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A pyrazole ligand yielding both chloro-bridged dinuclear and tetranuclear copper(II) compounds. The crystal and molecular structure of bis[μ-chloro-chloro(3,4-dimethyl-5-phenylpyrazole)(4,5-dimethyl-3-phenylpyrazole)copper(II)] and of (μ_4-oxo)hexakis(μ-chloro)tetrakis(3,4-dimethyl-5-phenylpyrazole)tetracopper(II)

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Abstract

The reaction of $CuCl_2 \cdot 2H_2O$ and 3(5),4-dimethyl-5(3)-phenylpyrazole (hereafter Hdmppz) gives green crystals that analyze as $CuCl_2(C_{11}H_{12}N_2)_2$ (**1**). The green filtrate produces brown crystals of composition $Cu_4OCl_6(C_{11}H_{12}N_2)_4$ (**2**). The crystal structure of both compounds was determined from single-crystal X-ray data. Crystals of bis[μ-chloro-chloro-(3,4-dimethyl-5-phenylpyrazole)-(4,5-dimethyl-3-phenylpyrazole)copper(II)] (1) are triclinic, space group $P\bar{1}$; $a = 9.071(1)$, $b = 11.008(1)$, $c = 11.358(1)$ Å, $\alpha = 93.42(1)$, $\beta = 97.50(1)$, $\gamma = 96.16(1)°$, $Z = 1$. The dinuclear unit is located on a crystallographic inversion center. The copper ion is five-coordinated by two pyrazole nitrogen atoms and one bridging and one non-bridging chloride anion. The coordination is best described as a distorted square pyramid with the long bridging chloride as the top. Surprisingly the two pyrazole ligands are coordinating through different nitrogen atoms, one through the nitrogen atom close to the phenyl substituent and the other through the nitrogen close to the methyl substituent. Crystals of (μ_4-oxo)hexakis(μ-chloro)tetrakis(4,5-dimethyl-3-phenyl-pyrazole)tetra-copper(II) (2) are monoclinic, space group $I2/a$; $a = 20.836(1)$, $b = 11.161(1)$, $c = 22.996(1)$ Å, $\beta = 104.54(1)°$, $Z = 4$. The copper ions are coordinated by five ligands in a trigonal-bipyramidal arrangement. The pyrazole nitrogen and the oxo-anion form the two tops of the bipyramid and the chlorides form the basal plane. Magnetic susceptibility measurements of **1** and **2** show that there is considerable antiferromagnetic interaction in these compounds as can be expected. For **1** the experimental data could be fitted to a model for a dinuclear compound with $2J$ as the singlet triplet splitting and zJ' the inter-dinuclear exchange. The best fit was found for $g = 2.13$, $J/k = -5.8$ K and $zJ'/k = -0.22$ K. For **2** a model was used with two different exchange parameters J_a and J_b. The best fit was obtained for $g = 2.11$ and $J_a/k = -51$ K and $J_b/k = -33$ K.

Introduction

Polynuclear compounds of copper(II), with small anions as bridging groups, are the subject of numerous papers in contemporary literature [1–5]. Compounds with fluoride as a bridging anion are the least-prominent family. With substituted azole ligands however, several compounds with fluoro bridges are known [6–13].

With 3(5)-methyl-5(3)-phenylpyrazole (Hmppz hereafter) as a ligand we were able to solve the first crystal structure of a fluoro-bridged dinuclear, planar copper(II) compound with a considerable magnetic interaction [8]. Recently we published the crystal structure of a rather uncommon compound [14] with 4-ethyl-3(5)-methyl-5(3)-phenylpyrazole (Hemppz hereafter), containing a non-linear chain of copper ions linked by fluoro bridges. For this and two other copper compounds, the magnetic and spectroscopic properties were studied in detail [15].

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In order to make a detailed comparison with other bridging anions, we undertook to prepare chloro-bridged compounds, isostructural to known fluoro compounds. From the reaction of $CuCl_2 \cdot 2H_2O$ and Hdmppz in ethanol green crystals formed that analyzed as $CuCl_2(C_{11}H_{12}N_2)_2$. Magnetic measurements indicated that this is a dinuclear compound, with a weak antiferromagnetic exchange. From the same solution brown, plate-like crystals were formed that analyzed as $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$. A single-crystal analysis was undertaken for both compounds, the results of which are discussed here.

Experimental

Starting materials

The ligand Hdmppz was synthesized from 1-phenyl-2-methyl-1,3-butadione and hydrazinehydrate [16]. $CuCl_2 \cdot 2H_2O$ was used as commercially available (J.T. Baker). Satisfactory C, H, N, Cl and metal analyses were obtained.

Synthesis and crystal growth

$[Cu(C_{11}H_{12}N_2)_2Cl_2]_2$ (**1**). To a warm solution of 1 mmol (0.170 g) of $CuCl_2 \cdot 2H_2O$ in 25 ml of ethanol a warm solution of 1.8 mmol (0.310 g) Hdmppz in 25 ml of ethanol was slowly added. The mixture was allowed to cool slowly. After several hours the compound crystallized in green parallelepipeds. The green crystals are separated from the solution by filtration. Upon standing brown, flat crystals $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (**2**) formed in the green filtrate.

Physical measurements and analyses

Infrared spectra were recorded on a Perkin-Elmer model 580B IR spectrometer in the region 4000–180 cm^{-1} as KBr pellets. Ligand field spectra were recorded in the region 28000–4000 cm^{-1} on a Perkin-Elmer 330 UV–Vis spectrometer, with the use of the diffuse-reflectance technique with MgO as a reference. EPR spectra were recorded on a Varian E3 (9.5 GHz) spectrometer by using powdered samples. Magnetic susceptibility data were obtained on powdered samples in the temperature region 2–300 K with a S.H.E. Corporation VTS superconducting SQUID susceptometer at a field of 5 kOe. The sample bucket was fabricated from an Al–Si alloy obtained from S.H.E. Corporation. The magnetic data were corrected for the magnetic susceptibility of the sample bucket, which was measured independently. The data were corrected for diamagnetism using Pascal constants; measurements and calibration procedures have been reported elsewhere [17]. Elemental analyses were performed by the Microanalytical Laboratory, University College, Dublin, Ireland.

TABLE 1. Crystal and diffraction data for $[CuCl_2(C_{11}H_{12}N_2)_2]_2$ (**1**) and for $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (**2**)

	1	**2**
Chemical formula	$C_{44}H_{48}Cl_4Cu_2N_8$	$C_{44}H_{48}Cl_6Cu_4N_8O$
Formula weight	957.82	1171.82
Space group	$P\bar{1}$	$I2/a$
a (Å)	9.071(1)	20.836(1)
b (Å)	11.008(1)	11.161(1)
c (Å)	11.358(1)	22.996(2)
α (°)	93.42(1)	
β (°)	97.50(1)	104.54(1)
γ (°)	96.16(1)	
V (Å^3)	1114.8(2)	5176.5(6)
Z	1	4
T (K)	295	295
λ (Å)	0.71073	0.71073
D_{calc} (g cm^{-3})	1.427	1.504
D_{obs} (g cm^{-3})	1.41	1.49
μ (cm^{-1})	12.4	19.8
Final R (F_o)	0.042	0.052
Final R_w (F_o)	0.045	0.063

X-ray data collection

X-ray data were collected on an Enraf-Nonius CAD4F diffractometer for crystals (**1** green; **2** brownish) glued on top of a glass fibre. Crystal data and numerical details of the structure determinations are given in Table 1. Unit-cell parameters and their standard deviations were derived from the SET4 setting angles of 25 reflections in the range $14 < \theta < 20°$ for **1** and $10 < \theta < 15°$ for **2**. The space group of **2** was determined from the observed systematic extinctions as Ia or $I2/a$. The latter one was adopted. There was no significant decay during data collection. The intensities were corrected for Lorentz and polarization effects but not for absorption (in view of only minor intensity variations observed for 360° ψ-scans for close to axial reflections). Crystal **2** was found to include a minor twin component affecting the intensities of a few reflections.

Structure determination and refinement

The structures were solved with standard Patterson and Fourier methods (SHELXS-86 [18]) and refined on F by full-matrix least-squares with SHELX-76 [19]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were introduced on calculated positions and refined with fixed geometry with respect to their carrier atoms with common isotropic thermal parameters, except for the two pyrazole hydrogen atoms in **1** that could be located from a difference map. Final

TABLE 2. Final coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of $[CuCl_2(C_{11}H_{12}N_2)_2]_2$ (1)

Atom	x	y	z	U_{eq}[a] (Å^2)
Cu	1.07796(4)	0.09562(4)	0.13326(3)	0.0354(1)
Cl(1)	0.84396(8)	0.06554(8)	0.02198(7)	0.0435(3)
Cl(2)	0.99132(9)	−0.01605(9)	0.27980(7)	0.0494(3)
N(11)	1.2973(3)	0.1242(3)	0.3477(2)	0.0371(8)
N(12)	1.2830(3)	0.1256(2)	0.2274(2)	0.0359(8)
N(31)	1.1059(4)	0.2461(3)	−0.0708(3)	0.049(1)
N(32)	1.1191(3)	0.2472(2)	0.0481(2)	0.0394(8)
C(13)	1.4204(3)	0.1615(3)	0.2024(3)	0.0369(9)
C(14)	1.5218(3)	0.1827(3)	0.3074(3)	0.042(1)
C(15)	1.4395(3)	0.1564(3)	0.3992(3)	0.0350(9)
C(16)	1.4521(4)	0.1743(4)	0.0782(3)	0.054(1)
C(17)	1.6859(4)	0.2250(5)	0.3114(3)	0.072(2)
C(18)	1.4792(3)	0.1580(3)	0.5292(3)	0.0361(9)
C(19)	1.6272(4)	0.1676(3)	0.5818(3)	0.051(1)
C(20)	1.6634(4)	0.1680(4)	0.7040(3)	0.055(1)
C(21)	1.5542(4)	0.1558(4)	0.7748(3)	0.056(1)
C(22)	1.4070(4)	0.1441(5)	0.7245(3)	0.072(2)
C(23)	1.3696(4)	0.1452(4)	0.6028(3)	0.062(1)
C(33)	1.1667(3)	0.3639(3)	0.0876(3)	0.042(1)
C(34)	1.1839(4)	0.4363(3)	−0.0083(3)	0.051(1)
C(35)	1.1436(4)	0.3567(3)	−0.1086(3)	0.052(1)
C(36)	1.1353(6)	0.3769(4)	−0.2382(3)	0.078(2)
C(37)	1.2292(5)	0.5719(4)	−0.0053(4)	0.074(2)
C(38)	1.1886(4)	0.3991(3)	0.2165(3)	0.048(1)
C(39)	1.0845(5)	0.3535(4)	0.2877(3)	0.059(1)
C(40)	1.1050(6)	0.3841(5)	0.4099(4)	0.082(2)
C(41)	1.2266(8)	0.4616(5)	0.4599(4)	0.099(3)
C(42)	1.3307(7)	0.5098(5)	0.3916(5)	0.096(2)
C(43)	1.3124(5)	0.4789(4)	0.2689(4)	0.071(2)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

TABLE 3. Final coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (**2**)

Atom	x	y	z	U_{eq}[a] (Å^2)
Cu(1)	0.21126(4)	1.03790(8)	0.04886(4)	0.0398(3)
Cu(2)	0.18230(4)	1.23993(8)	−0.04651(4)	0.0418(3)
Cl(1)	0.25	0.8777(3)	0.0	0.064(1)
Cl(2)	0.1102(1)	1.1407(2)	0.00215(9)	0.0602(8)
Cl(3)	0.25	1.3991(3)	0.0	0.064(1)
Cl(4)	0.2093(1)	1.1389(3)	−0.13440(9)	0.091(1)
O	0.25	1.1384(6)	0.0	0.034(2)
N(11)	0.2006(3)	0.9446(6)	0.1632(2)	0.044(2)
N(12)	0.1759(3)	0.9374(5)	0.1037(2)	0.040(2)
N(31)	0.1035(3)	1.3328(6)	−0.1589(3)	0.045(2)
N(32)	0.1164(3)	1.3434(6)	−0.0989(3)	0.046(2)
C(13)	0.1288(4)	0.8551(7)	0.0948(3)	0.047(3)
C(14)	0.1225(4)	0.8097(7)	0.1497(4)	0.05(3)
C(15)	0.1704(4)	0.8690(7)	0.1933(3)	0.045(3)
C(16)	0.0901(5)	0.8224(9)	0.0332(4)	0.077(4)
C(17)	0.0714(6)	0.720(1)	0.1566(6)	0.108(5)
C(18)	0.1887(4)	0.8647(7)	0.2590(3)	0.049(3)
C(19)	0.1704(5)	0.7714(9)	0.2902(4)	0.073(4)
C(20)	0.1879(6)	0.771(1)	0.3528(5)	0.084(5)
C(21)	0.2238(6)	0.862(1)	0.3853(4)	0.090(5)
C(22)	0.2446(5)	0.955(1)	0.3558(4)	0.090(5)
C(23)	0.2257(5)	0.9575(9)	0.2918(4)	0.075(4)
C(33)	0.0839(4)	1.4412(8)	−0.0897(4)	0.057(3)
C(34)	0.0498(4)	1.4914(8)	−0.1446(4)	0.061(3)
C(35)	0.0636(4)	1.4208(7)	−0.1878(4)	0.049(3)
C(36)	0.0857(5)	1.480(1)	−0.0269(5)	0.087(4)
C(37)	0.0108(6)	1.6069(9)	−0.1496(6)	0.107(5)
C(38)	0.0445(4)	1.4248(7)	−0.2538(4)	0.055(3)
C(39)	0.0844(5)	1.3744(8)	−0.2871(4)	0.067(3)
C(40)	0.0668(6)	1.3784(9)	−0.3499(4)	0.086(4)
C(41)	0.0100(7)	1.434(1)	−0.3789(5)	0.111(6)
C(42)	−0.0312(6)	1.481(1)	−0.3461(6)	0.111(6)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

coordinates are listed in Tables 2 and 3. Neutral scattering factors were obtained from ref. 20 and corrected for anomalous dispersion [21]. Three reflections, seriously affected by the minor twinning, were left out of the final weighted refinement cycles of **2**. The program PLATON of the EUCLID package [22] was used for the geometrical calculations and the thermal motion ellipsoid plots. All calculations were carried out on a Micro VAX cluster.

The corresponding labelling of the atoms is given in Figs. 1 and 2. See also 'Supplementary Material'.

Results and discussion

Description of the structure of $[CuCl_2(C_{11}H_{12}N_2)_2]_2$ (1)

The structure and atomic labelling of **1** is depicted in Fig. 1, and relevant interatomic distances and angles are given in Table 4. The unit cell of **1** is shown in Fig. 3. The copper ion is coordinated by two pyrazole nitrogen atoms at 2.005(3) and 2.003(2) Å and two chloride ions at 2.3047(9) and 2.297(1) Å. One chloride ion is bridging to the next copper ion, yielding a dinuclear unit, positioned around an inversion center. The long Cu–Cl(1)′ distance is 2.6420(9) Å. The copper–copper distance is 3.6164(7) Å and the Cu–Cl–Cu′ angle is 93.70(3)°. The coordination can be described as a distorted square pyramid [23], with Cl(1)′ at the apical position.

The basal plane is rather flat, the maximum deviation from the least-squares plane (N12, N32, Cl1, Cl2) is ±0.2 Å. The angle between this plane and the apical Cu–Cl(1)′ bond is 83.60(5)° and the copper ion is 0.23 Å above the plane. The next nearest copper is at 8.965(1) Å. The non-bridging chloride ion and the pyrazole N–H are linked by hydrogen bonding; distances and angles are given in Table 5. In the present literature there are several well characterized examples of dinuclear compounds, containing five-coordinated copper. Hodgson and coworkers [2] studied a series of these compounds and

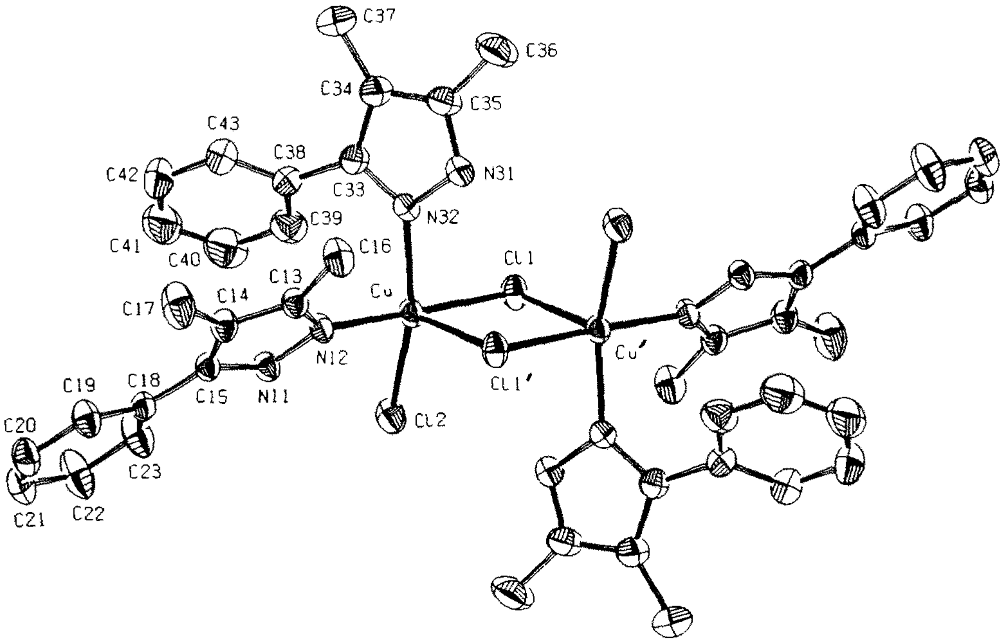

Fig. 1. Thermal motion ellipsoid plot (40% probability) of $[CuCl_2(C_{11}H_{12}N_2)_2]_2$ (1) with atomic labelling. The hydrogen atoms are omitted for clarity.

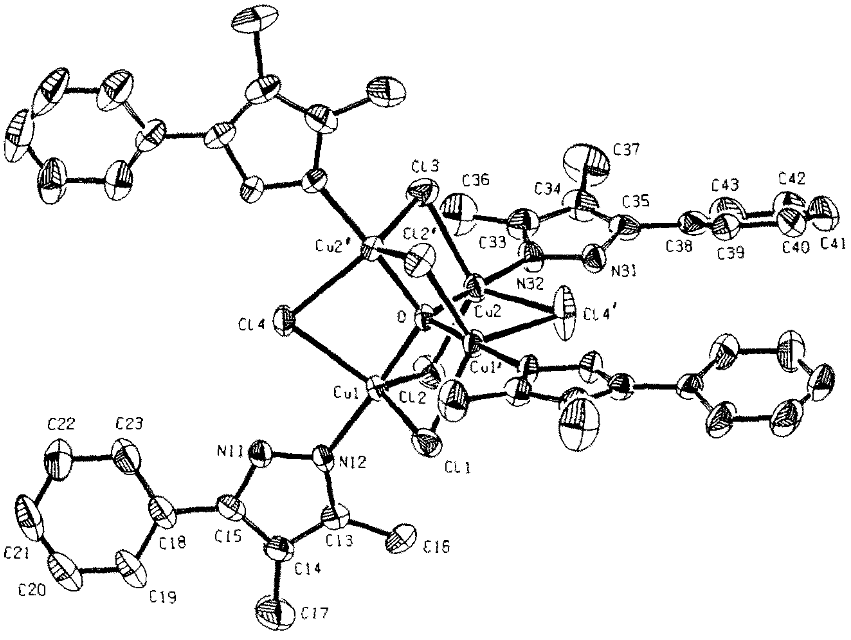

Fig. 2. Thermal motion ellipsoid plot (40% probability) of $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (2) with atomic labelling. The hydrogen atoms are omitted for clarity.

described an empirical relation between the structural and magnetic parameters. The distances and angles in 1 are normal, compared to the known compounds so far.

Most dinuclear compounds of this type, that are found so far, contain chelating ligands. The present compound contains two monodentate ligands per copper. Strikingly the two pyrazole ligands are coordinated in different ways, one via the nitrogen (N(12) next to the methyl group (hereafter L(N12)) and the other (hereafter L(N32)) via the nitrogen (N(32)) atom next to the phenyl substituent. In

TABLE 4. Relevant distances (Å) and angles (°) in $[CuCl_2(C_{11}H_{12}N_2)_2]_2$ (**1**). Primed atoms are generated by $2-x$, $-y$, $-z$; double primed by $2-x$, $-y$, $1-z$

Cu–Cl(1)	2.3047(9)
Cu–Cl(2)	2.297(1)
Cu–N(12)	2.005(3)
Cu–N(32)	2.003(2)
Cu–Cl(1)′	2.6420(9)
Cu–Cu′	3.6164(7)
Cu–Cu″	8.965(1)
Cu–Cl(1)′–Cu′	93.70(3)
Cl(1)–Cu–Cl(2)	90.70(3)
Cl(1)–Cu–N(32)	87.87(8)
Cl(2)–Cu–N(12)	90.79(7)
N(12)–Cu–N(32)	90.6(1)
Cl(1)–Cu–N(12)	178.44(7)
Cl(2)–Cu–N(32)	155.32(8)
Cl(1)′–Cu–Cl(1)	86.30(3)
Cl(1)′–Cu–Cl(2)	105.82(4)
Cl(1)′–Cu–N(12)	93.76(7)
Cl(1)′–Cu–N(32)	98.67(7)

solution of such ligands both tautomers are known to be present.

So far five crystal structures, containing 3(5)-phenylpyrazole derivatives as a ligand [8, 14, 24, 25] have been reported. In these structures the ligand coordinates via the nitrogen away from the phenyl substituent, i.e. as is found for ligand L(N12) in this compound, presumably for steric reasons. Coordination via the nitrogen close to the phenyl substituent is not impossible, two structures are known that contain 3,5-diphenylpyrazole coordinating to copper(II) [26, 27]. The angle between the phenyl and the pyrazole ring is 42.5(2)° for ligand L(N32); this relieves some of the steric hindrance.

As can be seen from Fig. 1 there is some interaction between the pyrazole ring of ligand L(N12) and the phenyl ring of ligand L(N32), that would not have been possible if both ligands were coordinated as ligand L(N12). The angle between the least-squares planes through these rings is 23.2(2)°. The shortest distance is N(12)–C(38) 3.222(4) Å.

Description of the structure of $Cu_4OCl_6(C_{11}H_{12}N_2)_4$ (2)

The final fractional atomic coordinates are given in Table 3. The structure and atomic labelling of **2** is depicted in Fig. 2, and relevant interatomic distances and angles are given in Table 6. A projection of the unit-cell packing of **2** is shown in Fig. 4. The structure consists of a μ_4-oxide surrounded by four copper ions, in a distorted tetrahedron. The cluster is positioned on a two-fold axis (through Cl(1) and Cl(3)). A chloride ion is bridging between each pair of copper ions. Two of the six chloride ions are positioned on the two-fold axis. The copper ions are

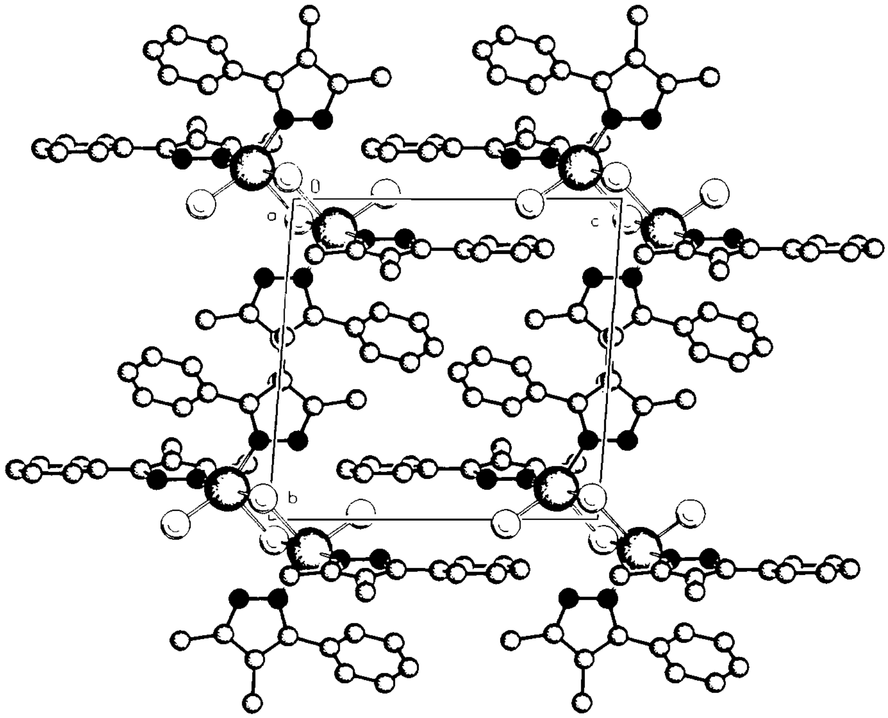

Fig. 3. Projection of the unit-cell contents of $[CuCl_2(C_{11}H_{12}N_2)_2]_2$ (**1**).

TABLE 5. Hydrogen bond distances (Å) and angles (°) for $[CuCl_2(C_{11}H_{12}N_2)_2]_2$ (**1**) and $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (**2**). Primed atoms are generated by $2-x$, $-y$, $-z$; double primed by $\frac{1}{2}-x$, y, $1-z$

D-H···A	D···A	D-H···A	H···A
1			
N(11)-H(11)···Cl(2)	3.010(3)	125(3)	2.40(4)
N(31)-H(31)···Cl(2)'	3.329(5)	163(3)	2.65(3)
2			
N(11)-H(11)···Cl(4)	3.047(7)	126.6(5)	2.383(7)
N(31)-H(31)···Cl(4)'	3.040(7)	126.1(5)	2.380(7)

TABLE 6. Relevant distances (Å) and angles (°) for $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (**2**). Primed atoms are generated by $\frac{1}{2}-x$, y, $1-z$

Cu(1)-Cu(2)	3.097(1)	Cu(1)-Cl(1)	2.359(3)
Cu(1)-Cu(1)'	3.079(1)	Cu(1)-Cl(2)	2.402(2)
Cu(1)-Cu(2)'	3.173(1)	Cu(1)-Cl(4)	2.499(3)
Cu(2)-Cu(2)'	3.083(1)	Cu(2)-Cl(2)	2.362(2)
Cu(1)-O	1.905(4)	Cu(2)-Cl(3)	2.352(3)
Cu(2)-O	1.913(4)	Cu(2)-Cl(4)'	2.499(3)
Cu(1)-N(12)	1.964(6)	Cu(2)-N(32)	1.960(7)
Cu(1)-Cl(1)-Cu(1)'	81.5(1)		
Cu(1)-Cl(2)-Cu(2)	81.10(7)		
Cu(2)-Cl(3)-Cu(2)'	81.9(1)		
Cu(1)-Cl(4)-Cu(2)'	78.81(7)		
Cu(1)-O(1)-Cu(2)	108.45(4)		
Cu(1)-O(1)-Cu(1)'	107.8(3)		
Cu(1)-O(1)-Cu(2)'	112.41(4)		
Cu(2)-O(1)-Cu(2)'	107.4(3)		
O(1)-Cu(1)-N(12)	176.3(2)		
Cl(1)-Cu(1)-Cl(2)	121.03(6)		
Cl(1)-Cu(1)-Cl(4)	118.60(8)		
Cl(2)-Cu(1)-Cl(4)	118.0(1)		
O(1)-Cu(2)-N(32)	175.8(2)		
Cl(2)-Cu(2)-Cl(3)	121.26(6)		
Cl(2)-Cu(2)-Cl(4)'	118.1(1)		
Cl(3)-Cu(2)-Cl(4)'	118.51(8)		

five-coordinated by three bridging chloride ions in equatorial and the oxide and a pyrazole nitrogen in axial positions, the ligands form an almost regular trigonal bipyramid. In this compound the pyrazole ligands are coordinating via the nitrogen next to the methyl group as is the case for ligand L(N32) of compound **1**. Cu–O distances are 1.905(4) and 1.913(4) Å, Cu–N_{pyr} distances 1.960(7) and 1.964(6) Å and Cu–Cl distances range from 2.352(3) to 2.499(3) Å. The Cu–Cu distances range from 3.079(1) to 3.173(1) Å and Cu–Cl–Cu angles from 78.8(7) to 81.9(1)°. Clusters of this type have been reported before [28, 29]. The pyrazole N–H are hydrogen bonding to Cl(4); distances and angles are given in Table 5.

Spectroscopic measurements

The infrared spectra of **1** and **2** show vibrations, characteristic for pyrazole and phenyl rings. The ligand field spectra are normal for five-coordinated copper(II) [30, 31]. The spectrum of **2** shows a maximum at 13.3×10^3 cm^{-1} with a pronounced low energy shoulder and a Cu–Cl charge transfer at about 24.6×10^3 cm^{-1}. The spectrum of **2** shows a symmetric maximum at 11.7×10^3 cm^{-1} with a charge transfer band at about 26.3×10^3 cm^{-1}.

The EPR spectrum of **1** is anisotropic with $g_\perp=2.06$ and $g_\parallel=2.26$ at room and liquid nitrogen temperature. The spectrum of **2** shows a very weak EPR signal, probably due to a small impurity in the bulk sample.

Magnetic measurements

The susceptibility of **1** and **2** was measured in the temperature region 2–300 K, the susceptibility per mole of copper ions is plotted as a function of the temperature in Figs. 5 and 6. For **1** the dominant feature of the data is a maximum near 7 K. A Curie–Weiss analysis of the data above 50 K gives the parameters $\theta=-3.2$ K and $C=0.42$ emu K/mol, $g=2.13$.

The equation for the susceptibility for a dinuclear molecule with spin $S_1=S_2=1/2$ is

$$\chi'=\frac{Ng^2\mu^2}{kT}\times\frac{\exp(2x)}{1+3\exp(2x)} \qquad (1)$$

where $x=-J/kT$ and $2J$ is the separation of the singlet and triplet energy levels with a negative J value denoting a ground-state singlet. Accounting for inter-dinuclear exchange zJ' and temperature independent paramagnetism (*TIP*) yields the following equation for the susceptibility

$$\chi=\frac{\chi'}{1-\left(\dfrac{2zJ'}{Ng^2\mu^2}\right)\chi'}+TIP \qquad (2)$$

The results were fitted to eqn. (2). During the fitting procedure the value of *TIP* was held constant (60×10^{-6} emu/mol). The results of the best fit are shown as the solid curve in Fig. 5. The best-fit parameters are $g=2.13$, $J/k=-5.8$ K, $zJ'/k=-0.22$ K. These parameters fit well with the empirical relation for these compounds, as described by Hodgson and co-workers [2].

For **2** a maximum in the susceptibility is found around 60 K, the maximum is broader than found for **1**. The data may be analyzed under a first approximation by using the simple model for di-

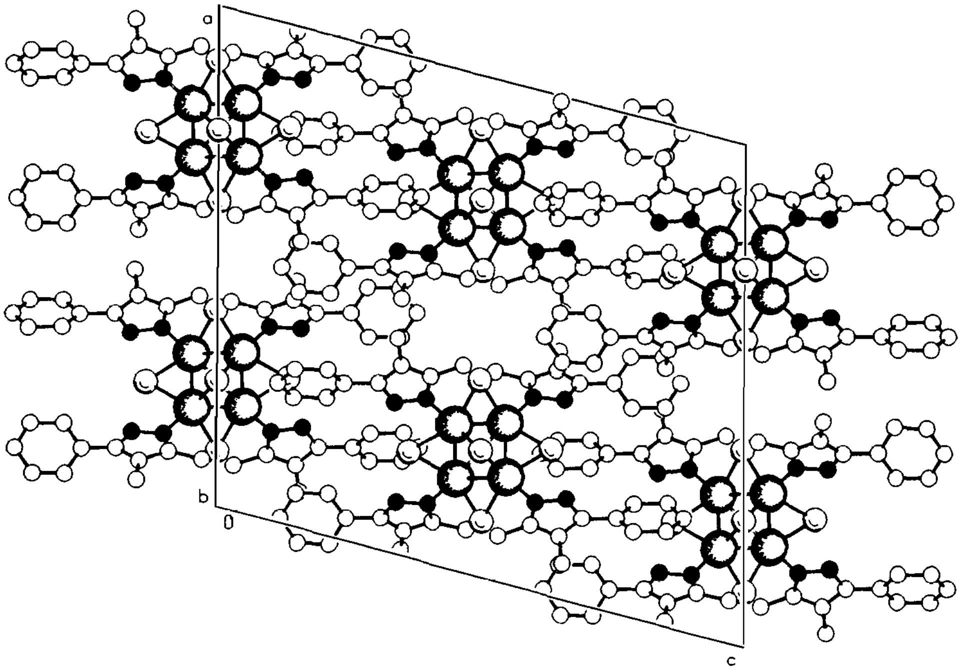

Fig. 4. Projection of the unit-cell contents of $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (2).

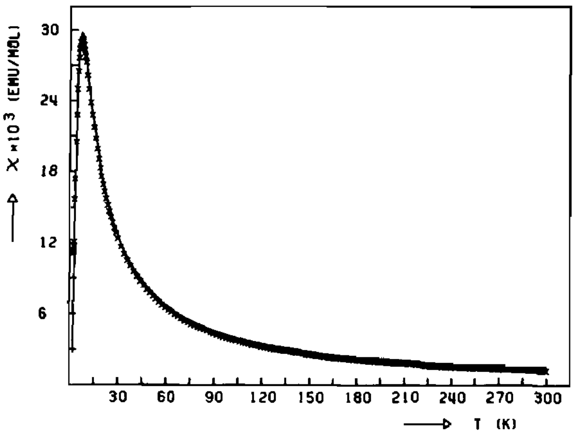

Fig. 5. Magnetic susceptibility measurements of $CuCl_2(C_{11}H_{12}N_2)_2]_2$ (1).

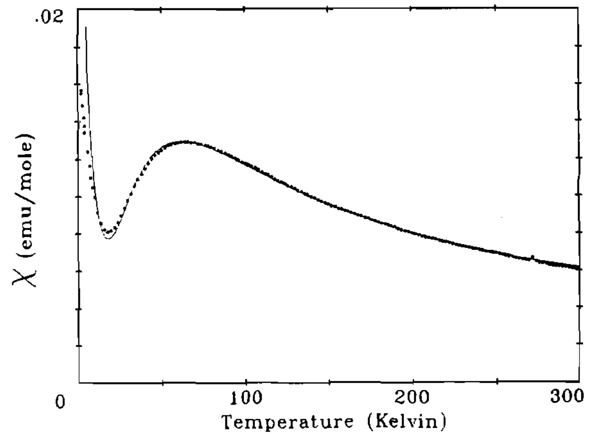

Fig. 6. Magnetic susceptibility measurements of $[Cu_4OCl_6(C_{11}H_{12}N_2)_4]$ (2).

nuclear compound (eqn. (1)), corrected for a weak interaction to compensate for the presence of a tetranuclear molecule (eqn. (2)).

A fit of the experimental magnetic susceptibility data to eqn. (2) gives the parameters $g=2.10$, $J/k=-54$ K, $zJ'/k=-8.5$ K. Here the *TIP* (this value is given per tetranuclear molecule) is 0.001717 emu/mol and there is 5.6% paramagnetic impurity. The zJ' is large enough, compared to the primary exchange interaction (J) to require a spin Hamiltonian for a tetranuclear cluster. The complete exchange interaction component of the spin Hamiltonian for a four spin system is given in eqn. (4).

$$\mathscr{H}=-2(J_{12}\hat{S}_1\cdot\hat{S}_2+J_{23}\hat{S}_2\cdot\hat{S}_3+J_{34}\hat{S}_3\cdot\hat{S}_4 +J_{14}\hat{S}_1\cdot\hat{S}_4+J_{13}\hat{S}_1\cdot\hat{S}_3+J_{24}\hat{S}_2\cdot\hat{S}_4) \qquad (3)$$

For a perfect tetrahedral arrangement of copper(II) ions, all exchange parameters J_{ij} are equal (J) and a closed form magnetic susceptibility equation may be generated as shown in eqn. (4).

$$\chi=\frac{Ng^2\mu^2}{kT}\times\frac{6\exp(2x)+10\exp(6x)}{2+9\exp(2x)+5\exp(6x)} \qquad (4)$$

where $x=2J/kT$

A fit of eqn. (4) to the magnetic susceptibility data gives the parameters $g=2.43$, $J/k=-52$ K, $TIP=0.00051$ emu/mol, and 4.8% paramagnetic impurity, however, this fit is not as good as the fit obtained from eqn. (2). The addition of a zJ' term to the susceptibility calculation (following eqn. (2)) resulted in an improvement of the goodness of fit and an improvement in the reasonableness of the parameters ($g=2.10$, $J/k=-52$ K, $zJ'/k=17$ K, $TIP=0.00133$ emu/mol, and 5.9% paramagnetic impurity), but the inter-tetranuclear exchange term (zJ') is too large and its use is difficult to rationalize in the context of the crystal structure data. Since the quality of the fit to eqn. (4) is only marginal, this indicates that the exchange symmetry is substantially less than tetrahedral. Therefore an attempt to improve the fit was made by reducing the high symmetry of the tetrahedral exchange field.

A square exchange model was attempted that retained a lower symmetry and two exchange values. The spin Hamiltonian in eqn. (4) was used with $J_{12}=J_{34}=J_a$ and $J_{13}=J_{23}=J_{24}=J_{41}=J_b$. By using the four spin $S=1/2$ basis set for copper(II) ($\Psi=|\phi_1, \phi_2, \phi_3, \phi_4\rangle$, where $\phi_1=1/2$ etc.) a 16×16 matrix is obtained. Diagonalization of this energy matrix yields energy levels corresponding to different total spin quantum numbers $S_T=0$, 1, 2, with degeneracies of 2, 3 and 1, respectively. By use of the van Vleck equation, the magnetic susceptibility may be calculated for this model. A fit of the exchange and g value parameters of this model to the magnetic susceptibility data gives the parameters $g=2.11$, $J_a/k=-51$ K, $J_b/k=-33$ K, $TIP=0.00141$ emu/mol, and 5.6% impurity. This fit gives a significant improvement over the simple tetrahedral model and indicates that the distortions from tetrahedral symmetry are significant, and a square model is preferred to the tetrahedral model.

A third model was attempted that consisted of a further reduction of the symmetry from square to rectangular. This model contains three exchange parameters. The spin Hamiltonian in eqn. (4) was used with the restriction $J_{12}=J_{34}=J_a$, $J_{23}=J_{41}=J_b$ and $J_{13}=J_{24}=J_c$. The fit of this model to the data gave the parameters $g=2.04$, $J_a/k=-51$ K, $J_b/k=-23$ K, $J_c=22$ K, $TIP=0.00149$ emu/mol, and 5.8% paramagnetic impurity. The quality of the fit of the 'rectangular' model to the magnetic susceptibility data was marginally better than the square model, however the degree of improvement is not sufficient to warrant the introduction of an additional term, and just two terms J_a and J_b are needed to adequately describe the magnetic behavior of this system.

Conclusions

The reaction of $CuCl_2 \cdot 2H_2O$ with 3(5),4-dimethyl-5(3)-phenylpyrazole in ethanol yields two chloro-bridged copper compounds. In the dinuclear compound **1** the pyrazole ligand is bonding to the copper ion in two different ways. The magnetic and spectroscopic properties of **1** and **2** are consistent with their crystal structures.

Supplementary material

The following material can be obtained from the authors on request.

Table S0 lists additional crystal and diffraction data. Tables S1 and S2 list the anisotropic temperature factors for the non-hydrogen atoms. Tables S3 and S4 list the positional and isotropic temperature factors of the hydrogen atoms. Tables S5, S6, S7 and S8 list bonding distances and angles in **1** and **2**. Tables S0 to S8 amount to a total of 11 pages. Table S9 (31 pages) and S10 (33 pages) list observed and calculated structure factors.

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