# Conformational Influences in Copper Co-ordination Compounds. Part VI.[1] Crystal Structure of a Fourth Crystalline Isomer of Bis-(2-hydroxy-*N*-methyl-1-naphthylmethyleneiminato)copper(II)

By **Dennis W. Martin** and **T. Neil Waters,*** Chemistry Department, University of Auckland, New Zealand

The title compound crystallises in the monoclinic system, $a = 10{\cdot}40$, $b = 5{\cdot}88$, $c = 15{\cdot}61$ Å, $\beta = 95{\cdot}2°$, with space group $P2_1/c$. The structure was solved from visually estimated photographic *X*-ray data by the heavy-atom method and refined by least-squares techniques to *R* 0·097 for 1024 reflections. It differs from polymorphs already studied in being strictly square-planar in co-ordination stereochemistry. It also shows a much higher degree of molecular planarity than expected. Intermolecular interactions of any significance are lacking so that the geometry of the complex can be discussed in terms of internal factors. The observations are interpreted in terms of a relationship between molecular conformation and metal–ligand bonding.

In introducing our study we draw attention to two features of the crystal and molecular structures of copper(II) co-ordination complexes reported recently. One is the solid-state polymorphism of a number of compounds,[2,3] the other the discovery that hydrogen bonding to donor oxygen atoms can alter molecular geometry.[4,5] The so-called α-,[6] β-,[7] and γ-[8] isomers of bis-(*N*-methylsalicylideneiminato)copper(II) in which the

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[1] Part V, D. Hall, T. N. Waters, and P. E. Wright, *J.C.S. Dalton*, 1973, 1508.

[2] D. Hall, A. J. McKinnon, and T. N. Waters, *J. Chem. Soc.*, 1965, 425.

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

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

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

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

[7] E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, 1959, **63**, 1908.

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

metal ion is respectively six- (or more strictly 4 + 2 co-ordinate), four-, and five-co-ordinate may be cited as examples of the first point and the changes in co-ordination number and molecular planarity seen in [*NN'*-ethylenebis(salicylideneiminato)]copper(II) as an illustration of the second.[4,9]

It appears that the co-ordination stereochemistry is an important structural force in stabilising polymorphs and we have supposed that crystals become locked into particular structures, some of which must be metastable, at the time of formation. The presence of bridging atoms to increase the number of donors per metal, from the four offered by the planar ligands used in these studies, has been related to their ligand-field strength.[4,10] Strict four-co-ordination, and lack of polymorphism, is thus seen in bis(salicylideneiminato)copper(II) [11] where the short Cu–N bonds ensure a stronger field than that of the isomeric *N*-methyl analogue.

The foregoing observations are pertinent to a consideration of bis-(*N*-methyl-2-hydroxynaphthylmethyleneiminato)copper(II), which exists in three polymorphic forms. A green, rather unstable, solid has not been studied in detail although it is well characterised,[12] but two brown modifications have been subjected to *X*-ray analysis. One shows 4 + 2 co-ordination (Cu–O 2·94 Å) in a polymeric arrangement; [13] the other has dimeric molecules, similar to those of γ-bis-(*N*-methylsalicylideneiminato)copper(II),[8] with Cu–O 2·59 Å.[14] Since the factors which determine polymorphism are still manifest in this complex despite the increased 'packing forces' associated with the larger ligands we have attempted to see whether we could induce further changes by varying the crystallisation environment. We did this by dissolving the complex in chloroform and then adding an equimolecular amount of 1,4-naphthaquinone in the hope of forming charge-transfer species [15] which would change the crystallisation conditions. The green needles which we produced are a further, hereafter δ, modification of the complex. We report its crystal structure.

## EXPERIMENTAL

*Crystal Data.*—$C_{24}H_{20}CuN_2O_2$, $M = 431{\cdot}5$, Monoclinic, $a = 10{\cdot}40(2)$, $b = 5{\cdot}88(1)$, $c = 15{\cdot}61(2)$ Å, β 95·2(1)° (standard deviations from the spread of independent film measurements), $U = 950{\cdot}6$ Å$^3$, $D_m = 1{\cdot}59$ (by flotation), $Z = 2$, $D_c = 1{\cdot}51$. Space group $P2_1/c$. Cu-$K_\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu$(Cu-$K_\alpha$) = 18·04 cm$^{-1}$ (Found: C, 67·35; H, 4·80; N, 6·45. Calc. for $C_{24}H_{20}CuN_2O_2$: C, 66·75; H, 4·65; N, 6·50%.)

Two crystals, of dimensions of 0·04 × 0·18 × 0·24 and 0·07 × 0·40 × 0·28 mm, were used for *a* and *b* axis photography respectively, the reciprocal lattice sections 0—8*kl* and *h*0—5*l* being recorded by Weissenberg methods. Intensity measurements were visual and they were brought to a common scale by a least-squares procedure.[16] No absorption corrections were made.

Structure solution used the heavy atom method and least squares refinement followed. A block-diagonal procedure was applied with data weighted by the factor $w = 1/[1 + (F_o - b)^2/a^2]$, the adjustable parameters *a* and *b* being altered to keep $\langle w\Delta^2\rangle$ constant over $|F_o|$ ranges. Scattering factors were those for neutral atoms [17] with a real dispersion correction of −2·1 e applied to copper values. The initial model, in which anisotropic thermal parameters for copper and isotropic parameters for oxygen and nitrogen were included for refinement, converged at *R* 0·135. A difference-Fourier synthesis was then computed to find hydrogen positions and *R* fell to 0·129, just significant at the 0·5% level.[18] All atoms, except those of hydrogen, which were given a fixed isotropic value of *B* 5·0 Å$^2$, were then refined on the assumption of vibrational anisotropy to reach a final *R* factor of 0·097, a reduction also statistically significant at the 0·5% level.

Atom co-ordinates are listed in Table 1, temperature parameters in Table 2, and calculated bond lengths and angles in Tables 3 and 4. Structure factor data are listed in Supplementary Publication No. SUP 20765 (10 pp., 1 microfiche).* The numbering scheme used is shown in Figure 1.

TABLE 1

Atom positions

| Atom | *x*<br>*a* | *y*<br>*b* | *z*<br>*c* |
|---|---|---|---|
| O(1) | 0·0207(6) | 0·2179(12) | 0·0884(4) |
| N(1) | 0·1554(7) | −0·1679(13) | 0·0491(5) |
| C(1) | 0·2019(8) | 0·0763(18) | 0·1750(6) |
| C(2) | 0·1042(8) | 0·2317(18) | 0·1557(6) |
| C(3) | 0·0911(9) | 0·4216(19) | 0·2096(7) |
| C(4) | 0·1695(10) | 0·4499(17) | 0·2819(7) |
| C(5) | 0·3505(9) | 0·3245(18) | 0·3822(6) |
| C(6) | 0·4463(9) | 0·1793(20) | 0·4057(6) |
| C(7) | 0·4652(11) | −0·0120(19) | 0·3538(8) |
| C(8) | 0·3885(9) | −0·0499(16) | 0·2802(6) |
| C(9) | 0·2885(7) | 0·1029(17) | 0·2529(6) |
| C(10) | 0·2698(9) | 0·2945(19) | 0·3062(6) |
| C(11) | 0·2206(9) | −0·1115(18) | 0·1202(6) |
| C(12) | 0·1972(9) | −0·3687(18) | 0·0055(6) |
| H(0) | 0·276 | −0·435 | 0·037 |
| H(1) | 0·223 | −0·327 | −0·055 |
| H(2) | 0·1248 | −0·484 | 0·005 |
| H(3) | 0·015 | 0·550 | 0·194 |
| H(4) | 0·154 | 0·598 | 0·322 |
| H(5) | 0·338 | 0·471 | 0·424 |
| H(6) | 0·506 | 0·219 | 0·466 |
| H(7) | 0·542 | −0·137 | 0·372 |
| H(8) | 0·403 | −0·197 | 0·241 |
| H(9) | 0·300 | −0·260 | 0·135 |

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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

[10] H. C. Freeman, 'The Biochemistry of Copper,' eds. J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York, 1966, p. 104.

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

[12] M. von Stackelberg, *Z. anorg. Chem.*, 1947, **253**, 136.

[13] D. Hall, A. J. McKinnon, J. M. Waters, and T. N. Waters, *Nature*, 1964, **201**, 607.

[14] G. J. Williams, M.Sc. Thesis, University of Auckland, 1967.

[15] E. E. Castellano, O. J. R. Hodder, C. K. Prout, and P. J. Sadler, *J. Chem. Soc.* (*A*), 1971, 2620.

[16] A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.

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

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

TABLE 2

Thermal parameters ($\times 10^4$) *

| Atom | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Cu | 26·2 | 209·8 | 25·2 | 6·3 | −14 | 5 |
| O(1) | 55 | 269 | 31 | 35 | −33 | 9 |
| N(1) | 37 | 190 | 29 | 6 | −16 | 13 |
| C(1) | 19 | 266 | 27 | 47 | −14 | 25 |
| C(2) | 44 | 286 | 27 | 48 | −8 | 12 |
| C(3) | 48 | 230 | 46 | 51 | −12 | −37 |
| C(4) | 71 | 193 | 40 | −26 | −11 | 29 |
| C(5) | 57 | 210 | 30 | −65 | −4 | −9 |
| C(6) | 51 | 369 | 26 | 83 | 13 | 18 |
| C(7) | 58 | 331 | 40 | 8 | −29 | −6 |
| C(8) | 45 | 185 | 33 | 5 | −15 | −5 |
| C(9) | 18 | 225 | 31 | −18 | −8 | 12 |
| C(10) | 49 | 251 | 31 | 1 | −12 | 0 |
| C(11) | 48 | 209 | 27 | 0 | 7 | 27 |
| C(12) | 52 | 279 | 33 | 92 | −29 | −19 |

* The scattering factors are expressed as: $f = f_0 \exp(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$.

TABLE 3

Bond lengths (Å)

| | | | |
|---|---|---|---|
| Cu–O(1) | 1·87(1) | C(3)–C(4) | 1·33(2) |
| Cu–N(1) | 1·98(1) | C(4)–C(10) | 1·41(1) |
| O(1)–C(2) | 1·29(1) | C(5)–C(6) | 1·33(1) |
| N(1)–C(12) | 1·44(1) | C(5)–C(10) | 1·39(1) |
| N(1)–C(11) | 1·28(1) | C(6)–C(7) | 1·41(2) |
| C(1)–C(2) | 1·38(1) | C(7)–C(8) | 1·40(1) |
| C(1)–C(9) | 1·45(1) | C(8)–C(9) | 1·40(1) |
| C(1)–C(11) | 1·42(1) | C(9)–C(10) | 1·42(1) |
| C(2)–C(3) | 1·41(1) | | |

TABLE 4

Bond angles (°)

| | | | |
|---|---|---|---|
| Cu–O(1)–C(2) | 131·0(6) | C(2)–C(3)–C(4) | 121·0(9) |
| Cu–N(1)–C(11) | 123·1(6) | C(3)–C(4)–C(10) | 121·3(9) |
| Cu–N(1)–C(12) | 119·6(6) | C(4)–C(10)–C(5) | 121·1(9) |
| O(1)–Cu–N(1) | 91·3(3) | C(4)–C(10)–C(9) | 119·6(8) |
| O(1)–Cu–N(1′) | 88·7(3) | C(5)–C(10)–C(9) | 119·3(8) |
| O(1)–C(2)–C(1) | 123·8(9) | C(5)–C(6)–C(7) | 119·4(9) |
| O(1)–C(2)–C(3) | 115·9(8) | C(6)–C(5)–C(10) | 121·6(9) |
| N(1)–C(11)–C(1) | 128·8(8) | C(6)–C(7)–C(8) | 121·1(9) |
| C(1)–C(2)–C(3) | 120·3(8) | C(7)–C(8)–C(9) | 120·6(9) |
| C(1)–C(9)–C(8) | 124·6(9) | C(8)–C(9)–C(10) | 117·7(8) |
| C(1)–C(9)–C(10) | 117·7(8) | C(11)–N(1)–C(12) | 117·3(6) |

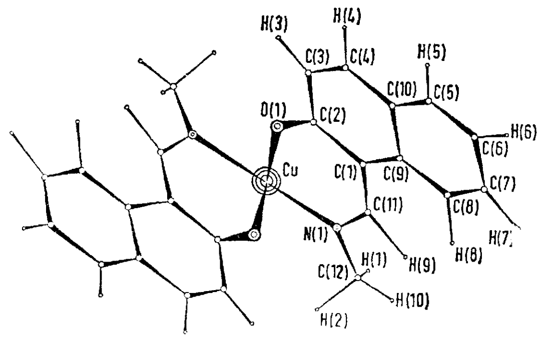

FIGURE 1 The numbering scheme

## DISCUSSION

The molecule is found to be four-co-ordinate and planar, there being no evidence for bonding in the ' octahedral ' positions of the copper ion, and it is closely represented by Figure 1. Table 5 compares geometrical details with those of similar compounds [6,11,19] analysed to similar levels of accuracy as well as with those of naphthalene.[20] The geometry is unexceptional, except for the Cu–N bond length of 1·98 Å which shows the increase over that in bis(salicylideneiminato)copper(II), resulting from the methyl substituent on the nitrogen atom.

TABLE 5

Comparison of bond lengths (Å) with those in similar compounds

| Compound | Cu–O | Cu–N | O(1)–C(2) | N(1)–C(11) | C(1)–C(11) |
|---|---|---|---|---|---|
| (1) | 1·91 | 1·90 | 1·31 | 1·28 | 1·44 |
| (2) | 1·90 | 1·90 | 1·32 | 1·31 | 1·44 |
| (3) | 1·90 | 2·02 | 1·30 | 1·31 | 1·46 |
| (4) | 1·88 | 1·98 | 1·30 | 1·29 | 1·42 |
| | C(1)–C(2) | C(1)–C(9) | C(2)–C(3) | C(3)–C(4) | |
| (4) | 1·38 | 1·45 | 1·41 | 1·33 | |
| (5) | 1·36 | 1·43 | 1·42 | 1·36 | |
| | C(4)–C(10) | C(5)–C(10) | C(5)–C(6) | C(6)–C(7) | |
| (4) | 1·41 | 1·39 | 1·33 | 1·41 | |
| (5) | 1·43 | 1·43 | 1·36 | 1·42 | |
| | C(7)–C(8) | C(8)–C(9) | C(9)–C(10) | | |
| (4) | 1·40 | 1·40 | 1·42 | | |
| (5) | 1·36 | 1·43 | 1·41 | | |

Compounds: (1) bis(salicylideneiminato)copper(II);[11] (2) α-bis-(*N*-methylsalicylideneiminato)copper(II);[6] (3) bis-(*N*-n-butylsalicylideneiminato)copper(II);[19] (4) present complex; (5) naphthalene.[20]

What is surprising about the geometry is the small size of the molecular ' step.' Table 6, listing planes of best fit, shows that it is only 0·19 Å and that the dihedral angle between the naphthalene and co-ordination planes is also small (2·9°). Table 7 compares the height of the step in a number of complexes; only bis(salicylideneiminato)-copper(II) has a similarly small value (0·29 Å). There is another similarity with this last-named complex in that there are no intermolecular approaches of any significance. Thus the δ-isomer is almost planar and purely four-co-ordinate, with no severe intermolecular restrictions forcing such a geometry. The molecule thus shows

TABLE 6

Equations of plane of best fit of naphthalene atoms, in the form $lX + mY + nZ + p = 0$, referred to orthogonal axes by the transformation $X = x + z \cos \beta$, $Y = y$, $Z = z \sin \beta$. Deviations (Å) of atoms from the plane are given

Plane: C(1)–(10)

Equation: $0.6762X + 0.5318Y - 0.05099Z - 0.0933 = 0$

Deviations: C(1)* 0·011, C(2)* −0·018, C(9)* 0·011, Cu −0·094, O(1) −0·051, N(1) 0·038, C(11) 0·041, C(12) 0·090

* Deviates from plane by >0·01 Å.

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[19] D. Hall, R. H. Summer, and T. N. Waters, *J. Chem. Soc.* (*A*), 1969, 420.

[20] D. W. J. Cruickshank, *Acta Cryst.*, 1957, **10**, 504.

the ' symptoms ' of an enhanced ligand-field strength without the shortened Cu–N bond of the unsubstituted salicylideneiminato-complex or hydrogen bonding to donor oxygens.

TABLE 7

Planarity of selected copper(II) complexes

| Complex | Height of molecular ' step '/Å |
|---|---|
| α-Cu(sal)$_2$ [a] | 0·39 |
| β-Cu(sal)$_2$ [b] | 0·37 |
| Cu(*N*-H-salim)$_2$ [c] | 0·29 |
| Cu(*N*-Bu$^n$-salim)$_2$ [d] | 0·74 |
| Cu(*N*-Ph-salim)$_2$ [e] | 0·89 |
| β-Cu(*N*-Me-naphthim)$_2$ [f] | 1·16 |
| γ-Cu(*N*-Me-naphthim)$_2$ [g] | 1·06 |
| Present complex | 0·19 |

[a] A. J. McKinnon, T. N. Waters, and D. Hall, *J. Chem. Soc.*, 1964, 3290. [b] Ref. 2. [c] Ref. 11. [d] Ref. 19. [e] L. Wei, R. M. Stogsdill, and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1058. [f] Ref. 13. [g] Ref. 14. Ligand abbreviations: sal = salicylaldehydato; salim = salicylaldiminato; naphthim = naphthaldiminato.

Figure 2 given an edge-on view of the asymmetric half of the molecule to illustrate this overall planarity and also to indicate how the methyl hydrogen atoms are placed with respect to this plane. The steric importance of the hydrogen atoms on the nitrogen substituent has been noted in another context.[3] Here they span the neighbouring oxygen donors and must provide some stabilising force in the maintenance of molecular planarity. It is interesting that this planarity is associated with unambiguous four-co-ordination so that it appears as if the ligand-field strength of the donors is enhanced. We interpret this by supposing that double bonding with the metal is increased by facilitating $d_\pi$–$p_\pi$, or perhaps $4p_z$–$p_\pi$, overlap.[4] Molecular planarity and ' extra ' co-ordination are therefore closely linked in these complexes and a change in planarity is, in itself, enough to alter the bonding at the metal centre without the intervention of a primary electronic interaction such as a hydrogen bond. In these terms the very weak axial interactions (Cu · · · Cu 3·33 Å) seen in α-bis-(*N*-methylsalicylideneiminato)copper(II) [6] become explicable. Here the molecules lie in mirror planes so that the methyl hydrogens must again be oriented to span oxygen donors. (The alternative to having the in-plane hydrogen adjacent to a donor is unlikely since O · · · H would be *ca.* 2·0 Å.)

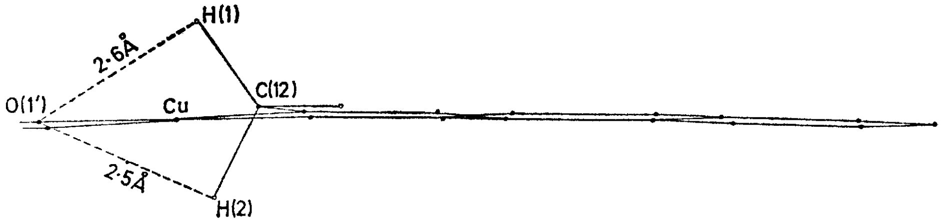

FIGURE 2 An ' edge-on ' view of one ligand and the co-ordination centre

The balancing forces, apart from 'non-bonding interactions,' responsible for crystal structure and polymorphism in these complexes are now becoming clear. The most obvious is that associated with ' extra ' co-ordination to the vacant metal positions, but the presence and extent of this bonding is seen to be dependent on the ligand-field strength of the in-plane donors. This latter factor is itself sensitive to molecular planarity, a state generally opposed by steric interactions between adjacent donors and their substituents but which, as in the compound herein described, is sometimes maintained by steric forces.

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