



# Synthesis and properties of $[\text{CuLCl}_2]$ and $[\text{CuL}(\text{N}_3)(\text{OClO}_3)] \cdot \text{H}_2\text{O}$ ( $\text{L} = \alpha, \alpha'$ -bis(pyrazolyl)-*m*-xylene): X-ray structure of $[\text{CuLCl}_2]_2$

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## Abstract

Using an *m*-xylyl based dinucleating ligand  $\alpha, \alpha'$ -bis(pyrazolyl)-*m*-xylene ( $\text{L}$ ), providing only one pyrazole nitrogen coordination to each copper(II) centre, two copper(II) complexes  $[\text{CuLCl}_2]$  (**1**) and  $[\text{CuL}(\text{N}_3)(\text{OClO}_3)] \cdot \text{H}_2\text{O}$  (**2**) have been synthesized. Complex **1** has been structurally characterized, revealing that the coordination sphere of each copper(II) ion is distorted square pyramidal. Two pyrazole nitrogens from two different ligands and two chloride ions form the equatorial plane and an additional weak bonding interaction by a chloride ion from an adjacent layer provide axial coordination. The dimeric repeat unit  $[\text{CuLCl}_2]_2$  having a  $\text{Cu}_2\text{Cl}_2$  bridging unit gives rise to an extended network. Based on physicochemical studies, a similar structure has been proposed for **2**; however, in **2** one azide ion and a coordinating perchlorate ion are in the equatorial plane. Magnetic susceptibility measurements (25–300 K) reveal that the two copper(II) centres in each 'pseudo dicopper(II) unit' are weakly antiferromagnetically coupled, with the relevant  $2J$  values of  $\approx -10 \text{ cm}^{-1}$  for **1** and  $\approx -9 \text{ cm}^{-1}$  for **2**. The square pyramidal stereochemistry of the copper(II) centres is revealed by absorption and EPR spectral properties. ©2000 Elsevier Science Ltd All rights reserved.

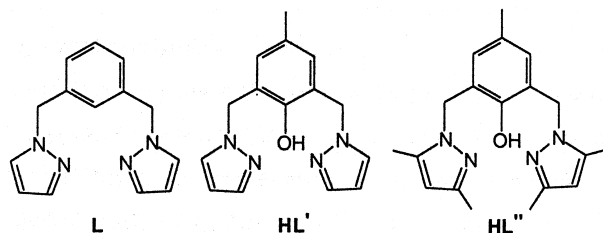
**Keywords:**  $\alpha, \alpha'$ -Bis(pyrazolyl)-*m*-xylene; Copper(II) complexes; X-ray structure; Network structures; Absorption spectroscopy; Electron spin resonance

## 1. Introduction

During the past few years we have investigated [1–13] the coordination chemistry of pyrazole-based chelating ligands. Recently, we have initiated a programme [14–16] to investigate the reactivity properties of binuclear Cu(I) complexes with dioxygen and pinpoint the effect of ligand topology on arene hydroxylation, using *m*-xylyl based ligands capable of providing only two N-coordination to each copper site. As part of this activity, using 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol ( $\text{HL}'$ ) and its 3,5-dimethyl pyrazole derivative ( $\text{HL}''$ ), we have synthesized and characterized two diphenoxo-bridged copper(II) complexes  $[\text{Cu}_2(\text{L}'/\text{L}'')_2(\text{OClO}_3)_2]$  and the complex  $[\text{Cu}_2(\text{L}')_2(\text{OClO}_3)_2]$  has been structurally characterized. The copper(II) centres in these complexes are strongly antiferromagnetically coupled [17].

With the aim of synthesizing and studying the magnetic properties of dichloro- and diazido-bridged copper(II) complexes, similar to diphenoxo-bridged copper(II) complexes  $[\text{Cu}_2(\text{L}'/\text{L}'')_2(\text{OClO}_3)_2]$ , we have investigated the reaction

between  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}/\text{NaN}_3$  and  $\text{L}$ . Here we present the properties of two dimeric copper(II) complexes  $[\text{Cu}^{\text{II}}\text{LCl}_2]_2$  (**1**) and  $[\text{Cu}^{\text{II}}_2(\text{L})_2(\text{N}_3)_2(\text{OClO}_3)_2] \cdot 2\text{H}_2\text{O}$  (**2**). We also present the molecular structure of **1** and comparative spectroscopic and temperature-dependent magnetic properties of **1** and **2**.



## 2. Experimental

### 2.1. Materials

All chemicals and reagents were obtained from commercial sources and used as received, unless otherwise stated. Purification of methanol was achieved by distillation from  $\text{Mg}(\text{OMe})_2$ . DMF was stored over BaO and distilled under

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inert atmosphere. Dichloromethane was washed thoroughly with aqueous solution of  $\text{Na}_2\text{CO}_3$  followed by distilled water before final reflux and distillation over anhydrous  $\text{CaCl}_2$ . 2,6-bis(1-bromomethyl)benzene was prepared following a reported procedure [18].

### 2.2. Synthesis of ligand $\alpha, \alpha'$ -bis(pyrazolyl)-*m*-xylene (L)

The methodology followed to prepare this ligand (which does not require phase-transfer catalysed conditions such as that reported [19]) is adapted from Sorrell et al. [20].

Pyrazole (0.26 g, 3.8 mmol) was added to a suspension of sodium hydride (0.24 g, 10.0 mmol) in DMF (7  $\text{cm}^3$ ), under a dry dinitrogen atmosphere. The mixture was then stirred for 1 h. To this was added 2,6-bis(1-bromomethyl)benzene in DMF (4  $\text{cm}^3$ ) dropwise, anaerobically. The resulting mixture was stirred magnetically for 4 days at 298 K. Addition of water (5  $\text{cm}^3$ ) followed by solvent evaporation under reduced pressure afforded a slurry, to which was added 10% sodium hydroxide solution (5  $\text{cm}^3$ ). The ligand was extracted with  $\text{CH}_2\text{Cl}_2$  and the organic layer washed with water, followed by drying over anhydrous  $\text{Na}_2\text{SO}_4$ . Solvent removal under reduced pressure afforded a thick yellowish-brown oil (yield ca. 90%).  $^1\text{H}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.5 (2H, s, aromatic protons), 7.3 (2H, d, aromatic protons), 7.10–6.73 (4H, m, aromatic protons), 6.30 (2H, t, aromatic protons), 5.30 (4H, s,  $\text{PhCH}_2$ ) [19].

### 2.3. Synthesis of $[\text{Cu}^{\text{II}}\text{LCl}_2]$

A methanolic solution (8  $\text{cm}^3$ ) of L (0.1 g, 0.42 mmol) was added to a solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.072 g, 0.42 mmol) in methanol (4  $\text{cm}^3$ ), under magnetic stirring at 298 K and a green mixture resulted. After 2 h, the solution was filtered to remove some yellow precipitate. On concentration of the filtrate a dark green crystalline material precipitated out. The crystalline product was collected by filtration, washed with methanol and dried in vacuo (yield ca. 64%). Single crystals suitable for X-ray diffraction studies were obtained from the filtrate within a day. *Anal.* Found: C, 45.4; H, 3.7; N, 15.3; Cl, 19.3. Calc. for  $\text{C}_{14}\text{H}_{14}\text{N}_4\text{Cl}_2\text{Cu}$ : C, 45.1; H, 3.8; N, 15.0, Cl 19.1%. Absorption spectrum (DMF solution):  $\lambda_{\text{max}}$  (nm) ( $\epsilon$  ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )) 434 (560), 945 (160).

### 2.4. Synthesis of $[\text{Cu}^{\text{II}}(\text{L})(\text{N}_3)(\text{OClO}_3)] \cdot \text{H}_2\text{O}$

A methanolic solution (8  $\text{cm}^3$ ) of L (0.1 g, 0.42 mmol) was added to a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.156 g, 0.42 mmol) in methanol (4  $\text{cm}^3$ ), followed by solid  $\text{NaN}_3$  (0.027 g, 0.42 mmol). The resulting brownish-green mixture was stirred for 2 h at 298 K. The diethyl ether was added to the filtrate, resulting in the formation of a dark green crystalline material. The product was collected by filtration, washed with methanol and dried in vacuo. Recrystallization from  $\text{MeCN}-(\text{C}_2\text{H}_5)_2\text{O}$  afforded microcrystalline solid (yield ca. 77%).

*Anal.* Found: C, 36.6; H, 3.4; N, 20.6. Calc. for  $\text{C}_{14}\text{H}_{16}\text{N}_7\text{O}_5\text{ClCu}$ : C, 36.4; H, 3.5; N, 21.3%. IR (KBr,  $\text{cm}^{-1}$ , selected peaks): 2080 ( $\nu[\text{N}_3^-]$ ); 1100, 1060, 630, 625 ( $\nu[\text{ClO}_4^-]$ ). Absorption spectrum (DMF solution):  $\lambda_{\text{max}}$  (nm) ( $\epsilon$  ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )) 417 (2200), 655 (290).

### 2.5. Measurements

Elemental analysis was obtained from the Indian Association for the Cultivation of Science, Calcutta. Solution electrical conductivity measurements were carried out with an Elico (Hyderabad, India) type CM-82 T conductivity bridge. Spectroscopic data were obtained using the following instruments: IR spectra, Perkin-Elmer M-1320; electronic spectra, Perkin-Elmer Lambda 2; X-band EPR spectra, Varian E-109 C;  $^1\text{H}$  NMR spectra, Bruker WP-80 (80 MHz) NMR spectrometer. Variable-temperature (25–300 K) solid-state magnetic susceptibility measurements were recorded by the Faraday technique using a locally built magnetometer. The setup [21,22] consists of an electromagnet with constant gradient pole caps (Polytronic Corporation, Mumbai, India), Sartorius M25-D/S balance (Germany), a closed cycle refrigerator and a Lake Shore temperature controller (Cryo Industries, USA). All measurements were made at a fixed main field strength of  $\approx 10$  kG. Susceptibility was corrected for diamagnetic contribution using Pascal constants [23].

### 2.6. Structure determination and refinement

A green crystal of  $[\text{CuLCl}_2]$  (dimensions  $0.2 \times 0.1 \times 0.05$  mm) was used for data collection. Diffracted intensities were collected on an Enraf Nonius CAD4-Mach diffractometer using graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.710$  73 Å). The data were collected at 298 K using  $\theta$ - $2\theta$  scan techniques to a maximum  $2\theta$  value of  $45.0^\circ$ . 5810 reflections were measured of which 2614 were unique and 1376 reflections with  $I > 3\sigma(I)$  were used in the structure refinement. The cell parameters were obtained from least-squares analyses of 25 machine-centred reflections in the range  $16.02 \leq 2\theta \leq 27.18^\circ$ . Three standard reflections were measured at every hour to monitor instrument and crystal stability.

#### 2.6.1. Crystal data

$\text{C}_{14}\text{H}_{14}\text{N}_4\text{Cl}_2\text{Cu}$ ,  $M = 372.55$ , monoclinic, space group  $P2_1/c$ ,  $a = 7.797(1)$ ,  $b = 22.328(7)$ ,  $c = 8.699(9)$  Å,  $\beta = 101.77(5)^\circ$ ,  $V = 1482.8(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.670$  g  $\text{cm}^{-3}$ ,  $\mu = 18.3$   $\text{cm}^{-1}$ ,  $F(000) = 756$ .

Intensity data were corrected for Lorentz and polarization effects; analytical absorption corrections were applied. The structures were solved by the direct method and successive difference Fourier syntheses. All non-H atoms were refined anisotropically and H atoms were included at their calculated positions but not refined. All non-hydrogen atoms were refined with anisotropic thermal parameters. All refinements were performed by full-matrix least-squares procedures on  $F$  where the function minimized was  $\sum w(F_o - F_c)^2$  where

Table 1  
Selected bond distances (Å) and angles (°) for [CuLCl<sub>2</sub>]<sub>2</sub>

Cu–N(2)	2.003(6)	N(2)–Cu–N(3)	162.8(2)
Cu–N(3)	1.987(7)	Cl(1)–Cu–Cl(2)	178.8(1)
Cu–Cl(1)	2.281(2)	Cl(1)–Cu–N(2)	89.5(2)
Cu–Cl(2)	2.325(2)	Cl(1)–Cu–N(3)	90.1(2)
Cu–Cl(2a)	2.778(2)	Cl(2)–Cu–N(2)	91.3(2)
		Cl(2)–Cu–N(3)	89.5(2)

$w = 1/\sigma(F)$ . The final cycle of refinement included 190 variable parameters and converged with  $R = 0.046$ ,  $R_w = 0.036$  ( $I > 3\sigma(I)$ ),  $S = 1.892$ , final difference Fourier synthesis:  $-0.92 \leq \Delta\rho \leq 0.88 \text{ e \AA}^{-3}$ . All calculations were performed using the XTAL3.2 crystallographic software package [24]. Selected bond lengths and angles are given in Table 1.

### 3. Results and discussion

#### 3.1. Synthesis

The ligand L was prepared from the reaction between 2,6-bis(1-bromomethyl)benzene and sodium pyrazolate in DMF. A straightforward reaction between L and CuCl<sub>2</sub>·2H<sub>2</sub>O (1:1 mole ratio) in methanol afforded a dark green complex of composition [CuLCl<sub>2</sub>]. A single-crystal structural analysis (vide infra) revealed its dimeric nature [CuLCl<sub>2</sub>]<sub>2</sub> (**1**). A similar reaction using Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, L and NaN<sub>3</sub> (1:1:1 mole ratio) afforded a brownish-green solid of composition [Cu(L)(N<sub>3</sub>)(OCIO<sub>3</sub>)]·H<sub>2</sub>O. The IR spectrum of this complex clearly demonstrated the presence of azide ion [25], coordinated perchlorate ion [17] and water of crystallization. The electrical conductivity data of complex **1** in DMF ( $\Lambda_M = 50 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) revealed that it behaves as a 1:1 electrolyte (expected range for a 1:1 electrolyte: 65–90  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  [26]), implying that the chloride ions are partially dissociated in solution, i.e. in solution the copper(II) centre is bound by only one chloride ion with additional DMF coordination (vide infra). Complex **2** behaves almost as a 1:2 electrolyte in DMF ( $\Lambda_M = 130 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ; expected range 130–170  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  [26]), implying that both the anions are dissociated in solution. Based on physicochemical properties (vide infra) the azido complex has been proposed to be a dimer [Cu(L)(N<sub>3</sub>)(OCIO<sub>3</sub>)<sub>2</sub>]·2H<sub>2</sub>O (**2**). Microanalytical, IR (for **2**), and absorption spectral behaviour (vide infra) are in conformity with the suggested formulations for **1** and **2**.

#### 3.2. Description of the structure of [CuLCl<sub>2</sub>]<sub>2</sub>

Fig. 1 provides a perspective view of **1**. The dimeric unit sits on a crystallographically imposed inversion centre. Each copper(II) centre is coordinated by two pyrazole nitrogens from two L and two chloride ions. Interestingly, an additional bonding interaction exists at 2.778 Å, provided by a Cl atom of an adjacent layer (Cl(2a)). However, from each CuN<sub>2</sub>Cl<sub>2</sub>

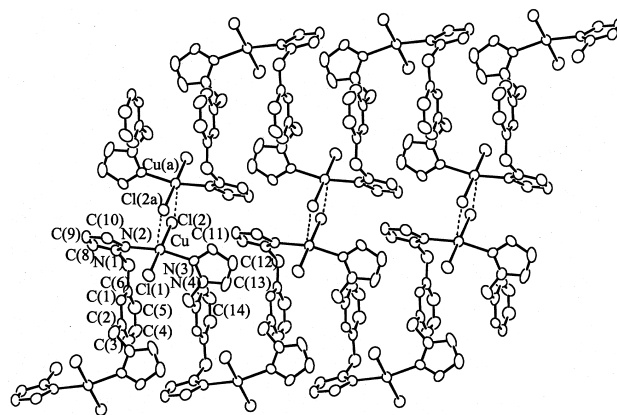


Fig. 1. View of the repeat unit of [CuLCl<sub>2</sub>]<sub>2</sub>. Hydrogen atoms are omitted for clarity. Unlabelled atoms are related to labelled atoms by the crystallographic centre of inversion.

moiety only one chloride ion is engaged in this type of interaction. Hence each copper(II) ion is present in a five-coordinate environment. The Cu···Cu separation between the two successive layers (Cu–Cu(a)) is 3.798(2) Å and within a layer (Cu–Cu') is 8.112(3) Å. The separation between Cl(2) and Cl(2a) is 3.20(6) Å. The angles Cu–Cl(2)–Cu(a) and Cu–Cl(2a)–Cu(a) are 86.78(4) and 75.29(3)°, respectively. The average Cu–N(pyrazole) distance of 1.995 Å is in line with the metric parameters of copper(II) complexes of pyrazole-based chelating ligands [1]. The average Cu–Cl distance in the equatorial plane is 2.303 Å. The N(2)–Cu–N(3) angle is 162.8(2)°, which is appreciably smaller than the expected 180° for a linear arrangement of two pyrazole nitrogens to a copper centre having a perfect square planar geometry. However, the Cl(1)–Cu–Cl(2) angle (178.77(8)°) is close to 180°. From this equatorial plane the Cu(II) ion is displaced towards a chloride ion of an adjacent layer by 0.1357 Å. The Addison structural distortion index parameter  $\tau$  [27] is 0.266. Therefore the coordination environment for each copper(II) centre is best described as distorted square pyramidal.

#### 3.3. Electronic properties

##### 3.3.1. Absorption spectroscopy

In the solid state (dispersed in mineral oil) compound **1** exhibits a peak at ~680 nm along with a low energy shoulder at ~950 nm, typical of square pyramidal geometry around the copper(II) centre [28]. However, in going from solid to solution (DMF), a red shift of the main absorption band was observed, which is known to occur as a result of increased coordination around the metal centre (tetragonal geometry) [13]. Thus this complex exhibits a d–d transition at 945 nm with an additional band at 434 nm. The latter band could be due to Cl<sup>−</sup> → Cu(II) charge transfer. In the solid state, complex **2** also shows a low energy band centred at 705 nm; however, a blue shift has been observed in the DMF solution (655 nm). This result implies that for **2** in the solid state a

'pseudo dimeric structure' exists [13], due to weak coordination of one azide ion of a Cu(II) centre to a nearby Cu(II) centre. We note that the extent of DMF coordination is more in **1** than in **2**. For **2** the band at 417 nm could be assigned as  $N_3^- \rightarrow Cu(II)$  charge-transfer transition.

### 3.3.2. EPR spectroscopy

In the polycrystalline state (77 K), the complex **1** exhibits an axial EPR spectrum with  $g_{\parallel} = 2.171$ ,  $g_{\perp} = 2.066$  and  $A_{\parallel} = 105$  G. The position of the high-field signal ( $g > 2.04$ ) is consistent with a  $d_{x^2-y^2}$  ground state [28]. In frozen DMF solution, superhyperfine interaction with chlorine atoms on the  $g_{\perp}$  component is clearly observable; however, the resolution is not sufficient to extract any meaningful information. Otherwise, the spectral parameters remain almost unaltered with slightly diminished signal intensity. Complex **2** is EPR silent in the solid state both at 300 K and at 77 K. This could be due to concentration broadening caused by magnetic dipolar interaction. However, in frozen DMF solution it exhibits a typical axial spectrum with  $g_{\parallel} = 2.396$ ,  $g_{\perp} = 2.077$  and  $A_{\parallel} = 120$  G.

### 3.4. Magnetic properties

To study (i) whether any magnetic exchange interaction exists between two copper(II) centres in **1** and (ii) to substantiate the proposed structure of **2** (unsymmetrical azide bridging), we investigated the temperature-dependent (25–300 K) magnetic susceptibility behaviour. The  $\mu_{\text{eff}}/Cu$  values at 300 K and at 25 K vary from 1.83 to 1.60  $\mu_B$  for **1** and 1.85 to 1.68  $\mu_B$  for **2**. The magnetic behaviour (Fig. 2) is typical of a very weak antiferromagnetic interaction. If we assume that the observed magnetic curve is intrinsic to the binuclear entity then  $\chi_M$  may be expressed as [15–17]

$$\chi_M = \frac{2N\beta^2 g^2}{kT} [3 + \exp(-2J/kT)]^{-1} + 2N_{\alpha} \quad (1)$$

where the symbols have their usual meanings. Keeping the temperature-independent paramagnetism ( $2N_{\alpha}$ ) fixed at  $120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ , the parameters  $J$  (the singlet–triplet energy gap is expressed in terms of  $2J$ ) and  $g$  were determined by looking for the minimum of  $R = \sum(\chi_M^{\text{obsd}} - \chi_M^{\text{calc}})^2 / \sum(\chi_M^{\text{obsd}})^2$ . Non-linear regression analysis of the data using Eq. (1) gave good data fits (Fig. 2):  $J = -4.9 \text{ cm}^{-1}$ ,  $g = 2.00$ ,  $R = 1.45 \times 10^{-6}$  for **1** and  $J = -4.4 \text{ cm}^{-1}$ ,  $g = 2.103$ ,  $R = 1.60 \times 10^{-6}$  for **2**. Inclusion of a corrective term for non-coupled copper(II) impurity gave no improvement in the fit.

Incorporation of a corrective term ( $\theta$ ) for interdimer interactions [29] in **1** and hence using Eq. (2),

$$\chi_M = \frac{2N\beta^2 g^2}{k(T-\theta)} [3 + \exp(-2J/kT)]^{-1} + 2N_{\alpha} \quad (2)$$

a similar data analysis gave rise to the following parameters:  $J = -4.67 \text{ cm}^{-1}$ ,  $g = 1.977$  ( $2N_{\alpha} = 120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ ,

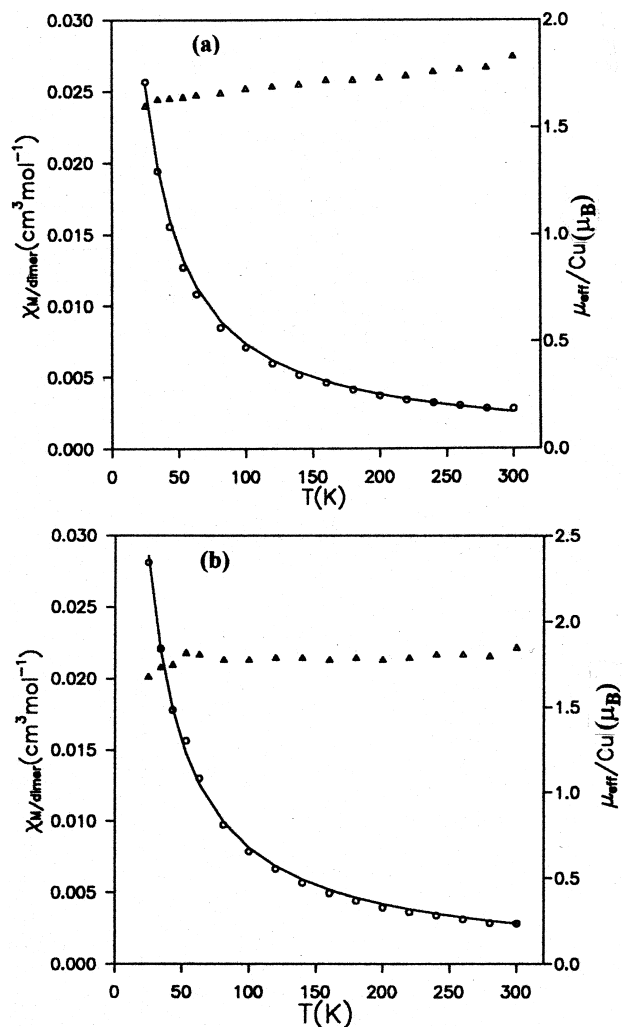


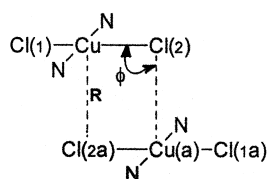
Fig. 2. Plot of magnetic susceptibility (left scale) per dimer and effective magnetic moment (right scale) per metal vs. temperature for polycrystalline samples of (a)  $[CuLCl_2]_2$  (**1**) and (b)  $[CuL(N_3)(OCIO_3)]_2 \cdot 2H_2O$  (**2**). The solid line represents theoretical fits using Eq. (1), as described in the text.

fixed),  $\theta = -0.055$  K, and  $R$  is then equal to  $9.37 \times 10^{-7}$ , which corresponds to an excellent agreement between observed and calculated magnetic data. The very small  $\theta$  value, however, indicates that intermolecular exchange effects are essentially non-existent. The observed behaviour is again pointing towards the weak nature of antiferromagnetic coupling between two copper centres.

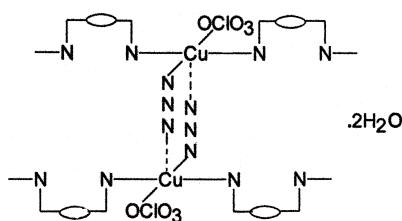
In the solid state of compound **1** (Fig. 1) one Cl atom at each Cu site occupies the fifth coordination of the Cu centre of an adjacent layer, resulting in a long intermolecular  $Cu \cdots Cl$  contact. However, the optimized  $2J$  parameter for this compound does not follow the empirical Hodgson correlation between structural parameter  $\phi/R$  and the coupling constant  $J$  [30,31]. Here  $\phi$  is the  $Cu-Cl(2)-Cu(a)$  bridging angle and  $R$  is the longer  $Cu-Cl(2a)$  separation. The dihedral angle between the planes  $Cu-Cl(2)-Cu(a)$  and  $Cu-Cl(2a)-Cu(a)$  is  $87.92^\circ$ , revealing that the four-membered ring  $Cu-$



Cl(2)–Cu(a)–Cl(2a) is non-planar. This could be the reason behind its deviation from this empirical correlation.



With asymmetric end-to-end azido bridges, with a short and a long Cu–N (azide) bond, it is well documented that the magnetic interaction is negligible when the geometry around the copper (II) ion is square pyramidal [32,33]. The observed magnetic behaviour of **2** is in line with this bonding interaction. In fact, in **2** the geometry around the copper centre is square-based pyramidal (vide absorption spectra). Two nitrogen atoms from two ligands are bonded to the Cu(II) ion; one oxygen atom from a perchlorate ion and a bridging azide ion are coordinated in the basal plane. The two copper(II) atoms are linked via one end-to-end bridging azide. The situation is very similar to what we have observed in **1**. Thus the structure of compound **2** can be proposed as shown below.



#### 4. Conclusions

Using an *m*-xylyl based pyrazole ligand L two dimeric copper(II) complexes  $[\text{CuLCl}_2]_2$  and  $[\text{CuL}(\text{N}_3)(\text{OClO}_3)]_2 \cdot 2\text{H}_2\text{O}$  have been synthesized. The presence of a dimeric structure containing a  $\{\text{Cu}_2\text{Cl}_2\}^{2+}$  structural unit, with an interacting  $\text{Cl}^-$  ion from an adjacent layer affording a network structure, is clearly established by a crystal structural analysis of one such complex **1**. The structure reveals that two L ligands are not capable of accommodating two copper centres at a distance capable of providing a discrete  $\text{Cu}_2\text{L}_2\text{Cl}_2$  bridged structure. The X-ray structure of the dicopper(I) complex of the 3,5-dimethylpyrazole derivative of L behaved similarly (each copper(I) centre had two pyrazole coordination from two ligands with a  $\text{Cu}\cdots\text{Cu}$  separation of 6.350 Å) [34]. Temperature-dependent magnetic measurements reveal very similar structures for **1** and **2**, exhibiting weak antiferromagnetic exchange coupling.

#### Supplementary data

Full tables of bond lengths and angles, tables of non-hydrogen and hydrogen atomic coordinates, anisotropic thermal

parameters for non-hydrogen atoms as well as hydrogen atom parameters are available as supplementary material from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), on request (CCDC deposition number 129652).

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