

# Synthesis and Structure of Di- and Tetra-copper(I) Complexes bridged by Pyridazine†

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Novel di- and tetra-copper(I) complexes of pyridazine (pydz) have been prepared and determined crystallographically. The yellow crystals of the dicopper(I) complex,  $[\text{Cu}_2(\text{pydz})_3(\text{MeCN})_2][\text{PF}_6]_2$  **1** are monoclinic, space group  $C2/c$ , with  $a = 21.720(6)$ ,  $b = 8.803(8)$ ,  $c = 15.778(6)$  Å,  $\beta = 114.33(2)^\circ$ ,  $Z = 4$ ,  $R = 0.056$  and  $R' = 0.072$ . Two copper atoms are triply bridged by three pydz ligands to give a binuclear structure, in which the  $\text{Cu} \cdots \text{Cu}$  separation is  $3.065(2)$  Å. Each Cu atom is co-ordinated by three N atoms of three pydz molecules and one N atom of a MeCN molecule, providing a distorted tetrahedral environment. The orange crystals of the tetracopper(I) complex,  $[\text{Cu}_4(\text{pydz})_6][\text{ClO}_4]_4 \cdot 2\text{Me}_2\text{CO}$  **2** are monoclinic, space group  $P2_1/a$ , with  $a = 16.368(2)$ ,  $b = 13.860(2)$ ,  $c = 10.542(2)$  Å,  $\beta = 102.25(1)^\circ$ ,  $Z = 2$ ,  $R = 0.050$  and  $R' = 0.058$ . Two Cu atoms are bridged by four N atoms of two pydz molecules to form a six-membered  $\text{N}_2\text{Cu}_2\text{N}_2$  framework. Furthermore, two parallel  $\text{N}_2\text{Cu}_2\text{N}_2$  frameworks are linked by two different pydz molecules to give a tetranuclear structure. Four Cu atoms are coplanar and each Cu atom is in a trigonal-square environment. The shortest  $\text{Cu} \cdots \text{Cu}$  separations are  $3.096(1)$  and  $3.264(1)$  Å. If in the preparation of **2** ethylene or CO atmospheres are employed instead of Ar, copper(I) pydz adducts with  $\text{C}_2\text{H}_4$  or CO are obtained which have been characterized by IR and  $^1\text{H}$  NMR spectroscopy. The former shows  $\nu_{\text{C-C}}$  of  $\text{C}_2\text{H}_4$  at  $1541 \text{ cm}^{-1}$ ; the latter shows  $\nu_{\text{CO}}$  at  $2108 \text{ cm}^{-1}$ .

It is established that  $\text{Cu}^I$  is co-ordinated by soft donor atoms such as P, S or N atoms to form relatively stable copper(I) complexes.<sup>1</sup> Copper(I) is also capable of bonding to small gaseous molecules such as olefins,<sup>2</sup> alkynes<sup>3</sup> and carbon monoxide<sup>2b,4</sup> to form  $\pi$  complexes. Polynuclear copper(I) complexes are expected to show novel properties and reactions, not found for mononuclear complexes. Only a few polynuclear  $\pi$  complexes however have been isolated. Pyridazine (pydz), which contains an N–N linkage, is a useful bridging ligand which forms bi- and poly-nuclear copper complexes similarly to bis(diphenylphosphino)methane,<sup>5</sup> 1,8-naphthyridine,<sup>6</sup> 2-(diphenylphosphino)pyridine<sup>7</sup> and pyrazolate.<sup>8,9</sup> In this study, novel di- and tetra-nuclear copper(I) pyridazine complexes have been prepared and their structures determined crystallographically. In addition ethylene and carbon monoxide adducts have been isolated and characterized by IR and  $^1\text{H}$  NMR spectroscopy.

## Experimental

**General.**—All preparations were performed using usual Schlenk techniques. The reagent  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  was prepared according to literature procedures.<sup>10</sup> Pyridazine (Aldrich) was used without further purification. Acetone was dried and distilled by a standard method before use. IR spectra as KBr discs were obtained with a JASCO 8000 FT IR spectrometer. Proton NMR spectra (relative to  $\text{SiMe}_4$ ) were measured with a JEOL GSX270 FT NMR spectrometer in  $[\text{D}_6\text{H}_6]$ acetone at 23 and  $-90^\circ\text{C}$ .  $^{14}\text{N}$  NMR spectra were measured relative to  $\text{MeNO}_2$  in  $\text{C}_6\text{D}_6$  (4:1 v/v).

**Preparations.**— $[\text{Cu}_2(\text{pydz})_3(\text{MeCN})_2][\text{PF}_6]_2$  **1**. A solution of pydz ( $14.5 \text{ cm}^3$ , 0.2 mmol) in acetone ( $10 \text{ cm}^3$ ) was added to

$[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  (74.5 mg, 0.2 mmol) under Ar. The resultant yellow solution was filtered after 15 min and the filtrate was sealed in a 5 mm diameter glass tube together with a small amount of diethyl ether. The glass tube was allowed to stand at ambient temperature and yellow crystals were obtained.‡ NMR:  $^1\text{H}$ ,  $\delta$  9.45 (t,  $\text{H}^{3,6}$ ), 8.07 (t,  $\text{H}^{4,5}$ ) and 2.18 (s,  $\text{CH}_3$ );  $^{14}\text{N}$ ,  $\delta$   $-145.50$ . IR (KBr,  $\text{cm}^{-1}$ ) 1571 ( $\nu_{\text{C-N}}$ ), 863 ( $\nu_{\text{P-F}}$ ).

$[\text{Cu}_4(\text{pydz})_6][\text{ClO}_4]_4$  **2**. Copper(II) perchlorate (55.6 mg, 0.15 mmol) was reduced with copper wire to  $\text{Cu}^I$  in acetone ( $10 \text{ cm}^3$ ) under ethylene. Pyridazine ( $21.8 \text{ cm}^3$ , 0.3 mmol) was added and a pale yellow solution was formed. After bubbling the reaction mixture with Ar a yellowish brown suspension was obtained. This suspension was filtered and the filtrate was sealed in a 5 mm diameter glass tube together with a small amount of diethyl ether under Ar. The solution was allowed to stand at ambient temperature and orange crystals of the product were collected (Found: C, 26.10; H, 2.25; N, 14.00. Calc. for  $\text{C}_{24}\text{H}_{24}\text{Cl}_4\text{Cu}_4\text{N}_{12}\text{O}_{16} \cdot \text{C}_3\text{H}_6\text{O}$ : C, 27.25; H, 2.55; N, 14.0%).

**Data Collection, Structure Solution and Refinement.**—Suitable yellow crystals of **1** and orange crystals of **2** for X-ray diffraction study were mounted on a Rigaku AFC-5R diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71069$  Å). The conditions for data collection and crystal data for **1** and **2** are listed in Table 1. A total of 1895 or 3040 independent reflections having  $F_o > 3\sigma(F_o)$  for **1** or **2** respectively was used. The structures of both **1** and **2** were solved by a direct method (MITHRIL)<sup>11</sup> and refined by full-matrix least squares with anisotropic thermal parameters. Isotropic hydrogen atoms were located by Fourier difference synthesis, using the program system TEXSAN.<sup>12</sup> Reliability

‡ When  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  and pydz were mixed in a mole ratio of 2:3, yellow crystals were also collected which gave the same IR spectra as complex **1**.

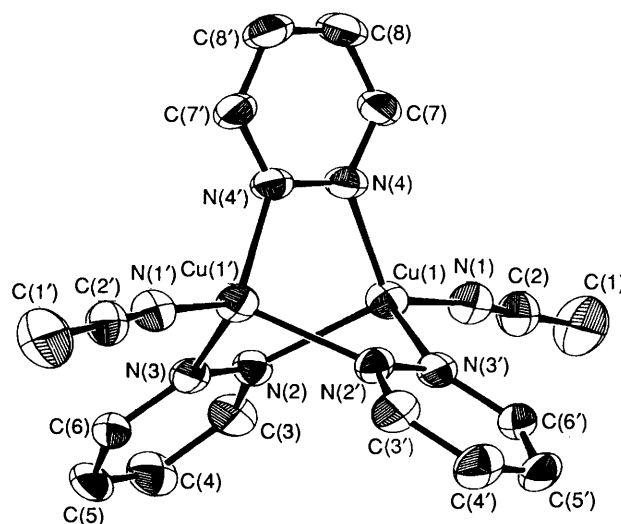
† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

**Table 1** Crystal data and measurement conditions for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Formula	C <sub>16</sub> H <sub>18</sub> Cu <sub>2</sub> F <sub>12</sub> N <sub>8</sub> P <sub>2</sub>	C <sub>24</sub> H <sub>24</sub> Cl <sub>4</sub> Cu <sub>4</sub> N <sub>12</sub> O <sub>16</sub> ·C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>
<i>M</i>	739.40	1248.68
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 <sub>1</sub> /a
<i>a</i> /Å	21.720(6)	16.368(2)
<i>b</i> /Å	8.803(8)	13.860(2)
<i>c</i> /Å	15.778(6)	10.542(2)
β/°	114.33(2)	102.25(1)
<i>U</i> /Å <sup>3</sup>	2749(3)	2337(1)
<i>Z</i>	4	2
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.786	1.774
λ(Mo-Kα)/Å	0.710 69	0.710 69
μ(Mo-Kα)/cm <sup>-1</sup>	17.68	21.12
Scan type	ω-2θ	ω-2θ
Scan rate/°min <sup>-1</sup>	8.0	8.0
Scan width/°	1.63 + 0.30 tan θ	1.47 + 0.30 tan θ
2θ <sub>max</sub> /°	55.0	55.0
No. of reflections measured	3461	5941
No. of observations [ <i>F</i> <sub>o</sub> > 3σ( <i>F</i> <sub>o</sub> )]	1895	3040
<i>R</i>	0.056	0.050
<i>R'</i>	0.072	0.058

**Table 2** Positional parameters for complex **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu(1)	0.936 86(4)	0.097 2(1)	0.657 97(5)
P(1)	0.651 7(1)	0.142 8(2)	0.101 3(1)
F(1)	0.625 5(3)	0.302 3(7)	0.110 4(4)
F(2)	0.674 0(4)	-0.018 9(7)	0.079 1(5)
F(3)	0.577 5(3)	0.086 2(8)	0.045 2(5)
F(4)	0.650 1(4)	0.201 5(8)	0.006 6(5)
F(5)	0.721 4(3)	0.196(1)	0.153 6(8)
F(6)	0.645 1(5)	0.074 9(9)	0.187 9(4)
N(1)	0.851 6(2)	0.087 9(6)	0.548 4(3)
N(2)	0.926 6(2)	-0.016 9(6)	0.765 9(3)
N(3)	0.983 9(2)	-0.027 8(6)	0.844 8(3)
N(4)	0.974 9(2)	0.306 1(5)	0.707 6(3)
C(1)	0.740 1(4)	0.044(1)	0.404 9(5)
C(2)	0.804 2(3)	0.067 7(8)	0.486 9(4)
C(3)	0.873 7(3)	-0.098 7(8)	0.758 1(5)
C(4)	0.872 9(4)	-0.198(1)	0.825 5(6)
C(5)	0.931 7(4)	-0.209 8(9)	0.904 1(5)
C(6)	0.985 7(3)	-0.120 4(7)	0.911 7(4)
C(7)	0.950 6(3)	0.436 6(8)	0.666 9(4)
C(8)	0.976 1(4)	0.575 5(8)	0.708 3(5)

**Fig. 1** An ORTEP view<sup>14</sup> of the [Cu<sub>2</sub>(pydz)<sub>3</sub>(MeCN)<sub>2</sub>]<sup>2+</sup> cation in **1** and atomic numbering scheme

factors are defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ , where  $w = 4 F_o^2 / \sigma^2(F_o^2)$ . Atomic scattering factors and anomalous dispersion terms were taken from ref. 13. The final *R* and *R'* values were 0.056 and 0.072 for **1**, and 0.050 and 0.058 for **2**, respectively. Atomic coordinates of non-hydrogen atoms for **1** and **2** are given in Tables 2 and 3.

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

## Results and Discussion

**Molecular Structure of Complex 1.**—The molecular structure of the [Cu<sub>2</sub>(pydz)<sub>3</sub>(MeCN)<sub>2</sub>]<sup>2+</sup> cation is shown in Fig. 1 together with the atomic numbering scheme. Selected bond distances and angles are listed in Table 4. Two copper atoms are triply bridged by six N atoms of three pydz ligands to form a binuclear structure. Three pydz ligands are located in the form of a propeller around the Cu(1)⋯Cu(1') vector and are slightly twisted. Each copper atom is co-ordinated by three N atoms from three pydz ligands and one N atom from a MeCN molecule, providing a distorted tetrahedral environment. This is the first complex having two triply bridged tetrahedral

coppers. Some dicopper(I) complexes with two trigonal coppers or one trigonal and one tetrahedral copper have been characterized crystallographically.<sup>5h,i,7e</sup>

The average Cu–N(pydz) distance of 2.054(5) Å is similar to those (2.02–2.07 Å) of four-co-ordinate copper(I) complexes,<sup>15</sup> and is longer than that [1.880(3) Å] of a three-co-ordinate copper(I) complex<sup>8a</sup> bridged by pyrazolate and is close to that [2.081(6) Å] of a two-co-ordinate copper(I) complex<sup>8b</sup> bridged by pyrazolate. A polynuclear Cu<sup>I</sup>-pydz complex has a long Cu–N(pydz) distance of 2.119(6) Å.<sup>16</sup> The Cu–N(MeCN) distance of 1.946(5) Å is in the midpoint of the range [1.859(17)–2.295(8) Å] found for four-co-ordinate copper(I) complexes<sup>5a,7e,17</sup> with MeCN and is longer than those [1.843(8)–1.933(5) Å] of three-co-ordinate copper(I) complexes with MeCN.<sup>7f,18</sup> The Cu(1)⋯Cu(1') separation of 3.065(2) Å is shorter than those [3.262(2)–3.406(1) Å] of copper(I) complexes bridged by pyrazolate<sup>8a,b</sup> and benzo[*c*]cinoline.<sup>19</sup> However, this separation is rather longer than those [2.566(2)–2.790(2) Å] of analogous dicopper(I) complexes triply bridged<sup>5h,i,7e</sup> and that (2.56 Å) in Cu metal. Therefore a significant Cu<sup>I</sup>⋯Cu<sup>I</sup> interaction is not expected.

The Cu(1)–Cu(1')–N(1') and Cu(1)–N(1)–C(2) angles are

**Table 3** Positional parameters for complex **2**

Atom	x	y	z	Atom	x	y	z
Cu(1)	0.027 32(5)	0.400 32(5)	0.174 00(7)	N(5)	-0.078 9(3)	0.364 3(3)	0.225 8(4)
Cu(2)	0.131 50(5)	0.493 76(5)	-0.027 87(7)	N(6)	-0.146 8(3)	0.415 7(3)	0.168 3(4)
Cl(1)	0.335 8(1)	0.407 6(1)	0.038 1(2)	C(1)	0.054 2(5)	0.586 8(5)	0.302 6(6)
Cl(2)	0.140 7(1)	0.343 2(1)	0.495 9(2)	C(2)	0.082 4(5)	0.679 4(5)	0.325 7(7)
O(1)	0.280 1(3)	0.479 2(3)	0.066 9(4)	C(3)	0.132 0(5)	0.715 4(5)	0.251 6(7)
O(2)	0.346 3(6)	0.420 2(5)	-0.087 7(6)	C(4)	0.147 6(5)	0.658 3(5)	0.153 6(7)
O(3)	0.412 1(4)	0.416 0(4)	0.129 3(7)	C(5)	0.048 8(4)	0.223 0(4)	0.037 0(7)
O(4)	0.304 1(4)	0.313 6(4)	0.051 4(6)	C(6)	0.070 0(5)	0.162 8(5)	-0.053 6(9)
O(5)	0.122 5(3)	0.324 7(4)	0.360 9(4)	C(7)	0.108 7(5)	0.202 5(6)	-0.141 8(8)
O(6)	0.217 5(5)	0.325(1)	0.550 7(8)	C(8)	0.124 5(5)	0.299 7(5)	-0.134 2(6)
O(7)	0.105 8(7)	0.425 2(7)	0.526 1(8)	C(9)	-0.087 2(4)	0.295 4(4)	0.308 4(6)
O(8)	0.099 7(8)	0.276 5(8)	0.555 2(8)	C(10)	-0.163 7(4)	0.273 2(4)	0.339 8(6)
O(9)	0.067 4(4)	0.891 4(4)	0.468 2(6)	C(11)	-0.230 1(4)	0.323 9(5)	0.284 0(7)
N(1)	0.070 7(3)	0.533 0(3)	0.208 4(4)	C(12)	-0.218 8(4)	0.396 4(5)	0.198 5(7)
N(2)	0.117 0(3)	0.570 3(3)	0.129 8(4)	C(13)	0.099 3(5)	0.969 9(6)	0.465 4(8)
N(3)	0.064 9(3)	0.315 2(3)	0.043 7(4)	C(14)	0.151 6(8)	1.012 8(7)	0.580(1)
N(4)	0.103 2(3)	0.356 4(3)	-0.044 5(4)	C(15)	0.085 9(6)	1.024 7(7)	0.343(1)

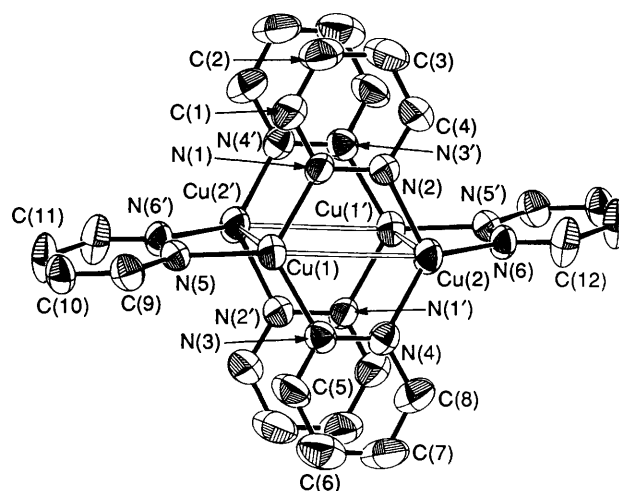
**Table 4** Selected bond lengths (Å) and angles (°) for complex **1**

Cu(1)···Cu(1')	3.065(2)	Cu(1)–N(1)	1.946(5)
Cu(1)–N(2)	2.067(5)	Cu(1)–N(3')	2.059(5)
Cu(1)–N(4)	2.037(5)	N(1)–C(2)	1.101(7)
N(2)–N(3)	1.353(6)	N(4)–N(4')	1.332(8)
N(1)–Cu(1)–N(2)	109.0(2)	N(1)–Cu(1)–N(3')	117.2(2)
N(1)–Cu(1)–N(4)	117.8(2)	N(2)–Cu(1)–N(3')	97.7(2)
N(2)–Cu(1)–N(4)	106.6(2)	N(3')–Cu(1)–N(4)	106.3(2)
Cu(1)–N(1)–C(2)	173.1(6)	Cu(1)–N(2)–N(3)	115.0(4)
Cu(1)–N(3')–N(2')	113.7(4)	Cu(1)–N(4)–N(4')	114.9(1)

173.9(1)° and 173.1(6)°, respectively, so that the two MeCN molecules are almost linear with the Cu(1)···Cu(1') vector. The N–Cu–N angles around each Cu atom are in the range 97.7(2)–117.8(2)°, *i.e.* within range found for usual four-coordinate copper(I) complexes.<sup>15</sup> It is interesting that one angle, N(2)–Cu(1)–N(3') 97.7(2)°, is rather shorter than the others [N(2)–Cu(1)–N(4) 106.6(2) and N(3')–Cu(1)–N(4) 106.3(2)°].

**Molecular Structure of Complex 2.**—There are two molecules of [Cu<sub>4</sub>(pydz)<sub>6</sub>][ClO<sub>4</sub>]<sub>4</sub> and four solvated acetone molecules in the unit cell. The molecular structure of the [Cu<sub>4</sub>(pydz)<sub>6</sub>]<sup>4+</sup> cation is shown in Fig. 2 together with the atomic numbering scheme. Selected bond distances and angles are listed in Table 5. Atoms Cu(1) and Cu(2) are bridged by four N atoms of two pydz ligands from the upper and lower sides of the Cu<sub>4</sub> plane to form a six-membered N<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub> framework. Furthermore, two parallel N<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub> frameworks are linked by two different pydz ligands from both sides to give a tetranuclear structure. Four three-coordinate copper atoms are coplanar and have a similar distorted trigonal co-ordination environment. Four pydz ligands of the N<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub> framework are perpendicular to the Cu<sub>4</sub> plane and the two pydz ligands of both sides are almost coplanar to the Cu<sub>4</sub> plane. The distance between the two N<sub>2</sub>Cu<sub>2</sub>N<sub>2</sub> framework moiety planes is *ca.* 3.2 Å, indicating the existence of π–π stacking among the pydz aromatic rings. To the best of our knowledge, three Cu<sub>4</sub> core arrangements, square-planar, cubane and stepped cubane arrangements, have been reported for tetracopper(I) complexes.<sup>1</sup> The copper atoms in square-planar and rectangular arrangements nearly always contain bridging bidentate halide ions or S atoms.<sup>1</sup> Complex **2** is the first tetracopper(I) complex having four three-coordinate coppers.

The Cu(1)···Cu(2) separation of 3.096(1) Å is slightly shorter than the Cu(1)···Cu(2') separation of 3.264(1) Å by *ca.*

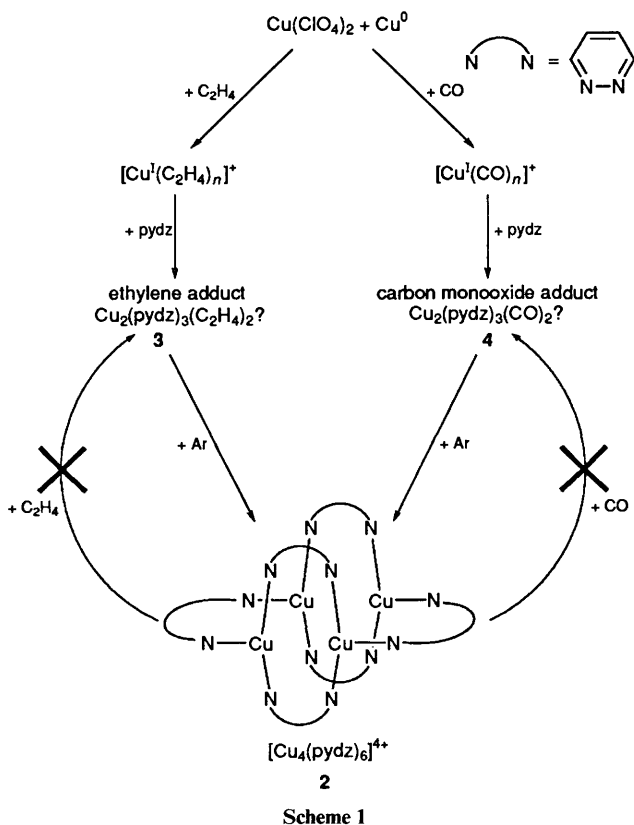
**Fig. 2** An ORTEP view<sup>14</sup> of the [Cu<sub>4</sub>(pydz)<sub>6</sub>]<sup>4+</sup> cation in **2** and atomic numbering scheme

0.17 Å. Both separations are shorter than those [3.280(2)–3.406(1) Å] of copper(I) complexes<sup>8a,b</sup> bridged by pyrazolate and that [3.3174(8), 3.4159(8) Å] of the analogous tetranuclear copper(II) complex<sup>9a</sup> bridged by pyrazolate. However, these separations are rather longer than those (2.45–2.80 Å) reported for tetracopper(I) complexes in square-planar arrangements<sup>20</sup> and that (2.56 Å) in Cu metal. Consequently, these separations are too long for a significant Cu···Cu interaction. The Cu–N distances around Cu(1) and Cu(2) atoms are 1.933(4)–2.004(4) Å and 1.959(5)–2.028(5) Å, respectively. These distances are similar to those (1.97–2.062 Å) of typical three-coordinate copper(I) complexes,<sup>21</sup> although they are longer than that [1.880(3) Å] of the three-coordinate copper(I) complex<sup>8a</sup> bridged by pyrazolate. The N–Cu–N angles around each Cu atom are 116.9–121.5° for Cu(1) and 109.5–121.0° for Cu(2). These angles are similar to those (112–135°) typically found for three-coordinate copper(I) complexes.<sup>22</sup>

**Ethylene and Carbon Monoxide Adducts.**—It is well established that Cu<sup>I</sup> readily binds to gaseous small molecules such as olefins<sup>2</sup> and alkynes.<sup>3</sup> In the preparation of **2**, an ethylene adduct **3** was isolated as colourless crystals if the pale yellow solution was sealed under C<sub>2</sub>H<sub>4</sub> (Scheme 1). This result is in contrast to the formation of orange crystals **2** when the pale yellow solution was sealed after bubbling of Ar gas through it.

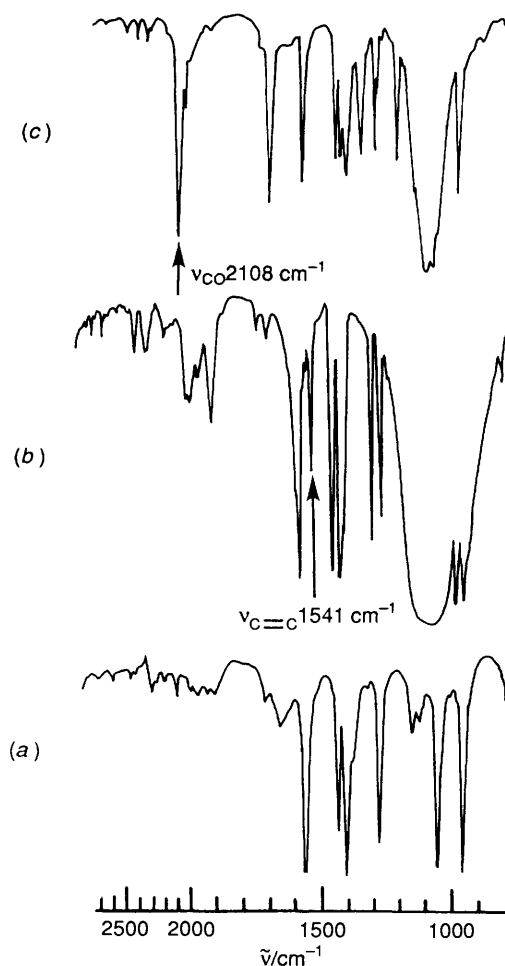
**Table 5** Selected bond distances (Å) and angles (°) for complex **2**

Cu(1)···Cu(1')	4.528(2)	Cu(2)···Cu(2')	4.470(2)
Cu(1')···Cu(2)	3.096(1)	Cu(1)···Cu(2)	3.264(1)
Cu(1)–N(1)	1.977(5)	Cu(1)–N(3)	2.004(4)
Cu(1)–N(5)	1.993(4)	Cu(2)–N(2)	2.028(5)
Cu(2)–N(4)	1.959(5)	Cu(2)–N(6)	1.997(4)
N(1)–N(2)	1.341(6)	N(3)–N(4)	1.352(6)
N(5)–N(6')	1.351(6)		
N(1)–Cu(1)–N(3)	121.5(2)	N(1)–Cu(1)–N(5)	118.9(2)
N(3)–Cu(1)–N(5)	116.9(2)	N(2)–Cu(2)–N(4)	121.0(2)
N(2)–Cu(2)–N(6)	109.5(2)	N(4)–Cu(2)–N(6)	127.5(2)
Cu(1)–N(1)–N(2)	118.3(3)	Cu(1)–N(1)–C(1)	122.9(4)
Cu(2)–N(2)–N(1)	119.0(3)	Cu(2)–N(2)–C(4)	122.2(4)
Cu(1)–N(3)–N(4)	118.5(3)	Cu(1)–N(3)–C(5)	121.7(4)
Cu(2)–N(4)–N(3)	118.9(3)	Cu(2)–N(4)–C(8)	123.0(4)
Cu(1)–N(5)–N(6)	115.3(3)	Cu(1)–N(5)–C(9)	125.5(4)
Cu(2)–N(6)–N(5)	116.3(3)	Cu(2)–N(6)–C(12)	124.6(4)



The colourless crystals are very unstable toward O<sub>2</sub> and moisture, and immediately turned orange in air. The IR spectrum of **3** [Fig. 3(b)] prepared as a KBr pellet under Ar showed  $\nu_{C=N}$  and  $\nu_{C=N}$  stretches of pydz in the range 1587–1431 cm<sup>-1</sup>, with co-ordination shifts ( $\Delta\tilde{\nu} = \tilde{\nu}_{\text{complex}} - \tilde{\nu}_{\text{free}}$ ) of 15–24 cm<sup>-1</sup>. The  $\nu_{C=C}$  stretching frequency of the co-ordinated ethylene is at 1541 cm<sup>-1</sup>. The co-ordination shift relative to free ethylene ( $\Delta\nu = -82$  cm<sup>-1</sup>) is smaller than those ( $\Delta\nu = -86$  to  $-118$  cm<sup>-1</sup>) found for other copper(I) ethylene complexes<sup>2g</sup> and that ( $\Delta\nu = -97$  cm<sup>-1</sup>) of K[PtCl<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>)]. A solution of **3** gave three well-resolved <sup>1</sup>H NMR signals at  $\delta$  9.59(H<sup>3,6</sup>), 8.40(H<sup>4,5</sup>) and 5.09(C<sub>2</sub>H<sub>4</sub>) at 23 °C in (CD<sub>3</sub>)<sub>2</sub>CO, with co-ordination shifts ( $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free}}$ ) of 0.37, 0.75 and  $-0.29$  ppm, respectively. The co-ordination shift of ethylene in the IR and <sup>1</sup>H NMR spectra is not very large compared with other copper(I) ethylene complexes,<sup>2g</sup> suggesting a relatively weak Cu<sup>I</sup>–olefin bond.

A carbon monoxide adduct **4** was also isolated by replacing the

**Fig. 3** IR spectra in the range 900–2700 cm<sup>-1</sup> of free pydz (a), **3** (b) and **4** (c)

C<sub>2</sub>H<sub>4</sub> atmosphere by CO (Scheme 1). The colourless crystals are even more air- and moisture-sensitive than **3**. The IR spectrum of **4** [Fig. 3(c)] showed  $\nu_{C=C}$  and  $\nu_{C=C}$  stretches of pydz in the region 1585–1414 cm<sup>-1</sup> ( $\Delta\nu = 1–22$  cm<sup>-1</sup>) and  $\nu_{CO}$  at 2108 cm<sup>-1</sup> ( $\Delta\nu = -47$  cm<sup>-1</sup>). For Cu<sup>I</sup>, both terminal<sup>4</sup> and bridging modes<sup>2,3</sup> of CO have been reported. The  $\nu_{CO}$  value of 2108 cm<sup>-1</sup> for **4** is in the range (2055–2117 cm<sup>-1</sup>) of copper(I) carbon monoxide complexes containing terminal CO.<sup>4</sup> A solution of **4** showed two broad <sup>1</sup>H NMR signals at  $\delta$  9.66(H<sup>3,6</sup>) and 8.35(H<sup>4,5</sup>) at 23 °C in (CD<sub>3</sub>)<sub>2</sub>CO. On the other hand, two sets of <sup>1</sup>H NMR signals were observed at  $-90$  °C: the major species showed signals at  $\delta$  9.96(t, H<sup>3,6</sup>) and 8.57(t, H<sup>4,5</sup>) and the minor species showed signals at  $\delta$  9.77(H<sup>3,6</sup>) and 8.46(H<sup>4,5</sup>), indicative of the existence of an equilibrium in solution.

The detailed structures of adducts **3** and **4** are not obvious, because these colourless crystals could not be characterized by X-ray crystal analysis\* or by elemental analysis owing to their instability. However, copper(I) complexes with pydz have a tendency to form binuclear triply bridged structures, as observed for complex **1**. These adducts are thus probably binuclear copper(I) complexes of formula [Cu<sub>2</sub>(pydz)<sub>3</sub>(L)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> (L = C<sub>2</sub>H<sub>4</sub> **3** or CO **4**). Once formed, complex **2** did not react with ethylene or carbon monoxide, indicating its rigid tetranuclear structure.

\* Reflection intensities of a colourless crystal of **3** decreased during data collection and only the crystal data are given: monoclinic, space group P2<sub>1</sub>/a,  $a = 14.876(9)$ ,  $b = 13.05(2)$ ,  $c = 11.220(6)$  Å,  $\beta = 109.09(4)^\circ$ ,  $U = 2058(6)$  Å<sup>3</sup>.

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