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FULL PAPER

Synthesis and structural characterisation of cadmium(II) and zinc(II) coordination polymers with an angular dipyridyl bridging ligand: parallel interpenetration of two-dimensional sheets with 4.8^2 topology†

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Coordination polymers formed between $Cd(NO_3)_2$ or $Zn(NO_3)_2$ and 2,4-bis(4-pyridyl)-1,3,5-triazine (dpt) have been synthesized and their single crystal structures determined. Reaction of a 1 : 1 ratio of $Cd(NO_3)_2$ with dpt in MeCN–CH_2Cl_2 affords the complex $[Cd_2(NO_3)_4(dpt)_2(MeCN)]_\infty$ **1** which exists as a doubly interpenetrated 4.8^2 two-dimensional sheet in the solid state. Each sheet is constructed from nitrate-bridged $[Cd(dpt)]_4$ metallacycles. In sharp contrast the analogous reaction performed using a 2 : 1 L : M ratio affords the discrete molecular complex **$[Cd(NO_3)_2(dpt)_2(MeCN)]$ 2** in which both dpt ligands act as terminal donors rather than bridging metal centres. Reaction of $Cd(NO_3)_2$ with dpt in EtOH–CH_2Cl_2 affords a one-dimensional coordination polymer $[Cd(NO_3)_2(dpt)(EtOH)]_\infty$ **3**. $Zn(NO_3)_2$ reacts with dpt in either a 1 : 1 or 2 : 1 L : M ratio to afford the one-dimensional polymer $[Zn(NO_3)_2(dpt)]_\infty$ **4** which can be isolated as two polymorphs **4a** and **4b** which differ in their nitrate binding modes. The product formed is independent of the L : M ratio used in the reaction. Only **4a** is formed when MeCN–CH_2Cl_2 is used as reaction solvent whereas both **4a** and **4b** are formed from either EtOH–CH_2Cl_2 or ^{i}PrOH–CH_2Cl_2.

Inorganic supramolecular chemistry is currently an area of extensive research which has led to the systematic design of both discrete coordination architectures[1] and polymeric coordination networks.[2,3] Whereas the discrete architectures are the convergent products of a self-assembly process, coordination polymers can be viewed as the divergent products from what are often similar reactions. We have become interested in the parallels between the two areas and how discrete supramolecular architectures can be aggregated into polymeric network structures.[4,5] This has involved the use of ligands that encourage the formation of convergent products which can also assemble into extended arrays. This is illustrated by the reaction of 1-(2-pyridyl)-4-(4-pyridyl)benzene with $Cd(NO_3)_2$ which forms a robust three-dimensional structure consisting of nitrate bridged dinuclear metallacycles.[4]

We now report the reaction of 2,4-bis(4-pyridyl)-1,3,5-triazine (dpt) with $Cd(NO_3)_2$ and $Zn(NO_3)_2$. This ligand provides a rigid 120° angle between the 4-pyridyl N-donors as observed in pyrimidine (pym) which has given rise to many unusual structures.[6,7] These include $[Ag(pym)X]_4$ ($X = NO_3^-$ or ReO_4^-) metallacycles which illustrate that such angular ligands can give rise to either convergent or divergent products when treated with a suitable metal centre (Scheme 1). In this paper both types of product are observed but it is also seen that the flexible coordinating nature of the nitrate anion in cadmium(II) and zinc(II) coordination polymers and the solvent of crystallisation have a significant role to play in the overall product architecture.[4,8]

Results and discussion

The reactions between $Cd(NO_3)_2$ and the ligand dpt[9] in either a 1 : 1 or 1 : 2 ratio in a MeCN–CH_2Cl_2 solvent mixture affords either $[Cd_2(NO_3)_4(dpt)_2(MeCN)]_\infty$ **1** or $[Cd(NO_3)_2(dpt)_2(MeCN)]$ **2** as colourless powders. The analogous reaction, in either a 1 : 1 or 1 : 2 M : L stoichiometry, affords $[Cd(NO_3)_2(dpt)(EtOH)]_\infty$ **3** when performed in EtOH–CH_2Cl_2. $Zn(NO_3)_2$ reacts with dpt in either MeCN–CH_2Cl_2, EtOH–CH_2Cl_2 or ^{i}PrOH–CH_2Cl_2 to afford $[Zn(NO_3)_2(dpt)]_\infty$ in two polymorphs **4a** and **4b**. The stoichiometry of the product from the reaction between $Zn(NO_3)_2$ and dpt was found to be the same when using either a 1 : 1 or 1 : 2 ratio of starting materials. All four compounds were insoluble not only in the reaction mixtures but also in all other common solvents.

Single crystals of compounds **1**–**4** were grown by slow diffusion of $Cd(NO_3)_2$, or $Zn(NO_3)_2$, in MeCN (**1**, **2** or **4a**), EtOH (**3**), or either EtOH or ^{i}PrOH (**4b**) into a solution of the ligand in CH_2Cl_2, and were analysed by X-ray diffraction studies.

Structures of $[Cd_2(NO_3)_4(dpt)_2(MeCN)]_\infty$ 1, $[Cd(NO_3)_2(dpt)_2(MeCN)]$ 2 and $[Cd(NO_3)_2(dpt)(EtOH)]_\infty$ 3

The structural determination of complex **1** revealed a most remarkable and unique structure. The four distinct cadmium(II) ions (Table 1) in the crystallographic asymmetric unit are each coordinated by two dpt ligands which link two adjacent cadmium(II) centres (Fig. 1). Thus two distinct pairs of cadmium(II) centres are formed; a formally monopositive "$Cd_2(NO_3)_3(MeCN)_2$" unit and a formally mononegative "$Cd_2(NO_3)_5$" unit (Scheme 2). The bridging *via* the dipyridyl ligand has the effect of generating "$Cd_4(dpt)_4$" metallacycles which have a distorted octagonal shape due to the angle of 120°

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† Electronic supplementary information (ESI) available: powder X-ray diffraction data for compounds **2**–**4**. See http://www.rsc.org/suppdata/dt/b0/b008715g/

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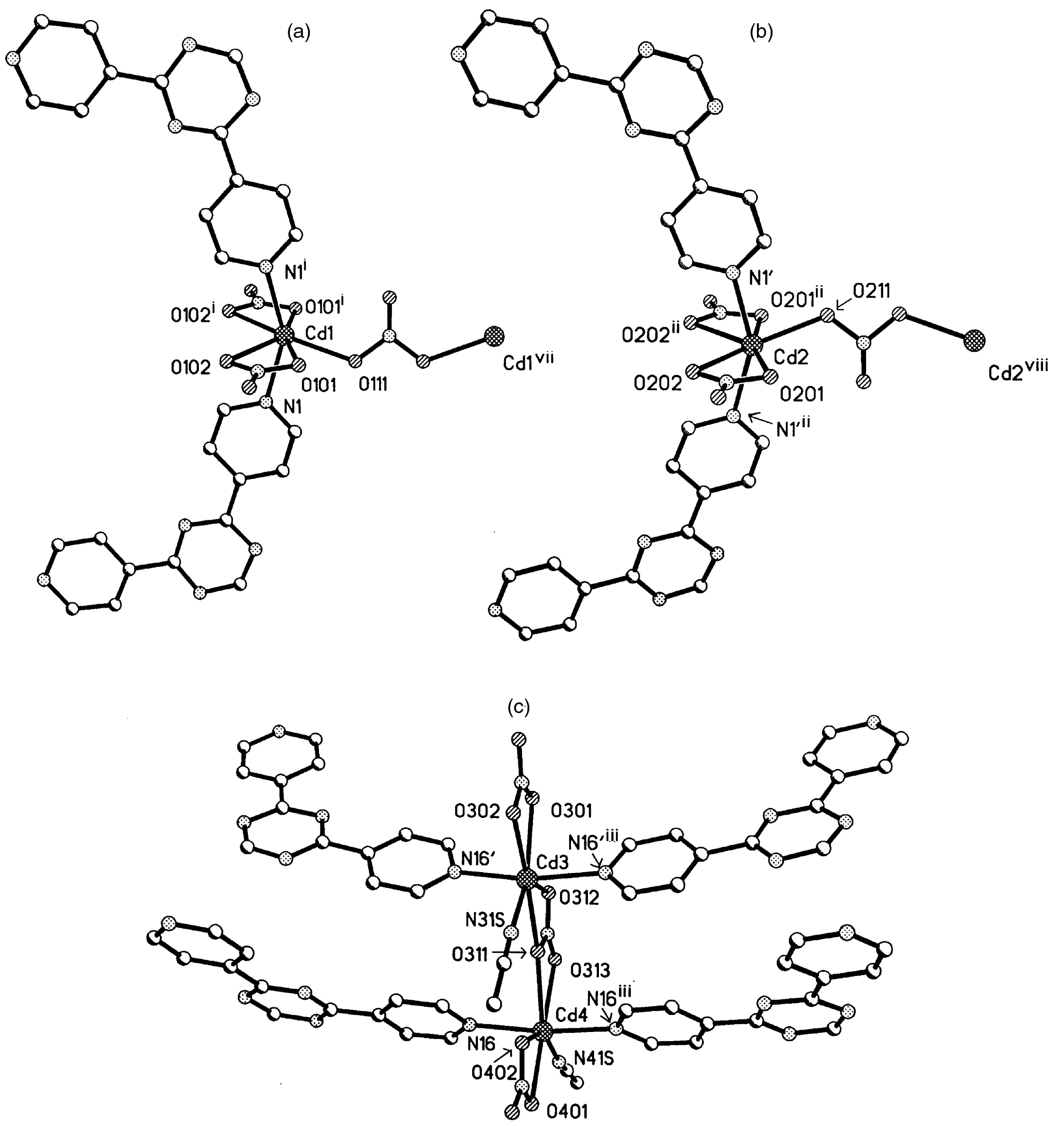
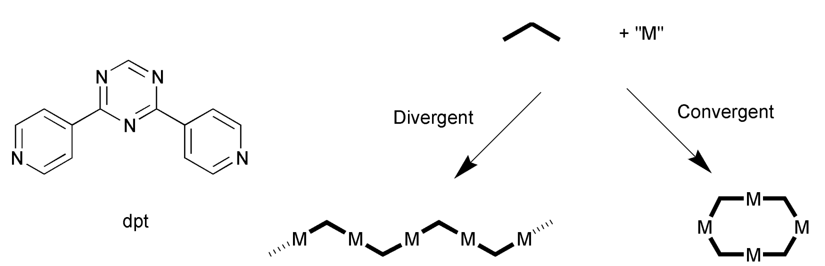
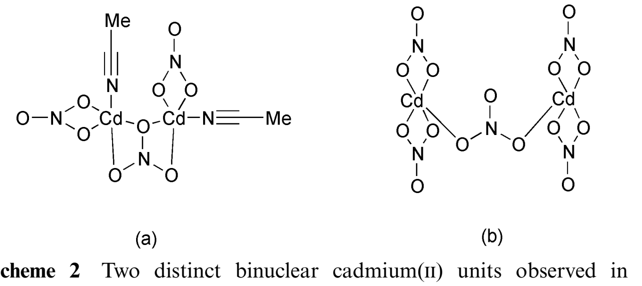


Fig. 1 Views of the cadmium(II) coordination environments in compound **1** showing the numbering scheme adopted. Hydrogen atoms are omitted for clarity (cadmium, cross-hatch; nitrogen, dotted; oxygen, left hatch). Symmetry codes: i $-x + 1, y, -z + 1$; ii $-x + 2, y, -z + 3$; iii $x, -y + 1, z$; vii $1 - x, 2 - y, 1 - z$; viii $2 - x, 2 - y, 3 - z$.



Scheme 1 Potential convergent and divergent products resulting from the reaction of an angular ligand, such as dpt, and a suitable metal centre.



Scheme 2 Two distinct binuclear cadmium(II) units observed in compound **1**: (a) formally monopositive "$Cd_2(NO_3)_3(MeCN)_2$" and (b) formally mononegative "$Cd_2(NO_3)_5$".

between the N-donors of dpt and an angle (N_{dpt}–Cd–N_{dpt}) of *ca.* 155–160° at each Cd^{II} (Fig. 2). This metallacycle can be viewed as the convergent product from the reaction of dpt and $Cd(NO_3)_2$. As this unit consists of four cadmium(II) ions and four ligand components it is, perhaps, most closely related to molecular squares[1] and will be discussed as such from now on. The nitrate bridging between cadmium(II) centres in adjacent metallacycles links these squares into a 2-D sheet with topology 4.8^2. Thus the "$Cd_4(dpt)_4$" metallacycles form a cyclic unit with four nodes and the nitrate bridges lead to further cyclic units with eight nodes around which dpt and nitrate bridges alternate (Scheme 3). A coplanar row of squares is linked to the next row

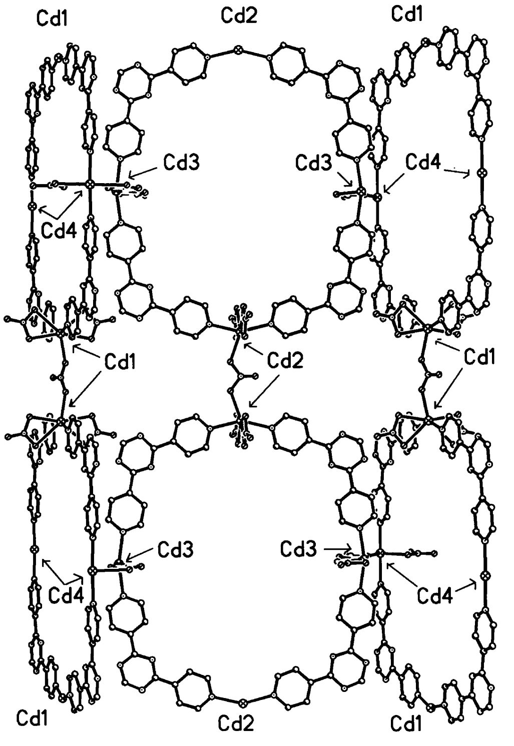
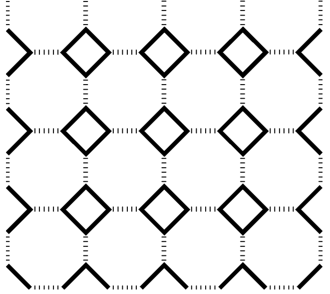


Fig. 2 View of a single 4.8^2 sheet in compound **1** illustrating the arrangement of the "$Cd_4(dpt)_4$" metallacycles which leads to an undulating array. Coordinated MeCN ligands, guest solvent molecules and hydrogen atoms are omitted for clarity. Shading as in Fig. 1.



Scheme 3 Representation of the 4.8^2 topology adopted by compound **1**. dpt and nitrate bridges are highlighted by solid and dashed lines, respectively.

in an almost perpendicular fashion resulting in formation of an undulating array (Fig. 2). However, the large spaces generated within each metallacycle (*ca.* 20 × 17 Å) allow catenation by two perpendicularly oriented squares from an adjacent sheet, resulting in the parallel interpenetration of two 2-D sheets (Fig. 3). Viewed parallel to the plane of these sheets, it can be seen that the arrangement of the nitrate anionic ligands results in interdigitation of adjacent interpenetrated layers. Further residual cavities in the structure are occupied by MeCN and CH_2Cl_2 solvent molecules.

Two-dimensional sheets can interpenetrate in two distinct fashions, namely parallel and perpendicular, affording 2-D or 3-D supermolecules, respectively.[2] Interestingly, both forms of interpenetration are far more common for (4,4) and (6,3) type nets than for any other.[2] In fact, in the case of parallel interpenetration of 2-D sheets there is only one previous example that does not involve these more common types of sheet, namely Hittorf's phosphorus which exists as a doubly interpenetrated 8^210 network.[10] The doubly interpenetrated 4.8^2 net described here is therefore unique.

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Cd1–N1	2.294(5)	Cd3–N16′	2.284(5)
Cd1–O101	2.364(5)	Cd3–N31S	2.300(8)
Cd1–O102	2.562(5)	Cd3–O301	2.443(7)
Cd1–O111	2.304(8)	Cd3–O302	2.390(7)
Cd2–N1′	2.306(5)	Cd3–O311	2.457(7)
Cd2–O201	2.352(5)	Cd3–O312	2.580(8)
Cd2–O202	2.519(5)	Cd4–N16	2.267(6)
Cd2–O211	2.296(9)	Cd4–N41S	2.298(10)
		Cd4–O401	2.416(8)
		Cd4–O402	2.409(8)
		Cd4–O311	2.496(7)
		Cd4–O313	2.580(9)
$N1^i$–Cd1–N1	151.6(3)	$N16'$–Cd3–$N16'^{iii}$	164.5(3)
$N1'$–Cd2–$N1'^{ii}$	152.6(3)	N16–Cd4–$N16^{iii}$	169.9(3)

Symmetry transformations used to generate equivalent atoms: i $-x + 1, y, -z + 1$; ii $-x + 2, y, -z + 3$; iii $x, -y + 1, z$.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **2** and **3**

2		**3**	
Cd1–N1	2.290(2)	Cd1–N1	2.297(2)
Cd1–N31	2.283(2)	Cd1–$N16^{iv}$	2.328(2)
Cd1–N1S	2.404(2)	Cd1–O1S	2.326(2)
Cd1–O101	2.335(2)	Cd1–O101	2.483(2)
Cd1–O102	2.529(2)	Cd1–O102	2.443(2)
Cd1–O201	2.422(2)	Cd1–O201	2.383(2)
Cd1–O202	2.396(2)	Cd1–O202	2.383(2)
N31–Cd1–N1	173.72(6)	N1–Cd1–$N16^{iv}$	108.35(7)

Symmetry transformation used to generate equivalent atoms: iv $x + 1, y, z - 1$.

In contrast to **1**, compound **2** somewhat surprisingly exists in the solid state as a discrete molecular complex $[Cd(NO_3)_2(dpt)_2(MeCN)]$ (Fig. 4). In this case the Cd^{II} is coordinated by two dpt ligands, a MeCN and two chelating NO_3^- anions. Although the coordination sphere in **2** (Table 2) is similar to those observed in **1** (Table 1) the major difference between the two complexes is that in **1** both "ends" of the dpt ligand are coordinated but in **2** only one of the pyridyl donors is coordinated to a Cd^{II} leaving the other pyridyl donor pendant. Therefore, **2** exists as a discrete molecular complex in the solid state. π–π Interactions between the pendant, uncoordinated, pyridyl groups and coordinated pyridyl groups link adjacent molecules into pairs (Fig. 4) (3.36 Å centroid–plane separation, 3.74 Å centroid–centroid separation) which in turn adopt π–π interactions between residual pendant pyridyl groups to form chains (3.37 Å centroid–plane separation, 3.71 Å centroid–centroid separation).

Compound **3**, $[Cd(NO_3)_2(dpt)(EtOH)]_\infty$, exists as a one-dimensional coordination polymer in which each Cd^{II} is coordinated by two dpt ligands, two nitrate anions and an EtOH molecule (Fig. 5). The two dpt ligands are arranged in a *cis* fashion such that their central triazine portions protrude from the same side of the 1-D chain. Adjacent chains are related by an inversion centre such that the dpt ligands are arranged in sheets separated by regions filled by NO_3^- anions and ligated EtOH molecules. However no π–π interactions are observed between separate chains.[11]

In the light of compounds **1** and **3** the isolation of $[Cd(NO_3)_2(dpt)_2(MeCN)]$ **2** as a discrete molecular species appears surprising, considering that uncoordinated pyridyl donors present within the complex may be expected to bridge cadmium(II) cations to afford a polymeric species, rather than the coordination of a MeCN ligand which is adopted. However, **2** was found to be insoluble not only in the reaction solvents but also in other common solvent systems, precluding its investigation by solution NMR experiments. It is reasonable to assume that the driving force behind the isolation of this complex is indeed its insolubility under the reaction conditions.

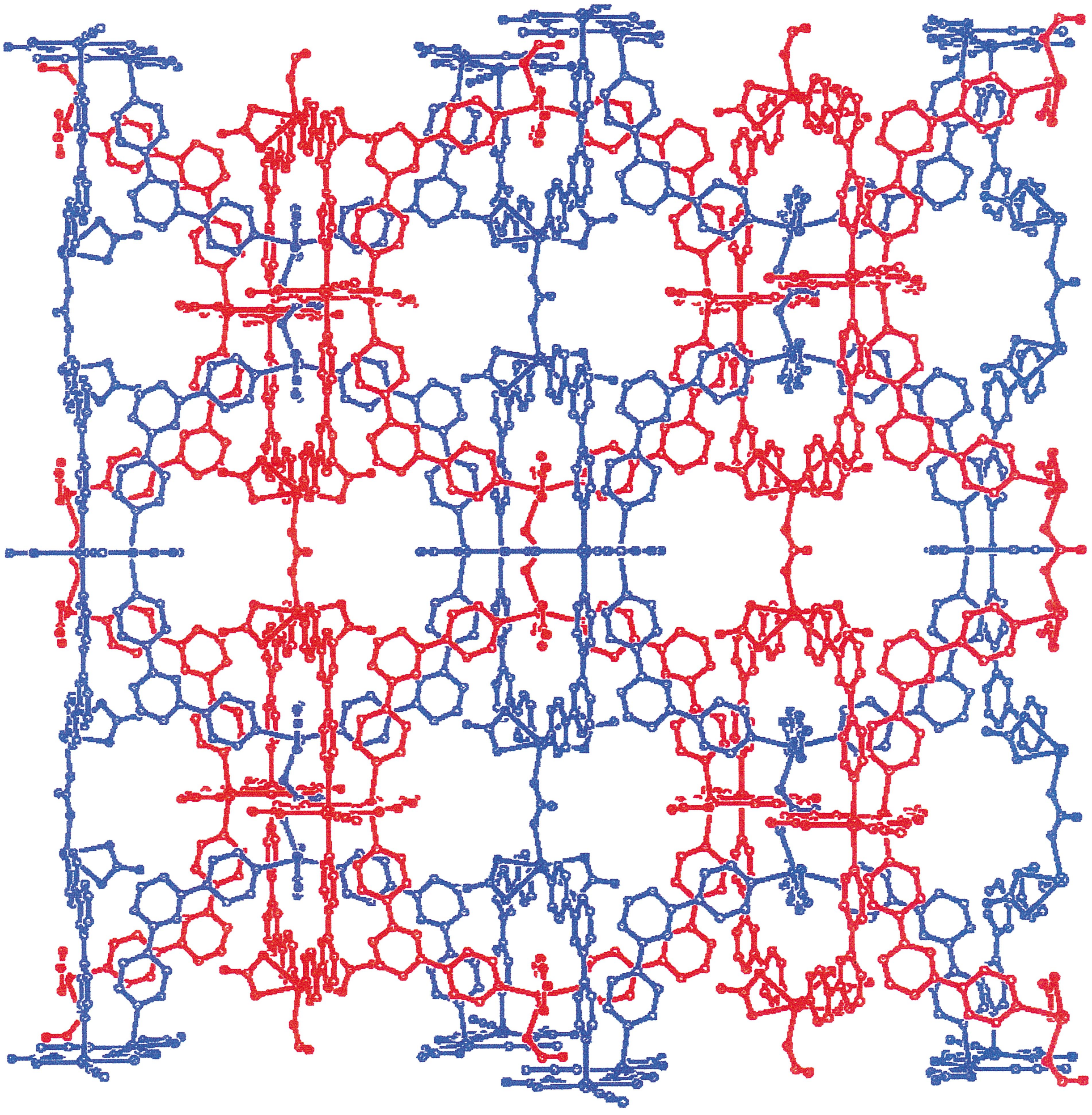


Fig. 3 View of two parallel interpenetrated 4.8^2 sheets formed by compound **1**.

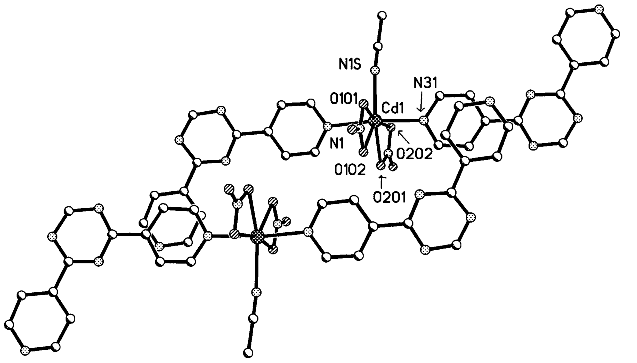


Fig. 4 Cyclic pairs of molecules of compound **2** formed by π–π interactions between the pendant dpt ligands showing the numbering scheme adopted. Hydrogen atoms are omitted for clarity. Shading as in Fig. 1.

The precise mechanism of coordination polymer formation remains unclear but can reasonably be thought of as being the result of the formation in solution of small building-blocks, or oligomers, which then link in a stepwise fashion to afford the polymeric species in the solid state. This mechanism implies a "virtual combinatorial library"[12] in the solution phase from which particular oligomers are used as the building-blocks of the resultant product. However, if the oligomeric species which are favoured in solution are themselves insoluble under the reaction conditions used then no polymerisation will take place, resulting in the isolation of discrete, molecular complexes in the solid state. This would appear to be the case for compound **2**.

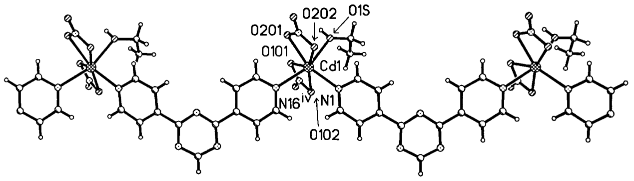


Fig. 5 View of the chains formed by compound **3** illustrating the cadmium(II) coordination sphere and showing the numbering scheme adopted. Shading as in Fig. 1. Symmetry code: iv $x + 1, y, z - 1$.

Bulk samples of compounds **1**–**3** were prepared so that the existence of a single phase could be confirmed. Unfortunately **1** always gave amorphous products when prepared by rapid precipitation from solution and so its purity as a single phase could not be assessed by powder X-ray diffraction studies. However,

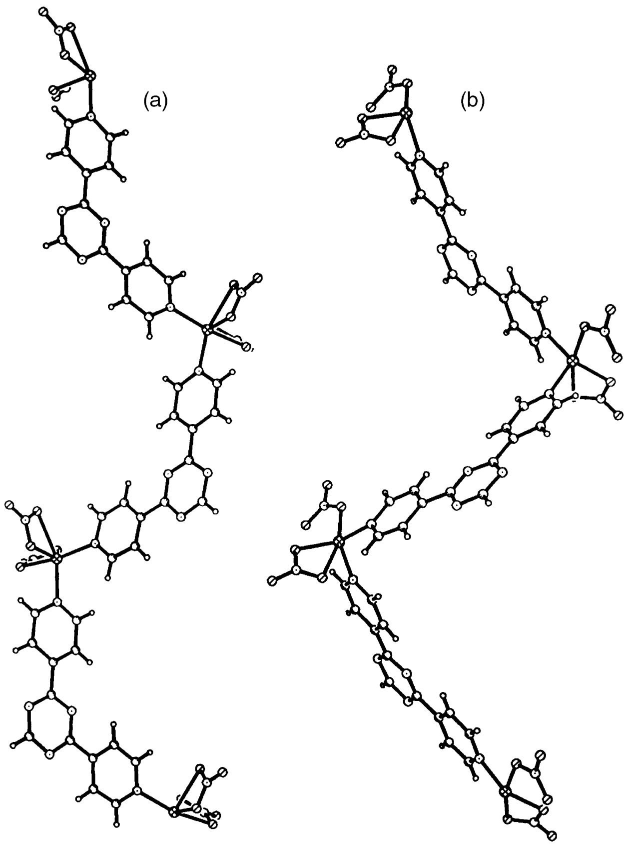


Fig. 6 View of compounds (a) **4a** and (b) **4b** drawn to the same scale showing the different pitches and diameters adopted due to variation in the zinc(II) coordination sphere. Zinc, cross-hatch; nitrogen, dotted; oxygen, left hatch.

when crystals were grown by slow diffusion over a period of a few days crystals of only a single morphology were observed indicating that diffusion experiments afforded only a single product. Powder X-ray diffraction studies of bulk samples of **2**, prepared by rapid precipitation from a 1 : 2 mixture of $Cd(NO_3)_2$ and dpt in MeCN–CH_2Cl_2, confirmed that a single compound was produced from this reaction. Similarly **3** was found to form a single product consistent with the single crystal X-ray diffraction studies when prepared from mixing a solution of the ligand in CH_2Cl_2 and $Cd(NO_3)_2$ in EtOH, in either a 1 : 1 or 1 : 2 M : L stoichiometry, as confirmed by powder X-ray diffraction.

Structure of $[Zn(NO_3)_2(dpt)]_\infty$ 4

The structure of compound **4a**, isolated from the reaction of $Zn(NO_3)_2$ with dpt in MeCN–CH_2Cl_2, forms a simple zigzag one-dimensional polymer, $[Zn(NO_3)_2(dpt)]_\infty$, instead of the two-dimensional sheets observed in **1**. Compound **4** was isolated even when higher L : M ratios were used and also when EtOH or ^{i}PrOH replaced MeCN in the crystallisation solvent mixture. However, in the cases where alcoholic solvents replaced MeCN a different polymorph of $[Zn(NO_3)_2(dpt)]_\infty$, **4b**, was crystallised. The structures of **4a** and **4b** are similar in that they can both be viewed as one-dimensional helical polymers (Fig. 6) but the environment at the Zn^{II} (Fig. 7) differs in the two compounds (Table 3). In **4a** both nitrate anions are coordinated in a chelating fashion with the two pyridyl donors in a *cis* arrangement at the distorted octahedral Zn^{II} (Fig. 7a). In **4b** the zinc(II) environment is essentially the same as that observed in **4a** except there is an elongation of one of the Zn–O distances such that one of the NO_3^- anions is coordinated in a monodentate, rather than chelating, fashion (Fig. 7b). The different binding modes of the nitrate anions in **4a** and **4b** also leads to a distinct difference in the overall geometry of the 1-D polymer. Since the Zn^{II} in **4a** is coordinated by two chelating nitrate anions the dpt pyridyl donors are pushed together such that an inter-pyridyl planar dihedral angle of 70.6° is adopted by the dpt ligands. In **4b** the one chelating and one monodentate nitrate anion provide less steric crowding at the Zn^{II} resulting in a larger inter-pyridyl planar angle of 104.9°. A decrease in the helix pitch from 22.576 Å in **4a** to 19.029 Å for **4b** and an increase in the helix diameter‡ from 6.343 Å in **4a** to 8.911 Å in **4b** is also observed.

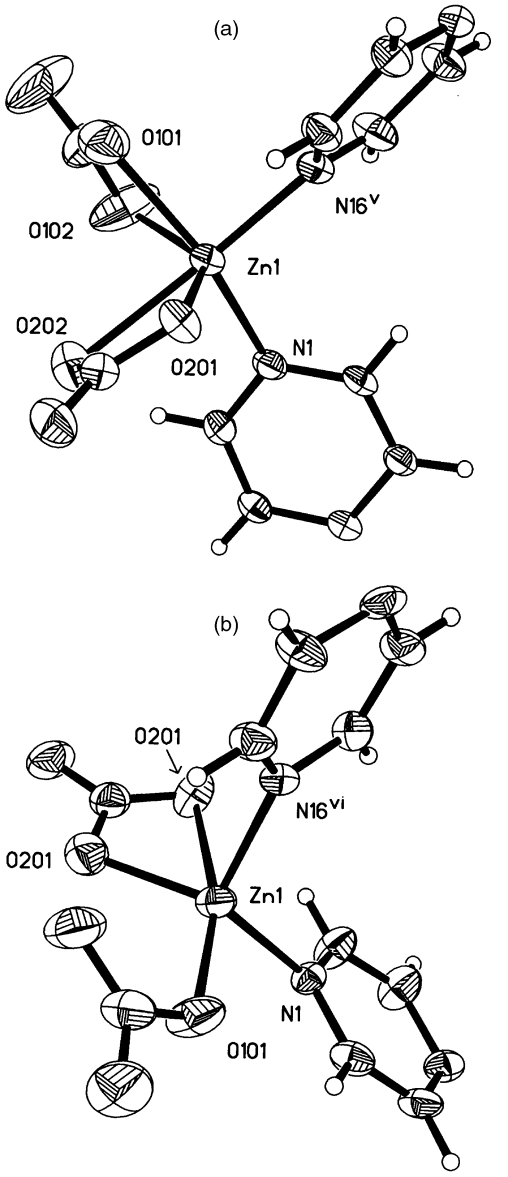


Fig. 7 The zinc(II) coordination environments adopted in compounds (a) **4a** and (b) **4b** showing the numbering scheme adopted. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: v $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; vi $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Powder X-ray diffraction studies of bulk samples of compounds **4a** and **4b** indicated that whereas the reaction in MeCN–CH_2Cl_2 gave exclusively **4a** that in EtOH or ^{i}PrOH afforded a mixture of **4a** and **4b**. This indicates that a subtle energy balance exists between the two forms, especially when the product is formed in the presence of alcoholic solvents. It is interesting that the crystallisation solvent affects the crystallised product despite not being included in the crystal lattice.

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‡ Helix diameter is defined as the Zn · · · Zn separation perpendicular to the axis of helical propagation.[13]

Table 3 Selected bond lengths (Å) and angles (°) for compounds **4a** and **4b**

4a		**4b**	
Zn1–N1	2.030(2)	Zn1–N1	2.039(7)
Zn1–N16^{v}	2.059(2)	Zn1–N16^{vi}	2.016(7)
Zn1–O101	2.197(2)	Zn1–O101	2.003(6)
Zn1–O102	2.144(3)	Zn1–O201	1.994(7)
Zn1–O201	2.069(2)	Zn1–O202	2.474(6)
Zn1–O202	2.428(2)		
N1–Zn1–N16^{v}	106.08(8)	N1–Zn1–N16^{vi}	113.2(3)

Symmetry transformations used to generate equivalent atoms: v $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; vi $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Comparison of the zinc(II) and cadmium(II) structures

The difference in the structures of these compounds can easily be explained by the tendency of Cd^{II} to adopt higher coordination numbers. This manifests itself in the coordination of an additional MeCN ligand, or bridging nitrate anion, in **1** and **2** which pushes the N$_{dpt}$–Cd–N$_{dpt}$ angle toward linearity (Tables 1, 2) whereas in the case of $[Zn(NO_3)_2(dpt)]_\infty$ **4** the N$_{dpt}$–Zn–N$_{dpt}$ angle is smaller (Table 3) due to the *cis* arrangement of the pyridyl donors at the octahedral metal centre. Thus in **1** the result of the N$_{dpt}$–Cd–N$_{dpt}$ angle approaching linearity is that this angle complements the 120° angle between the pyridyl donors of the dpt ligand thereby encouraging adoption of the cyclic "Cd$_4$(dpt)$_4$" unit which ultimately results in formation of the two-dimensional sheets observed. In compound **3** the relative orientation of the dpt ligands at the Cd^{II} [N$_{dpt}$–Cd–N$_{dpt}$ 108.35(7)°] precludes the adoption of cyclic structures and hence encourages the formation of 1-D chains as is similarly the case in **4** in which the more acute N$_{dpt}$–Zn–N$_{dpt}$ angle inhibits formation of cyclic species.

Conclusion

We have isolated a range of cadmium(II) and zinc(II) compounds of dpt, from molecular to one- and two-dimensional products, including the first example of doubly parallel-interpenetrated 4.8^2 sheets which are built from nitrate linked "Cd$_4$(dpt)$_4$" metallacycles. Using a 2 : 1 L : M ratio results in the isolation of a molecular complex with pendant pyridyl donors rather than the expected coordination polymer. One-dimensional polymers are isolated when the analogous reactions are performed in EtOH or when Zn(NO$_3$)$_2$ replaces Cd(NO$_3$)$_2$. Important points arise from the structural analysis of these compounds. First, the pitch of the 1-D Zn^{II} polymers, **4**, is significantly influenced in two dimorphs by a relatively small change in the mode of nitrate binding. Secondly, depending on the convergent or divergent pathway that the coordination polymer formation pursues, radically different structural forms are adopted. Both of these factors are significant when considering the design of new coordination polymer networks.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer (FTIR, samples in KBr discs). Elemental analytical data were obtained by the microanalytical service (Perkin-Elmer 240B analyser) at the University of Nottingham. 2,4-Bis(4-pyridyl)-1,3,5-triazine was prepared according to the literature method;[9] all other chemicals were purchased from Aldrich Chemicals and used without further purification.

Syntheses

$[Cd(NO_3)_2(dpt)(MeCN)]_\infty$ 1. A solution of Cd(NO$_3$)$_2$·4H$_2$O (105 mg, 0.34 mmol) in MeCN (15 cm^3) was added to a solution of dpt (81 mg, 0.34 mmol) in CH$_2$Cl$_2$ (3 cm^3). A creamy white precipitate formed immediately, was filtered off and dried *in vacuo*. Yield 70% (Found: C, 33.41; H, 2.42; N, 21.35. Calc. for C$_{28}$H$_{21}$Cd$_2$N$_{15}$O$_{12}$ [Cd$_2$(NO$_3$)$_4$(dpt)$_2$(MeCN)]: C, 34.16; H, 2.15; N, 21.35%). IR (KBr)/cm^{-1}: 2924w, 1571w, 1534m, 1511w, 1413m, 1384s, 1304w, 1056w, 1014w, 794m, 676w, 651w and 527w. Single crystals were grown by slow diffusion of layered solutions of Cd(NO$_3$)$_2$·4H$_2$O in MeCN over dpt in CH$_2$Cl$_2$.

$[Cd(NO_3)_2(dpt)_2(MeCN)]$ 2. A solution of Cd(NO$_3$)$_2$·4H$_2$O (75 mg, 0.24 mmol) in MeCN (20 cm^3) was added to a solution of dpt (114 mg, 0.48 mmol) in CH$_2$Cl$_2$ (3 cm^3). A creamy white precipitate formed immediately, was filtered off and dried *in vacuo*. Yield 92% (Found: C, 43.71; H, 2.60; N, 24.36. Calc. for C$_{28}$H$_{21}$CdN$_{13}$O$_6$: C, 44.95; H, 2.84; N, 24.35%). IR (KBr)/cm^{-1}: 3106w, 3066w, 2296w, 1615w, 1568m, 1547s, 1533s, 1425s, 1386s, 1294s, 1260w, 1215w, 1057w, 1032w, 1022w, 988w, 802m, 756w, 736w, 673w, 645m, 536w and 410w. Single crystals were grown by slow diffusion of layered solutions of Cd(NO$_3$)$_2$·4H$_2$O in MeCN over dpt in CH$_2$Cl$_2$.

$[Cd(NO_3)_2(dpt)(EtOH)]_\infty$ 3. A solution of Cd(NO$_3$)$_2$·4H$_2$O (64 mg, 0.21 mmol) in EtOH (15 cm^3) was added to a solution of dpt (49 mg, 0.21 mmol) in CH$_2$Cl$_2$ (2 cm^3). A creamy white precipitate formed over the period of *ca.* 30 min, was filtered off and dried *in vacuo*. Yield 74% (Found: C, 34.64; H, 2.83; N, 18.74. Calc. for C$_{15}$H$_{15}$CdN$_7$O$_7$: C, 34.80; H, 2.93; N, 18.94%). IR (KBr)/cm^{-1}: 3051w, 1570m, 1534m, 1512m, 1423m, 1413m, 1384s, 1303w, 1210w, 1055w, 1013w, 833w, 794m, 729w, 676w, 651m, 529w and 403w. Single crystals were grown by slow diffusion of layered solutions of Cd(NO$_3$)$_2$·4H$_2$O in EtOH over dpt in CH$_2$Cl$_2$.

$[Zn(NO_3)_2(dpt)]_\infty$ 4a. This was prepared analogously to compound **1**, replacing Cd(NO$_3$)$_2$ with Zn(NO$_3$)$_2$. Yield 72% (Found: C, 36.88; H, 2.12; N, 22.61. Calc. for C$_{13}$H$_9$N$_7$O$_6$Zn: C, 36.77; H, 2.14; N, 23.10%). IR (KBr)/cm^{-1}: 3052w, 1620w, 1572w, 1536m, 1517m, 1384s, 1302m, 1288w, 1219w, 1058w, 1029w, 806m, 737w, 679w, 660w and 537w.

$[Zn(NO_3)_2(dpt)]_\infty$ 4b. This was prepared analogously to compound **1**, replacing Cd(NO$_3$)$_2$ with Zn(NO$_3$)$_2$ and MeCN with either EtOH or ^{i}PrOH. Yield 70% (Found: C, 37.02; H, 2.16; N, 22.40%). IR (KBr)/cm^{-1}: 3057w, 1619w, 1572m, 1535m, 1514m, 1384s, 1302m, 1288m, 1208w, 1057w, 1029w, 804m, 737w, 681w, 660w and 537w.

Crystallography

All single crystal X-ray experiments were performed on either a Bruker AXS SMART CCD detector diffractometer (compounds **1**–**3**, **4a**) or a Stoë Stadi-4 four-circle diffractometer (**4b**), both equipped with an Oxford Cryosystems open flow cryostat[14] [graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å); ω scans]. Absorption corrections were applied by a semi-empirical approach (**1**–**3**, **4a**) or using ψ scans (**4b**). Other details of crystal data, data collection and processing are given in Table 4. All of the single-crystal structures were solved by direct methods using SHELXS 97[15] and all non-H atoms located using subsequent Fourier difference methods.[16]

In all cases hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Compound **1**, $\{[Cd_2(NO_3)_4(dpt)_2(MeCN)]\cdot 2.5MeCN\cdot 0.5CH_2Cl_2\}_\infty$, was found to contain both disordered and partially occupied guest solvent molecules. All of the nitrate anions were restrained to have equal N–O bond lengths and O–N–O angles. Two of the bridging nitrate anions (N110,O111,O112; N210,O211,O212) were found to be disordered around an inversion centre and were modelled accordingly. Of the

Table 4 Crystallographic data summary for compounds **1**–**4**

	1	**2**	**3**	**4a**	**4b**
Empirical formula	$C_{16.58}H_{12.28}CdCl_{0.5}N_{8.67}O_6$	$C_{28}H_{21}CdN_{13}O_6$	$C_{15}H_{15}CdN_7O_7$	$C_{13}H_9N_7O_6Zn$	$C_{13}H_9N_7O_6Zn$
M	559.09	747.98	517.74	424.64	424.64
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/m$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	26.578(5)	9.792(2)	8.9014(10)	11.891(1)	6.981(5)
b/Å	26.471(5)	10.319(2)	10.3249(12)	11.846(1)	19.029(7)
c/Å	16.037(3)	15.445(3)	10.4451(12)	11.804(1)	12.222(7)
α/°	—	102.529(3)	77.397(2)	—	—
β/°	1226.52(3)	96.953(3)	86.866(2)	110.352(2)	97.70(6)
γ/°	—	96.495(3)	86.988(2)	—	—
U/Å^3	9067(3)	1496.4(8)	934.6(2)	1558.9(2)	1608.9(16)
Z	16	2	2	4	4
T/K	150(2)	150(2)	150(2)	150(2)	150(2)
μ/mm^{-1}	1.073	0.797	1.225	1.629	1.578
Reflections collected	28328	15595	7088	10017	3276
Unique reflections (R_{int})	10763 (0.086)	6974 (0.029)	4102 (0.031)	3868 (0.039)	3164 (0.0)
Observed reflections [$F > 4\sigma(F)$]	8104	5968	3469	3038	2125
Final $R1$ [$F > 4\sigma(F)$]	0.0658	0.0302	0.0261	0.0364	0.0896
$wR2$ (all data)	0.1593	0.0802	0.0602	0.1078	0.2154

uncoordinated solvent molecules only one was fully occupied and in the other case the occupancy was refined and then fixed at half occupancy. One MeCN molecule (C1T,C1T′,N1T) and the CH_2Cl_2 molecule (Cl1A,C1A) were each disordered around a 2-fold axis. All non-H atoms of the uncoordinated molecules which were not fully occupied were refined isotropically and the hydrogen atoms not located but included in the formula sum.

CCDC reference numbers 151816–151820.

See http://www.rsc.org/suppdata/dt/b0/b008715g/ for crystallographic data in CIF or other electronic format.

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