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Modification of supramolecular motifs: some effects of incorporation of metal complexes into supramolecular arrays

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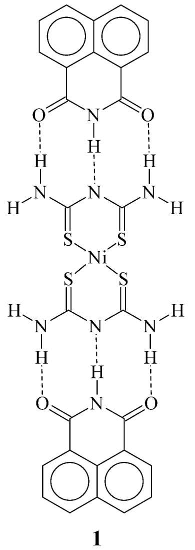
The structures of four supramolecular arrays incorporating concerted triple acceptor–donor–acceptor/donor–acceptor–donor (ADA/DAD) hydrogen bonds are described. The first is comprised of 1 : 1 phthalimide : 2,4-diamino-6-phenyl-1,3,5-triazine units linked into a one-dimensional strand by more loosely connected independent interposed triazine moieties. The second, composed of [bis(dithiobiureto)nickel(II):(3-iminoisoindolinone)$_2$] units, incorporates similar complementary triplet hydrogen bonding motifs. The third system involves a 1 : 2 assembly between the dianionic complex, bis(biureto)nickelate(II) and 2,4-diamino-6-phenyl-1,3,5-triazine to yield the bis(tetraethylammonium) salt of the [bis(biureto)nickelate(II):(2,4-diamino-6-phenyl-1,3,5-triazine)$_2$] dianion unit, the array again extended by secondary interactions. The final assembly investigated is composed of 'tri-component' units of type [bis(biguanidino)nickelate(II):(6,7-dimethoxy-2,4(1*H*, 3*H*)-quinazolinedione)$_2$] that feature an excess of hydrogen bond donor groups over acceptor groups. As in the above assemblies, it also incorporates hydrogen bonds between complementary triplet motifs as well as bridging hydrogen bonds between individual units. This last assembly is no longer planar; in the lattice being linked into a two dimensional network by dimethylsulfoxide molecules that act as 'ancillary' acceptors for the excess donors present and also as bridging molecules between neighbouring tri-component units. The hydrogen bond geometries in these assemblies are discussed comparatively and also compared with related arrays reported in the literature.

Introduction

There are good reasons for constructing supramolecular arrays that incorporate transition metal complexes. First, they provide an obvious mechanism for introducing components that have, or may acquire, interesting optical, magnetic or catalytic properties.[1] Secondly, it is sometimes possible to use metal ions and metal ion containing species to 'fine-tune' supramolecular structures—a goal of particular interest to crystal engineers.[2] For example, the presence of the metal ion may serve to moderate the intermolecular forces present, particularly hydrogen bonding, resulting in modification of the steric and/or electronic properties of the system.[3] In a related vein, we have recently demonstrated the perturbation (but not disruption) of the structure of an extended hydrogen bonded biuret array on interaction with an intercalated copper complex.[4]

In this paper we examine structure/function relationships arising from the incorporation of transition metal ion complexes into supramolecular assemblies that contain complementary hydrogen bonding donor–acceptor–donor (DAD) and acceptor–donor–acceptor (ADA) triplets.

In part, the present study was motivated by an earlier investigation by Mingos *et al.*[5] who demonstrated that co-crystallisation of Ni(dtb)$_2$ (where dtbH$_2$ = dithiobiuret) with either 1,8-naphthalimide or bemegride (3-ethyl-3-methylglutarimide) results in 1 : 2 products of type **1** and **2** incorporating hydrogen bonded DAD/ADA triplets,[6] showing that the established principles of creating hydrogen bonded organic co-crystals may be extended to transition metal containing systems. In the case of 1,8-naphthalimide, the 'three component' product is discrete since the bulky naphthalene groups sterically inhibit the adjacent carbonyl groups from forming inter-unit bridges *via* hydrogen bond formation. Conversely, the related tri-component system obtained with bemegride readily links with adjacent units such that a hydrogen bonded network is produced.



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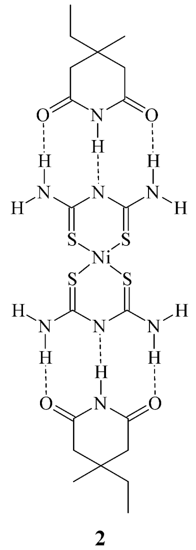

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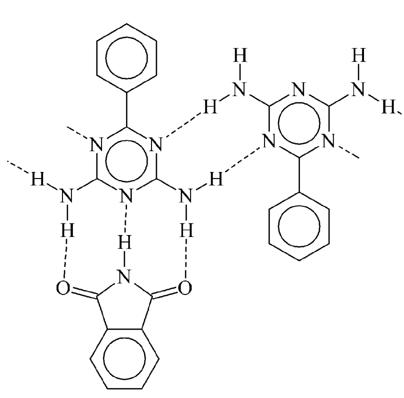
The assemblies studied are represented schematically by **3**–**6**. Within this series, the effect on hydrogen bonding of replacing an organic component with a neutral or a charged metal complex, of using five or six-membered rings to support the triplet motifs and of replacing a carbonyl group with an imino group are all examined.



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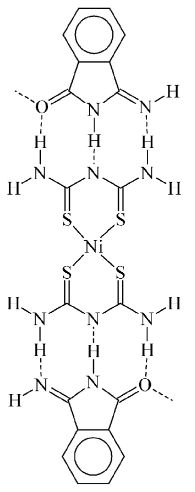

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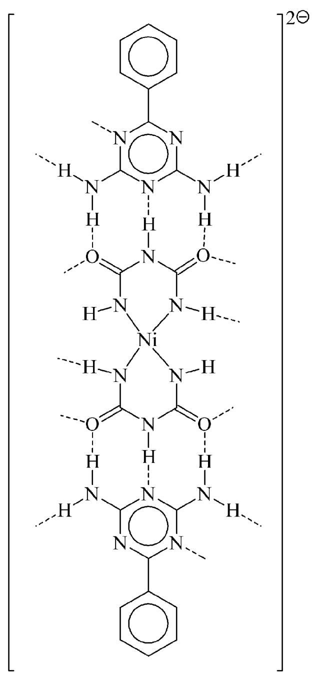

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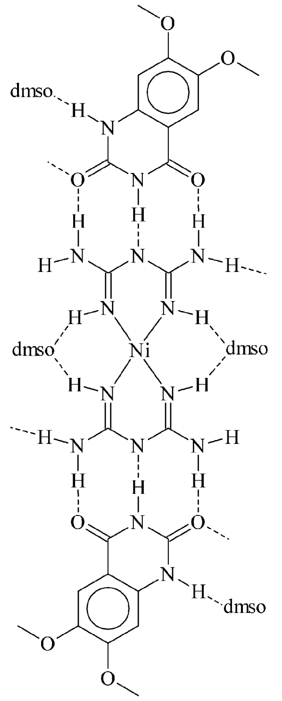

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Experimental

2,4-Diamino-6-phenyl-1,3,5-triazine (dapt), 3-iminoisoindolinone and 6,7-dimethoxy-2,4(1*H*, 3*H*)-quinazolinedione (dmq) were obtained from Aldrich Inc. Bis(dithiobiureto)nickel(II), Ni(dtb)$_2$, was prepared by the literature method.[7] Tetraethylammonium bis(biureto)nickelate(II), $(Et_4N)_2[Ni(bu)_2]$, was prepared according to the literature method for the corresponding potassium salt,[8] with tetraethylammonium hydroxide being substituted for potassium hydroxide. Biguanide sulfate dihydrate was prepared as reported previously.[9] Bis(biguanidino)nickel(II) dihydrate was prepared by dissolving biguanide sulfate dihydrate (1.41 g, 6 mmol) and sodium hydroxide (0.72 g, 18 mmol) in water (20 mL) and adding to this solution an ammoniacal solution of nickel(II) sulfate hexahydrate (0.75 g, 3 mmol). The neutral complex precipitated and was collected by filtration; yield 0.80 g, 90%.

Syntheses

[Phthalimide:(2,4-diamino-6-phenyl-1,3,5-triazine)$_2$], 3. 2,4-Diamino-6-phenyl-1,3,5-triazine (0.187 g, 1 mmol) was dissolved in hot absolute ethanol (30 mL) and phthalimide (0.147 g, 1 mmol) was added to the solution. Crystals of product formed on cooling (Found: C, 59.68; H, 4.35; N, 29.74. Calc. for $C_{26}H_{23}N_{11}O_2$: C, 54.88; H, 4.45; N, 29.54%); IR: νN–H 2710 cm^{-1} (broad).

[Bis(dithiobiureto)nickel(II):(3-iminoisoindolinone)$_2$], 4. 3-Iminoisoindolinone (45 mg, 0.30 mmol) was dissolved in a minimum volume of methanol and Ni(dtb)$_2$ (50 mg, 0.15 mmol) was added as a solid. The stirred mixture was heated and dimethylsulfoxide was added until dissolution of the complex was complete. The solution was let stand in a sealed container while it was subjected to methanol vapour diffusion; crystals suitable for X-ray crystallography were present after several days (Found: C, 39.05; H, 3.02; N, 22.41. Calc. for $C_{20}H_{20}NiN_{10}O_2S_4$: C, 38.78; H, 3.25; N, 22.61%); IR: νN–H 2770 cm^{-1} (broad).

Tetraethylammonium [bis(biureto)nickelate(II):(2,4-diamino-6-phenyl-1,3,5-triazine)$_2$], 5. $(Et_4N)_2[Ni(bu)_2]$ (0.09 g, 0.25 mmol) was dissolved in hot ethanol (7 mL). 2,4-Diamino-6-phenyl-1,3,5-triazine (0.10 g, 0.5 mmol) was added followed by dimethylsulfoxide until the solid dissolved. The hot solution was filtered. The mixture was left to stand at room temperature overnight after which time crystals suitable for X-ray crystallography had formed. (Found: C, 50.58; H, 6.93; N, 27.87. Calc. for $C_{38}H_{64}NiN_{18}O_4$: C, 50.91; H, 7.14; N, 28.13%).

[Bis(biguanidino)nickelate(II):(6,7-dimethoxy-2,4(1*H*, 3*H*)-quinazolinedione)$_2$], 6. Single crystals of the adduct suitable for X-ray diffraction were obtained by dissolving dmq (0.111 g, 0.5 mmol) in warm dimethylsulfoxide (10 mL) followed by the addition of $Ni(bg)_2{\cdot}2H_2O$ (0.074 g, 0.25 mmol). A little water was added. The solution was left to stand in air until crystals formed (Found: C, 39.13, H 5.10, N 22.67. Calc. for $C_{28}H_{44}NiN_{14}O_{10}S_2$: C, 39.11; H, 5.12; N, 22.81%).

Structure determinations

Full spheres of low-temperature CCD area-detector diffractometer data were measured (*T ca.* 153 K; Bruker AXS instrument, ω-scans, $2\theta_{max} = 58°$; monochromatic MoKα radiation, $\lambda = 0.7107_3$ Å) yielding $N_{t(total)}$ reflections, merging to N unique (R_{int} quoted) after 'empirical'/multiscan absorption correction (proprietary software), N_0 with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix least squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms, also $(x, y, z, U_{iso})_H$. Conventional residuals R, R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) are quoted on $|F|$ at convergence; neutral atom complex scattering factors were employed, within the Xtal 3.7 program system.[10] Pertinent results are given in the Tables and Figures, the latter showing labelling of the asymmetric unit (C denoted by number only) with 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

CCDC reference numbers 170261–170264.

See http://www.rsc.org/suppdata/dt/b1/b108070a/ for crystallographic data in CIF or other electronic format.

Crystal/refinement data. *3*. $C_{26}H_{23}N_{11}O_2$, $M = 521.6$. Monoclinic, space group $P2_1$ (C_2^2, No. 4), $a = 11.089(2)$, $b = 8.694(2)$, $c = 12.364(2)$ Å, $\beta = 94.446(3)°$, $V = 1188$ Å^3. D_c ($Z = 2$ f.u.) $= 1.45_7$ g cm^{-3}. $\mu_{Mo} = 1.0$ cm^{-1}; specimen: 0.50 × 0.28 × 0.08 mm; 'T'$_{min,max} = 0.62, 0.93$. $N_t = 13514$, $N = 3204$ ($R_{int} = 0.047$), $N_0 = 2530$; $R = 0.042$, $R_w = 0.044$. $|\Delta\rho_{max}| = 0.26(3)$ e Å^{-3}.

Variata. Refinement of x_{abs} gave an indeterminate chirality, 'Friedel pair' data being merged in the final least squares cycles.

4. $C_{20}H_{20}N_{10}NiO_2S_4$, $M = 619.4$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 7.502(1)$, $b = 7.681(1)$, $c = 12.061(2)$ Å, $\alpha = 91.773(2)$, $\beta = 107.638(2)$, $\gamma = 113.737(2)°$, $V = 596._9$ Å^3. D_c ($Z = 1$ f.u.) $= 1.72_3$ g cm^{-3}. $\mu_{Mo} = 12.1$ cm^{-1}; specimen: 0.32 × 0.21 × 0.17 mm; 'T'$_{min,max} = 0.59, 0.93$. $N_t = 7043$, $N = 2943$ ($R_{int} = 0.029$), $N_0 = 2607$; $R = 0.035$, $R_w = 0.042$. $|\Delta\rho_{max}| = 0.79(3)$ e Å^{-3}.

5. $C_{38}H_{64}N_{18}NiO_4$, $M = 895.7$. Triclinic, space group $P\bar{1}$, $a = 7.836(1)$, $b = 10.007(1)$, $c = 15.239(2)$ Å, $\alpha = 87.349(2)$, $\beta = 88.506(2)$, $\gamma = 69.232(2)°$, $V = 1116$ Å^3. D_c ($Z = 1$ f.u.) $= 1.33_3$ g cm^{-3}. $\mu_{Mo} = 5.0$ cm^{-1}; specimen: 0.40 × 0.14 × 0.12 mm; 'T'$_{min,max} = 0.45, 0.93$. $N_t = 13119$, $N = 5500$ ($R_{int} = 0.044$), $N_0 = 4686$; $R = 0.038$, $R_w = 0.044$. $|\Delta\rho_{max}| = 0.65(4)$ e Å^{-3}.

6. $C_{28}H_{44}N_{14}NiO_{10}S_2$, $M = 859.6$. Monoclinic, space group $P2_1/n$ (C^{15}_{2h}, No. 14), $a = 8.4180(7)$, $b = 14.256(1)$, $c = 15.927(1)$ Å, $\beta = 103.143(1)°$, $V = 1861$. D_c ($Z = 2$ f.u.) $= 1.53_4$ g cm^{-3}. $\mu_{Mo} = 7.1$ cm^{-1}; specimen: 0.1 × 0.1 × 0.07 mm; 'T'$_{min,max} = 0.76, 0.96$. $N_t = 21986$, $N = 4777$ ($R_{int} = 0.053$), $N_0 = 3543$; $R = 0.040$, $R_w = 0.044$. $|\Delta\rho_{max}| = 0.62(6)$ e Å^{-3}.

Results and discussion

The initial assembly investigated in the present study was obtained by co-crystallisation of phthalimide and 2,4-diamino-6-phenyl-1,3,5-triazine (dapt). Before discussing the crystal structure of this assembly it is instructive to first consider the reported structures of both phthalimide and 2,4-diamino-6-(4-pyridyl)-1,3,5-triazine (dapyt), the latter a close relative of dapt.

The crystal structure of phthalimide[11] shows that individual molecules are arranged in discrete dimers within which these molecules are joined by a centrosymmetric six-membered hydrogen bonded ring. One oxygen atom on each molecule is not involved in hydrogen bonding (which, as discussed elsewhere,[3a] is expected to weaken the latter bonding because of electrostatic repulsions). A weakening is also postulated in hydrogen bonded triplets of this type because of repulsions between the electronegative atoms present.[12]

While no X-ray structure of dapt has been reported, that of closely related dapyt, which might perhaps parallel that of dapt in broad terms, has been.[13] In the solid state dapyt occurs as two crystallographically independent molecules devoid of crystallographic symmetry (A and B) in the asymmetric unit; these are assembled into chains, along which the respective forms alternate. Both molecules have essentially identical bond lengths and angles but differ in the torsional relationships between their pyridyl and triazinyl rings. Individual A and B molecules are linked *via* hydrogen bonded rings formed between the triazinyl rings of 'antiparallel' (and certainly not coplanar) dapyt molecules. The (intermolecular) N–H ··· N hydrogen bonds are formed between the amino NH groups in positions 2 and 4 and the ring nitrogens in positions 1 and 5 of adjacent triazinyl rings. Type A molecules are also linked pairwise, by way of hydrogen bond formation between C_2 symmetry related counterparts *via* a pair of N–H ··· N hydrogen bonds between one of the amino group protons in one molecule and one of the triazinyl nitrogen atoms of the other (and *vice versa*). Molecules of type B are linked to each other *via* pairs of slightly less conventional N–H ··· N hydrogen bonds between one hydrogen atom from each amino group in one molecule and two of the triazinyl ring nitrogen atoms in another. Finally, it needs to be noted that while there are other interspecies interactions present in the crystal, these seem of less importance in terms of the following discussion.

By analogy with dapyt, dapt, which has four potential donor sites and three acceptor sites per molecule, might be expected to favour the formation of an extended (multiple) hydrogen bonding network.

In view of the above, the assembly formed between phthalimide and dapt was of interest because of the inherently different potential of these two components for forming extended solid arrays. Co-crystallisation of the above reagents led to the isolation of a product, **3**, of stoichiometry [phthalimide : (dapt)$_2$], one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. In this assembly (Fig. 1) triazinyl-containing moieties are joined side-to-side into chains by hydrogen bonded rings as found in dapyt; however, in the present case the chains are not linked in pairs. Rather, every second dapt forms a triplet of hydrogen bonds with the complementary motif on a phthalimide. The hydrogen bond geometry, which is summarised in Table 1, shows that the hydrogen bonding between triazinyl moieties in the adduct is similar to that reported for dapyt, with the individual hydrogen bond lengths being typical of interactions between organic species.[14]

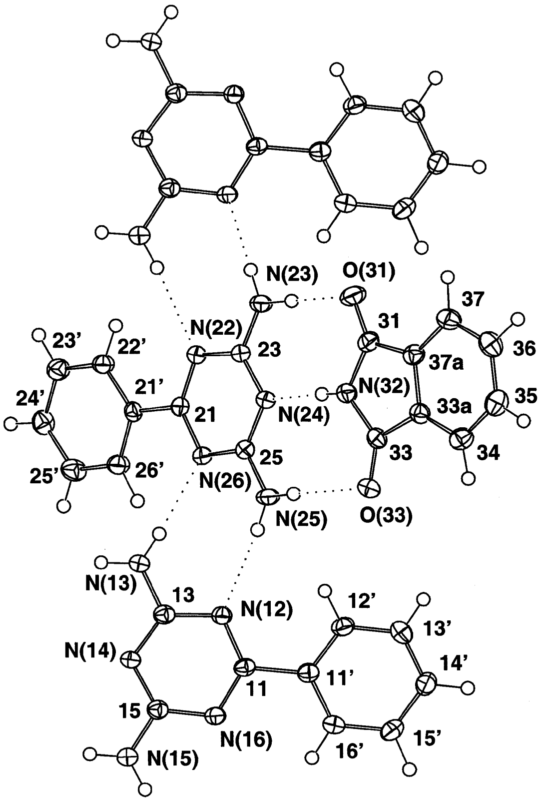

Fig. 1 Projection of **3**.

The hydrogen bonding present in the triplet is worthy of comment. The central N–H ··· N hydrogen bond is much shorter than the others of same type in the structure (by some 0.2 Å) so that we attribute the broad infrared absorption at 2710 cm^{-1} to this bond. It is also distinctly shorter (by 0.3 Å) than those present in corresponding hydrogen bonding triplets in adducts of the neutral complex bis(dithiobiureto)nickel(II), Ni(dtb)$_2$, with bemegride or 1,8-naphthalimide[5] (both of which lie in the range usually observed for N–H ··· N hydrogen bonds between organic molecules). The N–H ··· O hydrogen bonds are rather weak; they are longer by 0.1 Å than those in the above-mentioned complexes, and long, too, for bonds typically present between neutral organic species,[14] and phthalimide in particular.

The amino nitrogens of the dapt molecules not directly bonded to phthalimide are at a distance too far from a phthalimide oxygen for hydrogen bonding to occur (Table 1) but presumably there is still a weak electrostatic attraction between them. Interestingly, a corresponding hydrogen in dapyt is involved in a less conventional hydrogen bond with a triazinyl ring nitrogen, in which a non-bonding π-orbital is postulated as the acceptor.[13]

Within the dapt molecules, dihedral angles between the pairs of aromatic planes are 13.4(1), 7.3(1)°, between $N_3C_3(2)$ and the phthalimide 1.9(1)°; between $N_3C_3(2)$ and $N_3C_3(1)$ there is a substantial twist, the angle being 42.3(1)°. Intramolecular geometries of the two species in **3** are generally as expected.

The neutral metal complex bis(dithiobiureto)nickel(II), Ni(dtb)$_2$, and 3-iminoisoindolinone were co-crystallised to yield a product of type [bis(dithiobiureto)nickel(II):(3-iminoisoindolinone)$_2$], **4**; one half of the formula unit comprises the

Table 1 Hydrogen bond geometry in [phthalimide:(dapt)$_2$], **3**

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA angle/°
N(13)	H(13a)	O(33^{i})	0.91(4)	2.55(4)	3.280(5)	138(3)
N(13)	H(13b)	N(26)	0.85(3)	2.21(3)	3.046(4)	167(3)
N(15)	H(15b)	N(22^{ii})	0.87(3)	2.27(3)	3.140(4)	173(3)
N(23)	H(23b)	N(16)	0.92(4)	2.06(4)	2.986(4)	180(3)
N(25)	H(25b)	N(12)	0.85(4)	2.22(4)	3.060(4)	172(3)
N(32)	H(32)	N(24)	0.92(4)	1.89(4)	2.801(5)	175(3)
N(23)	H(23a)	O(31)	0.90(4)	2.20(4)	3.087(4)	168(3)
N(25)	H(25a)	O(33)	0.88(4)	2.36(4)	3.239(4)	174(3)

Transformations of the asymmetric unit: i $x, y - 1, z$; ii $x, y, z - 1$.

asymmetric unit of the structure, the nickel atom lying on a crystallographic inversion centre. It was thought that the supramolecular structure of this product, might resemble that reported by Mingos *et al.*[5] for [Ni(dtb)$_2$:(bemegride)$_2$] but with the acceptor–donor–acceptor (ADA) motif attached to a five-membered rather than a six-membered ring. In addition, in the present assembly an imino group has replaced one of the carbonyl groups in the corresponding triplet belonging to the latter, appearing in its E-configuration, to be capable of acting as a hydrogen bond acceptor in the triplet. It was anticipated that this change might not affect the hydrogen bonding arrangement greatly since, in any case, the crystal structure of [Ni(dtb)$_2$:(bemegride)$_2$] shows that the two bemegride carbonyl groups are not equivalent; one carbonyl, in addition to being part of the ADA triplet, forms a hydrogen bond bridge to a neighbouring complex while the other does not. Despite this asymmetry in the overall structure, the hydrogen bond length associated with this group in the triplet is not significantly affected. Thus, the 3-iminoisoindolinone might possibly be oriented so that the imino group, which is unable to function simultaneously as an acceptor in the bonded triplet and a bridge between three-component units, would replace the non-bridging carbonyl in the bonded triplet and be present in the E isomeric form. In this context, it is noted that incorporation of the E-isomer may offer a method for isomer recognition and the Z to E conversion of an imino group may offer a method for inducing a change in a hydrogen bonding motif in a different manner to that described recently by us[15] where such a change was achieved by means of facile acid/base behaviour.

The structure of **4**, an extended two dimensional sheet (Fig. 2), follows the above tendencies with details of the hydrogen bond geometry summarised in Table 2. The central N ··· N hydrogen bond is almost exactly linear and is significantly (0.2_0, 0.2_1 Å) shorter than that in the bemegride or 1,8-naphthalimide adducts with the same metal complex, but is 0.1_1 Å longer than that formed in **3**. The broad infrared absorption assigned to this bond occurs at 2770 cm^{-1}, 60 cm^{-1} higher than in adduct **3**. The lengths of the two outer hydrogen bonds of the triplet motif are essentially equal so that substitution of N for O has little or no influence on the individual distances. The hydrogen bonds which form bridges between the neighbouring complexes remain essentially the same as in the bemegride adduct; however such bridges do not form when 1,8-naphthalimide is substituted for 3-iminoisoindolinone, a feature which we exploit in **6**. The N ··· S distances between neighbouring complexes are shorter than observed in the bemegride (by 0.06_5 Å) and 1,8-naphthalimide (by 0.10_4 Å) adducts.

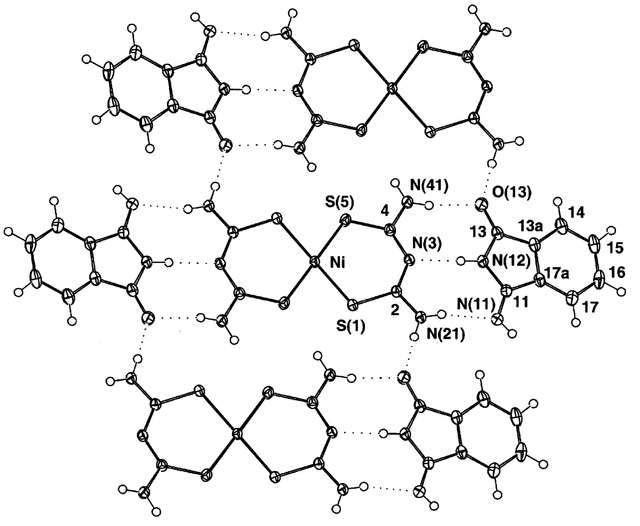

Fig. 2 Projection of **4**.

About the nickel atom, although the NiS$_4$ array is obligate planar, the six-membered chelate ring is appreciably distorted, torsions in the Ni–S bond being 22.4(1), −14.4(1), in the S–C bonds −23.8(3), 1.0(3) and in the N–C 6.3(4), 7.0(4)°; a weighted least squares plane through the six atoms makes a dihedral angle of 9.23(6)° with the phthalimide plane. Ni–S(1,5) 2.1665(6), 2.1636(5), S–C 1.735(2), 1.733(2) and N–C 1.344(2), 1.336(3) Å are nonetheless 'aromatic' in nature and comparable with counterpart values in the same molecule in numerous other determinations; C–N(H$_2$) are 1.330(3), 1.336(2) Å. Within the five-membered ring, dimensions are similar to those of phthalimide, generally, C(11)–N(11) being 1.266(3) Å.

The third assembly **5** synthesised, obtained by the interaction of tetraethylammonium bis(biureto)nickelate(II), (Et$_4$N)$_2$-[Ni(bu)$_2$] and dapt, was structurally characterised to explore whether the resulting supramolecular structure would resemble more closely that of the first assembly **3** or the second **4**. The effect of the use of a dicationic complex in the adduct on the nature of the hydrogen bonding formed was also of particular interest. The triplet motifs in this case are both incorporated on six-membered rings as are the related assemblies reported by Mingos *et al.*,[5] with the exception that the ADA motif is now on the metal complex component and the DAD motif on the organic component.

As perhaps suggested by its stoichiometry, [(Et$_4$N)$_2$-[Ni(bu)$_2$]:(dapt)$_2$], **5** has features of the aggregate structure (Fig. 3) that resemble those of **4**, one half of the formula unit comprising the asymmetric unit of the structure, with the nickel atom disposed on a crystallographic inversion centre. It contains chains of metal complex ions linked by interactions between ligands (N–H ··· O rather than N–H ··· S) and by a pair of hydrogen bonds formed between one of the amino groups of dapt and a carbonyl oxygen on the ligand in an adjacent complex, the anions forming a displaced sheet structure, with the cations between the sheets. Linked molecules of dapt are still found within the structure although the hydrogen bonds between the entities are much longer than those in **3**.

The strongest hydrogen bonds (Table 3) in the structure are those formed by the bridging amino group and ligand carbonyl groups.

Table 2 Hydrogen bond geometry in $[\mathrm{Ni(dtb)_2{:}(3\text{-}iminoisoindolinone)_2}]$, **4**

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA angle/°
N(12)	H(12)	N(3)	0.88(3)	2.03(3)	2.911(2)	178(4)
N(21)	H(21a)	N(11)	0.83(2)	2.18(3)	2.997(2)	167(3)
N(41)	H(41a)	O(13)	0.88(3)	2.12(2)	3.001(2)	171(3)
N(21)	H(21b)	O(13$^{\mathrm{i}}$)	0.85(3)	2.11(3)	2.935(2)	163(4)
N(41)	H(41b)	S(5$^{\mathrm{ii}}$)	0.87(2)	2.66(4)	3.495(2)	162(4)

Transformations of the asymmetric unit: i $x - 1, y - 1, z$; ii $1 - x, 1 - y, -z$.

Table 3 Hydrogen bond geometry in $[\mathrm{(Et_4N)_2[Ni(bu)_2]{:}(dapt)_2}]$, **5**

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA angle/°
N(3)	H(3)	N(14)	0.85(2)	2.16(2)	3.004(2)	174(2)
N(13)	H(13a)	O(2)	0.86(2)	2.04(2)	2.897(2)	171(2)
N(15)	H(15a)	O(4)	0.87(3)	2.20(3)	2.996(2)	152(3)
N(1)	H(1)	O(2$^{\mathrm{i}}$)	0.81(2)	2.48(2)	3.284(2)	170(2)
N(13)	H(13b)	O(4$^{\mathrm{ii}}$)	0.90(3)	1.90(3)	2.785(2)	168(2)
N(15)	H(15b)	N(16$^{\mathrm{iii}}$)	0.88(2)	2.47(2)	3.312(2)	162(2)

Transformations of the asymmetric unit: i $1 - x, -y, 1 - z$; ii $1 + x, y, z$; iii $-x, 1 - y, -z$.

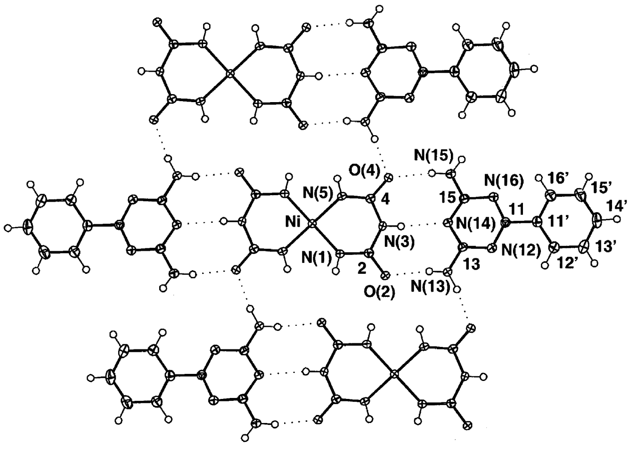

Fig. 3 Projection of **5**.

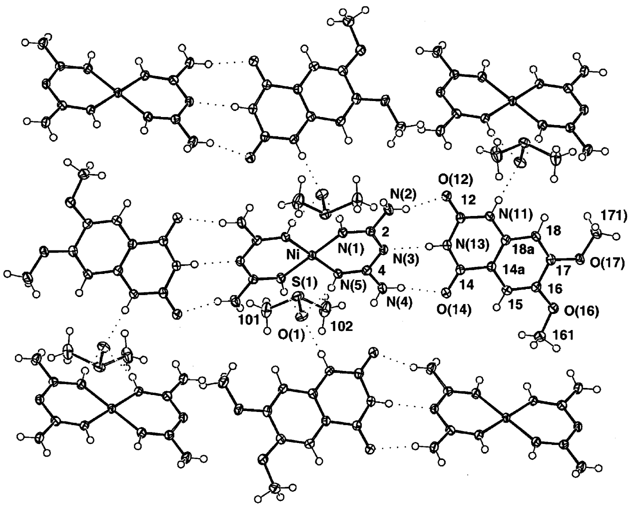

Fig. 4 Projection of **6**.

Of particular interest is the fact that the fused hydrogen bonded rings formed by the bound triplets are considerably distorted relative to the planar arrangement observed in the other adducts. If the supramolecular structure were planar (as occurs in **4**), the non-bridging amino group would be involved in the formation of just one hydrogen bond (as part of the triplet structure). Instead, the triazinyl ring is rotated with respect to the metal complex [$\mathrm{NiN_2C_2/C_3N_3}$ dihedral 23.23(5)°] so that, at the expense of weakening the triplet, a double interaction between anti-parallel triazinyl rings occurs. This leads to the same general geometry as that observed in the chains of dapt molecules in **3**, but with the 'hydrogen bonds' being much longer (by *ca* 0.3 Å). Despite the deviation from planarity, the lengths of the hydrogen bonds and the D–H ··· A angles of the triplets are only slightly different from those observed in **3** and **4**. There appears to be only one previously structurally characterised example of the $[\mathrm{Ni(bu)_2}]^{2-}$ anion[16] (as its $[\mathrm{Ag(NH_3)_2}]^+$ salt), its geometry essentially similar to that of the present one (Ni–N here 1.874(2), 1.865(1) Å).

The molecular aggregate of the fourth assembly **6**, formed by co-crystallisation of bis(biguanidino)nickel(II), $\mathrm{Ni(bg)_2}$, and 6,7-dimethoxy-2,4(1*H*, 3*H*)-quinazolinedione, dmq, is given in Fig. 4; again one half of the formula unit comprises the asymmetric unit of the structure, with the nickel atom on a crystallographic inversion centre. Unlike **5** (which contains both donor and acceptor groups outside its central triplet motif), the present three-component unit is characterised by an overall excess of donor over acceptor groups. Dmq incorporates two donor and two acceptor groups; its geometry allows it to act as an ADA triplet, with the NH group in position 1 available for additional interactions. Only one of the carbonyl acceptors (that in position 2) is available to form bridges with neighbouring three-component units (*cf.* the naphthalimide system mentioned earlier) because steric hindrance from the aryl ring effectively limits access to this site. The structure of **6** resembles that of **4** in that it has the same DAD motif on a neutral complex and the complementary ADA motif has one carbonyl group capable of forming a bridge between neighbouring tri-component assemblies (as well as one which cannot act as a bridge). However, it is unable to form the same extended structure linking the metal complexes in the second dimension (other than by way of the dmso) because donor NH groups now replace the S atoms in **4**.

The structure of **6** also shows the presence of a weak bridging bond between the dmq carbonyl group in position 2 and a biguanide $\mathrm{NH_2}$ on a neighbouring array (Table 4), similar to that observed in **4**. The components of individual units are not coplanar; the nickel chelate ring and dmq have an interplanar dihedral angle of 24.00(6)°, with the axis of rotation being the central hydrogen bond of the triplet rather than one of the outer ones, as was observed in **5**. Associated with this rotation are hydrogen bonds formed between the NH in position 1 of dmq and two ligand imino groups with the dimethylsulfoxide

Table 4 Hydrogen bond geometry in [Ni(bg)$_2$:(dmq)$_2$], **6**

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA angle/°
N(13)	H(13)	N(3)	0.83(3)	2.10(3)	2.928(3)	176(2)
N(2)	H(2a)	O(12)	0.84(3)	2.17(3)	2.978(3)	163(3)
N(4)	H(4a)	O(14)	0.85(3)	2.07(3)	2.914(3)	173(2)
N(4)	H(4b)	O(12)	0.80(3)	2.52(3)	3.255(3)	152(2)
N(1)	H(1)	O(1^{i})	0.85(3)	2.20(3)	3.018(3)	161(3)
N(5)	H(5)	O(1)	0.87(3)	2.24(2)	3.082(2)	162(2)
N(11)	H(11)	O(1^{ii})	0.84(3)	1.94(3)	2.776(3)	169(3)

Transformations of the asymmetric unit: i $1 - x, 1 - y, 1 - z$; ii $\frac{1}{2} - x, y - \frac{1}{2}, 1\frac{1}{2} - z$.

oxygen which forms another bridge between the neighbours. This results in the metal complexes also being linked indirectly through dimethylsulfoxide molecules. As in the previous cases tri-component arrays assemble into distinct layers but, unlike **4**, these layers are no longer planar but have an undulating structure with dimethylsulfoxide molecules running along the crests and troughs of the 'waves'. It is noted that dimethylsulfoxide molecules have been found by us to form similar bridges in the supramolecular array of type bis(2-guanidinobenzimidazolo)-nickel(II)·2dmso.[15] In the present system dmq molecules in neighbouring layers are aligned anti-parallel and are separated by van der Waals distances.

Concluding remarks

In this paper emphasis has been given to structural effects arising from the incorporation of transition metal ion complexes into arrays containing complementary hydrogen bonding motifs. For the systems studied, replacement of an organic component with either a neutral or a dicationic complex leads to a slight increase in the hydrogen bond lengths arising from bound DAD and ADA triplets. The use of a five-membered ring to support one of the triplet motifs, instead of a six-membered one, has resulted in a considerable shortening of the central bond of the corresponding hydrogen bound triplets, a feature clearly reflected in the infrared spectrum of the product. Replacing a carbonyl group with an imino group in one of the triplets had little effect on the corresponding hydrogen bond lengths. Donor and acceptor groups outside the bonded triplets were found capable of influencing the geometry of the triplets; the latter are not necessarily rigidly planar nor do they necessarily dominate the planarity (or otherwise) of the corresponding extended arrays.

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