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An unprecedented six-fold anion-type chiral diamondoid-like eight-coordinate Cd(II) coordination polymer with a second-order nonlinear optical effect

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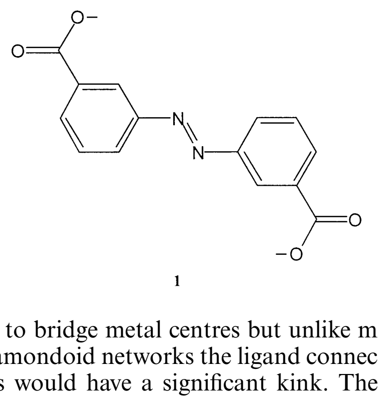
The reaction of $Cd(OH)_2$ with 3,3′-azodibenzoic acid affords an unprecedented anionic chiral diamondoid network, bis(3,3′-azodibenzoate)cadmium·(H_2NMe_2)·(NH_4) which contains eight-coordinate cadmium and displays strong SHG response and enantioselectivity for organic amines.

Many macro-physical properties of solid materials, such as triboluminescence, piezoelectricity and second-order nonlinear optical (NLO) effect (second-harmonic generation, SHG) essentially require the absence of a centre of symmetry.[1] Accordingly the rational design and synthesis of such acentric crystals or solids has been a continuing challenge for material chemists.[2] Recently, crystal engineering has demonstrated its usefulness in providing supramolecular architectures and acentric solid materials that display strong SHG properties.[3] To date, a low-temperature polymorph of potassium dideuterophosphate (KDP) remains as the only NLO-active inorganic diamondoid network although there are several metal–organic hybrid 3-D coordination polymer diamondoid-like networks with NLO properties.[3,4] On this basis it is anticipated that hybrid inorganic–organic metal-coordination polymers (HIOMCP) that are acentric (chiral) and have the diamond connectivity may find wide application as NLO materials. In addition such chiral networks may also be useful in enantioseparation.

The three-dimensional structure of a diamondoid network offers an inherent stability however the symmetry of the network often means that crystallization rarely occurs in a non-centrosymmetric space group.[5] One approach that may be employed to generate acentric diamond nets involves using low symmetry bridging ligands to link four-connecting centres. The dicarboxylate ligand, 3,3′-azodibenzoate (3,3′-AZDB), (**1**) has the potential to bridge metal centres but unlike many bridging ligands in diamondoid networks the ligand connection between metal centres would have a significant kink. The presence of such a kink offers the prospect of lower symmetry networks compared to those based upon “straight” ligands such as 4,4′-bipyridine, cyanide and 4-cyanopyridine. In addition the ligand incorporates electronic asymmetry (push–pull effects) which is essential for NLO behavior.



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In this communication, we report the synthesis and structure of acentric interpenetrating diamondoid networks formed by linking cadmium(II) centres with 3,3′-AZDB. We also report a preliminary investigation of NLO behaviour, and an examination of the thermal stability of this novel coordination polymer that has the formula $Cd(3,3'\text{-AZDB})_2$·(H_2NMe_2)·(NH_4). Brown-yellow crystals of **2** were obtained by treating 3,3′-azodibenzoic acid and $Cd(OH)_2$ under hydro(solvo)-thermal reaction conditions.† The IR spectrum of complex **2** shows two strong peaks at 1601 and 1391 cm^{-1}, indicating the existence of a typical carboxylate. Furthermore, ammonia and $HNMe_2$ molecules were detected by GCMS while heating a mixture of **2** and NaOH. Investigations into the thermal stability of **2** indicate that it is stable up to approximately 220 °C.

The three-dimensional polymeric structure of **2** was revealed by a single crystal X-ray diffraction study.‡ Each 3,3′-AZDB ligand chelates a cadmium(II) centre at each end and each cadmium is bound to four such ligands. Thus the cadmium(II) centres are eight-coordinate with a tetragonal antiprismatic geometry, as shown in Fig. 1. Dimethylammonium and ammonium ions are the counterions for the anionic network. The coordination environment of the cadmium(II) centres in **2** is unprecedented in multi-dimensional supramolecular architectures although there are some eight-coordinate Cd(II) macrocyclic monomeric compounds recorded in the literature.[6] Although all the 3,3′-AZDB ligands in the structure adopt a *trans* arrangement two distinct conformations of the ligand are apparent with differences arising because of rotation about the N–C bonds. In one conformation the N=N bond is close to being parallel with an imaginary line that links the bridged metal atoms. This conformation is shown above (**1**). In the other conformation the N=N bond is close to being perpendicular with such an imaginary line. The first conformation leads to metal–metal separations of 15.86 and 15.75 Å, while the second conformation leads to a corresponding separation of 14.45 Å.

Although the cadmium centre is eight-coordinate, from a topological perspective it may be treated as a four-connecting node. The connectivity of these four-connecting nodes is the same as that found for diamond. In Fig. 2, the 3,3′-AZDB ligands have been replaced by linear connections in order to illustrate an adamantane-type unit which is characteristic of diamondoid networks. Cd–Cd–Cd angles are in the range 92.7–123.2° which represents a significant distortion from the ideal tetrahedral angle of 109.5° found in diamond.

When intraframework voids are relatively large, interpenetration of a network by other independent networks is a common phenomenon. In this structure there are six independent diamondoid networks with all networks related by symmetry. Six

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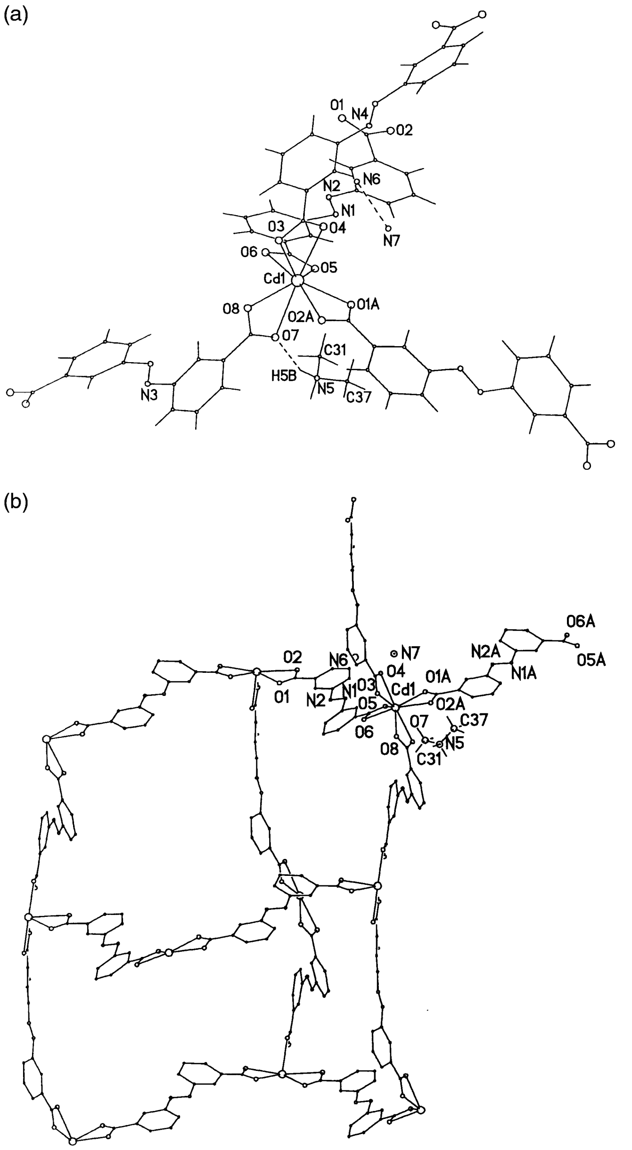

Fig. 1 (a) Eight-coordinate Cd(II) in **2** showing that there are strong hydrogen bonding interactions between O7 and N5 (2.727 Å), and N6 and N7 (2.612 Å); (b) Part of a single diamondoid net of bis(3,3′-azodibenzoate)cadmium·(H_2NMe_2)·(NH_4) (**2**). The open circles with increasing sizes represent C, N, O and Cd atoms while cation guest molecules NH_4^+ and $H_2N^+Me_2$ are highlighted by hatched circles.

adamantane-type units, each from a separate net are represented in Fig. 3. Normally diamondoid nets that interpenetrate are related to each other by a simple translation[5b] however in this case the interpenetration is more complex. As illustrated in Fig. 3 the nets may be divided into two groups. Within each group the nets are related by a translation along the *a* direction and the two groups are related to each other by a two-fold axis. On close inspection it is apparent that although the nets within a group of three are related by translation, the entanglement of the three nets is different to that normally observed (see ESI†). This interpenetrating phenomenon is unprecedented in the multi-fold interpenetrating diamondoid-like networks.[5b] A detailed description of this interpenetration will be reported at a later date.

It is clearly apparent that although the connectivity of the network is the same as diamond, the symmetry is lower. The adoption of the chiral space group *C*222$_1$, which belongs to the crystal class 222, means that specific physical effects relating to optical behaviour may be expected.[7] Our experimental results show that **2** displays strong powder SHG efficiencies, *ca.* 1.2 times that of urea.§ This behaviour is similar to that found for potassium dideuterophosphate (KDP), the only other known nonlinear optical (NLO)-active diamondoid network.

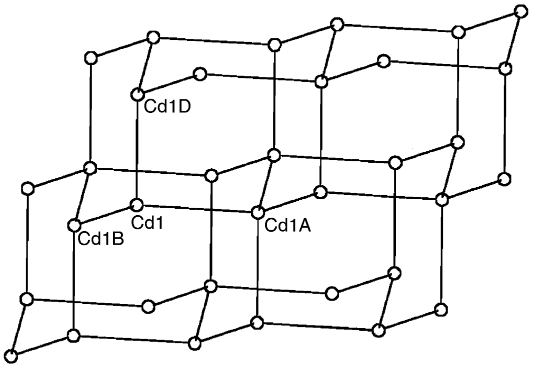

Fig. 2 An adamantane-type representation of bis(3,3′-azodibenzoate)cadmium·(H_2NMe_2)·(NH_4) (**2**) in which the diamondoid sides are not equal ($d_{Cd1-Cd1B}$ = 14.45 Å, $d_{Cd1-Cd1A}$ = 15.75 Å and $d_{Cd1-Cd1D}$ = 15.86 Å). The straight lines and open circles represent the 3,3′-azodibenzoate ligand and Cd atom respectively.

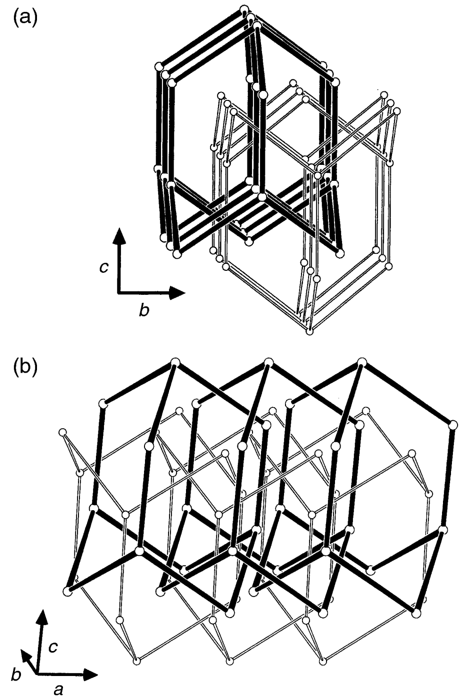

Fig. 3 A simplified view of the six-fold interpenetration within the structure. One adamantane-type unit from each of the six nets is represented. Circles represent cadmium(II) centres; lines between the circles represent the bridging ligands. The adamantane type units with "filled" bonds belong to one set of three nets; the units with "open" bonds belong to a second set. (a) Two group diamondoid nets; (b) different entanglement of each group (three nets).

According to a search of structures from the CCDC, anionic HIOMCPs involving dicarboxylate bridging ligands have not been previously reported. Given the chirality and charge of the framework the potential exists for resolution of cationic species. Preliminary investigations indicate that [bis(3,3′-azodibenzoate)Cd(II)]$^{2-}$ enantioselectively includes (−)-nicotine in a one-pot self-assembly reaction. Further examination of this material in regard to its usefulness in enantioseparation is currently underway.

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Notes and references

† Preparation of bis(3,3′-azodibenzoate)cadmium·(H_2NMe_2)·(NH_4) (**2**): Hydro(solvo)thermal treatment of $Cd(OH)_2$ (1.0 mmol), 3,3′-azodibenzoic acid (2.0 mmol), $HNMe_2$ (1 ml) and NH_3 (0.5 ml) for 2 days at 110 °C yielded a brown-yellow block crystalline product (only one pure phase). The yield of **2** was about 35% based on 3,3′-azodibenzoic acid. Anal. calc. for $C_{30}H_{28}N_6O_8Cd$: C, 50.49; H, 3.93; N, 11.78. Found: C, 50.35; H, 4.02; N,11.62%. IR (KBr, cm^{-1}): 3441(br,w), 3066(w), 2927(w), 2362(w), 1601(s), 1567(m), 1391(s), 1262(w), 1220(w), 1155(w), 1099(w), 1074(w), 1021(w), 927(w), 802(m), 774(m), 671(w), 593(w), 433(w).

‡ Crystal data for **2**: $C_{30}H_{28}N_6O_8Cd$, orthorhombic, $C222_1$, $a = 13.1187(10)$, $b = 23.3448(16)$, $c = 22.9554(17)$ Å, $V = 7030.2(9)$ Å^3, $Z = 8$, $M = 712.98$, $D_c = 1.347$ Mg m^{-3}, $R_1 = 7.09\%$, $wR_2 = 14.15\%$ (3536 reflections), $T = 293$ K, $\mu = 0.674$ mm^{-1}, $S = 0.951$, Flack parameter value $\chi = -0.08(6)$. CCDC reference number 166257. See http://www.rsc.org/suppdata/dt/b1/b105130j/ for crystallographic data in CIF or other electronic format.

§ SHG property measurement for **2**: The second-order nonlinear optical intensity was estimated by measuring a powder sample of 80–150 μm diameter in the form of a pellet (Kurtz powder test),[8] relative to that of urea. A pulse Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate the SHG signal from the sample. The backward scattered SHG light was collected using a spherical concave mirror and passed through a filter which transmits only 532 nm radiation. It is estimated that the SHG efficiency of **2** is slightly stronger than that of urea by about 1.2 times.

1 (*a*) J. Zyss, *Molecular Nonlinear Optics: Material, Physics, and Devices*, Academic Press, New York, 1993; (*b*) R. E. Newnhan, *Structure–Property Relationships*, Springer, New York, 1975; (*c*) X.-R. Zeng, R.-G. Xiong, X.-Z. You and K.-K. Cheung, *Inorg. Chem. Commun.*, 2000, **3**, 341 and references therein.

2 (*a*) G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, 1989; (*b*) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH Publishers, New York, 1995.

3 (*a*) O. R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong and W. Lin, *Angew. Chem., Int. Ed.*, 1999, **38**, 536; (*b*) R.-G. Xiong, J.-L. Zuo, X.-Z. You, B. F. Abrahams, Z.-P. Bai, C.-M. Che and H.-K. Fun, *Chem. Commun.*, 2000, 2061; (*c*) W. Lin, O. R. Evans, R.-G. Xiong and Z. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 13272.

4 (*a*) B. C. Frazer and R. Pepinsky, *Acta Crystallogr.*, 1953, **6**, 273; (*b*) S. Endo, T. Chino, S. Tsuboi and K. Koto, *Nature*, 1989, **340**, 452.

5 For reviews on diamondoid-like networks see: (*a*) S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1461; (*b*) M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, 283; (*c*) C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431; (*d*) O. M. Yaghi, H. Li, C. Davis, D. Richard and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; (*e*) S. R. Batten, A. R. Harris, P. Jensen, K. S. Murray and A. Ziebell, *J. Chem. Soc., Dalton Trans.*, 2000, 3829; (*f*) A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *J. Chem. Soc., Dalton Trans.*, 2000, 3811; (*g*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *J. Chem. Soc., Dalton Trans.*, 2000, 3821; For diamondoid-like nets with a centric space group see: (*h*) K. A. Hirsch, S. R. Wilson and J. S. Moore, *Chem. Eur. J.*, 1997, **3**, 765; (*i*) O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747; (*j*) E. Siebel, A. M. A. Ibrahim and R. D. Fischer, *Inorg. Chem.*, 1999, **38**, 2530; (*k*) M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa and M. Maekawa, *J. Am. Chem. Soc.*, 1996, **118**, 3117; (*l*) A. J. Blake, N. R. Champness, S. S. M. Chung, W. S. Li and M. Schroder, *Chem. Commun.*, 1997, 1005; (*m*) J. Zhang, W. Lin, Z.-F. Chen, R.-G. Xiong, B. F. Abrahams and H.-K. Fun, *J. Chem. Soc., Dalton Trans.*, 2001, 1806; For diamondoid-like nets with a polar space group see: (*n*) T. Kuroda-Sowa, T. Horino, M. Yamamoto, Y. Ohno, M. Maekawa and M. Munakata, *Inorg. Chem.*, 1997, **36**, 6382; (*o*) K.-W. Kim and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1992, **114**, 4878.

6 (*a*) K. R. Adam, S. Donnelly, A. J. Leong, L. F. Lindov, B. J. McCool, A. Bashall, M. R. Dent, B. P. Murphy, M. McPartlin and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1990, 1625; (*b*) M. G. B. Drew, J. D. O. Cabral, M. F. Cabral, F. S. Esho and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 1033; (*c*) A. Jantti, M. Wagner, R. Suontamo, E. Kolehmainen and K. Rissanien, *Eur. J. Inorg. Chem.*, 1998, 1555; (*d*) A. Neels and H. Stoeckli-Evans, *Inorg. Chem.*, 1999, **38**, 6164; (*e*) D. C. Bebout, S. W. Stokes and R. J. Butcher, *Inorg. Chem.*, 1999, **38**, 1126.

7 (*a*) C. Janiak, T. G. Scharmann, P. Albrecht, F. Marlow and R. Macdonald, *J. Am. Chem. Soc.*, 1996, **118**, 6307; (*b*) H. Zhang, X. Wang and B. K. Teo, *J. Am. Chem. Soc.*, 1996, **118**, 11813; (*c*) R.-G. Xiong, J.-L. Zuo, X.-Z. You, H.-K. Fun and S. S. Sundara, *New J. Chem.*, 1999, **23**, 1051.

8 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.