Methyl groups control coordination number, stoichiometry, network and magnetism in a Cu(II)-azide-pyrazine (6,3) 2D net

Alshima’a A. Massoud†*, Morsy A. M. Abu-Youssef†, Jana PoltieroVá Vejpravová†, Vratislav Langer† and Lars Öhrström†*

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The methyl groups of [Cu2(2,5-dimethylpyrazine)(N3)3]n, 1, force penta-coordination on the Cu(II) ions, which, together with the di-µ1,3-azido zigzag chains, result in a (6,3) 2D net with dominant ferromagnetic interactions.

To synthesise molecule-based magnetic materials is an attractive, but difficult, goal for crystal engineers.1 Many of the reported high Tc systems have been created with the help of coordination chemistry, although the complete structures of these materials remain unknown,2 with the exception of the hexacyanomellitate systems.3

The azide ligand, another pseudo-halide, commonly mediates strong magnetic couplings between transition metal compounds, but has not yet yielded any such materials magnetic at room temperature. In addition to this challenge, the many possible bridging modes (scheme 1)5, 6 of the azide ion make the rational preparation of such structures a crystal engineering problem of some dignity. Consequently, the structure and magnetism of these compounds continue to attract attention.6

![Scheme 1](image)

Scheme 1: Most common bridging modes for azides ions illustrated by double bridged end-on, µ1,3-N3, EO (left) and double bridged end-to-end, µ1,2-N3, EE (right). M is commonly 4, 5 or 6 coordinated.

A way of increasing the dimensionality of these systems is to add a bridging co-ligand (scheme 2), and recently we have shown that [{Cu(N3)4}2Cu(N3)(methylpyrazine)]2-, 7 is a 3D coordination polymer with the unusual (4.102)2(4.104)-dmd topology,8 where the pyrazine transmits weak antiferromagnetic couplings, as reported in many other cases.9

In this communication we report on the synthesis, and the distinctively different structure and magnetism of the compound obtained with the related 2,5-dimethylpyrazine ligand: [Cu2(2,5-dimethylpyrazine)(N3)3]n, completing a triad begun by Dong et al. with the pyrazine compound.10

![Scheme 2](image)

Scheme 2: Bridging co-ligands pyrazine, methylpyrazine and 2,5-dimethylpyrazine used to prepare respectively 2D,10 3D and 2D (this paper) coordination polymers with Cu(II) and azide ions.

[Cu2(2,5-dimethylpyrazine)(N3)3]n, 1 was obtained by reaction of the ligand with Cu(NO3)2·3H2O in an ethanol : water mixture with excess NaN3.11 X-ray diffraction5 revealed the structural unit shown in Fig. 1.

![Figure 1](image)

Fig. 1 Perspective view of [Cu2(2,5-dimethylpyrazine)(N3)3]n. 1. Atomic displacement ellipsoids drawn at 50% probability level. Symmetry codes: (i) -x+1, -y+1, -z (ii) -x, -y+1, -z (iii) -x, -y+1, -z+1

The 2,5-dimethylpyrazine ligand, as well as the Cu2N2 units lie about independent inversion centres. The Cu(II) ion is penta-coordinated (CuN5), in a distorted trigonal bipyramidal geometry, binding four nitrogens from azido anions and one nitrogen from 2,5-dimethylpyrazine (see Fig. 1). The three equatorial Cu-N7, Cu-N11, Cu-N4 bond distances are 2.095(3), 2.190(4) and 2.009(3) Å, respectively, with bond angles 137.60(16), 121.88(15) and 100.00(13)°. The two apical Cu-N1 and Cu-N4 bond distances are 1.965(3) and 1.981(4) Å with a N-Cu-N angle 171.46(15)°. These data are consistent with known (CuN5) trigonal bipyramidal complexes.3, 11, 12 The azide ions are coordinated to the Cu ions in a di-EO (µ1,1-N3) fashion giving Cu2N2 units forming a zigzag chain along the a-axis. The dimethylpyrazines connect these chains along the c-axis giving rise to a (6,3) 2D net in the ac-plane as shown in Fig. 2.

This 2D grid-like structure shows weak C–H···N hydrogen bonds between the crystallographically well defined -CH3 group of the dimethylpyrazine ligand and the azido terminal N.
atoms, affecting also the asymmetry of the EO bridging azido groups and the rectangular Cu₂N₂ units. On the first-level of the graph-set they form chains C(8) and C(10).

Despite the richness of metal-azide structures, (>1000 entries in the Cambridge Structural Database) there are few structures containing a doubly bridged end-to-end coordination polymer chain. Moreover, double end-to-end chains are even rarer than the end-on chains found in compound 1. We tentatively attribute this to the spacing of ~5 Å of the metal ions, which is too far apart to obtain π-π stacking of axial aromatic ligands, but not far enough to conveniently fit in another molecule. Thus rigid objects such as polymeric rods of this type may be difficult to pack.

![Fig.2](image)

**Fig.2** The (6,3) 2D-net in [Cu₃(2,5-dimethylpyrazine)(N₃)₄]ₙ, 1.

For end-on azide polymers, the situation is different. For example in [Cu₂(pyrazine)]₂(N₃)₄ there is efficient π-π stacking between ligands on adjacent octahedral Cu centres. Replacing the pyrazine with 2,5-dimethylpyrazine efficiently blocks the π-π stacking, so an iso-structural compound is inconceivable. Efficient packing in the pyrazine compound is also manifested by the higher density (disregarding the different stoichiometry), 2.12 g/cm³ vs. 1.95 g/cm³ for 1.

The stoichiometry and the coordination number of Cu(II) will be determine the kind of net formed. Methyl groups ortho to a coordinated nitrogen will decrease the coordination number because of steric crowding, imposing 5-coordination around the metal ion. In [Cu₂(pyrazine)]₂(N₃)₄ with an octahedral Cu(II), a very regular (4,4) 2D grid was obtained. Terminal N...H-C weak hydrogen bonds connect the 2D sheets in this compound, as in 1, but with a more regular packing.

[Cu(N₃)₂Cu(N₃)₂(methylpyrazine)₅]₃ shows yet another stoichiometry, Cu/pyrazine 3:2, and has both penta- and hexacoordinated Cu(II), resulting in a 3D (4.10⁻²)₄(4.10⁻³)-dmd̂-net. It is not clear why this particular stoichiometry leads to a 3D net, but it may be related to the fact that the 2D, three- and four-connected net that can be constructed with a 2:1 relation between the nodes is the Cairo tiling of pentagons.

The molar magnetic susceptibility data are shown in Fig. 3. At 2 K χ is near 0 cm³/mol, reacing a maximum at 33 K and then moderately decreasing to χ=0.0017 cm³/mol at room temperature. The corresponding room-temperature value of the effective magnetic moment, μₑff=2.02 Nabcdefg (μₑff=2.82χ(T)⁻¹/²) is considerably enhanced in comparison with the single Cu²⁺-value (1.73 Nabcd). Taking into account the α temperature independent susceptibility term, χ₀= 3.0 x 10⁻⁴ cm/mol obtained from the χ vs. T analysis this value decreases to the more relevant 1.84 Nabcd.

The maximum in the temperature dependence of χ suggest a ferromagnetic coupling of the Cu ions, and absolute values of χ are also typical for Cu complexes with intermediate-strength ferromagnetic coupling.

![Fig.3](image)

**Fig.3** The magnetism for 1 presented as χT vs. T (squares) and as χ vs. T (circles). The solid line represents the best fit of χ vs. T using a 1D chain model with 2D corrections giving J=24.0 cm⁻¹ and J’=0.4 cm⁻¹.

To test this, a model considering a chain of Cu-azides coupled by J, (H=~2EZS₈₈i₋₁) and additional small coupling J', was fitted to the data, yielding, J = 24.0 ± 0.09 cm⁻¹ and J’= 0.4 ± 0.05 cm⁻¹.

The ferromagnetic coupling through the azides was expected, although it has been suggested that end-on coupling should be antiferromagnetic if the Cu-N-Cu bond angle is larger than 104° (the angles in 1 are 102.95(16)° and 100.13(15)°). However, the small ferromagnetic coupling tentatively assigned to the pyrazine bridge needs accounting for, as these interactions are normally antiferromagnetic (i.e. in the related pyrazine and methyl-pyrazine compounds). The existing examples of ferromagnetic interactions through pyrazine bridges in Cu(II) compounds have been explained by orthogonal magnetic orbitals. In the case of 1, the distinctively longer equatorial bond lengths suggest that the unpaired electrons reside in a d-orbital in the equatorial plane, and for neighbouring Cu(II)s these orbitals are related by a centre of inversion and thus cannot be orthogonal.

However, a tentative explanation can be provided by spin-polarization. Through the covalent part of the coordination bond, spin will be delocalized onto the Cu-N₈p α-bond, and inducing a positive spin polarization of the N₈p pₐ-orbital. As the total spin density is constant, this will be compensated by negative spin polarization of the other pₐ-orbitals in the highest MO with a large N₈p pₐ-component (see Scheme 3).

Now, for symmetry reasons this orbital will have a large component also on the second nitrogen, and only small components on the remaining carbon atoms. Consequently, negative spin density will build up on the nitrogen close to the second Cu atom, and this in turn will generate a ferromagnetic coupling through what has been described as the third case of...
the McConnell-I Mechanism\(^{21}\).

![Scheme 3](image)

**Scheme 3** Schematic view of the interactions MOs and spin densities in 1; a and b: the magnetic orbitals on Cu (\(d_{z^2}\)) will give the same result). c: the \(\pi\)-HOMO has no components on N; d: the \(\pi\)-HOMO-1 will be spin polarized; e: the resulting spin polarization (green positive, mauve negative) giving negative spin density on the remote nitrogen atom.

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**Notes and references**