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Assembly of a Three-Dimensional Polyknotted Coordination Polymer

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Abstract: The coordination polymer $\{[Cd_2(4,4'\text{-pytz})_3(\mu\text{-}NO_3)(NO_3)_3(MeOH)]\}_\infty$, **1**, displays a unique polyknotted structure in which each Cd(II) center is coordinated by three pyridyl N-donors arranged in an approximate T-shaped geometry to form a ladder motif. Within this structure, each ladder is interpenetrated perpendicularly by two other ladders. Significantly, each of the Cd(II) centers at the intersections of one ladder is bridged by a coordinated NO_3^- anion to a Cd(II) center located at the corner of a square section of one of the perpendicularly interpenetrated ladders. Thus, all the ladders are linked together to give a three-dimensional polymer where the overall architecture is constructed of one molecule in a fused "polyknot".

Many examples of discrete supramolecular architectures including molecular squares,[1] knots,[2] rotaxanes,[2] catenanes,[1,2] and cages[1] have been reported. The level of sophistication achieved in these systems is such that recent advances have been linked to the development of potential "molecular machines".[3] More recently, this chemistry has been extended to the assembly of polymeric arrays derived from and based upon metal-coordination networks,[4] ranging from simple chains[5] to ladders,[6,7] sheets,[8] diamondoid nets,[9] and other fascinating architectures.[10] Interpenetration[6,7,8a,9,10b] (or polycatenation) is a phenomenon exhibited by some of these compounds and, recently, examples of polyrotaxane networks have been identified.[11] It is clear that there is a crossover between discrete and polymeric systems, and that both can exhibit the phenomena of catenation/polycatenation and rotaxanation/polyrotaxanation. We report herein a knotted three-dimensional polymer,[12] which can be thought of as the polymeric equivalent of the discrete molecular knots reported by Sauvage and others.[2]

Using the extended bis(pyridin-4-yl) spacer ligand, 3,6-bis(pyridin-4-yl)-1,2,4,5-tetrazine[13] (4,4′-pytz), we have synthesized the metalloorganic coordination polymer $\{[Cd_2(4,4'\text{-pytz})_3(\mu\text{-}NO_3)(NO_3)_3(MeOH)]\}_\infty$, **1**, which displays the unique knotted motif. Pink sphenoidal crystals of the complex were prepared by diffusion of toluene into the pink mother liquor

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(1) (a) Fujita, M.; Ogura, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471. (b) Olenyuk, B.; Fechtenkötter, A.; Stang, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 1707. (c) Fujita, M. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, 1996; Vol. 9, p 253.

(2) For example see: (a) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725. (b) Chambron, J. C.; Dietrich-Buchecker, C.; Sauvage, J. P. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, 1996; Vol. 9, p 43. (c) Amabilino, D. B.; Raymo, F. M.; Stoddart, J. F. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, 1996; Vol. 9, p 85. (d) Ashton, P. R.; Boyd, S. E.; Lee, J. Y.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2070. (e) Gillard, R. E.; Raymo, F. M.; Stoddart, J. F. *Chem. Eur. J.* **1997**, *3*, 1933. (f) Cárdenas, D. J.; Sauvage, J. P. *Inorg. Chem.* **1997**, *36*, 2777. (g) Ashton, P. R.; Matthews, O. A.; Menzer, S.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Liebigs Ann. Recl.* **1997**, 2485. (h) Dietrich-Buchecker, C. O.; Sauvage, J. P.; Armaroli, N.; Ceroni, P.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1119. (i) Dietrich-Buchecker, C.; Rapenne, G.; Sauvage, J. P. *Chem. Commun.* **1997**, 2053. (j) Carina, R. F.; Dietrich-Buchecker, C.; Sauvage, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 9110.

(3) (a) Sauvage, J. P. *Acc. Chem. Res.* **1998**, *31*, 611. (b) Balzani, V.; Gomez-Lopez, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405.

(4) For recent reviews see: (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1461. (b) Blake, A. J.; Champness, N. R.; Hubberstey, H.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (c) Champness, N. R.; Schröder, M. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 419. (d) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.

(5) (a) Batsanov, A. S.; Begley, M. J.; Hubberstey, P.; Stroud, J. *J. Chem. Soc., Dalton Trans.* **1996**, 1947. (b) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327.

(6) (a) Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 2027. (b) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zawarotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972. (c) Losier, P.; Zawarotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779.

(7) (a) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Inorg. Chem.* **1999**, *38*, 2259. (b) Fujita, M.; Kwon, Y.-J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995** *117*, 7287. (c) Carlucci, L.; Ciani, G.; Proserpio D. M. *New. J. Chem.* **1998**, 1319. (d) Fujita, M.; Sasaki, O.; Watanbe, K.; Ogura, K.; Yamaguchi, K. *New J. Chem.* **1998**, 189. (e) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *New J. Chem.* **1999**, *23*, 573. (f) For recent discussion of T-shaped linkers see: Gudbjartson, H.; Biradha, K.; Poirier, K. M.; Zawarotko, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 2599.

(8) (a) Subramanian, S.; Zawarotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127. (b) Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1677. (c) Blake, A. J.; Hill, S. J.; Hubberstey, P.; Li, W-S. *J. Chem. Soc., Dalton Trans.* **1997**, 913. (d) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (e) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A *J. Chem. Soc., Dalton Trans.* **1997**, 1801. (f) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676.

(9) (a) MacGillivarrry, L. R.; Subramanian, S.; Zaworotko, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1325. (b) Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1005. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755. (d) Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 1339.

(10) (a) Abrahams, B. F.; Jackson, P. A.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2656. (b) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M. *Chem. Commun.* **1998**, 1837.

(11) (a) Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 2952. (b) Hoskins, B. F.; Robson, R.; Slizys, D. A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2336. (c) Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451. (d) Whang, D.; Heo, J.; Kim, C.-A.; Kim, K. *Chem. Commun.* **1997**, 2361.

(12) Busch, D. H.; Vance, A. L.; Kolchinski, A. G. *Comprehensive Supramolecular Chemistry*; Pergamon Press: Oxford, 1996; Vol. 9, p 1. The word 'knot' is used in the usual sense of the Webster's Dictionary most general definition: "an interlacement of parts of a cord, rope or the like, forming a lump or knob".

(13) Charonnat, R.; Fabiani, P. *C. R. Hebd. Seances Acad. Sci.* **1955**, *241*, 1783.

10.1021/ja991698n CCC: $19.00

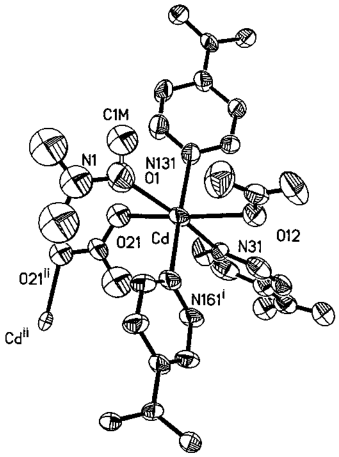
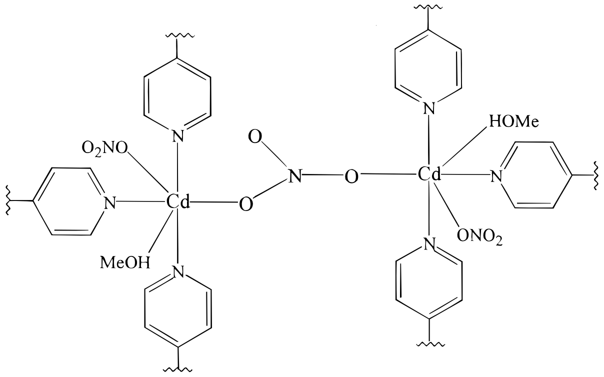


Figure 1. The coordination sphere about the Cd(II) center in **1** illustrating the nitrate bridge between Cd(II) centers; displacement ellipsoids at 50% probability. Selected interatomic distances (Å) and angles (deg): Cd−N(31) = 2.444(11), Cd−N(131) = 2.256(9), Cd−N(161)^{i} = 2.274(10), Cd−O(12) = 2.390(9), Cd−O(1) = 2.447(13), Cd−O(21) = 2.381(14); ∠N(31)−Cd−N(131) = 95.4(4)°, ∠N(31)−Cd−N(161) = 87.1(4)°, ∠N(131)−Cd−N(161) = 175.1(5)° (symmetry codes, i = $x - {}^{1}/_{2}$, $y + {}^{1}/_{2}$, z; ii = $2 - x$, y, $1{}^{1}/_{2} - z$).

Scheme 1. A Schematic Diagram Showing the Linking of Cd(II) Centers by the Bridging NO_3^- Anions in **1**



obtained by layering solutions of 4,4′-pytz in CH_2Cl_2 and Cd$(NO_3)_2$·$4H_2O$ in MeOH. A single-crystal X-ray structure determination revealed that $\{[Cd_2(\mu\text{-}4,4'\text{-pytz})_3(\mu\text{-}NO_3)(NO_3)_3(MeOH)]\}_\infty$ exists as a 3:2 ligand/metal coordination polymer,[14] with each Cd(II) center (Figure 1) coordinated by three pyridyl N-donors arranged in an approximate T-shaped geometry. Two monodentate NO_3^- anions (one-half-occupied), a MeOH (half-occupied) and a disordered bridging NO_3^-, complete the coordination at Cd(II) (Figure 1).[14]

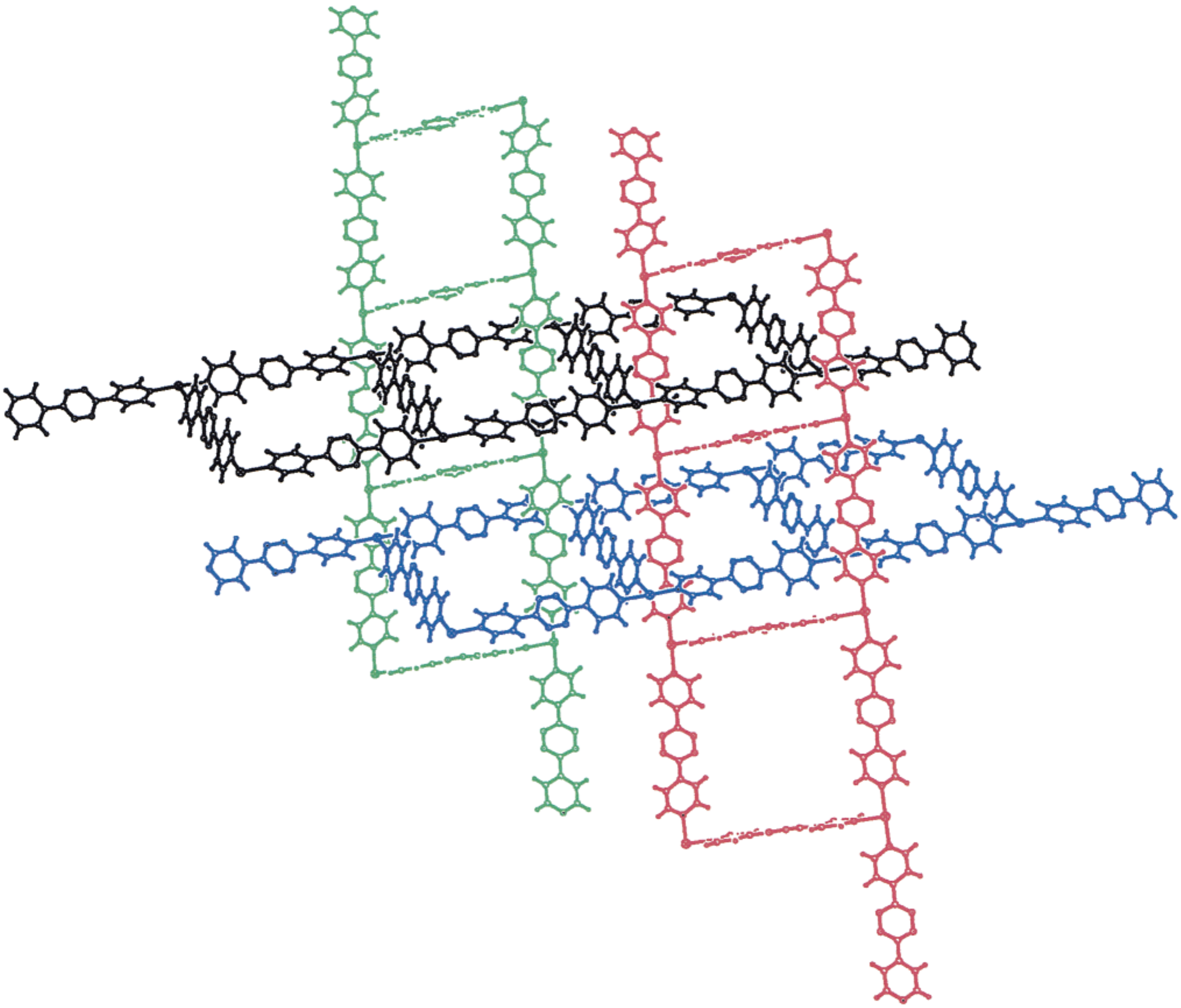


Figure 2. The perpendicular interpenetration of ladders formed in **1**.

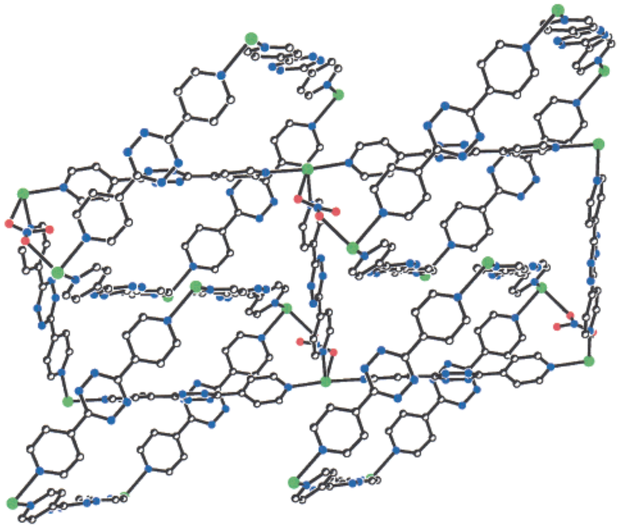
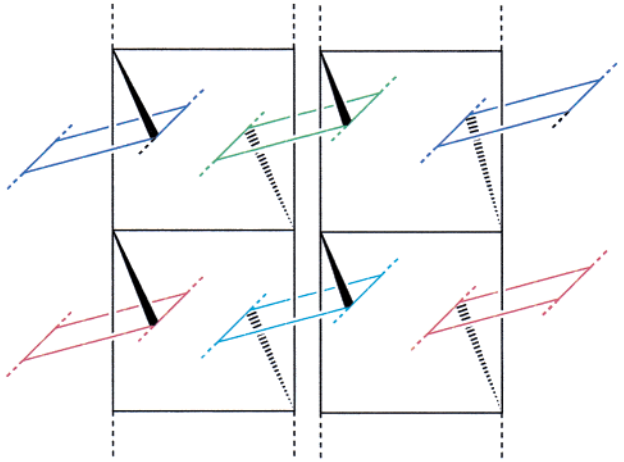


Figure 3. Expanded view of the interpenetration of the ladders in **1** with the bridging NO_3^- anions clearly evident. These anions link the ladders to produce a three-dimensional polymer, effectively a single molecule.

T-shaped connecting units, as exemplified by the Cd(II) center in **1**, have given rise to ladder,[6b,c,7] brick-wall[7b,c] and herringbone[7e] architectures. The structure of **1** can be regarded as a ladder-type motif in which large cavities are created within each square of the ladder, defined as two rungs and two edges [Cd···Cd ('rung') = 15.53 Å, Cd···Cd ('edge') = 16.01 Å]. These cavities (23.1% of the crystal volume[15]) are filled by intercalated solvent and by further ladders which interpenetrate perpendicularly through the original ladder (Figure 2). Interpenetration of molecular ladders *must* result in a polycatenated structure and in this case a total of two ladders are catenated through each square of any given ladder. Each of the Cd(II) centers at the intersections of the ladder is bridged to one other Cd(II) center by a coordinated NO_3^- anion (Scheme 1), and this second Cd(II) is located at the corner of a square section of a perpendicularly interpenetrated ladder (Figure 3, Scheme 2). As a consequence of the bridging NO_3^- anion, all the ladders are linked together resulting in the formation of a three-dimensional polymer where the total architecture is constructed of one molecule. As this single polymeric network also exhibits polycatenation, this coordination polymer can be regarded as a fused polyknotted array, or a "polyknot".[17] The role of the MeOH solvent is influential in determining the structure of **1** as when EtOH is used, instead of MeOH, a simpler, noninterpenetrated, molecular ladder motif **2** is observed.[16]

Interpenetrating ladders have been reported for the complex $\{[Cd_2(1,4\text{-bis(pyrid-4-ylmethyl)benzene})_3(NO_3)_4]\}_\infty$, **3**.[7b] This structure is related to that of **1** as both exhibit perpendicularly interpenetrated ladders. However, in **3** all the anions act as bidentate donors to individual Cd(II) centers and so the individual ladders are independent of each other and are not connected through bridging NO_3^- anions as in **1**. Therefore **3** is an example of a polycatenated complex but is not knotted. Polyrotaxanes have been identified in $\{[Ag_2(bix)_3(NO_3)_2]\}_\infty$,[11a] **4**, and $\{[Zn(bix)_2(NO_3)_2]4.5H_2O\}_\infty$,[11b] **5**, [bix = 1,4-bis(imidazol-1-ylmethyl)benzene]. In **4** and **5**, chains and sheets, respectively, are intertwined by rotaxanated linkages where again each chain or sheet is independent of each other (i.e. not coordinatively linked). The superstructure of **1** is neither a polycatenane nor a polyrotaxane: this is because each ladder in **1** is not independent of the other interpenetrating ladders due to the linking NO_3^- bridges joining them together. Therefore, **1** is best described as a knotted coordination polymer as it is a single polymeric molecule that loops around itself. **1** is the first example of this type of knotting in coordination polymers,[17] and we are currently investigating whether this phenomenon is transferable to other metal/ligand combinations.

Scheme 2. A Schematic Showing the Knotting of the Interpenetrated Ladders in **1**[a]



[a] Bridging NO_3^- anions are represented by dashes and wedges.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates and anisotropic displacement parameters for **1**, **1a**, and **2**, a synthetic scheme for complex preparation, and figures giving the numbering scheme for **1**, **1a,** and **2** and a view of the molecular ladder formed by **2** (PDF); X-ray crystallographic files for **1**, **1a,** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Crystal Data for **1**: crystal size 0.45 × 0.25 × 0.15 mm, monoclinic, space group $C2/c$, $a = 19.46(2)$ Å, $b = 24.20(3)$ Å, $c = 13.81(2)$ Å, $\beta = 121.17(13)°$, $U = 5565(12)$ Å^3, $2\theta_{max} = 50°$, Mo Kα radiation ($\lambda = 0.71073$ Å) for $Z = 8$. Least-squares refinement on 4807 independent reflections, 2905 of which have $I > 2\sigma(I)$, of 367 parameters on convergence gave a final value of $R_1 = 0.0971$. Determination of the unit cell for five separate single crystals revealed small variations in the unit cell parameters, most noticeably in a which varied from 19.46(2) to 19.835(7) Å. X-ray diffraction analysis of the crystals with the longest value for a revealed a slight modification of the structure with a hydroxide anion replacing one of the monodentate nitrates but with retention of the coordination polymer's knotted architecture. See Supporting Information. Crystal Data for **1a**: crystal size 0.50 × 0.16 × 0.12 mm, monoclinic, space group $C2/c$, $a = 19.835(7)$ Å, $b = 23.936(5)$ Å, $c = 13.841(6)$ Å, $\beta = 122.48(4)°$, $U = 5543(3)$ Å^3, $2\theta_{max} = 50°$, Mo Kα radiation ($\lambda = 0.71073$ Å) for $Z = 8$. Least-squares refinement on 4887 independent reflections, 3521 of which have $I > 2\sigma(I)$, of 369 parameters on convergence gave a final value of $R_1 = 0.0668$.

[15] Spek, A. L.; PLATON *Acta Crystallogr., Sect. A* **1990**, *46*, C-34.

[16] Crystal Data for **2**: crystal size 0.59 × 0.30 × 0.15 mm, monoclinic, space group $C2/c$, $a = 27.314(6)$ Å, $b = 15.701(4)$ Å, $c = 15.514(5)$ Å, $\beta = 116.70(2)°$, $U = 5944(2)$ Å^3, $2\theta_{max} = 50°$, Mo Kα radiation ($\lambda = 0.71073$ Å) for $Z = 8$. Least-squares refinement on 3624 independent reflections, 2886 of which have $I > 2\sigma(I)$, of 330 parameters on convergence gave a final value of $R_1 = 0.0854$.

[17] We are most grateful to a referee for bringing to our attention three previous examples of coordination polymers which demonstrate related topological features related to those reported here (Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Sutherland, E. E. *J. Chem. Soc., Chem. Commun.* **1994**, 1049. Hardie, M. J. Ph.D. Thesis, University of Melbourne, 1995. Abrahams, B. F.; Batten S. R.; Grannas M. J.; Hamit H.; Hoskins, B. F.; Robson, R. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1475. The latter paper describes the structural type as a "self-entangled net" but other descriptions including "self-catenating" and "self-penetrating" are also valid. The structural description is somewhat subjective and we prefer the term "polyknotted" as we believe it describes most clearly the subtle complexity of this remarkable class of compounds.