Synthesis, Crystal Structure and Magnetic Properties of a Dinuclear Copper(II) Complex with 1,1′-(4-Methylpyrazole-3,5-diyl)diacetaldehyde Dioxime. Evidence for both Classical and Zwitterion Structures†

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The reaction of 1,1′-(4-methylpyrazole-3,5-diyl)diacetaldehyde dioxime (H_3L) with $CuCl_2{\cdot}2H_2O$ produces two different isomeric dinuclear co-ordination compounds according to the temperature. Analytical results indicated the same composition $[Cu_2(H_2L)_2Cl_2]{\cdot}2H_2O$. One isomer (**1**) crystallized at 15 °C in the monoclinic space group $P2_1/a$ with $a = 11.490(5)$, $b = 16.287(14)$, $c = 6.253(4)$ Å, $\beta = 97.78(4)°$ and $Z = 2$. Refinement of 1983 reflections with $I > 3\sigma(I)$ gave a final $R = 0.025$ ($R' = 0.027$). The second isomer (**2**) crystallized at 25 °C in the triclinic system, space group $P\bar{1}$ and $a = 8.520(15)$, $b = 8.607(18)$, $c = 8.671(14)$, $\alpha = 75.27(15)$, $\beta = 69.96(17)$, $\gamma = 76.66(15)°$ and $Z = 1$; $R = 0.027$ ($R' = 0.031$) for 2964 significant reflections. The molecular structures of the two isomers are closely related; the centrosymmetric dinuclear $[Cu_2(H_2L)_2Cl_2]$ unit is almost planar. Each copper atom is five-co-ordinated in a distorted square-based pyramid involving an N_3O in-plane donor set, with the oxygen atom of the zwitterionic form of the oxime group, the nitrogen atom of the classical form of the oxime group and two nitrogen atoms of the pyrazole heterocycle; the axial ligand is a chloride ion. The two water molecules are linked by hydrogen bonds to the oxime function. In **1** the bonding is $O{-}H \cdots OH_2$ (classical structure), in **2** it is $N{-}H \cdots OH_2$ (zwitterionic structure). In the IR spectrum the ν(N–H) vibration is observed only for compound **1**. Magnetic susceptibility measurements performed from 5 to 300 K provides evidence of the existence of strong antiferromagnetic exchange interactions between the copper(II) ions ($J = -159$ cm^{-1} for isomer **2**). These results are discussed on the basis of the structural features.

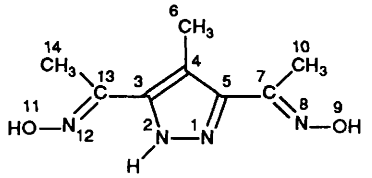
Dinuclear compounds of transition metals form a field of continuing research interest. The best known examples are those of copper(II). Useful correlations between magnetic spin exchanges and structural properties have been established.[1–5] The design of ligands capable of binding two metal ions in close proximity is, therefore, an important subject in this field and numerous polyfunctional ligands have been used for this purpose. Among them, polyaza derivatives in which the N_2 diazine fragment is incorporated into rigid heterocyclic structures derived from pyrazole,[6–12] triazole,[13–15] phthalazine[16–28] and pyridazine[26–32] afford an interesting field of investigations.

In this work we report two isomeric copper(II) complexes built from a dinucleating functionalized pyrazole derivative, namely 1,1′-(4-methylpyrazole-3,5-diyl)diacetaldehyde dioxime (H_3L). The two isomers are similar and differ only in the hydrogen bonding. The molecular structures reveal the nature of the co-ordination of the metal centre in the dimeric units and allow its correlation with the intramolecular magnetic interaction.

Experimental

Synthesis.—The ligand H_3L was synthesised as previously described.[33]

$[Cu_2(H_2L)_2Cl_2]{\cdot}2H_2O$ **1** *and* **2**. A solution of copper(II) chloride dihydrate (341 mg, 2 mmol) in water (100 cm^3) was added to a solution of H_3L (392 mg, 2 mmol) in water (400 cm^3). It became slowly cloudy and after 3 h was filtered to remove any precipitated material. A small amount (< 1 mg) of green microcrystalline powder, not suitable for X-ray diffraction study, was removed. The resulting clear solution was divided into several batches which were allowed to stand at different temperatures. In one experiment at 15 °C a very few brown crystals of isomer **1** deposited within 2 months. They were filtered off, washed with water and air dried. At 25 °C, dark green crystals of isomer **2** were formed after 2 months. The obtention of isomer **1** is not easily repeatable (Found for **1**: C, 30.75; H, 4.25; Cl, 11.20; Cu, 20.25; N, 17.90; O, 15.30. Found for **2**: C, 30.75; H, 4.20; Cl, 11.25; Cu, 20.20; N, 17.70; O, 15.25. Calc. for $C_8H_{13}ClCuN_4O_3$: C, 30.75; H, 4.20; Cl, 11.35; Cu, 20.35; N, 17.95; O, 15.40%).



Crystal Structure Determinations.—Pertinent data for the crystals used and the measurement of diffraction intensities are summarized in Table 1. Intensity data for isomer **1** were collected on a Philips PW 1100 diffractometer, those for isomer **2** on an Enraf-Nonius CAD-4 diffractometer. Lorentz and polarization factors were applied for the two compounds but no

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Summary of crystal data, intensity measurement, and structure refinement[a]

	1	2
Crystal size/mm	0.094 × 0.100 × 0.350	0.095 × 0.110 × 0.273
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
a/Å	11.490(5)	8.520(15)
b/Å	16.287(14)	8.607(18)
c/Å	6.253(4)	8.671(14)
α/°	90	75.27(15)
β/°	97.78(4)	69.96(17)
γ/°	90	76.66(15)
U/Å^3	1159.4(14)	570.5(20)
Z	2	1
D_c/g cm^{-3}	1.79	1.82
F(000)	636	318
μ/cm^{-1}	21.9	22.3
2θ/°	4–54	4–60
No. of measured reflections	2858	3287
No. of unique reflections [$I > 3\sigma(I)$]	1983	2964
Maximum shift/σ for non-H atoms	0.32	0.14
Maximum shift/σ for H atoms	0.86	0.21
Maximum and minimum Δρ/e Å^{-3}	−0.11, 0.14	−0.37, 0.31
R, R'[b]	0.025, 0.027	0.027, 0.031

[a] Details in common: formula $C_{16}H_{26}Cl_2Cu_2N_8O_6$; $M = 624.3$; Mo-Kα radiation (λ = 0.7107 Å); 193 parameters. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, where $w = 1$.

Table 2 Fractional coordinates (× 10^5 for Cu, Cl, × 10^4 for O, N, C and × 10^3 for H atoms) for compound **1**

Atom	x	y	z
Cu	62 790(3)	−2 258(2)	−15 844(5)
N(1)	6 125(2)	507(1)	862(4)
N(2)	5 303(2)	647(1)	2 127(3)
C(3)	5 721(2)	1 211(2)	3 636(4)
C(4)	6 821(2)	1 453(2)	3 289(4)
C(5)	7 074(2)	981(2)	1 535(4)
C(6)	7 659(3)	2 081(2)	4 454(6)
C(7)	8 058(2)	889(2)	280(4)
N(8)	7 817(2)	389(2)	−1 309(4)
O(9)	8 697(2)	256(2)	−2 575(4)
C(10)	9 199(3)	1 332(2)	816(6)
O(11)	3 429(2)	558(1)	4 404(3)
N(12)	4 047(2)	1 122(2)	5 589(4)
C(13)	5 043(2)	1 448(2)	5 334(4)
C(14)	5 468(3)	2 089(2)	6 978(6)
Cl	22 205(6)	65 167(5)	4 179(11)
O$_w$(15)	9 045(3)	−689(2)	−5 965(5)
HC(6)	799(4)	233(3)	357(7)
H′C(6)	827(4)	187(3)	537(7)
H″C(6)	742(4)	231(3)	549(8)
HO(9)	835(4)	−8(3)	−359(7)
HC(10)	969(4)	120(3)	−1(7)
H′C(10)	905(4)	194(3)	68(7)
H″C(10)	949(4)	129(3)	220(7)
HN(12)	366(3)	128(2)	667(6)
HC(14)	496(4)	215(3)	800(7)
H′C(14)	555(4)	260(3)	623(7)
H″C(14)	622(4)	196(3)	770(7)
HO$_w$(15)	860(5)	−88(3)	−700(7)
H′O$_w$(15)	961(5)	−64(4)	−649(9)

Table 3 Fractional coordinates (× 10^5 for Cu, Cl, × 10^4 for O, N, C and × 10^3 for H atoms) for compound **2**

Atom	x	y	z
Cu	66 503(3)	54 195(3)	−21 320(3)
N(1)	5 947(2)	6 412(2)	−148(2)
N(2)	4 931(2)	6 102(2)	1 399(2)
C(3)	5 041(3)	7 160(2)	2 272(3)
C(4)	6 203(3)	8 204(2)	1 212(3)
C(5)	6 741(3)	7 667(2)	−301(3)
C(6)	6 775(4)	9 548(3)	1 595(4)
C(7)	7 919(3)	8 146(2)	−1 958(3)
N(8)	7 945(2)	7 307(2)	−3 003(2)
O(9)	9 037(3)	7 676(2)	−4 602(2)
C(10)	8 982(4)	9 430(3)	−2 357(4)
O(11)	2 943(2)	4 695(2)	4 427(2)
N(12)	3 140(3)	5 979(2)	4 887(2)
C(13)	4 051(3)	7 094(3)	4 011(3)
C(14)	4 024(4)	8 339(3)	4 965(3)
Cl	91 803(8)	33 147(7)	−16 421(9)
O$_w$(15)	1 379(3)	5 844(3)	8 118(2)
HC(6)	767(5)	984(5)	92(5)
H′C(6)	588(5)	1 027(5)	205(5)
H″C(6)	747(5)	909(5)	232(5)
HO(9)	903(5)	714(5)	−507(5)
HC(10)	970(5)	913(5)	−162(5)
H′C(10)	825(5)	1 041(5)	−215(5)
H″C(10)	981(5)	943(5)	−328(5)
HN(12)	249(3)	592(4)	600(4)
HC(14)	334(5)	812(5)	601(5)
H′C(14)	516(5)	825(5)	499(5)
H″C(14)	354(5)	939(5)	454(5)
HO$_w$(15)	85(6)	529(5)	828(6)
H′O$_w$(15)	135(5)	603(5)	895(5)

absorption correction. The structures were solved by heavy-atom methods and refined by full-matrix least squares using a local modification of the program SFLS-5.[34] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic thermal parameters fixed to values of the equivalent isotropic coefficients of the atoms to which they are attached. Scattering factors were taken from ref. 35.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Spectra and Magnetic Measurements.—Routine IR spectra were recorded on a Perkin Elmer 1310 instrument using KBr pellets (4000–600 cm^{-1}).

Magnetic susceptibility was measured with a Faraday-type magnetometer (MANICS) equipped with a continuous-flow cryostat. The data were corrected for underlying diamagnetism and temperature-independent paramagnetism (60 × 10^{-6} cm^3 mol^{-1} per mol Cu). Data were corrected for diamagnetism of the ligands estimated from Pascal constants.[36] They were not corrected for the presence of any paramagnetic impurity.

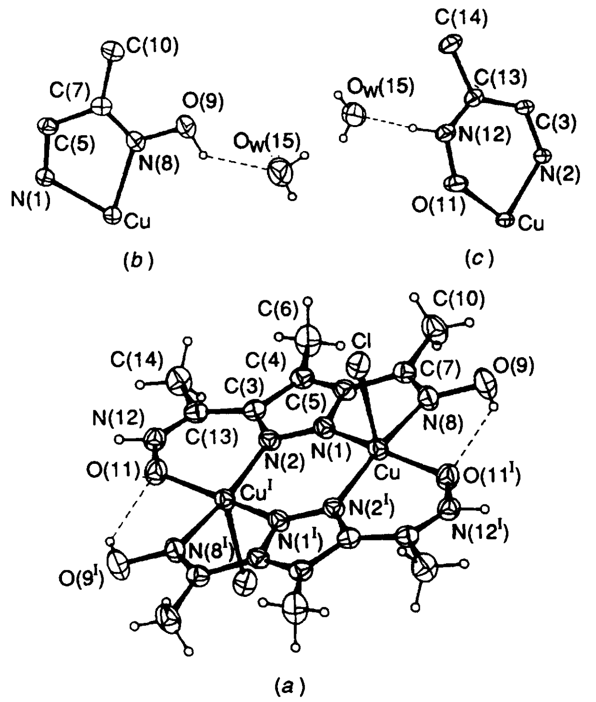

Fig. 1 Perspective view of the dinuclear complex $[Cu_2(H_2L)_2Cl_2]$ (*a*), the water molecule in isomer **1** (*b*) and in **2** (*c*)

Table 4 Selected bond distances (Å) with estimated standard deviations (e.s.d.s) in parentheses for compounds **1** and **2***

	1	**2**
Cu···Cu^{I}	3.832(1)	3.815(1)
Cu–N(1)	1.967(2)	1.963(2)
Cu–N(8)	2.018(3)	2.015(2)
Cu–N(2^{I})	1.929(2)	1.933(2)
Cu–O(11^{I})	1.917(2)	1.924(2)
N(1)–N(2)	1.331(3)	1.322(2)
N(2)–C(3)	1.357(3)	1.360(3)
C(3)–C(4)	1.413(3)	1.414(3)
C(4)–C(6)	1.495(4)	1.501(4)
C(4)–C(5)	1.388(4)	1.394(4)
C(5)–C(7)	1.469(4)	1.464(4)
C(7)–C(10)	1.494(4)	1.488(4)
C(7)–N(8)	1.285(4)	1.286(3)
N(8)–O(9)	1.385(4)	1.385(2)
C(3)–C(13)	1.452(4)	1.448(3)
C(13)–C(14)	1.499(4)	1.503(4)
C(13)–N(12)	1.291(4)	1.292(3)
N(12)–O(11)	1.324(3)	1.328(3)
Cu–Cl	2.605(1)	2.558(1)

* Symmetry operation I: translation $\vec{a}$ for compound **1** and $\vec{a} + \vec{b}$ for **2**.

Table 5 Selected bond angles (°) with e.s.d.s in parentheses for compounds **1** and **2**

	1	**2**
N(1)–Cu–N(2^{I})	99.8(2)	100.0(2)
N(2^{I})–Cu–O(11^{I})	90.9(2)	90.6(1)
O(11^{I})–Cu–N(8)	87.6(2)	87.3(1)
N(8)–Cu–N(1)	78.6(2)	78.7(1)
Cu–N(8)–O(9)	125.0(4)	125.5(2)
Cu–N(8)–C(7)	118.3(3)	118.2(3)
O(9)–N(8)–C(7)	116.4(5)	115.8(4)
N(8)–C(7)–C(10)	124.7(6)	124.5(6)
N(8)–C(7)–C(5)	112.1(4)	112.1(4)
C(10)–C(7)–C(5)	123.1(5)	123.4(5)
C(7)–C(5)–N(1)	114.9(4)	115.1(3)
C(7)–C(5)–C(4)	135.2(7)	135.1(6)
N(1)–C(5)–C(4)	109.9(4)	109.8(4)
C(5)–C(4)–C(6)	127.0(6)	127.3(6)
C(5)–C(4)–C(3)	103.5(4)	103.3(3)
C(3)–C(4)–C(6)	129.5(6)	129.4(6)
N(1)–N(2)–C(3)	108.4(4)	108.9(3)
N(1)–N(2)–Cu^{I}	124.2(6)	123.6(2)
C(3)–N(2)–Cu^{I}	126.8(4)	127.0(3)
C(5)–N(1)–Cu	115.7(3)	115.4(3)
C(5)–N(1)–N(2)	108.9(4)	109.1(3)
N(2)–N(1)–Cu	135.4(4)	135.6(3)
C(4)–C(3)–N(2)	109.3(4)	109.1(3)
C(4)–C(3)–C(13)	129.7(6)	130.3(5)
N(2)–C(3)–C(13)	120.9(5)	120.5(4)
C(14)–C(13)–C(3)	122.0(6)	121.8(5)
C(3)–C(13)–N(12)	123.6(5)	124.2(4)
C(14)–C(13)–N(12)	114.4(5)	114.0(5)
C(13)–N(12)–O(11)	129.3(6)	128.5(5)
N(12)–O(11)–Cu^{I}	124.3(3)	123.1(3)
Cl–Cu–N(1)	101.0(1)	100.9(1)
Cl–Cu–N(8)	96.3(1)	94.6(1)
Cl–Cu–O(11^{I})	95.9(1)	97.3(1)
Cl–Cu–N(2^{I})	96.8(1)	95.9(1)

Results and Discussion

Structures of the Complexes.—The atomic parameters are given in Tables 2 (isomer **1**) and 3 (isomer **2**). An ORTEP[37] drawing of complex **1** showing the atom numbering scheme is given in Fig. 1. The drawing for **2** is practically superimposable. Selected bond distances and angles for **1** and **2** are listed in Tables 4 and 5 respectively. Intra- and inter-molecular hydrogen bonds are in Table 6.

In the $[Cu_2(H_2L)_2]^{2+}$ system the copper atoms are linked by two pyrazolate groups *via* their N(1)–N(2) bridging mode. The equatorial co-ordination is completed by the nitrogen atom N(8) of the classical form and the oxygen O(11) of the zwitterion form of the oxime groups. There is an inversion centre at the centre of the cation.

The copper atom forms a five-membered chelate ring [Cu–N(1)–C(5)–C(7)–N(8)] with the H_2L^- anion when the co-ordination involves the nitrogen atom of the oxime group [Fig. 1(*b*)], a six-membered chelate ring [Cu–N(2)–C(3)–C(13)–N(12)–O(11)] when the oxygen atom of the zwitterion form is the co-ordinating atom [Fig. 1(*c*)]. The role of the two oxime functions of the ligand (H_3L) is therefore quite different. The former function is present in the classical structure $R_2C{=}N{-}OH$, the latter with the zwitterion structure $R_2C{=}^{+}NH{-}O^{-}$.[38,39] The co-ordination mode and the location of hydrogen atoms allow us to state the actual structure of the oximes in our compounds: astonishingly the two structures are simultaneously present to permit the two ligand molecules to be in favourable geometrical position so as to co-ordinate two copper atoms.

Within the pyrazolate Cu_2N_4 chelate ring the two Cu–N–N angles are very different; this illustrates beautifully the consequences of the differently sized chelate rings at each end of the molecule. The angle Cu–N(1)–N(2) (135°) is equal to the values calculated for the complex $[\{Cu(\mu\text{-bpt})(CF_3SO_3)(H_2O)\}_2]$[14] [Hbpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazole] in which the N atom is shared by a Cu_2N_4 ring, a triazolate and a terminal five-membered Cu–N–C–C–N ring; on the other hand, the Cu^{I}–N(2)–N(1) angle is close to that obtained when the N atom is involved in a Cu_2N_4 ring, a pyridazine (six-membered ring) and a terminal five-membered ring.[32] The mean planes of the N_3O and Cu_2N_4 systems are not rigorously coplanar, the angles between them being 7.9 and 7.8° for compounds **1** and **2** respectively. The copper(II) ion is co-ordinated in equatorial position by two tetradentate ligands and in axial position by one Cl^- ion, *i.e.* the co-ordination is 4 + 1. It is displaced from the plane of the equatorial chelating atoms [N(1), N(2^{I}), N(8) and O(11^{I})] toward the Cl^- ion by 0.231(1) Å in compound **1** and by 0.246(1) Å in **2**. In the dimeric unit the bond distances

Table 6 Intra- and inter-molecular hydrogen bonds with e.s.d.s in parentheses *

X–HX ··· X′	X–H/Å	H ··· X/Å	X ··· X′/Å	X–H ··· X′/°
Compound **1**				
O(9)–HO(9) ··· O(11$^{\mathrm{I}}$)	0.89(5)	2.18(5)	2.877(3)	134(7)
O(9)–HO(9) ··· O_w(15)	0.89(5)	2.04(5)	2.693(4)	130(6)
O_w(15)–HO_w(15) ··· $Cl_{00\bar{1}}$	0.83(5)	2.35(5)	3.169(3)	172(20)
O_w(15)–H′O_w(15) ··· O(9$^{\mathrm{I}}$)$_{20\bar{1}}$	0.77(6)	2.20(6)	2.950(4)	166(21)
N(12)–HN(12) ··· Cl^{I}_{101}	0.90(4)	2.23(4)	3.124(3)	172(17)
Compound **2**				
O(9)–HO(9) ··· O(11$^{\mathrm{I}}$)$_{110}$	0.69(5)	2.40(5)	2.879(3)	128(7)
N(12)–HN(12) ··· O_w(15)	0.93(3)	1.75(3)	2.674(2)	176(18)
O_w(15)–HO_w(15) ··· $Cl_{\bar{1}01}$	0.69(5)	2.43(6)	3.111(3)	170(23)
O_w(15)–H′O_w(15) ··· Cl^{I}_{111}	0.77(5)	2.40(5)	3.171(2)	172(21)

* X_{pqr} from symmetry operation translation $p\vec{a} + q\vec{b} + r\vec{c}$.

and angles are not significantly different, except for the Cu–Cl distances which differ by more than 3σ. Consequently, the two structures represent distortion isomers due to the plasticity effect.[40] In both compounds an intramolecular hydrogen bond is established between the oxygen atom O(9) of the classical form and that [O(11)] of the zwitterion form through the hydrogen atom HO(9) [Fig. 1(*a*)]. The cohesion of the crystal is maintained by intermolecular hydrogen bonds (Table 6). The difference between the two structures lies essentially in the type of hydrogen bonds established by the water molecule [Fig. 1(*b*) and 1(*c*)]. In the $[Cu_2(H_2L)_2Cl_2]\cdot 2H_2O$ complexes the water molecule is linked to the dimer $[Cu_2(H_2L)_2Cl_2]$ by a hydrogen bond with the hydrogen atom HO(9) of the classical oxime function in isomer **1** and with the hydrogen atom HN(12) of the zwitterion form in isomer **2**. In isomer **2** the hydrogen atom HO(9) is only involved in the intramolecular bond, while in **1** it is involved in one intra- and one inter-molecular bond; however the intramolecular hydrogen bond does not seem stronger in isomer **2**. In the two compounds the water molecule links three different dimeric units, one by the previously described hydrogen bond and the other two by hydrogen bonds involving water hydrogen atoms (Table 6).

Infrared Spectra.—The infrared spectra of compounds **1** and **2** are very similar in the range 4000–600 cm^{-1} except for a very strong sharp band observed at 3600 cm^{-1} for **1**. This vibration can be ascribed to ν(N–H) of the zwitterionic co-ordinated oxime group. Indeed the structure of isomer **2** shows the participation of the hydrogen atom of the zwitterionic form in a hydrogen bond involving one water molecule [Fig. 1(*c*)]. In contrast, the hydrogen atom of the zwitterionic structure in isomer **1** is not involved in hydrogen bonding [Fig. 1(*b*)] and the infrared spectrum therefore exhibits the free ν(N–H) stretching vibration at 3600 cm^{-1}. To our knowledge no data have been published so far for comparison.

Magnetic Properties.—Variable-temperature magnetic susceptibility measurements were performed on a powdered sample of complex **2** up to 300 K. The results are displayed in Fig. 2. Unfortunately compound **1** was not obtained in sufficient amount for such measurements. The shape of the susceptibility plot is typical of an antiferromagnetically coupled dinuclear species with the maximum of susceptibility occurring just above room temperature (at about 320 K). The best fit of the experimental data was obtained using equation (1) where $2J$ is

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

the singlet–triplet energy gap related to the intradimer interaction. The other symbols have their usual meaning[15,41] The exchange integral J was found to be -159 cm^{-1} and g = 2.1; the fitting coefficient $R = \Sigma(\chi_{\text{exptl}} - \chi_{\text{calc}})^2/\Sigma\chi^2_{\text{exptl}}$ was 0.001 56.

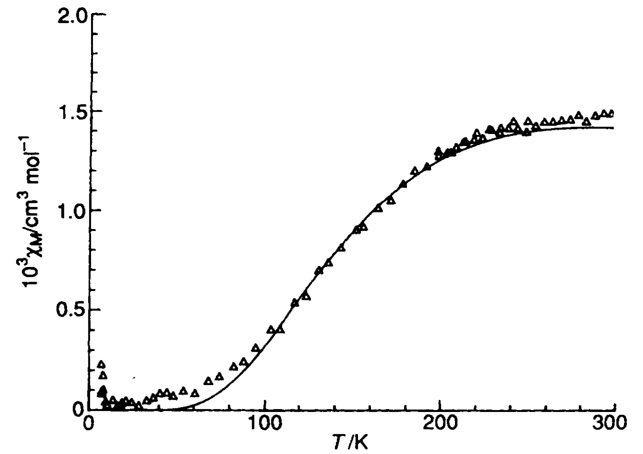

Fig. 2 Plot of molar susceptibility *versus* T for complex **2**. The line drawn represents the theoretical values

As previously reported,[42] for interacting copper(II) ions bridged by extended ligands, the ferromagnetic component is expected to be very small and only the antiferromagnetic contribution is significant. The latter is proportional to the square of the overlap intergral of the magnetic orbitals. In the present compound the copper(II) ions adopt a 4 + 1 co-ordination with three nitrogen and one oxygen atom as nearest neighbours in the basal plane. In such an environment, the most destabilized orbital occupied by the unpaired electron of copper(II) is the d_{xy} orbital.[5] It points from the metal toward the four nearest neighbours in an antibonding fashion. Considering the large intradimer copper–copper distance, a superexchange pathway is likely to be responsible for the strong antiferromagnetic interaction, although the Cu–N(1)–N(2), N(1)–Cu–N(2$^{\mathrm{I}}$) and N(1)–Cu–N(8$^{\mathrm{I}}$) angles deviate strongly from ideal values. Nevertheless the magnitude of the J value indicates that there is a strong transfer *via* the pyrazole species. Accordingly the exchange is mainly determined by the σ and η superexchange pathways.[22,43] The copper atom is displaced from the N_3O basal plane toward the apical chloride by 0.231(1) Å; however, as reported earlier, that displacement has almost no effect on the magnitude of the interaction.[5] A quantitative discussion on the magnetostructural correlations would be questionable in the present case due to the lack of information on dinuclear copper(II) complexes involving two bridging pyrazole groups.

The majority of the dinuclear copper complexes for which antiferromagnetic exchange has been observed have one N_2

bridge plus at least one other bridging group including hydroxide, halides and bidentate anions such as nitrate, sulfate or iodate. In some cases, magnetostructural correlations have been established. For example, in hydroxo-bridged diazine complexes, a linear relationship was found between J and the Cu–O(H)–Cu hydroxide bridge angle for a number of systems involving six-membered chelate rings;[23] on the other hand, no such correlation can be established for systems involving five-membered chelate rings.[23] Examples of dinuclear copper(II) complexes involving just two in-plane diazine bridges are rare: in a series of complexes of the ligands μ-3,5-bis(pyridin-2-yl)-1,2,4-triazole[14] and μ-4-amino-3,5-bis(aminomethyl)-4*H*-1,2,4-triazole[15] with Cu···Cu distances of about 4.07 Å, exchange integrals J were observed in the range -102 to -118 cm^{-1}; in the first and only example of a di-μ-pyrazolato-dicopper complex a larger exchange integral was obtained (-214 cm^{-1})[12] and strong exchange was observed with two pyridazine groups bridging two six-co-ordinate copper centres ($J \approx -270$ cm^{-1} in complexes of the ligand μ-pyridazine-3,6-dicarbaldehyde dioxime[32]). All these systems involved five- or six-membered chelate rings; our compounds are the first examples of dinuclear complexes containing both five- and six-membered chelate rings. Studies of other copper complexes with the ligand H$_3$L are planned.

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