# Properties and Structural Characterization of Copper(II) Mixed Complexes with 2,2′-Bipyridyl and Iminodiacetate or Pyridine-2,6-dicarboxylate

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*X*-Ray analysis of the mixed complexes $[Cu(bipy)(ida)]\cdot 6H_2O$ (1) and $[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$ (2b) (bipy = 2,2′-bipyridyl, ida = iminodiacetate, and pydca = pyridine-2,6-dicarboxylate) shows that different stereochemistries are involved in the solid state in spite of the similarity of the two chromophores around the copper(II) ion. In the crystals of (1) the copper is five-co-ordinate and the co-ordination polyhedron may be described as a distorted square pyramid. The crystal structure of (2b) consists of binuclear units in which $Cu(bipy)_2$ and $Cu(pydca)_2$ moieties are bound through an oxygen bridge, the former having a distorted square-pyramidal geometry, the latter a trigonal-bipyramidal arrangement. Cell parameters: (1) $a = 11.200(7)$, $b = 13.252(8)$, $c = 7.975(7)$ Å, $\alpha = 66.8(1)$ $\beta = 115.3(1)$, $\gamma = 102.0(1)°$, triclinic, space group $P\bar{1}$; (2b) $a = 13.103(6)$, $b = 17.815(7)$, $c = 15.302(7)$, $\beta = 90.8(2)°$, monoclinic, space group $P2_1/c$. Both structures have been solved by conventional Patterson and Fourier methods and refined to *R* factors of 0.043 and 0.041 respectively.

IT is well known that copper(II) complexes can display various co-ordination polyhedra, the usual co-ordination number varying from four to six.[1] While many reports on the crystal and molecular structures of simple copper(II) complexes have appeared, relatively few cases concern ternary complexes. Recently, some structures of copper(II) compounds containing two different organic ligands have been determined,[2-8] because of the important role played by ternary complexes in biological systems.[9] Also of interest are systems where the $Cu^{II}$ is bound to two chelating ligands; in particular, the way in which each ligand influences the formation of a typical structure.

The thermodynamic and spectroscopic properties of copper(II) mixed complexes with 2,2′-bipyridyl (bipy) and some dicarboxylic acids have been studied by some of us in order to obtain information on their bonding and geometries in aqueous solution.[10-12] We have now extended these studies to the solid state and report here the structure of the ternary complexes $[Cu(bipy)(ida)]\cdot 6H_2O$ and $[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$ (where ida and pydca are iminodiacetate and pyridine-2,6-dicarboxylate, respectively). The structure of these ternary complexes is of interest since thermodynamic functions, e.s.r. and electronic spectroscopic parameters [12] have shown that these tridentate ligands are arranged differently around $[Cu(bipy)]^{2+}$, giving rise to different stereochemistries and co-ordination numbers.

## EXPERIMENTAL

B.D.H. Iminodiacetic acid, Fluka purum pyridine-2,6-dicarboxylic acid, and Merck analytical grade 2,2′-bipyridyl were employed in the preparation of the mixed complexes. All solvents used were reagent grade.

*Preparation and Characterization of the Complexes.*—The [Cu(ida)] and [Cu(pydca)] salts were used as starting materials in the synthesis of the mixed complexes with 2,2′-bipyridyl; their preparation is described elsewhere.[13,14] Suitable crystals were obtained in the case of [Cu(bipy)(ida)] (1) by dissolving the microcrystalline powder in water–ethanol and slowly evaporating the solution. In the case of the preparation of crystals from $[Cu(bipy)(pydca)]\cdot 2H_2O$ powder (2), obtained following the procedure of Murtha and Walton,[14] a complication arose, since different products could be synthesized from an ethanolic solution of the mixed complex. From our previous potentiometric [15] and e.s.r. studies [12] there was no doubt that only one species predominated in aqueous or aqueous alcohol solutions. This species was the mixed complex [Cu(bipy)(pydca)]. When the complex was crystallized at room temperature from a dilute solution a product (2a) was obtained. (A large amount of n-butanol was added to the complex dissolved in ethanol, avoiding immediate precipitation, and after 1 week blue crystals were formed.) If the complex was crystallized from a hot (50—60 °C) ethanol solution, blue-green crystals (2b) were obtained before the solution dried up. The same product was also formed when the blue powder was dissolved in water and the solution evaporated to a volume of 1—3 cm³; air-drying left a vitreous material which dissolved in ethanol and slowly evaporated at 50—60 °C to yield blue-green crystals. Product (2a) transformed into (2b) when dissolved in ethanol. This behaviour can be ascribed to the following dismutation reaction.

$$\underset{(2a)}{2[Cu(bipy)(pydca)]\cdot 2H_2O} \rightleftharpoons \underset{(2b)}{[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O}$$

Analytical data and i.r. spectra of these products did not show any difference between them, in contrast to the visible-reflectance and powder e.s.r. spectra (see Figures 1 and 2). The thermoanalytical behaviour of the two species was also different (Figure 3). Loss of water molecules occurred at different temperatures; in particular, the temperature of initial dehydration of product (2a) was 110 °C,[16] but 70 °C for (2b). The mass loss was different for the complexes, but the above temperatures suggested that one water molecule was bound to the copper(II) ion in (2a), while for the (2b) the water molecules were not co-ordinated. When dissolved in water, ethanol, or n-butanol both (2a) and (2b) yielded the same species, the spectral patterns being the same in these solvents [13 890 (41) in water, 13 250 (83) in ethanol, and 13 120 $cm^{-1}$ (100 $dm^3$ $mol^{-1}$ $cm^{-1}$) in n-butanol]. A molecular-weight determination carried out on a n-butanol solution of both products gave a mean value of 401—403, corresponding to $[Cu(bipy)(pydca)(OH_2)]$.

*Equipment.*—An Optica CF-4-NI spectrophotometer equipped with a standard reflectance attachment, a Varian E-109 e.s.r. spectrometer, a Hewlett-Packard 3028 vapour-pressure osmometer, and a Mettler thermoanalyzer were used for reflectance spectra, e.s.r. powder spectra, molecular-weight determination, and thermal analysis respectively.

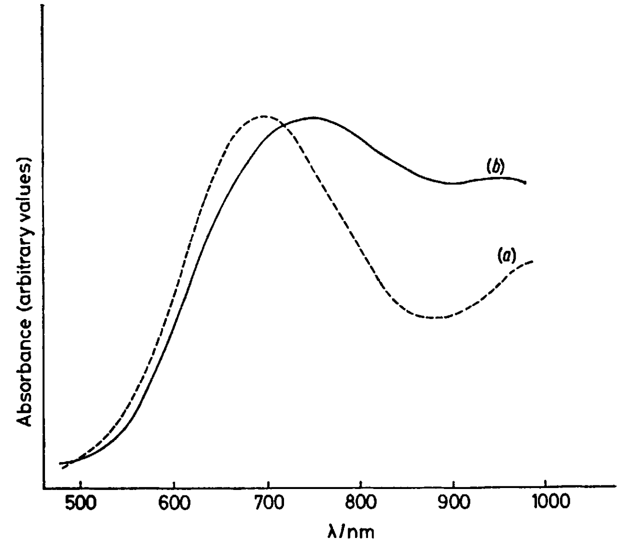

FIGURE 1 Visible-reflectance spectra of [Cu(bipy)(pydca)]·$2H_2O$ (*a*) and $[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$ (*b*). There are many absorption peaks in the spectrum (*b*), the main ones being at 15 040, 14 183, 13 300, and 10 410 $cm^{-1}$; two significant absorptions are present in the spectrum (*a*) at 14 080 and 10 200 $cm^{-1}$

*Crystal Data*.—(1), $C_{14}H_{12}CuN_3O_4\cdot 6H_2O$, $M = 457.6$, Triclinic, space group $P\bar{1}$ (from the final refinement), $a = 11.200(7)$, $b = 13.252(8)$, $c = 7.975(7)$ Å, $\alpha = 66.8(1)$, $\beta = 115.3(1)$, and $\gamma = 102.0(1)°$, $U = 982.3$ Å$^3$, $D_m = 1.57$, $Z = 2$, $F(000) = 476$, $D_c = 1.55$ g $cm^{-3}$, $\mu$(Mo-$K_\alpha$) = 11.6 $cm^{-1}$, $\lambda = 0.710\ 7$ Å.

(2b), $C_{34}H_{22}Cu_2N_6O_8\cdot 4H_2O$, $M = 841.4$, Monoclinic, space group $P2_1/c$, $a = 13.103(6)$, $b = 17.815(7)$, $c = 15.302(7)$ Å, $\beta = 90.8(2)°$, $U = 3\ 571.6$ Å$^3$, $D_m = 1.58$, $Z = 4$, $F(000) = 1\ 720$, $D_c = 1.57$ g $cm^{-3}$, $\mu$(Mo-$K_\alpha$) = 13.1 $cm^{-1}$, $\lambda = 0.710\ 7$ Å.

Cell parameters for both (1) and (2b) were determined from Weissenberg and precession photographs, and refined by a least-squares fit of the 2θ, χ, and φ setting angles of the Siemens AED diffractometer for 20 accurately centred reflections. Intensity data were collected by the θ—2θ scan mode with Mo-$K_\alpha$ radiation to $\theta_{max.} = 27°$ for both crystals. Reflections with $I \leqslant 3\sigma(I_0)$ were rejected; the remainder, 3 735 (1) and 4 472 (2b), were corrected for Lorentz-polarization factors and used in the subsequent calculations. No absorption correction was applied, since the crystals used were approximately parallelepipeds with nearly equal edges [0.5 (1) and 0.4 mm (2b)].

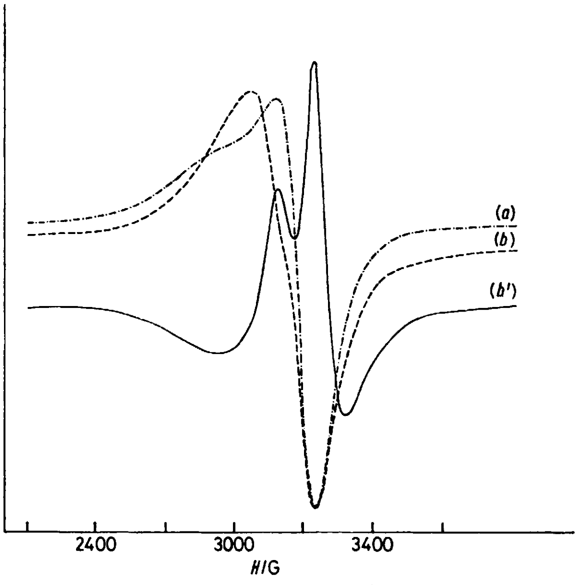

FIGURE 2 E.s.r. powder spectra of [Cu(bipy)(pdyca)]·$2H_2O$ (*a*), $[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$ (*b*), and second-derivative e.s.r. spectrum of the latter compound (*b'*) at 130 K (1 G = $10^{-4}$ T)

*Structure Determination and Refinement*.—Both structures were solved by conventional Patterson and Fourier methods. After the anisotropic refinement, a three-dimensional difference Fourier synthesis was calculated to locate H atoms. Calculated positions of all the latter occurred in positive regions of the electron-density map. The final anisotropic block-diagonal matrix least-squares refinement, including the fixed contribution of hydrogen atoms ($B = 5$ Å$^2$), gave $R$ 0.043 for (1) and 0.041 for (2b). The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$, where $A = 2.7$ and $B = 0.008$ for (1) and $A = 24.0$ and $B = 0.006$ for (2b) were chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta)/\lambda$. The numbering schemes for (1) and (2b) are shown in Figures 4 and 7 respectively. Final co-ordinates are listed in Tables 1 and 2 for (1) and (2b), observed and calculated structure factors and anisotropic temperature factors are given in Supplementary Publication No. SUP 22664 (40 pp.).* Atomic scattering factors were those of Moore.[17]

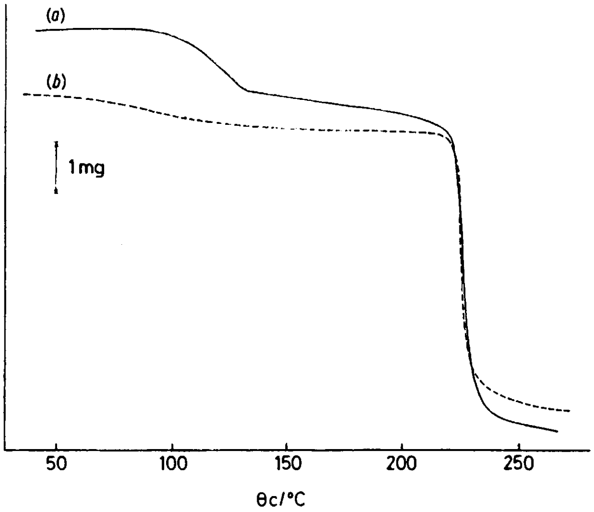

FIGURE 3 Thermal gravimetric curves at φ = 2 °C $min^{-1}$ of 13.3 mg of [Cu(bipy)(pydca)]·$2H_2O$ (*a*) and of 11.1 mg of $[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$ (*b*)

## RESULTS AND DISCUSSION

*Structure of* (1).—The crystals of (1) consist of molecules [Cu(bipy)(ida)], in which the copper is five-co-ordinate as shown in Figure 4. The co-ordination polyhedron around the metal atom may be described as a distorted square pyramid, with the bidentate bipy ligand [Cu–N(1) 1.989(3), Cu–N(2) 2.026(3) Å] and the N(3) and O(3) atoms of the tridentate ida ligand in the basal positions [Cu–N(3) 2.034(2), Cu–O(3) 1.952(2) Å]. The O(2) atom of ida occupies the apical position

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

[Cu-O(2) 2.249(2) Å]. The atoms of the basal plane are displaced from it by −0.16 to 0.16 Å with a tetrahedral distortion, and the copper atom is displaced by 0.075 Å from the mean plane towards O(2). Such distortion has been already discussed for other copper(II) compounds, particularly those of small peptides.[18]

The whole bipy ligand is nearly planar, the torsion angle between the two pyridine rings being 1°. The tridentate dianionic ligand ida is arranged in such a way that its two chemically equivalent halves (planar within ±0.02 and ±0.15 Å respectively) are bent along the Cu-N(3) direction, making an angle of 105°. In contrast with other tridentate ligands such as pydca (see below) and glycylglycinate(2−) (Ogly-glyO),[5,19] where the trigonal nature of the central nitrogen requires the whole ligand to be either planar or slightly bent, the

TABLE 1

Atomic fractional co-ordinates ($\times 10^4$) of compound (1)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu | 3 592(0) | 1 161(0) | 1 116(0) |
| O(1) | 5 408(3) | 3 718(3) | −2 207(4) |
| O(2) | 4 374(2) | 2 104(2) | −1 226(3) |
| O(3) | 5 097(2) | 224(2) | 2 869(3) |
| O(4) | 7 099(3) | 126(2) | 5 281(4) |
| A(1) | 3 020(4) | 1 918(3) | 5 005(5) |
| A(2) | 1 436(3) | 3 569(3) | 4 158(5) |
| A(3) | 8 711(3) | 3 722(3) | 2 706(5) |
| A(4) | 7 557(4) | 5 032(3) | 3 543(5) |
| A(5) | 5 234(4) | 4 024(3) | 4 089(4) |
| A(6) | 7 965(5) | 4 687(4) | 8 728(6) |
| N(1) | 1 827(3) | 1 867(2) | −150(4) |
| N(2) | 2 495(2) | 82(2) | −121(4) |
| N(3) | 4 764(2) | 2 316(2) | 2 308(3) |
| C(1) | 1 566(3) | 2 778(3) | −37(5) |
| C(2) | 336(4) | 3 228(3) | −1 114(6) |
| C(3) | −649(4) | 2 731(3) | −2 351(6) |
| C(4) | −398(3) | 1 766(3) | −2 459(5) |
| C(5) | 859(3) | 1 366(3) | −1 327(4) |
| C(6) | 1 237(3) | 348(3) | −1 310(4) |
| C(7) | 376(3) | −289(3) | −2 413(5) |
| C(8) | 836(4) | −1 230(3) | −2 266(5) |
| C(9) | 2 137(4) | −1 501(3) | −1 055(5) |
| C(10) | 2 945(3) | −835(3) | 14(5) |
| C(11) | 4 984(4) | 3 285(3) | 678(4) |
| C(12) | 4 927(3) | 3 001(3) | −1 041(4) |
| C(13) | 5 996(3) | 1 788(3) | 3 890(5) |
| C(14) | 6 079(3) | 629(3) | 4 105(4) |
| H(C1) | 2 350 | 3 180 | 940 |
| H(C2) | 150 | 3 970 | −980 |
| H(C3) | −1 620 | 3 090 | −3 250 |
| H(C4) | −1 170 | 1 340 | −3 410 |
| H(C7) | −650 | −50 | −3 380 |
| H(C8) | 170 | −1 750 | −3 100 |
| H(C9) | 2 520 | −2 230 | −940 |
| H(C10) | 3 970 | −1 050 | 990 |
| H1(C11) | 4 220 | 3 870 | 100 |
| H2(C11) | 5 960 | 3 670 | 1 300 |
| H1(C13) | 6 850 | 2 290 | 3 600 |
| H2(C13) | 6 000 | 1 750 | 5 300 |
| H1(A1) | 3 600 | 2 200 | 6 150 |
| H2(A1) | 2 250 | 1 350 | 5 500 |
| H1(A2) | 1 700 | 4 150 | 3 000 |
| H2(A2) | 1 700 | 2 750 | 4 300 |
| H1(A3) | 8 400 | 4 160 | 3 300 |
| H2(A3) | 8 500 | 4 100 | 1 300 |
| H1(A4) | 7 000 | 4 500 | 4 250 |
| H2(A4) | 8 000 | 5 600 | 4 200 |
| H1(A5) | 5 200 | 3 800 | 5 400 |
| H2(A5) | 5 000 | 4 800 | 3 400 |
| H1(A6) | 7 150 | 4 150 | 8 200 |
| H2(A6) | 7 450 | 5 450 | 8 400 |
| H(N3) | 4 300 | 2 500 | 3 100 |

TABLE 2

Atomic fractional co-ordinates ($\times 10^4$) of compound (2b)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu(1) | 2 579(0) | 4 333(0) | 3 609(0) |
| Cu(2) | 2 551(0) | 4 218(0) | 883(0) |
| O(1) | 4 578(2) | 3 850(2) | 3 122(2) |
| O(2) | 3 166(2) | 4 201(2) | 2 401(2) |
| O(3) | 4 025(3) | 3 732(2) | −1 435(2) |
| O(4) | 2 841(2) | 4 263(2) | −592(2) |
| O(5) | 634(3) | 2 456(2) | 615(3) |
| O(6) | 2 065(2) | 3 125(2) | 796(2) |
| O(7) | 1 381(2) | 6 284(2) | 1 387(3) |
| O(8) | 2 502(2) | 5 374(2) | 1 078(2) |
| W(1) | 5 400(3) | 2 439(2) | 3 571(3) |
| W(2) | 7 475(3) | 2 514(2) | 3 908(3) |
| W(3) | 7 797(4) | 3 016(4) | 2 124(4) |
| W(4) | 8 501(3) | 2 082(2) | 550(4) |
| N(1) | 3 017(3) | 4 190(2) | 4 898(2) |
| N(2) | 3 291(2) | 5 307(2) | 3 803(2) |
| N(3) | 1 068(3) | 4 758(2) | 3 570(2) |
| N(4) | 1 806(3) | 3 387(2) | 3 444(2) |
| N(5) | 4 040(2) | 4 045(2) | 841(2) |
| N(6) | 1 119(2) | 4 364(2) | 992(2) |
| C(1) | 2 871(4) | 3 582(3) | 5 399(3) |
| C(2) | 3 209(4) | 3 554(3) | 6 271(3) |
| C(3) | 3 698(4) | 4 173(4) | 6 636(3) |
| C(4) | 3 850(4) | 4 814(3) | 6 119(3) |
| C(5) | 3 499(3) | 4 800(3) | 5 247(3) |
| C(6) | 3 627(3) | 5 440(2) | 4 633(3) |
| C(7) | 4 456(4) | 6 211(3) | 4 876(3) |
| C(8) | 4 139(4) | 6 680(3) | 4 244(4) |
| C(9) | 3 824(4) | 6 537(3) | 3 387(3) |
| C(10) | 3 400(3) | 5 845(2) | 3 183(3) |
| C(11) | 748(4) | 5 468(3) | 3 723(4) |
| C(12) | −265(4) | 5 654(3) | 3 781(4) |
| C(13) | −981(4) | 5 089(4) | 3 655(5) |
| C(14) | −664(4) | 4 375(3) | 3 489(5) |
| C(15) | 366(3) | 4 211(2) | 3 468(3) |
| C(16) | 783(3) | 3 451(2) | 3 330(3) |
| C(17) | 189(4) | 2 839(3) | 3 101(4) |
| C(18) | 651(4) | 2 139(3) | 3 005(3) |
| C(19) | 1 683(4) | 2 065(3) | 3 152(3) |
| C(20) | 2 239(4) | 2 706(2) | 3 365(3) |
| C(21) | 4 634(3) | 3 983(2) | 1 570(3) |
| C(22) | 4 096(3) | 4 010(2) | 2 432(3) |
| C(23) | 5 684(3) | 3 901(3) | 1 517(3) |
| C(24) | 6 129(3) | 3 896(3) | 693(3) |
| C(25) | 5 513(3) | 3 940(3) | −58(3) |
| C(26) | 4 457(3) | 4 003(2) | 43(3) |
| C(27) | 3 710(3) | 4 012(3) | −734(3) |
| C(28) | 504(3) | 3 767(2) | 891(3) |
| C(29) | 1 103(3) | 3 041(2) | 750(3) |
| C(30) | −546(3) | 3 854(3) | 926(3) |
| C(31) | −936(3) | 4 579(3) | 1 056(4) |
| C(32) | −274(3) | 5 186(3) | 1 161(3) |
| C(33) | 760(3) | 5 055(2) | 1 122(3) |
| C(34) | 1 614(3) | 5 628(2) | 1 198(3) |
| H(1) | 2 476 | 3 087 | 5 111 |
| H(2) | 3 100 | 3 038 | 6 658 |
| H(3) | 3 963 | 4 164 | 7 329 |
| H(4) | 4 235 | 5 320 | 6 391 |
| H(7) | 4 320 | 6 221 | 5 590 |
| H(8) | 4 454 | 7 238 | 4 427 |
| H(9) | 3 908 | 6 973 | 2 875 |
| H(10) | 3 149 | 5 726 | 2 500 |
| H(11) | 1 327 | 5 918 | 3 802 |
| H(12) | −503 | 6 238 | 3 920 |
| H(13) | −1 807 | 5 214 | 3 675 |
| H(14) | −1 225 | 3 901 | 3 379 |
| H(17) | −644 | 2 905 | 2 996 |
| H(18) | 195 | 1 647 | 2 805 |
| H(19) | 2 059 | 1 512 | 3 100 |
| H(20) | 3 068 | 2 655 | 3 486 |
| H(23) | 6153 | 3 834 | 2 119 |
| H(24) | 6 969 | 3 856 | 635 |
| H(25) | 5 854 | 3 922 | −719 |
| H(30) | −1 055 | 3 362 | 847 |
| H(31) | −1 773 | 4 671 | 1 076 |
| H(32) | −563 | 5 760 | 1 280 |

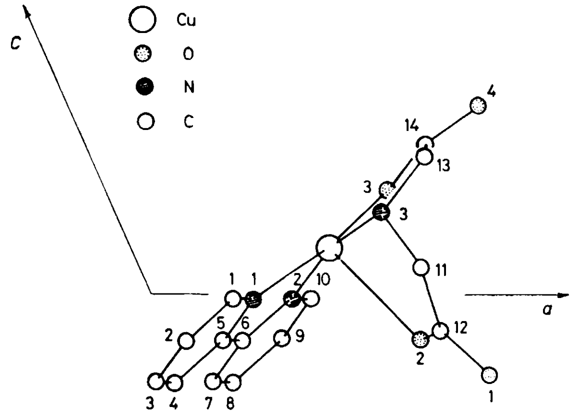
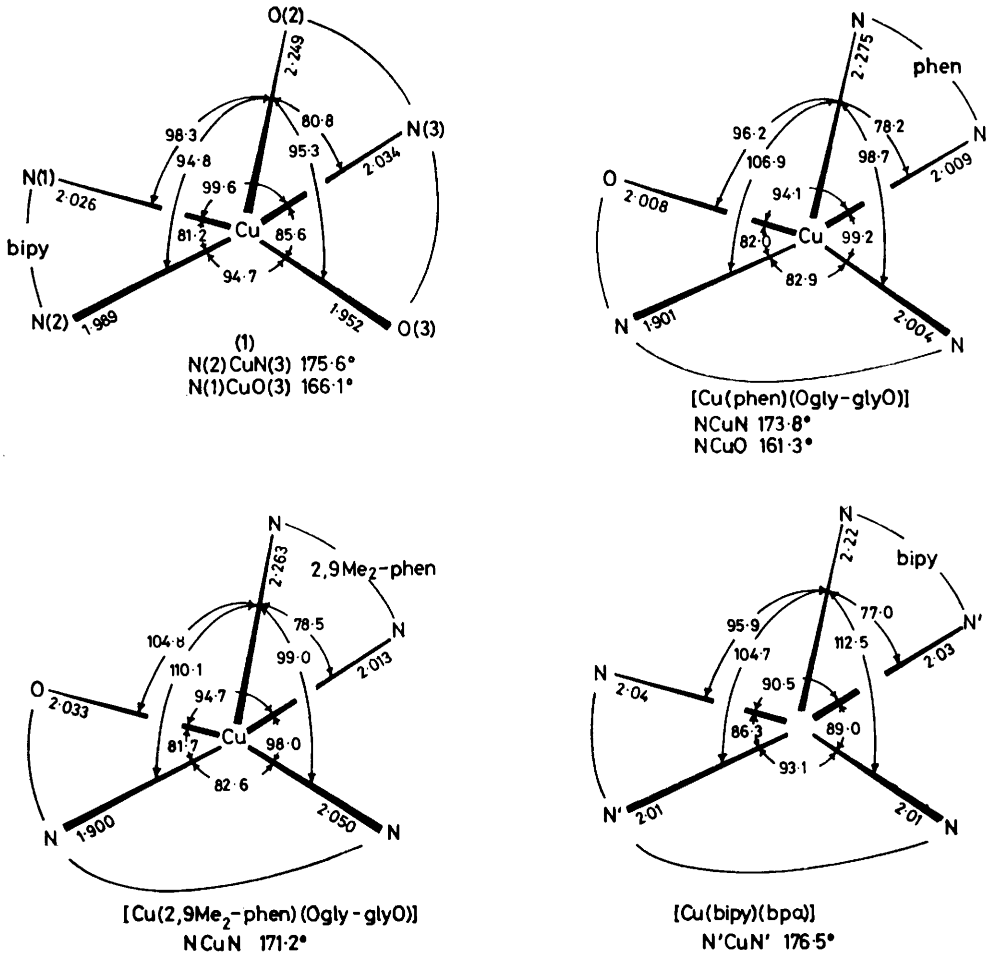


FIGURE 4 Side view of (1) along the *b* axis, together with the atom-numbering scheme

tetrahedral nature of N in ida, associated with the geometrical requirements of the two five-membered rings formed upon co-ordination, imposes a much greater bending. Thus the bipy ligand occupies two basal positions and ida the other two basal and the apical positions, whereas in [Cu(phen)(Ogly-glyO)] and [Cu-(2,9Me$_2$-phen)(Ogly-glyO)] (phen = 1,10-phenanthroline, 2,9Me$_2$-phen = 2,9-dimethyl-1,10-phenanthroline) the bidentate ligand occupies only one basal and the apical position. That the tetrahedral nature of N is not sufficient to ensure co-ordination as in (1) is demonstrated by the co-ordination polyhedron of [Cu(bipy)(bpa)]$^{2+}$ [bpa = bis(3-aminopropyl)amine].[20] In this compound the tridentate ligand occupies three basal positions, whereas the bipy ligand occupies one basal and the apical positions of a distorted square pyramid. The ' full ' basal co-ordination of the tridentate ligand results in a more distorted square-pyramidal arrangement as is shown by a comparison of co-ordination bond lengths and angles in such compounds with those of [Cu(bipy)(ida)] (Figure 5). It is also of interest to compare the geometry of the neutral ligand H$_2$ida with the co-ordinated dianion ida.[21] Besides the different conformations, which determine the angles between the two halves of the molecule [105° in (1) and 41° in H$_2$ida], the N–C and C–C distances and CNC angles are very similar in both molecules (Table 3). The CCN



(1)
N(2)CuN(3) 175·6°
N(1)CuO(3) 166·1°

[Cu(phen)(Ogly-glyO)]
NCuN 173·8°
NCuO 161·3°

[Cu(2,9Me$_2$-phen)(Ogly-glyO)]
NCuN 171·2°
NCuO 154·8°

[Cu(bipy)(bpa)]
N'CuN' 176·5°
NCuN 150·7°

FIGURE 5 Comparison of the co-ordination geometries in the five-co-ordinate compounds (1) [Cu(bipy)(bpa)], [Cu(phen) (Ogly-glyO)], and [Cu(2,9Me$_2$-phen)(Ogly-glyO)]. Estimated standard deviations of bond angles are 0.1 [complex (1)] and 0.5–0.7, 0.2, and 0.08° in pba, phen, and 2,9Me$_2$-phen respectively angles are slightly larger [113.5(3)° (mean)] in ida than in $H_2$ida. On the other hand, deprotonation of $H_2$ida, followed by co-ordination to copper, provokes significant variations in the $CO_2$ groups. Bond lengths and angles (Table 4) indicate that these two groups, which are not equivalent in $H_2$ida, one being formulated as $CO_2^-$ and the other as $CO_2H$, become equivalent in ida. We observe that the bond O(3)–C(14) [1.271(4) Å] is slightly longer than O(2)–C(12) [1.254(5) Å] and the Cu–O(3) distance of 1.952(2) Å is correspondingly shorter than the Cu–O(2) distance of 2.249(2) Å.

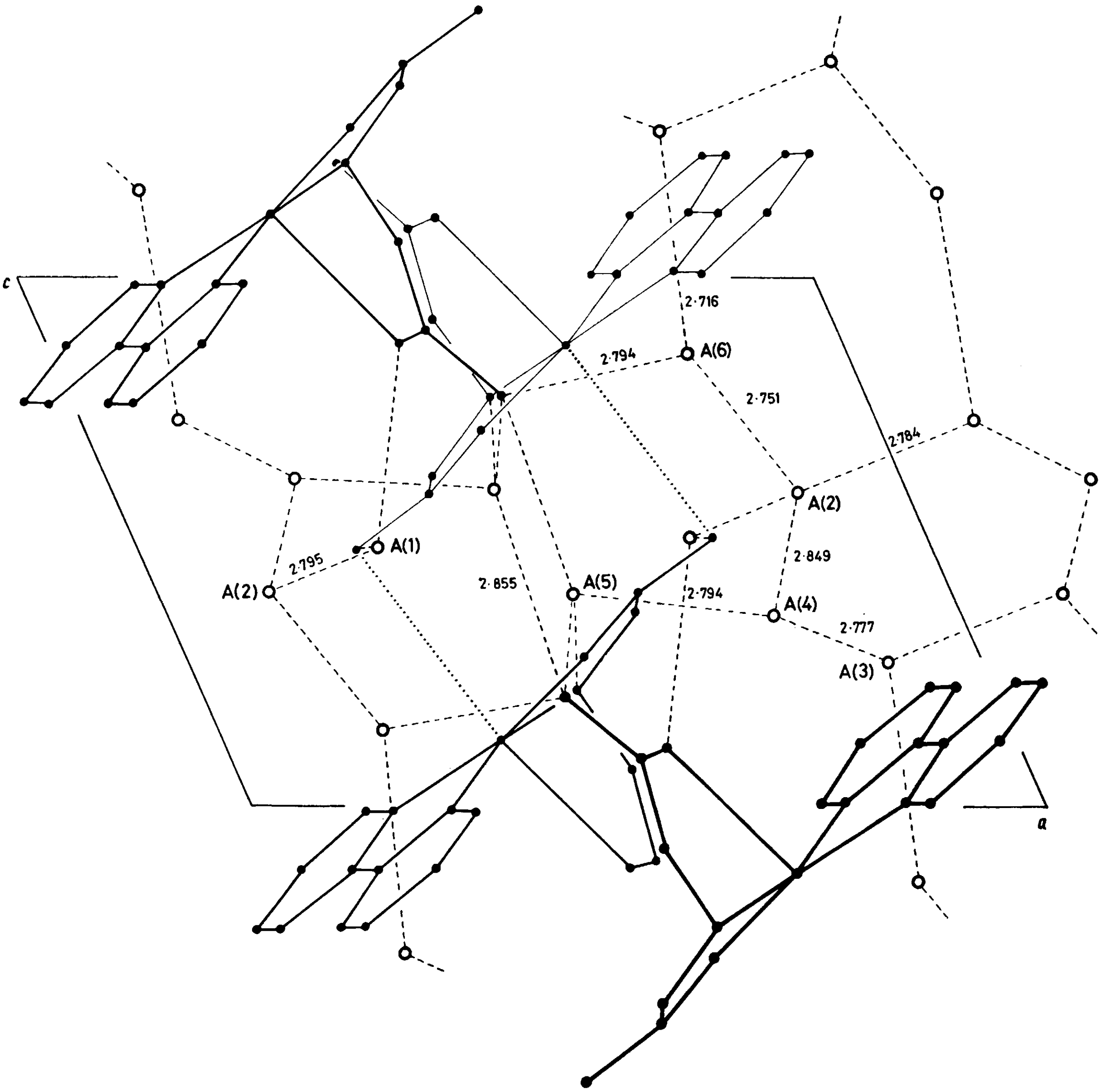


FIGURE 6 Crystal packing of (1) showing also the hydrogen-bonding network

The crystal packing (Figure 6) may be described as built up by dimeric [{Cu(bipy)(ida)}$_2$] species arranged around the symmetry centre at $x = \frac{1}{2}, y = 0, z = \frac{1}{2}$ and loosely bound by further co-ordination of the O(4) atom of one molecule to the sixth vacant position of the copper atom of the other molecule (Figure 6), with distances Cu–O(4) $(1 - x, \bar{y}, 1 - z)$ of 3.008(4) Å. The dimers, arranged approximately along the *c* axis, are held together by van der Waals contacts and by hydrogen bonds formed both between the O and N atoms of the complex and the water molecules with A(1) and A(5) (Figure 6). The remaining four water molecules of crystallization form corrugate double chains of hydrogen-bonded molecules running along the crystallographic *c* axis of the cell. The double chain is formed by two single chains $\cdots$ A(3)–A(4)–A(2)–A(6) $\cdots$, with O $\cdots$ O distances ranging from 2.716(5) to 2.849(6) Å, cross-linked by hydrogen bonds of 2.784(5) Å every two water molecules along the single chain. Thus the double chain is built up by six-membered rings of two kinds sharing a side and arranged around the symmetry centres at

$x = 0$. Finally, the double chain forms further hydrogen bonds with A(5) and O(1) (Figure 6).

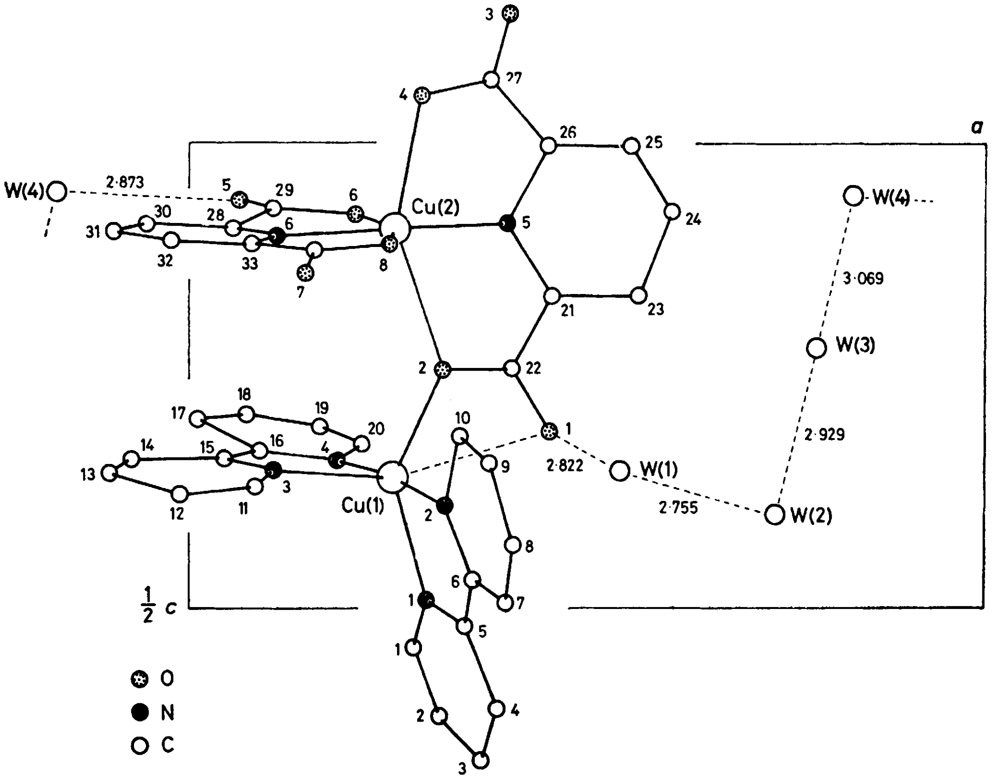


FIGURE 7 View of (2b) along the *b* axis together with the atom-numbering scheme

TABLE 3

Comparison of the free and co-ordinated ida ligand. The numbering scheme is that of Figure 4. O(1) bears the H atom in $H_2$ida

| | $H_2$ida | ida |
|---|---|---|
| (*a*) Bond lengths (Å) | | |
| C–N (mean) | 1.489(2) | 1.488(4) |
| C–C (mean) | 1.517(2) | 1.526(6) |
| C(12)–O(1) | 1.306(2) | 1.255(4) |
| C(12)–O(2) | 1.202(2) | 1.254(5) |
| C(14)–O(3) | 1.267(2) | 1.253(4) |
| C(14)–O(4) | 1.229(2) | 1.271(4) |
| (*b*) Bond angles (°) | | |
| C(1)–C(2)–O(1) | 114.6(2) | 116.3(3) |
| C(1)–C(2)–O(2) | 122.6(2) | 118.7(3) |
| O(1)–C(2)–O(2) | 125.8(2) | 125.0(4) |
| C(3)–C(4)–O(3) | 114.2(2) | 118.0(3) |
| C(3)–C(4)–O(4) | 119.9(2) | 117.6(3) |
| O(3)–C(4)–O(4) | 125.9(2) | 124.4(4) |
| CNC | 115.4(1) | 114.0(3) |
| NCC (mean) | 110.5(1) | 113.5(3) |

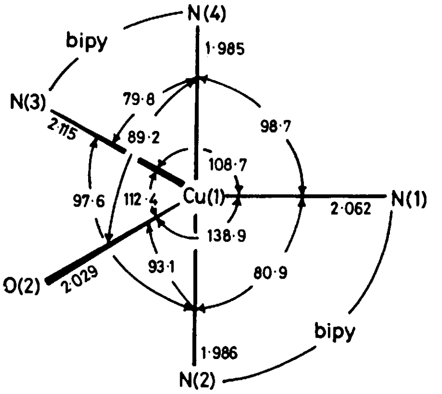


FIGURE 8 Geometrical parameters of the co-ordination around Cu(1) in (2b). Estimated standard deviations are 0.2 °C for bond angles and 0.003—0.004 Å for bond lengths

*Structure of* (2b).—The crystal structure of (2b) consists of binuclear units, one of which is shown in Figure 7. One copper atom is co-ordinated by two bipy molecules and by the O(2) atom of the one pydca ligand with a distorted bipyramidal arrangement, where O(2) occupies an equatorial position (Figure 8). The two bipy ligands are nearly planar, with small torsion angles of 4.3 and 9.8° between the two pyridine residues. The equatorial donor atoms are coplanar with Cu(1), as shown by the sum of equatorial angles at Cu(1)(360.0°). The two bipy molecules are symmetrically bonded to the metal, the axial Cu–N distances being *ca.* 0.1 Å shorter than the equatorial ones. The compression along the axial direction is a well known effect in bipyramidal copper(II) complexes. The Cu(1)–O(1) contact of 2.866(3) Å may be indicative of a possible interaction between a symmetrically chelated carboxyl group and copper. The other crystallographically independent copper atom is co-ordinated by two tridentate pydca units in a distorted octahedral environment, in the same way as that found in $[Cu(Hpydca)_2]$ [22] and with similar co-ordination bond lengths and angles (Table 4). The equatorial donors are coplanar within ±0.003 Å with Cu(2) displaced 0.058 Å from their mean plane towards O(4). This plane makes an angle of 84.8° with that passing through the O(2), O(4), N(5), and N(6) atoms, which are coplanar within ±0.08 Å. It is worth noting that one pydca ligand acts both as a chelating and bridging ligand, as already observed in $[\{Cu(pydca)(OH_2)_2\}_2]$.[23] In our case, however, the Cu–O distance involving the chelated copper atom Cu(2) [2.447(3) Å] is longer than that involving the bridged Cu(1) [2.029(3) Å], in contrast to the corresponding distances of 2.050(4) and 2.423(3) Å found in $[\{Cu(pydca)(OH_2)_2\}_2]$. The geometry around O(2) indicates its trigonal nature, the sum of the angles at O(2) being 359.8°. The carboxyl groups in the pydca molecule, acting only as a tridentate ligand, are nearly coplanar with their pyridine ring, the torsion angles being 3.1 and 4.6°. In contrast, in the other pydca ligand the torsion angles around C(26)–C(27) and C(21)–C(22) are 22.1 and 11.1° respectively. The C–O distances are indicative of a complete delocalization on to the $CO_2^-$ groups. The four crystallographically independent water molecules are present as crystallization solvent, making hydrogen bonds between themselves and with O(1) and O(5) (Figure 7).

TABLE 4

Comparison of co-ordination bond lengths (Å) and angles (°) between compounds (2) and $[Cu(Hpydca)_2]\cdot H_2O$. Numbering scheme is that of Figure 7. For the latter complex the mean values of two crystallographically independent molecules, together with estimated standard deviations of the single values in parentheses, are reported

| | (2) | $[Cu(Hpydca)_2]\cdot H_2O$ |
|---|---|---|
| (*a*) Distances | | |
| Cu–O(2) | 2.447(3) | 2.39(1) |
| Cu–O(4) | 2.296(3) | 2.31(1) |
| Cu–O(6) | 2.053(3) | 2.04(1) |
| Cu–O(8) | 2.084(3) | 2.04(1) |
| Cu–N(5) | 1.976(3) | 2.00(1) |
| Cu–N(6) | 1.904(3) | 1.90(1) |
| (*b*) Angles | | |
| O(6)–Cu–N(5) | 98.9(1) | |
| O(6)–Cu–N(6) | 80.2(1) | 79.9(4) |
| O(6)–Cu–O(8) | 159.6(1) | 160.4(4) |
| O(6)–Cu–O(4) | 91.3(1) | 91.7(4) |
| O(6)–Cu–O(2) | 98.6(1) | 91.7(4) |
| N(6)–Cu–O(8) | 79.6(1) | 80.5(4) |
| N(6)–Cu–N(5) | 176.6(1) | 178.8(4) |
| N(6)–Cu–O(2) | 103.4(1) | |
| N(6)–Cu–O(4) | 105.0(1) | |
| O(8)–Cu–N(5) | 101.1(4) | |
| O(8)–Cu–O(2) | 83.4(1) | 92.5(4) |
| O(8)–Cu–O(4) | 96.6(1) | 93.8(4) |
| N(5)–Cu–O(2) | 73.5(1) | 76.8(4) |
| N(5)–Cu–O(4) | 78.2(1) | 74.4(4) |
| O(2)–Cu–O(4) | 151.2(1) | 151.1(4) |

These systems, previously investigated in solution,[12] have shown a noteworthy difference in their co-ordination environment; in particular, five-co-ordination in a square-pyramidal structure for the complex [Cu(bipy)(ida)] and six-co-ordination through a water molecule in a distorted octahedral geometry in the case of [Cu(bipy)(pydca)]. The crystal structure of $[Cu(bipy)(ida)]\cdot 6H_2O$ confirms the previous hypothesis, suggested on the basis of thermodynamic, electronic, and e.s.r. spectral data, that the solid structure is preserved in solution. On the other hand, in the case of the pydca complex the co-ordination in the solid state is different from that in solution, probably as a consequence of the ligand rigidity. The *X*-ray pattern obtained for the crystals of $[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$ shows an unusual arrangement around the copper. Two chemically different copper atoms are present in the solid state with no co-ordinated water molecules having co-ordination numbers of six and five. This environment is destroyed in solution (water, ethanol, or n-butanol) giving rise to the mixed octahedral complex $[Cu(bipy)(pydca)(OH_2)]$. This result is in agreement with Murtha and Walton,[14] since the product prepared and characterized by them is our product (2a).

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