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Control of molecular architecture by the degree of deprotonation: self-assembled di- and tetranuclear copper(II) complexes of *N*,*N′*-bis(2-pyridylmethyl)pyrazine-2,3-dicarboxamide†

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In the absence of added base, a deep navy-blue dimeric copper complex $[Cu^{II}(H_2L)(MeCN)]_2(BF_4)_4$ (1) of the non-deprotonated bis-terdentate diamide ligand H_2L self-assembles whereas in the presence of base a grass-green [2 × 2] grid complex $[Cu^{II}(HL)]_4(BF_4)_4$ (2) of the monodeprotonated ligand HL^-, a rare example of a discrete grid of pyrazine-bridged metal ions, is formed.

A large number of self-assembled grid-type structures containing tetrahedral metal centres, such as Ag(I) and Cu(I), or octahedral metal centres, such as Fe(II), Fe(III), Co(II), Co(III), Ni(II) or Cu(II), have been reported.[1,2] With regard to advanced materials, grid complexes containing octahedral metal ions are expected to give rise to a broader range of potentially useful properties, including electrochemical and magnetic properties. The development of rigid ligands with terdentate rather than bidentate binding pockets is therefore of interest. The use of amide ligands for this purpose is advantageous, as they are easily synthesised and access to their homologues is straightforward. Extending the approach of Raymond and co-workers,[3] who chose the amide group in order to reduce the degrees of freedom of the ligands, we have chosen to also exploit its potential to coordinate to the metal ions. With simple unidentate amide ligands, coordination often occurs at the carbonyl oxygen atom, as the coordination of the amide nitrogen atom requires its deprotonation. However, multidentate ligands bearing an amide functionality are often coordinated to the metal ion through the amide nitrogen atom.[4] Amongst other ligand types, several pyridine-containing amide ligands are known to function as chelating ligands and therefore to facilitate the deprotonation of an amide nitrogen atom.[4–7]

The symmetrical diamide ligand H_2**L** (Fig. 1) features a central bridging pyrazine unit flanked by two terdentate binding pockets.[8] The 1:1 reaction of $Cu(BF_4)_2 \cdot xH_2O$ with H_2**L** in acetonitrile, in the absence of added base, followed by vapour diffusion of diethyl ether, gave a deep navy-blue crystalline solid (**1**). Conductivity measurements, not in accord with the expected [2 × 2] grid-type structure, indicated a 1:2 ratio of Cu(II) complex to BF_4^-, thus suggesting that no deprotonation of the ligand had occurred. Elemental analysis confirmed this and led to the formulation of **1** as $\{[Cu^{II}(H_2\mathbf{L})(MeCN)](BF_4)_2\}_n$. The X-ray crystal structure determination†‡ subsequently revealed compound **1** to be a centrosymmetric dimer, $[Cu^{II}(H_2\mathbf{L})(MeCN)]_2(BF_4)_4$, of the non-deprotonated zwitterionic form of the ligand H_2**L** (Fig. 2).

The Cu(II) ions are in a distorted square-pyramidal N_4O coordination environment and are separated by 6.5470(5) Å. The pyrazine ring does not bridge the two Cu(II) ions as only one of the nitrogen donor atoms is coordinated and therefore only one of the terdentate binding pockets of H_2**L** is used for metal complexation. The nitrogen donor atoms of this binding pocket, including the deprotonated amide nitrogen, occupy three equatorial coordination sites of the Cu(II) ion with the fourth site occupied by an acetonitrile coligand. The Cu(II)–N bond lengths are comparable to those of similar *N*-(2-picolyl)picolinamide complexes,[5] with shorter Cu(II)–N_{amide} (1.913 Å) than Cu(II)–$N_{heterocycle}$ (2.044 and 2.017 Å) distances. Remarkably the amide proton, H(6), has relocated to the pyridine nitrogen atom belonging to the non-chelating binding pocket of the ligand, where it is involved in a strong N–H···O hydrogen bond to the carbonyl oxygen atom of the deprotonated N-coordinated amide group. The carbonyl oxygen atom of the

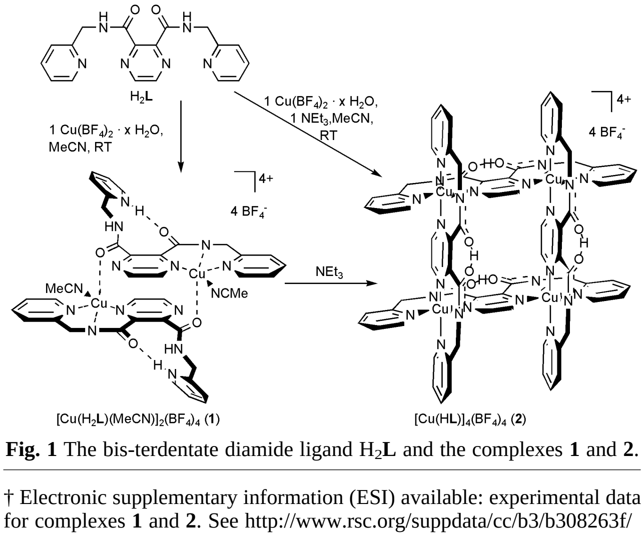

Fig. 1 The bis-terdentate diamide ligand H_2**L** and the complexes **1** and **2**.

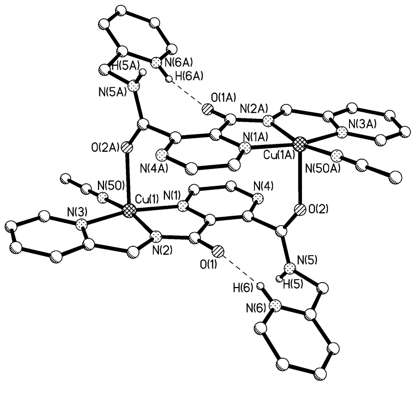

Fig. 2 Molecular structure of $[Cu^{II}(H_2\mathbf{L})(MeCN)]_2^{4+}$, the cation of complex **1**. Hydrogen atoms, except H(5), H(5A), H(6) and H(6A), have been omitted for clarity. Selected distances (Å) and angles (°): Cu(1)–N(1) 2.0442(16), Cu(1)–N(2) 1.9126(16), Cu(1)–N(3) 2.0165(16), Cu(1)–N(50) 1.9790(17), Cu(1)–O(2A) 2.2703(14), N(6)···O(1) 2.657(3); N(1)–Cu(1)–N(2) 81.08(6), N(1)–Cu(1)–N(3) 162.85(6), N(1)–Cu(1)–N(50) 98.90(7), N(1)–Cu(1)–O(2A) 92.22(6), N(2)–Cu(1)–N(3) 81.82(7), N(2)–Cu(1)–N(50) 165.93(7), N(2)–Cu(1)–O(2A) 106.16(6), N(3)–Cu(1)–N(50) 97.39(7), N(3)–Cu(1)–O(2A) 93.70(6), N(50)–Cu(1)–O(2A) 87.91(6). Symmetry operation used to generate equivalent atoms: $A = -x + 2, -y + 2, -z + 1$.

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† Electronic supplementary information (ESI) available: experimental data for complexes **1** and **2**. See http://www.rsc.org/suppdata/cc/b3/b308263f/

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non-deprotonated amide coordinates axially to the Cu(II) ion in a second complex, thereby forming the dimer. The proton, H(5), of this non-deprotonated amide group is involved in an N–H···F hydrogen bond to a BF_4^-. Both H(5) and H(6) were located from a difference map and freely refined.

The addition of one equivalent of NEt_3 to a dark navy-blue acetonitrile solution of the dimeric complex **1** afforded a light grass-green solution which, on vapour diffusion of diethyl ether, gave complex **2** as shiny grass-green octahedra. Complex **2** also resulted from the 1:1:1 reaction of $H_2\mathbf{L}$, $Cu(BF_4)_2{\cdot}xH_2O$ and NEt_3. Elemental analysis revealed the formulation of **2** to be $\{[Cu^{II}(H\mathbf{L})](BF_4)\}_n$, suggesting the loss of just one proton from $H_2\mathbf{L}$. The [2 × 2] grid structure (n = 4) of compound **2**·3.5MeCN was revealed by the X-ray crystal structure determination (Fig. 3)†‡. Here, both binding pockets of each ligand, and therefore both deprotonated amide nitrogen atoms, are involved in terdentate chelation, leading to a distorted octahedral coordination sphere for all four Cu(II) ions. Complex **2** is a rare example of a discrete grid of pyrazine-bridged metal ions[2] and the first example of an amide-based grid.

Each of the four pyrazine rings bridge two Cu(II) ions. The Cu(II)···Cu(II) distances are similar but not equal, as two shorter [Cu(3)···Cu(4) 7.101(3) Å and Cu(2)···Cu(3) 7.108(3) Å] and two slightly longer [Cu(1)···Cu(4) 7.132(3) Å and Cu(1)···Cu(2) 7.150(3) Å] distances are observed. The Cu(II) ions are shifted by *ca.* 0.28 Å in an up-down-up-down fashion relative to the Cu^{II}_4 mean plane, leading to a small tetrahedral distortion of the Cu^{II}_4 square. The average Cu(II)–N_{amide} bond length (1.941 Å) is significantly shorter than the average Cu(II)–N_{pyz} (2.215 Å) and Cu(II)–N_{py} (2.142 Å) bond lengths. The formulation of $[Cu^{II}(H\mathbf{L})]_4(BF_4)_4{\cdot}3.5MeCN$ clearly requires the presence of one retained proton per ligand strand. However, unlike in complex **1**, all nitrogen atoms of the complex cation of **2**·3.5MeCN are employed in the Cu(II) coordination sphere and therefore cannot be involved in retaining this proton. Here, these protons are, presumably, located in symmetrical O···H···O hydrogen bonds between the two amide oxygen atoms of each ligand strand. The O···O separations in the resulting seven-membered rings are in the range of 2.31–2.46 Å for all four ligands. This feature has been observed earlier by Fleischer and co-workers in the polymeric complex $[Cu^{II}_2(H\text{-}\mathbf{L'})(Cl)_3]_n$ of the homologous ligand *N*,*N′*-bis[2-(2-pyridyl)ethyl]pyrazine-2,3-dicarboxamide.[9]

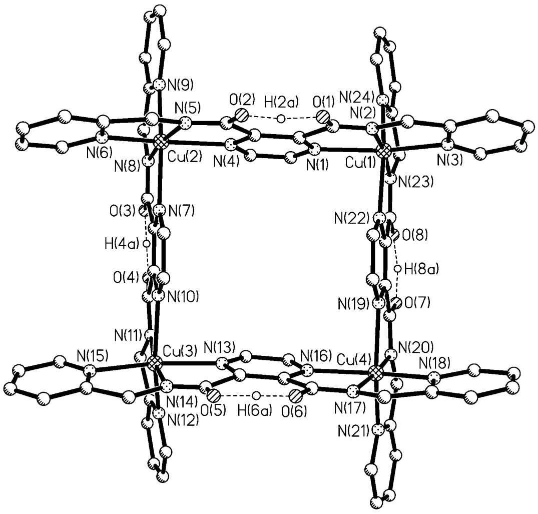

Fig. 3 Molecular structure of the monoclinic tetragonally twinned $[Cu^{II}(H\mathbf{L})]_4^{4+}$, the cation of complex **2**·3.5MeCN. Hydrogen atoms, except H(2a), H(4a), H(6a) and H(8a), have been omitted for clarity. Selected distances (Å) and angles (°): Cu(1)–N(2) 1.902(12), Cu(1)–N(23) 2.002(11), Cu(1)–N(3) 2.170(9), Cu(1)–N(24) 2.193(9), Cu(1)–N(22) 2.217(12), Cu(1)–N(1) 2.232(8), Cu(1)···Cu(3) 10.051(3), Cu(2)···Cu(4) 10.035(3), O(1)···O(2) 2.44(2), O(3)···O(4) 2.31(2), O(5)···O(6) 2.46(2), O(7)···O(8) 2.35(2), N(2)–Cu(1)–N(23) 172.6(4), N(2)–Cu(1)–N(3) 79.1(4), N(23)–Cu(1)–N(3) 104.9(3), N(2)–Cu(1)–N(24) 108.4(4), N(23)–Cu(1)–N(24) 77.2(3), N(3)–Cu(1)–N(24) 100.5(3), N(2)–Cu(1)–N(22) 96.7(4), N(23)–Cu(1)–N(22) 77.0(4), N(3)–Cu(1)–N(22) 93.2(3), N(24)–Cu(1)–N(22) 153.2(4), N(2)–Cu(1)–N(1) 76.7(4), N(23)–Cu(1)–N(1) 98.9(3), N(3)–Cu(1)–N(1) 155.7(3), N(24)–Cu(1)–N(1) 89.1(3), N(22)–Cu(1)–N(1) 87.6(4).

Only in the N-deprotonated state can the amide-containing terdentate binding pockets of $H_2\mathbf{L}$ provide the chelating coordination mode required for the formation of grids of octahedrally coordinated metal ions. As the 1:1 reaction of $H_2\mathbf{L}$ with Cu(II) ions does not lead to deprotonation of the ligand, the formation of the grass-green [2 × 2] grid species **2** requires deliberate deprotonation of the deep navy-blue precursor complex **1**. The deprotonation of **1** and formation of **2** can be monitored by UV-vis spectroscopy (ESI†), emphasising that the product architecture is controlled by the degree of ligand deprotonation.[7,8]

In both **1** and **2** one amide proton of the $H_2\mathbf{L}$ ligand is shifted and retained. When both binding pockets are occupied by Cu(II) ions, the shifted amide proton is presumed to be located in a symmetrical O···H···O hydrogen bond between the amide oxygen atoms of the ligand strand (**2**). If one of the pyridine arms is not coordinated, the shifted amide proton is bound to the nitrogen atom of the non-coordinating pyridine (**1**). To date no transition metal complexes of the doubly deprotonated ligand ($\mathbf{L}^{2-}$) have been isolated. Attempts to further deprotonate the complexes of the monodeprotonated ligand ($H\mathbf{L}^-$) do not lead to well defined reaction products.

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Notes and references

‡ CCDC 212607–212609. See http://www.rsc.org/suppdata/cc/b3/b308263f/ for crystallographic data in .cif or other electronic format.

1 For example: G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483; S. Brooker, S. J. Hay and P. G. Plieger, *Angew. Chem. Int. Ed.*, 2000, **39**, 1968; M. Ruben, E. Breuning, J.-P. Gisselbrecht and J.-M. Lehn, *Angew. Chem. Int. Ed.*, 2000, **39**, 4139; E. Breuning, M. Ruben, J.-M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Gütlich, E. Wegelius and K. Rissanen, *Angew. Chem. Int. Ed.*, 2000, **39**, 2504; S. Toyota, C. R. Woods, M. Benaglia, R. Haldimann, K. Wärnmark, K. Hardcastle and J. S. Siegel, *Angew. Chem. Int. Ed.*, 2001, **40**, 751; H. Gang, G. Dong, D. Chun-Ying, M. Hong and M. Qing-jin, *New J. Chem.*, 2002, **26**, 1371; L. K. Thompson, *Coord. Chem. Rev.*, 2002, **233–234**, 193; E. C. Constable, C. E. Housecroft, B. M. Kariuki, N. Kelly and C. B. Smith, *C. R. Chimie*, 2002, **5**, 425; M. Ruben, E. Breuning, M. Barboiu, J.-P. Gisselbrecht and J.-M. Lehn, *Chem. Eur. J.*, 2003, **9**, 291; L. K. Thompson, L. Zhao, Z. Xu, D. O. Miller and W. M. Reiff, *Inorg. Chem.*, 2003, **42**, 128; C. J. Matthews, S. T. Onions, G. Morata, M. B. Salvia and M. R. J. Elsegood, *Chem. Commun.*, 2003, 320; J. P. Plante, P. D. Jones, D. R. Powell and T. E. Glass, *Chem. Commun.*, 2003, 336; Y. Lan, D. K. Kennepohl, B. Moubaraki, K. S. Murray, J. D. Cashion, G. B. Jameson and S. Brooker, *Chem. Eur. J.*, 2003, **9**, 3772.

2 T. Bark, M. Duggeli, H. Stoeckli-Evans and A. von Zelewsky, *Angew. Chem. Int. Ed.*, 2001, **40**, 2848.

3 D. L. Caulder, C. Brückner, R. E. Powers, S. König, T. N. Parac, J. A. Leary and K. N. Raymond, *J. Am. Chem. Soc.*, 2001, **123**, 8923 and references therein.

4 H. Sigel and R. B. Martin, *Chem. Rev.*, 1982, **82**, 385; O. Clement, B. M. Rapko and B. P. Hay, *Coord. Chem. Rev.*, 1998, **170**, 203.

5 C.-Y. Wu and C.-C. Su, *Polyhedron*, 1997, **16**, 383.

6 For example: F. A. Chavez, M. M. Olmstead and P. K. Mascharak, *Inorg. Chem.*, 1996, **35**, 1410; S. Brooker, G. S. Dunbar and G. B. Jameson, *Polyhedron*, 1999, **18**, 679; S. Brooker, G. S. Dunbar and P. G. Plieger, *Inorg. Chim. Acta*, 2000, **304**, 204; D. S. Marlin, M. M. Olmstead and P. K. Mascharak, *Inorg. Chim. Acta*, 2001, **323**, 1.

7 T. Yano, R. Tanaka, T. Nishioka, I. Kinoshita, K. Isobe, L. J. Wright and T. J. Collins, *Chem. Commun.*, 2002, 1396.

8 J. Hausmann and S. Brooker, *unpublished results*.

9 E. B. Fleischer, D. Jeter and R. Florian, *Inorg. Chem.* , 1974, **13**, 1042.