

# Glycine coupled to a bis(imidazole): a tetradentate ligand rendering dinuclear copper(II) compounds through ligand sharing

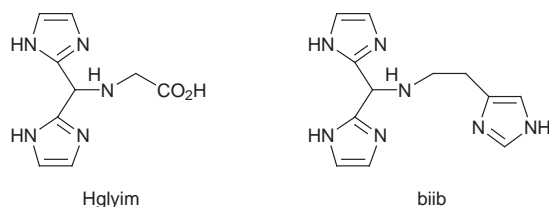
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The tetradentate ligand (carboxymethylamino)bis(imidazole-2-yl)methane (Hglyim), obtained through the reaction of glycine with bis(imidazol-2-yl)nitromethane, rendered several dinuclear copper(II) compounds, *viz.* [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl<sub>2</sub>]·6H<sub>2</sub>O **1**, [Cu<sub>2</sub>(glyim)<sub>2</sub>Br<sub>2</sub>]·5H<sub>2</sub>O **2**, [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl(H<sub>2</sub>O)](CF<sub>3</sub>SO<sub>3</sub>)·2H<sub>2</sub>O **3** and [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl(H<sub>2</sub>O)](ClO<sub>4</sub>)·2H<sub>2</sub>O **4**. The single crystal structure of **1** was determined. It consists of [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl<sub>2</sub>] units and several, mostly disordered, water molecules. The ligands and the anions are grouped in dimers of formula [Cu<sub>2</sub>(glyim<sup>-</sup>)<sub>2</sub>(Cl<sup>-</sup>)<sub>2</sub>] in which the two copper(II) ions are entangled by two ligands. Each copper is in a square pyramidal N<sub>3</sub>OCl environment with the chloride ion occupying the apical position. Two of the co-ordinating nitrogens are from the imidazole groups of one ligand, while an amine nitrogen and a carboxyl oxygen are donated by the other ligand. This 2+2 ligand-sharing arrangement imposes a rather short distance on the two copper(II) ions, *i.e.* 3.249(2), 3.357(2) and 3.373(2) Å. A well resolved EPR spectrum of 10<sup>-3</sup> M **3** in MeOH was obtained at 77 K with *g*<sub>eff</sub> values for H<sub>z1</sub>, H<sub>xy1</sub>, H<sub>z2</sub> and H<sub>xy2</sub> at 2.69, 2.26, 1.89 and 1.86 respectively, an *A*<sub>||</sub> value of 87 G and a half-field signal at *g* = 4.24, indicating the preservation of the dinuclearity in solution (*D* = 0.047 cm<sup>-1</sup>). At concentrations of 10<sup>-4</sup> M and lower the dinuclear signals break down and the complex decomposes into monomeric species (*g*<sub>||</sub> = 2.27 and *g*<sub>⊥</sub> = 2.10).

Modelling strategies for the active sites<sup>1-3</sup> of hemocyanin and tyrosinase have employed a variety of ligand systems, most of which possess N-heterocycles as potential co-ordinating groups.<sup>4,5</sup> Suitable models should at least accommodate two copper ions, preferably at distances comparable to those found in the natural systems. In a previous study,<sup>6</sup> dinuclear copper(II) complexes of the ligand 1,1-bis(imidazol-2-yl)-4-[imidazol-4(5)-yl]-2-azabutane (biib) have been reported. A novel feature of the structures of these complexes was the full sharing of two ligands by two copper(II) ions. In the present paper, the synthesis and characterisation of dinuclear copper(II) complexes formed from the ligand (carboxymethylamino)bis(imidazol-2-yl)methane (Hglyim) are reported. The ligand combines the donor functions of two imidazoles with those of an amino acid. It was anticipated that it would not only give rise to structurally interesting dinuclear copper(II) complexes, but also that the glycinate arm might modulate the co-ordination properties and help maintain the structural continuity in solution.



## Experimental

### General

All synthetic and spectroscopic procedures were performed in air. All reagents were commercially available and of sufficient purity for use without further treatment. The starting material for the preparation of the ligand Hglyim, bis(imidazol-2-yl)nitromethane hydrochloride, was prepared by a literature method.<sup>7</sup> The NMR spectra were recorded on a Bruker WM-300 MHz spectrometer, FT-IR spectra as samples pressed

in KBr or milled in Nujol on a Bruker IFS 113V FT IR spectrophotometer, ligand field spectra of the solids (300–2000 nm) in the VIS/NIR region on a Perkin-Elmer Lambda 900 spectrophotometer in reflectance mode, X-band EPR spectra of the powdered solids at room temperature and as frozen solutions at 77 K on a JEOL RE2X ESR spectrometer, employing diphenylpicrylhydrazyl (dpph, *g* = 2.0036) as an external reference and mass spectra on a Finnigan MAT TSQ-70 instrument equipped with a custom-made electrospray interface. Halide analyses were carried out by potentiometric titration with AgNO<sub>3</sub>.<sup>8</sup> Elemental analyses (C,H,N) were done in the Microanalytical Laboratory of University College, Dublin, Ireland.

### Synthesis of (carboxymethylamino)bis(imidazol-2-yl)methane (Hglyim)

The ligand was synthesized by a modification of the method reported by Joseph *et al.*<sup>7</sup> At ambient temperature, bis(imidazol-2-yl)nitromethane hydrochloride (0.50 g, 2.26 mmol) was dissolved in 2 M NaOH (3.3 cm<sup>3</sup>, 6.60 mmol) with vigorous stirring and glycine (0.17 g, 2.26 mmol) was added to the stirred solution. The resulting orange solution was heated at 80 °C for 15 min, after which time it was left standing at room temperature. The pH was then adjusted to 6 by dropwise addition of HCl (11 M). Acetone (50 cm<sup>3</sup>) was added with stirring and the combined solvents were decanted off the resulting oil. The oil was solidified by the addition of EtOH (3 cm<sup>3</sup>), followed by diethyl ether (12 cm<sup>3</sup>) with moderate stirring. The product was filtered off, washed with ether and air dried. The resulting dry solid appeared to be the hydrogen chloride salt, which was sufficiently pure for the preparation of the complexes. Yield 0.47 g, 94%. A small amount was treated with an excess of NaOH and recrystallised from hot EtOH (Cl<sup>-</sup> < 0.2%):  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup> in KBr) 3339 [ν(OH)], 2920–3143 [ν(NH)], 1614 [ν(C=O)] and 755 [ν(heterocyclic ring vibration)]. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25 °C): δ<sub>H</sub> 7.17–7.12 (4 H, imidazole), 5.46 (1 H, CH), 3.51 (1 H, imidazole) and 3.22 (2 H, CH<sub>2</sub>). Mass spectrum (ESI): *m/z* 222, [*M* + H]<sup>+</sup>.

**Table 1** Selected infrared bands for compounds **1–4**, and corresponding tentative assignments

Compound	$\nu(\text{H}_2\text{O})$	$\nu(\text{N-H})$ amine <sup>a</sup>	$\nu(\text{C=O})$	$\nu(\text{ClO}_4)$	$\nu(\text{SO}_3)$	$\nu(\text{imid})^b$
<b>1</b>	3420	3116	1618	—	—	792, 768, 740
<b>2</b>	3430	3118	1615	—	—	792, 767, 740
<b>3</b>	3446	3118	1616	—	1272	793, 766, 740
<b>4</b>	3427	3118	1618	626, 1091	—	791, 768, 741

<sup>a</sup> Split band, value of stronger band given. <sup>b</sup> Heterocyclic ring breathing vibrations.<sup>13</sup>

### Preparation of the copper complexes

An ethanolic solution (5 cm<sup>3</sup>) of the appropriate copper salt, *i.e.* CuCl<sub>2</sub>·2H<sub>2</sub>O (30 mg, 2.26 × 10<sup>-1</sup> mmol), CuBr<sub>2</sub> (50 mg, 2.26 × 10<sup>-1</sup> mmol), Cu(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> (82 mg, 2.26 × 10<sup>-1</sup> mmol) or Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (77 mg, 2.26 × 10<sup>-1</sup> mmol), was added to an aqueous solution (8 cm<sup>3</sup>) of Hglyim (50 mg, 2.26 × 10<sup>-1</sup> mmol). Dark blue solutions resulted, which were filtered and set aside at room temperature. Dark blue crystals emerged in 2–4 weeks. These were harvested by filtration or decantation and dried on filter-paper. [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl<sub>2</sub>]·6H<sub>2</sub>O **1** (32 mg, 19%) (Found: C, 28.8; H, 4.3; Cl, 9.3; N, 18.8. C<sub>9</sub>H<sub>16</sub>ClCuN<sub>5</sub>O<sub>5</sub> requires C, 29.0; H, 4.3; Cl, 9.5; N, 18.8%); [Cu<sub>2</sub>(glyim)<sub>2</sub>Br<sub>2</sub>]·5H<sub>2</sub>O **2** (33 mg, 18%) (Found: C, 26.2; H, 3.8; N, 16.9. C<sub>18</sub>H<sub>30</sub>Br<sub>2</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>9</sub> requires C, 26.5; H, 3.7; N, 17.1%); [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl(H<sub>2</sub>O)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O **3** (30 mg, 16%) (Found: C, 28.0; H, 3.2; N, 17.0. C<sub>19</sub>H<sub>26</sub>ClCu<sub>2</sub>F<sub>3</sub>N<sub>10</sub>O<sub>10</sub>S requires C, 28.3; H, 3.3; N, 17.4%); [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O **4** (30 mg, 18%) (Found: C, 29.1; H, 4.2; N, 18.6. C<sub>18</sub>H<sub>26</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>11</sub> requires C, 28.6; H, 3.5; N, 18.5%).

### Crystallography

X-Ray data for complex **1** were collected at room temperature on an Enraf-Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K $\alpha$  radiation: monoclinic, space group *C2/c* (no. 15), *a* = 28.5364(17), *b* = 17.810(2), *c* = 25.887(3) Å,  $\beta$  = 120.763(7)°, *U* = 11 305(2) Å<sup>3</sup>, *Z* = 16 for C<sub>18</sub>H<sub>20</sub>Cl<sub>2</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>4</sub>·3H<sub>2</sub>O (without the disordered solvent molecules), *D*<sub>c</sub> = 1.613 g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha)$  = 17.5 cm<sup>-1</sup>. A total of 21 005 reflections were measured ( $\theta_{\text{min/max}}$  = 2.6/26.4°). Data were corrected for Lorentz polarisation and averaged [*R*(int) = 0.103] into a unique set of 4649 reflections with *I* > 2.0 $\sigma$ (*I*). The structure was solved with DIRDIF/PATT<sup>9</sup> and refined on *F*<sup>2</sup> using full-matrix least-squares techniques with SHELXL 97.<sup>10</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions, riding on their parent atom and refined with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C or N). Refinement converged at *R* = 0.099 (*S* = 0.95) with residual density peaks (maximum +2.70 e Å<sup>-3</sup>) in four symmetry related cavities, *viz.* at  $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$ , at  $\frac{3}{4}, \frac{1}{2}, \frac{1}{4}$ , at  $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$ , and at  $\frac{3}{4}, \frac{3}{4}, \frac{1}{2}$ . No discrete solvent model could be refined. The BYPASS<sup>11</sup> procedure, as implemented in the program PLATON,<sup>12</sup> was used to take this electron density into account. Each cavity contained 39 electrons in a volume of 393 Å<sup>3</sup>, probably due to strongly disordered water molecules. The correct occupancy of the cavities could not be assessed. Further refinement resulted in a convergence of *R* = 0.083 (*S* = 0.75) for 4649 observed [*I* > 2 $\sigma$ (*I*)] reflections and 673 parameters with minimum and maximum residual electron densities of -1.27 and +2.44 e Å<sup>-3</sup> in the final difference map. Geometric calculations and molecular graphics were performed with PLATON/PLUTON.<sup>12</sup>

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## Results and Discussion

### General

The four complexes [Cu(glyim)<sub>2</sub>X<sub>2</sub>]·*n*H<sub>2</sub>O, X = Cl, *n* = 6 **1**, X = Br, *n* = 5 **2**, [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl(H<sub>2</sub>O)](X)·*n*H<sub>2</sub>O, X = CF<sub>3</sub>SO<sub>3</sub>,

*n* = 2 **3** and X = ClO<sub>4</sub>, *n* = 2 **4**, were characterised by elemental analyses and by infrared, VIS/NIR and EPR spectroscopy. Compound **1** was also characterised by X-ray crystallography, but the coordinates of only three of the six waters could be determined (see above).

The infrared spectra of the complexes **1–4** are quite similar to those of the ligand, with some bands shifted and/or split. In the case of **3** and **4** additional bands are present due to vibrations arising from the triflate and perchlorate anions respectively. These bands are characteristic for non-co-ordinated triflate<sup>13</sup> and perchlorate<sup>14</sup> (see Table 1). Bands arising from breathing vibrations of the imidazole rings,<sup>15</sup> water of crystallisation<sup>16</sup> and co-ordinated carboxylate<sup>17</sup> are present in the IR spectra of all four complexes, and are listed and assigned tentatively in Table 1.

The diffuse reflectance VIS/NIR spectra of complexes **1–4** are quite similar, as expected, due to the fact that the axially co-ordinated ligands are all of comparable donor strength. The positions of the  $\lambda_{\text{max}}$  values at 630, 632, 600 and 629 nm respectively are typical for similar chromophores with square-pyramidal geometries.<sup>18</sup>

### Structure of [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl<sub>2</sub>]·6H<sub>2</sub>O **1**

There are four independent asymmetric units {Cu(glyim)Cl} in the unit cell, arranged in such a way that one [Cu<sub>2</sub>(glyim)<sub>2</sub>(Cl<sup>-</sup>)<sub>2</sub>] dimer hosts two asymmetric units with two crystallographic independent copper ions at a distance of 3.249(2) Å, while two other dimers each host one asymmetric unit. In each of the latter dinuclear dimers the other half is generated by a twofold rotation axis with Cu...Cu distances of respectively 3.357(7) and 3.373(2) Å. A representation of the structure is given in Fig. 1. So, the contents of the unit cell consist of 16 dinuclear dimers of formula [Cu<sub>2</sub>(glyim)<sub>2</sub>(Cl<sup>-</sup>)<sub>2</sub>] together with a number of water molecules, which are mostly disordered (see above). The arrangements of the dinuclear dimers are the same, *viz.* each copper is co-ordinated by the two nitrogens of both imidazoles of one ligand and the amine nitrogen and the carboxyl oxygen of the other, as well as by a chloride ion at the apex of the square pyramid (see Fig. 1). The bond distances are normal for this type of co-ordination. The Cu...Cu distances, which vary slightly (see Table 2), are quite short, obviously as a consequence of the close entanglement by the ligands. The formation of dinuclear dimers through ligand sharing is not unprecedented, as reported in our previous study on the ligand 1,1-bis(1,1-imidazol-2-yl)-4-[imidazol-4(5)-yl]-2-azabutane (biib).<sup>6</sup> In the case of biib the ligand contributes three of its donor atoms to one copper and one donor atom to the other, *viz.* a [3 + 1] type of ligand sharing, whereas in the present case the ligand sharing is of the [2 + 2] type. Extensive hydrogen bonding interactions occur, but these are apparently not sufficiently regular to keep (some of) the water molecules from being disordered.

Recently a ligand similar to Hglyim, *i.e.* one which arose from the 'coupling' of a bis(imidazole) and propionic acid, was reported. Its copper(II) complex appears, however, to be very different from the present complexes, in being mononuclear, while also the carboxylic acid group does not participate in the co-ordination to the copper ion.<sup>19</sup>

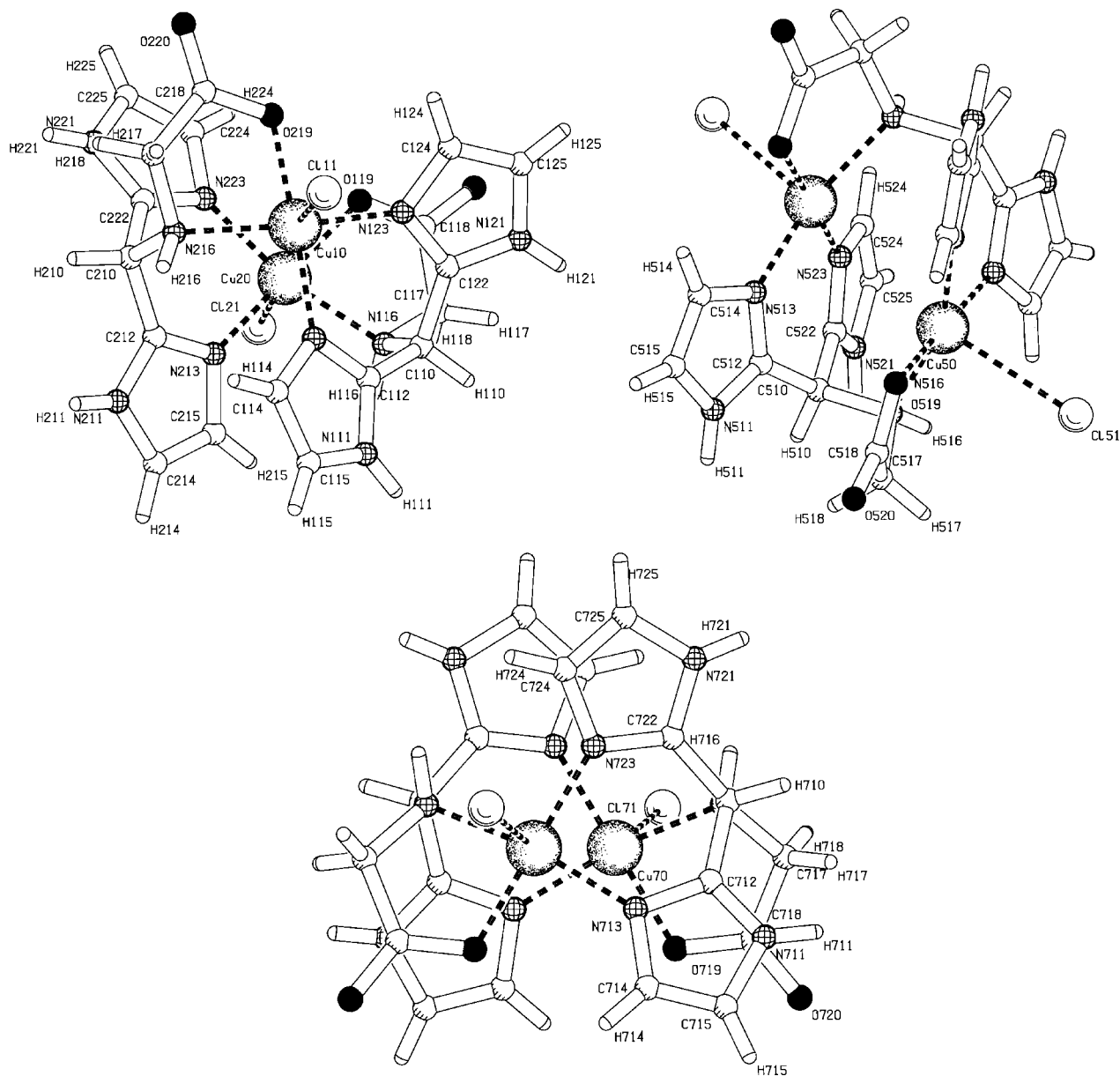


Fig. 1 The PLUTON<sup>12</sup> plots of the dinuclear sub-units  $[\text{Cu}_2(\text{glyim})_2\text{Cl}_2]$  of complex 1

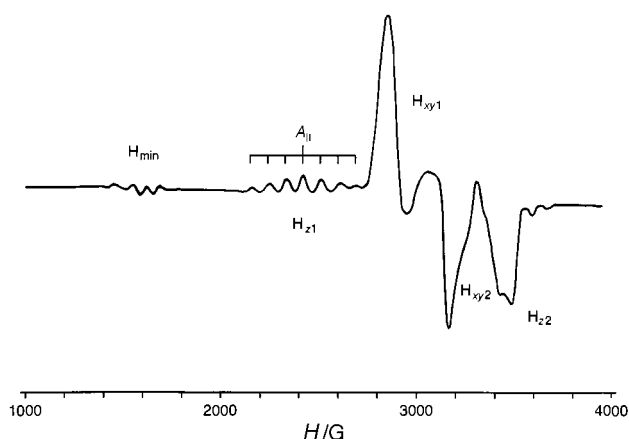


Fig. 2 The EPR spectrum of  $[\text{Cu}_2(\text{glyim})_2\text{Cl}(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3) \cdot 2\text{H}_2\text{O}$  3 in MeOH ( $10^{-3}$  M) at 77 K;  $G = 10^{-4}$  T

### EPR spectroscopy

The X-band EPR spectra of powdered samples of the polycrystalline complexes **1–4**, recorded at room temperature are asymmetric with  $g_{\text{iso}} = 2.10$  for **1**, **2** and **4** and 2.07 for **3**. The

triplet signal is poorly resolved in these spectra, and is masked by the substantially more intense isotropic signal, resulting from intertriplet interactions. Unsatisfactory matrices for reproducible EPR spectra with good resolution were obtained when freezing solutions of **1**, **2** and **4** in MeOH, water, MeCN, dmf, dmsO, dichloromethane, toluene or judiciously chosen mixtures of the solvents with liquid nitrogen. The spectrum of **3** in MeOH was recorded at 77 K at concentrations of  $10^{-3}$ ,  $2 \times 10^{-4}$ , and  $10^{-4}$  M. Fortunately, the spectrum at  $10^{-3}$  M exhibits well resolved triplet features, see Fig. 2. Seven well resolved lines due to copper hyperfine interactions superimposed on the  $H_z$  absorptions are observed with  $A_{\parallel} = 87$  G. The half-field signal at  $g \approx 4$  is well resolved (centred at  $g = 4.24$ ), and indicative of a dinuclear copper(II) complex.<sup>6</sup> The  $H_{z1}$ ,  $H_{xy1}$ ,  $H_{z2}$  and  $H_{xy2}$  absorptions are also well resolved and arise at  $g_{\text{eff}}$  values of 2.69, 2.26, 1.89 and 1.86, respectively ( $g_z = 2.20$  and  $D = 0.047 \text{ cm}^{-1}$ ). Some monomeric species is also observed at this concentration with a  $g_{\perp}$  value of 2.06. A well resolved triplet spectrum is still observed for this complex at a concentration of  $2 \times 10^{-4}$  M, suggesting that the dinuclearity of **3** is maintained at low concentrations. The analogous complex of biib was seen to decompose into its monomeric constituents at this concentration. The enhanced stability of **3** in dilute solutions may be due to the co-ordination of the strongly binding

**Table 2** Selected distances (Å) and angles (°) for [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl<sub>2</sub>]  
3H<sub>2</sub>O<sup>a</sup>

Cu10–Cl11	2.527(3)	Cu50–N523	1.986(9)
Cu10–O219	1.964(9)	Cu50–Cl51	2.782(4)
Cu10–N113	1.981(9)	Cu50–N513	1.975(10)
Cu10–N123	1.973(9)	Cu50–O519 <sup>b</sup>	1.934(8)
Cu10–N216	2.082(8)	Cu50–N516 <sup>b</sup>	2.074(9)
Cu20–Cl21	2.501(3)	Cu70–N716 <sup>c</sup>	2.059(9)
Cu20–O119	1.962(8)	Cu70–N723	1.956(8)
Cu20–N116	2.071(8)	Cu70–Cl71	2.813(3)
Cu20–N213	1.987(10)	Cu70–N713	1.956(10)
Cu20–N223	1.954(10)	Cu70–O719 <sup>b</sup>	1.943(7)
Cu10...Cu20	3.249(2)	Cu70...Cu70 <sup>c</sup>	3.373(2)
Cu50...Cu50 <sup>b</sup>	3.357(7)		
Cl11–Cu10–O219	91.0(2)	O519 <sup>b</sup> –Cu50–N513	89.7(4)
Cl11–Cu10–N113	96.2(3)	N513–Cu50–N516 <sup>b</sup>	159.0(3)
Cl11–Cu10–N123	96.0(3)	O519 <sup>b</sup> –Cu50–N523	178.6(4)
Cl11–Cu10–N216	97.3(3)	N516 <sup>b</sup> –Cu50–N523	97.7(4)
O219–Cu10–N113	172.7(4)	O519 <sup>b</sup> –Cu70–N516 <sup>b</sup>	82.5(3)
O219–Cu10–N123	90.8(4)	Cl51–Cu50–O519 <sup>b</sup>	91.0(2)
O219–Cu10–N216	82.4(4)	Cl51–Cu50–N516 <sup>b</sup>	91.2(2)
N113–Cu10–N123	89.3(4)	N513–Cu50–N523	90.5(4)
N113–Cu10–N216	95.8(4)	Cl51–Cu50–N523	87.6(3)
N123–Cu10–N216	165.1(5)	Cl51–Cu50–N513	108.5(3)
Cl21–Cu20–O119	92.6(2)	Cl71–Cu70–N723	88.4(3)
Cl21–Cu20–N116	94.3(3)	Cl71–Cu70–N713	109.4(3)
Cl21–Cu20–N213	94.3(3)	O719 <sup>c</sup> –Cu70–N716 <sup>c</sup>	83.6(3)
Cl21–Cu20–N223	102.5(3)	Cl71–Cu70–O719 <sup>c</sup>	89.3(2)
O119–Cu20–N116	82.2(4)	Cl71–Cu70–N716 <sup>c</sup>	90.7(2)
O119–Cu20–N213	172.8(4)	O719 <sup>c</sup> –Cu70–N713	89.5(3)
O119–Cu20–N223	91.6(4)	N713–Cu70–N716 <sup>c</sup>	158.7(4)
N116–Cu20–N213	95.3(4)	O719 <sup>c</sup> –Cu70–N723	177.6(4)
N116–Cu20–N223	162.4(4)	N716 <sup>c</sup> –Cu70–N723	97.1(3)
N213–Cu20–N223	88.9(4)	N713–Cu70–N723	90.7(4)

<sup>a</sup> Without disordered solvent contribution. <sup>b</sup> 1 – x, y, 0.5 – z. <sup>c</sup> –x, y, 0.5 – z.

glycinate oxygen from glyim, as well as the fact that glyim coordinates to the metal ion in a different way to that of biib (see below). At 10<sup>–4</sup> M both the dinuclear and mononuclear signals have similar intensities, suggesting substantial decomposition of **3** into monomeric species ( $g_{\parallel} = 2.27$  and  $g_{\perp} = 2.10$ ).

## Conclusion

Four new copper complexes involving a novel type of ligand sharing have been prepared from the ligand Hglyim. The crystal structure of [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl<sub>2</sub>] $\cdot$ 6H<sub>2</sub>O reveals that each copper(II) ion is shared by two ligands in a 2+2 manner. Solution EPR studies of [Cu<sub>2</sub>(glyim)<sub>2</sub>Cl(H<sub>2</sub>O)][(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O show that

dinuclearity is maintained in methanolic solutions at low concentrations, down to 2  $\times$  10<sup>–4</sup> M.

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