

Magnetic properties and crystal structure of $\{\mu\text{-pyrazine}\}$ -bis[(aqua)(2,6-xylylaminodiacetato)copper(II)]. A pyrazine-bridged dinuclear copper(II) complex

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Abstract

The preparation, spectroscopic and magnetic study, and crystal structure of the complex $\{\mu\text{-pyrazine}\}$ bis[(aqua)(2,6-xylylaminodiacetato)copper(II)], $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$, are reported. It crystallizes in the monoclinic space group $P2_1/n$ with cell constants $a = 13.309(3)$, $b = 7.590(2)$, $c = 15.459(3)$ Å, $\beta = 100.90(3)^\circ$, $Z = 2$, $R = 0.038$, $R_w = 0.045$. The structure consists of neutral dinuclear $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ molecules, in which the copper(II) ions are bridged by a molecule of pyrazine, with a $\text{Cu} \cdots \text{Cu}$ distance of 5.786 Å. Each of the CuN_2O_3 coordination polyhedra can be described as a square-based pyramid with a small distortion toward trigonal-bipyramid. The bridging pyrazine molecule is bonded in equatorial position and canted out of the basal coordination plane by 20.8° . The magnetic study indicates that a weak antiferromagnetic interaction operates between the copper(II) ions with an exchange coupling constant of -3.7 cm^{-1} . The magnitude of the exchange interaction is discussed on the basis of structural data.

Key words: Crystal structures; Copper complexes; Bidentate ligand complexes; Dinuclear complexes

Introduction

Numerous structural and magnetic studies on polynuclear bridging pyrazine copper(II) complexes have been reported [1–13], most of them dealing with chain and two-dimensional layer compounds [1–10]. These studies have shown that, in spite of the length of the exchange pathway, pyrazine can support significant spin–spin interactions between metal ions. The magnitude of the exchange coupling in these systems is significantly affected by the structural features of the bridging pyrazine network. Thus, it has been suggested [4] that for copper–pyrazine complexes in which the unpaired electron is the $d_{x^2-y^2}$ orbital and the pyrazine

is bonded in the equatorial xy plane, the magnitude of the antiferromagnetic exchange is mainly determined from the overlap of the $d_{x^2-y^2}$ orbital and the pyrazine π system. Simple systems such as dinuclear species are good candidates for evaluating in a better way how the structural factors involving the bridging pyrazine network affect the magnetic properties. It should be noted that only a few examples exist of well structurally and magnetically characterized dinuclear bridging pyrazine complexes [11–13], which are obtained by adding a coordinating substituent group to the pyrazine ring.

In this paper, we report on the synthesis, X-ray structure determination and magnetic studies of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ (where H_2L stands for 2,6-xylylaminodiacetic acid). To the best of our knowledge, this compound represents the first example reported so far

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of a dinuclear bridging pyrazine copper(II) complex in which the nitrogen atoms of the pyrazine molecule occupy equatorial sites on the copper(II) coordination polyhedra.

Experimental

Physical measurements

Microanalyses of C, H and N were performed with a Perkin-Elmer 240 C analyzer. Copper was determined thermogravimetrically, as CuO, using a Mettler TG 50 thermobalance. The IR spectrum was recorded in the 4000–180 cm^{-1} range on a Perkin-Elmer 983 G spectrometer, using KBr pellets. ESR spectra of the compound were recorded at X-band frequencies with a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz, at room temperature and 90 K.

Magnetic susceptibility data were collected on powdered samples with use of a Faraday type magnetometer fitted with a helium continuous-flow cryostat. Independence of the magnetic susceptibility versus magnetic field was checked at each temperature. Mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C = 16.44×10^{-6} cgsu) was used as susceptibility standard. All data were corrected of diamagnetism of the ligands estimated from Pascal constants and for TIP. The electronic reflectance spectrum was obtained with a Shimadzu MPC 3100 spectrometer, using BaSO₄ as reference.

Preparation of the compounds

The ligand 2,6-xylylamino diacetic acid and the complex $[\text{Cu}(\text{L})_2] \cdot 3\text{H}_2\text{O}$ were prepared as described previously [14].

The complex $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ was prepared by adding 2 g (25 mmol) of pyrazine to a suspension of 0.2 g (0.57 mmol) of $[\text{Cu}(\text{L})_2] \cdot 3\text{H}_2\text{O}$ in 50 ml of EtOH/pyridine (20:1) mixture and then was held at reflux for 30 min. The resulting blue solution was filtered and allowed to stand at room temperature. After two days well developed blue crystals of the complex $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ were obtained. *Anal.* Found: C, 47.01; H, 4.93; N, 7.70; Cu, 17.45. Calc. for $\text{C}_{28}\text{H}_{34}\text{N}_4\text{O}_{10}\text{Cu}_2$: C, 47.12; H, 4.80; N, 7.85; Cu, 17.81%. IR (cm^{-1}): 3366 $\nu(\text{OH})$, 3100, 3000 $\nu(\text{CH})_{\text{arom}}$, 2966 $\nu(\text{CH})_{\text{alkyl}}$, 1630 $\nu_{\text{as}}(\text{COO})$, 1380 $\nu_{\text{s}}(\text{COO})$.

X-ray data collection and structure determination of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$

A blue crystal (0.08 × 0.12 × 0.23 mm) was selected for single-crystal X-ray diffraction analysis. Data collection was performed at ambient temperature with a Siemens-Stoe AED-2 four circle diffractometer using monochromatized Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$).

The unit cell parameters were obtained from least-squares refinement of 25 well-centred reflections ($25 > 2\theta > 35^\circ$).

Intensity data were collected by ω - 2θ scan mode ($3 < 2\theta < 60^\circ$, $-23 \leq h \leq 21$, $-9 \leq k \leq 13$, $-6 \leq l \leq 27$). A total of 13 366 reflections was measured, of which 3738 with $F > 6\sigma(F)$ were considered to have observable intensity and were used in the structure analysis. Intensities of four check reflections measured every 120 min showed only statistical variation. The data were corrected for Lorentz and polarization effects and an empirical absorption correction (ψ scan) was performed using the XEMP program of the SHELXTL-Plus program package [15].

Crystal data. $\text{C}_{28}\text{H}_{34}\text{N}_4\text{O}_{10}\text{Cu}_2$, $M = 713.7$, monoclinic, space group $P2_1/n$, $a = 13.309(3)$, $b = 7.590(2)$, $c = 15.459(3) \text{ \AA}$, $\beta = 100.90(3)^\circ$, $U = 1533.4(6) \text{ \AA}^3$, $Z = 2$, $D_c = 1.546 \text{ g cm}^{-3}$, $F(000) = 736$, $\mu(\text{Mo K}\alpha) = 1.449 \text{ mm}^{-1}$.

The structure was solved by a combination of direct methods and Fourier techniques by using the SHELXTL-Plus program package on a MicroVAX II computer. In the final refinement, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions. Isotropic thermal parameters were refined for pyrazine hydrogen atoms H13 and H14.

The function minimized was $\sum w(\Delta F)^2$ ($w = 1/\sigma_F^2$), resulting in a final $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ value of 0.038 and $R_w = \sum w[(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.045$. The goodness-of-fit ratio was 1.85 for 204 parameters. Atomic coordinates for the non-hydrogen atoms are listed in Table 1.

Results and discussion

Crystal structure of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$

The structure of the complex consists of neutral dinuclear $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ molecules, in which the copper(II) ions are bridged by a molecule of pyrazine, resulting in a Cu...Cu distance of 5.786 Å. A perspective view of the molecular structure is given in Fig. 1 together with the atomic labelling system. Selected bond lengths and angles are listed in Table 2.

Within the $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ molecule, two five-coordinated CuN_2O_3 chromophores are related by a crystallographic centre of symmetry. Each of the Cu(II) atoms forms four short bonds of about 2.0 Å with one nitrogen and two oxygen atoms from the doubly deprotonated ligand L^{2-} and one nitrogen atom of the pyrazine molecule, while a water molecule is coordinated in axial position at a longer distance (2.390(3) Å).

The angles of the coordination polyhedron are not far from those corresponding to a square-based py-

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
N(1)	344(2)	-6(4)	2576(2)	28(1)
O(1)	-741(2)	-474(3)	926(2)	44(1)
O(2)	-1122(2)	2349(3)	746(2)	43(1)
O(4)	2414(2)	-2752(4)	3642(2)	48(1)
O(3)	1162(2)	-3288(3)	2501(2)	39(1)
C(1)	-357(3)	109(6)	3211(3)	39(2)
C(11)	1420(3)	-324(5)	3049(3)	35(2)
C(10)	-642(3)	1144(5)	1146(3)	32(2)
C(9)	177(3)	1534(5)	1963(3)	34(2)
C(12)	1688(3)	-2285(5)	3076(3)	30(2)
O(5)	1704(2)	-1111(4)	1041(2)	49(1)
N(2)	51(4)	-3832(4)	703(3)	32(1)
C(7)	-1301(4)	-2716(8)	2601(4)	87(3)
C(2)	-1127(4)	-1142(8)	3205(4)	62(2)
Cu	241(1)	-1961(1)	1631(1)	35(1)
C(6)	-251(4)	1539(7)	3807(4)	58(2)
C(8)	559(4)	2948(7)	3898(4)	75(2)
C(5)	-928(6)	1655(11)	4377(5)	98(4)
C(3)	-1782(5)	-930(12)	3806(5)	97(4)
C(4)	-1688(6)	457(15)	4379(5)	116(5)
C(14)	781(3)	-5034(5)	675(3)	33(2)
C(13)	-727(3)	-3805(5)	9(3)	32(2)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

ramidal geometry. Distortion can be measured by using the index τ [16], which is unity for perfect trigonal-bipyramidal geometry and zero for square-pyramidal geometry. The calculated value for $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ is 0.097, indicating that the coordination polyhedron could be well described as a square-based pyramid with a small trigonal-bipyramidal distortion. In this square-pyramidal geometry, the basal plane is defined by O(1), N(1), O(3) and N(2), whereas the apical position is occupied by O(5) from a water molecule, in accordance with the relatively large Cu–O(5) distance. Deviations from planarity up to 0.0173 Å are observed for the equatorial donor atoms. As usual, the copper atom is lifted 0.059 Å out of the basal plane toward the O(5) axial donor.

The tridentate behaviour of the ligand results in the formation of two five-membered rings which have in common the Cu–N(1) bond. The dihedral angle between the mean planes of these two rings is 15°. The pyrazine ring is essentially planar, as expected. The dihedral angle between the pyrazine plane and the mean equatorial plane around copper is 20.8°.

Neighbouring dinuclear molecules are interconnected by hydrogen bonds, which are established from an axially coordinated water molecule to the O(4) and O(2) carboxylate oxygen atoms. The donor–acceptor distances O(5)–O(2)ⁱ ($i = \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) and O(5)–O(4)ⁱⁱ ($ii = -x, -y, -z$) are 2.810 and 2.882 Å, respectively.

Electronic and magnetic properties

The electronic reflectance spectrum of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ exhibits a band maximum at 650 nm. Taking into account the assignment of the electronic spectrum of copper(II) complexes with trigonal-bipyramidal and square-pyramidal geometries reported by Hathaway and co-workers, [17], that band can be assigned to the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition for a square-pyramidal system. In DMSO solution, the complex exhibits a band maximum at 730 nm, indicating that the distortion of the CuO_3N_2 chromophore from the ideal square-pyramidal geometry is higher in solution than in solid state.

The polycrystalline EPR spectrum of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ at 297 K is almost axial with a small anisotropy in the g_{\perp} component ($g_z = 2.21$; $g_y = 2.06$; $g_x = 2.05$) and only consistent with a $d_{x^2-y^2}$ ground state, as expected for a square-pyramidal coordination [18]. The spectrum is devoid of any signal assignable to either half-field transition of hyperfine interaction. Lowering the temperature from 297 to 90 K does not alter the overall appearance of the spectrum.

Magnetic susceptibility data were collected on a powdered sample in the temperature range 280–4.5 K. The temperature dependence of χ_M and μ_{eff} are given in Fig. 2. On lowering the temperature, the effective

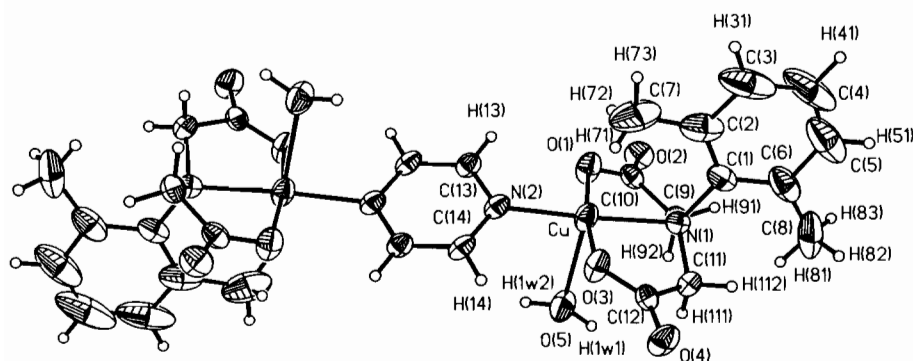
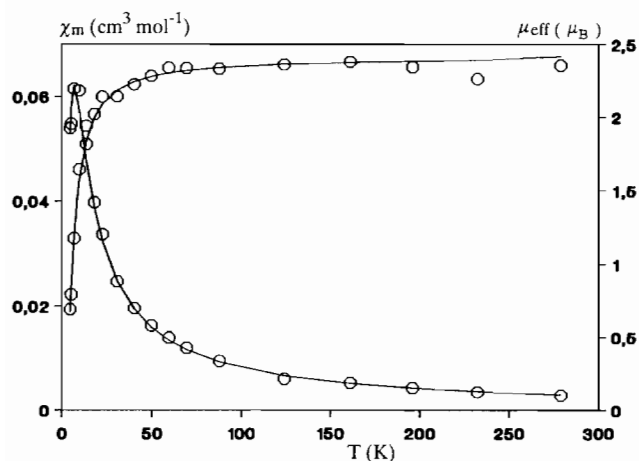


Fig. 1. A perspective view of the $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2(\text{pyz})]$ molecule with the atom labelling.

TABLE 2. Selected bond lengths (Å) and angles (°) of [Cu₂(L)₂(H₂O)₂(pyz)]

N(1)–Cu	2.069(3)	C(6)–C(8)	1.506(8)
N(2)–Cu	2.000(4)	N(1)–C(9)	1.495(5)
O(1)–Cu	1.906(3)	C(10)–C(9)	1.533(6)
O(3)–Cu	1.924(3)	O(2)–C(10)	1.215(5)
O(5)–Cu	2.390(3)	O(1)–C(10)	1.274(5)
N(1)–C(1)	1.479(6)	N(1)–C(11)	1.500(5)
C(1)–C(2)	1.396(7)	C(11)–C(12)	1.529(5)
C(2)–C(3)	1.399(10)	O(3)–C(12)	1.275(5)
C(3)–C(4)	1.366(13)	O(4)–C(12)	1.228(5)
C(5)–C(4)	1.361(12)	N(2)–C(13)	1.343(5)
C(6)–C(5)	1.376(10)	N(2)–C(14)	1.339(5)
C(1)–C(6)	1.414(7)	C(14)–C(13A)	1.368(6)
C(7)–C(2)	1.506(9)		
N(1)–Cu–O(1)	85.7(1)	C(8)–C(6)–C(5)	116.0(6)
O(1)–Cu–O(3)	170.8(1)	C(1)–N(1)–C(9)	109.7(3)
O(1)–Cu–O(5)	98.2(1)	C(1)–C(2)–C(7)	124.8(5)
N(1)–Cu–N(2)	176.6(1)	C(7)–C(2)–C(3)	117.4(6)
O(3)–Cu–N(2)	96.1(1)	N(1)–C(1)–C(6)	118.7(4)
N(1)–Cu–O(3)	86.2(1)	O(1)–C(10)–O(2)	124.9(4)
N(1)–Cu–O(5)	97.3(1)	O(2)–C(10)–C(9)	119.8(4)
O(3)–Cu–O(5)	87.2(1)	O(1)–C(10)–C(9)	115.3(3)
O(1)–Cu–N(2)	91.7(1)	N(1)–C(9)–C(10)	111.6(3)
O(5)–Cu–N(2)	85.4(1)	N(1)–C(11)–C(12)	111.5(3)
N(1)–C(1)–C(2)	120.7(4)	O(4)–C(12)–O(3)	125.4(4)
C(2)–C(1)–C(6)	120.6(5)	O(3)–C(12)–C(11)	117.9(3)
C(1)–C(2)–C(3)	117.8(6)	C(1)–N(1)–C(11)	110.5(3)
C(2)–C(3)–C(4)	121.8(7)	C(11)–N(1)–C(9)	116.6(3)
C(5)–C(4)–C(3)	119.4(8)	O(4)–C(12)–C(11)	116.7(3)
C(6)–C(5)–C(4)	122.4(7)	C(14)–N(2)–C(13)	116.0(4)
C(1)–C(6)–C(5)	118.0(5)	N(2)–C(13)–C(14A)	121.8(4)
C(1)–C(6)–C(8)	125.9(5)	N(2)–C(14)–C(13A)	122.1(4)

Fig. 2. Experimental and calculated temperature dependence of μ_{eff} and χ for [Cu₂(L)₂(H₂O)₂(pyz)].

magnetic moment per dinuclear molecule decreases from a value of 2.36 μ_{B} at 280 K to a value of 0.69 at 4.5 K, indicating that a weak antiferromagnetic interaction operates between the copper(II) ions. In good accordance with this, the temperature dependence of χ_{M} shows a maximum at 6.7 K. The experimental

susceptibilities are well fitted to the Bleaney-Bowers equation with an isotropic exchange Hamiltonian ($\mathcal{H}_{\text{ex}} = -2JS_1S_2$):

$$\chi_{\text{M}} = \frac{Ng^2\mu_{\text{B}}^2}{kT} \left[\frac{2}{3 + \exp\left(\frac{-2J}{kT}\right)} \right] + N\alpha$$

The best fit parameters for the data are $J = -3.7 \text{ cm}^{-1}$, $g = 2.14$ and $R = \Sigma(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \Sigma(\chi_{\text{obs}})^2 = 5 \times 10^{-3}$.

To the best of our knowledge, with the exception of the ferromagnetic polynuclear complex [Cu(pzdc)-ClH]_n [9], all pyrazine-bridged complexes reported so far exhibit either weak antiferromagnetic or no significant exchange coupling between the copper ions (Table 3). However, it should be noted that the exchange interaction in these complexes is much weaker than that in other inorganic nitrogen heterocyclic bridging systems such as imidazolate, triazolate and triazole groups. In connection with this, an extended Hückel molecular orbital (EHMO) calculation recently performed on the model compound [Cu₂(pyz)(NH₃)₈]⁴⁺ [13] revealed that the HOMO–LUMO (both of σ type) energy gap, which determines the magnitude of the antiferromagnetic contribution to $2J$ (triplet–singlet energy difference), is similar to that calculated for [Cu₂(triazole)₂(NH₃)₄(OH)₂(H₂O)₂]²⁺, in spite of the very weak magnitude of the antiferromagnetic interaction observed for pyrazine-bridged copper(II) complexes. The disagreement between experimental and EHMO calculation results was interpreted on the basis of the larger electron transfer energy between two copper centres for pyrazine than for triazole. As some authors have indicated [4], the π electron exchange pathway may also contribute to the overall antiferromagnetic coupling. Moreover, spectroscopic evidence suggests that the π pathway is the more important [6]. In contrast to the σ type pathway, which is cylindrically symmetrical about the bond axis and the overlap integral would not be affected by a colinear rotation of the bridging orbitals, the overlap integral of the π -exchange pathway would depend on the orientation of the pyrazine π and metal d electrons. Thus for pyrazine-bridged copper(II) systems where the unpaired electron is predominantly in the $d_{x^2-y^2}$ orbital, as the distorted square-pyramidal geometry suggests it is in [Cu₂(L)₂(H₂O)₂(pyz)], this orbital overlaps with the highest occupied $\pi(b_{1g})$ orbital of pyrazine. If the pyrazine ring is coplanar with the copper(II) coordination plane, then the π system of the pyrazine would be orthogonal to the $d_{x^2-y^2}$ orbital and no antiferromagnetic interaction would be observed. This case was observed for [Cu(pyza)₂(ClO₄)₂] [5] (where pyza is pyrazine-2-

TABLE 3. Magnetic and structural data related with the exchange coupling in some pyrazine-bridged copper(II) complexes

Complex no.	Compound ^a	Geometry	Magnetic orbital	Location of Pyz molecule	Canting angle (°)	<i>J</i> (cm ⁻¹)	Reference
1	[Cu ₂ (L) ₂ (H ₂ O) ₂ (pyz)]	distorted square-pyramid	d _{x²-y²}	equatorial	20.8	-3.7	this work
2	[Cu(NO ₃) ₂ (pyz)] _n	distorted octahedral	d _{x²-y²}	equatorial	50	-7.4	1
3	[Cu(py ₂) ₂ (ClO ₄) ₂] _n	distorted octahedral	d _{x²-y²}	equatorial	66.1	-5.3	8
4	[Cu(py ₂) ₂ (CH ₃ -SO ₃) ₂] _n	distorted octahedral	d _{x²-y²}	equatorial	28.5	-2.5	10
5	[Cu(py ₂ A) ₂ (ClO ₄) ₂] _n	distorted octahedral	d _{x²-y²}	equatorial	0	<0.5 ^b	5
6	[Cu ₂ (dapz)(dien) ₂](ClO ₄) ₂	distorted trigonal-bipyramid	d _{z²}	axial		-1.7	13
7	[Cu(L ¹)Cl ₂](ClO ₄) ₂ ·2CH ₃ OH	distorted trigonal-bipyramid	d _{z²}	equatorial	77.6	<0.5	11
8	[Cu(L ¹)Cl ₂](ClO ₄) ₂	distorted square-pyramid	d _{x²-y²}	axial		<0.5	11
9	[Cu(hfac) ₂ (pyz)] _n	distorted octahedral	d _{x²-y²}	axial		<0.5	4

^aAbbreviations for ligands: L = 2,6-xylylaminoacetato dianion; pyzA = pyrazine-2-carboxamide; dapz = 2,5-bis[(dimethylamino)methyl]pyrazine; L¹ = 2,5-bis[(2'-pyridylmethyl)aminomethyl]pyrazine; hfac = hexafluoroacetylacetonato anion. ^bIn these cases there are no signs of an exchange interaction in the susceptibility data to 4.2 K and so $|J| \leq 0.5 \text{ cm}^{-1}$.

carboxamide), where the pyrazine ring lies in the *xy* plane giving rise to a magnetic-dilute system (see Table 3). However, canting of the equatorially bonded ring relative to the *xy* coordination plane would locate the $\pi(b_{1g})$ orbital of pyrazine in a good orientation for overlapping positively with the d_{x²-y²} orbitals on the Cu(II) centres. This case was observed for the complexes 1–4 in Table 3.

As mentioned above, in [Cu₂(L)₂(H₂O)₂(pyz)] (1), the equatorially bonded pyrazine ring, which is canted out of the *xy* coordination plane by 20.8°, is suitably oriented to have a π -exchange pathway, leading to an antiferromagnetic interaction with $J = -3.7 \text{ cm}^{-1}$.

The magnetic behaviour exhibited by complexes 6–9 in Table 3 can also be interpreted on the basis of their structural data. Thus, in [Cu₂(dapz)(dien)₂](ClO₄)₂ [13] (dapz is 2,5-bis[(dimethylamino)methyl]pyrazine and dien is diethylenetriamine), where the copper atoms exhibit a distorted-trigonal pyramidal geometry with the pyrazine ligand bonded in axial position, the presence of significant exchange interaction ($J = -1.7 \text{ cm}^{-1}$) must be a consequence of the distortion of the CuN₅ chromophore towards a square-pyramidal geometry

($\tau = 0.64$), which incorporates a small amount of unpaired electron density in the d_{x²-y²} orbital, thus allowing a $\pi(b_{1g})$ -d_{x²-y²} exchange pathway.

Finally, it must be pointed out that in complexes 7–9, the magnetic orbitals are perpendicular to the Cu–Npyz bonds, which does not allow a d- σ exchange pathway. Moreover, the long Cu–Npyz distances relative to the others in the coordination polyhedron and the orientation of the pyrazine ring does not allow effective d- π overlap with copper. All this is in agreement with the fact that no significant exchange interaction has been observed for these complexes.

Supplementary material

Hydrogen atom coordinates, thermal parameters, tables of observed and calculated structure factors, and remaining bond distances and angles are available from the authors on request.

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