

A Binuclear Copper(II) Complex Containing the Pyrazine-2,5-dicarboxylate Ligand: Study of the Magnetic Exchange through the Pyrazine Bridge

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The compound $[\text{Cu}_2(\mu\text{-pzdc})(\text{phen})_4](\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ (**1**; pzdc = pyrazine-2,5-dicarboxylate; phen = 1,10-phenanthroline) has been structurally and magnetically characterised. Theoretical calculations have allowed us to establish a plausible magneto-structural correlation for pyrazine-bridged complexes.

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Introduction

A lot of work has been devoted to the study of the magnetic interactions between two paramagnetic centres bridged by an aromatic ring.^[1] The study of the spin delocalisation and polarisation effects is helpful in order to understand the nature of these magnetic interactions. The spin-polarisation mechanism itself provides a key tool for predicting the kind of magnetic interactions in high-spin organic molecules, and therefore for designing molecule-based magnets.^[2] Nevertheless, the application of this strategy to transition metal complexes, which provide a more stable spin source than those based on organic radicals, is more tricky, and the spin-delocalisation effect must also be taken into account.^[3] Metal complexes containing pyrazine-2,5-dicarboxylate (pzdc) ligands have seldom been investigated.^[4] Until now, as far as we aware, a three-dimensional Mn^{II} complex^[5] and a binuclear V^{V} complex^[6] are the only structurally characterised examples with this ligand.

We report here the synthesis,^[7] crystal structure^[8] and magnetic properties of a complex with formula $[\text{Cu}_2(\mu\text{-pzdc})(\text{phen})_4](\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$ (**1**). In addition, a plausible magneto-structural correlation for pyrazine-bridged complexes is analysed by DFT methods.

Results and Discussion

The structure of compound **1** consists of water molecules of crystallisation, nitrate counterions and centrosymmetric

$[\text{Cu}_2(\mu\text{-pzdc})(\text{phen})_4]^{2+}$ binuclear units (Figure 1) in which a bidentate pzdc ligand bridges two copper atoms with an $\text{M}\cdots\text{M}$ distance of 7.112 Å. The distorted octahedral environment around each copper atom is completed by four nitrogen atoms of two phen ligands (phen1 and phen2). We can distinguish two long bonds in the *trans* position formed by an oxygen of the carboxylate group and a nitrogen of the phen2 ligand [$\text{Cu1}-\text{O41}$ 2.271(3) Å, $\text{Cu1}-\text{N38}$ 2.210(3) Å]. The four shortest bonds are nearly coplanar and are to two N atoms from phen1 [$\text{Cu1}-\text{N11}$ 2.115(3) Å, $\text{Cu1}-\text{N18}$ 2.011(2) Å], another one from phen2 [$\text{Cu1}-\text{N31}$ 2.003(2) Å] and a one from the bridging ligand [$\text{Cu1}-\text{N1}$ 2.184(2) Å]. This equatorial plane is almost perpendicular to the mean plane of the pzdc ligand [dihedral angle 81.7(2)°]. Similar distorted octahedral environments have been reported for other phen or 2,2'-bipyridine copper complexes.^[9] The deviation of the metal atom from the pyrazine ring is quite significant [0.209(1) Å], probably due to the steric hindrance of the terminal ligands.

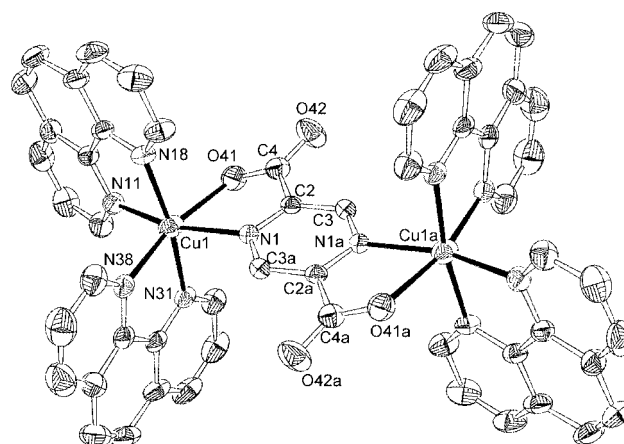


Figure 1. ORTEP view of the dimeric entity in compound **1**.

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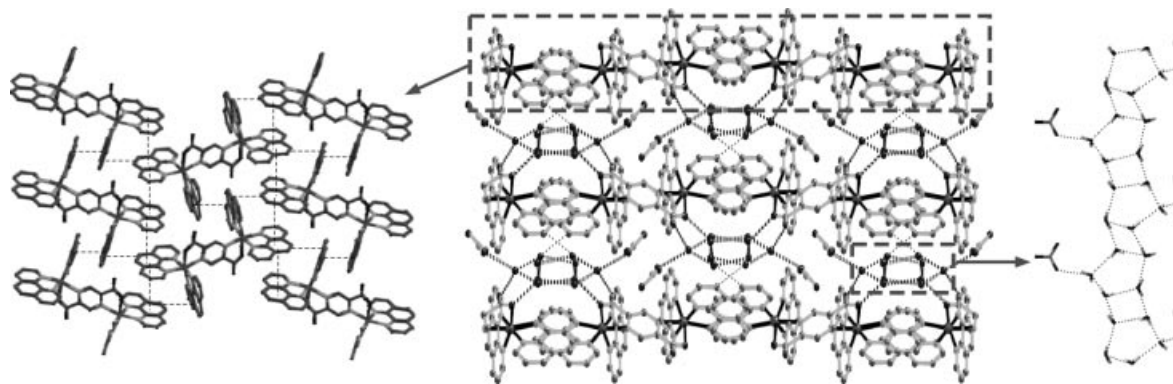


Figure 2. Crystal structure viewed along the [001] direction showing π - π interactions (dashed lines) within the cationic layers and hydrogen-bonded (dotted lines) chains of water molecules.

In the crystal structure (Figure 2), the cationic complexes are held together by means of face-to-face and edge-to-face π - π interactions between the aromatic phen ligands to form corrugated layers parallel to the bc plane. The water molecules are inserted in the interlayer space and are linked themselves by $O_w-H\cdots O_w$ hydrogen bonds to form zig-zag strips comprised of an alternating sequence of fused water pentamers and tetramers running along the [001] direction. The nitrate anions are attached to the edges of the pentagonal water ring by a hydrogen bond. There are no significant interactions between adjacent strips, therefore the water strips act as bridges between the cationic layers by means of a highly complex network of non-covalent interactions. Compound **1** shows a different crystal packing to those described in a recent study^[10] of the most common packings of complexes based on phen ligands, and bears a very close resemblance to the compound $[\{Cu(ox)(phen)_2\}\cdot 5H_2O]$.^[11] Both compounds show a similar π - π interaction scheme within the corrugated complex layers. Due to this conformation, there is a similarity between the hydrophilic holes in the interlayer space, which leads to a similar arrangement of the solvated water molecules.

Variable-temperature magnetic-susceptibility measurements (2–200 K) show the presence of weak antiferromagnetic coupling, with values of $J = -5.7 \text{ cm}^{-1}$ and $g = 2.14$ obtained from the Bleaney–Bowers expression ($H = -JS_A \cdot S_B$) for a binuclear copper(II) complex. This antiferromagnetic coupling is mainly attributed to the magnetic interaction through the pyrazine ring. The contribution of the carboxylate groups can be considered negligible due to the long magnetic pathway involving these groups.

DFT methods have shown to give good estimates of the magnetic interactions.^[12] A detailed description of the computational strategy adopted in this work is given elsewhere.^[13] For the evaluation of the coupling constant, two separate DFT calculations were carried out, from which the energy of the highest spin (E_{HS}) and broken-symmetry singlet configuration (E_{BS}) are obtained. The magnetic coupling constant results from the energy difference between the triplet and singlet states ($E_{HS} - E_{BS} = -J$). The hybrid B3LYP method, as implemented in Gaussian 03, was used in all calculations.^[14] The exact Hartree–Fock-type exchange was

mixed with Becke's expression for the exchange functional and the Lang–Yong–Parr correlation functional was used. A basis set of double- ζ quality (triple- ζ for the transition metal atoms), proposed by Schäfer et al.,^[15] was employed throughout.

The calculations were performed for an isolated $[Cu_2(phen)_4(\mu\text{-pzdc})]^{2+}$ dimer with an experimental geometry of C_i symmetry, leading to a value of the magnetic interaction ($J_{calc} = -8.4 \text{ cm}^{-1}$) similar to the experimental one ($J_{exp} = -5.7 \text{ cm}^{-1}$). Figure 3 illustrates the spin densities for the ground state ($S = 0$) of the title compound. The spin-density distribution around the metal centre resembles a $d_{x^2-y^2}$ orbital with a significant contribution of d_{z^2} . The coordinated Cu1 and pzdc atoms (N1 and O41) carry spin densities with the same sign due to the spin-delocalisation effect. This situation is in sharp contrast to that of organic high-spin materials bridged by m -phenylenes,^[2] in which the spin density alternates throughout the π -conjugated hydrocarbon network, as predicted by the spin-polarisation mechanism.

Most of the previously reported Cu^{II} complexes with pyz-type (pyz = pyrazine) bridging ligands coordinated at

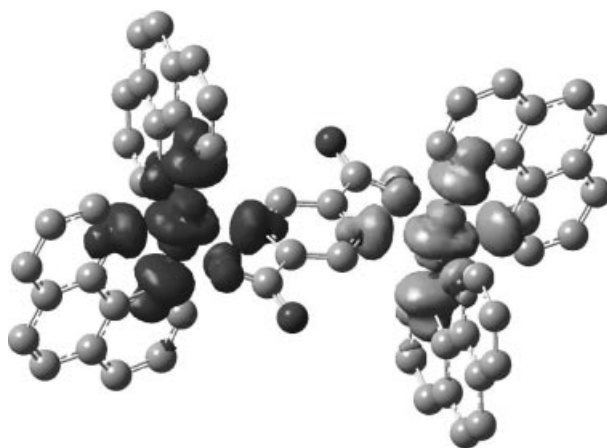
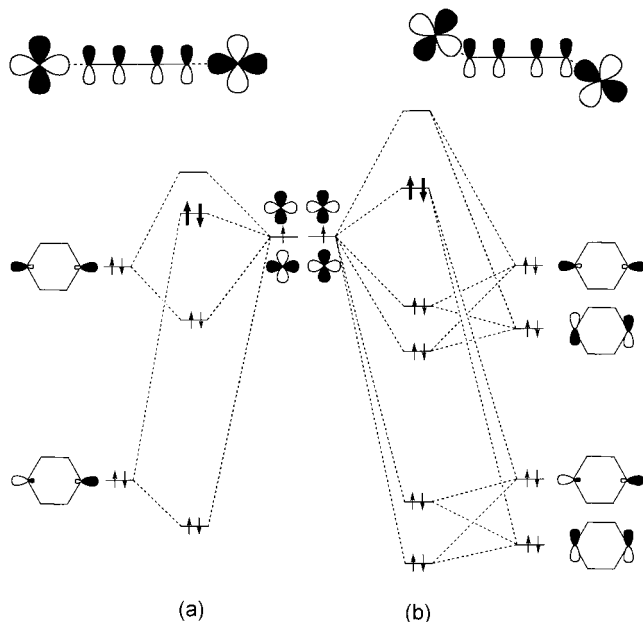


Figure 3. Calculated spin-density distribution for the ground state ($S = 0$) of $[Cu_2(phen)_4(\mu\text{-pzdc})]^{2+}$ with a surface threshold level of 0.001. Hydrogen atoms have been omitted for clarity. Spin densities: Cu1 0.667, N31 0.105, N11 0.057, N18 0.099, O41 0.025, N1 0.043, N38 0.020, C2 -0.006, C3a -0.008.

the equatorial sites show very weak antiferromagnetic interactions ($|J| < 4 \text{ cm}^{-1}$).^[16] However, there are a handful of pyz-bridged Cu^{II} complexes, specially with the tppz ligand [1,3,5,6-tetra(2-pyridyl)pyrazine], that present unusually large antiferromagnetic interactions,^[17] with J values ranging from -35 to -61 cm^{-1} . A common structural feature of the latter compounds is the large displacement of the metal from the mean plane of the pyrazine bridge (0.34 – 0.56 \AA) and/or the distortion of the pyrazine ring (dihedral angles between the two C–N–C planes of the pyz ring range between 8.8 and 11.0°). Due to the structural features of the title compound, we have restricted the present work to the analysis of the former structural parameter, which allows a σ -overlap between the metal $d_{x^2-y^2}$ orbital and the π -orbitals of the pyrazine ring; in an ideal planar system this $d_{\sigma}-p_{\pi}$ overlap is not allowed (part a in Scheme 1). Taking into account these facts, the observed values of J could be attributable to an important contribution of the π -orbitals of the pyz-type ligand through a $d_{\sigma}-p_{\pi}$ interaction, which is allowed by the structural distortion (Scheme 1, part b). The title compound represents an intermediate situation between the negligible values commonly observed and the cited unusually high values.



Scheme 1. Orbital interaction diagram showing the interaction between the two Cu $d_{x^2-y^2}$ orbitals and a) the σ -symmetry orbitals and b) the σ - and π -orbitals.

In order to determine the contribution of the π -orbitals of the bridging ligand to the magnetic behaviour, we carried out DFT calculations on a pyrazine-bridged dimeric Cu^{II} model for different values of the $\text{Cu}-\text{N}_{\text{pyz}}\cdots\text{N}_{\text{pyz}}$ angle (see details in Figure 4). The values obtained for the magnetic coupling constant indicate an exponential increase of the J value with a decrease of the $\text{Cu}-\text{N}_{\text{pyz}}\cdots\text{N}_{\text{pyz}}$ angle. The J value is -6.8 cm^{-1} at 180° , but reaches values as high as -144 cm^{-1} for an angle of 130° .

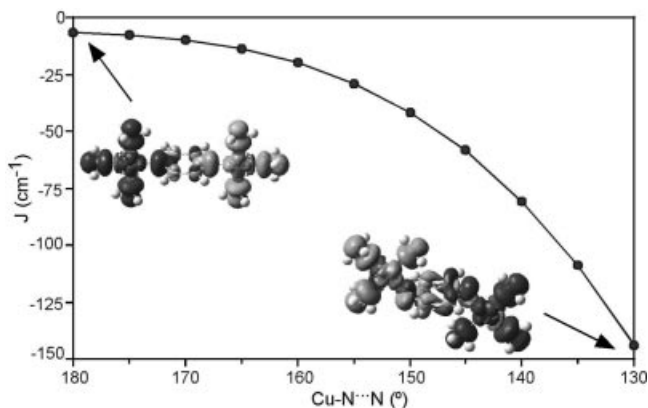


Figure 4. Calculated coupling constants for $[\text{Cu}_2(\text{NH}_3)_6(\mu\text{-pyz})]^{4+}$ as a function of the $\text{Cu}-\text{N}_{\text{pyz}}\cdots\text{N}_{\text{pyz}}$ angle. The inset graphics represent the spin-density distribution for the two extreme angles. Calculations have been performed in an idealised C_{2h} symmetry using the following bond lengths [\AA] and angles [$^\circ$]: Cu–N 2.00, C–N: 1.35, C–C 1.42, C–H 1.00, N–H 1.00, N–Cu–N 90.0 , N–Cu–N–C 90.0 , $\text{Cu}-\text{N}_{\text{pyz}}\cdots\text{N}_{\text{pyz}}$ 130.0 – 180.0 .

As depicted in Scheme 1 (part a), when the $\text{Cu}-\text{N}_{\text{pyz}}\cdots\text{N}_{\text{pyz}}$ angle is 180° , the two Cu $d_{x^2-y^2}$ orbitals overlap with the two symmetry-adapted σ -orbitals of the pyrazine. The energy of these σ -orbitals is not equal, leading to a substantial energy difference between the two singly occupied orbitals of the dimer and, consequently, an antiferromagnetic coupling through the pyrazine is observed. If the $\text{Cu}-\text{N}_{\text{pyz}}\cdots\text{N}_{\text{pyz}}$ angle is not linear the overlap of the two Cu $d_{x^2-y^2}$ orbitals involves the symmetry-adapted σ - and π -orbitals of the bridge, and the energy difference between the two SOMOs increases, leading to an increase of the antiferromagnetic interaction (part b in Scheme 1). No simple relation between the spin density at the pyrazine bridge and the magnetic coupling constant has been found.

The experimental J value (-5.7 cm^{-1}) is comparable to that obtained for the model compound with a similar $\text{Cu}-\text{N}_{\text{pyz}}\cdots\text{N}_{\text{pyz}}$ angle (-9.8 cm^{-1}) taking into account the small singlet–triplet gap. In agreement with the trend shown in Figure 4, the pyrazine-bridged complex with the highest J value^[16a] (-61.1 cm^{-1}) shows the greatest deviation of the metal from the mean plane of the pyrazine. However, the values of other tppz-based complexes cannot be fitted easily, due to the high distortion that the pyrazine ring presents.

Other structural factors, such as the $\text{Cu}-\text{N}_{\text{pyz}}$ distance, the dihedral angle between the Cu^{II} equatorial plane and the pyrazine plane, the influence of the axial ligand, etc. seem to have a less decisive role on the magnetic properties (see Supporting Information).

Acknowledgments

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- [1] a) A. M. W. Cargill Thompson, D. Gatteschi, J. A. McCleverty, J. A. Navas, E. Rentschler, M. D. Ward, *Inorg. Chem.* **1996**, *35*, 2701–2703; b) O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, **1993**.
- [2] a) S. K. Silverman, D. A. Dougherty, *J. Phys. Chem.* **1993**, *97*, 13273–13283; b) H. Iwamura, *Adv. Phys. Org. Chem.* **1990**, *26*, 179–253; c) A. Rajca, *Chem. Rev.* **1994**, *94*, 871–893.
- [3] J. Cano, E. Ruiz, S. Álvarez, M. Verdaguer, *Comments Inorg. Chem.* **1998**, *20*, 27–56.
- [4] a) L. R. Harlow, S. H. Simonsen, *Acta Crystallogr. Sect. B* **1974**, *30*, 1370–1372; b) H. Ptasiwicz-Bak, J. Leciejewicz, *J. Coord. Chem.* **1998**, *44*, 299–309; c) H. Ptasiwicz-Bak, J. Leciejewicz, *J. Coord. Chem.* **1998**, *44*, 237–246.
- [5] G. Beobide, O. Castillo, A. Luque, U. García-Couceiro, J. P. García-Terán, P. Román, *Inorg. Chem. Commun.* **2003**, *6*, 1224–1227.
- [6] G. Süß-Fink, L. González Cuervo, B. Therrien, H. Stoeckli-Evans, G. B. Shul'pin, *Inorg. Chim. Acta* **2004**, *357*, 475–484.
- [7] Compound **1** was prepared in aqueous solution (30 mL) from the stoichiometric reaction between $\text{H}_2\text{pzdc} \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and phen. The reaction yielded a blue, polycrystalline precipitate of compound **1**. After filtering off the precipitate the resulting solution was allowed to stand at room temperature. Single crystal growth was observed after six days. Yield: 65%. $\text{C}_{54}\text{H}_{54}\text{Cu}_2\text{N}_{12}\text{O}_{20}$: calcd. C 48.97, H 3.99, Cu 9.51, N 12.69; found C 49.20, H 4.13, Cu 9.64, N 12.75.
- [8] Crystal data for **1**: Monoclinic, space group $P2_1/c$, $a = 10.421(1)$, $b = 26.566(3)$, $c = 10.718(2)$ Å, $\beta = 108.24(1)^\circ$, $U = 2818.1(7)$ Å³, $Z = 2$, $\mu(\text{Cu}-\text{K}\alpha) = 1.5418 \text{ mm}^{-1}$. Final R [4330 with $I \geq 2\sigma(I)$] = 0.0496 and wR_2 (4687 unique reflections) = 0.1337. CCDC-254764 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [9] a) D. Choquesillo-Lazarte, M. J. Sánchez-Moreno, E. Bugella-Altamirano, M. J. Moyano-Gallego, J. D. Martín-Ramos, J. M. González-Pérez, R. Carballo, J. Niclos-Gutiérrez, *Z. Anorg. Allg. Chem.* **2003**, *629*, 291–296; b) H. J. He, L. G. Zhu, *Chin. J. Inorg. Chem.* **2003**, *19*, 317–320; c) O. Costisor, M. Brezeanu, Y. Journaux, K. Mereiter, P. Weinberger, W. Linert, *Eur. J. Inorg. Chem.* **2001**, 2061–2066.
- [10] V. Russel, M. Scudder, I. Dance, *J. Chem. Soc., Dalton Trans.* **2001**, 789–799.
- [11] O. Castillo, A. Luque, P. Román, *J. Mol. Struct.* **2001**, *559–601*, 181–188.
- [12] E. Ruiz, J. Cano, S. Álvarez, P. Alemany, *J. Comput. Chem.* **1999**, *20*, 1391–1400.
- [13] a) E. Ruiz, P. Alemany, S. Álvarez, J. Cano, *J. Am. Chem. Soc.* **1997**, *119*, 1297–1303; b) E. Ruiz, A. Rodríguez-Fortea, J. Cano, S. Álvarez, P. Alemany, *J. Comput. Chem.* **2003**, *24*, 982–989.
- [14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh PA, **2003**.
- [15] a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577; b) A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829–5835.
- [16] a) H. Grove, J. Sletten, M. Julve, F. Lloret, *J. Chem. Soc., Dalton Trans.* **2000**, 515–522; b) T. Okubo, M. Kondo, S. Kitawaga, *Synth. Met.* **1997**, *85*, 1661–1662; c) J. Suárez-Varela, E. Colacio, A. Romerosa, J. C. Ávila-Rosón, M. A. Hidalgo, J. Romero, *Inorg. Chim. Acta* **1994**, *217*, 39–44.
- [17] a) M. Graf, H. Stoeckli-Evans, A. Escuer, R. Vicente, *Inorg. Chim. Acta* **1997**, *257*, 89–97; b) E. Burkholder, V. Golub, C. J. O'Connor, J. Zubieta, *Inorg. Chem.* **2003**, *42*, 6729–6740; c) J. Carranza, J. Sletten, C. Brennan, F. Lloret, J. Cano, M. Julve, *Dalton Trans.* **2004**, 3997–4005.

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