[Zn_n(polyox)(pmtz)$_n$]: the first polyoxalate-containing coordination polymer from an unforeseen chemical rearrangement of 5-pyrimidyl-tetrazole under hydrothermal conditions

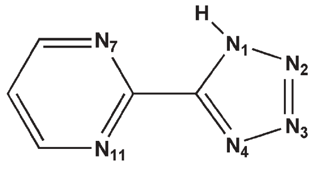
A. Rodríguez-Diéguez and E. Colacio*

Received (in Cambridge, UK) 14th June 2006, Accepted 31st July 2006
First published as an Advance Article on the web 21st August 2006
DOI: 10.1039/b608403f

The compound [Zn_2(polyox)(pmtz)$_2$], which has been prepared by the hydrothermal reaction of $ZnCl_2$ and Napmtz (5-pyrimidyl-tetrazolate), exhibits a unique 2D network with (6,3) topology, in which Zn^{II} ions are connected by pmtz- and polyoxalate-bridging ligands (generated *in situ* from the breaking of the pmzt$^-$ ligand). This is the first structural report on a polyoxalate species.

In recent years, there has been increasing research interest in the design and synthesis of extended coordination frameworks as potential zeolitic, magnetic, conducting, nonlinear optical materials, *etc.*[1] Although most of these systems have been synthesized by controlled mixing of suitable soluble molecular components, solvothermal conditions have provided increasing success in alternative pathways to the preparation of single-crystalline supramolecular solids, including metal–organic coordination networks and hydrogen-bonded systems. In this context, 5-substituted-1-*H*-tetrazole ligands have been shown to be excellent and versatile building blocks, with charge and multi-connectivity ability, to produce under hydrothermal conditions multidimensional coordination polymers with interesting optical properties.[2] Recently, by using hydrothermal methods, we have succeeded in obtaining the first example of a 5-substituted tetrazolate-bridged extended system with paramagnetic metal ions [Co(pmtz)$_2$] (pmtz = 5-pyrimidyl-tetrazolate, Chart 1), which behaves as a spin-canted antiferromagnet and magnetically orders at T_c = 12 K.[3]

As a part of our work in this area, we report here the structural properties of the complex [Zn_n(polyox)(pmtz)$_n$], which contains an unforeseen polyoxalate (polyox) ligand. This compound has been prepared[4] by reaction of $ZnCl_2$ and Napmtz under hydrothermal conditions and exhibits a 2D metal–polyoxalate network, in which Zn^{II} ions are connected through polyoxalate and pmtz$^-$ ligands. The polynucleating polyoxalate ligand is generated *in situ* from an unforeseen chemical rearrangement of the pmtz$^-$ ligand. The mechanism of this process might consist in the oxidation of the pmtz$^-$ ligand to oxalic acid and further polymerization to polyoxalate assisted by the Zn^{II} ions. The fact that under hydrothermal conditions the pmtz$^-$ ligand affords in some cases oxalate-containing complexes[5] seems to support the proposed mechanism. In connection with this, it has been shown recently that pyridinecarboxylate species afford oxalate-bridged polymeric complexes under hydrothermal conditions.[6] It should be noted that in the absence of Zn^{II} ions, the reaction does not lead to polyoxalate but to a mixture of oxalate and pmzt$^-$. Moreover, preliminary results indicate that counterions of the Zn^{II} salt do not play a significant role in the formation of the polyoxalate ligand.



Hpmtz

Chart 1

The structure of [Zn_n(polyox)(pmtz)$_n$]† consists of polyoxalate–Zn^{II} infinite chains running along the *a* axis (Fig. 1) connected by pmtz$^-$ bridging ligands, to give rise to an unique 2D network with (6,3) topology in the *ac* plane (Fig. 2). Because of the imposed crystallographic symmetry, all atoms except O_1 and C_{12} lie on mirror planes.

Neighbouring polyoxalate–Zn^{II} chains are not in the same plane, but in parallel planes with an interplanar distance of 2.141 Å. Within the polyoxalate–Zn^{II} chain, metal ions are alternatively located at both sides of the chain adopting a zig-zag disposition. The polyoxalate ligand has in plane–tridentate–O_3 sites, which, when coordinated to the Zn^{II} ions, generate two five-membered rings. Zn^{II} ions, which are related by a twofold axis located at the middle of the oxalate C–C bond, exhibit a distorted octahedral ZnN_3O_3 coordination polyhedron. In this description, three *mer* coordination positions are occupied by the three oxygen atoms of each nucleating site of the polyoxalate ligand, whereas three tetrazole nitrogen atoms occupy the other remaining three *mer* positions, the mean planes of the polyoxalate chain and pmtz$^-$ ligand being mutually perpendicular. Each pmtz$^-$ ligand is coordinated to a Zn^{II} ion in a chelate fashion through the N1 tetrazole and the N7 pyrimidyl nitrogen atoms, and to the

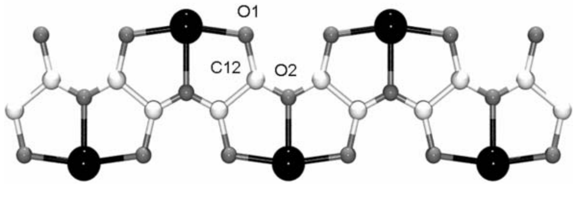


Fig. 1 A view of the polyoxalate–Zn^{II} chain.

Departamento de Química Inorgánica, Universidad de Granada, Avenida Fuentenueva s/n, 18071, Granada, Spain. E-mail: ecolacio@ugr.es; Fax: 34-958248526

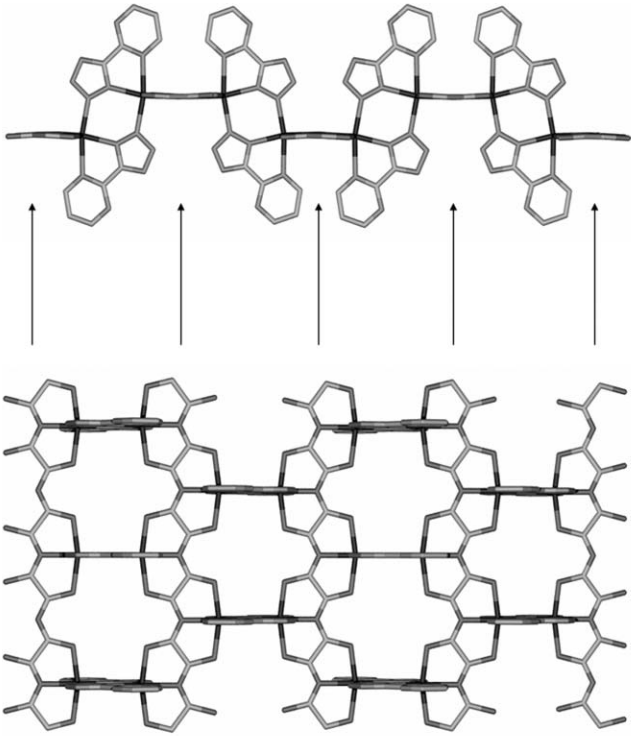


Fig. 2 Views of a layer of [Zn_n(polyox)$(pmtz)_n$] showing the dinuclear units [$Zn_2(pmtz)_2$] in the *bc* plane (top) and the linking of the polyoxalate–Zn^{II} chains by $pmtz^-$ ligands in the *ac* plane (bottom).

neighbouring Zn^{II} ion through the N_2 tetrazole atom, thus acting as a tridentate bridging ligand. This is the first time that the κ^2-N_1,N_7 : κ-N_2 coordination mode of the ligand is observed in 5-substituted-tetrazolate bridged complexes. The Zn–O and Zn–N bond distances are in the 2.062(8)–2.135(4) Å and 2.114(5)–2.250(6) Å ranges, respectively, whereas *cis* and *trans* X–Zn–X angles are in the 76.1(2)–99.2(3)° and 164.5(3)–168.55(19)° ranges, respectively.

Each two Zn^{II} ions in neighbouring polyoxalate–Zn^{II} chains are connected by a pair of $pmtz^-$ bridging ligands generating centrosymmetric $Zn_2(\mu\text{-pmtz})_2$ dinuclear units. Each of these Zn^{II} ions is linked to three other Zn^{II} ions (two belonging to the same chain and one to a neighbouring one) giving rise to layers with (6,3) topology (Fig. 2). The Zn···Zn distance through the pmtz- ligand is 4.282 (5) Å , whereas the shortest Zn···Zn distances through the polyoxalate ligand between metal atoms at the same side and at opposite sides of the chain are of 5.656(5) and 7.030(5) Å, respectively.

Layers, with the $pmtz^-$ ligands pointing outwards, are stacked in such a fashion as to align the $pmtz^-$ ligands above and below one layer with the cavities in neighbouring networks, leading to an ABAB…. repeating pattern with a shortest interlayer separation of 7.812 Å.

Although several oxalate and metal oxalate compounds have been employed as precursors in the hydrothermal preparation of novel oxalate-bridged coordination polymers, however, in no case is a polyoxalate ligand formed.[8] Therefore, it seems that the $pmtz^-$ anion plays an important role in the formation of polyoxalate species. Further work remains to be done in order to check the influence of factors such as temperature, pH, the presence of Lewis acids, the use of other metal ions, *etc.*, on the polymerization reaction and the products distribution.

This work was supported by the Spanish Ministerio de Ciencia y Tecnología through Projects BQU 2001/3221 and CTQ 2005/09023 and the Junta de Andalucía. A.R. thanks the Ministerio de Ciencia y Tecnología for a predoctoral fellowship. We thank reviewers for their interesting suggestions.

Notes and references

† *Crystal data* of [Zn_n(polyox)$(C_5H_3N_6)_2$], M = 256.51, orthorhombic, space group *Cmca*, a = 7.0292(8), b = 15.6245(17), c = 16.1876(17)Å, V = 1777.8(3) Å^3, Z = 8, ρ_{calcd} = 1.917 g cm^{-3}, μ(Mo-$K\alpha$) = 2.751 mm^{-1}, T = 100 K, $F(000)$ = 1016, R1(Fo) = 0.0798, (wR2(Fo^2) = 0.2243) for 1113 unique reflections (Rint = 0.0314) with a goodness-of-fit on F^2 1.226. Data were collected by $\omega/2\theta$ scans ($2\theta_{max}$ = 56°) on a Bruker SMART CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 by the SHELX-97 program.[7] CCDC 611209. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b608403f

1 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **34**, 319; A. Oxtoby and N. R. Champness, *Coord. Chem. Rev.*, 2003, **246**, 145; C. Janiak, *Dalton Trans.*, 2003, 2781; S. Kitagawa, R. Kitaura and S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; M. Eddaoudi, D. B. Moler, H.-L. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109; G. Férey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, 2005, **38**, 217; S. R. Batten, *Curr. Opin. Solid State Mater. Sci.*, 2001, **5**, 107; O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; Y. García, V. Niel, M. C. Muñoz and J. A. Real, *Top. Curr. Chem.*, 2004, **233**, 229; M. Yoshizawa, T. Kusukawa, M. Kawano, T. Ohhara, I. Tanaka, K. Kurihara, N. Niimura and M. Fujita, *J. Am. Chem. Soc.*, 2005, **127**, 2798; B. Kensali and W. B. Lin, *Coord. Chem. Rev.*, 2003, **246**, 305; *Magnetism: Molecules to Materials*, ed. J. S. Miller and M. Drillon, **volumes I–V**, VCH, Weinheim, 2001–2005; E. Coronado and P. Day, *Chem. Soc. Rev.*, 2004, **104**, 5419.

2 X. Xue, X.-S. Wang, L.-Z. Wang, R.-G. Xiong, B. F. Abrahams, X.-Z. You, Z.-L. Xue and C.-M. Che, *Inorg. Chem.*, 2002, **41**, 6544; R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams and Z. Xue, *Angew. Chem., Int. Ed.*, 2002, **41**, 3800; L.-Z. Wang, Z.-R. Qu, H. Zhao, X.-S. Wang, R.-G. Xiong and Z.-L. Xue, *Inorg. Chem.*, 2003, **42**, 3969; F. A. Mautner, C. Gspan, K. Gatterer, M. A. S. Goher, M. A. M. Abu-Youssef, E. Bucher and W. Sitte, *Polyhedron*, 2004, **23**, 1217; C. Jiang, Z. Yu, S. Wang, C. Jiao, J. Li, Z. Wang and Y. Cui, *Eur. J. Inorg. Chem.*, 2004, 3662; J. Tao, Z.–J. Ma, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2004, **43**, 6133; X.-J. Mo, E.-Q. Gao, Z. He, W.-J. Li and C.-H. Yan, *Inorg. Chem. Commun.*, 2004, **7**, 353; H. Zhao, Q. Ye, Q. Wu, Y.-M. Song, Y.-J. Liu and R.-G. Xiong, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1367; T. Wu, B.-H. Yi and D. Li, *Inorg. Chem.*, 2005, **44**, 4130; T.-T. Luo, H.-L. Tsai, S. L. Yang, Y. H. Liu, R. D. Yadav, C.-C. Su, C.-H. Ueng, L-G. Lin and K.-L. Lu, *Angew. Chem., Int. Ed.*, 2005, **44**, 6063; P. Lin, W. Clegg, R. W. Harrington and R. A. Henderson, *Dalton Trans.*, 2005, 2388.

3 A. Rodríguez, R. Kivekäs and E. Colacio, *Chem. Commun.*, 2005, 5228.

4 Synthesis of [Zn_n(polyox)$(pmtz)_n$]: A mixture of $ZnCl_2$ (0.16 g, 1.18 mmol), Napmtz (0.20 g, 1.18 mmol) and water (10 mL) was added to a Teflon-lined stainless steel Parr acid digestion vessel and heated at 180 °C for 12 h under autogenous pressure. Slow cooling of the resulting solution to room temperature afforded colourless crystals of the [Zn_2(polyox)$(pmtz)_2$] complex. Yield: 55% (based on Zn). Anal. Calcd. for $C_{12}H_8N_{12}O_4Zn_2$: C, 27.98; H, 1.57; N, 32.63. Found: C, 27.32; H, 1.43; N, 32.21. IR (KBr, cm^{-1}): 3104 ν(CH); 1637, 1393 ν(CO); 1587, 1562 ν(C=C).

5 A. Rodríguez, R. Kivekäs, R. H. Sakiyama, A. Debdoubi and E. Colacio, unpublished results.

6 J. Y. Lu, J. Macías, J. Lu and J. E. Cmaidalka, *Cryst. Growth Des.*, 2002, **6**, 485.

7 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

8 D. J. Price, A. K. Powell and P. T. Wood, *J. Chem. Soc., Dalton Trans.*, 2000, 3566; S. O. H. Gutschke, D. J. Price, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed.*, 1999, **38**, 1088; S. Natarajan, R. Vaidhyanathan,

C. N. R. Rao, S. Ayyappan and A. K. Cheetham, *Chem. Mater.*, 1999, **11**, 1633; R. Vaidhyanathan, S. Natarajan, A. K. Cheetham and C. N. R. Rao, *Chem. Mater.*, 1999, **11**, 3636; P. A. Prasad, S. Neeraj, S. Natarajan and C. N. R. Rao, *Chem. Commun.*, 2000, 1251; R. Vaidhyanathan, S. Neeraj, P. A. Prasad, S. Natarajan and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 2000, **39**, 3470; R. Vaidhyanatha, S. Natarajan and C. N. R. Rao, *J. Chem. Soc., Dalton Trans.*, 2001, 699.