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## Supramolecular Chemistry

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Michael M. Bishop<sup>ab</sup>; Leonard F. Lindoy<sup>a</sup>; Peter Turner<sup>a</sup>

<sup>a</sup> School of Chemistry, University of Sydney, Sydney, NSW, Australia <sup>b</sup> Sydney Grammar School, Darlinghurst, NSW, Australia

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# Supramolecular Assembly: A Comparative Structural Study of the Incorporation of Bis(2-guanidinobenzimidazolo)nickel(II) into Supramolecular Arrays

MICHAEL M. BISHOP<sup>a,b</sup>, LEONARD F. LINDOY<sup>a,\*</sup> and PETER TURNER<sup>a</sup>

<sup>a</sup>School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia; <sup>b</sup>Sydney Grammar School, College Street, Darlinghurst, NSW 2010, Australia

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Dedicated to Professor E. Kimura on the Occasion of His Official Retirement

The structural effects of incorporating a non-planar neutral metal complex, bis(2-guanidinobenzimidazolo)nickel(II), into three supramolecular arrays are described. The complex has a donor–acceptor–donor (DAD) hydrogen bonding motif on each ligand and this motif is used to link it to bis(biureto)nickelate(II) ions, or to 1,8-naphthalimide or phthalimide molecules, all of which incorporate a complementary acceptor–donor–acceptor (ADA) hydrogen bonding motif. The geometry about the metal ion as well as the nature of the network of hydrogen bonds formed have significant influences on the supramolecular structure adopted. An interesting combination of intramolecular hydrogen bonding and close  $\pi$ -stacking interactions also occur in each species.

*Keywords:* X-ray crystallography; Diffraction; Hydrogen bond; Nickel C4; Crystal engineering; Supramolecular Chemistry

## INTRODUCTION

One reason for including transition metal complexes in supramolecular arrays is to use the metal coordination geometry to influence the overall geometry adopted by the resulting supramolecular system.

In this paper, we examine the effect of incorporating a transition metal complex, which for steric reasons cannot be planar, into extended arrays by

means of matching donor–acceptor–donor (DAD) motifs to complementary acceptor–donor–acceptor (ADA) motifs incorporated on a second molecular entity. The complex chosen for the study was bis(2-guanidinobenzimidazolo)nickel(II),  $\text{Ni}(\text{gb})_2$ , which has the required DAD motif on each ligand and which a previous structural study has shown does not adopt a planar configuration because of steric interactions between the coordinated ligands. It has been observed that in cationic bis(2-guanidinobenzimidazolo)nickel(II),  $[\text{Ni}(\text{gbH})_2]^{2+}$ , and in the isolated neutral complex  $[\text{Ni}(\text{gb})_2]$ , the nickel lies at a centre of symmetry but the ligands do not occupy the  $\text{NiN}_4$  plane; the complexes have a step-like structure [1,2]. In contrast, the structure of  $\text{Ni}(\text{gb})_2$  (crystallised from dimethylsulfoxide/water) shows that this species contains its four donor nitrogens arranged in a tetrahedrally distorted geometry, with the latter reflecting the presence of steric interactions between the bound ligands [3]. Each ligand in  $\text{Ni}(\text{gb})_2$  also presents a DAD hydrogen bonding motif and, indeed, this complex was observed to self-assemble into four-sided tubes using hydrogen bonding between ligands on adjacent complexes and between bridging dimethylsulfoxides that link to hydrogen bond donor groups on adjacent complexes [3].

Other supramolecular assemblies between planar metal complexes and organic species incorporating complementary DAD–ADA motifs have been reported in Ref. [4]. In the present context, it is

\*Corresponding author.

noted that hydrogen bonding triplets of the type DAD–ADA are (partially) destabilised by secondary interactions within the triplet [5]. Furthermore, hydrogen bonding triplets of the present type are not necessarily planar but rotation may occur about the central hydrogen bond or about one of the outer two bonds when the triplet forms part of an extended hydrogen bonding network [6].

Even though no stacking interactions occur in crystalline 2-guanidinobenzimidazole (gbH) [7] or in  $\text{Ni}(\text{gb})_2 \cdot 2\text{dmsO} \cdot \text{H}_2\text{O}$  [3] (or, indeed, in phthalimide [8]), it was anticipated that co-crystallisation of selected aromatic species containing complementary hydrogen bonding triplets might lead to interesting  $\pi$ -stacking interactions. The prospect that the geometry of the central complex might also influence the structure adopted was also of interest.

The goal of the present study was thus to generate arrays of the above type based on  $\text{Ni}(\text{gb})_2$ . The species chosen to form the assemblies were selected so that the assemblies might be expected, by comparison with those reported earlier, to form discrete three-component units as well as extended structures, chains and sheets, held together by hydrogen bonding and, in one case, by  $\pi$ -stacking. Three assemblies of stoichiometries  $(\text{Et}_4\text{N})_2[\text{Ni}(\text{bu})_2]:[\text{Ni}(\text{gb})_2]$ , **1**, (where  $\text{buH}_2$  is biuret),  $[\text{Ni}(\text{gb})_2]:(\text{1,8-naphthalimide})_2 \cdot 2\text{-dimethylsulfoxide}$ , **2**, and  $[\text{Ni}(\text{gb})_2]:(\text{phthalimide})_2$ , **3**, were synthesised during the present investigation.

## EXPERIMENTAL

Bis(2-guanidinobenzimidazolo)nickel(II) was prepared by the addition of an ammoniacal solution of nickel(II) chloride to a methanolic solution of 2-guanidinobenzimidazole [3].

### [Tetraethylammonium Bis(biureto)nickelate(II): Bis(2-guanidinobenzimidazolo)nickel(II)] **1**

Tetraethylammonium bis(biureto)nickelate(II),  $(\text{Et}_4\text{N})_2[\text{Ni}(\text{bu})_2]$ , was prepared according to the literature method described for the corresponding potassium salt [9], except that tetraethylammonium hydroxide was used instead of potassium hydroxide and the product was precipitated by the addition of acetone.

Single crystals of **1** suitable for X-ray crystallography were obtained as follows.  $(\text{Et}_4\text{N})_2[\text{Ni}(\text{bu})_2]$  (0.12 g, 0.23 mmol) was dissolved in methanol (5 ml) and 2-guanidinobenzimidazole (0.05 g, 0.5 mmol) was added with gentle warming. The orange solution that resulted was allowed to evaporate slowly in air. After several days, the dark orange-red crystals that formed were filtered off and washed with ethanol.

Analysis: % by mass calculated for  $\text{C}_{36}\text{H}_{62}\text{NiN}_{18}\text{O}_4$ : C 46.28, H 6.64, N 27.00; found C 46.47, H 6.58, N 26.87.

### [Bis(2-guanidinobenzimidazolo)nickel(II): (1,8-naphthalimide)<sub>2</sub>·2dimethylsulfoxide] **2**

Bis(2-guanidinobenzimidazolo)nickel(II) was prepared as described previously. Crystals of **2** suitable for X-ray crystallography were obtained by dissolving a mixture of 1,8-naphthalimide (0.04 g, 0.2 mmol) and bis(2-guanidinobenzimidazolo)nickel(II) (0.04 g, 0.1 mmol) in hot dimethylsulfoxide (6 ml). The solution was then left to stand and clusters of red-brown crystals of product formed overnight in near quantitative yield.

Analysis: % by mass calculated for  $\text{C}_{44}\text{H}_{42}\text{N}_{12}\text{NiO}_6\text{S}_2$ : C 55.18, H 4.39, N 17.56; found C 55.29, H 4.54, N 17.31. IR  $\nu(\text{N}-\text{H} \cdots \text{N})$  2794 (br), 2740 (br), 2673 (br)  $\text{cm}^{-1}$ .

### [Bis(2-guanidinobenzimidazolo)nickel(II): (phthalimide)<sub>2</sub>] **3**

Crystals of **3** suitable for X-ray crystallography were obtained by dissolving a mixture of phthalimide (0.074 g, 0.5 mmol) and bis(2-guanidinobenzimidazolo)nickel(II) (0.10 g, 0.25 mmol) in dimethylsulfoxide (2 ml). The solution was let stand and clusters of dark green crystals formed over several days.

Analysis: % by mass calculated for  $\text{C}_{32}\text{H}_{26}\text{NiN}_{12}\text{O}_4$ : C 54.80, H 3.74, N 23.97; found C 54.70, H 3.85, N 23.66. IR  $\nu(\text{N}-\text{H} \cdots \text{N})$  2500 (br)  $\text{cm}^{-1}$ .

## X-ray Crystal Structure Determinations

Diffraction data for assembly **1** were obtained on mounting a red prismatic crystal on a Bruker SMART 1000 CCD diffractometer employing graphite monochromated  $\text{MoK}\alpha$  radiation generated from a sealed tube. Diffraction data for assembly **2** and **3** were obtained on mounting a red blade like crystal for **2** and a green acicular crystal of **3** on a Rigaku AFC7R diffractometer, employing graphite monochromated  $\text{CuK}\alpha$  radiation generated from a rotating anode. The structures were solved by direct methods with SIR97 [10], and extended and refined with SHELXL-97 [11], using the teXsan interface [12] Pertinent details are summarised in Table I. ORTEP [13, 14] depictions of the molecules with 20% displacement ellipsoids are shown in Figs. 1–3.

### $\text{Ni}(\text{gb})_2:(\text{Et}_4\text{N})_2[\text{Ni}(\text{bu})_2]$

Cell constants were obtained from a least squares refinement against 4769 reflections located between  $4.36$  and  $56.08^\circ 2\theta$ . Data were collected at  $297(2)\text{K}$  with  $0.3^\circ$  increment  $\omega$  scans to  $56.60^\circ 2\theta$ . The

intensities of 155 standard reflections recollected at the end of the experiment did not change significantly during the data collection. An empirical absorption correction determined with SADABS [14, 15] was applied to the data. The data integration and reduction were undertaken with SAINT and XPREP, [16,17]. The asymmetric unit contains two complex molecules each centred on inversion sites (0,0,0 and 0.5,0.5,0.5, respectively), and a tetraethylammonium counter-ion. Anisotropic displacement parameters were refined for the non-hydrogen atoms of the structure model, and in general, a riding atom model was used for hydrogen atoms. The N(5) and N(8) hydrogens were located and modelled with isotropic displacement parameters and distance restraints.

### *Ni(gb)<sub>2</sub>:(1,8-naphthalimide)<sub>2</sub>·2dmsO*

Cell constants were obtained from a least squares refinement against 25 reflections located between 83.40 and 107.20° 2 $\theta$ . Data were collected at 294(2) K with  $\omega - 2\theta$  scans to 135.50° 2 $\theta$ . The intensities of three standard reflections measured every 150 reflections did not change significantly during the data collection. An empirical absorption correction based on azimuthal scans of three suitable reflections

was also applied to the data. Processing and calculations were undertaken with teXsan [12]. The asymmetric unit contains a complex molecule centred on an inversion site, a co-crystallised 1,8-naphthalimide molecule and a dmsO solvate molecule. The dmsO molecule exhibits sp<sup>3</sup> inversion disorder. The S(1) and S(2) populations were refined and then fixed at 0.85 and 0.15, respectively. The solvate disorder required two model carbon atoms occupying the same site, with complementary occupancies, for each methyl carbon atom (C(21A) and C(21B), and C(22A) and C(22B)). In general, the non-hydrogen atoms were modelled with anisotropic thermal parameters and a riding atom model was used for the hydrogen atoms. Isotropic thermal parameters were used for the 0.15 population C(21B) and C(22B) sites. The amine hydrogens were located in difference maps.

### *Ni(gb)<sub>2</sub>:(phthalimide)<sub>2</sub>*

Cell constants were obtained from a least squares refinement against 25 reflections located between 22.60 and 56.40° 2 $\theta$ . Data were collected at 294(2) K with  $\omega - 2\theta$  scans to 135.66° 2 $\theta$ . The intensities of three standard reflections measured every 150

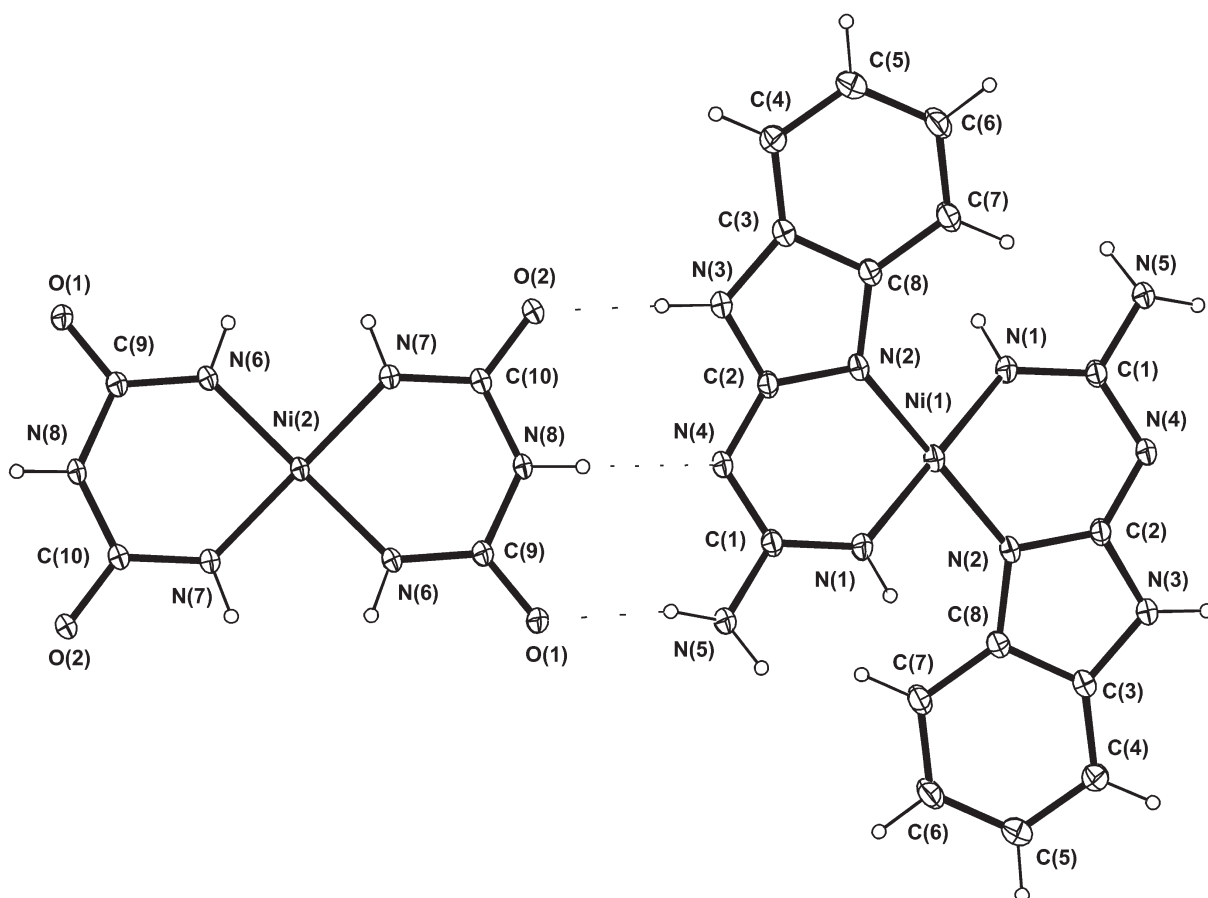


FIGURE 1 ORTEP [13,14] depiction of **1** with displacement ellipsoids at the 20% level. Both of the metal complex molecules reside on inversion centres, such that the hydrogen bonded complex is trimeric (the second symmetry related Ni(bu)<sub>2</sub> complex is not shown).

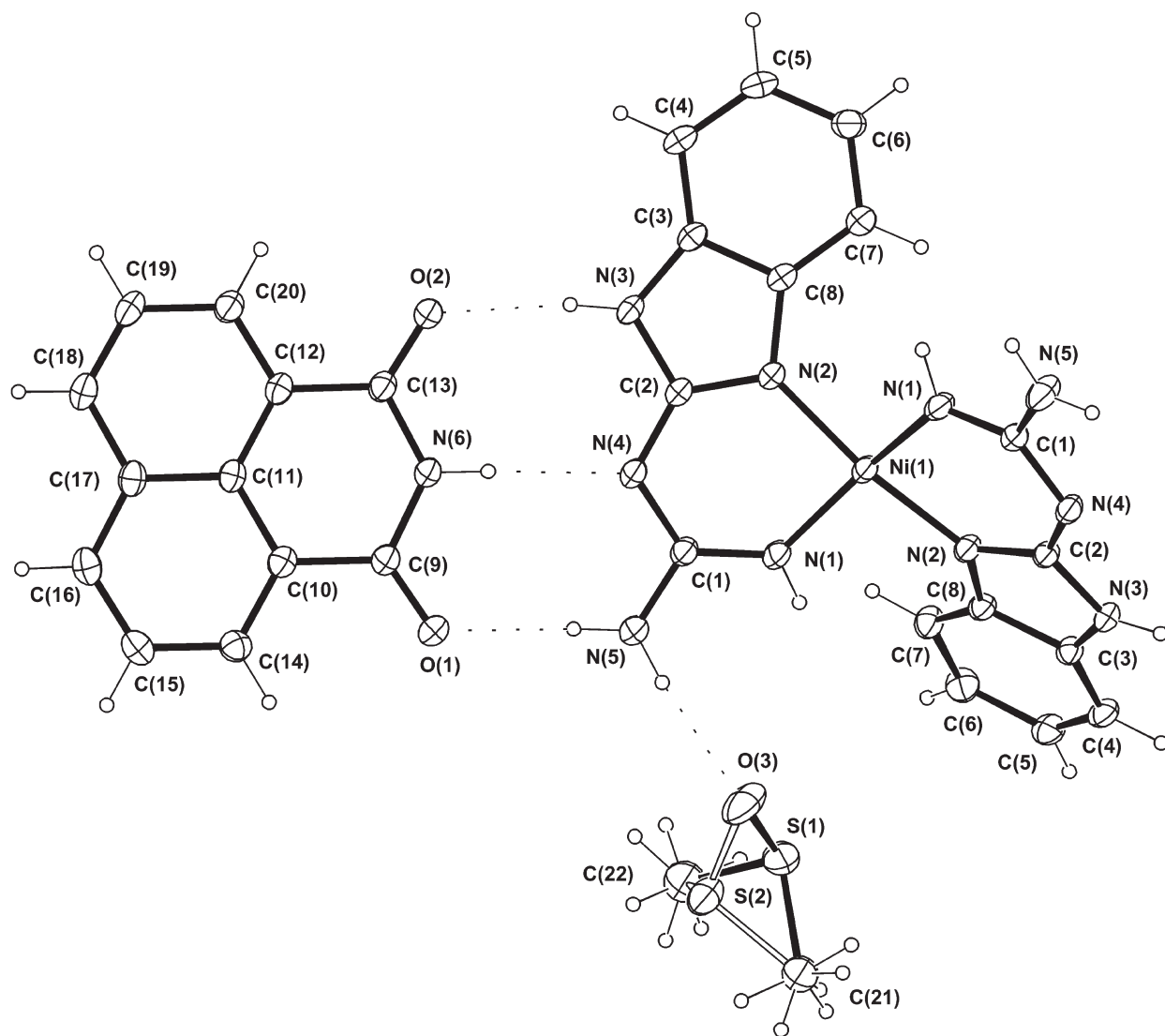


FIGURE 2 ORTEP [13,14] depiction of **2** with displacement ellipsoids at the 20% level. The metal complex is located on an inversion site, and the hydrogen bonded complex is thus trimeric (the second symmetry related 1,8-naphthalimide is not shown).

reflections changed by  $-7.72\%$  during the data collection and a correction was accordingly applied to the data. An empirical absorption correction based on azimuthal scans of three suitable reflections was also applied to the data. Processing and calculations were undertaken with *teXsan*. Anisotropic thermal parameters were refined for the non-hydrogen atoms, and in general, a riding atom model was used for the hydrogen atoms included in the model. The terminal amine hydrogen H(5NA), H(5NB), H(101) and H(102) atoms were located and modelled with isotropic thermal parameters.

## RESULTS AND DISCUSSION

Details of the crystallography are summarised in Table I and Tables II and III provide a comparative

summary of the differences between the metal complex geometries within the metallarings.

As shown in Fig. 4, the  $[\text{Ni}(\text{bu})_2]^{2-}$  and  $\text{Ni}(\text{gb})_2$  molecules comprising assembly **1** are linked through a continuous hydrogen bond network. The metal ion of the  $[\text{Ni}(\text{bu})_2]^{2-}$  complex ion is located on the inversion site at the centre of the unit cell and is linked through hydrogen bonds to other  $[\text{Ni}(\text{bu})_2]^{2-}$  complex ions aligned in the direction of the *c*-axis (along  $[1/2, 1/2, 1]$ ) of the unit cell. These complexes are linked to neighbouring  $\text{Ni}(\text{gb})_2$  complexes through an essentially coplanar triplet of hydrogen bonds, with the biureto ligand providing a DAD motif and the guanidinobenzimidazolo ligand providing the complementary ADA motif. The  $\text{Ni}(\text{gb})_2$  complexes are accordingly stacked along the *c*-axis, with the metal residing at the unit cell vertices. The hydrogen bond geometries of the assembly are typical of those found in organic

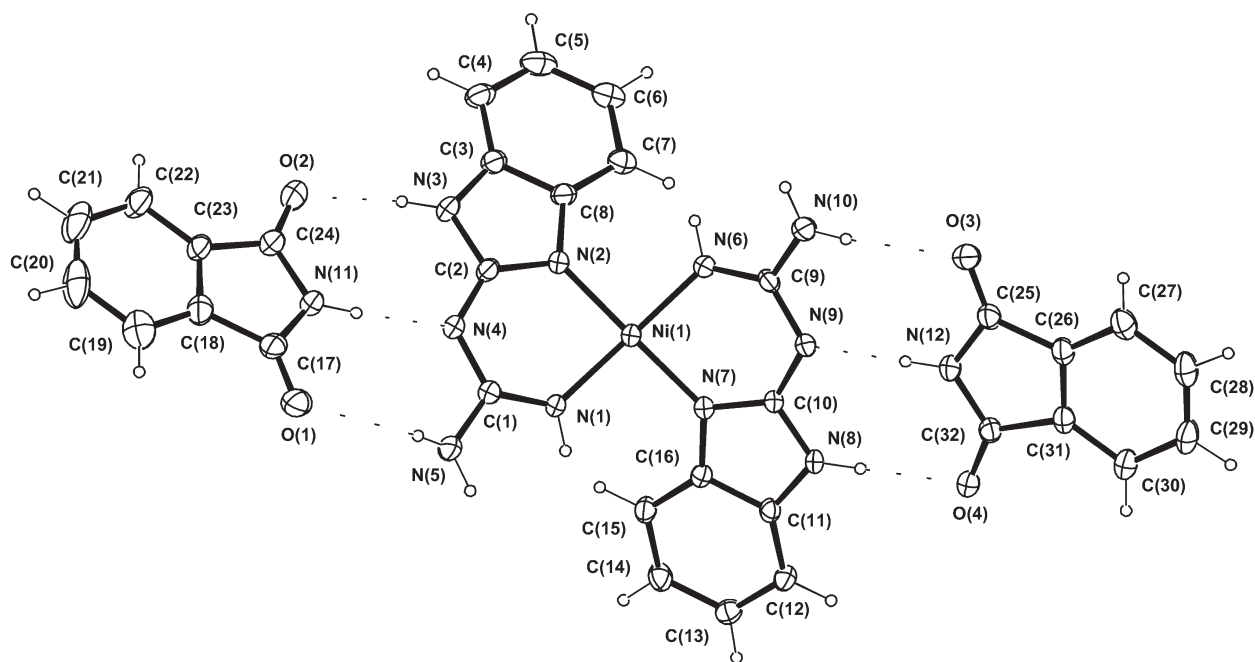


FIGURE 3 ORTEP [13,14] depiction of **3** with displacement ellipsoids at the 20% level. Although a hydrogen bond is shown between O(1) and N(5), it is much weaker than in **1** and **2**; the O(1) to N(5) distance is 3.399(5) Å

assemblies [18], and are summarised in Table IV. There are no intermolecular hydrogen bonds between the Ni(gb)<sub>2</sub> complex molecules.

The least squares plane of the square planar [Ni(bu)<sub>2</sub>]<sup>2-</sup> complex ion forms a dihedral angle of

approximately 12 degrees with the (1,1,0) unit cell plane. The six atoms comprising the hydrogen triplet are approximately co-planar with, for instance, the deviations of O(1) and O(2) from the least squares plane defined by N(1), N(2), N(4), C(1) and C(2)

TABLE I Summary of the crystallographic data for the three supramolecular assemblies

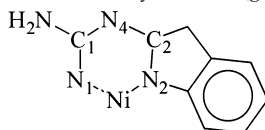
	1	2	3
Formula of the refinement model	C <sub>36</sub> H <sub>62</sub> N <sub>18</sub> Ni <sub>2</sub> O <sub>4</sub>	C <sub>22</sub> H <sub>21</sub> N <sub>6</sub> Ni <sub>0.50</sub> O <sub>3</sub> S	C <sub>32</sub> H <sub>26</sub> N <sub>12</sub> NiO <sub>4</sub>
Model molecular weight	928.46	478.86	701.36
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (#2)	<i>C</i> 2/ <i>c</i> (#15)	<i>P</i> $\bar{1}$ (#2)
<i>a</i>	9.4863(5) Å	23.376(3) Å	10.804(5) Å
<i>b</i>	15.0934(8) Å	7.695(4) Å	15.357(7) Å
<i>c</i>	7.8630(4) Å	25.142(3) Å	9.667(4) Å
$\alpha$	98.3600(10)°		97.95(5)°
$\beta$	96.3130(10)°	109.257(7)°	91.91(5)°
$\gamma$	81.5860(10)°		76.30(4)°
<i>V</i>	1097.34(10) Å <sup>3</sup>	4269(2) Å <sup>3</sup>	1543.3(12) Å <sup>3</sup>
<i>D</i> <sub>c</sub>	1.405 g cm <sup>-3</sup>	1.490 g cm <sup>-3</sup>	1.509 g cm <sup>-3</sup>
<i>Z</i>	1	8	2
Crystal size	0.303 × 0.158 × 0.116 mm	0.550 × 0.200 × 0.038 mm	0.38 × 0.05 × 0.02 mm
Crystal colour	Red	Red	Green
Crystal habit	Cut prismatic fragment	Blade	Acicular
$\lambda$ (MoK $\alpha$ )	0.71073 Å	1.54178 Å	1.54178 Å
$\mu$ (MoK $\alpha$ )	0.918 cm <sup>-1</sup>	2.116 mm <sup>-1</sup>	1.418 mm <sup>-1</sup>
<i>T</i> (SADABS) <sub>min,max</sub>	0.689, 1.000	0.724, 0.998	0.875, 0.997
2 $\theta$ <sub>max</sub>	56.60°	135.50°	135.66°
<i>hkl</i> range	-12 12, -20 20, -10 10	0 28, 0 8, -30 28	0 12, -17 18, -11 11
<i>N</i>	10,226	3776	5804
<i>N</i> <sub>ind</sub>	5056( <i>R</i> <sub>merge</sub> 0.0216)	3678( <i>R</i> <sub>merge</sub> 0.0560)	5491( <i>R</i> <sub>merge</sub> 0.034)
<i>N</i> <sub>obs</sub>	4117( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	2834( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	3204( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))
<i>N</i> <sub>var</sub>	294	307	459
Residuals* <i>R</i> 1( <i>F</i> ), <i>wR</i> 2( <i>F</i> <sup>2</sup> )	0.0477, 0.1461	0.0491, 0.1574	0.0465, 0.136
GoF(all)	1.006	1.063	0.974
Residual extrema	-0.812, 0.943 e <sup>-</sup> Å <sup>-3</sup>	-0.464, 0.560 e <sup>-</sup> Å <sup>-3</sup>	-0.505, 0.367 e <sup>-</sup> Å <sup>-3</sup>

\* *R*1 =  $\sum ||F_o| - |F_c|| / \sum |F_o|$  for  $F_o > 2\sigma(F_o)$ ; *wR*2 =  $(\sum w(F_o^2 - F_c^2)^2 / \sum wF_c^2)^{1/2}$  all reflections.

*P* =  $(F_o^2 + 2F_c^2) / 3$  and  $w = 1 / [\sigma^2(F_o^2) + (0.0934P)^2 + 0.6956P]$  for **1**,  $w = 1 / [\sigma^2(F_o^2) + (0.07P)^2 + 2.0584P]$  for **2** and  $w = 1 / [\sigma^2(F_o^2) + (0.05P)^2]$  for **3**.

TABLE II Summary of angles (in degrees) showing the variation of the geometry about the nickel in the Ni(gb)<sub>2</sub> in the arrays

	1	Ni(gb) <sub>2</sub> ·2dmsO·H <sub>2</sub> O [3]	2	3
<i>Trans-nitrogen angles</i>				
N1–Ni–N1	180	163.03	158.44(16)	157.58(14)
N2–Ni–N2	180	172.94	165.92(14)	165.80(12)
<i>Angles in the metallaring at the nickel</i>				
N1–Ni–N2	87.18(9)	89.46; 88.56	89.11(9)	89.28(13); 89.67(13)
<i>Angles in the metallaring at the coordinated nitrogens</i>				
Ni–N1–C1	127.40(18)	128.4; 128.3	128.51(18)	126.2(2); 126.9(2)
Ni–N2–C2	120.05(17)	122.6; 123.1	124.63(17)	124.1(2); 124.4(2)

TABLE III Summary of bond lengths (in angstrom) in the metallacycles in Ni(gb)<sub>2</sub>. Numbering scheme as shown below.

Typical bond lengths: C–N 1.47 Å; C = N 1.30 Å

	1	2	3	Ni(gb) <sub>2</sub> ·2dmsO·H <sub>2</sub> O [3]
N1–C1	1.330(3)	1.319(3)	1.313(4); 1.313(4)	1.314; 1.318
C1–N4	1.345(3)	1.350(3)	1.344(4); 1.343(4)	1.355; 1.353
N4–C2	1.338(3)	1.336(3)	1.345(5); 1.347(4)	1.339; 1.353
C2–N2	1.356(3)	1.348(3)	1.331(4); 1.335(4)	1.352; 1.349
N2–Ni	1.909(2)	1.882(2)	1.878(3); 1.873(3)	1.896; 1.887
Ni–N1	1.867(2)	1.868(2)	1.879(3); 1.877(3)	1.875; 1.875

TABLE IV Hydrogen bond geometry for assembly 1

Donor Angle(°)	Hydrogen	Acceptor	D–H (Å)	H–A (Å)	D–A (Å)	DHA
N(3)	H(3N)	O(2)	0.89(4)	1.90(4)	2.785(3)	175(4)
N(5)	H(5NA)	O(2*)	0.890(10)	2.012(14)	2.864(3)	160(3)
N(5)	H(5NB)	O(1)	0.890(10)	1.981(16)	2.836(3)	160(3)
N(6)	H(6N)	O(1†)	0.86	2.40	3.236(3)	165.4
N(8)	H(8N)	N(4)	0.886(10)	2.133(11)	3.014(3)	173(3)

\*x, y, z + 1. †1 – x, 1 – y, 2 – z.

being, respectively, approximately 0.6 and 0.4 Å. The N(3) and N(5) atoms both deviate from this plane by 0.2 Å. The structure can thus be regarded as having sheets of hydrogen bond linked complex molecules lying diagonally across the unit cell. The sheets are comprised of rows or chains of alternating complexes running in the direction of the *c*-axis. The oxygen atoms of the biuret ligands not only participate in the “inter-row” triplet hydrogen bonding between the two complex types, but they also act as “intra-row” hydrogen bond acceptors for neighbouring biuret ligands.

The complex molecule sheets are separated by the tetraethylammonium counter-ions and are distorted by a “step” in the Ni(gb)<sub>2</sub> complex. The complex resides on an inversion centre so the normals to the two ligand planes are parallel, however, the least squares plane of one of the ligands is displaced approximately 0.9 Å from that of the second ligand. Each ligand least squares plane, therefore, forms a dihedral angle of 31.7° with the square planar

nitrogen coordination least squares plane. The step reduces contact between the two ligands of the metal complex, and it also allows the lower ligand of one complex to “slip” under the upper ligand of a neighbouring complex (on the *c*-axis), without rupturing the hydrogen bond network. The distance between the least squares planes of the two overlapping ligands is approximately 3.5 Å. The phenylene ring of one ligand partially eclipses the imidazolyl ring of the second, with the ring centroids separated by 3.5 Å. The angle between the ligand least squares plane normal and the line joining the centroids is 7°.

There is some deformation of the guanidinobenzimidazolo ligand with the dihedral angle between the least squares planes defined by the two rings of the benzimidazolyl group and by the guanidinyl residue being 16°. The nickel is approximately 0.5 Å from both of these least squares planes.

In the crystal structure of assembly 2, both of the ligands of the bis(2-guanidinobenzimidazolo)nickel(II)

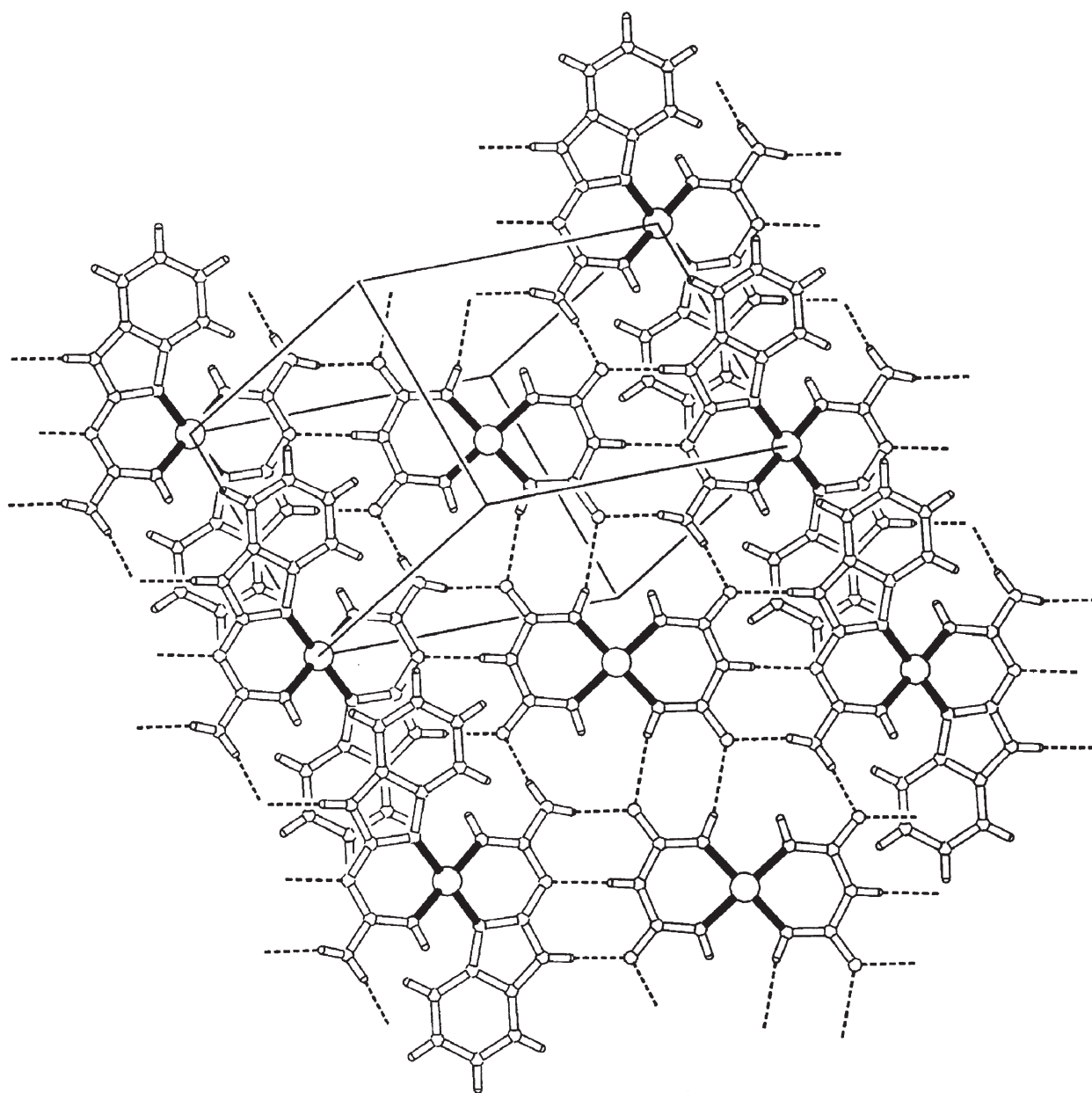


FIGURE 4 A depiction of the extended structure of 1 showing the stacking of the benzimidazole rings.

complex are linked to a 1,8-naphthalimide molecule by the same triplet hydrogen bond motif observed in assembly 1. Access to the carbonyl oxygen atoms is hindered by the naphthyl residue in assembly 2, in contrast to 1, and this restriction apparently prevents the hydrogen bond network extending significantly beyond the trimeric [bis(2-guanidinobenzimidazolo)nickel(II):(1,8-naphthalimide)<sub>2</sub>] complex. However, there is an additional hydrogen bond between the terminal amine residue of the guanidinobenzimidazolo ligand and a nearby dimethylsulfoxide solvate molecule (Fig. 2, Table V). Accommodating the hydrogen bond to the dmsol molecule is associated with a significant distortion of the otherwise square planar co-ordination geometry of the Ni(gb)<sub>2</sub> com-

plex. In particular, the symmetry related nitrogens opposite the metal coordinating nitrogens of a guanidinobenzimidazolo ligand deviate by 0.240(5) and 1.382(5) Å from plane defined by the N(1), N(2), N(4), C(1) and C(2) atoms of the ligand. The dihedral angle formed between the least squares planes of the two ligands is 57°, and this "tilting" reduces unfavourable steric contact between the ligands. The benzimidazole is partially sandwiched between two naphthalimide molecules, being involved in offset  $\pi$ -stacking interactions with least squares plane separations of 3.4 and 3.3 Å.

In assembly 3, phthalimide replaces 1,8-naphthalimide, and the carbonyl groups are more exposed. As in assembly 2, the two ligands of the metal



TABLE V Hydrogen bond geometry for assembly 2

Donor Angle(°)	Hydrogen	Acceptor	D-H (Å)	H-A (Å)	D-A (Å)	DHA
N(3)	H(3N)	O(2)	0.86	2.03	2.878(3)	171.0
N(5)	H(5NB)	O(1)	0.86	2.05	2.906(3)	170.1
N(5)	H(5NA)	O(3)	0.86	2.09	2.922(3)	162.0
N(6)	H(6N)	N(4)	0.86	2.07	2.929(3)	178.2

complex are both linked to phthalimide molecules, however, one of the hydrogen bonds in one of the two hydrogen bond triplets in the three-component unit has been significantly weakened and essentially ruptured (Table VI). The distance between N(5) and O(1) is 3.399(5) Å. The weakening of the hydrogen bond is associated with the same coordination geometry distortion observed in **2**, and it occurs for similar reasons. The least squares planes for the two ligands of the complex are inclined at 66° with respect to each other, N(1) is displaced 1.135(5) Å from the N(2), N(6) and N(7) plane and likewise N(6) is 1.140(5) Å from the N(1), N(2) and N(7) plane. The metal ion is 0.218(1) Å from the N(2), N(6) and N(7) plane and 0.221(1) Å from the N(1), N(2) and N(7) plane. The distortion of the square planar coordination geometry reduces intra-complex ligand contact and facilitates hydrogen bonding between the ligand terminal amine residues and the phthalimide oxygens in adjacent trimers (Fig. 5). The relative tilting of the ligands allows an oxygen of a phthalimide within a trimer to hydrogen bond with the terminal amine of the metal complex ligand in another trimer. The use of phthalimide, with its carbonyl groups more exposed than those of 1,8-naphthalimide, thus admits a more complex three-dimensional hydrogen bond network in assembly **3** (Fig. 5).

In addition to the hydrogen bond network, there are  $\pi$ -stacking interactions between the ligand benzimidazole rings and the phthalimide molecules. The phenyl centroid of the N(11)-containing phthalimide is 3.418(3) Å from the least squares plane of the N(2)-containing benzimidazole residue. The angle between the line joining the two phenyl ring centroids and the normal to the benzimidazole plane is 26° and the two centroids are separated by 3.8 Å. The N(7)-containing benzimidazole system is

involved in two stronger  $\pi$ -stacking interactions. The separation between the centroid of the phenylene ring of the N(12)-containing phthalimide and the least squares plane of the N(7)-containing benzimidazole is 3.386(1) Å and this centroid is 3.4 and 3.8 Å from the centroid of the N(7)-benzimidazole five- and six-membered rings, respectively. The angles formed between the lines joining the phthalimide phenylene centroid to the two benzimidazole centroids and the normal to the benzimidazole plane, are 6° and 29° for the five- and six-membered ligand rings, respectively. The other face of the N(7)-benzimidazole ligand is involved in a  $\pi$  stacking with the N(7)-benzimidazole ligand of an adjacent metal complex. The centroids of the respective five- and six-membered rings are separated by 3.6 Å, and the least squares planes are 3.2 Å apart. The latter separation is very short compared with the distance between, for example, the layers in graphite (3.35 Å), the distance between bases in DNA (ca 3.4 Å) [19] or the distances observed by Sanders and Hunter between stacked porphyrins (3.4–3.6 Å) [20]. It corresponds to the shortest interplanar distances observed in some copper(I) and silver(I)-containing polymers incorporating aromatic moieties (some of which display “special” properties such as low energy charge transfer bands) [21].

The solid state adsorbance spectrum of **3** shows a clear maximum at 600 nm which is not present in **2**. Although there are coordination geometry differences between the metal complexes of **2** and **3**, the origin of the colour difference seems more likely to be associated with the ligand–ligand interactions present in **3**. The 3.2 Å between the planes of adjacent N(7) benzimidazole ligands is similar to that recently reported between phthalimide and 2-guanidinobenzimidazole [22]. The [2-guanidinobenzimidazo-

TABLE VI Hydrogen bond geometry for assembly 3

Donor Angle(°)	Hydrogen	Acceptor	D-H (Å)	H-A (Å)	D-A (Å)	DHA
N(3)	H(3N)	O(2)	0.86	2.04	2.897(5)	171.2
N(5)	H(5NA)	O(4*)	0.85(4)	2.23(4)	3.055(5)	163(3)
N(5)	H(5NB)	O(1)	0.78(4)	2.63(4)	3.399(5)	171(4)
N(6)	H(61)	O(1†)	0.86	2.44	3.183(4)	145.4
N(8)	H(8N)	O(4)	0.86	2.06	2.922(4)	175.9
N(10)	H(101)	O(1†)	0.84(4)	2.28(4)	3.004(5)	145(3)
N(10)	H(102)	O(3)	0.80(4)	2.33(4)	3.124(5)	172(4)
N(11)	H(111)	N(4)	0.86	1.93	2.783(5)	174.6
N(12)	H(121)	N(9)	0.86	1.89	2.746(4)	176.6

\*1 - x, -y, 1 - z. †x, y, z - 1.

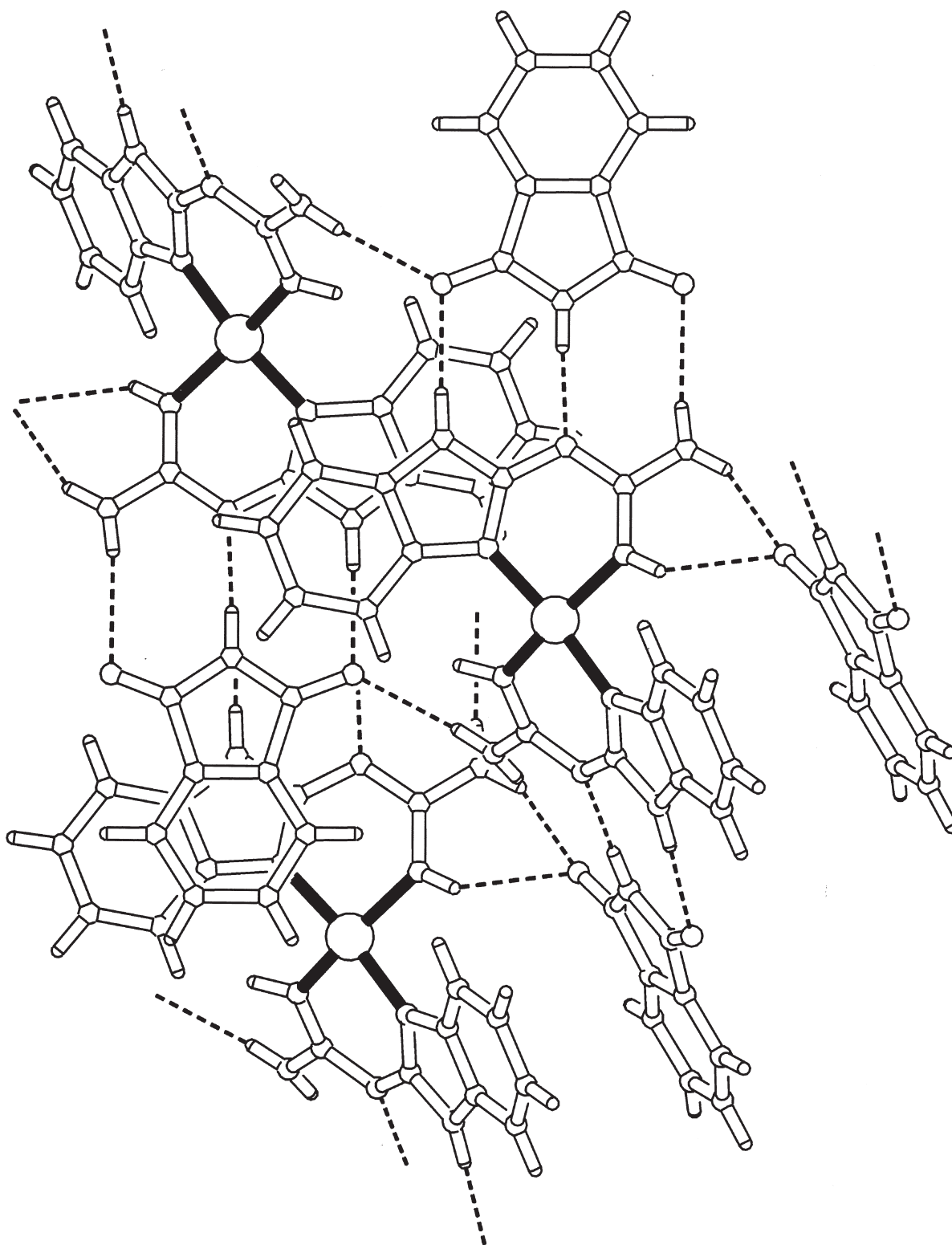


FIGURE 5 A depiction of the extended structure of **3**, showing the stacking of the benzimidazole rings, and the stacking of the phthalimide with benzimidazole.

le:phthalimide] assembly is linked by a triplet of hydrogen bonds, in which the central proton has been transferred from phthalimide to the 2-guanidinobenzimidazole. The central nitrogen to nitrogen distance in this ion paired hydrogen bond linked

system is just  $2.692(4)$  Å. It is intriguing that the central nitrogen to nitrogen distance between the N(7) benzimidazole and the N(12) phthalimide in **3** is  $2.746(4)$  Å, being only  $0.1$  Å longer than N–H $\cdots$ N hydrogen bonds observed in some “proton sponges”

[23]. Regrettably, the data did not permit the location of the central protons in **3**.

## CONCLUSION

Triplet hydrogen bond motifs have been used to link non-planar metal complex Ni(gb)<sub>2</sub> into tri-component assemblies that underpin extended structures. A change from the use of 1,8-naphthalimide in **2** to phthalimide in **3**, results in a three dimensional hydrogen bond network, a notably short nitrogen to nitrogen hydrogen bond distance and an unusually small inter-planar separation between  $\pi$  interacting molecules. The metal complexes in **2** and **3** suffer similar tetrahedral distortions from square planar coordination geometry, whereas **1** adopts a step-like structure.

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