# Co-ordination Behaviour of *N*-Protected Aspartic Acid in Binary and Ternary Copper(II) Complexes. Crystal and Molecular Structure of [*N*-Acetyl-L-aspartato(2−)-*O*]bis(2,2′-bipyridine)copper(II)-Ethanol Tetrahydrate†

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The complexes [Cu(bipy)$_2$(acaspOO′)]·EtOH·4H$_2$O (**1**), [Cu(bipy)$_2$(bzaspOO′)]·2H$_2$O (**2**) and [Cu(bipy)$_2$(bzloaspOO′)]·EtOH·H$_2$O (**3**) [bipy = 2,2′-bipyridine, acaspOO′ = *N*-acetyl-L-aspartate(2−), bzaspOO′ = *N*-benzoyl-L-aspartate(2−), and bzloaspOO′ = *N*-benzyloxycarbonyl-L-aspartate(2−)] were synthesized. The crystal and molecular structure of (**1**) has been determined by *X*-ray diffraction. The compound crystallises in the space group $P\bar{1}$, with $a$ = 12.947(4), $b$ = 12.462(4), $c$ = 11.152(3) Å, $\alpha$ = 115.44(6), $\beta$ = 106.53(5), $\gamma$ = 74.32(5)°, and $Z$ = 2. The structure involves monomeric [Cu(bipy)$_2$(acaspOO′)] units with the copper atom in a basically trigonal-bipyramidal stereochemistry. The in-plane co-ordination is from a nitrogen atom of each bipy ligand and a β-carboxylate oxygen of the aspartate anion. Two nitrogen atoms, one from each bipy molecule, are the axial donors. The distortion is toward square-pyramidal stereochemistry with the oxygen atom at the apex. The second oxygen of the β-carboxylate group is at a distance of 2.875(8) Å from copper to give a 4 + 1 + 1* type co-ordination. The crystal packing is determined by hydrogen bonds between water molecules, α-carboxylate and acetyl groups, and ethanol molecules. The stack between symmetry related (and hence parallel) bipy moieties involves interatomic distances of 3.47 and 3.45 Å, respectively. Spectroscopic results suggest that the metal co-ordination geometry is the same in all the complexes.

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The involvement of the amino group of aspartic acid in a peptidic bond allows the ligand to restore co-ordination properties typical of α,β-dicarboxylic acids. Indeed, we have found that *N*-acetyl-, *N*-benzoyl- and *N*-benzyloxycarbonyl-aspartic acids behave as simple dicarboxylic acids with copper(II) and form binary complexes, where they, in an extended configuration, join metal ions to yield three-dimensional tetracarboxylate-bridged structures.[1] A bridging co-ordination mode was observed also in the ternary complexes of the above ligands with 2,2′-bipyridine (1:1:1 molar ratio) and, in particular, in di-μ-[*N*-benzyloxycarbonyl-L-aspartato-(2−)]-bis(2,2′-bipyridine)dicopper(II)·2.5H$_2$O·0.5NaClO$_4$, where bridge formation results from the co-ordination of monodentate α- and bidentate β-carboxylate groups.[1] To investigate further the co-ordination behaviour of the ligands, we have prepared the 2,2′-bipyridine (bipy) bis adducts of the Cu$^{II}$ complexes and here describe their structural and spectroscopic properties.

## Experimental

*Preparation of Complexes.*—All the compounds were prepared by dissolving the corresponding binary complexes [{Cu(acaspOO′)(H$_2$O)}$_n$]·$n$H$_2$O, [{Cu(bzaspOO′)(H$_2$O)}$_n$]·1.5$n$H$_2$O, and [{Cu(bzloaspOO′)(H$_2$O)}$_n$]·0.25$n$NaClO$_4$ ($1 \times 10^{-2}$ mmol dm$^{-3}$), prepared as described previously,[1] in an ethanolic solution of 2,2′-bipyridine ($3 \times 10^{-2}$ mmol dm$^{-3}$). By evaporating the solutions at room temperature (∼20 °C) pale blue crystalline compounds separated: [Cu(bipy)$_2$(acaspOO′)]·EtOH·4H$_2$O [acaspOO′ = *N*-acetyl-L-aspartate(2−)] (Found: C, 50.15; H, 5.20; N, 10.90; EtOH + H$_2$O, 17.1. Calc. for $C_{28}H_{37}CuN_5O_{10}$: C, 50.40; H, 5.60; N, 10.50; EtOH + H$_2$O, 17.70); [Cu(bipy)$_2$(bzaspOO′)]·2H$_2$O [bzaspOO′ = *N*-benzoyl-L-aspartate(2−)] (Found: C, 56.50; H, 4.25; N, 10.80; H$_2$O, 5.3. Calc. for $C_{31}H_{29}CuN_5O_7$: C, 57.40, H, 4.65; N, 10.80; H$_2$O, 5.55); [Cu(bipy)$_2$(bzloaspOO′)]·EtOH·H$_2$O [bzloaspOO′ = *N*-benzyloxycarbonyl-L-aspartate(2−)] (Found: C, 57.85; H, 4.80; N, 9.80; EtOH + H$_2$O, weight-loss too close to decomposition. Calc. for $C_{34}H_{35}CuN_5O_8$: C, 57.90; H, 5.00; N, 9.95; EtOH + H$_2$O, 9.10%).

*Crystallography.*—*Crystal data for* [Cu(bipy)$_2$(acaspOO′)]·EtOH·4H$_2$O. $C_{28}H_{37}CuN_5O_{10}$, $M$ = 667.17, $a$ = 12.947(4), $b$ = 12.462(4), $c$ = 11.152(3) Å, $\alpha$ = 115.44(6), $\beta$ = 106.53(5), $\gamma$ = 74.32(5)°,‡ $U$ = 1 535(1) Å$^3$ (by least-squares refinement from the 2θ values of 15 accurately measured reflections, $\lambda$ = 1.541 78 Å), space group $P\bar{1}$, $Z$ = 2, $D_c$ = 1.44 g cm$^{-3}$, $F(000)$ = 698. A crystal of approximate dimensions 0.13 × 0.23 × 0.32 mm was used, $\mu$(Cu-$K_\alpha$) = 15.09 cm$^{-1}$.

*Data collection and processing.* Siemens AED diffractometer, ω–2θ mode with scan width = 1.2 + 0.35 tan θ, scan speed 3.0° min$^{-1}$, Cu-$K_\alpha$ radiation; 4 086 reflections measured ($6 < 2\theta < 120°$, $+h, +k, +l$) 2 081 being considered observed [$I > 3\sigma(I)$].

*Structure analysis and refinement.* Patterson and Fourier methods, full-matrix least-squares calculations with all non-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ $a$ = 12.947, $b$ = 12.462, $c$ = 11.152 Å, $\alpha$ = 64.56, $\beta$ = 73.47, and $\gamma$ = 74.32°. The triacute reduced cell can be obtained by applying the transformation matrix $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

**Table 1.** Final fractional atomic co-ordinates ( × $10^4$) with e.s.d.s in parentheses for $[Cu(bipy)_2(acaspOO')]\cdot EtOH\cdot 4H_2O$

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Cu | 2 055(1) | 645(1) | 2 598(1) | C(7) | 1 625(7) | −299(9) | −1 628(10) |
| O(1) | 874(4) | 1 413(5) | 3 655(6) | C(8) | 2 045(8) | 545(10) | −1 801(11) |
| O(2) | 1 798(5) | 416(6) | 4 950(6) | C(9) | 2 446(7) | 1 454(9) | 714(11) |
| O(3) | −1 782(5) | 2 845(5) | 4 081(6) | C(10) | 2 408(7) | 1 565(9) | 564(10) |
| O(4) | 677(5) | 3 997(6) | 4 182(7) | C(11) | 2 376(8) | 3 173(8) | 4 118(10) |
| O(5) | 1 034(6) | 3 671(7) | 8 378(7) | C(12) | 2 989(8) | 4 079(9) | 4 798(10) |
| O(6) | 3 484(8) | 6 826(9) | 7 928(11) | C(13) | 4 113(8) | 3 787(9) | 5 086(10) |
| $O_w(1)$ | −2 678(5) | 2 028(6) | 5 392(6) | C(14) | 4 605(7) | 2 591(8) | 4 664(9) |
| $O_w(2)$ | 5 070(8) | 5 017(8) | 1 258(9) | C(15) | 3 951(6) | 1 711(8) | 3 949(9) |
| $O_w(3)$ | 1 385(8) | 4 608(8) | 1 177(8) | C(16) | 4 402(6) | 410(8) | 3 438(8) |
| $O_w(4)$ | 3 173(11) | 5 855(16) | 2 311(17) | C(17) | 5 505(7) | −60(8) | 3 599(10) |
| N(1) | 1 338(5) | −732(6) | 1 318(8) | C(18) | 5 836(7) | −1 304(9) | 3 099(10) |
| N(2) | 2 021(5) | 765(6) | 754(7) | C(19) | 5 077(7) | −2 037(8) | 2 460(10) |
| N(3) | 2 861(5) | 1 986(6) | 3 684(7) | C(20) | 3 987(7) | −1 501(8) | 2 327(10) |
| N(4) | 3 651(5) | −316(6) | 2 807(7) | C(21) | 1 020(6) | 1 167(7) | 4 691(10) |
| N(5) | 651(5) | 3 816(6) | 6 364(8) | C(22) | 185(6) | 1 802(7) | 5 602(9) |
| C(1) | 976(7) | −1 445(8) | 1 682(10) | C(23) | −229(6) | 3 128(8) | 5 834(9) |
| C(2) | 470(7) | −2 403(8) | 745(11) | C(24) | −934(8) | 3 363(8) | 4 587(10) |
| C(3) | 350(7) | −2 657(8) | −624(11) | C(25) | 1 215(7) | 4 041(8) | 7 603(12) |
| C(4) | 724(7) | −1 940(8) | −997(10) | C(26) | 2 129(9) | 4 735(13) | 8 046(18) |
| C(5) | 1 221(6) | −983(8) | −5(10) | C(27) | 4 170(12) | 7 508(19) | 7 852(20) |
| C(6) | 1 621(6) | −151(8) | −325(10) | C(28) | 4 681(15) | 8 231(21) | 9 104(20) |

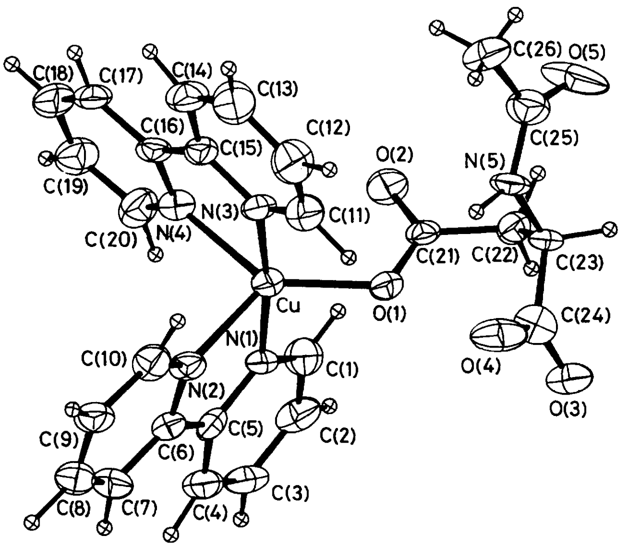

**Figure 1.** Structure of $[Cu(bipy)_2(acaspOO')]\cdot EtOH\cdot 4H_2O$, showing the atom labelling scheme and 35% probability thermal ellipsoids. The hydrogen atoms are represented as spheres of arbitrary radius

**Table 2.** Selected bond distances (Å) and angles (°) for $[Cu(bipy)_2(acaspOO')]\cdot EtOH\cdot 4H_2O$

| | | | |
|---|---|---|---|
| Cu–O(1) | 1.977(6) | Cu–N(3) | 1.958(7) |
| Cu–N(1) | 1.961(7) | Cu–N(4) | 2.094(6) |
| Cu–N(2) | 2.112(9) | | |
| N(3)–Cu–N(4) | 80.1(3) | N(1)–Cu–N(2) | 80.0(3) |
| N(2)–Cu–N(4) | 96.7(3) | O(1)–Cu–N(4) | 138.1(3) |
| N(2)–Cu–N(3) | 93.3(3) | O(1)–Cu–N(3) | 92.3(3) |
| N(1)–Cu–N(4) | 97.2(3) | O(1)–Cu–N(2) | 125.0(3) |
| N(1)–Cu–N(3) | 172.5(3) | O(1)–Cu–N(1) | 94.3(3) |
| Cu–N(1)–C(5) | 117.2(7) | Cu–N(2)–C(6) | 112.2(6) |
| Cu–N(1)–C(1) | 124.3(7) | Cu–N(3)–C(15) | 117.1(7) |
| Cu–N(2)–C(10) | 128.3(6) | Cu–N(3)–C(11) | 123.9(7) |
| Cu–O(1)–C(21) | 115.3(6) | Cu–N(4)–C(20) | 128.6(7) |

hydrogen atoms anisotropic and hydrogens isotropic. Weighting scheme used: $w = 1.0961/[\sigma^2(F_o) + 0.001\,814\,F_o^2]$. Final $R$ and $R'$ values were 0.0496 and 0.0514, respectively. Calculations were performed on a CRAY X/MP (Centro di Calcolo dell'Italia Nord-Orientale, Bologna) computer using SHELX.[2] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 3. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond parameters.

*Physical Measurements.*—Thermogravimetric determination of $H_2O$ and EtOH was carried out on a Mettler TA3000 instrument using a scan rate of 5 °C $min^{-1}$. *X*-Band e.s.r. spectra (~9.15 GHz) were recorded on a Varian E-9 spectrometer with diphenylpicrylhydrazyl (dpph) as reference. Electronic spectra were obtained with Varian Cary-2300 and Beckman Acta M IV spectrophotometers.

## Results and Discussion

*Description of the Structure.*—The structure of complex (**1**), Figure 1, consists of monomeric $[Cu(bipy)_2(acaspOO')]$ units, with a basically five-co-ordinate stereochemistry involving two bipyridine molecules and one *N*-acetyl-L-aspartate ion. Bond distances and angles are listed in Table 2. The *N*-acetyl-L-aspartate ligand participates in the co-ordination through one β-carboxylate oxygen, while the second β-carboxylate oxygen atom occupies the sixth co-ordination position at a distance of 2.875(8) Å from the copper atom to give a 4 + 1 + 1* co-ordination. Such structural features have been previously reported for complexes such as $[Cu(bipy)_2(O_2CMe)]ClO_4\cdot H_2O$,[4] $[Cu(bipy)_2(O_2CMe)]BF_4$,[4] $[Cu(bipy)_2(ONO)]NO_3$,[5] $[Cu(bipy)_2(O_2CH)]BF_4\cdot 0.5H_2O$,[6] and the $[Cu(bipy)_2(pydca)]$ unit of the complex $[Cu_2(bipy)_2(pydca)_2]\cdot 4H_2O$[7] (pydca = pyridine-2,6-dicarboxylate). The $CuN_4O$ chromophore can be described as a distorted bipyramid with a nitrogen atom from each bipy ligand and the carboxylic oxygen in the basal plane, and the other two bipy nitrogen atoms, N(1) and N(3), as the

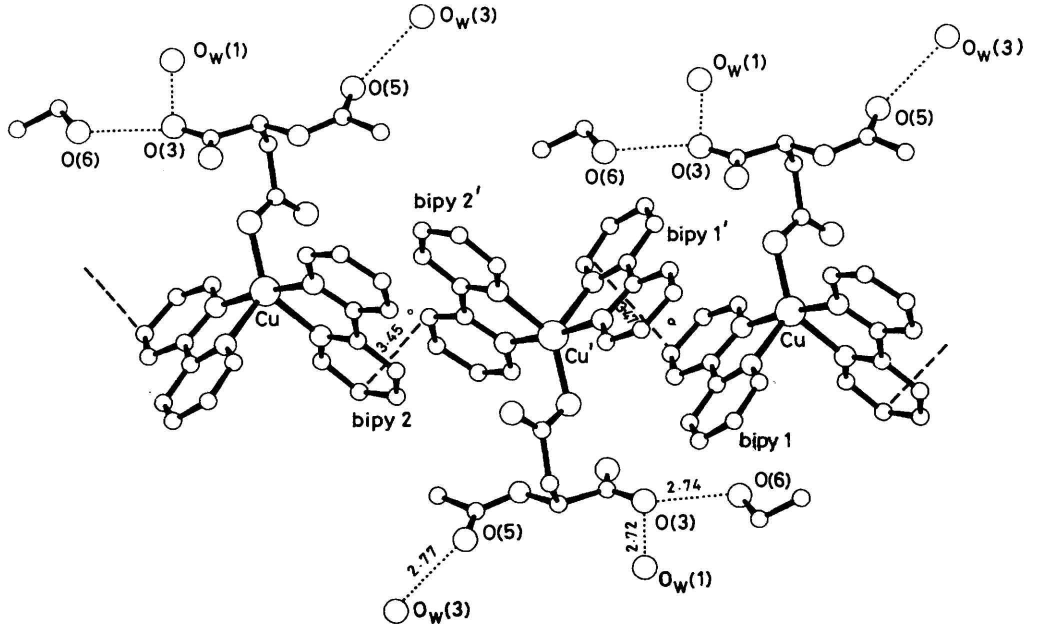

Figure 2. Ring-stacking (dashed lines) and hydrogen-bonding (dotted lines) interactions (Å)

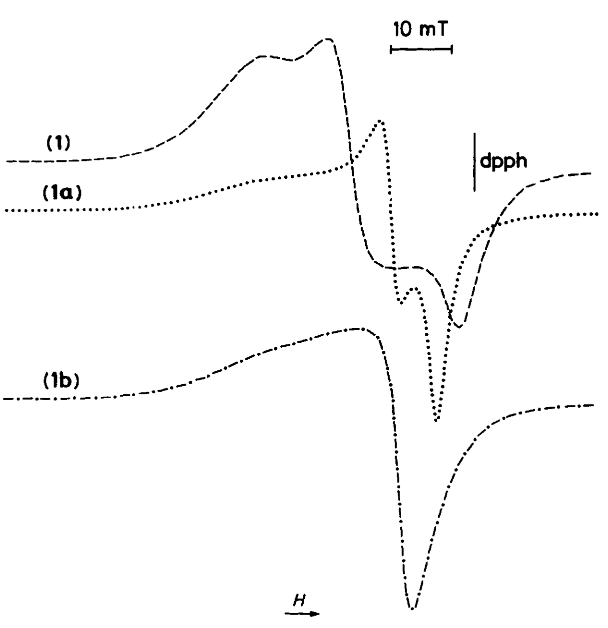

Figure 3. E.s.r. spectra recorded at 123 K on powdered samples of $[Cu(bipy)_2(acaspOO')]\cdot EtOH\cdot 4H_2O$ (**1**) and its dehydration, (**1a**), and re-hydration, (**1b**), products

axial donors [N(1)–Cu–N(3) = 172.5(3)°]. The copper atom lies 0.052(3) Å out of the equatorial plane.

The distortion of $Cu(bipy)_2X$ and $Cu(bipy)_2OXO$ chromophores (X is a unidentate ligand and $OXO^-$ a bidentate chelate ligand) from regular trigonal-bipyramidal stereochemistry toward square-pyramidal stereochemistry may occur through two alternative routes,[6] depending on the ligand atom involved in the elongation of the fifth position. In this case, the bond angles in the equatorial plane are $\alpha_1 = 138.1(3)$, $\alpha_2 = 125.0(3)$, and $\alpha_3 = 96.7(3)°$, which suggest that the distortion is toward the square pyramid with the oxygen atom at the apex. Also, the Cu–N(2) and Cu–N(4) distances are almost equivalent, while the difference between the Cu–O distances is *ca.* 0.9 Å. Thus, the present structure is an example of 4 + 1 + 1* type co-ordination with near equivalent Cu–N(2) and Cu–N(4) distances (C-type in ref. 6), *i.e.* distortion occurs along the Cu–O axis, and a very asymmetrically bound $OXO^-$ group. Comparable features were found previously for $[Cu(bipy)_2(pydca)]$[7] and associated with geometrical factors arising from the co-ordination of a carboxylate group belonging to a complex ligand.

The main interest in this class of $CuN_4O_2$ chromophores (4 + 1 + 1*) is their temperature-variable stereochemistry.[8] Unfortunately, our structural (and e.s.r., see later) data do not provide evidence for any fluxional behaviour.

It is also noteworthy to observe that in the present structure the metal binding by the aspartate moiety occurs through a β-carboxylate group, whereas the α-carboxylic oxygens are involved only in hydrogen-bonding interactions. Previous studies on aspartate and glutamate complexes[9] have always shown mono- or bi-dentate α-carboxylate functions and, sometimes, 'free' β- or γ-carboxylate groups. In the *N*-protected-aspartate complexes, the presence of the protecting group, while preventing metal binding to the nitrogen atom, activates the β-carboxylate co-ordination. In fact, in the complex di-μ-[*N*-benzyloxycarbonyl-L-aspartato(2–)]-bis(2,2'-bipyridine)-dicopper(II)$\cdot 2.5H_2O\cdot 0.5NaClO_4$,[1] the β- and α-carboxylate groups are bidentate and monodentate, respectively. In the present case, the peculiar stereochemistry dictated by metal co-ordination of two bipy molecules favours only a very asymmetrical bidentate bonding of the β-carboxylate function.

Bond distances and angles in the aspartate ligand are similar to those found in other $Cu^{II}$–aspartate complexes,[9] while the metal–nitrogen distances are in the range usually observed for $Cu^{II}$–bipy complexes.[4–7]

Packing is determined by hydrogen bonds involving water molecules, α-carboxylate and acetyl groups, and ethanol molecules, the shortest of these being shown in Figure 2. Ring stacking interactions between bipy molecules complete the packing; the stack between symmetry related (and hence parallel) bipy moieties involves shortest interatomic distances of 3.47 and 3.45 Å, respectively (Figure 2).

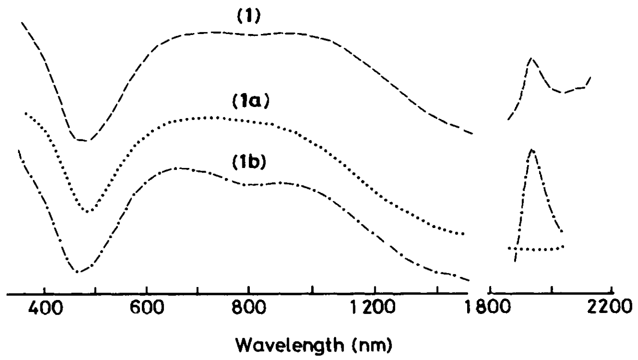

**Figure 4.** Diffuse-reflectance spectra of [Cu(bipy)$_2$(acaspOO′)]•EtOH•4H$_2$O and its dehydration (**1a**) and re-hydration (**1b**) products. The combination band at *ca.* 1 940 nm (attributable to $\nu_{H_2O} + \delta_{H_2O}$) is diagnostic of the presence of water

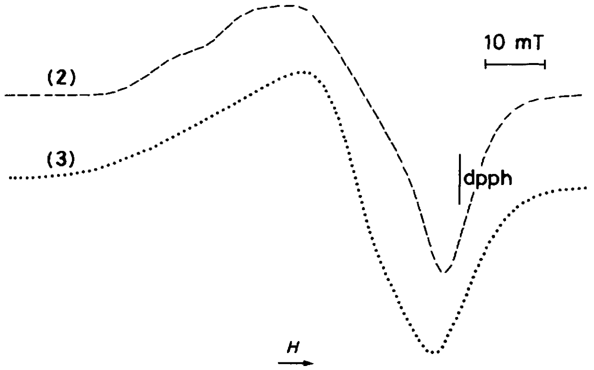

**Figure 5.** E.s.r. spectra recorded at 123 K on powdered samples of complexes (**2**) and (**3**)

*E.S.R. and Electronic Spectra.*—The e.s.r. spectrum of complex (**1**), Figure 3, is clearly rhombic with *g* values (2.24, 2.14 and 2.02) consistent with a $d_{z^2}$ ground state, conforming to essentially trigonal-bipyramidal stereochemistry. The square-planar distortion is well reflected by the electronic spectrum, Figure 4, consisting of two almost equally intense peaks at *ca.* 13.4 and 10.6 × $10^3$ cm$^{-1}$.

Compounds [Cu(bipy)$_2$(bzaspOO′)]•2H$_2$O (**2**) and [Cu(bipy)$_2$(bzloaspOO′)]•EtOH•H$_2$O (**3**) also exhibit twin-peaked spectra [bands at *ca.* 14.1 and 10.6, and 14.1 and 10.0 × $10^3$ cm$^{-1}$ for (**2**) and (**3**), respectively], but the increased splitting indicates a more distorted structure.[8] The e.s.r. spectra of these compounds are shown in Figure 5. However, that of (**3**) is nearly isotropic, probably due to exchange coupling and misalignment of the molecular axes, while the spectrum of (**2**) seems to give evidence for copper hyperfine splitting at low fields and is grossly reminiscent of the spectrum of (**1**) with *g* values of 2.21, 2.13, and 2.02. On the whole, these results suggest that complexes (**2**) and (**3**) have the same geometry as (**1**), but with different distortion.

As anticipated in the previous section, the e.s.r. spectra are almost insensitive to the temperature variation, at least in the 298—123 K temperature range, suggesting insignificant change in structure. However, it has been found that packing effects due to unbound H$_2$O and EtOH molecules influence the copper stereochemistry. In fact, when water and ethanol molecules are removed by heating at 120 °C, complex (**1**) undergoes a colour change from pale blue to green and, on standing, it recovers four water molecules from the air-moisture to return to blue. Spectral results obtained on the anhydrous, (**1a**), and re-hydrate, (**1b**), products are shown in Figures 3 and 4. The e.s.r. spectrum of (**1a**), also if exchange-narrowed, is still rhombic (*g* 2.23, 2.09, and 2.04), while that of (**1b**) is axial ($g$ = 2.24 and 2.08). On the other hand, the electronic spectra (Figure 4) differ from that of (**1**) mainly in the blue-shift of the higher-energy *d–d* bands [absorption maxima: 14.2 × $10^3$ cm$^{-1}$ with a shoulder at 11.4 × $10^3$ cm$^{-1}$ for (**1a**), and 15.0 and 21 × $10^3$ cm$^{-1}$ for (**1b**)]. Although difficult to interpret in detail, these results seem to be consistent with a rearrangement of the copper chromophore and the attainment of a strong distortion toward square-pyramidal stereochemistry in (**1b**) with a concomitant change from an essentially $d_{z^2}$ to a $d_{x^2-y^2}$ ground state. This may be further evidence for the flexible copper(II) stereochemistry or the plastic effect of the $d^9$ configuration.[10]

When dissolved in methanol, the complexes yield axial e.s.r. spectra [$g$ = 2.251—2.255 and 2.054—2.060; $A_{\parallel}$ = (156—165) × $10^{-4}$ cm$^{-1}$] and twin-peaked electronic spectra with absorptions at 14.7 and 10.7 × $10^3$ cm$^{-1}$ (ε *ca.* 100 and 50 dm$^3$ mol$^{-1}$ cm$^{-1}$, respectively). These spectral features suggest similar environments about the copper ion in solution, as a consequence of a common rearrangement of the geometry toward a distorted square pyramid. Therefore, the major differences in the solid state may be considered as due to packing effects.

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## References

1 L. Antolini, L. P. Battaglia, A. Bonamartini Corradi, L. Menabue, G. Micera, and M. Saladini, *Inorg. Chem.*, 1986, **25**, 3301.
2 G. M. Sheldrick, SHELX System of Computing Programs, University of Cambridge, 1976.
3 J. A. Ibers and W. C. Hamilton, 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
4 B. J. Hathaway, N. J. Ray, D. Kennedy, N. O'Brien, and B. Murphy, *Acta Crystallogr., Sect. B*, 1980, **36**, 1371.
5 I. M. Procter and F. S. Stephens, *J. Chem. Soc. A*, 1969, 1248.
6 W. Fitzgerald and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 567.
7 G. Nardin, L. Randaccio, R. Bonomo, and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 1980, 369.
8 B. J. Hathaway, *Struct. Bonding (Berlin)*, 1984, **57**, 55.
9 L. Antolini, L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue, G. C. Pellacani, M. Saladini, and M. Sola, *Inorg. Chem.*, 1986, **25**, 2901.
10 J. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Coord. Chem. Rev.*, 1976, **21**, 253.

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