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[Ni(cyclam)(OCOR)₂], a finite molecular complex: hydrogen-bonded supramolecular aggregation in one, two and three dimensions, and coordination polymers in one and two dimensions

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In the complexes [Ni(cyclam)(OCOR)₂] (cyclam = 1,4,8,11-tetraazacyclotetradecane), where $(RCOO)^-$ is 2-naphthoate [bis-(2-naphthoato)-1,4,8,11-tetraazacyclotetradecane-nickel(II), (I), monoclinic $P2_1/c$, $Z' = 0.5$], 3,5-dinitrobenzoate [bis-(3,5-dinitrobenzoato)-1,4,8,11-tetraazacyclotetradecane-nickel(II), (II), triclinic $P\bar{1}$, $Z' = 0.5$], 4-nitrobenzoate [bis-(4-nitrobenzoato)-1,4,8,11-tetraazacyclotetradecanenickel(II), (III), monoclinic $P2_1/n$, $Z' = 0.5$], 3-hydroxybenzoate [bis-(3-hydroxybenzoato)-1,4,8,11-tetraazacyclotetradecanenickel(II), (IV), monoclinic $P2_1/c$, $Z' = 0.5$] and 4-aminobenzoate [bis-(4-aminobenzoato)-1,4,8,11-tetraazacyclotetradecanenickel(II), (V), monoclinic $C2/c$, $Z' = 0.5$], the Ni lies on a centre of inversion with monodentate carboxylato ligands occupying *trans* sites. Compound (I) consists of isolated molecules. In (II) and (III), N—H···O hydrogen bonds link the complexes into chains. Compounds (IV) and (III) form two- and three-dimensional structures generated entirely by hard hydrogen bonds. The 5-hydroxyisophthalate(2−) anion forms a hydrated complex, [Ni(cyclam)(5-hydroxyisophthalate)(H₂O)]·4H₂O {[aqua-(5-hydroxyisophthalato)-1,4,8,11-tetraazacyclotetradecanenickel(II)] tetrahydrate, (VI), monoclinic Cc, $Z' = 1$}, in which the monodentate carboxylato ligand and a water molecule occupy *trans* sites at Ni: extensive hydrogen bonding links the molecular aggregates into a three-dimensional framework. The terephthalate(2−) anion forms a hydrated linear coordination polymer {*catena*-poly[terephthalato-1,4,8,11-tetraazacyclotetradecanenickel(II)] monohydrate, (VII), monoclinic $C2/c$, $Z' = 0.5$}. In 1,2,4,5-benzenecarboxylate tris[1,4,8,11-tetraazacyclotetradecane-nickel(II)] diperchlorate hydrate (VIII), [Ni(cyclam)]₃·[1,2,4,5-benzenetetracarboxylate(4−)]·[ClO₄]₂·[H₂O]₃, there are two distinct Ni sites: [Ni(cyclam)]²⁺ and centrosymmetric $[C_{10}H_2O_8]^{4-}$ units form a two-dimensional coordination polymer, whose sheets are linked by centrosymmetric [Ni(cyclam)(H₂O)₂]²⁺ cations.

1. Introduction

In the square-planar [Ni(cyclam)]²⁺ cation [cyclam = 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$], the macrocyclic ligand adopts an almost planar, disk-like conformation with two axial N—H bonds on each face (Prasad & McAuley, 1983; Barefield *et al.*, 1986; Adam *et al.*, 1991), and there are two axial coordination sites available at the Ni (Ito *et al.*, 1984; Mochizuki & Kondo, 1995; Choi *et al.*, 1999; Glidewell *et al.*, 2000; Zakaria *et al.*, 2001). The [Ni(cyclam)]²⁺ cation thus provides an attractive building block for supramolecular chemistry, in that there

is an essentially rigid and pre-organized arrangement of coordination sites and hydrogen-bond forming N—H bonds. We have previously reported the three-dimensional aggregation of the 4-hydroxybenzoate derivative (Glidewell *et al.*, 2000) as well as the three-dimensional aggregation of a binuclear system $[\{Ni(C_{10}H_{24}N_4)(H_2O)\}_2(C_8H_4O_4)](ClO_4)_2$ containing the terephthalate (1,4-benzenedicarboxylate) anion as a bridging ligand (Zakaria *et al.*, 2001). In the only other example of the use of this cation in supramolecular chemistry, the *trans*-diaqua cation $[Ni(cyclam)(H_2O)_2]^{2+}$ was found to form a highly hydrated framework structure with the 1,3,5-benzenetricarboxylate(3−) anion but, in this case there was no coordination of the carboxylate anions to the Ni (Choi *et al.*, 1999). In this paper we report the results of a systematic study of $[Ni(cyclam)(OCOR)_2]$ complexes in which the carboxylate ligand $(RCOO)^-$ has been selected to manifest different modes of supramolecular aggregation, including aromatic $\pi\cdots\pi$ stacking interactions, hard and soft (Braga *et al.*, 1995) hydrogen bonds and coordination polymer formation. To this end, we have determined and analysed the supramolecular structures for monocarboxylate examples where $(RCOO)^-$ is 2-naphthoate, expected to lead to $\pi\cdots\pi$ stacking, compound (I); 3,5-dinitrobenzoate and 4-nitrobenzoate, where there is an excess of hard hydrogen-bond acceptors, compounds (II) and (III), respectively; and 3-hydroxybenzoate and 4-aminobenzoate, with an excess of hard hydrogen-bond donors, compounds (IV) and (V), respectively. In addition, we have studied three polycarboxylate derivatives in which the anionic ligands are 5-hydroxyisophthalate(2−), where the pentahydrate, compound (VI), yields a three-dimensional framework; 1,4-benzenedicarboxylate(2−), which leads to cation–anion chain formation in a coordination polymer, compound (VII); and 1,2,4,5-benzenetetracarboxylate(4−) where the product $[Ni(cyclam)]_3\cdot[1,2,4,5$-benzenetetracarboxylate(4−)]$\cdot2ClO_4\cdot3H_2O$, compound (VIII), contains a two-dimensional coordination polymer. We have also prepared the $[Ni(cyclam)(OCOR)_2]$ complexes from adamantane-1-carboxylate, as a dihydrate compound (IX), and from 3,5-dihydroxybenzoate, compound (X), but we have so far been unable to obtain these materials in suitably crystalline form.

2. Experimental

2.1. Syntheses

Stoichiometric quantities of $[Ni(cyclam)][ClO_4]_2$ and the sodium salt of the carboxylic acid were separately dissolved in water: these solutions were mixed and then set aside to crystallize, producing pale purple crystals of the products in analytically pure form. Analyses: (I), found C 63.7, H 6.4, N 9.1%; $C_{32}H_{38}N_4NiO_4$ requires C 63.9, H 6.4, N 9.3%; (II), found C 42.2, H 3.4, N 16.1%; $C_{24}H_{30}N_8NiO_{12}$ requires C 42.3, H 4.4, N 16.4%; (III), found C 48.8, H 5.0, N 13.9%; $C_{24}H_{32}N_6NiO_8$ requires C 48.8, H 5.4, N 14.2%; (IV), found C 53.9, H 6.1, N 10.5%; $C_{24}H_{34}N_4NiO_6$ requires C 54.0, H 6.4, N 10.5%; (V), found C 54.7, H 5.8, N 15.9%; $C_{24}H_{36}N_6NiO_4$

requires C 54.3, H 6.8, N 15.8%; (VI), found C 41.1, H 7.6, N 10.8%; $C_{18}H_{38}N_4NiO_{10}$ requires C 40.9, H 7.2, N 10.6%; (VII), found C 49.3, H 7.0, N 12.9%; $C_{18}H_{30}N_4NiO_5$ requires C 49.0, H 6.9, N 12.7%; (VIII) found C 38.3, H 6.6, N 13.1%; $C_{40}H_{80}Cl_2N_{12}Ni_3O_{19}$ (idealized composition) requires C 37.5, H 6.3, N 13.1%; $C_{40}H_{78}Cl_2N_{12}Ni_3O_{19}$ (composition found in X-ray analysis) requires C 37.6, H 6.32, N 13.2%; (IX), found C 59.4, H 9.3, N 8.7%; $C_{32}H_{58}N_4NiO_6$ requires C 58.8, H 9.0, N 8.6%; (X), found C 50.7, H 5.7, N 9.8%; $C_{24}H_{34}N_4NiO_8$ requires C 51.0, H 6.1, N 9.9%. Crystals of (I)–(VIII) suitable for single-crystal X-ray diffraction were selected directly from the analytical samples. No suitable crystals have yet been obtained for (IX) and (X).

2.2. Data collection, structure solution and refinement

Diffraction data for (I)–(VIII) were collected at 150 (2) K [293 (2) K for (II)] using a Nonius KappaCCD diffractometer, using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Other details of cell data, data collection and refinement are summarized in Table 1.

For (I), (IV) and (VIII) the space group $P2_1/c$ was uniquely assigned from the systematic absences: the space group $P2_1/n$ was similarly assigned for (III). Compound (II) is triclinic: the space group $P\bar{1}$ was selected and subsequently confirmed by the successful structure solution and refinement. For each of (V)–(VII) the systematic absences permitted space groups Cc and $C2/c$: bearing in mind the stoichiometries, space group Cc was selected for (VI) and $C2/c$ was selected for both (V) and (VII), and these choices were subsequently confirmed by the successful structure solutions and refinements. The structures were solved by direct methods and refined with all data on F^2. A weighting scheme based upon $P = [F_o^2 + 2F_c^2]/3$ was employed in order to reduce statistical bias (Wilson, 1976). In each of (I)–(V) the Ni is located at a centre of inversion, chosen for convenience as that at (0.5, 0.5, 0.5). In (VII) the Ni is located at a centre of inversion and the terephthalate unit also lies across a centre of inversion: these inversion centres were chosen as (0.25, 0.25, 0) for Ni and the origin for the terephthalate anion: there is also a water molecule present in (VII), located on the twofold axis (0, y, 0.25). For (VI) the coordinates of the H atoms on the five water molecules were obtained from difference maps and allowed to refine subject to a common $DFIX$ restraint; the resulting O—H distances are in the range 0.85 (3)–0.92 (3) Å. In (VII) the water molecule oxygen (O3) lies on a twofold axis and the coordinates of its unique H atom (H3) were obtained from a difference map and then refined with an O—H restraint of 0.85 (3) Å. For (VIII) the coordinates of the H atoms (H1A, H1B) on coordinated water oxygen O1 were determined from a difference map and then allowed to refine with $DFIX$ restraints. In the determination of the structure it became apparent that there was another water molecule with only partial occupancy, filling what would have been a void in the asymmetric unit; the occupancy of this O atom (O2) was refined and its final value is 0.430 (9). It was not possible to determine coordinates for the H atoms on this partial occupancy O atom. It was also

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Table 1
Experimental details.

	(I)	(II)	(III)	(IV)	(V)
Crystal data					
Chemical formula	$C_{32}H_{38}N_4NiO_4$	$C_{24}H_{30}N_8NiO_{12}$	$C_{24}H_{32}N_6NiO_8$	$C_{24}H_{34}N_4NiO_6$	$C_{24}H_{36}N_6NiO_4$
Chemical formula weight	601.37	681.27	591.27	533.26	531.3
Cell setting, space group	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$
a, b, c (Å)	11.4970 (4), 10.6563 (4), 11.9407 (4)	7.7663 (3), 9.7845 (6), 10.4026 (7)	12.8106 (3), 8.4187 (2), 12.8397 (4)	8.5180 (3), 13.2496 (5), 10.7720 (4)	18.4430 (4), 8.4149 (2), 16.8262 (4)
α, β, γ (°)	90, 92.2080 (17), 90	99.826 (2), 97.966 (2), 108.388 (2)	90, 114.2543 (10), 90	90, 101.161 (2), 90	90, 107.8774 (14), 90
V (Å³)	1461.83 (9)	723.30 (7)	1262.51 (6)	1192.74 (8)	2485.27 (10)
Z	2	1	2	2	4
D_x (Mg m⁻³)	1.366	1.564	1.555	1.485	1.420
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	3144	5718	2781	2748	2913
θ range (°)	2.61–27.51	2.82–27.19	2.93–27.79	2.88–27.53	2.81–27.50
μ (mm⁻¹)	0.707	0.748	0.831	0.862	0.823
Temperature (K)	150 (2)	293 (2)	150 (2)	150 (2)	150 (2)
Crystal form, colour	Block, purple	Plate, colourless	Block, colourless	Needle, colourless	Block, colourless
Crystal size (mm)	$0.36 \times 0.26 \times 0.18$	$0.30 \times 0.24 \times 0.02$	$0.26 \times 0.24 \times 0.22$	$0.40 \times 0.28 \times 0.22$	$0.42 \times 0.40 \times 0.38$
Data collection					
Diffractometer	Kappa–CCD	Kappa–CCD	Kappa–CCD	Kappa–CCD	Kappa–CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.7848	0.8067	0.8130	0.7243	0.7236
T_{max}	0.8832	0.9852	0.8384	0.8330	0.7449
No. of measured, independent and observed parameters	9394, 3328, 2895	17 662, 3135, 2560	8828, 2894, 2456	9996, 2721, 2194	12 342, 2823, 2395
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.022	0.075	0.040	0.040	0.032
θ_{max} (°)	27.51	27.19	27.79	27.53	27.50
Range of h, k, l	$0 \to h \to 14$	$0 \to h \to 9$	$0 \to h \to 16$	$0 \to h \to 11$	$0 \to h \to 23$
	$0 \to k \to 13$	$-12 \to k \to 11$	$0 \to k \to 10$	$0 \to k \to 17$	$0 \to k \to 10$
	$-15 \to l \to 15$	$-13 \to l \to 13$	$-16 \to l \to 15$	$-13 \to l \to 13$	$-21 \to l \to 20$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0297, 0.0765, 1.029	0.0421, 0.0968, 1.055	0.0303, 0.0797, 1.038	0.0319, 0.0759, 1.041	0.0283, 0.0738, 1.05
No. of reflections and parameters used in refinement	3328, 187	3135, 206	2894, 178	2721, 162	2823, 161
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0155P)^2 + 0.7435P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2)P)^2 + 0.3293P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 0.5307P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 0.6219P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 2.6861P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.000	0.001	0.001	0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.287, −0.367	0.285, −0.431	0.367, −0.39	0.333, −0.362	0.32, −0.344
Extinction method	None	*SHELXL*	None	*SHELXL*	*SHELXL*
Extinction coefficient	–	0.013 (3)	–	0.0036 (10)	0.0023 (3)

	(VI)	(VII)	(VIII)
Crystal data			
Chemical formula	$C_{18}H_{30}N_4NiO_6 \cdot 4H_2O$	$C_{18}H_{28}N_4NiO_4 \cdot H_2O$	$2C_{15}H_{25}N_4NiO_4 \cdot C_{10}H_{28}N_4NiO_2 \cdot 2ClO_4 \cdot 0.86H_2O$
Chemical formula weight	529.23	441.17	1277.62
Cell setting, space group	Monoclinic, C_c	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	18.4057 (8), 9.6927 (4), 13.4648 (5)	16.2155 (4), 16.0404 (6), 8.8937 (3)	10.8295 (3), 16.9416 (5), 14.9596 (5)
β (°)	96.724 (2)	118.4900 (16)	93.6260 (13)
V (Å³)	2385.61 (17)	2033.14 (11)	2739.13 (14)
Z	4	4	2
D_x (Mg m⁻³)	1.474	1.441	1.550

Table 1 (continued)

	(VI)	(VII)	(VIII)
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	2739	2402	6029
θ range ($^\circ$)	2.75–27.48	2.63–27.49	2.56–27.53
μ (mm^{-1})	0.873	0.991	1.199
Temperature (K)	150 (2)	150 (2)	150 (2)
Crystal form, colour	Plate, purple	Block, purple	Plate, purple
Crystal size (mm)	$0.36 \times 0.34 \times 0.04$	$0.18 \times 0.16 \times 0.16$	$0.40 \times 0.36 \times 0.12$
Data collection			
Diffractometer	Kappa–CCD	Kappa–CCD	Kappa–CCD
Data collection method	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets	φ scans, and ω scans with κ offsets
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.7441	0.8418	0.6455
T_{max}	0.9659	0.8576	0.8694
No. of measured, independent and observed parameters	9912, 5106, 4757	12 978, 2333, 1622	20 675, 6277, 5362
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.051	0.088	0.039
θ_{max} ($^\circ$)	27.48	27.49	27.53
Range of h, k, l	$-23 \rightarrow h \rightarrow 23$	$0 \rightarrow h \rightarrow 20$	$0 \rightarrow h \rightarrow 14$
	$-12 \rightarrow k \rightarrow 12$	$0 \rightarrow k \rightarrow 20$	$0 \rightarrow k \rightarrow 21$
	$-17 \rightarrow l \rightarrow 17$	$-11 \rightarrow l \rightarrow 10$	$-19 \rightarrow l \rightarrow 19$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0344, 0.0817, 1.031	0.0515, 0.1471, 1.067	0.0342, 0.0904, 1.032
No. of reflections and parameters used in refinement	5106, 342	2333, 134	6277, 377
H-atom treatment	Constrained	Constrained	Constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + 2.7841P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2 + 1.8839P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.009	0.000	0.002
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.348, −0.362	0.831, −0.853	0.448, −0.616
Extinction method	*SHELXL*	*SHELXL*	*SHELXL*
Extinction coefficient	0.0014 (3)	0.0193 (17)	0.0031 (6)

Computer programs used: *Kappa-CCD* (Nonius, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997*b*), *PLATON* (Spek, 2001), *PRPKAPPA* (Ferguson, 1999).

apparent that the perchlorate O atoms were disordered unequally over two orientations and refinement yielded occupancy factors of 0.914 (4) and 0.086 (4) for O atoms. The O atoms of the minor occupancy site were refined with appropriate *DFIX* restraints and with an overall U_{iso} vibration parameter. All other H atoms were located from difference maps and all were fully ordered: they were included in the refinements as riding atoms with O—H 0.84–0.85, N—H 0.88–0.93 and C—H 0.93–0.99 Å. Refinement of the Flack parameter (Flack, 1983) for (VI) gave the value 0.434 (11), indicative of racemic twinning (Flack & Bernardinelli, 2000).

Supramolecular analyses were made and the diagrams were prepared with the aid of *PLATON* (Spek, 2001). Hydrogen-bonding details are given in Table 2.[1] Figs. 1–23 show the

molecular aggregates, with the atom-labelling schemes, and aspects of the supramolecular structures.

3. Results and discussion

3.1. General aspects of the structures

There are two carboxylate anions per [Ni(cyclam)]$^{2+}$ unit in each of (I)–(V): in (VI) there is one 5-hydroxy-isophthalate(2−) anion per [Ni(cyclam)]$^{2+}$ unit, accompanied by five water molecules, one of which is coordinated to the Ni atom. The one-dimensional coordination polymer (VII) contains equal numbers of [Ni(cyclam)]$^{2+}$ cations, terephthalate(2−) anions and water molecules, while the two-dimensional coordination polymer (VIII) contains both [Ni(cyclam)]$^{2+}$ and [Ni(cyclam)(H$_2$O)$_2$]$^{2+}$ cations in a 2:1 ratio, as well as 1,2,4,5-benzenetetracarboxylate(4−) and perchlo-

rate anions in a 1:2 ratio, and neutral water molecules. In (I)–(V) and (VII), the Ni(cyclam) moiety lies across a centre of inversion with the two carboxylate ligands in axial sites; in (VI) only one of the two available carboxylate groups is bound to Ni and the second axial site is occupied by one of the five independent water molecules. Of the two types of Ni(cyclam) unit present in (VIII), the aquated cation [Ni(cyclam)(H$_2$O)$_2$]$^{2+}$, observed previously in the salt formed with the 1,3,5-benzenetricarboxylate(3−) anion (Choi *et al.*, 1999), but not in any of (I)–(VII), lies across a centre of inversion: in the other non-centrosymmetric cation the two axial sites are occupied by carboxylate O, similar to the coordination pattern in (I)–(V). In each compound the cyclam ligand adopts the near-planar *trans*-(III) conformation (Barefield *et al.*, 1986) with almost perfect staggering about each of the C—C and C—N bonds in the macrocycle, and with two axial N—H bonds potentially available for hydrogen-bond formation on each face of the macrocycle. The axial carboxylate ligands are bound to Ni in a monodentate fashion and the uncoordinated O of each ligating carboxyl group acts as the acceptor in an N—H···O hydrogen bond, generating an unusual S(6) synthon which has previously been observed in the 4-hydroxybenzoate complex (XI) (Glidewell *et al.*, 2000) and in the terephthalate-bridged binuclear cation [{(H$_2$O)-Ni(cyclam)}$_2$(OCOC$_6$H$_4$COO)]$^{2+}$, which has been analysed as its perchlorate salt (Zakaria *et al.*, 2001).

In the centrosymmetric systems, formation of the S(6) motifs on each face of the macrocycle leaves two N—H bonds, one on each face, potentially available for intermolecular hydrogen-bond formation, while in (VI) there are three such N—H bonds available. In (VIII) the formation of the S(6) motifs with the carboxylate ligands in the non-aquated Ni(cyclam) unit leaves two N—H bonds available, one on each face: in the aquated Ni(cycalm) units of (VIII) all four N—H bonds are available. In addition, where there is an excess of hydrogen-bond acceptors over hard hydrogen-bond donors, the formation of C—H···O hydrogen bonds is also to be expected and it is convenient to consider the supramolecular structures in terms of the dimensionality generated by the hard and soft (Braga *et al.*, 1995) hydrogen bonds in turn.
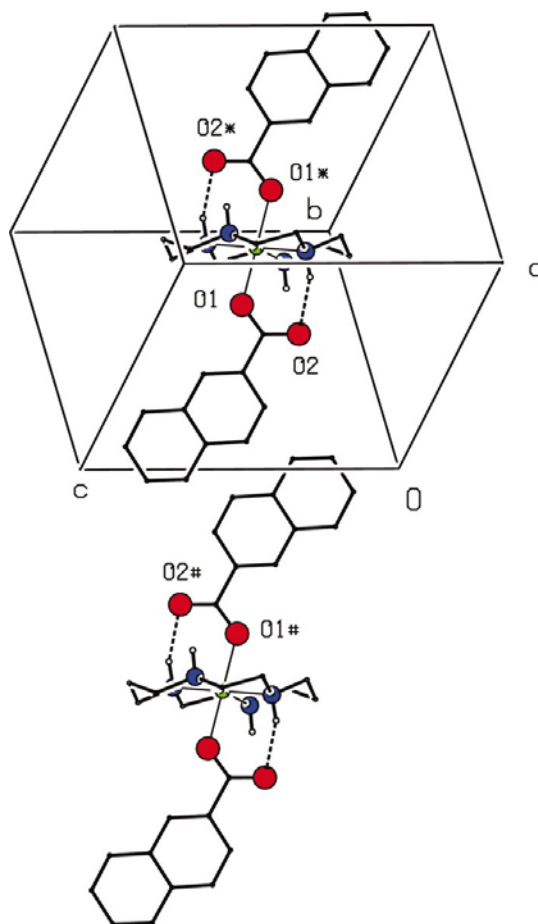

Figure 1
The centrosymmetric molecular aggregate in compound (I), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a' are at the symmetry position $(1 − x, 1 − y, 1 − z)$.

Figure 2
The molecular packing in (I), showing the mutual avoidance of the adjacent naphthyl rings related by the centres of inversion. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 − x, 1 − y, 1 − z)$ and $(−x, −y, 1 − z)$, respectively.

Table 2
Hydrogen-bond parameters (Å, °).

$D-H\cdots A$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(I)			
N1—H1$\cdots$O2	2.22	2.994 (2)	140
(II)			
N1—H1$\cdots$O12	2.33	3.056 (3)	137
N4—H4$\cdots$O52^{i}	2.35	3.132 (3)	144
C2—H2A$\cdots$O12^{ii}	2.40	3.287 (4)	152
(III)			
N1—H1$\cdots$O12	1.99	2.845 (2)	153
N4—H4$\cdots$O41^{iii}	2.52	3.221 (2)	132
C16—H16$\cdots$O42^{iv}	2.60	3.439 (2)	148
(IV)			
N1—H1$\cdots$O12	2.09	2.943 (2)	152
O13—H3$\cdots$O12^{v}	1.81	2.645 (2)	172
(V)			
N1—H1$\cdots$O12	2.00	2.868 (2)	155
N14—H14A$\cdots$O12^{vi}	2.25	3.043 (2)	150
N14—H14B$\cdots$O12^{vii}	2.10	2.954 (2)	165
(VI)			
N1—H1$\cdots$O2	2.06	2.903 (3)	150
N8—H8$\cdots$O7	2.13	3.032 (3)	164
N11—H11$\cdots$O9^{viii}	2.20	3.018 (3)	147
O5—H5$\cdots$O3^{ix}	1.69	2.519 (3)	169
O6—H6A$\cdots$O7	1.80 (3)	2.670 (3)	161 (4)
O7—H7A$\cdots$O8	1.88 (3)	2.719 (3)	164 (4)
O8—H8A$\cdots$O9	1.84 (4)	2.712 (3)	169 (4)
O9—H9A$\cdots$O10	1.97 (3)	2.824 (3)	176 (4)
O6—H6B$\cdots$O5^{iv}	2.00 (3)	2.864 (3)	160 (4)
O7—H7B$\cdots$O10^{ix}	1.91 (3)	2.793 (3)	172 (4)
O8—H8B$\cdots$O5^{x}	1.97 (3)	2.824 (3)	167 (5)
O9—H9B$\cdots$O4^{xi}	1.93 (3)	2.801 (3)	174 (4)
O10—H10A$\cdots$O2^{xii}	1.83 (3)	2.739 (3)	169 (3)
O10—H10B$\cdots$O4^{x}	1.85 (3)	2.718 (3)	174 (8)
(VII)			
N1—H1$\cdots$O2	2.08	2.927 (4)	151
N4—H4$\cdots$O2^{iv}	2.33	3.182 (3)	152
O3—H3$\cdots$O2	2.09 (4)	2.865 (3)	152 (5)
(VIII)			
N1—H11$\cdots$O4^{xiii}	2.18	3.066 (3)	159
N1—H11$\cdots$O24^{xiii}	2.25	3.12 (2)	156†
N4—H4$\cdots$O31	2.10	3.017 (2)	167
N21—H21$\cdots$O31	2.10	2.928 (2)	148
N24—H24$\cdots$O34^{xiv}	2.07	2.911 (2)	150
N211—H211$\cdots$O34	2.16	3.045 (2)	159
O1—H1A$\cdots$O3	2.12 (3)	2.965 (3)	177 (3)
O1—H1A$\cdots$O24	2.17 (4)	2.87 (2)	139 (3)†
O1—H1B$\cdots$O31	1.80 (3)	2.662 (2)	173 (3)

Symmetry codes: (i) $1+x, y, 1+z$; (ii) $-x, 1-y, 1-z$; (iii) $1+x, y, z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $x, -y, \frac{1}{2}+z$; (vii) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (viii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ix) $x, 1-y, -\frac{1}{2}+z$; (x) $\frac{1}{2}+x, -\frac{1}{2}+y, 1+z$; (xi) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (xii) $\frac{1}{2}+x, \frac{1}{2}+y, 1+z$; (xiii) $1-x, 1-y, 1-z$; (xiv) $x, \frac{3}{2}-y, -\frac{1}{2}+z$. † O24 is a component of the minor occupancy perchlorate anion [s.o.f. = 0.086 (4)].

3.2. Supramolecular structures

3.2.1. Hydrogen bonds are absent: a finite molecular complex.
Compound (I), the bis-2-naphthoate derivative (Fig. 1) (monoclinic $P2_1/c$, $Z' = 0.5$), contains both hard hydrogen-bond donors and hard hydrogen-bond acceptors, in the form of the free axial N—H bonds and the carboxylate groups, two

each per [Ni(cyclam)(OCOC$_{10}$H$_7$)$_2$] aggregate. However, the crystal structure of (I) contains neither hard nor soft hydrogen bonds between the aggregates: the free N—H bonds in fact play no role in the structure.

The most surprising feature of this structure, however, is the complete absence of aromatic $\pi\cdots\pi$ stacking interactions, which we had expected to make a significant contribution to

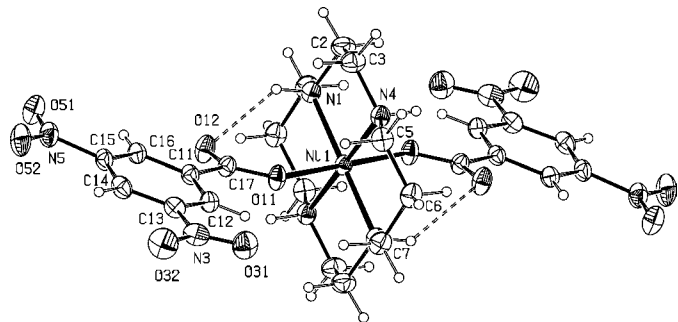**Figure 3**
The centrosymmetric molecular aggregate in (II), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
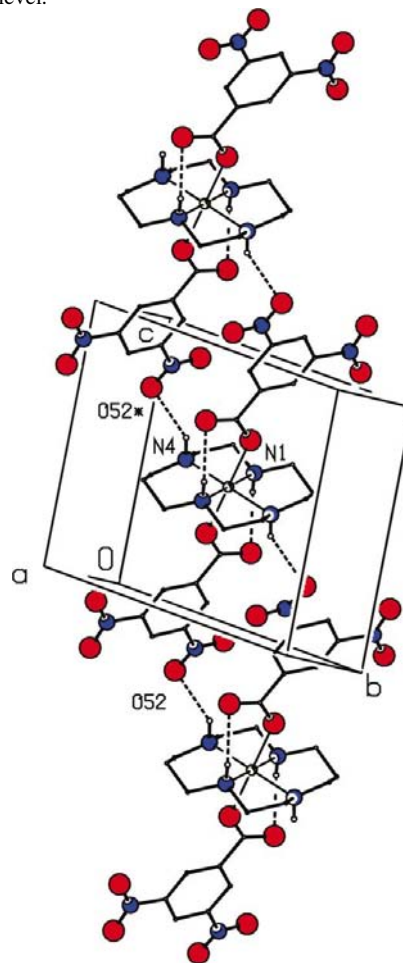
Figure 4
Part of the crystal structure of (II), showing the formation by the hard hydrogen bonds of a [101] chain. For the sake of clarity, H atoms bonded to C are omitted. The atom marked with an asterisk (*) is at the symmetry position $(1+x, y, 1+z)$.

supramolecular aggregation in the form of $\pi\cdots\pi$ stacked chains. Indeed, (I) was designed with this expected mode of aggregation specifically in mind. In the event, the closest approach of parallel naphthoate rings is across the centres of inversion and, while the interplanar distance is only 3.122 (2) Å, the shortest distance between ring centroids is 5.260 (2) Å with a corresponding centroid offset of 4.2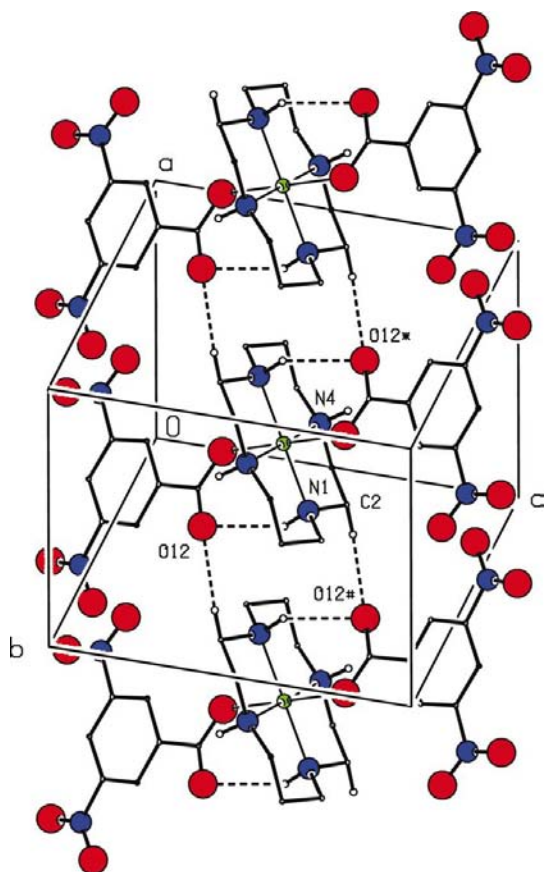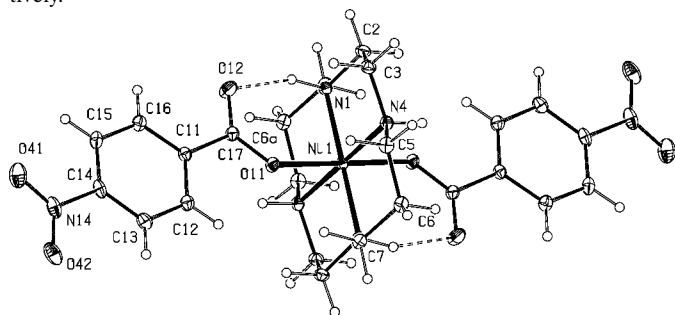3 Å, so that there is no ring overlap whatsoever. Thus, even simple molecular-design principles can readily fail in practice, as just a modest rotation of the complex around the [100] vector would replace the apparent mutual avoidance of adjacent naphthyl rings with $\pi\cdots\pi$ stacking interactions across the centres of inversion (Fig. 2).

3.2.2. Hard hydrogen bonds generate one-dimensional structures.

Compound (II): soft hydrogen bonds generate a two-dimensional structure. In (II), bis(3,5-dinitrobenzoate) (Fig. 3; triclinic $P\bar{1}$, $Z' = 0.5$), there is an excess of hard hydrogen-bond acceptors, in the four nitro groups and two carboxyl groups per [Ni(cyclam)(OCOR)$_2$] aggregate, over hard hydrogen-bond donors, two N—H bonds per aggregate. The hard hydrogen bonds, which generate a one-dimensional structure, are thus augmented by soft C—H$\cdots$O hydrogen bonds, which expand the supramolecular aggregation to two-dimensional.
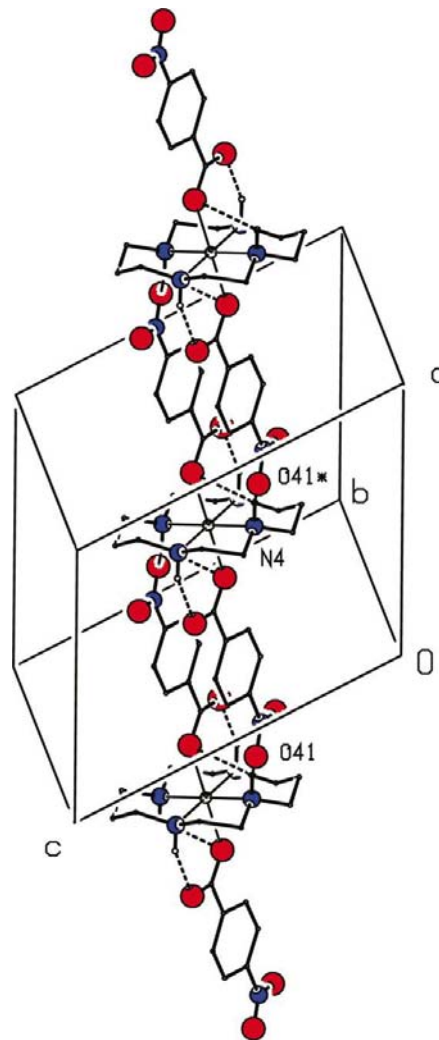

Figure 5
Part of the crystal structure of (II), showing the linking of the [101] chains into a (010) sheet by the soft hydrogen bonds. For the sake of clarity, H atoms bonded to C and not involved in the hydrogen bonding are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$ and $(-x, 1 - y, 1 - z)$, respectively.

Figure 6
The centrosymmetric molecular aggregate in (III), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atom marked 'a' is at the symmetry position $(1 - x, 1 - y, 1 - z)$.

Figure 7
Part of the crystal structure of (III), showing the formation by the hard hydrogen bonds of a [100] chain. For the sake of clarity, H atoms bonded to C are omitted. The atom marked with an asterisk (*) is at the symmetry position $(1 + x, y, z)$.

The ring amino N4 at (x, y, z) is a component of the [Ni(cyclam)(OCOR)₂] aggregate centred at (0.5, 0.5, 0.5) and it acts as a hydrogen-bond donor to nitro O52 at $(1 + x, y, 1 + z)$, which is a component of the aggregate centred at (1.5, 0.5, 1.5). At the same time, the symmetry-related N4 at $(1 - x, 1 - y, 1 - z)$ in the aggregate centred at (0.5, 0.5, 0.5) acts as a hydrogen-bond donor to O52 at $(-x, 1 - y, -z)$, which is a component of the aggregate centred at (−0.5, 0.5, −0.5). Propagation of this interaction by translation and inversion thus generates a $C(10)[R_4^2(10)]$ chain of rings running parallel to the [101] direction (Fig. 4). Along the length of this chain the Ni centres are at $(n + 0.5, 0.5, n + 0.5)$ (n = zero or integer) and the $R_2^2(20)$ rings are centred at $(n, 0.5, n; n$ = zero or integer).

The [101] chains are linked by C—H···O hydrogen bonds to form (010) sheets. Ring atom C2 at (x, y, z) is a component of the [Ni(cyclam)(OCOR)₂] aggregate centred at (0.5, 0.5, 0.5) and it acts as a hydrogen-bond donor to carboxyl O12 at $(-x, 1 - y, 1 - z)$, which is a component of the aggregate centred at (−0.5, 0.5, 0.5): the symmetry-related C2 in the aggregate centred at (0.5, 0.5, 0.5) is at $(1 - x, 1 - y, 1 - z)$ and this atom acts as a hydrogen-bond donor to O12 at $(1 + x, y, z)$, a component of the aggregate centred at (1.5, 0.5, 0.5). Propagation of this interaction generates a second chain of rings, here of $C(7)[R_2^2(10)]$ type, running parallel to the [100] direction, in which the $R_4^2(10)$ rings are centred at $(n, 0.5, 0.5)$ (n = zero or integer); Fig. 5). The combination of the [101]

chains of rings (Fig. 4) and the [100] chains of rings (Fig. 5) generates a (010) sheet and a single (010) sheet is sufficient completely to define the supramolecular structure.

Compound (III): soft hydrogen bonds generate a three-dimensional structure. In (III), bis-(4-nitrobenzoate) (Fig. 6; monoclinic $P2_1/n$, $Z' = 0.5$), there is again an excess of hard hydrogen-bond acceptors over hard hydrogen-bond donors: the hard hydrogen bonds generate a one-dimensional supramolecular structure, as for (II), but although the excess of hard acceptors over donors is less in (III) than in (II), the effect of the soft hydrogen bonds in (III) is to generate a three-dimensional supramolecular structure.

Figure 9
The centrosymmetric molecular aggregate in (IV), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
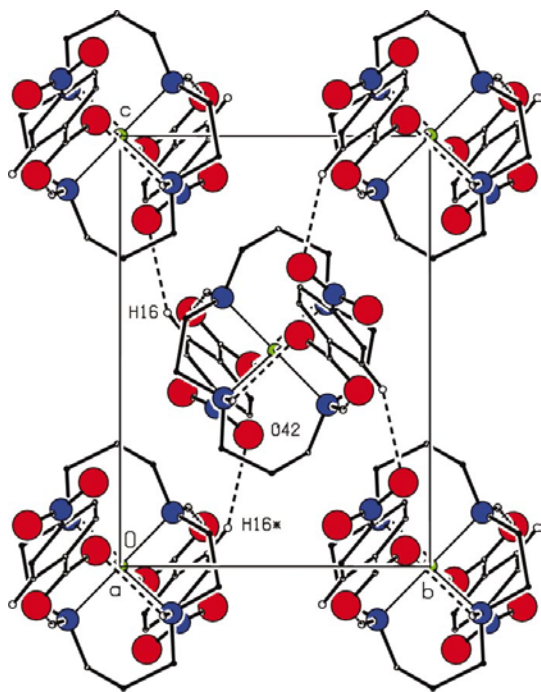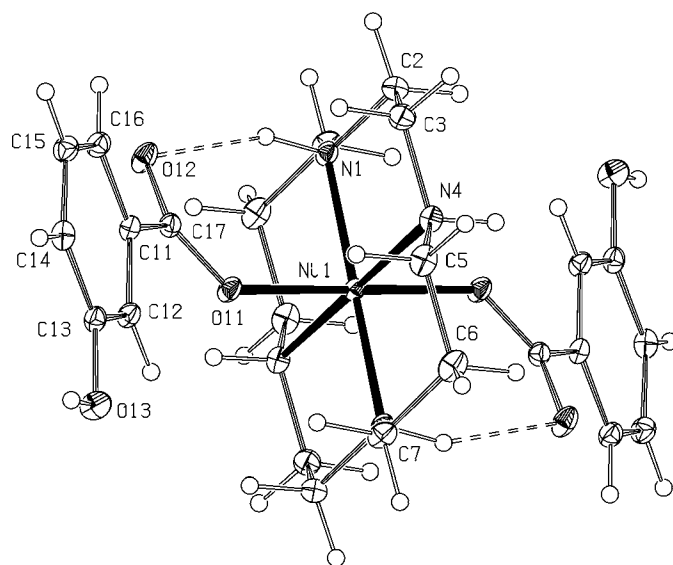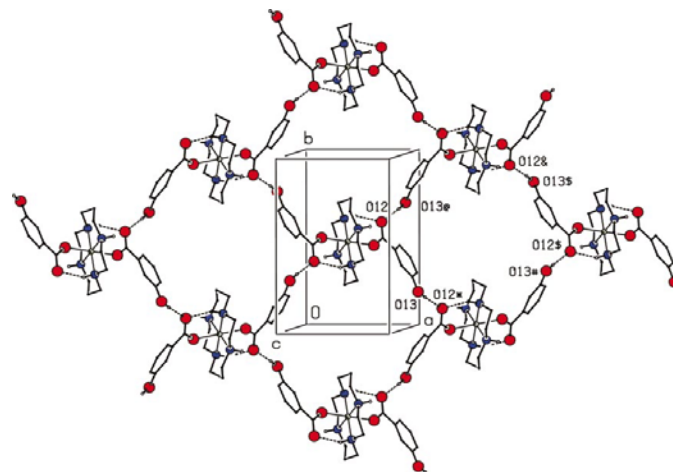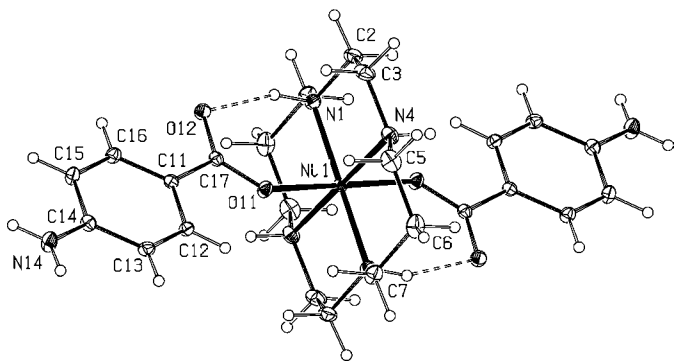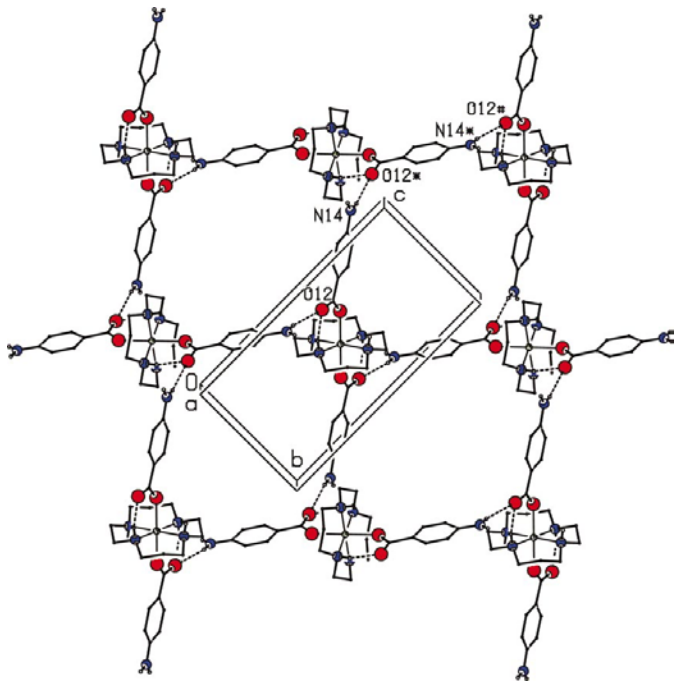

Figure 8
Projection of part of the crystal structure of (III) showing the linking of the [100] chains into a continuous framework by the soft hydrogen bonds. For the sake of clarity, H atoms bonded to C and not involved in the hydrogen bonding are omitted. The atom marked with an asterisk (*) is at the symmetry position $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$.

Figure 10
Part of the crystal structure of (IV), showing the formation of a (102) sheet. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or at sign (@) are at the symmetry positions $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, $(1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, $(3 - x, 1 - y, -z)$, $(1 + x, \frac{3}{2} - y, -\frac{1}{2} + z)$ and $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

The amino N4 at (x, y, z), part of the aggregate centred at (0.5, 0.5, 0.5), acts as a hydrogen-bond donor to nitro O41 at $(1 + x, y, z)$, which itself is part of the [Ni(cyclam)(OCOR)$_2$] aggregate centred at (1.5, 0.5, 0.5): in this manner a $C(11)[R_2^2(22)]$ chain of rings is generated running parallel to the [100] direction, in which the $R_2^2(22)$ rings are centred at $(n,$ 0.5, 0.5) (n = zero or integer; Fig. 7). Within the $R_2^2(22)$ rings, the planes of the two parallel aromatic rings are separated by 3.501 (3) Å, with a centroid offset of 1.465 (3) Å, consistent with the presence of a weakly attractive aromatic $\pi\cdots\pi$ stacking interaction between these rings. Two such chains of rings run through each unit cell, along the lines $(x, 0.5, 0.5)$ and $(x, 0, 0)$.

A single C—H$\cdots$O hydrogen bond is sufficient, when propagated by the operators of space group $P2_1/n$, to link all of the [100] chains into a single three-dimensional framework. Atom C16 in the aryl ring at (x, y, z), which is part of the [Ni(cyclam)(OCOR)$_2$] aggregate centred at (0.5, 0.5, 0.5), acts as a hydrogen-bond donor to nitro O42 at $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, which is a component of the aggregate centred at (1, 0, 1). Each centrosymmetric [Ni(cyclam)(OCOR)$_2$] aggregate acts as a twofold donor and as a twofold acceptor of C—H$\cdots$O hydrogen bonds: the aggregate centred at (0.5, 0.5, 0.5), part of the chain of rings along $(x, 0.5, 0.5)$, provides donors of C—H$\cdots$O hydrogen bonds to acceptors in the aggregates centred at (1, 0, 1) and (0, 1, 0), which lie in the chains along $(x, 0, 1)$ and $(x, 1, 0)$, respectively, and it provides acceptors from donors in the aggregates centred at (0, 0, 0) and (1, 1, 1), which

Figure 11
The centrosymmetric molecular aggregate in (V), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.
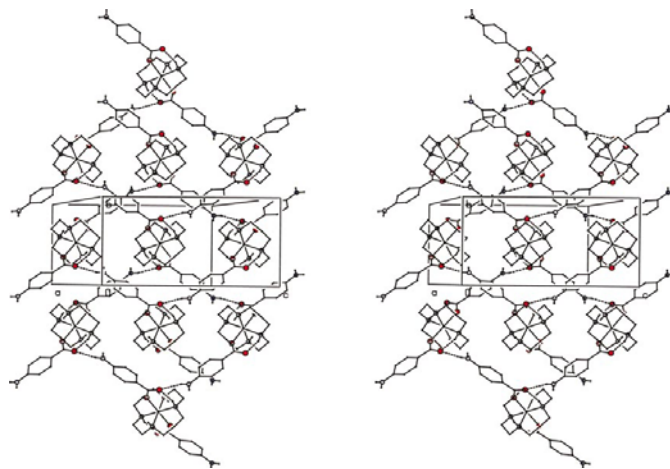

Figure 13
Stereoview of part of the crystal structure of (V), showing the interweaving of two (100) sheets. For the sake of clarity, H atoms bonded to C are omitted.
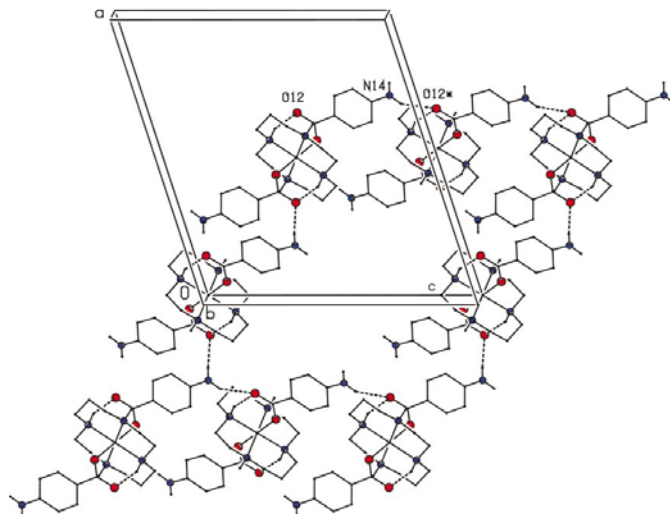

Figure 12
Part of the crystal structure of (V), showing the formation of a (100) sheet. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, -y, \frac{1}{2} + z)$ and $(x, y, 1 + z)$, respectively.

Figure 14
Part of the crystal structure of (V), showing the formation of a (010) sheet. For the sake of clarity, H atoms bonded to C are omitted. The atom marked with an asterisk (*) is at the symmetry position $(x, -y, \frac{1}{2} + z)$.

lie in the chains along (x, 0, 0) and (x, 1, 1), respectively (Fig. 8). In this manner, each [100] chain is directly linked to its four immediate neighbours, so that all of the [100] are linked by the soft hydrogen bonds into a single continuous bundle.

General comments on the structures of (II) and (III). The structures of (II) and (III), taken together, provide a gentle warning against the naive application of simple counts of hydrogen-bond donors *versus* acceptors when attempting to rationalize, predict or 'design' supramolecular structures. Both compounds have a substantial excess of C—H bonds over potential hydrogen-bond acceptors, while (II) actually has 50% more acceptors per molecular aggregate than (III). Despite this, the soft hydrogen bonds generate a two-dimensional structure in (II), which has the larger number of hydrogen-bond acceptors, as against a three-dimensional structure in (III), with the smaller number of acceptors.

Despite the differing number of hydrogen-bond acceptors, there is in each structure only one soft hydrogen bond of structural significance. The key to the dimensionality of the overall structure is thus not the number of distinct C—H···O hydrogen bonds, but the manner in which the single such bond is, in each case, propagated by the space group. In (II) the soft hydrogen bond links the reference complex (and its associated
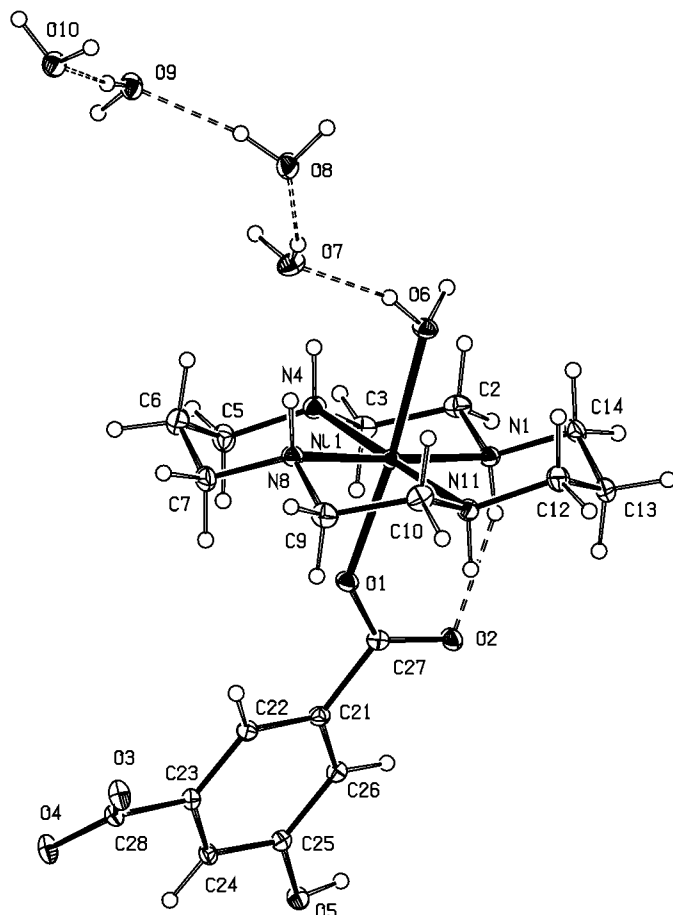
[101] chain) to another related to it by a centre of inversion: thus, although each centrosymmetric complex acts as a twofold donor and as a twofold acceptor of C—H···O hydrogen bonds, each is thereby linked to only two others, leading to sheet formation. By contrast, in (III) the soft hydrogen bond links the reference complex (and its associated [100] chain) to another related to it by an *n*-glide plane: it follows from this that each centrosymmetric complex is thereby linked to four others, giving a three-dimensional structure overall. The space groups of (II) and (III), respectively, thus provide the interpretation of the overall dimensionality of the structures of these compounds. That is not, of course, to say that the space groups determine the structures; rather that the space groups encode the underlying supramolecular aggregation.

3.2.3. Hard hydrogen bonds generate a two-dimensional structure. In (IV), the bis(3-hydroxybenzoate) (Fig. 9; monoclinic $P2_1/c$, $Z' = 0.5$), there are equal numbers of potential hard hydrogen-bond donors and acceptors, if the hydroxyl substituent on the aryl ring is reckoned as both a potential donor and a potential acceptor. In the event, the hydroxyl group only acts as a hydrogen-bond donor, while the N—H unit in the macrocycle does not in this instance parti-
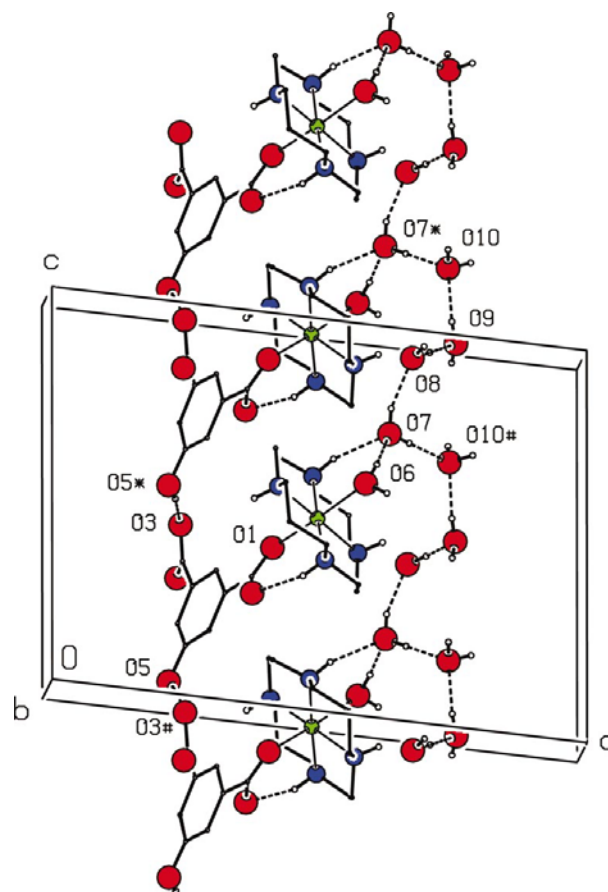

Figure 15
The molecular aggregate in (VI), showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Figure 16
Part of the crystal structure of (VI), showing the formation of a molecular ladder along [001]. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(x, 1 - y, \frac{1}{2} + z)$ and $(x, 1 - y, -\frac{1}{2} + z)$, respectively.

cipate in the hydrogen bonding: nor are there any soft hydrogen bonds in the structure of (IV). Thus, the only inter-aggregate hydrogen bond is a single type of O—H···O hydrogen bond, with each centrosymmetric aggregate acting as a twofold donor and as a twofold acceptor. Each aggregate is thus linked by O—H···O hydrogen bonds to four others, so generating a two-dimensional array in the form of a (4,4) net (Batten & Robson, 1998; Fig. 10).

Hydroxyl O13 at (x, y, z) forms part of the aggregate centred at (0.5, 0.5, 0.5): this hydroxyl acts as a hydrogen-bond donor to carboxyl O12 at $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, which forms part of the aggregate centred at (1.5, 0, 0). In this latter aggregate, the hydroxyl groups are at $(2 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, and the second of these acts as a hydrogen-bond donor to O12 at $(3 - x, 1 - y, -z)$, which is a component of the aggregate centred at (2.5, 0.5, −0.5). Hydroxyl O13 at $(3 - x, 1 - y, -z)$ in turn acts as a donor to O12 at $(1 + x, \frac{3}{2} - y, -\frac{1}{2} + z)$, part of the aggregate centred at (1.5, 1, 0), and the hydroxyl O13 in this aggregate at $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ acts as a donor to O12 at (x, y, z); this completes the formation of an $R_4^4(36)$ ring centred at (1.5, 0.5, 0) (Fig. 10). Propagation of this motif generates a (102) sheet, and two such sheets are required completely to define the structure, although the sheets are not interwoven: the cyclam ligands in one sheet nestle into the cavities of the $R_4^4(36)$ rings in the two adjacent sheets.

The two-dimensional structure of (IV) may be contrasted with the three-dimensional structure of the isomeric compound (XI) derived from 4-hydroxybenzoate (Glidewell *et al.*, 2000), in which both the hydroxyl O4 and the ring amino N4 act as hydrogen-bond donors: in (X) the hydroxyl again acts as an inter-aggregate hydrogen-bond donor to a carboxyl O, but it also accepts an inter-aggregate N—H···O hydrogen bond from the ring N. However, despite this the structure of (X) exhibits one major feature in common with the structure of (IV), in that the O—H···O hydrogen bond similarly
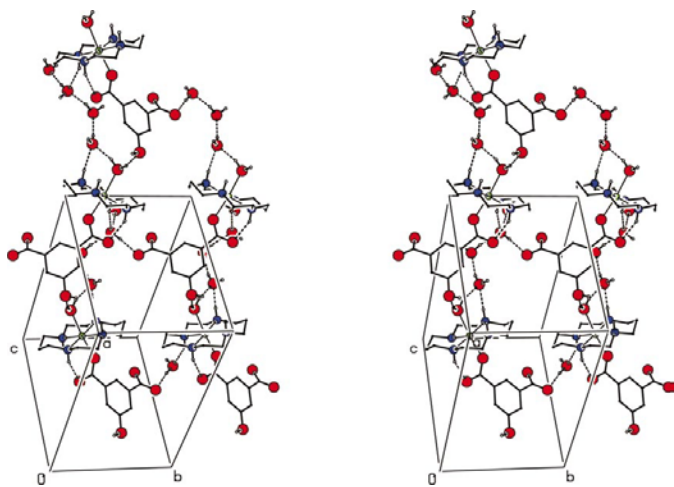
generates a (4,4) net, also in space group $P2_1/n$, built in the case of (XI) from $R_4^4(40)$ rings: since there are four carboxylate units in each of these rings, the larger ring size in (XI) is simply a consequence of the different site of the hydroxyl substitution. In (XI) it is the linking of these (4,4) nets by the N—H···O hydrogen bonds which generates the three-dimensional framework and the mode of this linking *via* the formation of a $C(10)[R_2^2(20)]$ chain of rings resembles the hard hydrogen bonding already described for (II) and (III) (§3.2.2).

3.2.4. Hard hydrogen bonds generate three-dimensional structures.

The anhydrous bis(4-aminobenzoate) (V). The supramolecular aggregation of (V) (Fig. 11; monoclinic $C2/c$, $Z' = 0.5$), is determined by N—H···O hydrogen-bond formation. Although the ring amino N4 does not participate, the aryl NH$_2$ substituent acts as a twofold donor in N—H···O hydrogen bonds: with an excess of hard hydrogen-bond donors over acceptors, the carboxylate O12 acts as a threefold acceptor, but there are no soft hydrogen bonds. Just two inter-aggregate hydrogen bonds generate the three-dimensional structure, and this is most simply analysed and described in terms of the formation of sheets parallel to (100) and (010), the combination of which is sufficient to generate the overall framework.
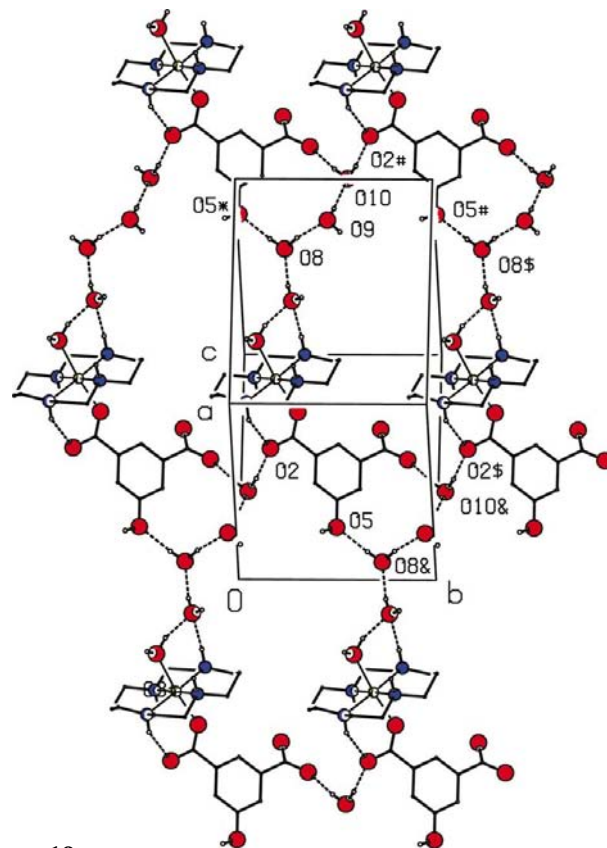

Figure 18
Part of the crystal structure of (VI), showing the formation of a (20$\bar{1}$) sheet. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions $(\frac{1}{2} + x, -\frac{1}{2} + y, 1 + z)$, $(\frac{1}{2} + x, \frac{1}{2} + y, 1 + z)$, $(x, 1 + y, z)$ and $(-\frac{1}{2} + x, \frac{1}{2} + y, -1 + z)$, respectively.

Figure 17
Stereoview of part of the crystal structure of (VI), showing the formation of a (10$\bar{1}$) sheet. For the sake of clarity, H atoms bonded to C are omitted.

The amino N14 at (x, y, z), which lies in the aggregate centred at (0.5, 0.5, 0.5), acts as a hydrogen-bond donor, *via* H14*A*, to carboxyl O12 at $(x, -y, \frac{1}{2}+z)$, which is a component of the aggregate centred at (0.5, −0.5, 1): the symmetry-related N14 at $(1-x, 1-y, 1-z)$ in the aggregate centred at (0.5, 0.5, 0.5) similarly acts as a hydrogen-bond donor to O12 at $(1-x, 1+y, \frac{1}{2}-z)$, which lies in the aggregate centred at (0.5, 1.5, 0), thus generating a chain running parallel to the [0$\bar{2}$1] direction. In an entirely similar fashion, the carboxyl O12 atoms in the aggregate centred at (0.5, 0.5, 0.5), which are at (x, y, z) and $(1-x, 1-y, 1-z)$, accept N—H···O hydrogen
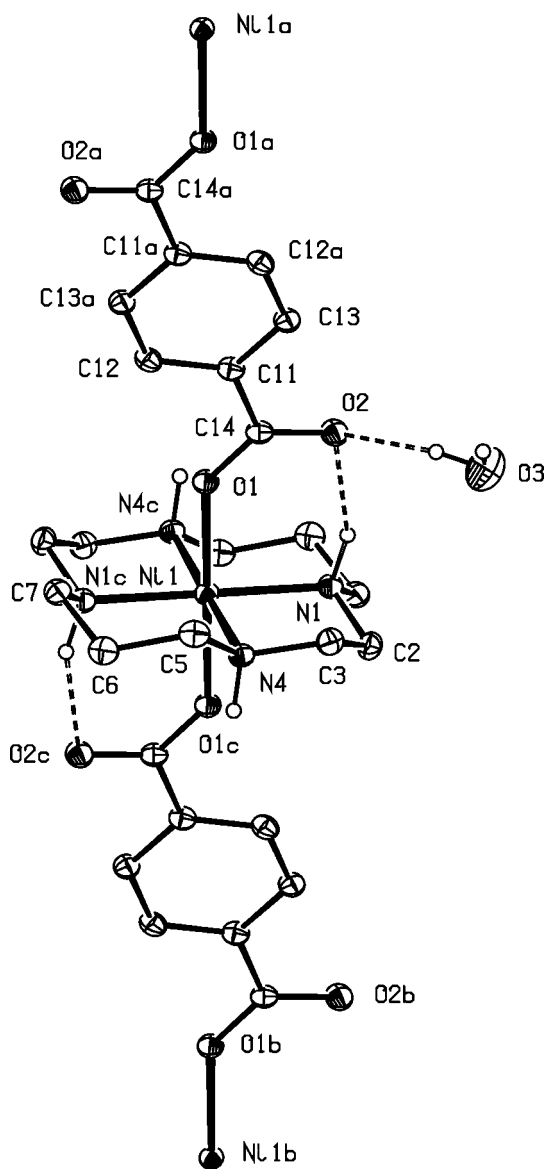

Figure 19
Part of the crystal structure of (VII), showing both the atom-labelling scheme and the formation of a [110] chain of alternating cations and anions. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked Ni1, Ni1a and Ni1b are at (0.25, 0.25, 0), (−0.25, −0.25, 0) and (0.75, 0.75, 0), respectively: the atoms marked with 'a', 'b' and 'c' are at the symmetry positions $(-x, -y, -z)$, $(\frac{1}{2}+x, 0.5+y, z)$ and $(\frac{1}{2}-x, \frac{1}{2}-y, -z)$, respectively.

bonds from amino N14 atoms at $(x, -y, -\frac{1}{2}+z)$ and $(1-x, 1+y, \frac{3}{2}-z)$, respectively; these N14 atoms are components of the aggregates centred at (0.5, −0.5, 0) and (0.5, 1.5, 1), respectively, and in this manner a chain running parallel to the [021] direction is generated. The combination of the [0$\bar{2}$1] and [021] chains generates a (100) sheet in the form of a (4,4) net built from $R_4^4(40)$ rings (Fig. 12). These (100) sheets are deeply puckered and they are pairwise interwoven (Fig. 13).

The formation of the (010) sheet utilizes both of the N—H···O hydrogen bonds and it is most simply analysed in terms of two one-dimensional motifs. As in the formation of the (100) sheet, amino N14 at (x, y, z) acts as a hydrogen-bond donor, *via* H14*A*, to O12 at $(x, -y, \frac{1}{2}+z)$, while N14 at $(x, -y, \frac{1}{2}+z)$ in turn acts as a donor to O12 at $(x, y, 1+z)$. In this manner a $C(8)$ chain is formed running parallel to [001], generated by the glide plane at $y = 0$ and linking the [Ni(cyclam)(OCOR$_2$)] aggregates centred at (0.5, 0.5, 0.5), (0.5, −0.5, 1) and (0.5, 0.5, 1.5) (Fig. 14). The amino N14 at (x, y, z) also acts as a hydrogen-bond donor, *via* H14*B*, to O12 at $(\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z)$, which is a component of the aggregate centred at (1, 0, 1): of the two amino N14 donors in this latter aggregate, that at $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ acts similarly as a hydrogen-bond donor to O12 at $(2-x, 1-y, 2-z)$, which lies in the aggregate centred at (1.5, 0.5, 1.5). Propagation of this interaction produces a $C(12)$ chain running parallel to [101] and generated by the *n*-glide plane at $y = 0.25$ (Fig. 14). The combination of the [001] and [101] chains generates the (010) sheet: the combination of the (010) sheet and the pairwise-interwoven (100) sheets generates the entire three-dimensional framework.

[Ni(cyclam)(5-hydroxyisophthalate)(H$_2$O)]·4H$_2$O   (VI). Compound (VI) (monoclinic *Cc*, *Z'* = 1) differs from (I)–(V) in that, although the overall stoichiometry provides two carboxylate groups per [Ni(cyclam)]$^{2+}$ unit as usual, only one of the carboxylates is bonded to the Ni, while the second axial coordination site is occupied by a water molecule. Thus, in this instance the Ni cannot lie at a centre of inversion. In addition to the coordinated water, there are four other water molecules present, although not anticipated, in the asymmetric unit, and it is possible to select the asymmetric unit so that the water molecules are all arranged in an essentially linear, hydrogen-bonded chain (Fig. 15). Within the asymmetric unit, where the 5-hydroxyisophthalate ligand carries a formal charge of (2−), N1 acts as a hydrogen-bond donor to carboxyl O2, as before, and N8 acts as a donor to water O7: in addition, there are four intra-aggregate O—H···O hydrogen bonds generating the chain of water molecules.

These neutral aggregates (Fig. 15) are linked by one N—H···O and seven O—H···O hydrogen bonds into a single three-dimensional framework. All available hydrogen-bond donors except N4 and all potential hydrogen-bond acceptors except O8 participate in the inter-aggregate hydrogen bonding: this is thus of considerable complexity, but it can readily be analysed in terms of just a small number of low-dimensional sub-structures (Gregson *et al.*, 2000).

The first sub-structure is one dimensional and it is generated by the action of a *c*-glide plane. The unionized hydroxyl O5 in the anionic ligand at (x, y, z) acts as a hydrogen-bond donor to carboxylate O3 at $(x, 1 - y, -\frac{1}{2} + z)$, thus producing a $C(7)$ chain running parallel to the [001] direction and generated by the glide plane at $y = 0.5$. Similarly, water O7 at (x, y, z) acts as a hydrogen-bond donor to water O10 at $(x, 1 - y, -\frac{1}{2} + z)$, thus producing a $C_4^3(8)$ chain parallel to [001]. These two [001] chains are generated by the same glide plane and together they form the uprights of a molecular ladder where the rungs are provided by the [Ni(cyclam)(H$_2$O)] units (Fig. 16).

The other two substructures are both two-dimensional, but each can be analysed in terms of a combination of one-dimensional components. The second substructure is generated by the combined action of the two *n*-glide planes at $y = 0.25$ and $y = 0.75$. Coordinated water O6 at (x, y, z) acts as a hydrogen-bond donor to hydroxyl O5 at $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$, producing a $C(9)$ chain running parallel to [101] and generated by the *n*-glide plane at $y = 0.25$. Likewise, N11 at (x, y, z) acts as a donor to water O9 at $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, giving a $C_4^3(10)$ chain along [101] generated by the same glide plane. In addition, water O9 at (x, y, z) acts as a donor to carboxylate O4 at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, thus producing a $C_4^4(16)$ chain, also running parallel to the [101] direction, but this time generated by the *n*-glide plane at $y = 0.75$. The combination of the [101] chains produced by the two glide planes generates a $(10\bar{1})$ sheet (Fig. 17).

The two substructures so far described utilize five of the eight inter-aggregate hydrogen bonds. The third substructure, which utilizes the remaining three hydrogen bonds, is again two-dimensional and arises by the action of the C-centring translation. Atoms O8 and O10 in water molecules at (x, y, z) act as hydrogen-bond donors, respectively, to hydroxyl O5 and carboxylate O4, both at $(\frac{1}{2} + x, -\frac{1}{2} + y, 1 + z)$, thus producing $C_3^3(13)$ and $C_5^5(18)$ chains, respectively, running parallel to [11\bar{2}]. The water O10 at (x, y, z) also acts as a donor to carboxylate O2 at $(\frac{1}{2} + x, \frac{1}{2} + y, 1 + z)$, thus producing a $C_5^5(14)$ chain running parallel to [11\bar{2}]. Thus, the two hydrogen bonds arising from water O10 produce a pair of chains whose combined action is production of a $(20\bar{1})$ sheet (Fig. 18). Of these three readily identified substructures, the [001] ladder and the $(10\bar{1})$ and $(20\bar{1})$ sheets, the combination of any two is
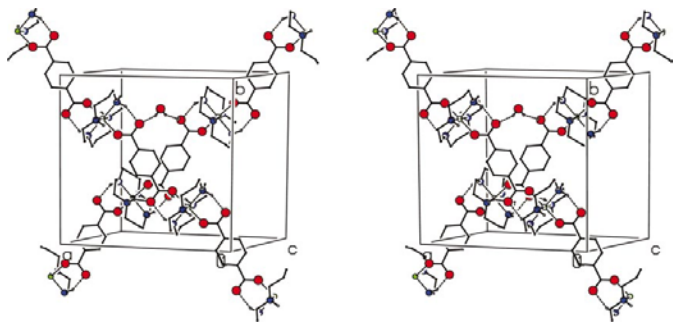

Figure 20
Stereoview of part of the crystal structure of (VII), showing the linking of the [110] and [1$\bar{1}$0] chains by the water molecules. For the sake of clarity, H atoms bonded to C are omitted.
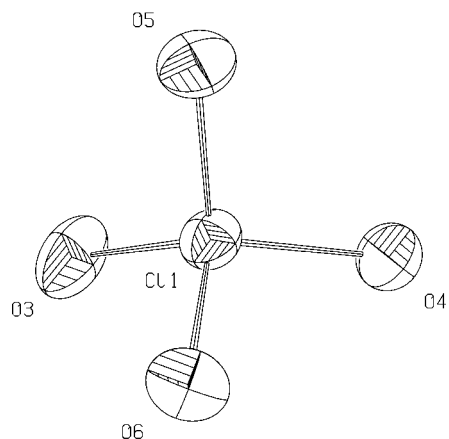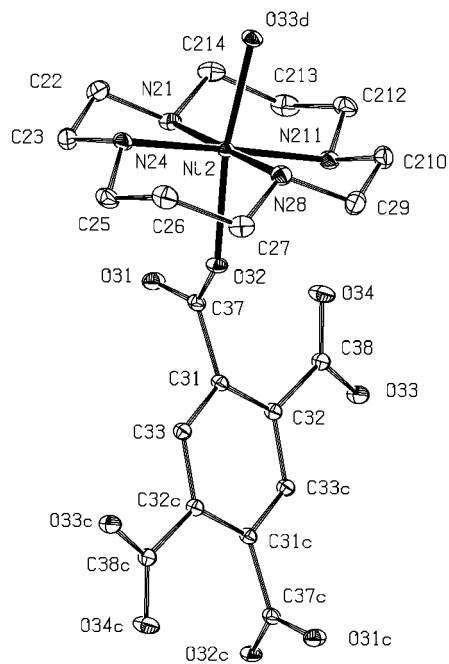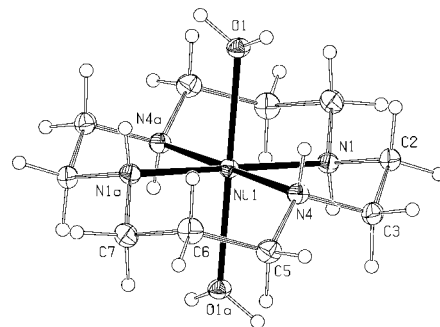

Figure 21
The molecular components of (VIII), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. The atoms marked 'a', 'c' and 'd' are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(-x, 1 - y, 1 - z)$ and $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, respectively.

sufficient to generate a continuous three-dimensional framework structure.

3.2.5. Hard hydrogen bonds link coordination-polymer chains into a three-dimensional structure. In the coordination polymer [{Ni(cyclam)(OCOC$_6$H$_4$COO)}·nH$_2$O] (VII) (Fig. 19) (monoclinic $C2/c$, $Z' = 0.5$), there are equal numbers of cations, anions and water molecules. The reference Ni atom lies at the centre of inversion at (0.25, 0.25, 0) and the reference terephthalate anion lies across the centre of inversion at the origin. The Ni atom at (0.25, 0.25, 0) is thus coordinated by the anions centred at (0, 0, 0) and (0.5, 0.5, 0), respectively, while the reference anion acts as a bridging ligand between the Ni at (0.25, 0.25, 0) and (−0.25, −0.25, 0). Thus, by the combined action of the C-centring operation and the inversion centres, a continuous chain of alternation [Ni(cyclam)]$^{2+}$ and [OCOC$_6$H$_4$COO]$^{2-}$ units is generated, running parallel to the [110] direction. Related to this [100] chain by the action of the 2_1 axes and the glide planes is a [1$\bar{1}$0] chain. There is one chain of each type running through each unit cell in alternating layers stacked like cordwood: the layers of [110] chains are at $z = n$ (n = zero or integer), while the [1$\bar{1}$0] chains are at $z = (n + 0.5)$ (n = zero or integer). Although there are no direct connections between adjacent chains of either type, the chains are, in fact, linked into a 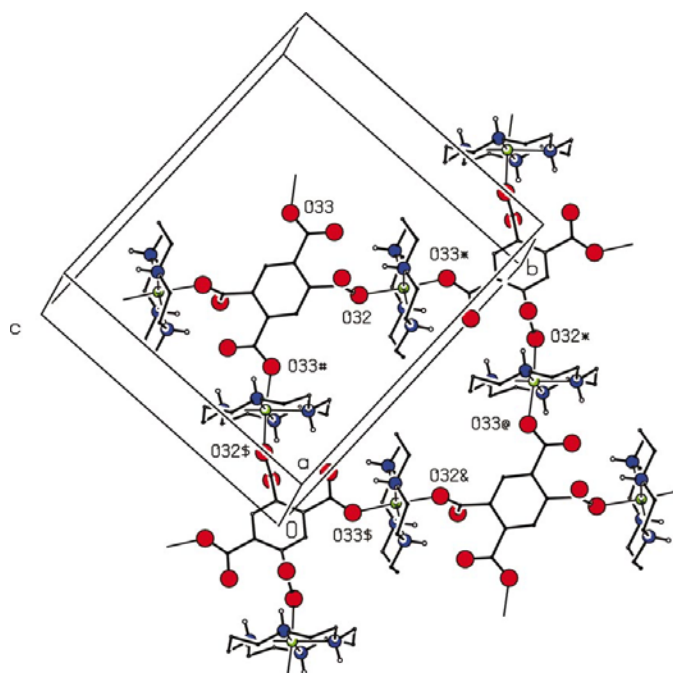continuous three-dimensional array by the water molecules, which act as twofold donors in O—H···O hydrogen bonds, but not as hydrogen-bond acceptors.

The water molecule at (x, y, z) which lies on the twofold rotation axis along $(0, y, 0.25)$ acts as a hydrogen-bond donor to carboxylate O2 at (x, y, z), which thus acts as a threefold acceptor of hydrogen bonds (Table 2). This O2 is a component of a [110] chain at $z = 0.0$: the same water molecule also acts as a hydrogen-bond donor to O2 at $(−x, y, \frac{1}{2} − z)$, which is a component of a [1$\bar{1}$0] chain at $z = 0.5$. The water molecule at $(x, 1 − y, \frac{1}{2} + z)$, on the other hand, which lies on the twofold axis along $(0, y, 0.75)$ acts as a hydrogen-bond donor to the two carboxylate O2 atoms at $(x, 1 − y, \frac{1}{2} + z)$ and $(−x, 1 − y, 1 − z)$, which lie respectively in a [1$\bar{1}$0] chain at $z = 0.5$, and in a [110] chain at $z = 1.0$. In this way, each water molecule links [110] and [1$\bar{1}$0] chains in different domains of z, such that all of the chains are linked into a single three-dimensional framework (Fig. 20).

In the reaction between the [Ni(cyclam)]$^{2+}$ cation {or its diaqua form [Ni(cyclam)(H$_2$O)$_2$]$^{2+}$} and the terephthalate anion [C$_8$H$_4$O$_4$]$^{2-}$ in methanol or aqueous methanol, where the end product is (VII), it is reasonable to envisage that the growth of the coordination polymer (VII) proceeds in a stepwise fashion *via* low- and medium-molecularity intermediates, at least in the early stages of chain growth. We have previously isolated and structurally characterized a binuclear anion-bridged complex [{Ni(C$_{10}$H$_{24}$N$_4$)(H$_2$O)}$_2$-(C$_8$H$_4$O$_4$)]·2ClO$_4$ (Zakaria *et al.*, 2001), which may be regarded as an early intermediate on the pathway to the polymer (VII).

Figure 22
Part of the crystal structure of (VIII) showing the formation of a coordination polymer sheet parallel to (100) utilizing the type 2 cations and the tetracarboxylate anions only. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked with an asterisk (*), hash (#), dollar sign ($), ampersand (&) or at sign (@) are at the symmetry positions $(x, \frac{3}{2} − y, −\frac{1}{2} + z)$, $(−x, 1 − y, 1 − z)$, $(−x, −\frac{1}{2} + y, \frac{1}{2} − z)$, $(−x, 1 − y, −z)$ and $(x, y, −1 + z)$, respectively.
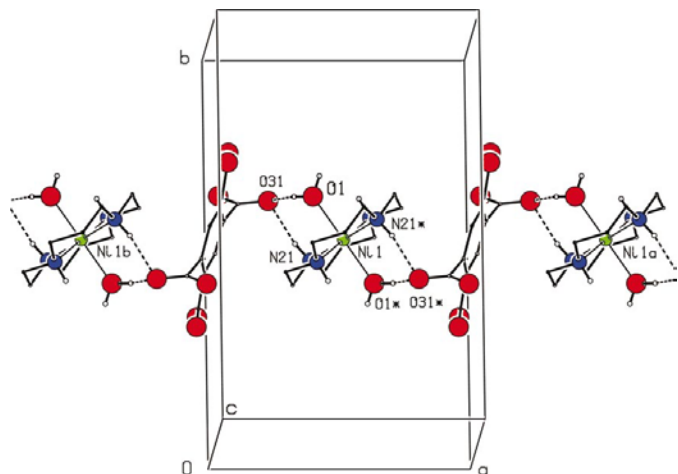

Figure 23
Part of the crystal structure of (VIII) showing the formation of a [100] chain linking the (100) sheets, built from the type 1 cations and the tetracarboxylate anions only. For the sake of clarity, H atoms bonded to C are omitted. The atoms marked Ni1, Ni1a and Ni1b are at (0.5, 0.5, 0.5), (1.5, 0.5, 0.5) and (−0.5, 0.5, 0.5), respectively: the atoms marked with an asterisk (*) are at the symmetry position $(1 − x, 1 − y, 1 − z)$.

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[Ni(cyclam)]²⁺ + ⁻OCO—X—COO⁻

↓ H₂O/MeOH

$$\left[\text{H}_2\text{O}\text{—Ni(cyclam)}\text{—O}\diagdown\text{C}\diagup\text{X—COO}\right]$$

↓ [Ni(cyclam)]²⁺

$$\left[\text{H}_2\text{O}\text{—Ni(cyclam)}\text{—O—C—X—C—O—Ni(cyclam)—OH}_2\right]^{2+}$$

↓

↓ (steps)

↓

$$\left[\text{—Ni(cyclam)—O—C—X—C—O—}\right]_n$$
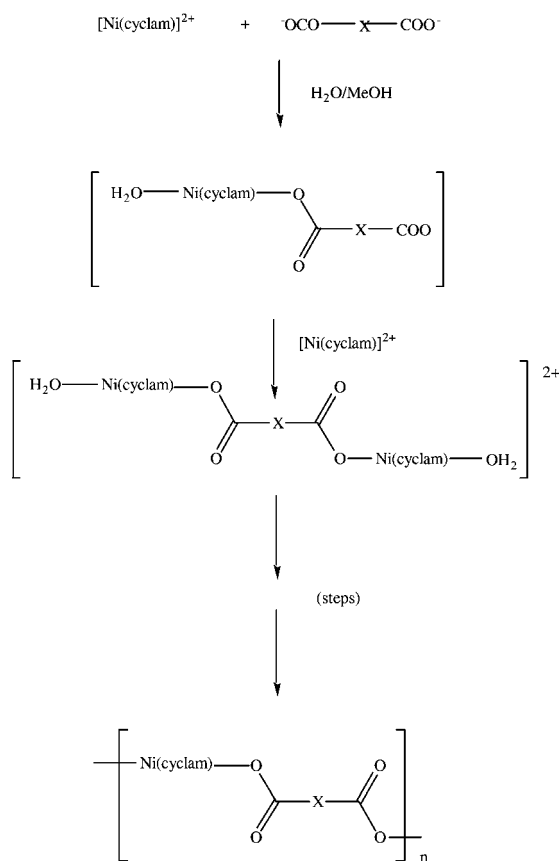
Compound (VI), albeit formed from the 5-hydroxy-isophthalate(2−) anion rather than from terephthalate(2−) can be regarded as the very first intermediate on this pathway, whose formation is then followed directly by that of a product such as (VII). Efforts are currently in progress aimed at the isolation of an analogue of (VI) derived from the terephthalate(2−) anion.

3.2.6. Hard hydrogen bonds link coordination polymer sheets into a three-dimensional structure. Both the composition and the constitution of product (VIII) (Fig. 21), isolated from the reaction between [Ni(cyclam)][ClO₄)]₂ and the tetrasodium salt of 1,2,4,5-benzenetetracarboxylic acid, are unusual and unexpected. Despite this, the supramolecular structure exhibits both simplicity and elegance. The composition, which was not correctly deduced from the microanalytical data, comprises three Ni(cyclam) units, one 1,2,4,5-benzenetetracarboxylate(4−) anion, two perchlorate anions and three water molecules. There is one hydrated cation [Ni(cyclam)(H₂O)₂]²⁺ which lies across a centre of inversion, chosen for convenience as that at (0.5, 0.5, 0.5); this cation contains Ni1 and will be referred to in the following discussion as the type 1 cation. The tetracarboxylate anion also lies across a centre of inversion, chosen as that at (0, 0.5, 0.5), while the other cation, of [Ni(cyclam)]²⁺ type containing Ni2 (the type 2 cation), lies in a general position. There is a perchlorate anion lying in a general position, disordered over two closely similar sets of atomic sites with site occupation factors of 0.915 (4) and 0.085 (4): only the major site will be discussed here.

Finally, there is a water molecule in a general position, having occupancy 0.5, for which the H atoms could not be located. For each perchlorate anion there are thus 1.5 [Ni(cyclam)] units, 0.5 tetracarboxylate units and 1.5 water molecules, consistent with the overall composition [Ni(cyclam)]₃·[1,2,4,5-benzene-tetracarboxylate(4−)]·[ClO₄]₂·3H₂O. The microanalytical data suggested 13.5 or 13.67 C per four N, rather than the 13.33 C per four N observed, and this confused the interpretation of these data.

The tetracarboxylate anions and the type 2 cations together generate a two-dimensional coordination polymer and adjacent sheets of this polymer are linked together by hydrogen bonds, where the donors are ring N and coordinated water in the type 1 cations. The perchlorate anions are linked to the resulting three-dimensional framework by further hydrogen bonds, but their presence is not essential to the formation of the framework.

Although the type 2 cation lies in a general position, the cyclam ligand adopts the usual conformation so that the Ni and the ligating N atoms are essentially coplanar: the two axial sites are occupied by O atoms from two different tetracarboxylate anions. The atom Ni2 at (x, y, z) is bonded to O32 at (x, y, z), which is a component of the tetracarboxylate anion centred at (0, 0.5, 0.5), and to O33 at $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, which is a component of the tetracarboxylate anion centred at (0, 1, 0). Each centrosymmetric tetracarboxylate anion is, in turn, bonded to four different Ni2 atoms: thus, the anion centred at (0, 0.5, 0.5) is bonded to the Ni2 atoms at (x, y, z), $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$, $(-x, 1 - y, 1 - z)$ and $(x, \frac{3}{2} - y, \frac{1}{2} + z)$. Propagation of these Ni—O bonds by the space group generates a continuous (100) sheet in the form of a square net containing a single type of 30-membered ring (Fig. 22), whose local stoichiometry [Ni(cyclam)]₂·[C₁₀H₂O₈] firstly reflects the mutual coordination behaviour of the cations and anions involved, twofold and fourfold, respectively, and secondly indicates that the sheets carry no net charge.

Two sheets of this type run through each unit cell: that in the domain $-0.31 < x < 0.31$ is centred at $x = 0$ and that in the domain $0.69 < x < 1.31$ is centred at $x = 1$. These sheets are linked by the type 1 cations to give a pillared layer framework. In the type 1 cation centred at (0.5, 0.5, 0.5), the two water O1 atoms are at (x, y, z) and $(1 - x, 1 - y, 1 - z)$: these act as hydrogen-bond donors *via* the H1*B* atoms, to the carboxylate O31 atoms at (x, y, z) and $(1 - x, 1 - y, 1 - z)$, respectively. These O31 atoms are parts of the tetracarboxylate anions centred at (0, 0.5, 0.5) and (1, 0.5, 0.5), respectively, which lie in adjacent (100) sheets. The O—H···O hydrogen bonds linking the (100) sheets are reinforced, albeit weakly, by N—H···O hydrogen bonds: N4 acts as a donor to the same O31 as in the O—H···O hydrogen bond (Table 2). The effect of these O—H···O and N—H···O hydrogen bonds is to produce a [100] chain, generated by successive inversion operations, in the form of a $C_2^2(13)$ motif (Fig. 23) and by these means all the (100) sheets are linked into a single three-dimensional framework.

The perchlorate anion makes no contribution to the development of the framework, but it is attached to the type 1

cation by two hydrogen bonds, one each of $O—H\cdots O$ and $N—H\cdots O$ types (Fig. 21). The perchlorate O3 and O4 atoms at (x, y, z) act as hydrogen-bond acceptors, respectively, from O1 (*via* H1*A*) at (x, y, z) and from N1 at $(1 - x, 1 - y, 1 - z)$, both of which are components of the type 1 cation centred at (0.5, 0.5, 0.5). The minor disorder of the perchlorate may be associated with the fact that this anion is tethered to the framework at only two points, allowing some rotation about the $O3\cdots O4$ vector. By contrast, in the perchlorate salt of the binuclear cation $[\{(H_2O)Ni(cyclam)\}_2(OCOC_6H_4COO)]^{2+}$, the fully ordered perchlorate anions are tethered to the cation by three hydrogen bonds and hence are effectively immobilized (Zakaria *et al.*, 2001).

The H atoms of the half-occupancy water molecule could not be located, despite extensive searches. There are three O atoms within a plausible hydrogen-bonding distance: $O2^{xv}$ [(xv) $1 - x, 2 - y, 1 - z$] at 2.694 (9) Å, $O5^{xv}$ at 2.885 (6) Å and O5 at 2.890 (6) Å. The angle $O5\cdots O2\cdots O5^{xv}$ is 124.4 (2)°, whereas the corresponding angles $O5\cdots O2\cdots O2^{xv}$ and $O2^{xv}\cdots O2\cdots O5^{xv}$ are 62.1 (2) and 62.3 (2)°, respectively, suggesting that the H atoms bonded to O2 may well be directed towards O5 and $O5^{xv}$ provided, that is, that they are ordered. However, further searches based on this possibility failed to reveal these atoms.

4. Concluding comments

The structures reported here, taken together with the two related structures reported earlier (Glidewell *et al.*, 2000; Zakaria *et al.*, 2001), exhibit a very wide range of supramolecular aggregation patterns, ranging from isolated, finite (zero-dimensional) species in (I), *via* hard hydrogen bonding in one, two or three dimensions and augmented in the case of the one-dimensional systems by soft hydrogen bonding in two or three dimensions, to a coordination polymer in one or two dimensions, in compounds (VII) and (VIII). However, in a number of these structures, the expectations of simple supramolecular design principles have been confounded by the aggregation patterns actually observed. Moreover, the extent of hydration in (VI) and (VII) is neither predictable nor indeed readily rationalized after the event: the entire constitution of (VIII) is wholly unpredictable On the other hand, the dihydrate formation for (IX), whose structure has not yet been analysed, may indicate an ionic constitution $[Ni(cyclam)(H_2O)_2]^{2+}\cdot[(RCOO)^-]_2$.

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[Ni(cyclam)(OCO*R*)₂], a finite molecular complex: hydrogen-bonded supramolecular aggregation in one, two and three dimensions, and coordination polymers in one and two dimensions. Erratum

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In the paper by Zakaria *et al.* (2002) *Acta Cryst.* (2002), B**58**, 78–93 the title was printed incorrectly. The correct title should read: [Ni(cyclam)(OCO*R*)₂]: a finite molecular complex; hydrogen-bonded supramolecular aggregation in one, two and three dimensions; and coordination polymers in one and two dimensions

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