Co-ordinative Versatility of the dmcpz Ligand (Hdmcpz = 3,5-dimethoxycarbonylpyrazole) in Copper Compounds. Synthesis, Characterization and Crystal Structures of $[Cu(dmcpz)_2(py)_2]$ and $[Cu_3(dmcpz)_6]$ (py = pyridine)†

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The oxidation of $[\{Cu(dmcpz)\}_n]$ (Hdmcpz = 3,5-dimethoxycarbonylpyrazole) with dioxygen in pyridine (py) leads to the formation of the violet complex $[Cu(dmcpz)_2(py)_2]$ **1**. Crystals of **1** are monoclinic, space group $P2_1/n$ (no. 14), $a = 11.441(2)$, $b = 9.339(3)$, $c = 12.493(3)$ Å, $\beta = 99.95(1)°$, $Z = 2$; $R = 0.033$ for 2308 reflections having $I > 3\sigma(I)$. Pyridine abstraction from **1** *via* azeotropic distillation with benzene allows the isolation of the blue trinuclear linear complex $[Cu_3(dmcpz)_6]$ **2**. Crystals of **2** are monoclinic, space group $P2_1/c$ (no. 14), $a = 17.286(3)$, $b = 20.649(4)$, $c = 16.498(2)$ Å, $\beta = 114.51(1)°$, $Z = 4$; $R = 0.034$ for 4710 reflections having $I > 3\sigma(I)$. Rapid equilibria between **1**, **2** and a still uncharacterized species **3** have been verified to occur in solution. A CH_2Cl_2 solution of **1** is violet below −10 °C, deep blue at around 15 °C and green at temperatures higher than 35 °C; it has been confirmed that these colours are associated with the presence of the distinct species **1**, **2** and **3**. The chemical, spectroscopic and structural properties of **1** and **2** are discussed.

The synthesis of di- and poly-nuclear complexes having ligands which maintain the metal centres in close proximity is an important objective in transition-metal chemistry. Interest in such systems arises because of their potential role in multi-metal centred catalysis in both biological and industrial reactions, and also because of their peculiar magnetic properties.[1] As a part of a systematic study of the chemical properties of new and already known copper(I) complexes containing neutral pyrazoles or pyrazolate groups as ligands, we have reported the reaction of $[\{Cu(Hpz)_2Cl\}_2]$ (Hpz = pyrazole) and of the recently structurally characterized[2] $[\{Cu(dmpz)\}_3]$ (Hdmpz = 3,5-dimethylpyrazole) with dioxygen, which allowed the isolation and characterization of the polynuclear copper(II) derivatives $[Cu_3(pz)_3(py)_2(OH)Cl_2]$[3] (py = pyridine) and $[Cu_8(dmpz)_8(OH)_8]$,[4] respectively. In an attempt to gain more insight into the reactions of these types of copper(I) complexes with dioxygen, we decided to use different pyrazoles, whose donor capabilities were modified by introducing heteroatoms in the ring substituent groups.

The dmcpz ligand (Hdmcpz = 3,5-dimethoxycarbonylpyrazole), possessing four nucleophilic centres, seems to be, among other pyrazolate ions, highly suitable for stabilizing polynuclear systems. However, the extended π net of the heterocyclic ring and the two carboxylic branches make the donor capability of each nucleophilic centre somehow dependent on the electronic situation of all other atoms of the molecule; therefore, only a limited number of co-ordination modes is expected. Throughout this paper, the most simple dmcpz co-ordination modes will be referred to with roman numerals, followed by alphabetic characters (if needed), as sketched in Fig. 1.

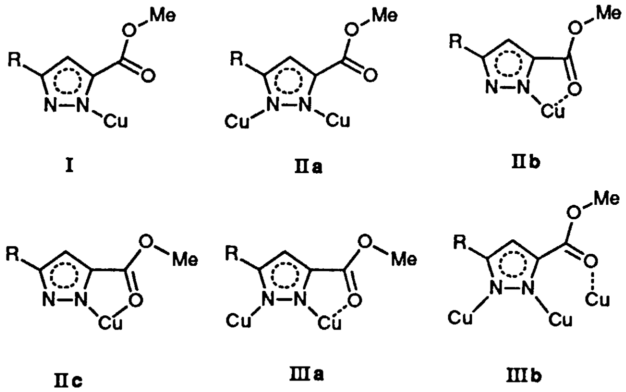

Fig. 1 Summary of simple co-ordination modes for the dmcpz ligand. Those with four (or more) donor centres have been omitted

While the form **I** has never been structurally evidenced,‡ the complexes $[Cu(dmcpz)_2(py)_2]$ **1** and $[Cu_3(dmcpz)_6]$ **2** contain dmcpz ligands in the **IIb**, **IIc**, **IIIa**, **IIIb** modes; notably, the **IIa** co-ordination type has recently been observed and reported by us in the copper(I) compounds $[Cu_2(dmcpz)_2(py)_2(CO)]$ and $[\{Cu(dmcpz)(RNC)\}_2]$ (R = cyclohexyl).[5]

Results and Discussion

The complex $[\{Cu(dmcpz)\}_n]$[5] reacts with molecular oxygen in pyridine at room temperature affording the violet mononuclear copper(II)–pyrazolate complex $[Cu(dmcpz)_2(py)_2]$ **1** which was recovered as an insoluble material. It has been verified that complex **1** was formed even if traces of water were present. The

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

‡ A unidentate 3,5-dimethoxycarbonylpyrazolate has however been suggested to be present in the still elusive compound $[Cu(dmcpz)(py)_2(CO)]$.[5]

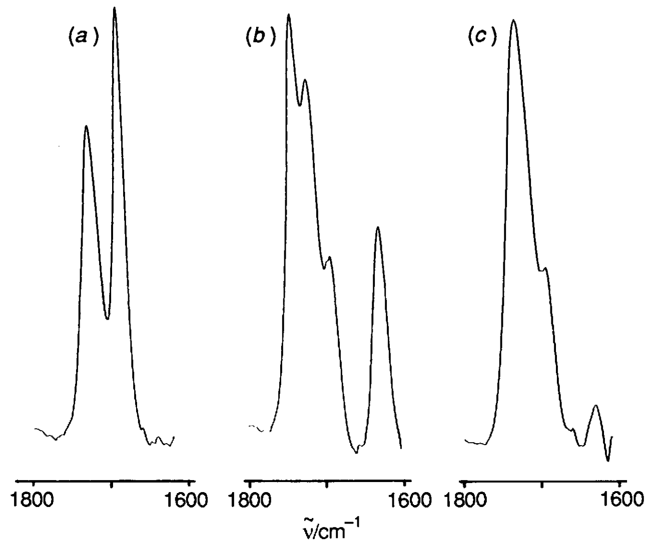

Fig. 2 IR spectra (CH_2Cl_2 solutions) in the carbonyl region for compounds **1** (*a*) (in excess pyridine), **2** (*b*) (at 0 °C) and **3** (*c*) (at 35 °C)

formation of **1** is accompanied by the concomitant presence in solution of a green copper(II) species. This green product contains pyrazolato and pyridine ligands (IR evidence) and probably oxo and/or hydroxo groups derived from the four-electron reduction of dioxygen. Attempts to characterize this species failed because of the lability of the pyridine ligands, which prevented the isolation of an analytically pure product. Notably, $[\{Cu(dmpz)\}_3]$ gave quantitatively, under similar experimental conditions, the unprecedented octanuclear copper(II)–hydroxo complex, $[Cu_8(dmpz)_8(OH)_8]$.[4]

Complex **1** has been obtained alternatively by the direct reaction of $CuCl_2$ with Hdmcpz in the presence of pyridine (see Experimental section). Complex **1** obtained by the two different routes was checked for structural identity by comparing the lattice parameters of well crystallized samples.

Complex **1** was shown to contain the two pyrazolate ligands co-ordinated in a unidentate fashion (see later). Transition-metal complexes containing monohapto pyrazolate ligands, although not common, are known.[6] However, complexes having two monohapto pyrazolate ligands are rare and invariably exhibit a *cis* conformation. Thus, to our knowledge, complex **1** appears to be the first example of a structurally characterized bis-pyrazolato species containing two unidentate pyrazolate groups *trans* to each other.

The IR spectrum of **1** (Nujol mull) shows in the 1600–1800 cm^{-1} region two absorptions at 1689 and 1712 cm^{-1} (1681 and 1720 cm^{-1} in CH_2Cl_2 solution, see Fig. 2), assignable to $\nu(C{=}O)$ of the CO_2Me substituents of the pyrazolate ring. The presence of two bands is in agreement with the results obtained from the X-ray structure determination of **1**, which confirmed that only one $-CO_2Me$ group per pyrazole ring is involved in co-ordination with the metal centre.

The EPR spectrum of complex **1** (frozen CH_2Cl_2 solution) is typical for a tetragonally elongated octahedral copper(II) centre, with a $d_{x^2-y^2}$ ground state ($g_{\parallel} = 2.238$, $g_{\perp} = 2.044$). The hyperfine splitting due to the copper nucleus is evident in the parallel region of the spectrum, showing $A_{\parallel}$ of 191×10^{-4} cm^{-1}, a value in the range found for other complexes of this type.[7]

Behaviour of Complex **1** *in Solution.*—We have observed that CH_2Cl_2 solutions of **1** maintain their violet colour only at temperatures lower than −10 °C. By raising the temperature to *ca.* 20 °C, the colour becomes blue; further raising of the temperature (to 35 °C or higher) causes a further change in colour to green. These changes in colour are reversible, even after keeping the solution in a sealed tube for several months; accordingly, by lowering the temperature of the green solutions, the blue and finally violet colours are restored.

These observations suggest the presence of the following equilibria between three different species **1**–**3**, which are responsible for the three different colours. Moreover, by adding excess pyridine to the blue solutions, their colour definitively becomes violet, irrespective of the temperature. This fact strongly supports the hypothesis that pyridine plays an important role in the aforementioned equilibria.

$$\begin{array}{ccccc} \mathbf{1}\ \text{(Violet)} & \rightleftharpoons & \mathbf{2}\ \text{(Blue)} & \rightleftharpoons & \mathbf{3}\ \text{(Green)} \\ < -10\,^{\circ}\text{C} & & 20\,^{\circ}\text{C} & & > 35\,^{\circ}\text{C} \end{array}$$

In particular, these observations suggest that the violet complex **1**, when in solution at room temperature, dissociates releasing pyridine and giving complex **2**. The blue species **2**, as a pure product, has been obtained by removing pyridine from benzene solutions of **1** by azeotropic distillation, shifting the equilibrium toward the right [equation (1)].

$$\underset{\mathbf{1}}{3[\mathrm{Cu(dmcpz)_2(py)_2}]} \rightleftharpoons \underset{\mathbf{2}}{[\mathrm{Cu_3(dmcpz)_6}]} + 6\mathrm{py} \qquad (1)$$

The transformation of complex **2** into **1** can be easily followed by 'titration' of species **2** with pyridine and monitoring by means of UV/VIS spectroscopy. Fig. 3 shows the alteration of the visible spectrum of **2** as a consequence of the addition of predetermined amounts of pyridine. The absence of clear isosbestic points indicates that the transformation $\mathbf{2} \rightleftharpoons \mathbf{1}$ takes place *via* one or more intermediate species and not *via* a one-step reaction. These results are consistent with the marked structural differences between **1** and **2**.

Attempts have been made to prepare complex **2** from genuine anhydrous copper(II) salts [*e.g.* $CuCl_2$, $Cu(ClO_4)_2$ or $CuSO_4$], Hdmcpz and triethylamine, in the absence of pyridine, according to the method reported for the synthesis of complex **1** [see Experimental section, method (*b*)] and in all cases, copper(II)–pyrazolato derivatives have been isolated. Their nature is at the moment unknown, but they do not exhibit the behaviour already described for complex **2**.

The crystal and molecular structure of **2** has been determined by single-crystal X-ray diffraction, revealing the presence of the three copper atoms disposed in a pseudo-linear fashion.

The IR spectrum of **2** (Nujol mull) shows in the 1600–1800 cm^{-1} region four bands at 1620, 1685, 1721 and 1735 cm^{-1}, which are attributed to the $\nu(C{=}O)$ of the CO_2Me substituents of the pyrazolate rings differently involved in co-ordination with the copper centres. In particular, the absorption at 1620 cm^{-1} is assigned to the CO_2Me groups co-ordinated in an enolic form to the terminal copper atoms (see crystal structure). The spectrum recorded in CH_2Cl_2 solution exhibits four significant absorptions in the 1600–1800 cm^{-1} region (1627, 1690, 1714 and 1733 cm^{-1}, see Fig. 2). The close similarity between the two IR spectra suggests that species **2** maintains its identity in solution and in the solid state. Additional support to this hypothesis is given by its EPR spectra which show the same pattern when recorded either as a microcrystalline powder or as a frozen glass. Moreover, the same analogy was found in the reflectance and in the UV/VIS spectra (CH_2Cl_2 solution).

The room-temperature powder EPR spectrum of complex **2** is interpretable as a quartet-state resonance showing the effects of strong axial zero-field splitting. Three signals at 2250, 2874 and 3526 G (G = 10^{-4} T) have been detected in the $\Delta M_S = 1$ region; in addition, in the low-field region of the spectrum, three signals are observed at 1872, 1181 and 665 G. The magnetic moment of complex **2** at room temperature, gave a value μ of 3.2 per trimeric unit, in agreement with the observed EPR spectrum. The EPR spectrum of **2** recorded at 123 K, exhibits substantial differences from the room-temperature spectrum

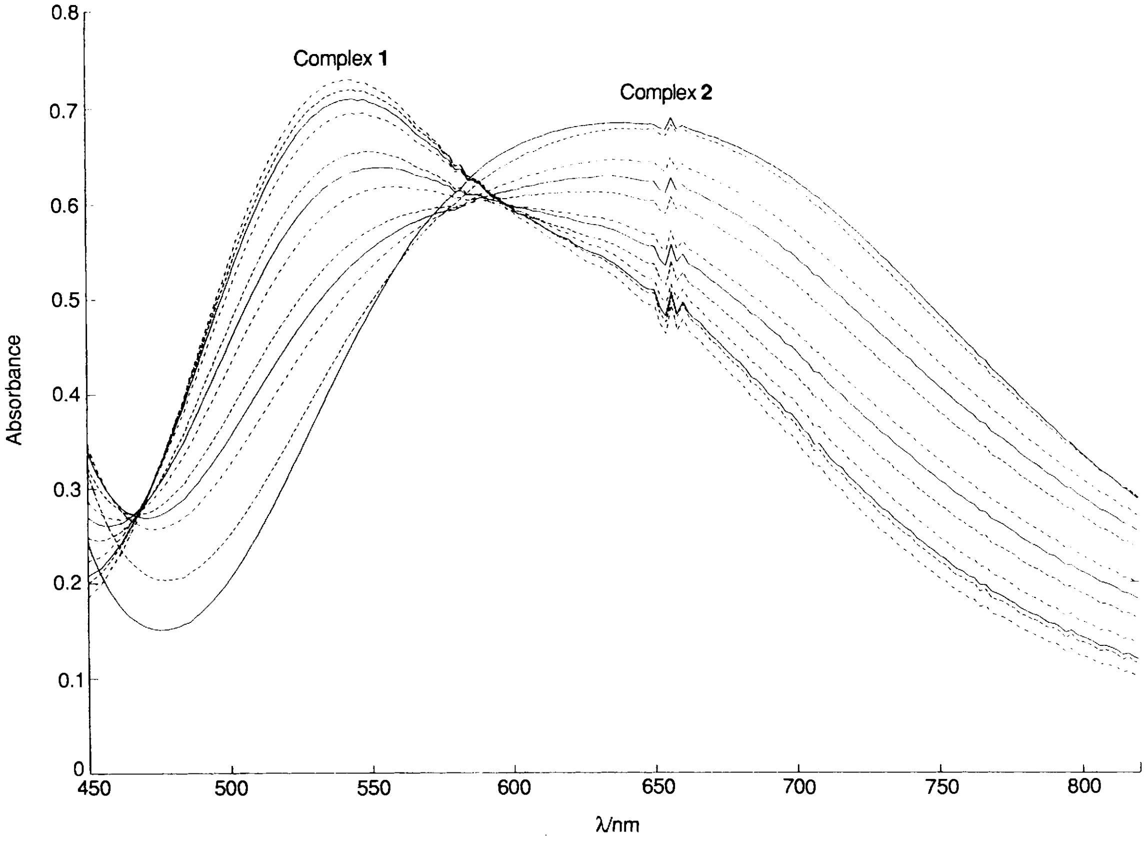

Fig. 3 Series of UV/VIS spectra of the equilibrium 1 $\rightleftharpoons$ 2, obtained by gradually adding pyridine to a CH_2Cl_2 solution of 2 up to a 5:1 molar ratio

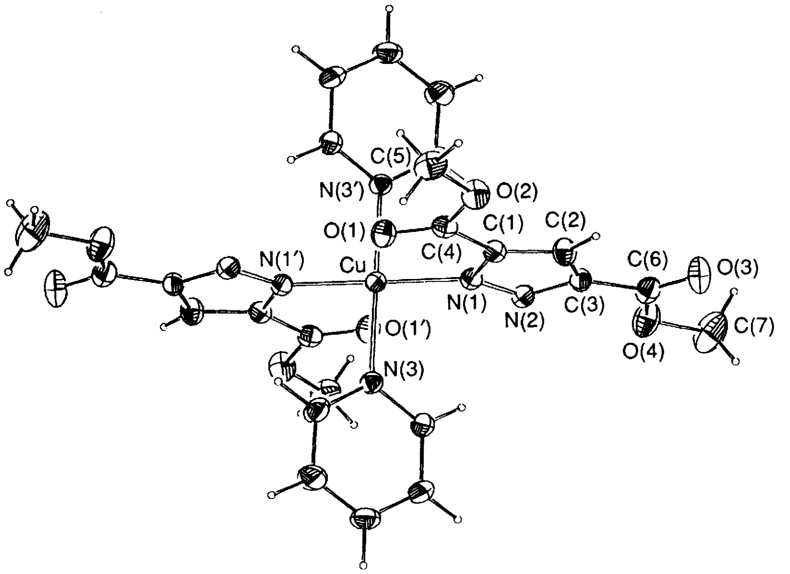

Fig. 4 An ORTEP drawing of the $[Cu(dmcpz)_2(py)_2]$ molecule 1, with partial labelling scheme. Thermal ellipsoids are drawn at the 30% probability level

and its features could be explainable in terms of an overlap between the quartet and ground-state doublet resonances. Further and more detailed work (variable-temperature EPR and magnetic susceptibility studies) however is required in order to verify this statement.

In the room-temperature NMR spectrum of complex 2 in CD_2Cl_2 only broad peaks were detected, in accord with the paramagnetic character of the molecule.

In the IR spectrum of complex 3 a significant strong band is present at 1720 cm^{-1}, which we attribute to $-CO_2Me$ groups not involved in co-ordination with the copper centres. The weak absorptions at 1627 and 1688 cm^{-1} are probably related to the presence of 2 as a consequence of the 2 $\rightleftharpoons$ 3 equilibrium.

Hence, as far as the formulation of 3 is concerned, we put forward the hypothesis that it could be a structural isomer of complex 2. This hypothesis will be more usefully discussed at the end of the next section.

Description of the Structures of Complexes 1 *and* 2.—Relevant bond distances and angles are reported in Tables 1 and 2, for compounds **1** and **2**, respectively. Figs. 4 and 5 contain the ORTEP[8] drawings of the [Cu(dmcpz)$_2$(pz)$_2$] and [Cu$_3$(dmcpz)$_6$] molecules, with partial labelling schemes.

Table 1 Relevant bond distances (Å) and angles (°) for [Cu(dmcpz)$_2$(py)$_2$] **1** with estimated standard deviations (e.s.d.s) in parentheses

Cu–N(1)	1.950(2)	C(1)–C(4)	1.455(4)
Cu–N(3)	2.057(2)	C(3)–C(6)	1.463(4)
Cu ··· O(1)	2.680(2)	C(4)–O(1)	1.204(3)
N(1)–N(2)	1.335(3)	C(6)–O(3)	1.192(4)
N(1)–C(1)	1.366(3)	C(4)–O(2)	1.330(3)
N(2)–C(3)	1.354(3)	C(6)–O(4)	1.343(4)
C(1)–C(2)	1.369(4)	C(5)–O(2)	1.435(4)
C(2)–C(3)	1.371(4)	C(7)–O(4)	1.435(4)
N(1)–Cu–N(3)	89.28(9)	N(1)–N(2)–C(3)	106.2(2)
N(1)–Cu ··· O(1)	72.21(8)	N(2)–C(3)–C(2)	110.8(2)
N(3)–Cu ··· O(1)	83.07(8)	C(3)–C(2)–C(1)	105.2(2)
Cu–N(1)–N(2)	126.8(2)	N(1)–C(1)–C(2)	108.1(2)
Cu–N(1)–C(1)	123.1(2)		

Table 2 Relevant bond distances (Å) and angles (°) for [Cu$_3$(dmcpz)$_6$] **2** with e.s.d.s in parentheses

Cu(1) ··· Cu(2)	3.500(1)	Cu(2)–N(9)	1.937(3)
Cu(1) ··· Cu(3)	3.480(1)	Cu(2)–O(17)	2.102(3)
Cu(1)–N(1)	2.012(3)	Cu(2) ··· O(3)	2.558(3)
Cu(1)–N(3)	2.015(3)	Cu(2) ··· O(13)	2.513(3)
Cu(1)–N(5)	2.003(3)	Cu(3)–N(6)	1.969(3)
Cu(1)–N(7)	2.007(3)	Cu(3)–N(8)	1.979(3)
Cu(1) ··· O(5)	2.701(3)	Cu(3)–N(11)	1.930(3)
Cu(1) ··· O(13)	2.729(3)	Cu(3)–O(21)	2.084(3)
Cu(2)–N(2)	1.979(3)	Cu(3) ··· O(5)	2.553(3)
Cu(2)–N(4)	1.969(3)	Cu(3) ··· O(11)	2.693(3)
N(1)–Cu(1)–N(3)	86.4(1)	N(2)–Cu(2)–N(4)	89.2(1)
N(1)–Cu(1)–N(5)	99.6(1)	N(2)–Cu(2)–N(9)	168.2(1)
N(1)–Cu(1)–N(7)	165.4(1)	N(4)–Cu(2)–N(9)	101.7(1)
N(3)–Cu(1)–N(5)	166.4(1)	O(21)–Cu(3)–N(6)	90.7(1)
N(3)–Cu(1)–N(7)	91.0(1)	O(21)–Cu(3)–N(8)	175.2(1)
N(5)–Cu(1)–N(7)	86.3(1)	O(21)–Cu(3)–N(11)	80.1(1)
O(17)–Cu(2)–N(2)	90.0(1)	N(6)–Cu(3)–N(8)	88.4(1)
O(17)–Cu(2)–N(4)	171.3(1)	N(6)–Cu(3)–N(11)	170.0(1)
O(17)–Cu(2)–N(9)	79.8(1)	N(8)–Cu(3)–N(11)	101.1(1)

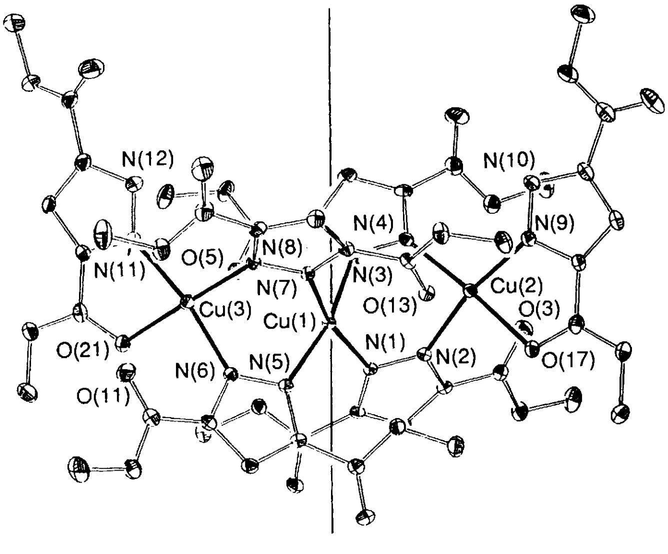

Fig. 5 An ORTEP drawing of the [Cu$_3$(dmcpz)$_6$] molecule **2**, with partial labelling scheme. Thermal ellipsoids are drawn at the 30% probability level. The trace of the idealized two-fold axis is also sketched

The crystals of **1** consist of a molecular packing of discrete monomeric complexes, possessing crystallographic C_i symmetry. Each Cu^{II} ion is surrounded by two *trans* pyridine ligands and two dmcpz ligands bonded in the **IIb** fashion, with short Cu–N bond distances [Cu–N(1) 1.950(2) and Cu–N(3) 2.057(2) Å] and loose Cu ··· O contacts [2.680(2) Å, the sum of the van der Waals radii being 2.95 Å]. The overall geometry described by the ligands (a Jahn–Teller-elongated octahedron, with a T^* value[9] of 0.73) can also be interpreted in terms of a square-planar CuN$_4$ chromophore stabilized by weak 'apical' *semi-co-ordinating* Cu ··· O interactions. The value of the (crystallographically unique) Cu ··· O contact, which is intermediate between those found in compound **2** (see below), confirms the plasticity of the co-ordination sphere of the copper atom. The dihedral angle between the pyridine and the pyrazolate five-membered ring is 78.9°; this tilt, in conjunction with the slightly elongated Cu–N(3) distance, lowers the possible steric strain derived by the presence of the –CO$_2$Me substituents on the dmcpz ligands; however, as described in the previous section, the behaviour of **1** when in solution clearly indicates that the pyridine ligands in **1** are fairly labile.

The crystals of **2** consist of a molecular packing of discrete [Cu$_3$(dmcpz)$_6$] complexes, each trinuclear* molecule possessing idealized C_2 symmetry, with the unique axis passing through the Cu(1) atom and bisecting the N(1)–Cu(1)–N(5) and N(3)–Cu(1)–N(7) angles. The only evident features which do not follow the two-fold axis are two –CO$_2$Me residues, plus a slight distortion of the co-ordination sphere of Cu(2) *vs.* Cu(3), with slightly different Cu ··· O contacts [range 2.513(3)–2.693(3) Å; see Table 2 and Fig. 5].

Each copper atom it roughly square-planar [although the central copper atom suffers of a tetrahedral twist, with *trans* N(1)–Cu(1)–N(7) and N(3)–Cu(1)–N(5) angles of 165.4(1) and 166.4(1)°, respectively, and a dihedral angle between the N(1)–Cu(1)–N(5) and N(3)–Cu(1)–N(7) planes of 18.3°], with 'apical' contacts involving some of the carbonylic oxygen atoms of the dmcpz ligands for the 'external' Cu(2) and Cu(3) atoms. The closest Cu(1) ··· O contacts are with the weakly interacting O(5) and O(13) atoms [2.701(3) and 2.729(3) Å, respectively], which are however to be considered mainly as donors on the 'external' copper atoms, owing to their significantly shorter contacts with Cu(3) and Cu(2) atoms, of 2.553(3) and 2.513(3) Å, respectively.

The non-bonding Cu ··· Cu interactions [Cu(1) ··· Cu(2) 3.500(1), Cu(1) ··· Cu(3) 3.480(1) Å] are slightly longer than the few values reported for other $\overline{\mathrm{Cu{-}N{-}N{-}Cu{-}N{-}N}}$ systems with three or four ligands on each metal centre[11a–e] (range 3.15–3.44 Å), in agreement with the aforementioned observation that the co-ordination spheres of the Cu(2) and Cu(3) atoms also include the loosely interacting oxygen atoms; moreover, in contrast to what is observed in [{Cu(dmpz)(RNC)}$_2$][12] (R = cyclohexyl), where strict coplanarity of the pz rings was found, the $\overline{\mathrm{Cu{-}N{-}N{-}Cu{-}N{-}N}}$ metallocycles of **2** are in a boat conformation, characterized by 'wing-tip' N–Cu–N angles of 88.4(1), 86.3(1), 86.4(1) and 89.2(1)° (see Table 2) and by dihedral angles between the dmcpz rings of 105.3 and 103.0°. A similar feature has been observed in the dinuclear complexes [Cu$_2$(dmcpz)$_2$(py)$_2$(CO)] and [{Cu(dmcpz)(RNC)}$_2$] (R = cyclohexyl), and, in conformity with the geometrical model presented in ref. 5, it shows that boat conformations are likely to be stable if a narrow N–Cu–N angle can be achieved. A detailed study of the $\overline{\mathrm{M{-}N{-}N{-}M'{-}N{-}N}}$ (M = Ga, M′ = Ga, Cu or Ni) ring conformation in pyrazolylgallate derivatives

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* Several (more or less) linear trinuclear copper complexes, mostly stabilized by the presence of macrocyclic and/or polydentate ligands have appeared in the literature. The widespread distribution of Cu ··· Cu interactions found, with bond distances as low as 2.47 Å,[10] suggests that metal–metal contacts are heavily influenced by the shape of the ligands and, hence, by geometrical constraints.

Table 3 Summary of crystal data for $[Cu(dmcpz)_2(py)_2]$ **1** and $[Cu_3(dmcpz)_6]$ **2**[a]

Compound	1	2
Formula	$C_{24}H_{24}CuN_6O_8$	$C_{42}H_{42}Cu_3N_{12}O_{24}$
M	588.03	1289.49
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	11.441(2)	17.286(3)
b/Å	9.339(3)	20.649(4)
c/Å	12.493(3)	16.498(2)
β/°	99.95(1)	114.51(1)
U/Å^3	1315(1)	5358(3)
Z	2	4
D_c/g cm^{-3}	1.485	1.598
F(000)	606	2628
μ/cm^{-1}	8.9	12.7
Scan range/°	$2.2 + 0.35 \tan\theta$	$1.0 + 0.35 \tan\theta$
Max. scan time/s	75	45
No. collected reflections	5861	9686
No. unique observed reflections [$I > 3\sigma(I)$]	2308	4710
Min., max. transmission factors	0.84, 1.32	0.85, 1.20
No. of refined variables	178	730
R[b]	0.033	0.034
R'[c]	0.041	0.041
Goodness of fit[d]	1.430	1.359
Max. peak final Fourier difference map/e Å^{-3}	0.27	0.30

[a] Details in common: crystal system, monoclinic; θ range, 3–25°; pre-scan speed 20° min^{-1}; pre-scan acceptance criterion $\sigma(I)/I < 0.66$; required $\sigma(I)/I < 0.02$; collected octants, $\pm h, k, l$. [b] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$. [c] $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [d] Goodness-of-fit $= [\Sigma w(F_o - k|F_c|^2)/(N_o - N_v)]^{\frac{1}{2}}$ where N_o, N_v = number of observations and number of variables respectively.

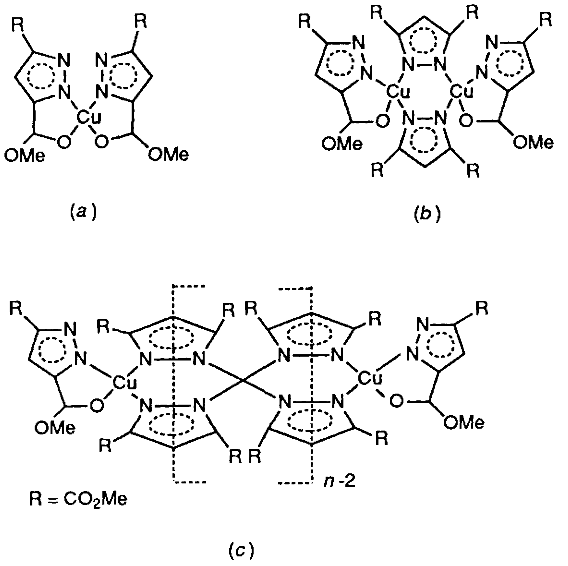

Fig. 6 Schematic representation of the topologies of $[\{Cu(dmcpz)_2\}_n]$ complexes: (*a*) monomer ($n = 1$); (*b*) dimer ($n = 2$); (*c*) oligo- or poly-meric (stepped-ribbon) complexes (for $n = 3$, compound **2**)

$\{[Cu(GaMe_2L_2)_2]$ (L = pz or dmpz): topologically equivalent to compound **2**$\}$ is reported in ref. 13.

The best planes defined by the CuL_4 fragments are at an angle of 84.7 and 83.8°, for Cu(1)–Cu(2) and Cu(1)–Cu(3), respectively, giving the molecule a stepped ribbon shape. The nature of the six crystallographically independent dmcpz ligands is markedly different: two co-ordinate in a **IIIa** fashion, two in a **IIIb** fashion and two exhibit a fairly peculiar 'enolic' **IIc** co-ordination mode; together with the remaining non-co-ordinating $-CO_2Me$ residues, a total of four different ν(C=O) stretching modes are expected and indeed observed.

While the geometrical parameters of the **IIb** (compound **1**), **IIIa** and **IIIb 2** dmcpz ligands are not significantly different, in the **IIc** dmcpz ligands a definite elongation of the co-ordinating C=O distances relative to the other modes (average value 1.226 *vs.* 1.200 Å*) is found, and is accompanied by shortening of the adjacent C–C interactions (average value 1.448 *vs.* 1.470 Å*). The change in the conjugated π system, if not relevant at the ring level, is however also reflected in the significant changes observed in the non-co-ordinated $-CO_2Me$ moieties, where C=O shortening and C–C elongation occurs (average value 1.181 and 1.491 Å, respectively*). While the structure of the trimer suggests that all the homologues of general formula $[\{Cu(dmcpz)_2\}_n]$ (n = 1,2,...), with the ribbon-like structures reported in Fig. 6, could be *theoretically* copresent in solution, and possibly isolated also in the solid state, the precipitation of $[Cu_3(dmcpz)_6]$ **2** might be interpreted as a result of a particularly favourable isomer (n = 3, compound **2**) stabilized by the presence of a stereochemically suitable arrangement of the net of C=O ••• Cu contacts.

The nature of complex **3**, which has never been recovered as an analytically pure material, can only be inferred on the basis of its spectroscopic properties and of the nature of **2**, from which it is obtained by moderate heating of the solutions. We tentatively suggest that **3** might be an oligomeric (maybe still trimeric) compound which lacks loose 'axial' C=O•••Cu contacts, possibly due to conformational changes in the extended net of the $-CO_2Me$ residuals. On the basis of the absence of the 'enolic' ν(C=O) absorption band in the IR spectrum of **3**, a cyclic trimer of idealized D_{3h} symmetry $\{$topologically analogous to the previously reported $[\{Ni(pz)_2\}_3]$[14] derivative and to the structurally characterized $[Pd_3(MeCO_2)_6]$ complex[15]$\}$, obtained by combining three boat-shaped Cu_2N_4 rings around a common axis, is also inferred.

Experimental

Infrared spectra were recorded on a Bio-Rad FTS 7PC instrument, EPR spectra with a Varian E-g spectrometer equipped with an X-band microwave radiation source; the equilibrium studies were carried out employing a HP 8452A UV/VIS instrument. NMR spectra were recorded on a Bruker

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* Typical estimated standard deviations are 0.004–0.006 Å.

WP80 spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory of this University. Solvents were dried and distilled by standard methods. The synthesis of $[\{Cu(dmcpz)\}_n]$ was as reported.[5]

Table 4 Fractional atomic coordinates for $[Cu(dmcpz)_2(py)_2]$ **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu	0.0000	0.0000	0.0000
O(1)	−0.0257(2)	0.2712(3)	0.0620(2)
O(2)	−0.1851(2)	0.3827(2)	0.1050(2)
O(3)	−0.5054(2)	−0.0669(3)	0.1488(2)
O(4)	−0.4106(2)	−0.2579(3)	0.0989(2)
N(1)	−0.1467(2)	0.0114(3)	0.0591(2)
N(2)	−0.2230(2)	−0.0950(3)	0.0661(2)
N(3)	−0.0900(2)	0.0734(3)	−0.1466(2)
C(1)	−0.1923(3)	0.1373(3)	0.0893(3)
C(2)	−0.3003(3)	0.1091(4)	0.1176(3)
C(3)	−0.3169(3)	−0.0353(3)	0.1021(3)
C(4)	−0.1241(3)	0.2679(4)	0.0840(3)
C(5)	−0.1279(4)	0.5187(4)	0.1000(3)
C(6)	−0.4209(3)	−0.1176(4)	0.1190(3)
C(7)	−0.5091(4)	−0.3442(5)	0.1170(4)
C(8)	−0.0399(3)	0.1657(4)	−0.2072(3)
C(9)	−0.0978(3)	0.2167(4)	−0.3046(3)
C(10)	−0.2105(3)	0.1734(4)	−0.3438(3)
C(11)	−0.2633(4)	0.0830(5)	−0.2823(3)
C(12)	−0.2017(3)	0.0352(4)	−0.1844(3)

Synthesis of $[Cu(dmcpz)_2(py)_2]$ **1**.—(*a*) The complex $[\{Cu(dmcpz)\}_n]$ (0.15 g, 0.61 mmol) was dissolved in pyridine (10 cm^3) under an oxygen atmosphere. In a few minutes the solution turned green and a violet precipitate separated. The suspension was maintained under stirring for 6 h, then the solid was filtered off, washed with pyridine and diethyl ether and dried under vacuum (0.14 g, 38% yield). Crystals suitable for X-ray analysis were obtained by slow diffusion of dioxygen through a degassed pyridine solution of $[\{Cu(dmcpz)\}_n]$.

(*b*) To a solution of Hdmcpz (1.0 g, 5.4 mmol) in acetonitrile (40 cm^3) anhydrous $CuCl_2$ (0.35 g, 2.6 mmol) was added under stirring. A deep green solution formed. After 30 min stirring, pyridine (0.44 cm^3, 5.4 mmol) was added. The resulting sky-blue suspension was maintained under stirring for 2 h and then NBu_3 (1.5 cm^3) added. A violet suspension formed in about 10 min. The suspension was stirred for an additional hour, then the solid was filtered off, washed with pyridine and acetonitrile and dried in vacuum (1.32 g, 87% yield), m.p. 166 °C (decomp.) (Found: C, 48.95; H, 3.90; N, 14.35. $C_{24}H_{24}CuN_6O_8$ requires C, 49.0; H, 4.10; N, 14.30%).

Synthesis of $[Cu_3(dmcpz)_6]$ **2**.—Complex **2** was prepared from **1** by azeotropic distillation of pyridine with benzene. The complex $[Cu(dmcpz)_2(py)_2]$ (0.45 mg, 0.77 mmol) was suspended in benzene (50 cm^3). The temperature was raised to 60 °C and a green solution formed. The application of vacuum [*ca.* 10^{-1} Torr ($\approx$13.3 Pa)] allowed the distillation of the azeotrope. This cycle was repeated four times by adding fresh

Table 5 Fractional atomic coordinates for $[Cu_3(dmcpz)_6]$ **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.249 85(3)	0.306 04(2)	0.492 62(3)
Cu(2)	0.468 30(3)	0.279 46(3)	0.564 71(3)
Cu(3)	0.034 01(3)	0.271 36(3)	0.415 27(3)
O(1)	0.251 0(2)	0.507 9(2)	0.639 1(2)
O(2)	0.189 9(2)	0.411 3(1)	0.595 4(2)
O(3)	0.589 7(2)	0.337 0(2)	0.691 4(2)
O(4)	0.601 4(2)	0.438 4(2)	0.743 4(2)
O(5)	0.154 1(2)	0.251 3(2)	0.568 5(2)
O(6)	0.178 0(2)	0.166 4(2)	0.661 6(2)
O(7)	0.521 1(2)	0.090 5(2)	0.730 2(3)
O(8)	0.561 0(2)	0.192 5(2)	0.719 3(2)
O(9)	0.248 1(2)	0.516 4(2)	0.378 0(2)
O(10)	0.300 4(2)	0.415 9(2)	0.393 7(2)
O(11)	−0.094 1(2)	0.337 2(2)	0.289 4(2)
O(12)	−0.102 3(2)	0.442 5(2)	0.253 1(2)
O(13)	0.351 0(2)	0.266 8(1)	0.411 5(2)
O(14)	0.331 8(2)	0.189 8(2)	0.307 8(2)
O(15)	−0.011 8(2)	0.104 5(2)	0.212 5(3)
O(16)	−0.055 3(2)	0.196 3(2)	0.253 7(2)
O(17)	0.526 5(2)	0.342 1(2)	0.506 3(2)
O(18)	0.628 6(2)	0.342 2(2)	0.456 6(2)
O(19)	0.681 5(2)	0.058 9(2)	0.473 1(3)
O(20)	0.593 7(2)	0.030 2(2)	0.531 7(3)
O(21)	−0.033 9(2)	0.322 5(2)	0.473 3(2)
O(22)	−0.146 6(2)	0.309 4(2)	0.504 6(2)
O(23)	−0.085 8(3)	0.005 0(2)	0.407 3(3)
O(24)	−0.131 2(2)	0.026 8(2)	0.512 0(3)
N(1)	0.334 9(2)	0.368 2(2)	0.576 9(2)
N(2)	0.417 3(2)	0.354 8(2)	0.598 6(2)
N(3)	0.316 4(2)	0.235 7(2)	0.577 6(2)
N(4)	0.398 5(2)	0.221 6(2)	0.602 0(2)
N(5)	0.161 7(2)	0.369 2(2)	0.416 5(2)
N(6)	0.080 2(2)	0.352 7(2)	0.391 3(2)
N(7)	0.188 6(2)	0.240 2(2)	0.398 1(2)
N(8)	0.107 2(2)	0.223 7(2)	0.369 8(2)
N(9)	0.536 7(2)	0.218 1(2)	0.534 1(2)
N(10)	0.544 4(2)	0.154 0(2)	0.538 5(2)
N(11)	−0.027 3(2)	0.201 0(2)	0.438 7(2)
N(12)	−0.027 3(2)	0.136 9(2)	0.428 4(2)
C(1)	0.333 0(3)	0.422 6(2)	0.622 3(3)
C(2)	0.414 8(3)	0.444 0(2)	0.672 6(3)
C(3)	0.466 1(2)	0.399 6(2)	0.657 1(2)
C(4)	0.255 3(3)	0.452 5(2)	0.619 8(3)
C(5)	0.109 4(3)	0.438 5(3)	0.583 7(3)
C(6)	0.558 5(3)	0.387 8(2)	0.698 3(3)
C(7)	0.692 6(3)	0.430 4(3)	0.788 4(3)
C(8)	0.284 2(3)	0.195 4(2)	0.619 3(2)
C(9)	0.346 4(3)	0.152 1(2)	0.670 3(3)
C(10)	0.418 1(3)	0.170 3(2)	0.658 7(3)
C(11)	0.198 7(3)	0.207 6(2)	0.612 1(3)
C(12)	0.096 0(3)	0.171 4(3)	0.662 9(3)
C(13)	0.505 1(3)	0.145 8(3)	0.705 0(3)
C(14)	0.649 5(3)	0.174 9(3)	0.756 4(4)
C(15)	0.163 0(3)	0.428 1(2)	0.380 5(3)
C(16)	0.081 0(3)	0.450 4(2)	0.333 0(3)
C(17)	0.030 4(3)	0.400 8(2)	0.339 2(3)
C(18)	0.240 7(3)	0.459 3(2)	0.384 7(3)
C(19)	0.379 9(3)	0.440 0(3)	0.399 1(3)
C(20)	−0.061 6(3)	0.388 8(2)	0.292 4(3)
C(21)	−0.191 4(4)	0.435 5(3)	0.198 1(4)
C(22)	0.222 3(2)	0.208 7(2)	0.349 2(2)
C(23)	0.160 8(3)	0.169 0(2)	0.288 7(3)
C(24)	0.089 6(3)	0.180 3(2)	0.302 7(3)
C(25)	0.308 5(3)	0.225 0(2)	0.361 7(2)
C(26)	0.415 2(3)	0.201 8(3)	0.310 9(3)
C(27)	0.002 9(3)	0.154 8(3)	0.252 1(3)
C(28)	−0.142 6(3)	0.175 5(4)	0.218 1(4)
C(29)	0.590 0(3)	0.243 9(2)	0.501 6(3)
C(30)	0.634 3(3)	0.195 2(3)	0.483 4(3)
C(31)	0.604 4(3)	0.140 2(2)	0.507 5(3)
C(32)	0.579 6(3)	0.313 2(2)	0.488 6(3)
C(33)	0.617 0(3)	0.411 4(3)	0.443 5(4)
C(34)	0.629 7(3)	0.072 5(3)	0.500 1(3)
C(35)	0.614 4(4)	−0.037 1(3)	0.528 3(7)
C(36)	−0.083 6(3)	0.217 6(2)	0.472 3(3)
C(37)	−0.122 0(3)	0.163 0(3)	0.485 3(3)
C(38)	−0.084 2(3)	0.113 7(2)	0.457 5(3)
C(39)	−0.086 0(3)	0.287 1(2)	0.483 7(3)
C(40)	−0.152 9(3)	0.379 7(3)	0.506 3(4)
C(41)	−0.100 2(3)	0.042 2(3)	0.453 1(4)
C(42)	−0.149 3(4)	−0.040 9(3)	0.515 8(5)

benzene. Finally, 20 cm^3 of benzene were added to the blue residue, the temperature kept constant at 40 °C and the suspension filtered. The resulting blue solid was washed with benzene and *n*-hexane and dried under vacuum (0.247 g, 75% yield). The crystals used in the X-ray structure determination were obtained by slow diffusion of *n*-pentane into a CH_2Cl_2 solution of complex **2**; m.p. 233 °C (decomp.) (Found: C, 39.25; H, 3.15; N, 12.95. $C_{42}H_{42}Cu_3N_{12}O_{24}$ requires C, 39.10; H, 3.25; N, 13.05%).

X-Ray Crystal Structure Determination of Compounds **1** *and* **2**.—Crystal data and experimental conditions are summarized in Table 3. A violet octahedral **1** or blue prismatic crystal **2** of approximate dimensions 0.20 × 0.15 × 0.05 and 0.30 × 0.10 × 0.08 mm, respectively, were mounted on the tip of a glass fibre and put onto a goniometer head. The intensity data were collected at room temperature using the ω scan method on an Enraf-Nonius CAD4 automated diffractometer with Mo-Kα radiation ($\lambda = 0.710\ 73$ Å). A least-squares fit of 25 randomly oriented intense reflections with θ ranging from 8 to 12° provided the unit-cell parameters. Intensities were collected using a variable scan range with a 25% extension at each end for background determination. Three standard reflections were measured at regular intervals and showed no decay of the scattering power of the crystals over the data collection period. Both data sets were corrected for Lorentz and polarization effects. Empirical absorption corrections (DIFABS[16]) were later performed after complete isotropic refinements.

The structures were solved by conventional three-dimensional Patterson and Fourier difference methods and refined by full-matrix least squares using the Enraf-Nonius Structure Determination Package (SDP[17]) and the physical constants tabulated therein, on a PDP 11/73 computer. Individual weights were assigned as: $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}/2F_oL_p$, the 'ignorance factor' p being set at 0.04 in both cases. Anomalous scattering terms were taken from ref. 18. The final values of the agreement indices are also reported in Table 3. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen-atom contribution to the scattering factors was included in the last stages of the refinements assuming placement in ideal positions (C–H 0.95 Å, $B = 5.0$ and 6.0 Å^2, for **1** and **2**, respectively). The peaks in the final Fourier difference map were randomly distributed. The final values of the positional parameters for compounds **1** and **2** are reported in Tables 4 and 5, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Conclusion

The results achieved in the course of this study confirmed that the nature of the products of the reactions between copper(I)–pyrazolate complexes and dioxygen greatly depends on the nature of the substituents on the pyrazole ring. Both electronic and steric effects seem to play an important role in determining the reaction path. It is noteworthy that [{Cu(dmpz)}$_3$] gave [Cu$_8$(dmpz)$_8$(OH)$_8$] when treated with dioxygen.[4] Assuming that the initial step of these reactions is, in all cases, the formation of an O_2 adduct with the metal centre, as previously suggested by other authors,[19] attention will be devoted to the reaction of dioxygen with copper(I)–pyrazolato complexes having bulky (and electron-withdrawing) substituents on the pyrazole ring, with the aim to isolate dioxygen complexes or other intermediates, preventing the complete four-electron reduction of dioxygen. Moreover, in view of the presence in complex **1** of two nucleophilic nitrogen atoms not yet involved in co-ordination with the metal centre, studies are in progress on the potential role of complex **1** as a 'ligand', in order to obtain hetero(bi- or tri-)metallic derivatives.

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