Magnetic properties of dinuclear copper(II) complexes with simple pyrazolate bridges


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Three new copper(II) complexes with simple pyrazolate bridges have been prepared, [Cu₂(pz₂)(dpa)₃(H₂O)]Cl·H₂O 1, [Cu₂(pz₂)(phen)₂Cl₂]·2CH₂OH 2 and [Cu₂(pz₂)(phen)₂Cl₂]·2H₂O 3 (H₂pz = pyrazole, dpa = di(2-pyridyl)amine, phen = 1,10-phenanthroline) and their crystal and molecular structures determined. The copper centres in the binuclear cation in 1 have a square pyramidal geometry at Cu1 and a distorted octahedral geometry at Cu2. The neutral complexes 2 and 3 have the copper atoms in a distorted square pyramidal geometry. Complexes 1 and 2 are bibradiated by pyrazolate while 3 is monobridged by this ligand. Variable temperature magnetic studies on all three complexes indicate the existence of antiferromagnetic exchange phenomena (−2J = 191, 169, 42 cm⁻¹ for 1, 2 and 3 respectively). Extended Hückel calculations showed a HOMO/LUMO gap which is in agreement with the experimental data.

The pyrazolate ligand functions as a bridge through its two nitrogen atoms to afford bi- and poly-nuclear copper(II) complexes. However well characterised discrete binuclear complexes with simple pyrazolate bridges are still rare. The pyrazolate bridge in binuclear copper(II) co-ordination compounds is generally present with another bridging group such as alcohols, phenolate, thiolate, acetate or azide. Another possibility is the use of pyrazole derived ligands, which present chelating arms at the 3 and 5 positions of the pyrazole moiety, thus permitting the incorporation of two metal centres in close proximity. 3h-16

We herein report the syntheses, crystal structure and magnetic properties of binuclear copper(II) complexes, bibradiated or monobridged by simple pyrazolate ligands. The 2J values of these compounds are related to geometrical factors.

Results and discussion

Crystal structures

[Cu₂(pz₂)(dpa)₃(H₂O)]Cl·H₂O 1 [dpa = di(2-pyridyl)amine]. Compound 1 (Fig. 1) is a binuclear cationic copper(II) complex, crystallising in the P2₁2₁2₁ crystal system. The copper nuclei are bridged by two pyrazolate ligands and one chloride ion; each is also chelated by a di(2-pyridyl)amine molecule. The copper–copper distance is 3.426(1) Å, and the Cu1–Cl1–Cu2 angle is 79.65(5)°. Bond distances and angles relevant to the copper co-ordination sphere are given in Table 1.

Atom Cu1 has a square pyramidal environment. The apical position is occupied by the shared Cl1 atom (Cu1–Cl1 2.572(2) Å) and the basal plane is formed by the dpa-nitrogen atoms (N1, N3) and by the nitrogen atoms from each of the two pyrazolate rings (N4, N10). The basal plane defined by these four nitrogen atoms is planar (major deviation from the best mean plane observed for N3 0.032(5) Å). The copper atom is found at 0.257(1) Å from this best mean plane, and Cl1 deviates from the normal to this plane by 5.49(9)°.

Fig. 1 Diagram showing the structure with atom labels for compound 1. Hydrogen atoms are omitted for clarity.

Atom Cu2 has an octahedral co-ordination, with a basal plane defined by the four nitrogen atoms N5, N6, N8, N9 (major deviation from the best mean plane for N9 0.047(5) Å) similar to Cu1. One apical position is occupied by the same Cl1 atom (Cu2–Cl1 2.772(2) Å) and the other by a water oxygen with a relatively long bond distance (Cu2⋯O1 2.801(6) Å). The copper atom lies at 0.048(1) Å from the nitrogen mean plane, Cl1 deviates by 1.59(8)° and O1 by 175.2(1)° from the normal to this basal plane. Both nitrogen mean planes surrounding the copper atoms define a dihedral angle of 75.3(1)°.

The two pyrazolate rings are planar (major deviation from the best mean plane is 0.002(6) Å for Cl2 and 0.010(7) Å for Cl2), and form a dihedral angle of 98.2(2)°. The N4–N5 bond length is 1.379(7) Å and N9–N10 is 1.362(7) Å.

The ligands are twisted with respect to the copper basal plane. The dpa chelate mean planes defined by N1, N2, N3, C5, C6 and N6, N7, N8, C18, C19 form 59.2(2) and 34.1(2)° dihedral angles with the copper basal plane they are joined to.
Table 3 Bond distances in Å and angles in ° for compound 3 relevant to the copper co-ordination sphere

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cu–CuA</th>
<th>Cu–CuN1</th>
<th>Cu–CuN2</th>
<th>Cu–CuN3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–Cl1</td>
<td>2.286(2)</td>
<td>2.081(3)</td>
<td>2.033(3)</td>
<td></td>
</tr>
<tr>
<td>Cu–Cl2</td>
<td>2.570(4)</td>
<td>1.960(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu–Cl2–CuA</td>
<td>94.7(4)</td>
<td>87.4(9)</td>
<td>87.4(9)</td>
<td></td>
</tr>
<tr>
<td>Cu–N3–N3A</td>
<td>125.5(1)</td>
<td>91.86(9)</td>
<td>91.86(9)</td>
<td></td>
</tr>
<tr>
<td>Cu–Cl–Cu–Cl2</td>
<td>116.7(1)</td>
<td>93.3(1)</td>
<td>93.3(1)</td>
<td></td>
</tr>
<tr>
<td>Cu–Cl–Cu–Cl2</td>
<td>140.9(1)</td>
<td>80.2(1)</td>
<td>80.2(1)</td>
<td></td>
</tr>
<tr>
<td>Cu–Cl–Cu–N3</td>
<td>91.89(9)</td>
<td>172.1(1)</td>
<td>172.1(1)</td>
<td></td>
</tr>
<tr>
<td>Cu–Cl–Cu–N1</td>
<td>91.39(9)</td>
<td>92.4(1)</td>
<td>92.4(1)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3 Diagram showing the structure with atom labels for compound 3. Hydrogen atoms are omitted for clarity.

Bipyramidal (apical atoms N1 and N3). The calculated z value for this complex is 0.35. The largest Cu–N distance observed is 2.081(3) Å for N2 from a phenanthroline molecule, and the smallest one is 1.960(3) Å for N3, from the pyrazole bridge.

The pyrazole ring is planar with the main deviation observed for C13 (0.002(4) Å). This complex presents a larger Cu–N3–N3A angle of 125.5(1)°, as compared to 2 where the Cu–N3–N4 angles are 120.2(3)°. The pyrazole ring forms with the Cu–Cl2–Cu–A plane a dihedral angle of 16.4(1)°.

Compound 3 can be compared to the complex reported by Matsumoto et al.18 [Cu(dien)2(pz)(Br)][ClO4]溶解–H2O. Both complexes are described as having a distorted square pyramidal geometry around the copper atoms. The Cu–Cl2–Cu–A angle is 94.7(1)° in 3, compared to Cu(1)–Br(1)–Cu(2) 87.1(1)° and Cu3–Br2–Cu4 89.0(1)° for the two independent molecules of [Cu(dien)2(pz)(Br)][ClO4]溶解–H2O.

EPR Spectra

At 300 K the X-band EPR spectra consist of a single asymmetric line, at g = 2.16 for compound 1, 2.14 for 2 and 2.13 for 3 (with a shoulder on the low-field side at 3350 G). A weak half-field band (ΔM = 2) transition can be observed at 1610 G for 1 (g = 4.32). The latter is a so-called forbidden transition but often appears for compounds of triplet state with a large zero-field splitting. No hyperfine splitting was observed since exchange effects normally broaden the EPR spectra of the copper(II) complexes in the solid state to an extent that hyperfine data are masked.38 This spectrum can be interpreted as a triplet state spectrum originating from exchange-coupled pairs of copper(II) atoms.

Upon cooling the samples from 300 to 80 K the spectrum of compound 3 remains unresolved. The 80 K spectra of 1 and 2 lose intensity, but show an improved resolution. The half-field transition (ΔM = 2) appears at g = 4.36 and 4.58 for 1 and 2 respectively. The ΔM = 1 transition shows three signals that can be associated to the rhombic values 2.48, 2.12 and 1.76 (1) and 2.56, 2.13 and 1.78 (2).

The zero-field splitting parameter, D, can be estimated from the position of the half-field transition through eqn. (1),32 as 0.663 and 0.699 cm⁻¹ for 1 and 2 respectively.

\[ H = (\hbar \omega)^2 - \frac{1}{4} D^2 \frac{1}{Tg^2} \]

(1)

Magnetic measurements

The temperature dependence of the magnetic susceptibility measured in the range 300–5 K is shown in Figs. 4 and 6 for compounds 1, 2 and 3. The small rise in susceptibility at low temperature for 1 and 2 is associated with negligible amounts of paramagnetic impurities.

The solid lines have been computed by using the modified Bleaney–Bowers equation33 (2) for exchange-coupled pairs of copper(II) ions, based on the spin Hamiltonian \(-2JS_i\cdot S_j\). In this expression all symbols have their usual meaning, \(x_m\) is expressed per mole of dimer, \(N_e\) is the temperature independent paramagnetism of the copper atom, and \(\theta\) is a Weiss-like correction to account for possible intermolecular exchange effects. Small \(\theta\) corrections are often included in magnetic data analyses, and negative values are indicative of the presence of antiferromagnetic intermolecular exchange effects. The corrections are usually small and may result from weak lattice interactions or hydrogen-bonding interactions. The monomeric impurity \(p\) was modelled as a Curie paramagnet. The

\[ x_m = \frac{N\beta g^2}{3kT} \left[ 1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} (1 - p) + \frac{N\beta g^2}{3kT} \rho + N_e \]

(2)

\[ \rho = \frac{N\beta g^2}{3kT} \]

Such a treatment allows for the determination of \(N_e\) and \(\theta\) from the difference between the experimental and calculated magnetic susceptibility.

\[ x_m = x_m (T) - x_m (0) \]

The magnetic susceptibility for compound 3 is shown in Fig. 4 corrected for the paramagnetic impurity. The temperature dependence of the magnetic susceptibility for compound 2 is shown in Fig. 5 corrected for the paramagnetic impurity.
Table 4 Magnetic data for pyrazolate bridged dicopper(II) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>$T_M$/K</th>
<th>$g$</th>
<th>$-2J$/cm$^{-1}$</th>
<th>$-\theta$/K</th>
<th>$\rho$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[\text{Cu}_2(\text{pz})_2(\text{dpa})_2(\text{H}_2\text{O})\text{Cl}\right]\text{CH}_2\text{O}$</td>
<td>195</td>
<td>2.12</td>
<td>191</td>
<td>2.0</td>
<td>4.5</td>
</tr>
<tr>
<td>$\left[\text{Cu}_2(\text{pz})_2(\text{phen})_2\text{Cl}_2\text{Cl}_2\text{H}_2\text{O}\right]$</td>
<td>171</td>
<td>2.09</td>
<td>169</td>
<td>2.0</td>
<td>4.3</td>
</tr>
<tr>
<td>$\left[\text{Cu}_2(\text{pz})_2(\text{phen})_2\text{Cl}_2\right]$</td>
<td>171</td>
<td>1.97</td>
<td>169</td>
<td>2.0</td>
<td>4.3</td>
</tr>
<tr>
<td>$\left[\text{Cu}_2(\text{pz})_2(\text{phen})_2\text{Cl}_2\text{H}_2\text{O}\right]$</td>
<td>40</td>
<td>2.10</td>
<td>42</td>
<td>2.3</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Fig. 6 Corrected magnetic susceptibility vs. temperature for $\left[\text{Cu}_2(\text{pz})_2(\text{phen})_2\text{Cl}_2\text{H}_2\text{O}\right]$.

parameters giving the best fit were obtained by using a non-linear regression analysis. Since compound 2 loses solvent quite easily, two fits were done considering the solvated structure as observed by crystallography and an anhydrous structure. Corrected magnetic susceptibility data with this last formula weight gave a lower $g$ value, while the $J$ value remained unchanged (Table 4).

The data of compounds 1 and 2 are typical of a moderate antiferromagnetically coupled dicopper(II) complex, while for 3 a weak antiferromagnetic interaction is present. For the three complexes the susceptibility rises to a maximum and drops at higher temperatures.

The magnitude of the exchange interaction is of the same order in compounds 1 and 2, thus making evident that the axial co-ordinated Cl atom in 1 does not appreciably contribute to the antiferromagnetic coupling ($-2J=191$, 1; 169 cm$^{-1}$, 2). Compound 2 presents only two pyrazolate bridges, which are responsible for the propagation of the moderate antiferromagnetic coupling between the metal centres in the dicopper complex.

Magnetic structure correlations were considered by Bencini and co-workers$^3$ using extended Hückel molecular orbital calculations. Their predictions suggest that the deviation from coplanarity of the two pyrazolate bridges has the largest effect on the exchange interaction. They recorded an experimental 2J value of $-240$ cm$^{-1}$ for the $\left[\text{FeHCl}_{2}(\text{pz})_2(\mu-pz)_2(\mu-\text{Cl})\right]$ complex while Kamiusuki et al.$^{12}$ obtained a value of $-428$ cm$^{-1}$ for the $\left[\text{Cu}_{12}(\text{pz})_2\text{BPh}_2\text{Cl}_2\right]$ complex ($L=3,5$-bis-[2-(diethyldiamino)ethylphenyl]pyrazole) in this latter complex the two pyrazolate bridges are coplanar, while Bencini and co-workers$^3$ reported an angle of 92° between the planes of the pyrazolate anions. The geometry around the copper atoms in 2 is distorted from square pyramidal to trigonal bipyramidal as compared to 1 and that reported by Bencini, and therefore a direct comparison between the 2J values is rather difficult. It has been reported that in pyrazolate bridged complexes the J value is larger when the co-ordination of the copper(II) atoms is planar or square pyramidal ($-J=120$–210 cm$^{-1}$) and relatively smaller when tetrahedral or trigonal bipyramidal ($-J=5$–100 cm$^{-1}$).$^{20}$

For the mono-bridged complex $\left[\text{Cu}_2(\text{dien})_2(\mu-pz)(\mu-\text{Br})\right]_2\text{ClO}_4\cdot\text{H}_2\text{O}$ the copper(II) atoms can be considered as having a $d_{x^2-y^2}$ ground state due to their square-pyramidal geometry.

Therefore the bridging halogen atom will be unfavourable for magnetic exchange since it shares the common apical position of the two square pyramids. Wang and co-workers$^{20}$ reported a monobridged pyrazolate complex with a square-planar geometry around the copper atoms $\left[\text{Cu}_2(\text{H}_2\text{O})_2\right]_2\text{ClO}_4$ ($L=5$-methoxy carbonyl pyrazole-3-carboxylic acid). The exchange interaction between the copper atoms propagated by the monopyrazolate bridge is reported to be antiferromagnetic with $J=-12.3$ cm$^{-1}$. This magnetic coupling is of the same order of magnitude as the one reported by Matsumoto et al.$^{24}$ ($J=-14$ cm$^{-1}$) for $\left[\text{Cu}_2(\text{dim})(\mu-pz)(\mu-\text{Br})\right]_2\text{ClO}_4\cdot\text{H}_2\text{O}$. Both values are lower than the exchange observed for 3 ($J=-21$ cm$^{-1}$).

In order to get a better insight into the bonding and magnetic coupling in the studied compounds, extended Hückel (EH) calculations$^{26}$ were performed, with the use of the CACAO package.$^{27}$ The experimental X-ray molecular geometries were considered in the calculations. The EH atomic parameters used are the same as in a previous study on related compounds.$^{28}$ The calculated single–triplet HOMO/LUMO gap (i.e. separating the two magnetic MOs) is 0.30, 0.23 and 0.14 eV for 1, 2 and 3, respectively. These values are in good qualitative agreement with the magnetic behaviour of these molecules since the HOMO/LUMO gap is expected to vary as the square root of the antiferromagnetic coupling constant.$^{28}$ In the studied compounds the metal atom ligand spheres can be described as being either an octahedron (Cu2 in compound 1) or a square pyramid, more or less distorted toward a trigonal bipyramid (Cu1 in compound 1 and both copper centres in 2 and 3). In all these types of environment the singly occupied orbital of CuII can be roughly described as being of dominant $d_{x^2}$ character.$^{29}$ It follows that the magnetic MOs of the binuclear species 1, 2 and 3 are the in-phase ($\psi_L$) and out-of-phase ($\psi_R$) combinations of the $d_{x^2}$ copper AO's with some ligand participation mixed in an antibonding way. As found previously by us$^{25}$ and others$^{24,30}$ for complexes in which the two metal centres are bridged by one (or two) NN bond(s), the magnetic orbitals differ mainly by their character on the NN bridge(s). These orbitals are schematized in Fig. 7.

As mentioned above, the nitrogen ligand lone pair mixes in an antibonding way with the metal AOs. It follows that the in-phase $d_{x^2}$ combination ($\psi_L$) gets some N-N bonding character, while the out-of-phase combination ($\psi_R$) gets some N-N antibonding character. Therefore, the lowest magnetic orbital is the more bonding one, i.e. $\psi_L$.

Whatever is the real symmetry and possible distortion of the molecule, the topology, phase relationship and level ordering of the magnetic MOs appear to be always that of the idealized $\psi_L$ and $\psi_R$ orbitals.
shown in Fig. 7. The computed N–N overlap population in ϕ1, is −0.035, −0.039 and −0.045 for compound 1, 2 and 3, respectively. The corresponding N–N overlap population in ϕ2 is +0.25, +0.27 and +0.38, respectively. It thus appears that the electronic factors of the two pyrazolato bridges in 1 and 2 are very similar. The moderate difference between their magnetic behaviour comes from the different nature and number of the other ligands. The lower magnetic coupling of 3 originates mainly from the fact that it has a unique pyrazolato bridge.

### Experimental

#### Syntheses of complexes

[Cu(phen)(pz)2]Cl2·2C2H5OH 1. An anethol solution of sodium pyrazid (5 cm³) containing one millimole of sodium pyrazolato (from pyrazole and sodium ethoxide) was mixed with an equimolar solution of copper(ll) chloride in the same solvent (5 cm³). One millimole of the chelating ligand (di(pyridyl)amine) (5 cm³ ethanol) was added with stirring and the product precipitated immediately. Suitable violet crystals for X-ray analysis were obtained by recrystallisation from an acetone–n-butanol solvent mixture. Found: C: 42.5; H: 4.01; Cu, 17.4; N: 19.1. Calc. for [Cu(phen)(pz)2]Cl2·2C2H5OH: C, 43.95; H, 3.79; Cu, 17.88; N, 19.71%.

[Cu(phen)(pz)(H2O)]Cl2·2C2H5OH 2. An equimolar solution of sodium pyrazid was added to a solution of copper chloride (1 mmol) in ethanol (5 cm³), followed by the 1,10-phenanthroline ligand (1 mmol in 5 cm³ ethanol) which was mixed with stirring. The resulting slurry was filtered off, washed with ethanol and dried under vacuum. On standing for several days the remaining solution gave green crystals suitable for X-ray analysis. Owing to solvent loss, two empirical formulae have been used to calculate the percentages of C, H, N and Cu. Found: C: 50.7; H: 4.01; Cu, 16.5; N, 14.8. Calc. for [Cu(phen)(pz)(H2O)]Cl2·2C2H5OH: C, 52.04; H, 4.37; Cu, 16.20; N, 14.28. Calc. for [Cu(phen)(pz)(H2O)]Cl2·2H2O: C, 49.40; H, 3.60; Cu, 17.43; N, 15.37%.

[Cu(phen)(pz)2](H2O)Cl2·2H2O 3. A solution of the ligand phen (2 mmol) in ethanol (5 cm³) was added with stirring to a solution containing copper chloride (2 mmol in 5 cm³ ethanol) and sodium pyrazid (1 mmol) in the same solvent (2.5 cm³). The green precipitate was filtered off, washed with ethanol and vacuum dried. Green crystals suitable for X-ray analysis were obtained by recrystallisation from an acetone–water solvent mixture. Found: C, 45.5; H, 3.25; Cu, 18.1; N, 11.9. Calc.: C, 46.53; H, 3.33; Cu, 18.23; N, 12.06%.

#### Physical measurements

The analyses of C, H, N were performed by Centro de Estudios para el Desarrollo de la Química, University of Chile. X-Band EPR spectra were recorded on an ECE 106 Bruker spectrometer. Magnetic susceptibilities were measured between 5 and 300 K using a SHE 906 SQUID magnetometer, at a field strength of 1 Koe (10³ A/m). Pascal’s constants were used to estimate the diamagnetic correction of the samples.[11]

#### X-Ray crystallography

Compound 2 was diffacted in a capillary tube saturated with solvent, since the crystals were unstable over time. The loss of solvating molecules from the crystal under ambient conditions determined the decay of the measured reflections, even when the crystal was covered with a protective coating of a hydrocarbon oil. Crystal data, data collection and processing, structure analysis and refinement for complexes 1, 2 and 3 are summarised in Table 5. Crystallographic programs employed were the Siemens data collection software and SHELXTL PLUS.[12] Scattering factors were from ref. 33.

CCDC reference number 185/1553.

### Acknowledgements

This research was supported in part by Fundación Andes and Fondo Nacional de Ciencia y Tecnología (project 7980050). We are also grateful to the Evaluation-orientation de la Cooperation Scientifique (France)-Comisión Nacional de Investigación Científica y Tecnológica (Chile) collaboration program (project C97E01).

#### References
