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A new isomer of $[\{Zn(IX)_2(NO_3)_2\}{\cdot}2.5H_2O]_n$ [IX = 1,4-bis(imidazole-1-methylene)-benzene] as a rare example of topological isomerism in coordination polymers

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The title topological isomer possessing a 3D interpenetrated framework formed from alternate rectangular and puckered rhombic like repeat units was synthesised and characterised by X-ray diffraction analysis.†

A challenge of modern inorganic chemistry is to design molecular extended systems possessing architectures with predictable physical properties, but the challenge is even greater when a flexible angular ligand is employed as a building block.[2–5] Bifunctional semiflexible ligand IX [IX = 1,4-bis(imidazole-1-methylene)benzene] can adopt either *syn* or *anti* conformation with imidazole nitrogen binding the metal ion with angles from below 90 to 180°. Therefore, this ligand has a potential to yield both convergent (macrocyclic) and divergent (polymeric) products. The hybrid of the two processes by assembling the discrete molecular products into polymeric arrays by bridging the metal ions of metallocycles, using a suitable bifunctional moiety, is another possibility. Flexibility induces an additional ability in such ligands to adopt the most suitable conformation for efficient packing, and many fascinating interlocked/intertwined species (rotaxanes, catenanes, knots, helicates, *etc.*) have been generated.[6] Polymers exhibiting topological isomerism due to more than one conformations of the ligand and interpenetration of two frameworks with different conformations of the same ligand have been reported in some of the complexes derived from flexible bis(pyridyl)alkanes (R = methane, ethane or propane).[4] Similarly disulfide ligands such as bis(phenylthio)alkanes (R = methane or butane) and bis(4-pyridyl)disulfide (pds) result in a variety of networks exhibiting both chiral and topological isomerisms.[3,5] In general, it is common to obtain widely different structural assemblies from the same set of components under different or even identical reaction conditions when a flexible ligand is employed as a building block.

Apart from the structural isomerism due to different conformations of the ligand, the lack of directional bonding approach in these ligands also enables them to exhibit different metal–ligand coordination connectivity even with the same conformation of the ligand. This results in a new kind of topological isomerism. Herein, we report a new structural isomer of $[Zn(IX)_2(NO_3)_2]{\cdot}2.5H_2O$. Robson *et al.*[1] reported a 2D polyrotaxane structure for a compound with the empirical formula $[Zn(IX)_2(NO_3)_2]{\cdot}2.5H_2O$. Characteristically, both structural isomers have the same geometry around the Zn ion and in both cases two ligands IX bind to each zinc in a *syn* conformation while the other two in an *anti* conformation. However, four ligands IX co-ordinated to the central Zn cation differ in the manner in which they coordinate to their neighbouring zinc ions. To the best of our knowledge, there is only one example reported by Blake *et al.*[3] where $[(CuI)_2(pds)]$ exhibits a similar kind of isomerism. In this case, tetrahedral Cu_4I_4 cubane junctions are linked together by pds either in tubular or in necklace fashion.

For the preparation of the complex, a methanolic solution of IX (0.046 g, 0.2 mmol in 5 ml) was layered over an aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.03 g, 0.1 mmol in 5 ml). Suitable colourless crystals were obtained during a week, which were collected, washed with methanol and air dried. The elemental analysis of polymer **1** is consistent with the formula $[Zn(IX)_2(NO_3)_2]{\cdot}2.5H_2O$ [found (%): C, 46.7; H, 4.6; N, 19.5; calc. for $C_{14}H_{16.50}N_5O_{4.25}Zn_{0.50}$ (%): C, 47.2; H, 4.6; N, 19.6]. The IR spectrum of the complex in KBr pellet records a broad peak in the region 3350–3450 cm^{-1} suggesting the presence of water in the complex, while peaks at 1480 (s), 1250 (br.) and 815 (w) cm^{-1} are attributed to the NO_3 anion.

Both the Zn ions of the asymmetric unit are nearly equivalent, and the geometry around either of the Zn ions is close to tetrahedral with the angles varying from 101.8 to 116.9°. Each Zn ion is coordinated to four imidazole nitrogens from four different IX ligands with an average Zn–N distance of 1.991 Å. The other ends of these ligands bind to different neighbouring

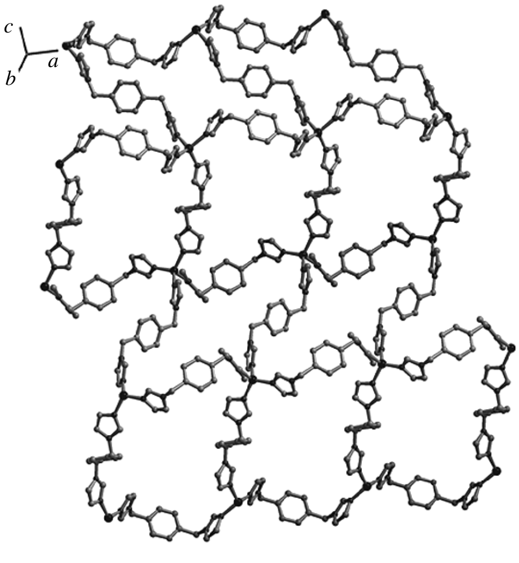

Figure 1 2D sheet structure of polymer **1**.

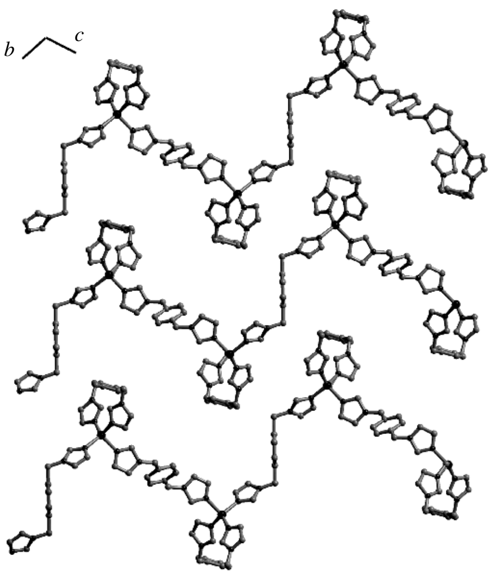

Figure 2 The wavelike structure formed by layers of **1**, seen along the *a* axis. *Syn* and *anti* conformations of the ligand are clearly depicted.

[†] Earlier, Robson *et al.*[1] reported a 2D polyrotaxane isomer **2** for the same compound; the two isomers differ only in the manner the various IX ligands are connected to their neighbouring Zn ions.

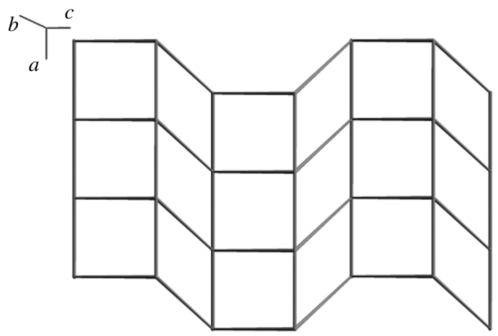

Figure 3 Stick model of the wavelike structure of a 2D sheet as seen along the *a* axis.

Zn ions. The IX ligands alternatively adopt *syn* and *anti* conformations while binding to Zn. Although the geometry around each Zn ion is close to tetrahedral but due to the angular nature of IX (node and spacer approach) it serves as a pseudosquare planar node in the present case. Earlier, the polymer derived from the Zn ion and angular bifunctional nicotinate was also reported to exhibit a similar geometry.[7] A 2D sheet with 4^4 grid structure was generated, which propagates in the *ac* plane (Figure 1). Within 2D sheets, the alternate pairs of Zn ions are slightly displaced from one another so that the sheet appears wave like (Figures 2, 3). The wave form is probably due to the puckering of layers thereby resulting in two different locations of Zn ions. Overall two types of 56 membered parallelograms; rectangular and puckered rhombic like repeating units are formed (Figures 1, 3). The short (Zn···Zn 11.8 Å) and long arms (Zn···Zn 14.8 Å) of the rectangle are formed from the *syn* and *anti* conformations of the ligand, respectively. To the best of our knowledge the present work is the first example of a rectangular grid assembly, where both the long and the short arms have been generated from the same ligand. All the rectangular grids reported so far have been obtained from two linear ligands of variable lengths.[8] The two nearest rhombic rows are arranged so that they form mirror images of each other and the centre of inversion passes through the centre of rectangular block (Figure 3). The separation between two 2D layers is 9.2 Å. The rectangular cavity is sustained through interpenetration within 2D sheets. All the 2D sheets are equivalent and cut each other so that the nodes of the two networks overlap. As a result, their mean planes are parallel. Overall 3D entangled structure enclosing channels perpendicular to the plane of rectangular grid with a cavity size of 10×5.5 Å is generated. This kind of parallel/parallel interpenetration is common with 4^4 grids.[2] The uncoordinated anions and water molecules are present in the channels and are highly ordered through hydrogen bonding.

Robson *et al.*[1] reported a different 2D polyrotaxane isomer (polymer **2**) for the same compound. Polymer **2** can be interpreted as a hybrid product generated by the aggregation of a $Zn_2(IX)_2$ metallocycles (convergent product) through IX bridging [Figure 4(*a*)]. Each Zn centre is connected by three types of bridging IX units. Two IX in their *syn* conformation form a $Zn_2(IX)_2$ metallocycle (Zn···Zn 11.902 Å). The second kind of bridging IX in an *anti* conformation connects two metallocycles (Zn···Zn 15.037 Å) generating a linear tape of $Zn_2(IX)_3$, while the third kind of bridging IX in an *anti* form connects two metallocyclic rings of adjacent tapes together (Zn···Zn 14.146 Å). This mode of overall connectivity results in the formation of a 2D sheet assembly enclosing two types of cavities, one within the metallocycle $Zn_2(IX)_2$ and the other enclosed within the columns of the two adjacent 2D tapes [Figure 4(*a*)]. The sufficiently large sizes of these cavities facilitate the interpenetration of another similiar sheet yielding a polyrotaxane type motif [Figure 4(*b*)]. On the other hand, there is a single mode of IX bridging in polymer **1**.

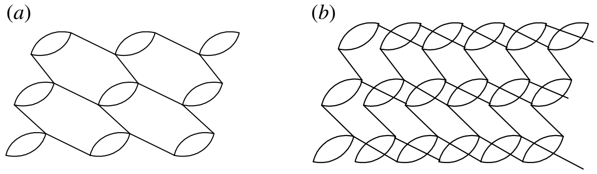

Figure 4 (*a*) Stick model representation of polymer **2** showing three types of bridging IX leading to the formation of a 2D sheet structure. (*b*) Interpenetration of two 2D sheets resulting in a polyrotaxane motif in polymer **2**.

In both of the isomers, the Zn ion provides four-fold connectivity with approximately the same range of binding angles (polymer **1**, 101.8–116°; polymer **2**, 96.2–125.0°), and the Zn centre acts as a pseudo-square planar node. Interestingly, in both of the polymers, each Zn node is connected to two IX ligands in *syn* and the other two in *anti* conformations. However, the position of coordination of *syn* and *anti* ligands to the Zn ion alternates in polymer **1**, whereas in polymer **2** *syn* and *anti* IX ligands are arranged in a *cis* configuration around the Zn ion. The *cis* configuration of *syn* ligands around the Zn ion in the latter case enables it to generate $Zn_2(IX)_2$ metallocycle, which derives the other ligands to a rotaxane motif. On the other hand, the alternate configuration of *syn* and *anti* forms of ligands in polymer **1** facilitates their coordination to four different Zn ions. Hence, the basic difference in two polymers is the position of attachment of *syn* and *anti* IX ligands to the Zn ion, which leads to structural diversity in the polymers.

The two polymorphs could be obtained under different conditions. The homogeneous solution of IX and $Zn(NO_3)_2{\cdot}6H_2O$ in methanol–water on slow evaporation provides a polyrotaxane isomer of $[\{Zn(IX)_2(NO_3)_2\}{\cdot}2.5H_2O]_n$, but the slow diffusion of ligand solution in methanol into aqueous solution of the metal ion, in our case, generates its 4^4 grid isomer.‡ Probably, under homogeneous conditions, the higher concentration of the ligand facilitated the initial formation of the metallomacrocycle $Zn_2(IX)_2$ and interpenetration of the free ligand in the large void of the macrocycle. It is well known that intertwined and interlocked structures are preferred at high concentrations of reactants, and these structures even show concentration dependent equilibria with their non-interwoven counterparts in some cases.[9] Moreover, the stability achieved through π–π interactions between the phenylenes of macrocycle and interpenetrated ligand is expected to further promote the formation of interwoven species. The special propensity of ligands derived from 1,4-xylyl moiety to form catenane and rotaxane motifs may be accounted for due to the extra stability achieved through π–π interactions between the phenylenes of the macrocycle and the guest ligand present in the cavity.[10] But under a slow diffusion process, since the species are available at a low concentration, the interweaving of the ligand does not take place and empty voids are filled by the anions and solvent water molecules. The $[\{Zn(IX)_2(NO_3)_2\}{\cdot}2.5H_2O]_n$ isomers are very rare examples of metal organic frameworks, which exhibit topological isomerism

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‡ *X-ray data.* Molecular formula, $C_{14}H_{16.50}N_5O_{4.25}Zn_{0.50}$; molecular weight, 355.51; crystal system, triclinic; space group, $P\bar{1}$ (no. 2); $a = 11.5400(2)$, $b = 14.9643(2)$, $c = 21.4525(4)$ Å, $\alpha = 109.435(1)°$, $\beta = 89.949(1)°$, $\gamma = 112.812(2)°$, $V = 3185.07(10)$ Å^3, $Z = 8$, $d_{calc} =$ $= 1.483$ g cm^{-3}, $\mu = 0.838$ mm^{-1}, $F(000) = 1476$; reflections collected/unique, 19971/11867 ($R_{int} = 0.0328$); data/restraints/parameters, 11867/15/886. Final R indices $[I > 2\sigma(I)]$, $R_1 = 0.0892$, $wR_2 = 2052$; R indices (all data), $R_1 = 0.1075$, $wR_2 = 0.2141$.

The single-crystal X-ray diffraction was done with a Nonius Kappa CCD diffractometer with graphite monochromatised MoKα ($\lambda = 0.71073$ Å) radiation. Collect software was used in the measurement and DENZO-SMN[11(*a*)] in processing of the data. The structure was solved and refined by full-matrix least-squares on F^2 with the WinGX software package[11(*b*)] utilising SHELXS97 and SHELXL97[11(*c*)] modules. Hydrogen atoms were refined by a riding model. The graphic presentations of the structure were created with the Diamond software.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 208912. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

arising solely due to the difference in the way the various ligands are connected to the metal ions and illustrate the profound influence of reaction conditions on the resultant architecture.[1,3] The flexibility of the ligand enables it to adjust according to small changes in the coordination environment.

Thus, the formation of two different arrays from the same set of components under different reaction conditions reveals the high capability of bifunctional flexible ligands to be incorporated in the structural framework. These ligands not only conveniently adopt the suitable conformation but also allow significant variations in their length, as well as binding angle for efficient packing; therefore, opening a new gateway to the structural diversity. Unfortunately, the control over the design of polymeric species is lost completely and currently the accurate prediction of the overall architecture is almost impossible when a flexible ligand is employed. A complete understanding of crystal packing is needed to develop proper synthetic strategies to generate a functional framework.

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