Dicopper(II) Complexes of Novel Polyfunctional Pyridazines: Crystal Structure and Magnetic Properties of Bis[μ-pyridazine-3,6-dicarbaldehyde dioximato(1−)-$\kappa N^1,N'$:N^2,N'']-bis[aqua(perchlorato-κO)copper(II)]†

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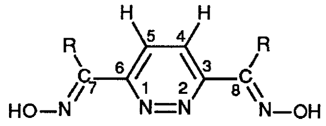
Two novel pyridazine ligands with 3,6-CR=NOH (R = H, H_2L^1; Ph, H_2L^2) oxime side chains were synthesised. The related copper(II) dinuclear complexes $[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2]$ **1** and $[Cu_2(HL^2)_2(ClO_4)_2(MeOH)_n]$ **2** were obtained subsequently. The crystal structure of **1** was determined: space group $P2_1/n$, $a = 12.031(6)$, $b = 9.517(4)$, $c = 9.973(5)$ Å, $\beta = 100.16(4)°$ and $Z = 2$. The copper(II) ions of the binuclear unit are bridged by the two diazine fragments of the two essentially planar tetradentate ligands with the oxime nitrogen atoms completing the equatorial co-ordination. Two intra-complex hydrogen bridges link the terminal oximato moieties to give dinucleating macrocyclic complexes. In complexes **1** and **2** the copper(II) is in a classical 4 + 2 environment. The magnetic properties of those compounds revealed a spin-singlet ground state in each case. The singlet–triplet energy gaps were found to be −536(2) for **1** and −545(4) cm^{-1} for **2**. The low-lying states of the complexes are discussed in relation to the nearly planar structure of the macrocyclic complexes.

Polyfunctional ligands derived from pyrazole,[1–3] triazole,[4–6] phthalazine[7–11] and pyridazine[12,13] form transition-metal complexes in which the metals are brought into close proximity because of the presence of the N_2 diazine fragments in these systems. Antiferromagnetic exchange between the adjacent metal centres has been demonstrated in some of these complexes.[4–13] The best known examples are dinuclear copper(II) compounds. Useful correlations between the singlet–triplet (S–T) splitting and structural parameters have been made.[14,15] Another interesting aspect of these compounds is their potential use as models for biological dimetallic sites.[4–6,16–18] In addition, conductive molecular crystals based on metallomacrocyclic complexes have been reported[19,20] and the size of the substituents in the side chain of the macrocycle could be partly responsible for the increasing stacking distance in the crystal structure.

In an effort to obtain novel dinuclear planar macrocyclic complexes with an organic backbone stable against chemical and electrochemical oxidation and without a bulky side chain substituent, we have synthesised pyridazines, functionalized with dioxime side chains. The macrocyclic system is obtained through intra hydrogen bonds between two ligands by a template effect. An advantage of the macrocyclic system is that variation of ring size and other geometric parameters should enable systematic control of the disposition of the metal ions. The syntheses and crystal-structure determination of dicopper(II) complexes of novel pyridazines with 3,6-side chains have been undertaken to establish the nature of the co-ordination and its consequence upon the singlet–triplet splitting.



	R
H_2L^1	H
H_2L^2	Ph

Experimental

Syntheses.—H_2L^1. 3,6-Bis(hydroxymethyl)pyridazine (0.05 mol), prepared from 2,5-bis(hydroxymethyl)furan,[21] was smoothly oxidized[22] to the corresponding dialdehyde at −60 °C (argon atmosphere) by a mixture of oxalyl chloride (0.11 mol) and dimethyl sulphoxide (0.22 mol) in dichloromethane. After completion of the reaction with triethylamine (0.1 mol) the reaction mixture was allowed to return to room temperature, then extracted with water. The organic layer was separated. The ligand H_2L^1 precipitated directly from the aqueous layer after the addition of an excess of $NH_2OH\cdot HCl$. Yield: 0.045 mol (90%) (Found: C, 43.50; H, 3.50; N, 33.70; O, 19.10. Calc. for $C_6H_6N_4O_2$: C, 43.40; H, 3.65; N, 33.45; O, 19.25%). Mass spectrum: m/z 166 and 79. Infrared: ν(C=N) 1500; ν(N–O) 1000 cm^{-1}. ^1H NMR (reference $SiMe_4$): δ 7.8 (2 H), 8.4 (2 H) and 11 (2 H).

H_2L^2. Pyridazine-3,6-dicarboxylic acid (0.05 mol) prepared as previously described[21] was converted into the corresponding dichloride using an excess of thionyl chloride in the presence of a catalytic amount of dimethylformamide. Unreacted thionyl chloride was removed under reduced pressure at nearly room

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Details of the data collection and structure refinement for compound **1** *

Formula	$C_{12}H_{14}Cl_2Cu_2N_8O_{14}$
M	692.24
crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.031(6)
b/Å	9.517(4)
c/Å	9.973(5)
β/°	100.16(4)
U/Å^3	1124(8)
Z	2
D_c/kg m^{-3}	2.05×10^3
μ(Mo-Kα)/cm^{-1}	22.9
F(000)	692
Scan range/°	1.2
Reflections collected	3329
Reflections kept for refinement [$I > 3\sigma(I)$]	1356
Average shift/e.s.d. in last cycle	
for non-H atoms	0.006
for H atoms	0.015
R	0.043
R'	0.048
Number of data per variable	7.0

* Other details: colour, dark orange-red; Philips PW 1100 diffractometer, graphite monochromator; Mo-Kα radiation (λ = 0.7107 Å); 20 °C; θ–2θ scan mode; 2θ range 4–58°, scan speed 0.03° s^{-1}; background half of scan time in fixed positions before and after every scan; three standard reflections measured every 2 h; reflections measured for four octants; computer program, SFLS-5;[23] atomic form factors from ref. 24; function minimized ΣwF^2; $R = \Sigma|F|/\Sigma F_o$; $R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}}$; no secondary extinction observed; absorption correction applied,[25] crystal bounded by (100) at 0.90, (101) at 0.076, (101) at 0.079, (010) at 0.027 and (010) at 0.027 mm from an origin within the crystal; transmission factor ranges 0.74 (223)–0.090 (101); unit weight for all reflections.

Table 2 Atomic parameters for non-hydrogen atoms (×10^4) in compound **1**

Atom	*x*	*y*	*z*
Cu	768(1)	1630(1)	713(1)
N(1)	−35(4)	1306(6)	−1226(5)
N(2)	−510(4)	130(6)	−1737(5)
C(3)	−932(6)	25(9)	−3077(6)
C(4)	−879(6)	1149(10)	−3943(7)
C(5)	−403(6)	2349(10)	−3442(7)
C(6)	34(5)	2410(8)	−2030(7)
C(7)	581(6)	3637(8)	−1355(8)
N(3)	974(5)	3495(7)	−81(7)
O(1)	1482(5)	4588(6)	614(7)
C(8)	−1446(6)	−1333(9)	−3498(7)
N(4)	−1458(5)	−2229(7)	−2568(6)
O(2)	−1900(5)	−3492(7)	−2870(6)
O(3)	2395(4)	632(6)	208(5)
Cl	−1712(2)	2408(2)	2194(2)
O(4)	−1190(5)	2464(7)	1017(5)
O(5)	−2845(5)	2818(10)	1823(7)
O(6)	−1154(7)	3349(8)	3187(7)
O(7)	−1626(6)	1042(7)	2756(6)

temperature (30 °C) and the pyridazine-3,6-dicarboxylic acid dichloride immediately suspended in anhydrous benzene. After addition of $AlCl_3$ (0.15 mol) and completion of the reaction, the mixture was hydrolysed (pH 5). 3,6-Dibenzoylpyridazine extracted from the organic layer was recrystallized from light petroleum. The ligand H_2L^2 (0.026 mol) was obtained from oximation of this compound and recrystallized from ethanol (Found: C, 68.10; H, 4.50; N, 17.50; O, 9.90. Calc. for $C_{18}H_{14}N_4O_2$: C, 67.90; H, 4.45; N, 17.60; O, 10.05%]. Mass spectrum: m/z 318, 287 and 77. Infrared: ν(C=N) 1435, ν(N–O) 1000 cm^{-1}. ^{1}H NMR: δ 7–7.8 (10 H) and 8.5 (2 H).

Table 3 Main interatomic distances (Å) and bond angles (°) for compound **1**

Cu···Cu^I	3.760(2)		
Copper surroundings			
Cu–N(3)	1.977(7)	Cu–N(4^I)	1.974(6)
Cu–N(1)	2.027(5)	Cu–O(3)	2.310(6)
Cu–N(2^I)	2.014(6)	Cu–O(4)	2.554(6)
N(3)–Cu–N(1)	80.0(4)	C(6)–N(1)–Cu	112.6(7)
N(1)–Cu–N(2^I)	105.5(4)	N(2)–N(1)–Cu	126.8(7)
N(2^I)–Cu–N(4^I)	80.9(4)	N(1)–N(2)–Cu	127.3(8)
N(4)–Cu–N(3)	93.1(5)	C(3)–N(2)–Cu	112.1(7)
O(1)–N(3)–Cu	124.7(9)	C(8)–N(4)–Cu	115.9(8)
N(2)–N(1)–Cu	126.8(7)	O(2)–N(4)–Cu	124.0(9)
O(4)–Cu–N(3)	87.2(4)	O(3)–Cu–N(3)	96.4(4)
O(4)–Cu–N(1)	82.3(3)	O(3)–Cu–N(1)	90.4(3)
O(4)–Cu–N(2^I)	88.3(4)	O(3)–Cu–N(2^I)	88.9(3)
O(4)–Cu–N(4^I)	92.5(4)	O(3)–Cu–N(4^I)	95.2(4)
HL^1-anion			
N(3)–O(1)	1.337(9)	C(3)–N(2)	1.347(8)
N(3)–C(7)	1.282(10)	N(2)–N(1)	1.318(8)
C(7)–C(6)	1.447(10)	N(1)–C(6)	1.333(9)
C(6)–C(5)	1.415(9)	C(3)–C(8)	1.462(12)
C(5)–C(4)	1.335(12)	C(8)–N(12)	1.262(10)
C(4)–C(3)	1.383(12)	N(4)–O(2)	1.327(9)
O(1)–N(3)–C(7)	119.1(13)	C(5)–C(4)–C(3)	119.5(13)
N(3)–C(7)–C(6)	115.7(12)	C(4)–C(3)–C(8)	124.6(16)
C(7)–C(6)–N(1)	115.3(12)	C(8)–C(3)–N(2)	114.6(11)
C(7)–C(6)–C(5)	123.7(14)	C(4)–C(3)–N(2)	120.7(13)
C(5)–C(6)–N(1)	121.0(12)	C(3)–N(2)–N(1)	120.6(11)
C(6)–N(1)–N(2)	120.4(12)	C(3)–C(8)–N(4)	116.4(13)
C(6)–C(5)–C(4)	117.9(13)	C(8)–N(4)–O(2)	120.1(14)

Symmetry related position: I = $\bar{x}, \bar{y}, \bar{z}$.

$[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2]$ **1**. Copper(II) perchlorate (2 mmol) was added to a solution of H_2L^1 (2 mmol) in warm water (50 cm^3) (50 °C). The mixture was stirred for 10 min and filtered. Orange-red single crystals of complex **1** deposited within a few days at room temperature. They were suitable for X-ray analysis (Found: C, 20.80; H, 2.10; Cl, 10.0; Cu, 18.20; N, 15.90; O, 32.20. Calc. for $C_{12}H_{14}Cl_2Cu_2N_8O_{14}$: C, 20.80; H, 2.05; Cl, 10.25; Cu, 18.35; N, 16.20; O, 32.35%). Infrared: ν(C=N) 1590, ν(N–O) 1080 cm^{-1}.

$[Cu_2(HL^2)_2(ClO_4)_2(MeOH)_n]$ **2**. Copper(II) perchlorate (2 mmol) was added to a solution of H_2L^2 (2 mmol) in methanol (50 cm^3). The mixture was stirred for 10 min at room temperature and filtered. Slow evaporation of the solution afforded within a few days well formed dark green crystals of complex **2**. These decomposed within 2 h at room temperature and were not suitable for X-ray analysis. All attempts to obtain stable crystals using other solvents failed. Compound **2** crystallizes probably as a solvate which loses its solvent molecules rapidly. The elemental analysis was carried out on a carefully dried sample. **CAUTION**: Care must be taken when working with solvent-free perchlorate complexes (Found: C, 45.70; H, 2.80; Cl, 7.25; Cu, 13.20; N, 11.80; O, 19.50. Calc. for $C_{36}H_{26}Cl_2Cu_2N_8O_{12}$: C, 45.00; H, 2.75; Cl, 7.40; Cu, 13.25; N, 11.65; O, 20.00%). Infrared: ν(C=N) 1580 cm^{-1}.

Crystallography.—The structure of compound **1** was determined by X-ray diffraction. Preliminary Weissenberg photographs revealed $2/m$ symmetry. The space group $P2_1/n$ was deduced from systematic absences. The unit-cell parameters were refined by least squares from a Guinier powder spectrum. Data collection and structure refinement details are given in Table 1.

All non-hydrogen atoms were refined with anisotropic

Table 4 Structural hydrogen-bonding parameters

D–H	A	D–H (Å)	H $\cdots$ A (Å)	D $\cdots$ A (Å)	D–H $\cdots$ A (°)	Symmetry transformation of A
O(1)–HO(1)	O(2)	1.09(9)	1.39(9)	2.450(9)	161(23)	$\bar{x}, \bar{y}, \bar{z}$
O(3)–HO(3)	O(2)	0.79(9)	2.24(9)	2.823(8)	131(12)	$\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$
O(3)–HO(3′)	O(6)	0.80(9)	2.33(9)	3.048(9)	149(19)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

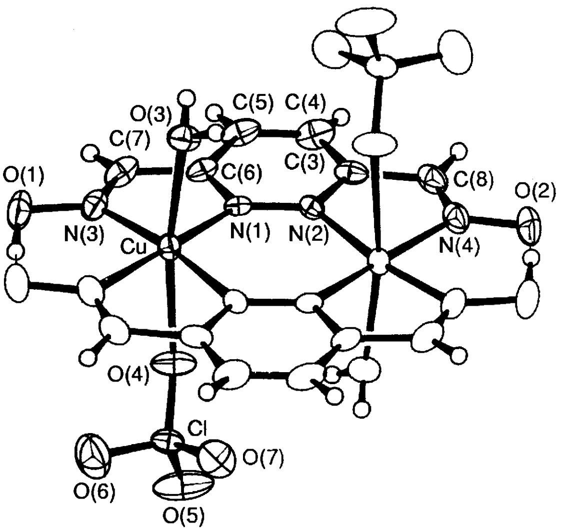

Fig. 1 Perspective view of the dinuclear complex $[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2]$ with the atom labelling system

thermal parameters. The hydrogen atoms were refined with isotropic thermal parameters fixed to those of the atoms to which they are bonded. Table 2 shows the atomic parameters, Table 3 the main interatomic distances and bond angles.

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

The well formed single crystals of complex **2** decomposed at room temperature over 2 h. Thus the crystal data collection failed and only poor X-ray diffraction data were obtained. The crystal system is triclinic with a = 14.16(1), b = 13.89(1), c = 12.82(1) Å, α = 111.11(4), β = 108.66(5) and γ = 90.18(2)°.

Magnetic Measurements.—These were carried out with a Faraday-type magnetometer equipped with a continuous-flow cryostat. In order to minimize the amount of paramagnetic impurities, *ca.* 10 mg samples were prepared by selecting single crystals under a binocular lens. The data were corrected for underlying diamagnetism and temperature-independent paramagnetism (t.i.p.) (60×10^{-6} cm^3 mol^{-1} per mol Cu). The diamagnetic correction was estimated as -280×10^{-6} cm^3 mol^{-1} for complex **1** and -290×10^{-6} cm^3 mol^{-1} for **2**. EPR spectra were recorded at X-band on a Varian E 109 spectrometer at room and liquid-nitrogen temperatures using powder samples. The magnetic field was calibrated with a diphenylpicrylhydrazyl (dpph) marker.

Spectroscopy.—The ^1H NMR spectra were recorded on a Bruker WP80 spectrometer in [$^2H_6$]dimethyl sulphoxide solvent and with $SiMe_4$ as internal reference, IR spectra on a Perkin-Elmer 1310 instrument using KBr discs or Nujol mulls (4000–600 cm^{-1}), and electronic spectra of Nujol mulls with a Jobin Yvon DUOSPAC 203 instrument.

Results

Syntheses.—Two new pyridazine oxime ligands, H_2L^1 and H_2L^2, have been synthesised. Full details will be given in a paper devoted to the preparation and the characterization of a new series of pyridazine derivatives. The procedures are described in the Experimental section.

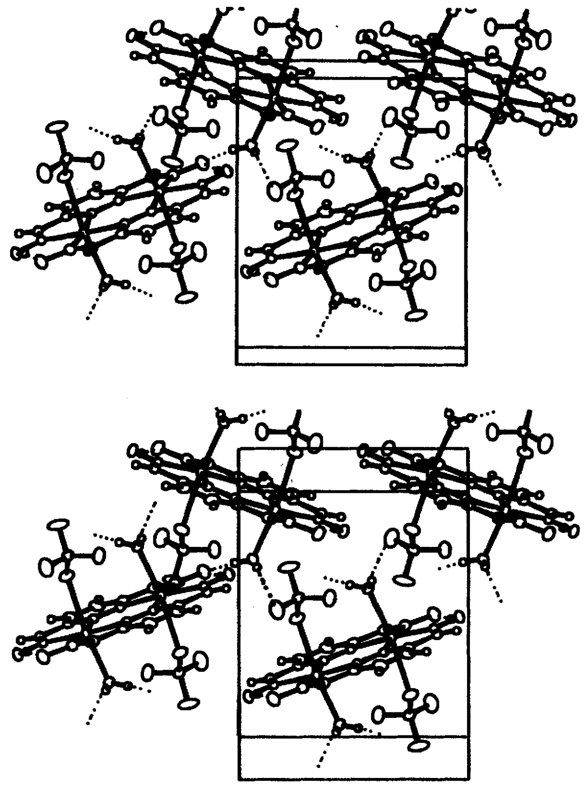

Fig. 2 Stereoscopic view of the unit cell for $[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2]$

Structure of Compound **1**.—The crystal structure consists of two $[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2]$ dinuclear molecules per unit cell, held together by hydrogen bridges. There is an inversion centre at the centre of the molecule. A perspective view of the structure is presented in Fig. 1 together with the atomic labelling system. The $Cu_2(HL^1)_2{}^{2+}$ moiety is nearly planar. The distance of the copper atoms to the least-squares plane through the ligand is 0.095 Å. In this plane the copper atoms are linked by two diazine fragments [N(1)–N(2)] in an essentially planar dimeric arrangement of two tetradentate ligands with oxime nitrogen atoms completing the equatorial co-ordination. The Cu $\cdots$ Cu distance in the dimer is 3.760(2) Å. Both halves of the ligand show different pyridazine and oxime nitrogen to copper distances and angles. These features have also been observed for related copper(II) and nickel(II) compounds. The interatomic bond distances and angles of the HL^1 anion are analogous to those previously reported[26] for the parent free ligand and metallic derivatives. The co-ordination does not induce significant deformation of the backbone of the ligand. The intra complex hydrogen bridges (Table 4) link the terminal oximato moieties of the two HL^1 anions to give a binucleating macrocycle type molecule. The hydrogen bridge is asymmetric with the hydrogen atom bonded to one oxygen atom of a ligand and hydrogen bonded to the other one. This arrangement occurs in several metallic glyoxime complexes.[27]

The copper(II) ion has 4 + 2 surroundings. Each basal plane

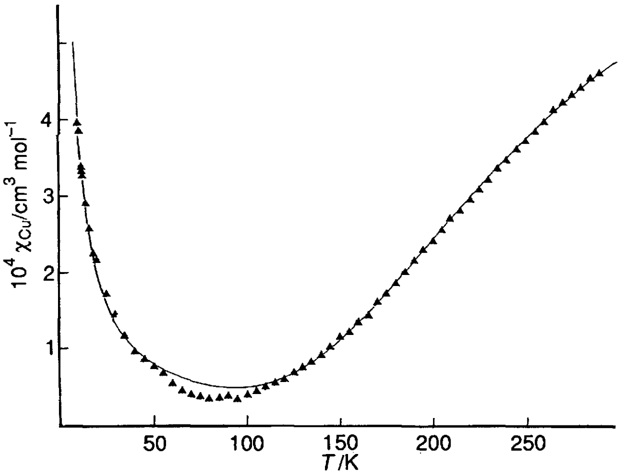

Fig. 3 Experimental and calculated temperature dependences of the magnetic susceptibility of $[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2]$ **1**

includes two nitrogen atoms of the oximato groups and two nitrogen atoms of the pyridazine rings. The apical positions are occupied by oxygen atoms of a water molecule Cu–O(3) 2.310(5) Å and a perchlorate anion at a significantly larger distance Cu–O(4) 2.554(6) Å. The interatomic distances and angles of the perchlorate anion indicate that its tetrahedral geometry is slightly distorted by co-ordination to copper.

The crystal structure is further stabilized by intermolecular hydrogen bonds. The hydrogen atoms of co-ordinated water O(3) bridge one oxygen atom O(6) of one perchlorate anion and one oxygen atom O(2) of an oximato group. A stereoscopic view of the unit cell is given in Fig. 2.

Magnetic Properties.—The temperature dependence between 300 and 12 K of the molar magnetic susceptibility χ_{Cu} for an isolated copper(II) dimer is expected to obey equation (1)

$$\chi_{Cu} = \frac{2N\beta^2g^2}{kT}[3 + \exp(-J/kT)^{-1}(1 - P) + \frac{CP}{T} + \chi_{t.i.p.} \quad (1)$$

where J is the singlet–triplet (S–T) energy gap arising from the intradimer interaction and P the proportion of uncoupled copper(II) contained in the sample. The other symbols have their usual meanings.[4,5,28]

If we assume that the uncoupled impurity has the same molecular weight as those of compounds **1** and **2** then $C = N\beta^2g^2/2k$. The parameters J, g and P were determined by minimizing R defined as $\Sigma(\chi_{Cu}^{obs} - \chi_{Cu}^{calc})^2/\Sigma(\chi_{Cu}^{obs})^2$.

The magnetic susceptibilities of complexes **1** and **2** per copper atom at room temperature are low, typically 0.5×10^{-3} cm^3 mol^{-1}, and decrease on cooling to *ca.* 120 K (see Fig. 3). This behaviour is characteristic of a large S–T energy gap. At 300 K the excited triplet state is very weakly populated. The increase of χ_{Cu} below 120 K in a temperature range where the triplet state is totally depopulated is due to the proportion of uncoupled copper(II). For compound **1** the fitting of the experimental data (Fig. 3) in the range 20–292 K leads to $J = -536(2)$ cm^{-1}, $g = 2.12(2)$, $P = 0.009$, $R = 2.5 \times 10^{-6}$ (for 60 experimental points). For compound **2**, $[Cu_2(HL^2)_2(ClO_4)_2(MeOH)_n]$, the fitting of the experimental data in the range 20–300 K leads to $J = -545(4)$ cm^{-1}, $g = 2.14(3)$, $P = 0.012$, $R = 2.6 \times 10^{-6}$ (for 54 experimental points).

The polycrystalline powder EPR spectra of compounds **1** and **2** were recorded at X-band frequency at 300 and 77 K. Surprisingly the spectra are poorly resolved even at low temperature in the $m_s = \pm 1$ region near $g = 2.1$ and no $m_s = \pm 2$ absorption was clearly observed. However, there is a significant decrease in absorption intensities upon cooling the sample from room temperature to 77 K. This results from depopulation of the triplet state. Probably, the zero-field splitting tensor D and the g tensor are not coaxial, so that their principal values cannot be deduced from powder data as previously reported for highly coupled dicopper complexes.[6,29] In addition, it is possible that some contribution to the EPR signal is attributable to a low concentration (estimated as 1% by magnetic measurements) of a copper(II) monomer of unknown composition cocrystallized with the sample. The monomer apparently arises during either recrystallization or grinding of the dimer.

Electronic spectra for compounds **1** and **2** run between 350 and 850 nm in the solid state exhibit broad absorption maxima at about 620 nm. Absorptions in this region are commonly observed for tetragonally distorted octahedral copper(II) complexes.[30]

Discussion

The results described in this paper indicate that the 3,6-disubstituted pyridazines can act as tetradentate ligands through the diazine bridge and the nitrogen atoms of the oxime groups. The molecular structure of the $Cu_2(HL^1)_2^{2+}$ cation consists of a pair of copper(II) centres simultaneously bound to two tetradentate ligands and bridged by two diazine groups. The intramolecular hydrogen bonds between the hydrogen atom of the protonated oxime of one ligand and the deprotonated oximato group of another ligand form a dinucleating macrocycle ligand. The two intramolecular hydrogen bonds reinforce the stereoelectronic requirements imposing coplanarity of the two co-ordination planes of the copper(II) ions.

The distance between the O(2) oximato and O(1) oxime atoms linked together through the hydrogen bond is quite short at 2.450(9) Å compared to the corresponding distance of 2.49 Å in $[Cu(HL^3)(H_2O)]ClO_4$[31] and of 2.53(4) Å in $[Cu(Hdmg)_2]$ [L^3 = 3,3′-(trimethylenetrinitrilo)bis[butan-2-oneoximato(1−)], Hdmg = dimethylglyoximate(1−)].[32] The intermolecular hydrogen bond which bridges the O(3) co- ordinated water and the O(2) atom of the oximato group does not induce a significant distortion of the O(2) oximato atom from coplanarity. Nevertheless, it should be noted that the mean Cu–N distances of the oximato moieties are significantly greater in $Cu_2(HL^1)_2^{2+}$, 1.97 Å, than in the corresponding monomeric complexes, respectively 1.94 and 1.91 Å in $[Cu(HL^3)(H_2O)]ClO_4$ and $[Cu(Hdmg)_2]$. However the mean Cu–N(oxime) distance is quite short (1.97 Å) compared to the Cu–N(pyridazine) distance (2.02 Å). This phenomena is not apparent when the 3,6 substituents are 2-pyridyl. In this case, the four Cu–N distances are equivalent and close to 2.02 Å.[33]

From the structural data for compound **1** it is possible to give a reasonable interpretation of the magnetic data and particularly of the S–T energy gaps for compounds **1** and **2**. First, we will summarize briefly the key concepts which will be utilized. All these concepts have been discussed thoroughly in several papers and reviews.[14,15,29–31]

(*i*) In a copper(II) dinuclear system each magnetic centre has an unpaired electron described by a magnetic orbital the energy and the orientation of which depend on its environment.

(*ii*) The first approximation consists in assuming that all the electrons of the dinuclear system are passive, except for those two occupying the magnetic orbitals. In this active-electron approximation the S–T energy gap, J, arising from the intramolecular interaction appears as the result of a competition between a ferromagnetic component and an antiferromagnetic contribution.

As previously reported,[15] when the two copper(II) ions are bridged by an extended ligand the ferromagnetic component is actually very small and only the antiferromagnetic contribution is significant. The antiferromagnetic contribution is proportional to the square of the overlap integral of the magnetic orbitals.

In compounds **1** and **2** the copper(II) ions adopt a 4 + 2 co-ordination with four nitrogen atoms as nearest neighbours in the basal plane. In such an environment the most destabilized orbital occupied by the unpaired electron of copper(II) is of the d_{xy} type. It points from the metal toward the four nearest neighbours in an antibonding fashion. Without symmetry, in a 4 + 2 co-ordination the singly occupied orbital is delocalized toward all the six co-ordinated atoms. Nevertheless the co-ordination sphere is such that the xy plane is assumed to be a mirror plane, so the d_{xy} and d_{z^2} orbital mixing is assumed to be weak. In addition the copper atom is displaced from the basal plane toward the apical water by 0.095 Å; however, as reported earlier, this displacement has almost no effect on the magnitude of the interaction.

The hydrogen bonding between the oxime and oximato groups constrains the bridging pyridazine and the copper co-ordination planes to be nearly coplanar. The strong antiferromagnetic interaction in complexes **1** and **2** is due to the relative orientation of the magnetic orbitals and to their delocalization from the metal toward the nitrogen atoms of the diazine bridges bonded to the metal. Both the orientation and the delocalization of the magnetic orbitals favour their overlapping and thus the antiferromagnetic interaction.

With the present pyridazine dioxime ligands the possibilities of the orientation are nearly maximum since the magnetic orbitals are already located in the plane containing the bridging network and moreover point towards each other.

When the two copper(II) ions are bridged by an extended ligand[34] such as H_2L^1 and H_2L^2 each magnetic orbital is delocalized over a large number of bridge atoms, consequently the overlap density is spread over the whole bridge. Both the σ and π orbitals of the pyridazine heterocycles are capable of acting as superexchange pathways between copper(II) ions.

The overlap of the copper d_{xy} and the σ and π orbitals of the nitrogen-containing heterocycles is maximum in a planar arrangement when the Cu–N–N angle is close to 120°. The values reported for the present pyridazine and previous phthalazine compounds[8–11] explain the strong antiferromagnetic interaction. When the corresponding angle deviates significantly from the ideal value, as observed for triazole,[4,5] indazole[16,17] and pyrazole parent compounds, the exchange decreases but remains large, although the Cu $\cdots$ Cu distance increases. Considering previous investigations, it is suggested that the exchange is mainly determined by a σ-overlap superexchange pathway involving σ electrons of the heterocycle. Quantitative discussions on the correlation between exchange and geometric parameters are not undertaken because they can only be made when a series of structurally comparable compounds with related ligands having different bonding properties is investigated.

Conclusion

The planar structure of the macrocyclic dicopper moieties in $[Cu_2(HL^1)_2(ClO_4)_2(H_2O)_2]$ **1** and $[Cu_2(HL^2)_2(ClO_4)_2(MeOH)_n]$ **2** constrains the two copper(II) magnetic orbitals to be located in the plane containing the bridging network in order to favour their overlapping. This overlapping is mediated by the diazine bridge and is nearly maximum with the six-membered pyridazine heterocycle as compared with other heterocycles containing the diaza bridge. These two parameters appear as the main factors governing the antiferromagnetic superexchange in dicopper dimers with diaza bridges and represented by the S–T separation.

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