22(3)	247(3)	1(2)	92(5)	−49(2)
C(4)	193(2)	18(3)	298(4)	1(1)	159(6)	−15(2)
C(5)	186(2)	20(3)	297(4)	34(1)	−23(6)	21(2)
C(6)	168(2)	22(3)	214(3)	28(1)	−3(5)	25(2)
C(7)	259(3)	30(3)	280(5)	61(2)	−216(7)	−6(2)
C(11)	220(3)	24(3)	200(3)	−6(2)	−99(6)	−25(2)
C(12)	171(2)	19(3)	240(4)	−10(1)	58(5)	3(2)
C(13)	219(3)	25(3)	245(4)	−2(2)	76(6)	−48(2)
C(14)	198(2)	24(3)	259(4)	−3(1)	−14(6)	−40(2)
C(15)	167(2)	25(3)	313(4)	−2(2)	21(5)	7(2)
C(16)	159(2)	21(3)	309(4)	11(1)	−38(6)	−31(2)
C(17)	148(2)	17(2)	189(3)	−2(1)	−24(5)	21(2)

* The scattering factor for an atom is expressed by:

$$f = f_o\exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl).$$

(*b*) Isotropic temperature factors

	B/Å^2
C(8)	11·5(7)
C(9)	9·0(5)
C(10)	10·2(6)

---

[12] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1967.

[13] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

and bond angles are listed in Tables 1—4; the atom numbering scheme is shown in Figure 2. Structure factor data are *listed in* Supplementary Publication No. SUP 20663 (3 pp.).

TABLE 3

Bond lengths (Å)

Cu–N(1)	1·930(11)	N(2)–C(8)	1·57(3)
Cu–N(2)	1·880(13)	C(8)–C(9)	1·38(3)
Cu–N(3)	1·945(12)	C(9)–C(10)	1·73(3)
Cu–N(4)	1·899(11)	N(3)–C(9)	1·44(2)
N(1)–C(1)	1·36(2)	N(3)–C(11)	1·30(2)
C(1)–C(2)	1·45(2)	C(11)–C(12)	1·41(2)
C(2)–C(3)	1·36(2)	C(12)–C(13)	1·43(2)
C(3)–C(4)	1·40(2)	C(13)–C(14)	1·36(2)
C(4)–C(5)	1·36(2)	C(14)–C(15)	1·40(2)
C(5)–C(6)	1·41(2)	C(15)–C(16)	1·38(2)
C(6)–C(1)	1·41(2)	C(16)–C(17)	1·38(2)
C(6)–C(7)	1·44(2)	C(17)–C(12)	1·46(2)
N(2)–C(7)	1·30(2)	N(4)–C(17)	1·34(2)

TABLE 4

Bond angles (°)

N(1)–Cu–N(2)	91·5(5)	C(1)–C(6)–C(7)	122·0(13)
N(1)–Cu–N(3)	173·6(5)	C(5)–C(6)–C(7)	118·0(13)
N(1)–Cu–N(4)	95·0(5)	C(6)–C(7)–N(2)	124·1(15)
N(2)–Cu–N(3)	82·6(5)	C(7)–N(2)–C(8)	111·7(14)
N(2)–Cu–N(4)	170·0(5)	N(2)–C(8)–C(9)	104·7(17)
N(3)–Cu–N(4)	91·2(5)	N(3)–C(9)–C(8)	118·0(18)
Cu–N(1)–C(1)	127·4(9)	N(3)–C(9)–C(10)	107·8(15)
Cu–N(2)–C(7)	130·8(11)	C(8)–C(9)–C(10)	86·2(16)
Cu–N(2)–C(8)	117·2(11)	C(9)–N(3)–C(11)	119·0(13)
Cu–N(3)–C(9)	113·2(10)	N(3)–C(11)–C(12)	125·7(13)
Cu–N(3)–C(11)	127·5(10)	C(11)–C(12)–C(13)	117·7(12)
Cu–N(4)–C(17)	131·7(9)	C(11)–C(12)–C(17)	124·3(12)
N(1)–C(1)–C(2)	118·9(11)	C(13)–C(12)–C(17)	118·1(12)
N(1)–C(1)–C(6)	124·0(12)	C(12)–C(13)–C(14)	121·3(14)
C(2)–C(1)–C(6)	116·9(12)	C(13)–C(14)–C(15)	121·5(14)
C(1)–C(2)–C(3)	119·3(13)	C(14)–C(15)–C(16)	117·1(14)
C(2)–C(3)–C(4)	124·0(13)	C(15)–C(16)–C(17)	125·8(13)
C(3)–C(4)–C(5)	116·6(13)	N(4)–C(17)–C(12)	119·3(11)
C(4)–C(5)–C(6)	123·0(14)	N(4)–C(17)–C(16)	124·5(12)
C(1)–C(6)–C(5)	119·9(13)	C(12)–C(17)–C(16)	116·2(12)

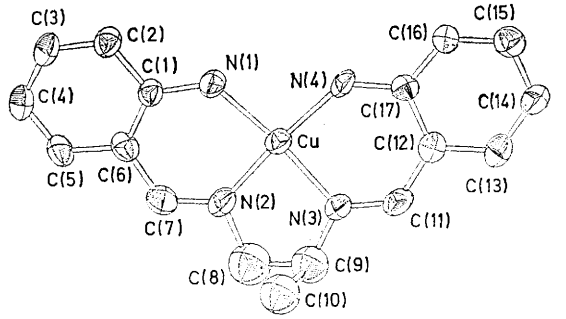

FIGURE 2 An ORTEP diagram (the three bridge atoms being represented isotropically), showing the atom numbering scheme used

DISCUSSION

Molecules of the title complex are monomeric and the copper atom is strictly four-co-ordinate. The nearest axial approaches are 3·95 and 3·96 Å and there are no other intermolecular distances less than accepted values for van der Waals approaches.

Overall, the molecule is similar to the analogous salicylaldimine complexes, as might be expected, and bond lengths and angles between the two systems are equal within the limits of accuracy. It is also similar to many salicylaldimine compounds in not being strictly planar and deviations from such a geometry are evidenced in various ways. Thus the angles N(1)–Cu–N(3) and N(2)–Cu–N(4) are 173·6 and 170·0° indicating a situation better illustrated by the planes of best fit and displacements therefrom listed in Table 5. The two chelate groups are inclined by 7·2 and 8·1° from the central co-ordination plane, so that atoms of both residues lie

TABLE 5

Equations of planes of best fit, in the form $lX + mY + nZ + p = 0$

Displacements (Å) of atoms from the planes are given in square brackets

Plane (I): N(1)—(4)

$$-0\cdot6527X - 0\cdot4945Y + 0\cdot5740Z - 2\cdot7546 = 0$$

[Cu 0·044, N(1) 0·074, N(2) −0·083, N(3) 0·082, N(4) −0·073, C(1) −0·026, C(2) −0·047, C(3) −0·211, C(4) −0·414, C(5) −0·334, C(6) −0·202, C(7) −0·185, C(8) −0·236, C(9) 0·160, C(10) 1·775, C(11) −0·060, C(12) −0·221, C(13) −0·394, C(14) −0·578, C(15) −0·605, C(16) −0·411, C(17) −0·223]

Plane (II): Cu, N(1), N(2)

$$-0\cdot7032X - 0\cdot4638Y + 0\cdot5388Z - 2\cdot7277 = 0$$

[C(1) −0·041, C(4) −0·311, C(6) −0·119, C(7) −0·058]

Plane (III): Cu, N(3), N(4)

$$-0\cdot6027X - 0\cdot5224Y + 0\cdot6032Z - 2\cdot6895 = 0$$

[C(11) −0·094, C(12) −0·164, C(14) −0·394, C(17) −0·113]

Plane (IV): N(1), C(2)—(7), N(2)

$$0\cdot7322X + 0\cdot4013Y - 0\cdot5503Z + 2\cdot4281 = 0$$

[N(1) 0·029, N(2) 0·014, C(1) −0·024, C(2) −0·019, C(3) −0·008, C(4) 0·047, C(5) −0·021, C(6) 0·000, C(7) −0·018, Cu 0·114, C(14) 1·351]

Plane (V): N(3), C(11)—(17), N(4)

$$-0\cdot5590X - 0\cdot6002Y + 0\cdot5720Z - 2\cdot7829 = 0$$

[N(3) −0·024, N(4) 0·003, C(11) 0·005, C(12) 0·012, C(13) 0·012, C(14) −0·004, C(15) −0·023, C(16) 0·003, C(17) 0·016, Cu −0·136, C(4) −1·254]

Plane (VI): C(1)—(6)

$$-0\cdot7389X - 0\cdot3868Y + 0\cdot5517Z - 2\cdot3200 = 0$$

[C(1) −0·003, C(2) 0·003, C(3) 0·013, C(4) −0·029, C(5) 0·030, C(6) −0·013, C(7) −0·004, Cu −0·180, N(1) −0·078, N(2) −0·056, N(3) −0·186, N(4) −0·555]

Plane (VII): C(12)—(17)

$$-0\cdot5493X - 0\cdot6070Y + 0\cdot5743Z - 2\cdot7394 = 0$$

[C(12) −0·007, C(13) 0·004, C(14) 0·004, C(15) −0·009 C(16) 0·006, C(17) 0·002, Cu −0·183, N(1) −0·259, N(2) −0·572, N(3) −0·072, N(4) −0·021]

Plane (VIII): Cu, N(2), N(3)

$$-0\cdot6965X - 0\cdot4356Y + 0\cdot5702Z - 2\cdot5820 = 0$$

[C(8) −0·14, C(9) 0·16]

Interplanar angles (°)

(II)–(III)	7·6	(I)–(VI)	8·0
(IV)–(V)	15·2	(I)–(VII)	8·8
(I)–(IV)	7·2	(II)–(IV)	4·0
(I)–(V)	8·1	(III)–(V)	5·4
(VI)–(VII)	16·8		

---

* For details see Notice to Authors No. 7 in *J.C,S. Dalton*, 1972. Items less than 10 pp. are supplied as full-sized copies.

beneath it. Since each residue is coplanar within itself, the molecule has an overall umbrella shape confirmed by comparing the distance of the copper atom from the central co-ordination plane (0·04 Å above) with its displacement from the planes of the residues (0·11 and 0·14 Å below). (The directional sense is such as to define the chelate groups as being below the co-ordination sphere.) The molecule thus bends along the lines N(1) $\cdots$ N(2) and N(3) $\cdots$ N(4) similar to the O $\cdots$ N bending found in co-ordinated salicylaldimines.

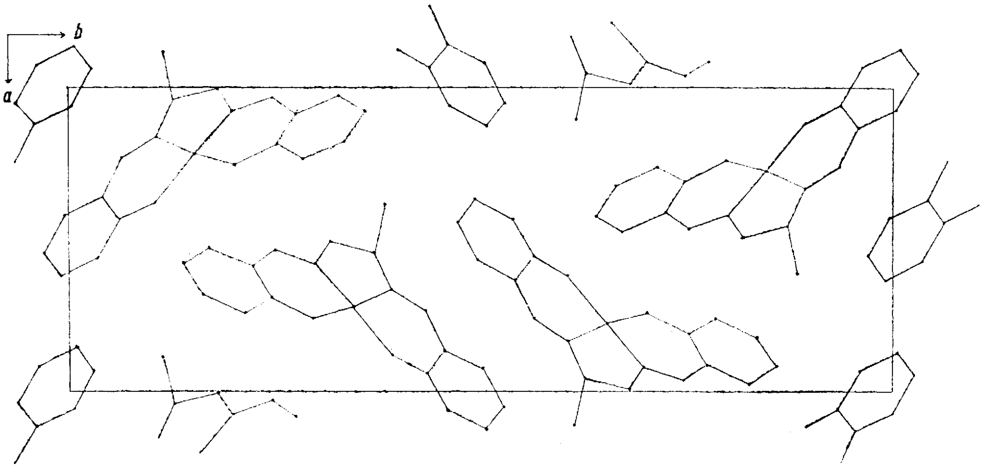

FIGURE 3 The unit cell contents projected down *c*

The supposedly unfavourable umbrella geometry is thus found without steric pressure from a ligand in a fifth co-ordination site and without any obvious demands from crystal-packing requirements. As mentioned earlier, a corollary of this, if the trigonal bonding at the imine nitrogens is to be maintained, is that either the bridging ethylene carbon atoms must be in the eclipsed conformation or there must be a tetrahedral distortion imposed on the basically square co-ordination stereochemistry. Table 5 shows that there is such a distortion, a circumstance which has been thought to be less likely with copper(II) than with adjacent first-row transition metals. In view of the disordered nature of the bridge atoms it is important that the tetrahedral distortion is static, the root-mean-square vibrational amplitudes (Table 6) and the ORTEP diagram (Figure 2) confirming that the two imine nitrogens suffer only average thermal oscillations.

The three bridge atoms are disordered over arcs of electron density which are 1·0—1·5 Å in length. Two reasons for this can be advanced. First it is to be noted that (±)-1,2-diaminopropane was used in the preparation of the complex and could lead to random disorder in the bridge. Since, however, it is clear that only C(9) carries the C(10) methyl group, disorder in C(8) and C(9) could only result from the δ to λ inversion of the bridge needed to maintain the observed axial position for C(10). This should lead to ' half-weight ' sitings for C(8) and C(9) and to a reversal of the tetrahedral distortion, both against the evidence. It is assumed therefore that individual crystals contain one optical isomer, as previously observed in a salicylaldimine analogue.[14] The alternative explanation, in which dynamic oscillation or static disorder over multisites cannot be distinguished, assumes a state of tension in the bridge arising from the particular geometry and bonding requirements of the complex. The steric positions obtained for C(8), C(9), and C(10) are more or less in the centre of their respective density arcs and show the bridge to be of *gauche* conformation ' on average ' but with much smaller displacements of the ethylene carbon atoms from the metal donor than is usual [*i.e.* plane VIII (Table 5) 0·16 and —0·14 Å]. There is scope within the density arcs to accommodate a more staggered bridge but this demands a further tetrahedral distortion of the central co-ordination sphere. Alternatively, a more eclipsed bridge can be fitted but this will only occur at the expense of hydrogen–hydrogen repulsion between the methylene groups. We are suggesting therefore that the

TABLE 6

Root-mean-square amplitudes of vibration (Å)

	Axis		
Atom	Minor	Medium	Major
Cu	0·207	0·238	0·278
N(1)	0·209	0·224	0·341
N(2)	0·210	0·275	0·365
N(3)	0·211	0·252	0·353
N(4)	0·167	0·262	0·310
C(1)	0·207	0·244	0·256
C(2)	0·221	0·254	0·305
C(3)	0·202	0·283	0·314
C(4)	0·219	0·242	0·325
C(5)	0·211	0·282	0·300
C(6)	0·211	0·248	0·293
C(7)	0·209	0·283	0·384
C(11)	0·204	0·279	0·312
C(12)	0·229	0·245	0·279
C(13)	0·214	0·291	0·318
C(14)	0·226	0·288	0·295
C(15)	0·262	0·275	0·288
C(16)	0·235	0·253	0·301
C(17)	0·203	0·239	0·254

---

[14] F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.* (*A*), 1960, 2639.

dictates of the umbrella-shaped molecule are competing with the conformational requirements of the bridge, preventing the full adoption of one or other of the alternative (*cis* or *gauche*) bridge geometries. It is not necessarily a consequence of this that the propane carbon atoms are dynamically or statically disordered, but there are precedents to this situation.[15]

That the molecule is four-co-ordinate, in contrast with the five-co-ordinate aquo-complex of its salicylaldimine analogue,[14] accords with the predicted effect of increasing the ligand-field strength of the donors. It is, however, unexpected that it should also be umbrella-shaped. In the absence of obvious crystal packing requirements (Figure 3 is a packing diagram), this must be assumed to be a bonding effect sufficiently strong to compete with the opposing demands of the substituted ethylene bridge. We regard this as evidence that the deviations from planarity and symmetry so often seen in copper(II) compounds have a partial electronic origin and are not solely due to geometrical pressures. We thus note that the oft-quoted asymmetrical *gauche* conformation of the simple bis(ethylenediamine)copper(II) ion can be redefined in terms of a symmetrical displacement from the appropriate copper-donor plane if a bending of the chelate ' plane ' about an N · · · N line be assumed.

[2/2273 *Received*, *2nd October*, 1972]

---

[15] Y. C. Leung and R. E. Marsh, *Acta Cryst.*, 1958, **11**, 17.