A [2 × 2] nickel(II) grid and a copper(II) square result from differing binding modes of a pyrazine-based diamide ligand

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Electronic Supplementary Information

Discussion of the results of the IR studies carried out on the complexes

IR spectra were obtained for all three complexes, prepared as KBr disks. In contrast to the preparation of the KBr disk of the related compound $[Cu^{II}_2(H_2\mathbf{L}^{\mathbf{Me}})_2(MeCN)_2](BF_4)_4$ **A** of the lower ligand homologue where, consistent with co-ligand exchange with bromide ions, a colour change from dark navy blue to grass green was observed, the preparation of the KBr disk of **3**·4H_2O did not result in a colour change. As might be expected from their very different structures, the respective IR spectra are quite different (**A**: *mu(bar)* = 1668, 1644, 1618, 1539 cm^{-1}). In the IR spectrum of **3**·4H_2O a very strong sharp split band was observed in the Amide I region, at *mu(bar)* = 1636 and 1607 cm^{-1}. In the Amide II region another very strong split band was observed, at *mu(bar)* = 1569 and 1542 cm^{-1}.

Consistent with the increased symmetry of complex **4**, and the lack of water molecules of solvation, the Amide I and II bands are less split than those of **3**·4H_2O, with a strong unsplit Amide I absorption band, at *mu(bar)* = 1636 cm^{-1}, and a very strong absorption peak in the Amide II region, at *mu(bar)* = 1569 cm^{-1}, with a shoulder to higher wavenumbers. The Amide I band occurred at 15 cm^{-1} lower wavenumbers than it did in the related complex **B** (1651 cm^{-1} with a shoulder to lower wavenumbers), of the lower ligand homologue.

The IR spectrum of the nickel(II) [2 × 2] grid complex **5**·10H_2O showed two strong bands in the Amide I region, at *mu(bar)* = 1652 and 1605 cm^{-1}, and a strong absorption band in the Amide II region, at *mu(bar)* = 1562 cm^{-1}. The 1652 cm^{-1} band is identical within experimental error to the Amide I vibration of the related copper(II) [2 × 2] grid complex **B** of the lower ligand homologue. Like for **3**·4H_2O, the second band may in fact be a result of the presence of significant numbers of water molecules of crystallisation (not present in **4**). The strong band at *mu(bar)* = 1562 cm^{-1} was comparable to the bands observed in the IR spectra of **3**·4H_2O (*mu(bar)* = 1565 cm^{-1}) and **4** (*mu(bar)* = 1569 cm^{-1}).

For all three complexes the expected presence of tetrafluoroborate counter ions was confirmed by the observation of a broad split absorption band/multiplet at around *mu(bar)* = 1080 cm^{-1}.

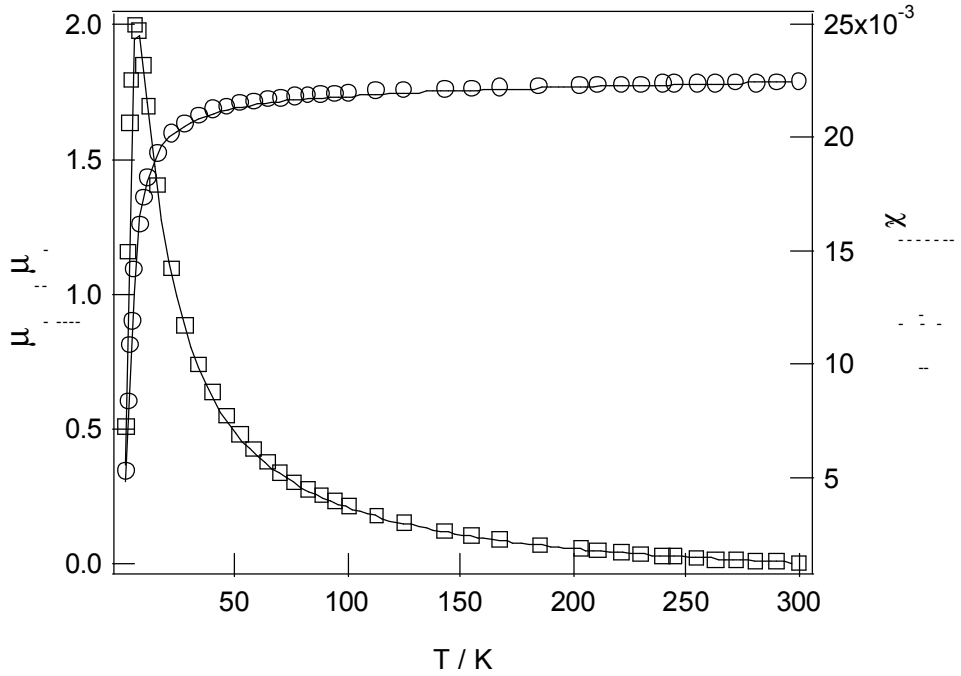

Figure S1. Thermal variation of μ_{eff} (○○) and χ_m (□□), per Cu(II), for $[Cu^{II}_4(H\mathbf{L}^{Et})_4](BF_4)_4$ (**4**). The solid lines represent the best fits using the parameters given in the text.

Table S1 Selected distances [Å] for the complexes **3**·3MeCN·0.5H_2O, **4** and **5**·10MeCN.

[Å]	**3**·3MeCN·0.5H_2O	**4**[a]	**5**·10MeCN	
M–N_{pz}	Cu(1)–N(1) 2.032(5)	Cu(1)–N(1) 2.024(6)	Ni(1)–N(1) 2.106(5)	Ni(5)–N(25) 2.141(5)
	Cu(1)–N(10) 2.316(5)	Cu(1)–N(2A) 2.226(7)	Ni(1)–N(13) 2.130(4)	Ni(5)–N(37) 2.148(4)
	Cu(2)–N(7) 2.052(5)		Ni(2)–N(4) 2.104(5)	Ni(6)–N(28) 2.119(5)
	Cu(2)–N(16) 2.247(5)		Ni(2)–N(19) 2.145(4)	Ni(6)–N(43) 2.135(4)
	Cu(3)–N(13) 2.039(5)		Ni(3)–N(7) 2.139(4)	Ni(7)–N(31) 2.137(4)
	Cu(3)–N(22) 2.275(5)		Ni(3)–N(16) 2.130(4)	Ni(7)–N(40) 2.174(4)
	Cu(4)–N(4) 2.313(5)		Ni(4)–N(10) 2.129(4)	Ni(8)–N(34) 2.117(5)
	Cu(4)–N(19) 2.027(5)		Ni(4)–N(22) 2.143(4)	Ni(8)–N(46) 2.154(4)
M–L_{am}	Cu(1)–N(2) 1.914(5)	Cu(1)–N(3) 1.895(6)	Ni(1)–N(2) 2.020(5)	Ni(5)–N(26) 2.017(5)
	Cu(1)–O(4) 1.958(4)	Cu(1)–O(2A) 1.966(5)	Ni(1)–N(14) 2.047(4)	Ni(5)–N(38) 2.035(4)
	Cu(2)–N(8) 1.915(5)		Ni(2)–N(5) 2.027(5)	Ni(6)–N(29) 2.028(5)
	Cu(2)–O(6) 1.974(4)		Ni(2)–N(20) 2.041(4)	Ni(6)–N(44) 2.019(4)
	Cu(3)–N(14) 1.931(5)		Ni(3)–N(8) 2.036(4)	Ni(7)–N(32) 2.036(5)
	Cu(3)–O(8) 1.997(4)		Ni(3)–N(17) 2.042(4)	Ni(7)–N(41) 2.043(4)
	Cu(4)–N(20) 1.924(5)		Ni(4)–N(11) 2.037(4)	Ni(8)–N(35) 2.024(4)
	Cu(4)–O(2) 1.993(4)		Ni(4)–N(23) 2.029(4)	Ni(8)–N(47) 2.044(4)
M–N_{py}	Cu(1)–N(3) 2.004(5)	Cu(1)–N(4) 2.009(6)	Ni(1)–N(3) 2.089(5)	Ni(5)–N(27) 2.116(6)
	Cu(2)–N(9) 2.027(5)		Ni(1)–N(15) 2.120(5)	Ni(5)–N(39) 2.122(5)
	Cu(3)–N(15) 2.007(5)		Ni(2)–N(6) 2.112(5)	Ni(6)–N(30) 2.124(8)
	Cu(4)–N(21) 2.012(5)		Ni(2)–N(21) 2.115(5)	Ni(6)–N(45) 2.117(5)
			Ni(3)–N(9) 2.114(4)	Ni(7)–N(33) 2.102(5)
			Ni(3)–N(17) 2.042(4)	Ni(7)–N(42) 2.122(4)
			Ni(4)–N(12) 2.108(4)	Ni(8)–N(36) 2.130(5)
			Ni(3)–N(18) 2.162(5)	Ni(8)–N(48) 2.120(4)
			Ni(4)–N(24) 2.163(4)	
M···M (pz-bridged)	Cu(1)···Cu(2) 7.051(1)	Cu(1)···Cu(1A) 6.922(2)	Ni(1)···Ni(2) 6.941(1)	Ni(5)···Ni(6) 7.009(1)
	Cu(2)···Cu(3) 6.997(1)	Cu(1)···Cu(1C) 6.922(2)	Ni(2)···Ni(4) 7.016(1)	Ni(5)···Ni(7) 7.004(1)
	Cu(3)···Cu(4) 7.009(1)		Ni(3)···Ni(1) 7.003(1)	Ni(6)···Ni(8) 7.026(1)
	Cu(4)···Cu(1) 7.037(1)		Ni(4)···Ni(3) 7.008(1)	Ni(7)···Ni(8) 6.987(1)
M···M (diagonal)	Cu(1)···Cu(3) 9.953(1)	Cu(1)···Cu(1B) 9.777(3)	Ni(1)···Ni(4) 9.776(1)	Ni(5)···Ni(8) 9.813(1)
	Cu(2)···Cu(4) 9.847(1)		Ni(2)···Ni(3) 9.999(1)	Ni(6)···Ni(7) 10.002(1)

[a] Symmetry operations used to generate equivalent atoms: **4**: (A) x–0.5, –y+0.5, –z+0.5.

Table S2 Selected bond angles [°] for the complexes **3**·3MeCN·0.5H_2O, **4** and **5**·10MeCN.

[°]	**3**·3MeCN·0.5H_2O	**4**[a]	**5**·10MeCN	
N_{pz}–M–N_{pz}	N(1)–Cu(1)–N(10) 99.6(2)	N(1)–Cu(1)–N(2A) 99.6(2)	N(1)–Ni(1)–N(13) 87.0(2)	N(25)–Ni(5)–N(37) 88.1(2)
	N(7)–Cu(2)–N(16) 98.5(2)		N(4)–Ni(2)–N(19) 86.1(2)	N(28)–Ni(6)–N(43) 87.7(2)
	N(13)–Cu(3)–N(22) 96.0(2)		N(7)–Ni(3)–N(16) 85.9(2)	N(31)–Ni(7)–N(40) 85.5(2)
	N(4)–Cu(4)–N(19) 96.9(2)		N(10)–Ni(4)–N(22) 87.0(1)	N(34)–Ni(8)–N(46) 86.5(2)
N_{pz}–M–L_{am}	N(1)–Cu(1)–N(2) 80.6(2)	N(1)–Cu(1)–N(3) 80.1(2)	N(1)–Ni(1)–N(2) 77.4(2)	N(25)–Ni(5)–N(26) 76.2(2)
	N(1)–Cu(1)–O(4) 93.5(2)	N(1)–Cu(1)–O(2A) 94.3(2)	N(1)–Ni(1)–N(14) 92.4(2)	N(25)–Ni(5)–N(38) 93.8(2)
	N(10)–Cu(1)–N(2) 105.2(2)	N(2A)–Cu(1)–N(3) 102.1(3)	N(13)–Ni(1)–N(2) 92.3(2)	N(37)–Ni(5)–N(26) 93.3(2)
	N(10)–Cu(1)–O(4) 74.3(2)	N(2A)–Cu(1)–O(2A) 76.5(2)	N(13)–Ni(1)–N(14) 77.1(3)	N(37)–Ni(5)–N(38) 76.8(2)
	N(7)–Cu(2)–N(8) 80.8(2)		N(4)–Ni(2)–N(5) 77.4(2)	N(28)–Ni(6)–N(29) 77.0(2)
	N(7)–Cu(2)–O(6) 90.9(2)		N(4)–Ni(2)–N(20) 92.1(3)	N(28)–Ni(6)–N(44) 93.8(2)
	N(16)–Cu(2)–N(8) 106.8(2)		N(19)–Ni(2)–N(5) 93.5(2)	N(43)–Ni(6)–N(29) 95.4(2)
	N(16)–Cu(2)–O(6) 75.0(2)		N(19)–Ni(2)–N(20) 76.1(2)	N(43)–Ni(6)–N(44) 76.6(2)
	N(13)–Cu(3)–N(14) 80.1(2)		N(16)–Ni(3)–N(8) 94.5(2)	N(31)–Ni(7)–N(32) 76.5(2)
	N(13)–Cu(3)–O(8) 95.4(2)		N(16)–Ni(3)–N(17) 76.8(2)	N(31)–Ni(7)–N(41) 94.0(2)
	N(19)–Cu(4)–O(2) 93.2(2)		N(7)–Ni(3)–N(8) 75.8(2)	N(40)–Ni(7)–N(32) 95.3(2)
	N(19)–Cu(4)–N(20) 80.4(2)		N(7)–Ni(3)–N(17) 93.7(2)	N(40)–Ni(7)–N(41) 75.6(2)
	N(22)–Cu(3)–N(14) 103.7(2)		N(10)–Ni(4)–N(11) 76.5(2)	N(34)–Ni(8)–N(35) 76.8(2)
	N(22)–Cu(3)–O(8) 74.0(2)		N(10)–Ni(4)–N(23) 93.3(2)	N(34)–Ni(8)–N(47) 93.9(2)
	N(4)–Cu(4)–N(20) 105.7(2)		N(22)–Ni(4)–N(11) 93.3(2)	N(46)–Ni(8)–N(35) 93.8(2)
	N(4)–Cu(4)–O(2) 73.2(2)		N(22)–Ni(4)–N(23) 76.5(2)	N(46)–Ni(8)–N(47) 75.8(2)
N_{pz}–M–N_{py}	N(1)–Cu(1)–N(3) 160.2(2)	N(1)–Cu(1)–N(4) 147.3(2)	N(1)–Ni(1)–N(3) 169.4(2)	N(25)–Ni(5)–N(27) 167.2(2)
	N(10)–Cu(1)–N(3) 100.3(2)	N(2A)–Cu(1)–N(4) 113.1(2)	N(1)–Ni(1)–N(15) 86.4(2)	N(25)–Ni(5)–N(39) 90.9(2)
	N(7)–Cu(2)–N(9) 163.0(2)		N(13)–Ni(1)–N(3) 90.8(2)	N(37)–Ni(5)–N(27) 88.4(2)
	N(16)–Cu(2)–N(9) 98.4(2)		N(13)–Ni(1)–N(15) 167.2(2)	N(37)–Ni(5)–N(39) 168.8(2)
	N(13)–Cu(3)–N(15) 159.3(2)		N(4)–Ni(2)–N(6) 167.8(2)	N(28)–Ni(6)–N(30) 166.7(2)
	N(22)–Cu(3)–N(15) 104.7(2)		N(4)–Ni(2)–N(21) 89.2(2)	N(28)–Ni(6)–N(45) 92.1(2)
	N(4)–Cu(4)–N(21) 99.4(2)		N(19)–Ni(2)–N(6) 90.8(2)	N(43)–Ni(6)–N(30) 87.6(3)

	N(19)–Cu(4)–N(21) 163.7(2)		N(19)–Ni(2)–N(21) 166.2(2)	N(43)–Ni(6)–N(45) 168.3(2)
			N(16)–Ni(3)–N(9) 86.6(2)	N(31)–Ni(7)–N(33) 166.1(2)
			N(16)–Ni(3)–N(18) 165.3(2)	N(31)–Ni(7)–N(42) 89.6(2)
			N(7)–Ni(3)–N(9) 165.6(2)	N(40)–Ni(7)–N(33) 88.6(2)
			N(7)–Ni(3)–N(18) 87.5(2)	N(40)–Ni(7)–N(42) 166.1(2)
			N(10)–Ni(4)–N(12) 168.2(2)	N(34)–Ni(8)–N(36) 167.5(2)
			N(10)–Ni(4)–N(24) 85.6(2)	N(34)–Ni(8)–N(48) 88.2(2)
			N(22)–Ni(4)–N(12) 88.0(2)	N(46)–Ni(8)–N(36) 90.6(2)
			N(22)–Ni(4)–N(24) 165.6(2)	N(46)–Ni(8)–N(48) 166.3(2)
L_{am}–M–L_{am}	N(2)–Cu(1)–O(4) 174.0(2)	O(2A)–Cu(1)–N(3) 174.0(3)	N(2)–Ni(1)–N(14) 165.8(2)	N(26)–Ni(5)–N(38) 166.3(2)
	N(8)–Cu(2)–O(6) 171.6(2)		N(5)–Ni(2)–N(20) 165.8(2)	N(29)–Ni(6)–N(44) 168.2(2)
	N(14)–Cu(3)–O(8) 174.9(2)		N(8)–Ni(3)–N(17) 166.9(2)	N(32)–Ni(7)–N(41) 167.4(2)
	N(20)–Cu(4)–O(2) 173.3(2)		N(11)–Ni(4)–N(23) 166.1(2)	N(35)–Ni(8)–N(47) 166.7(2)
L_{am}–M–N_{py}	N(2)–Cu(1)–N(3) 94.2(2)	N(3)–Cu(1)–N(4) 93.9(3)	N(2)–Ni(1)–N(3) 92.3(2)	N(26)–Ni(5)–N(27) 91.7(3)
	O(4)–Cu(1)–N(3) 91.8(2)	O(2A)–Cu(1)–N(4) 92.0(2)	N(2)–Ni(1)–N(15) 96.9(2)	N(26)–Ni(5)–N(39) 97.2(2)
	N(8)–Cu(2)–N(9) 94.9(2)		N(14)–Ni(1)–N(3) 97.2(2)	N(38)–Ni(5)–N(27) 97.4(2)
	O(6)–Cu(2)–N(9) 92.9(2)		N(14)–Ni(1)–N(15) 92.3(2)	N(38)–Ni(5)–N(39) 92.2(2)
	N(14)–Cu(3)–N(15) 93.7(2)		N(5)–Ni(2)–N(6) 91.0(2)	N(29)–Ni(6)–N(45) 95.9(2)
	O(8)–Cu(3)–N(15) 91.4(2)		N(5)–Ni(2)–N(21) 98.2(2)	N(29)–Ni(6)–N(30) 91.1(3)
	N(20)–Cu(4)–N(21) 94.0(2)		N(20)–Ni(2)–N(6) 98.7(2)	N(44)–Ni(6)–N(45) 91.8(2)
	O(2)–Cu(4)–N(21) 92.8(2)		N(20)–Ni(2)–N(21) 91.1(2)	N(44)–Ni(6)–N(30) 97.2(3)
			N(8)–Ni(3)–N(9) 92.6(2)	N(32)–Ni(7)–N(33) 91.5(2)
			N(8)–Ni(3)–N(18) 96.6(2)	N(32)–Ni(7)–N(42) 96.2(2)
			N(17)–Ni(3)–N(9) 96.5(2)	N(41)–Ni(7)–N(33) 96.8(2)
			N(17)–Ni(3)–N(18) 90.6(2)	N(41)–Ni(7)–N(42) 91.9(2)
			N(23)–Ni(4)–N(12) 95.9(2)	N(35)–Ni(8)–N(48) 97.3(2)
			N(23)–Ni(4)–N(24) 91.7(2)	N(35)–Ni(8)–N(36) 91.3(2)
			N(11)–Ni(4)–N(12) 93.1(2)	N(47)–Ni(8)–N(48) 92.0(2)
			N(11)–Ni(4)–N(24) 96.9(2)	N(47)–Ni(8)–N(36) 97.1(2)
N_{py}–M–N_{py}	–	–	N(3)–Ni(1)–N(15) 97.6(2)	N(27)–Ni(5)–N(39) 94.9(2)
			N(6)–Ni(2)–N(21) 96.3(2)	N(30)–Ni(6)–N(45) 95.1(3)
			N(9)–Ni(3)–N(18) 102.5(2)	N(33)–Ni(7)–N(42) 99.0(2)
			N(12)–Ni(4)–N(24) 101.5(2)	N(36)–Ni(8)–N(48) 97.2(2)

[a] Symmetry operations used to generate equivalent atoms: **4**: (A) x–0.5, –y+0.5, –z+0.5; (B) –x+1, –y, z; (C) –x+0.5, y+0.5, –z+0.5.

Table S3 Selected hydrogen-bond distances [Å] for the complexes **3**·3MeCN·0.5H_2O, **4** and **5**·10MeCN.

[Å]	**3**·3MeCN·0.5H_2O[a]	**4**[a]	**5**·10MeCN	
intramolecular	N(5)···O(1) 2.576(5)	N(5)···O(1) 2.551(9)	O(1)···O(2) 2.386(6)	O(9)···O(10) 2.362(6)
	N(11)···O(3) 2.561(5)		O(3)···O(4) 2.386(5)	O(11)···O(12) 2.408(5)
	N(17)···O(5) 2.547(5)		O(5)···O(6) 2.386(4)	O(13)···O(14) 2.395(5)
	N(23)···O(7) 2.557(5)		O(7)···O(8) 2.398(4)	O(15)···O(16) 2.397(5)
intermolecular	N(18)···N(6A) 2.703(5)	–	–	–
	N(24)···N(12B) 2.732(5)			

[a] Symmetry operations used to generate equivalent atoms: **3**·3MeCN·0.5H_2O: (A) –x+1, –y+1, –z+1; (B) –x+1, –y+1, –z; **4**: (A) x–0.5, –y+0.5, –z+0.5.