Four copper(II) pyrazolide complexes derived from reactions of 3{5}-substituted pyrazoles with CuF₂ or Cu(OH)₂†‡

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Treatement of CuF₂ with 2 equiv of 3{5}-(pyrid-2-yl)pyrazole (Hpz²⁺), 3{5}-phenylpyrazole (HpzPh)²⁺ or 3{5}-(4-fluorophenyl)pyrazole (HpzPhF)²⁺ in MeOH, followed by evaporation to dryness and recrystallisation of the solid residues, allows solvated crystals of [{Cu(µ-pz')(pz²⁺)}₂] (1), [{Cu(µ-pz²⁺)(pz²⁺)}₂] (2) and [{Cu₂F₃(µ₂-F)(µ-pz²⁺)}₄(HpzPh²⁺)₅] (3) to be isolated in moderate-to-good yields. Similar reactions of these three pyrazoles with Cu(OH)₂ in refluxing MeOH respectively afford 1,2 and [Cu(pz²⁺)(HpzPh²⁺)] (4) in ca. 10% yield. Crystalline 1·1.5·CH₂Cl₂ contains two independent dinuclear molecules with a puckered di-(1,2-pyrazolido) bridge motif, linked by a bridging, hydrogen-bonding water molecule. Compound 2·1.2C₅H₁₂, containing cyclic, square tetranuclear complex molecules, is the first homoleptic divalent metal pyrazolide to have a discrete molecular rather than polymeric structure, for a metal other than Pd or Pt. The two independent complex molecules in 3·3.5·CH₂Cl₂·HpzPhF²⁺ contain a unique tetrahedral [Cu₄(µ₂-F)]²⁺ core, three of whose edges are spanned by bridging pyrazolide groups. Magnetic data show that the copper centres in 1 and 3 are antiferromagnetically coupled, but that dried bulk samples of 2 do not retain their molecular structure.

Introduction

Pyrazoles are very versatile bridging ligands in transition metal chemistry. When deprotonated, they can link two metal ions through their two adjacent N donors, which typically places the metal ions 3.5–4.5 Å apart. A wide variety of dinuclear and polynuclear organometallic and coordination complexes have been prepared containing 1,2-pyrazolido bridges, including organometallic catalysts, cyclic toroidal host : guest complexes and other high-nuclearity structures. Conversely, in their neutral form, pyrazoles can bond simultaneously to metal ions (through their pyridinic N atom) and to anions (by donating hydrogen bonds with their pyrrolic N–H groups), making pyrazoles useful ditopic ligands for metal salts. While metal pyrazole complex chemistry is very well established, we have found that addition of base to reactions of copper salts with simple pyrazoles can lead to novel polymeric structures, containing both types of bridging pyrazole ligand. Of particular relevance here is the cyclic hexanuclear compound [{Cu₃(HpzPh)₅(µ₂-F)}₂].F₂, formed in good yield from the reaction of CuF₂, 3{5}-tert-butylpyrazole (HpzPh²⁺) and NaOH in MeOH, which contains two encapsulated fluoride ions within tripyrazole pockets on opposite sides of the molecule. We were keen to examine reactions of other pyrazole derivatives with CuF₂, to see if other similarly novel structures could be prepared. We report here three very different copper(II) complexes obtained in this way. One of these is a homoleptic copper(II) pyrazolide with a unique molecular, rather than polymeric, structure, while another is a tetranuclear complex with a novel fluoro-centred tetrahedral metal core.

Results and discussion

Treatement of CuF₂ with two molar equiv. of 3{5}-(pyrid-2-yl)pyrazole (Hpz²⁺)¹⁴ in MeOH at room temperature, in the presence of two equiv. of NaOH, yields a blue solution. This was filtered, evaporated to dryness and the solid residue extracted into chloroform. Addition of a large excess of pentane to the resultant solution and storage at –30 °C, led to the slow formation of blue crystals that were formulated as [{Cu(µ-pz²⁺)(pz²⁺)}₂].1/2H₂O.2CHCl₃, (1·1/2H₂O.2CHCl₃) by a crystal structure determination. An analogous reaction employing 3{5}-phenylpyrazole (HpzPhF)¹⁴ afforded the dark green hemipentane solvate of the tetranuclear product [{Cu₄(µ₂-F)}₂] (2·1/2C₅H₁₂). Interestingly, however, a very similar procedure...
with 3-[5-(4-fluorophenyl)pyrazole (HpzPhF)₃] and excess triethylamine as base, afforded blue-green crystals of a third, very different tetranuclear product of formula [Cu₄F₂(μ₄-F)(μ-PzPhF)₃](HpzPhF)₃/3/4CH₂Cl₂·HpzPhF (3-3/4CH₂Cl₂·HpzPhF). All these compounds were obtained in moderate yields, ranging from 30–68%. Reactions of HpzPy and HpzPh with Cu(OH)₂ in refluxing MeOH again afforded 1 and 2, albeit in much lower yields of ca. 10% reflecting the insolubility of the Cu(OH)₂ starting material. However, the only crystalline product obtained from reactions of HpzPhF with Cu(OH)₂ was instead mononuclear material. However, the only crystalline product obtained from reactions of HpzPhF with Cu(OH)₂ was instead mononuclear [Cu(PzPhF)₂(HpzPhF)₂] (4), which formed blue solvent-free crystals in 13% yield from CH₂Cl₂/Et₂O (ESI‡). The solvated crystals of 1–3 all collapsed upon drying in vacuo to powdered solids, whose microanalyses were consistent with the formulations of the unsolvated complexes. All magnetochemical and spectroscopic measurements were performed using these dried powders.

The asymmetric unit of 1-1/2H₂O·2CHCl₃ contains two unique complex molecules (labelled “A” and “B”) linked by a bridging hydrogen-bonded water molecule, and four molecules of chloroform, two of which also donate hydrogen bonds (Fig. 1). The two complex molecules have identical connectivities, being dimers of five-coordinate metal ions with apical pyridyl donors (Fig. 1, ESI†). The molecules differ, however, in that the copper ions in molecule A show stronger distortions away from an ideal square-pyramidal geometry than in molecule B. That is evident in their crystallographically ordered N-donors. This geometry is similar to that adopted by other copper(II) di(pyrazolide) salts, which adopt 1-D polymeric structures. The more regular geometry of molecule B is also reflected in its apical bond lengths Cu(1B)–N(31B) and Cu(2B)–N(42B), which are 0.048(4)–0.063(4) Å longer than the corresponding bonds in molecule A (ESI‡). The apical pyridyl groups C(30)–C(35) and C(41)–C(46) in the two molecules are syn to each other across their [Cu(μ₂-PzPhF)]₄⁺ bridges, being 3.2–3.4 Å apart at their closest approach. However, the large dihedral angles between these moieties [32.25(19)° in molecule A and 35.99(17)° in molecule B], which are a consequence of the puckered [Cu(μ₂-PzPhF)]₄⁺ geometry, means that these pyridyl rings do not form π–π interactions with each other. Three of the four uncoordinated pyrazolido N atoms in the two structures accept intermolecular hydrogen bonds. These are two O–H···N interactions, from water molecule O(63) to N(37A) and N(26B); and a C–H···N bond from chloroform molecule C(59)–Cl(62) to N(37B). There is also one further C–H···O interaction from another chloroform molecule C(47)–Cl(50) to O(63).

While the crystallographic data and refinement are good, the structure determination of 2-1/2C₂H₆O is complicated by disorder in both the solvent and three of the [pzPhF]⁺ ligands. The structure analysis showed that 2 has a cyclic tetrameric structure, with four four-coordinate Cu ions each linked to its neighbours by two [pzPhF]⁺ bridges (Fig. 2, ESI†). The molecule has approximate S₄ symmetry, although there are several local structural distortions away from this idealised symmetry. Each of the four Cu₄[pzPhF]⁺ moieties in the compound has a head-to-head disposition of phenyl groups, presumably to avoid steric clashes between them. The coordination geometry at the four Cu centres shows a substantial tetrahedral twist. The crystallographically ordered trans-N–Cu–N angles in the structure range from 142.78(9)–154.97(9)°, while the dihedral angle between the planes [Cu(3), N(49), N(60)] and [Cu(3), N(49), N(60)] is 43.97(9)° (Cu(3) is the only Cu atom in the structure bound to four crystallographically ordered N-donors). This geometry is similar to that adopted by other copper(II) dipyrazolide salts, which adopt 1-D polymeric...
The Cu–N bond lengths in 2 are typical for four-coordinate copper(II) centres, while the Cu···Cu distances between directly linked Cu ions lie between 3.2771(7)–3.3342(7) Å. Space-filling models of 2 show that there is no cavity within the cyclic molecule.

Crystals of 3·3/4CH2Cl2·HpzF both again contain two independent complex molecules labelled “A” and “B”, with identical connectivities, similar patterns of pyrazole ligand disorder (see Experimental section) and only small differences in their metric parameters (ESI†). The four copper ions in 3 are disposed in a distorted tetrahedral arrangement, that is approximately C3v-symmetric if the aryl substituents on the pyrazole groups are ignored. This copper tetrahedron is centred by a μ2-F− ion, forming four Cu–F bonds of 2.226(2)–2.324(2) Å (Fig. 3 and 4, ESI†). Two opposite edges of the copper tetrahedra are bridged by two μ1,2-[PzF]− bridging ligands, one pair having a head-to-head disposition of phenyl substituents and the other being head-to-tail. A third edge bears a single μ1,2-[PzF]− bridging ligand, while the other three edges are unbridged. The eight individual copper ions in the asymmetric unit all have geometries that are close to square pyramidal with F(1A) or F(1B) apical, with τ = 0.164(3)–0.321(3). The basal planes of Cu(1) and Cu(2) in each molecule are formed by two cis μ1-[PzF]− ligands, and by terminal F− and terminal HPzF ligands, while those of Cu(3) and Cu(4) are bound by three μ3-[PzF]− and one terminal HPzF ligands. Each terminal fluoride ligand accepts N–H···F hydrogen bonds from two of the four HPzF moieties in the molecules. The geometry at μ1,2-F− ligand F(1X) (X = A or B) is somewhat flattened, since two opposite edges of the [Cu2(μ1,2-F−)]4+ tetrahedron are spanned by very obtuse angles [Cu(1X)–F(1X)–Cu(3X) and Cu(2X)–F(1X)–Cu(4X)] of 133.68(9)–137.55(10)°, while three of the other four Cu–F(1X)–Cu angles in each molecule have contracted to 89.06(7)–93.10(8)° to compensate. However, the average of the six Cu–F(1X)–Cu angles in molecules A and B is 110.1(2) and 110.4(2)° respectively, showing that this geometry is best considered as distorted tetrahedral.

Crystals of 4 contain discrete, mononuclear [Cu(pzF)]2− ligands, whose square-planar geometry has a significant tetrahedral twist with trans-N–Cu–N angles of 140.69(16)–143.76(16)° (ESI†). The protonated and deprotonated pyrazole ligands are crystallographically distinguishable (see Experimental section), and form two intramolecular N–H···N hydrogen bonded pairs.

At room temperature /\gamma_m T for 1 is 0.7 cm−1 mol−1 K, slightly smaller than the value expected from two independent copper(II) ions with a sensible g value (ca. 0.8 cm−1 mol−1 K18). As the temperature is decreased /\gamma_m T also decreases steadily, reaching 0.05 cm−1 mol−1 K at 45 K and then continuing to decrease more slowly as the temperature is lowered further. These data were well-reproduced by the Bleaney–Bowers equation for a dicopper(II) complex (H = −2J1(S1 · S2)Hamiltonian).19 giving J = −88.7(5) cm−1, g = 2.13(1) and a paramagnetic impurity term ρ = 7.8(2)% . The refined value of g agrees well with the average g value predicted by the solid-state EPR spectrum of 1, g = 2.12 (see below).

The variable temperature susceptibility data for 3 are similar in form to those of 1, decreasing steadily from /\gamma_m T = 1.4 cm−1 mol−1 K at 330 K to 0.10 cm−1 mol−1 K at 40 K before decreasing more slowly as the temperature is lowered to 5 K (Fig. 5). These data were modelled using the Hamiltonian in eqn (1):

\[ H = -2J_1(S_1 \cdot S_2 + S_2 \cdot S_3 - 2J_2(S_1 \cdot S_3)) \]

where S1–S3 correspond to the equivalently numbered Cu atoms in the crystal structure of 3 (S1 = Cu1 etc., Fig. 3). Hence, J1 describes superexchange across the two [Cu2(μ-pzF)2(μ-F)]2− bridging groups, while J2 describes superexchange mediated by the [Cu2(μ-pzF)(μ-F)]2− moiety in the structure. Magnetic coupling between Cu(1) and Cu(2), Cu(1) and Cu(3), and Cu(2) and Cu(4),
Fig. 5 Variable temperature magnetic susceptibility data for 1 (♦) and 3 (○), and the best fits of these data (lines) to the equations described in the text. Data for 2 are given in the ESI‡.

is expected to be weak because these pairs of copper ions are only covalently bridged by the apical $\mu_2$-F$^-$ ligand, which does not interact directly with their d$_{xy}$ magnetic orbitals. Hence, to avoid over-parametrisation these interactions were neglected in the magnetochemical analysis. The spin-energy levels described by eqn (1) have been elucidated by others$^{19}$ and the susceptibility data for 3 were reproduced reasonably by the resultant van Vleck equation (Fig. 5), giving the parameters $J_1 = -97.9(7) \text{ cm}^{-1}$, $J_2 = -68(5) \text{ cm}^{-1}$ and $\rho = 10(1)\%$. Attempts to refine the g term in these fits led to strongly correlated g and J values. Hence g was fixed at 2.14, the value derived by EPR (see below), in the final fit. The small deviation of the simulation from the observed data below 50 K, and the slightly high value of $\rho$ (which is also governed by the low-temperature data), may reflect the approximations in the model used which neglects any weak superexchange mediated by the apical F$^-$ ligand.

The values of $J$ for 1 and $J_1$ for 3 derived from these analyses are typical values for copper centres linked by bis-pyrazolido bridges, for which $-240 \leq J \leq -70 \text{ cm}^{-1}$ is typically observed.$^{20-22}$ The value of $J_2$ for 3 is higher than usually found in dinuclear copper(II) complexes with a single pyrazolido bridge, which lie in the range $-32 \leq J \leq -12 \text{ cm}^{-1}$. However, a similar $J$ value ($J \approx -78 \text{ cm}^{-1}$) has been proposed for one other tetranuclear copper(II) complex containing mono-pyrazolido bridging groups.$^{24}$

In contrast to 1 and 3, magnetic data for 2 were sample-dependent. A typical measurement showed an almost monotonic decrease in $\chi_M T$ with temperature, from 1.5–1.7 cm$^3$ mol$^{-1}$ K at room temperature to near-zero at 5 K (ESI‡). This linear temperature dependence cannot be reproduced by the Hamiltonian describing a square of copper(II) spins (eqn (2)):

$$H = -2J_1(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1)$$

which predicts a $\chi_M T$ vs. $T$ curve of similar shape to that shown by 3 (ESI‡). Attempts to model the data as a 1-D polymer of copper(II) spins, the structure adopted by other homoleptic copper(II) pyrazolides,$^{13}$ were similarly unsuccessful. These data imply that, despite their apparent analytical purity, bulk samples of 2 do not contain purely the tetrameric molecule observed in the solvated crystals and are probably inhomogeneous.

The X-band (9.35 GHz) EPR spectrum of powdered 1 at 115 K is typical of a $S = 1$ spin-system, and shows a pronounced $\Delta m_s = \pm 2$ half-field resonance near 1590 G (ESI‡). This spectrum was further resolved at W-band (94.0 GHz) at 100 K, into a clearly rhombic spectrum with the six resonance lines expected from a randomly oriented rhombic spin–triplet (Fig. 6). Because of the low probability of the formally forbidden “half-field” transition at higher magnetic fields no such signal was observed at W-band.

Fig. 6 Observed (top) and simulated (bottom) W-band EPR spectrum of solid 1 at 100 K. Parameters derived from the simulation are given in the text.
From a simulation the following data were extracted: \( g_x = 2.100(1) \), \( g_y = 2.121(1) \), \( g_z = 2.135(1) \), \( |J| = 0.158(2) \) cm\(^{-1}\) and \( |E| = 0.041(2) \) cm\(^{-1}\) (Fig. 6). The value of \( |D| \) suggests only a limited level of delocalisation of the unpaired electron density, whereas \( |E| \) reflects significant distortion of the spectrum from the axial symmetry \( 3 \big| (1) \).

The EPR spectra of solid 2 and 3 are less informative, showing single isotropic lines at \( g = 2.12 \) (2) and 2.14 (3) at \( X\)-band at 115 K. Compound 3 (but not 2) also exhibits a weak half-field resonance under these conditions, consistent with its being an integer-spin system.

Conclusions

There are three other dicopper(II) complexes comparable to 1 in the literature. Of particular relevance is \( [\text{Cu}_2(\mu-\text{pzPh})_2(\text{HpzPh})][\text{ClO}_4]_2 \), the doubly protonated congener of 1 (\( [\text{H}_2][\text{ClO}_4] \)). While the basic connectivity in 1 and \( [\text{H}_2][\text{ClO}_4] \) is the same, they differ in that \( [\text{H}_2][\text{ClO}_4] \) crystallises with anti rather than syn apical pyridyl groups and has a perfectly planar \( [\text{Cu}_2(\mu-\text{pzPh})_2][\text{ClO}_4]_2 \) bridge motif. Several different magnetostuctural correlations have been proposed for \( [\text{Cu}_2(\mu-\text{pyrazolido})]_2^+ \) complexes, making it difficult to rationalise simply the weak antiferromagnetism of 1 (\( |J| = -88.7(5) \) cm\(^{-1}\)) compared to \( [\text{H}_2][\text{ClO}_4] \) (\( -105 \) cm\(^{-1}\)). However, the puckered \( [\text{Cu}_2(\mu-\text{pzPh})]_2^+ \) group in 1 is probably a contributing factor, since it has been shown that \( J \) is reduced if the two bridging pyrazoloido groups in these compounds are not coplanar.

Although we only achieved limited characterisation of bulk samples of 2, which apparently decompose upon exposure to air, its molecular structure is of some interest. First, 2 is notable as the first homoleptic divalent metal pyrazolide to have a discrete molecular structure containing a late transition metal in a moderate oxidation state. As in most (but not all\(^{36}\)) of these other examples the \( \mu_2-\text{F}^- \) in 3 is in an approximately tetrahedral environment.

Experimental

Ligands \( \text{HpzPh} \), \( \text{HpzPh} \) and \( \text{HpzPh} \) were synthesised according to the literature procedures. All other reagents and AR-grade solvents were purchased commercially and used as supplied.

Synthesis of \( [[\text{Cu}(\mu-\text{pz})_2(\text{pz})_2]] \) (1)

Addition of \( \text{HpzPh} \) (0.61 g, 4.2 mmol) to a solution of \( \text{CuF}_2 \) (0.21 g, 2.1 mmol), and \( \text{NaOH} \) (0.17 g, 4.2 mmol) in \( \text{MeOH} \) (50 cm\(^3\)) yielded an immediate blue precipitate, which dissolved upon stirring at room temperature for 2 h. The resultant dark blue solution was filtered and evaporated to dryness, and the solid residues extracted with the minimum volume of \( \text{CHCl}_3 \). Layering the filtered solution with a five-fold excess of pentane resulted in the formation of blue crystals over a period of days. These were collected, washed with pentane and dried in vacuo. Yield 0.36 g, 49%. Found C, 55.2; H, 4.1; N, 23.0%. Caled for \( \text{C}_{32}\text{H}_{24}\text{Cu}_{2}\text{N}_{12} \): C, 54.6; H, 3.4; N, 23.9%. FD mass spectrum (\( \text{CHCl}_3 \)): m/z 1467 ([\( \text{Cu}_4(\text{pzPh})_6 \)]\(^+\)), 1323 ([\( \text{Cu}_5(\text{pzPh})_6 \)]\(^+\)), 1260 ([\( \text{Cu}_6(\text{pzPh})_5 \)]\(^+\)), 1179 ([\( \text{Cu}_7(\text{pzPh})_4 \)]\(^+\)), 1116 ([\( \text{Cu}_8(\text{pzPh})_3 \)]\(^+\)), 1035 ([\( \text{Cu}_9(\text{pzPh})_2 \)]\(^+\)), 976 ([\( \text{Cu}_{10}(\text{pzPh})_2 \)]\(^+\)), 765 ([\( \text{Cu}_{11}(\text{pzPh})_1 \)]\(^+\)), 704 ([\( \text{Cu}_{12}(\text{pzPh})_1 \)]\(^+\)), 622 ([\( \text{Cu}_{13}(\text{pzPh})_1 \)]\(^+\)), 558 ([\( \text{Cu}_{14}(\text{pzPh})_1 \)]\(^+\)), 414 ([\( \text{Cu}(\text{pzPh})_2 \)]\(^+\)), 351 ([\( \text{Cu}(\text{pzPh})_3 \)]\(^+\)), 145 ([\( \text{HpzPh} \)]\(^+\)).

Synthesis of \( [[\text{Cu}(\mu-\text{pz})_2(\text{pz})_2]] \) (2)

A mixture of \( \text{CuF}_2 \) (0.21 g, 2.1 mmol), \( \text{HpzPh} \) (0.60 g, 4.2 mmol) and \( \text{NaOH} \) (0.17 g, 4.2 mmol) in \( \text{MeOH} \) (50 cm\(^3\)) was stirred at room temperature for 3 days, yielding a dark green solution. The mixture was then evaporated to dryness, and the solid residues extracted with the minimum volume of \( \text{CHCl}_3 \). Layering the filtered solution with a five-fold excess of pentane resulted in the formation of dark green crystals over a period of days. These were collected, washed with pentane and dried in vacuo. Yield 0.50 g, 68%. Found C, 61.9; H, 3.9; N, 16.3%. Caled for \( \text{C}_{35}\text{H}_{27}\text{Cu}_{2}\text{N}_{12} \): C, 62.4; H, 4.0; N, 15.7%. FD mass spectrum (\( \text{CHCl}_3 \)): m/z 765 ([\( \text{Cu}_4(\text{pzPh})_5 \)]\(^+\)), 665 ([\( \text{Cu}_5(\text{HpzPh})(\text{CHCN})_4 \)]\(^+\)), 558 ([\( \text{Cu}_6(\text{pzPh})_2 \)]\(^+\)), 455 ([\( \text{Cu}_7(\text{pzPh})_1 \)]\(^+\)), 414 ([\( \text{Cu}_8(\text{pzPh})_1 \)]\(^+\)), 351 ([\( \text{Cu}_9(\text{pzPh})_1 \)]\(^+\)), 207 ([\( \text{Cu}(\text{pzPh})_2 \)]\(^+\)), 146 ([\( \text{HpzPh} \)]\(^+\)).

Synthesis of \( [[\text{Cu}(\mu-\text{pz})_2(\text{pz})_2]] \) (3)

Reaction of \( \text{CuF}_2 \) (0.21 g, 2.1 mmol), \( \text{HpzPh} \) (0.68 g, 4.2 mmol) and \( \text{NEt}_3 \) (1.5 g, 15 mmol) in \( \text{MeOH} \) (50 cm\(^3\)) yielded a dark green solution, that was stirred at room temperature for 3 days. The mixture was evaporated to dryness, and the residues dissolved in the
minimum volume of CH₂Cl₂. Layering the filtered solution with a five-fold excess of hexanes resulted in the formation of blue–green crystals over a period of 2 weeks. These were collected, washed with pentane and dried in vacuo. Yield 0.28 g, 30%. Found C, 55.1; H, 3.4; N, 14.3%. Calcd for C₃₄H₂₇Cl₆Cu₂N₁₂O₀.₅ C, 60.9; H, 3.3; N, 14.3%. Calcd for C₈₁H₅₈Cu₄F₁₂N₁₈ C, 55.1; H, 3.3; N, 14.3%. Calcd for C₃₆H₂₆CaF₄N₈ C, 60.9; H, 3.3; N, 14.3%

Synthesis of [Cu(pzPhF)₂(HpzPhF)₂] (4)
A solution of Cu(OH)₂ (0.20 g, 2.1 mmol) and HpzPhF (0.68 g, 4.2 mmol) in MeOH (50 cm³) was refluxed for 3 days. The mixture was cooled, filtered and evaporated to dryness, and the turquoise residue redissolved in the minimum volume of CH₂Cl₂. Slow diffusion of Et₂O vapour into the filtered solution yielded dark blue crystals which were collected, washed with pentane and dried in vacuo. Yield 0.20 g, 13%. Found C, 61.0; H, 3.7; N, 15.8%. Calcd for C₃₄H₂₇Cl₆Cu₂N₁₂O₀.₅ C, 61.0; H, 3.4; N, 15.8%. Calcd for C₃₆H₂₆CaF₄N₈ C, 61.0; H, 3.4; N, 14.3%.

Single crystal X-ray structure determinations
Diffraction data for 2/1/2H₂Cl₂ were measured using a Bruker X8 Apex diffractometer, with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) generated by a rotating anode. The other three structure determinations were carried out on a Nonius KappaCCD area detector diffractometer, using graphite-monochromated Mo-Kα radiation from a sealed tube source. Both diffractometers were fitted with an Oxford Cryostream low temperature device. Experimental details of the structure determinations in this study are given in Table 1. All the structures were solved by direct methods (SHELXS97), and developed by full least-squares refinement on F² (SHELXL97). Figures were produced using XSEED, which incorporates POVRAY. More information about the crystal structure of 4 is given in the ESI.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618780c

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<td>wR(F²)</td>
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<td>R(F²)</td>
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* R = Σ||Fᵣ| − | Fₛ||/Σ|Fₛ|, * wR = [Σw(Fᵣ² − Fₛ²)/ΣwFᵣ²]⁰.⁵.
refined occupancies of 0.55 and 0.45. The following restraints were applied to these disordered groups: phenyl C–C = 1.39(2), phenyl 1,3-C–C = 2.41(1), C(pyrazole)–C(phenyl) = 1.46(1), N–N = 1.34(1), pyrazole C–N = 1.34(1), pyrazole C=C=N = 1.35(1), pyrazole C–C = 1.37(1) and pyrazole C=C = 1.39(1) Å. Two partial pentane solvent orientations were refined, each with occupancy 0.25 and sharing one common C atom. The C–C bonds in the disordered solvent were restrained to 1.54(1) Å, and 1.3–C···C distances to 2.51(1) Å. All non-H atoms were placed in calculated positions and refined using a riding model.

Single crystal X-ray structure of 3-3/4CH2Cl2-HPzRad

The asymmetric unit contains two molecules of the complex, labelled ‘A’ and ‘B’. Where required, partial disorder sites of atoms in molecule ‘A’ are given the label ‘C’, and those in molecule ‘B’ are labelled as ‘D’. The asymmetric unit also contains four weakly occupied dichloromethane environments C(1S)–Cl(3S), C(4S)–Cl(6S), C(5S)–Cl(7S) and partial ligand [N(11S), N(12S), C(51B)–F(60B)]. The following restraints were applied to these disordered groups: phenyl C–C = 1.35(1), pyrazole C–N = 1.39(1), pyrazole C=N = 1.35(1), pyrazole C–C = 1.37(1) and pyrazole C=C = 1.39(1) Å. Two partial pentane solvent orientations were refined, each with occupancy 0.25 and sharing one common C atom. The C–C bonds in the disordered solvent were restrained to 1.54(1) Å, and 1,3–C···C distances to 2.51(1) Å. All non-H atoms were placed in calculated positions and refined using a riding model. The protonated and deprotonated N atoms of each hydrogen-bonded pair were distinguished in two ways. First, because appropriately positioned residual Fourier peaks were present in the vicinity of N(3) and N(27), but not N(15) and N(39). Second, because the Cu–N bonds to the protonated pyrazole N atoms N(2) and N(26) are 6.3 Å than those to the deprotonated pyrazolido ligand donors N(14) and N(38). The deepest residual Fourier hole of –1.0 e. Å−3 is 0.9 Å from Cu(1).

Other measurements

Electrospray (ES) mass spectra were performed with a Micromass LCT TOF spectrometer using a MeCN feed solution, while field desorption (FD) mass spectra employed a Waters GCT premier spectrometer and were taken from chloroform solutions. All peaks show correct isotopic distributions for their assigned molecular ions. Mass peaks labelled as mixtures of monomeric and dimeric species show (m/z) : (m/z) + 2 isoerte ratios midway between that predicted for a mono-copper (0.44) and dicopper (0.89) species. CHN microanalyses were performed by the University of Leeds School of Chemistry microanalytical service. Variable temperature magnetic susceptibility measurements were obtained in the solid state using a Quantum Design SQUID magnetometer operating at 1000 G. Diamagnetic corrections for the sample (from Pascal's constants18) and the sample holder were applied to the data. Theoretical fits of the susceptibility data were carried out using SIGMAPLOT.42 X-band EPR spectra were obtained using a Bruker EMX spectrometer fitted with an ER419HS resonator and ER4131VT cryostat. W-band spectra were recorded using a commercial Bruker ELEXYSR spectrometer operating at 94 GHz frequency at 0–6 T field range. The temperature was stabilised by an Oxford Instrument ITC503 auto-tuning temperature controller at ±1 K precision. EPR spectra were analysed and simulated using XSophie commercial software.

Acknowledgements

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References
