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A new Zn(II) coordination polymer with 4-pyridylthioacetate: assemblies of homo-chiral helices with sulfide sites†

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Received (in Cambridge, UK) 19th June 2002, Accepted 2nd August 2002
First published as an Advance Article on the web 22nd August 2002

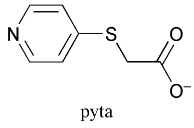
DOI: 10.1039/b205866a

A coordination polymer, [Zn(pyta)(OH)] (pyta = 4-pyridylthioacetate), was synthesized and structurally characterized; it is constructed by an alternating assembly of two types of homo-chiral helices, [Zn–OH] and [Zn-pyta], in which the sulfide moieties are fastened in the latter columns.

Coordination polymers with chiral frameworks are of great current interest because of their unique applications, such as asymmetric heterogeneous catalysis and optical resolution.[1,2] In general, the chiral compounds are derived from chiral organic ligands[1] or spontaneous resolution from achiral materials without any chiral sources.[2] Although the introduction of chemical interaction sites in the frameworks could be useful for these compounds,[3] to create new functional materials such as catalysts or molecular adsorption, this type of coordination polymer has not been explored to date. Thus, the introduction of chemical interaction sites in chiral frameworks is a challenging subject in developing new asymmetric catalytic systems.

We have focused on the sulfide group, a well-known functional group in organic chemistry, as the reaction site.[4,5] For example, the moiety can catalyse the transfer of oxygen atoms to produce hydroxy groups.[5] We have selected 4-pyridylthioacetate (pyta; Scheme 1) as a bridging ligand for the design of a new coordination polymer with sulfide moieties, and have found that the Zn-polymer obtained has an unprecedented asymmetric helical framework with the sulfide groups. Here, we report the synthesis and structural characterization of a novel coordination polymer [Zn(pyta)(OH)] that is constructed by assembly of two types of homo-chiral helices with sulfide groups.

Colourless crystals of the compound were obtained by the diffusion of an aqueous solution of Hpyta into an aqueous solution of $Zn(NO_3)_2·6H_2O$ in the presence of triethylamine. The structure was identified by elemental analysis‡ and X-ray diffraction.§ Each zinc centre is based on a distorted tetrahedron with two hydroxo oxygen atoms, a pyridine nitrogen atom, and a carboxylate oxygen atom, in which the bond angle (94.7(2)°) between the pyridine nitrogen (N(1*)) and the carboxylate oxygen (O(1)) is significantly smaller than the other bond angles (107.9(2)–123.8(3)°). As shown in Fig. 1, the carbonyl oxygen atom (O(2)) of the pyta ligand is tightly connected with the hydroxo anion (O(2)···O(3*) 2.739(9) Å) by a hydrogen bond.



pyta

Scheme 1

The structural feature of this network is the alternating assembly of the two types of cylindrical 2_1 helices along the *b* axis. One is formed by hydroxo bridges between zinc centres (Fig. 2(a)). The Zn···Zn distance bridged by a hydroxo anion is about 3.4 Å, and the repeating period in the helical column is about 5.1 Å. The other type is formed by pyta bridges between the zinc centres (Fig. 2(b)), showing an opposite helical orientation to the former helices. The Zn···Zn distance bridged by pyta is about 8.2 Å, and the repeating period in the helical column is about 5.1 Å. The diameter of the [Zn–pyta] helical column is about 10 Å, larger than that of the other (about 6 Å) due to the larger size of the pyta ligand. These two types of cylindrical columns are alternately connected, with the zinc atoms functioning as hinges. As a result, a unique two-dimensional layer forms in the *bc* plane. These two-dimensional layers stack along the *a* axis in an interlocking fashion. For each cylindrical column, only one helical orientation is involved in the crystal structure, which crystallizes in the asymmetric space group, $P2_1$. That is, the sulfide groups are fastened in the homo-chiral helices in each crystal. Although the bulk product is racemic due to the absence of programming of the chirality in the starting components, each crystal has a chirality that could be applicable for functional materials (crystals grow to a size of about 1.0 × 1.0 × 0.5 mm). Although there are numerous coordination polymers, this type of helix-assembled motif is, to the best of our knowledge, unprecedented.

The structure contains one crystallographically independent pyta ligand. The pyridine ring, sulfur atom, and C(2) carbon atom of the pyta ligand are planar, and tilt about 45° to the two-dimensional layer of the assembled columns. For the two lone pairs of the sulfide unit, one may lie parallel to the layer, while the other sticks out from the sheet. As a result, the two lone pairs of the sulfide are located in asymmetric circumstances.

Sulfide moieties are well known as redox active functional groups.[1] Partial oxidation of the sulfide is often necessary for creation of the unique functional properties of sulfide com-

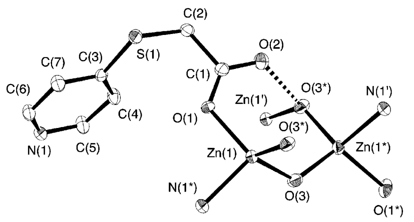


Fig. 1 A view of the coordination arrangement of the zinc centres of the network structure of [Zn(pyta)(OH)] (30% probability level, hydrogen atoms omitted for clarity). The hydrogen bond between the carbonyl oxygen (O(2)) and the hydroxo group (O(3*)) is illustrated by a broken line. Selected bond distances (Å) and angles (°): Zn(1)–O(1) 1.966(5), Zn(1)–O(3) 1.922(6), Zn(1)–N(1*) 2.063(5), O(2)–O(3*) 2.793(9); Zn(1)–O(3)–Zn(1*) 128.7(3), O(1)–Zn(1)–O(3) 123.8(3), O(1)–Zn(1)–O(3*) 112.2(2), O(1)–Zn(1)–N(1*) 94.7(2), O(3)–Zn(1)–N(1*) 107.9(2), O(3)–Zn(1)–O(3*) 104.8(1). O(3*)–Zn(1)–N(1*) 113.4(3). Symmetry equivalent positions * = −*x*, 1/2 + *y*, −*z*.

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† Electronic supplementary information (ESI) available: TG and DTA traces. See http://www.rsc.org/suppdata/cc/b2/b205866a/

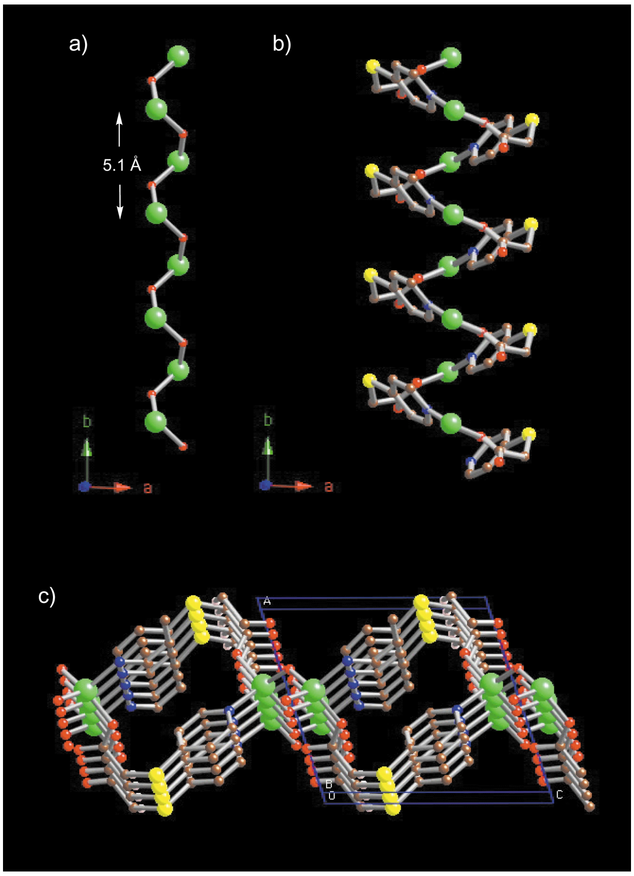

Fig. 2 A view of the cylindrical helices of [Zn–OH] (a) and [Zn–pyta] (b), and the two-dimensional structure formed by the alternating assemblies of these two types of chiral helices (c). The hydrogen atoms and hydrogen bonds between the carbonyl oxygen atoms (O(2)) and the hydroxo oxygen atoms (O(3)) are not illustrated for clarity.

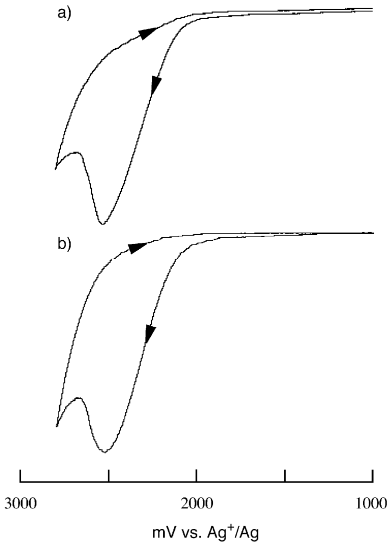

Fig. 3 Cyclic voltammograms of Hpyta in an acetonitrile solution (a) and [Zn(pyta)(OH)] in the solid state (b).

pounds.[4,6] In order to determine whether the properties of the sulfide are retained in the chiral framework, we measured the cyclic voltammograms (CV) of [Zn(pyta)(OH)] in the solid state. Fig. 3 illustrates the CV charts of [Zn(pyta)(OH)] in the solid state and Hpyta in acetonitrile for comparison. Oxidation of the sulfide of Hpyta is observed as an irreversible wave at 2540 mV (*vs.* Ag/Ag$^+$). [Zn(pyta)(OH)] also shows a similar irreversible oxidation at 2530 mV in the solid state. Apparently, the sulfide groups of the zinc compound retain their redox activity in the chiral framework.

We carried out a TG/DTA measurement of the compound in order to establish the thermal stability, which is an important factor for heterogeneous catalysts that activate substrates on a solid surface[7] or within pores.[8] The TG/DTA curve shows neither weight loss nor structural change up to about 220 °C, demonstrating that this chiral framework is retained up to this high temperature.

In summary, a new coordination polymer with pyta has been synthesized and structurally characterized. The X-ray diffraction study clarified that the compound comprises two types of cylindrical helices, [Zn–OH] and [Zn–pyta], in which the sulfide groups are fixed in the chiral framework. This study shows the high potentiality of the coordination polymers as chiral functional materials, such as new asymmetric heterogeneous catalysts.

This work was supported by the Foundation of Advanced Technology Institute.

Notes and references

‡ Anal: Calc. for $C_7H_7NO_3SZn$: C, 33.55; H, 2.82; N, 5.59. Found: C, 33.26; H, 2.71; N, 5.56%.

§ *Crystal data* for [Zn(pyta)(OH)]: M = 250.60, monoclinic, space group $P2_1$ (no. 4), a = 9.099(5), b = 5.098(2), c = 10.075(5) Å, β = 108.445(6)°, V = 443.4(3) Å^3, Z = 2, μ(Mo-Kα) = 2.975 mm^{-1}, T = 293 K, Flack parameter = −0.07(3), R = 0.059, wR = 0.081 for 1089 unique reflections (R_{int} = 0.082) with $I > 2\sigma(I)$ and 118 parameters. Highest electron density 0.75 e Å^{-3}. The data collection was performed on a Rigaku-CCD Mercury system. The structure was solved by direct methods using SIR-98. All non-hydrogen atoms were treated anisotoropically. Hydrogen atoms for the organic ligand were included but not refined. CCDC 188247. See http://www.rsc.org/suppdata/cc/b2/b205866a/ for crystallographic data in CIF or other electronic format.

1 (*a*) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; (*b*) Y. Cui, O. R. Evans, H. L. Ngo, P. S. White and W. Lin, *Angew. Chem., Int. Ed.*, 2002, **41**, 1159.

2 (*a*) T. Matsumoto, T. Kasai and K. Tatsumi, *Chem. Lett.*, 2002, 346; (*b*) M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem., Int. Ed.*, 1997, **36**, 2327; (*c*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; (*d*) M. Kondo, M. Shimamura, S. Noro, T. Yoshitomi, S. Minakoshi and S. Kitagawa, *Chem. Lett.*, 1999, 285; (*e*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (*f*) I. Katsuki, Y. Motoda, Y. Sunatsuki, N. Matsumoto, T. Nakashima and M. Kojima, *J. Am. Chem. Soc.*, 2002, **124**, 629; (*g*) M. Sasa, K. Tanaka, X.-H. Bu, M. Shiro and M. Shionoya, *J. Am. Chem. Soc.*, 2001, **123**, 10750; (*h*) I. Katsuki, N. Matsumoto and M. Kojima, *Inorg. Chem.*, 2000, **39**, 3350; (*i*) M. B. Ferrari, G. G. Fava, G. Pelosi, M. C. Rodriguez-Argüellers and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1995, 3035.

3 (*a*) K. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda and Y. Aoyama, *J. Am. Chem. Soc.*, 1997, **119**, 4117; (*b*) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 2186; (*c*) H.-P. Wu, C. Janiak, L. Uehlin, P. Klüfers and P. Mayer, *Chem. Commun.*, 1998, 2637; (*d*) H.-P. Wu, C. Janiak, G. Rheinwald and H. Lang, *J. Chem. Soc., Dalton Trans.*, 1999, 183; (*e*) C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski and T. G. Scharmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3121.

4 (*a*) T. Tsuchiya, T. Shimizu and N. Kamigata, *J. Am. Chem. Soc.*, 2001, **123**, 11534; (*b*) E. J. Goethals, V. Moss, D. A. Nole and G. H. Schmid, in *Topics in Sulfur Chemistry*, ed. A. Senning, Co-ed. P. S. Magee, Georg Thieme Publishers, Stuttgart, vol. 3, 1977.

5 (*a*) C. Francavilla, M. D. Drake, F. V. Bright and M. R. Detty, *J. Am. Chem. Soc.*, 2001, **123**, 57; (*b*) M. R. Detty, F. Zhou and A. E. Friedman, *J. Am. Chem. Soc.*, 1996, **118**, 313.

6 For example: (*a*) J. F. Rabolt, T. C. Clarke, K. K. Kanazawa, J. R. Reynolds and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 1980, 347; (*b*) K. Bechgaard, K. Carneiro, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen and J. C. Scott, *J. Am. Chem., Soc.*, 1981, **103**, 2440; (*c*) J. Ferraris, D. O. Cowan, V. Walatka Jr. and J. H. Perlstein, *J. Am. Chem. Soc.*, 1973, **95**, 948.

7 For example: (*a*) M. W. Anderson and J. Klinowski, *Inorg. Chem.*, 1990, **29**, 3260; (*b*) M. Chabanas, A. Baudouin, C. Copéret and J.-M. Basset, *J. Am. Chem. Soc.*, 2001, **123**, 2062; (*c*) M. R. Buchmeiser and K. Wurst, *J. Am. Chem. Soc.*, 1999, **121**, 11101.

8 (*a*) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151; (*b*) M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 1998, **37**, 1211; (*c*) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka and S. Kitagawa, *Angew. Chem., Int. Ed.*, 1997, **36**, 1725.