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Proton Controlled Supramolecular Assembly: A Comparative Structural Study of Bis(2-guanidinobenzimidazolo)nickel(II) with Bis(2-guanidinobenzimidazole)nickel(II) Nitrate and 2-guanidinobenzimidazole

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Previously studies have shown that when 2-guanidinobenzimidazole complexes with a number of transition metal ions it tautomerises so that, in contrast to the free ligand structure, no intermolecular hydrogen bonding between bound ligands occurs. In the present study it is demonstrated that ligand deprotonation to yield bis(2-guanidinobenzimidazolo)nickel(II) restores much of the original hydrogen bonding capability of the uncomplexed ligand. The structure of this neutral complex is compared to the previously reported structure of its diprotonated derivative, bis(2-guanidinobenzimidazole)nickel(II) nitrate, as well as to the structure of the uncomplexed ligand. In contrast to the dicationic species, the neutral complex exists in two enantiomeric forms that assemble to form an extended supramolecular lattice, containing channels through its structure. The walls of the channels are made up of 'strings' of complex molecules and are held in position by hydrogen bonding between the bound ligands and dimethyl sulfoxide (solvent) molecules as well as water molecules. Some of the solvent molecules lie within the channels and some outside. The hydrogen bonding motif responsible for chain formation differs from that found in the free ligand structure.

Keywords: Crystal engineering; Nickel(II); X-ray; Protonation

1. INTRODUCTION

Crystal engineering, the self-assembly of extended arrays using supramolecular interactions, continues to be a rapidly expanding field [1,2]. The self-assembly of inorganic and organic molecular solids, the aggregation of metal complexes with inorganic or organic molecules, and the self-association of metal complexes to form extended arrays have all been demonstrated to result in interesting supramolecular

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structures. Such structures have potential application in a number of areas that include their use as non-linear optical materials, as electron or ion conductors, and as porous zeolite-like structures for the selective uptake of small molecules and ions.

2-Guanidinobenzimidazole (gbH) has been demonstrated to form an extended hydrogen bonded structure in the solid state [3]. It has also been shown to function as a bidentate ligand towards cobalt(II), nickel(II) copper(II) and zinc(II) [4]. While the coordinated ligand incorporates a donor–donor–donor motif that in principle allows the formation of a triplet of hydrogen bonds, this is not observed in the above nickel complex which lacks appropriate acceptor sites. However, as discussed in the present paper, this motif readily changes between donor–donor–donor and donor–acceptor–donor arrangements, reflecting facile acid/base behaviour. Further, it is noted that each coordinated ligand possesses an additional NH group that is not part of the above (potentially) hydrogen bonding triplet. This leaves open the possibility that this group may also be involved in extended intermolecular interactions.

In this paper we report the preparation and supramolecular structure of the neutral complex, bis(2-guanidinobenzimidazolo)nickel(II). The latter is compared with the structure of the previously reported protonated form of this complex, bis(2-guanidinobenzimidazole)nickel(II) nitrate, as well as with structure of the uncomplexed ligand, gbH.

2. EXPERIMENTAL

2.1. Bis(2-guanidinobenzimidazolo) nickel(II)

Aqueous ammonia (25%, 10 mL) was added to nickel(II) chloride hexahydrate (0.24 g, 1 mmol) in water (8 mL). This solution was then added to a solution of 2-guanidinobenzimidazole (0.350 g, 2 mmol) in hot methanol (15 mL). The complex precipitated almost immediately. After stirring the mixture for 20 minutes, the solid was filtered off and washed with ethanol then ether. Yield: 74%.

Recrystallisation of this product from dimethyl sulfoxide gave orange crystals suitable for X-ray crystallography; the resulting formulation being $[(C_8H_8N_5)_2Ni] \cdot C_2H_6OS \cdot 1/2H_2O$. The latter is consistent with the result from microanalysis. *Anal.* Calc. for $C_{18}H_{23}N_{10}O_{1.5}S$: C, 43.71; H, 4.65; N, 28.33. Found: C, 43.9; H, 4.8; N, 28.0%.

2.2. Structure Determination

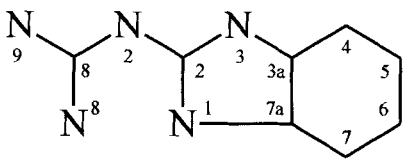
A full sphere of low-temperature CCD area-detector diffractometer data was measured to $2\theta_{max} = 58°$ (ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K), 24890 total reflections reducing, after 'empirical'/multiscan absorption correction, to 10364 unique ($R_{int} = 0.027$), 7767 with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement, refining anisotropic thermal parameter forms and $(x, y, z, U_{iso})_H$. (Exception: dmso sulfur atoms were modelled as disordered over two sets of sites, occupancies refining to similar values, possibly concerted: S(1), 0.889(2), S(2) 0.919(3) and complements, and considered as concerted with nearby residues modelled as disordered water molecule oxygen atoms.) Dmso and water hydrogen atoms were included constrained at values estimated from other geometry or difference maps (major components only). Conventional residuals R, R_w[weights: $[\sigma^2(F) + 0.0004(F)^2]^{-1}$] at convergence were 0.039, 0.043. Neutral atom complex scattering factors were employed within the context of the Xtal 3.4 program system [5].

Pertinent results are given below and in the Figures 1 and 2 and in Table I.

2.3. Crystal Data

$NiL_2 \cdot dmso \cdot 0.5H_2O \equiv C_{18}H_{23}N_{10}NiO_{1.5}S$, $M = 494.2$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2)· $a = 9.6136(9)$, $b = 13.456(1)$, $c = 16.807(2)$ Å, $\alpha = 88.482(2)$, $\beta = 79.477(2)$, $\gamma = 79.804(2)°$, $V = 2103.8$ Å^3· $D_c(Z = 4) = 1.56_0$ g cm^{-3}. $\mu_{Mo} = 10.6$ cm^{-1}; specimen: $0.25 \times 0.15 \times 0.12$ mm; $'T'_{min,max} = 0.72, 0.89$.

Ligand atoms are designated N,C(mnx), m = molecule 1 or 2, n = ligand 1 or 2, x = atom number as shown below.



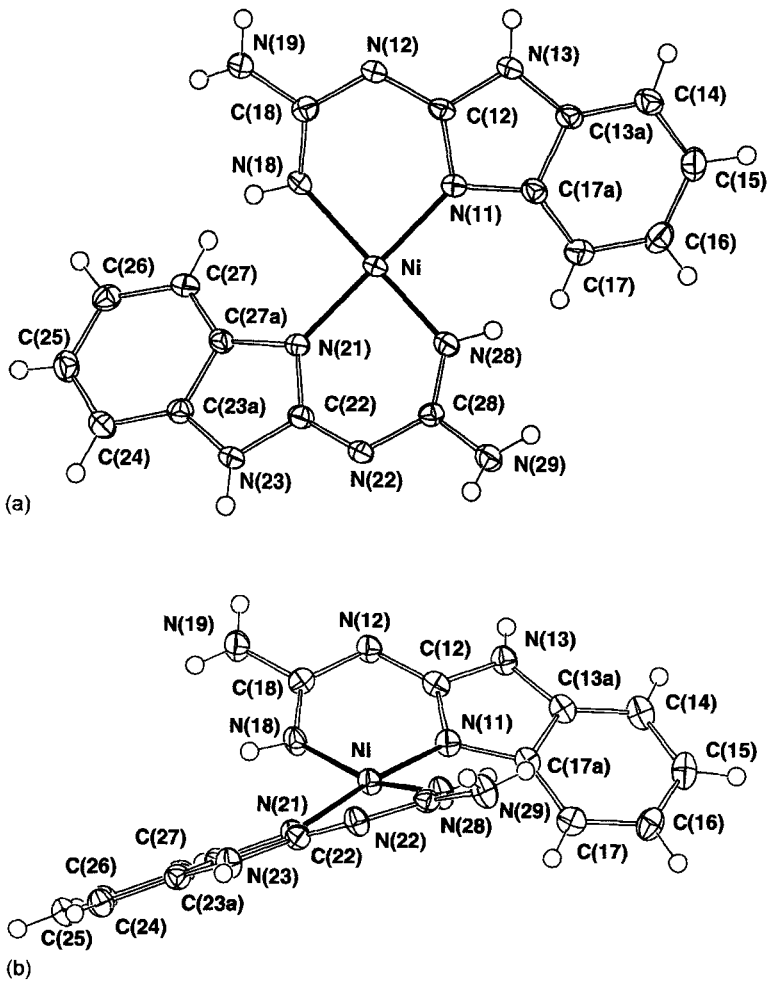


FIGURE 1 Projections of molecule 1; 50% 'thermal' ellipsoids are shown for the non-hydrogen atoms, hydrogen atom having arbitrary radii of 0.1 Å. Molecule 2 is similar. (a) Projection normal to the NiN_4 'plane'. (b) Projection oblique to the plane, showing the skewing of the two ligands.

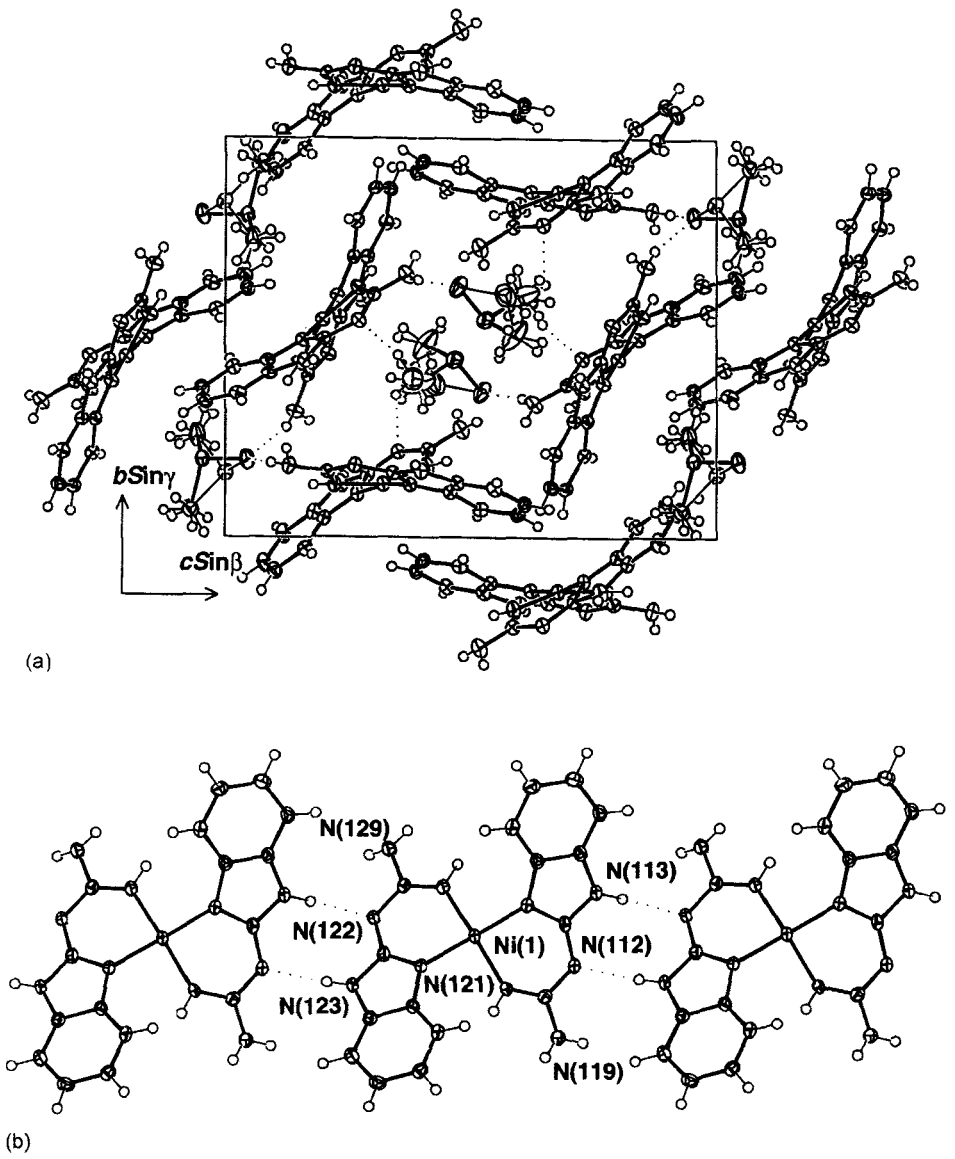


FIGURE 2 (a) Unit cell contents projected down *a*, showing the complex molecules lying with the planes parallel to that axis, forming a tube, maintained by hydrogen bonds to the solvent molecules at its core and periphery. (b) Column made up of successive molecules 1 generated by the unit *a* translation. (Molecule 2 generates a similar column.)

3. RESULTS AND DISCUSSION

3.1. Bis(2-guanidinobenzimidazolo)nickel(II)

Previous reports have described the structures of 2-guanidinobenzimidazole, gbH [3] and its complex formed from nickel(II) nitrate, $[Ni(gbH)_2](NO_3)_2$ [4]. In the present study the synthesis and structural characterisation of the corresponding deprotonated derivative $[Ni(gb)_2]$ are reported. The results of the low-temperature, single crystal X-ray structure determination are consistent, in terms of stoichiometry and connectivity, with the

TABLE I Comparative geometries, gbH, $[Ni(gbH)_2]^{2+}$, $[Ni(gb)_2]$. Two values in each entry, where given, are for the two ligands n = 1, 2 in the molecule

Compound (molecule)	gbH	$[Ni(gbH)_2]^{2+}$	$[Ni(gb)_2]$/1;2; ⟨⟩		
Distances (Å)					
Ni–N(n1)	–	1.901 (5)	1.887 (2), 1.895 (2);	1.882 (2), 1.893 (2);	1.889 (5)
Ni–N(n8)	–	1.881 (4)	1.874 (2), 1.875 (2);	1.878 (3), 1.873 (2);	1.875 (2)
N(n1)–C(n2)	1.339 (3)	1.338 (6)	1.349 (3), 1.352 (3);	1.347 (4), 1.344 (3);	1.348 (3)
N(n1)–C(n7a)	1.405 (3)	1.416 (8)	1.407 (3), 1.419 (3);	1.408 (3), 1.406 (3);	1.410 (5)
C(n2)–N(n3)	1.371 (3)	1.354 (7)	1.364 (4), 1.364 (4);	1.367 (3), 1.363 (3);	1.365 (2)
C(n2)–N(n2)	1.373 (3)	1.350 (7)	1.352 (3), 1.339 (3);	1.335 (3), 1.349 (3);	1.340 (7)
N(n2)–C(n8)	1.321 (4)	1.372 (8)	1.353 (4), 1.354 (4);	1.360 (3), 1.354 (3);	1.355 (3)
C(n8)–N(n8)	1.350 (4)	1.307 (7)	1.317 (3), 1.313 (3);	1.320 (4), 1.311 (3);	1.315 (3)
C(n8)–N(n9)	1.357 (4)	1.350 (8)	1.355 (3), 1.364 (3);	1.368 (4), 1.379 (4);	1.367 (9)
C(n7a)–C(n3a)	1.401 (4)	1.391 (7)	1.403 (4), 1.403 (4);	1.404 (4), 1.408 (3);	1.405 (2)
N(n3)–C(n3a)	1.388 (3)	1.412 (7)	1.379 (3), 1.382 (3);	1.383 (4), 1.376 (3);	1.381 (3)
C(n3a)–C(n4)	1.384 (4)	1.374 (9)	1.387 (4), 1.389 (4);	1.386 (3), 1.386 (3);	1.387 (1)
C(n4)–C(n5)	1.389 (4)	1.410 (9)	1.385 (4), 1.381 (4);	1.388 (5), 1.387 (4);	1.385 (3)
C(n5)–C(n6)	1.394 (4)	1.390 (1)	1.387 (4), 1.398 (4);	1.394 (4), 1.391 (4);	1.393 (4)
C(n6)–C(n7)	1.385 (4)	1.380 (1)	1.391 (4), 1.394 (3);	1.388 (3), 1.395 (4);	1.392 (3)
C(n7)–C(n7a)	1.396 (4)	1.406 (8)	1.392 (3), 1.385 (3);	1.397 (4), 1.390 (4);	1.391 (4)
Angles (degrees)					
N(n1)–Ni–N(n8)	–	89.1 (2)	88.55 (9), 89.43 (9);	88.56 (9), 89.33 (9);	89.0 (4)
N(11)–Ni–N(21)	–	180 (–)	172.94 (9);	169.95 (9);	171 (2)
N(18)–Ni–N(28)	–	180 (–)	163.0 (1);	161.4 (1);	162.2 (8)
N(n1)–Ni–N(n8′)	–	90.9 (2)	91.88 (9), 92.21 (9);	92.03 (9), 93.32 (9);	92.4 (6)
Ni–N(n8)–C(n8)	–	126.8 (4)	128.3 (2), 128.4 (2);	127.4 (2), 128.1 (2);	128.1 (4)
N(n8)–C(n8)–N(n9)	117.7 (3)	125.4 (6)	120.5 (3), 120.8 (3);	120.5 (2), 120.5 (2);	120.6 (1)
N(n8)–C(n8)–N(n2)	125.4 (2)	119.6 (5)	125.1 (2), 125.2 (2);	125.4 (2), 125.7 (2);	125.4 (2)
N(n9)–C(n8)–N(n2)	116.7 (2)	114.9 (5)	114.4 (2), 114.0 (2);	114.0 (2), 113.7 (2);	114.0 (2)
C(n2)–N(n2)–C(n8)	120.5 (2)	122.1 (5)	117.7 (2), 118.8 (2);	118.1 (2), 118.2 (1);	118.2 (4)
Ni–N(n1)–C(n2)	–	120.6 (4)	123.2 (2), 122.6 (2);	123.8 (2), 123.1 (2);	123.2 (4)
Ni–N(n1)–C(n7a)	–	134.3 (3)	130.7 (2), 130.7 (2);	130.4 (2), 130.6 (2);	130.6 (1)
C(n2)–N(n1)–C(n7a)	104.6 (2)	104.8 (4)	105.9 (2), 105.7 (2);	105.7 (2), 106.0 (2);	105.8 (1)
N(n1)–C(n2)–N(n2)	130.5 (2)	126.3 (5)	130.1 (3), 130.3 (3);	129.7 (2), 130.1 (2);	130.2 (2)
N(n1)–C(n2)–N(n3)	112.2 (2)	113.3 (5)	111.0 (2), 111.1 (2);	111.1 (2), 110.9 (2);	111.0 (1)
N(n2)–C(n2)–N(n3)	117.3 (2)	120.4 (4)	118.9 (2), 118.6 (2);	119.2 (2), 118.9 (2);	118.9 (2)
N(n3)–C(n3a)–C(n4)	131.8 (2)	128.9 (5)	131.1 (2), 130.7 (2);	131.8 (3), 131.4 (2);	131.3 (4)
N(n3)–C(n3a)–C(n7a)	104.9 (2)	106.2 (5)	106.4 (2), 106.3 (2);	106.0 (2), 105.9 (2);	106.2 (2)
C(n4)–C(n3a)–C(n7a)	123.2 (2)	124.9 (5)	122.5 (2), 122.9 (2);	122.2 (3), 122.6 (2);	122.6 (3)
N(n1)–C(n7a)–C(n3a)	110.4 (2)	109.1 (5)	108.4 (2), 108.3 (2);	108.8 (2), 108.4 (2);	108.5 (2)
N(n1)–C(n7a)–C(n7)	130.6 (2)	131.6 (5)	131.9 (3), 132.5 (3);	130.9 (2), 131.8 (2);	131.8 (6)
C(n3a)–C(n7a)–C(n7)	119.0 (2)	119.2 (6)	119.6 (3), 119.2 (2);	120.2 (2), 119.6 (2);	119.7 (4)
C(n2)–N(n3)–C(n3a)	107.9 (2)	106.5 (4)	108.1 (2), 108.5 (2);	108.1 (2), 108.6 (2);	108.3 (2)
C(n3a)–C(n4)–C(n5)	117.1 (3)	115.0 (5)	117.1 (3), 116.8 (3);	117.1 (3), 116.9 (2);	117.0 (1)
C(n4)–C(n5)–C(n6)	120.4 (3)	121.1 (7)	121.2 (3), 121.5 (3);	121.3 (2), 121.4 (2);	121.4 (1)
C(n5)–C(n6)–C(n7)	122.3 (3)	122.8 (6)	121.7 (2), 120.8 (2);	121.7 (3), 121.4 (3);	121.4 (4)
C(n6)–C(n7)–C(n7a)	118.0 (2)	116.8 (6)	117.9 (3), 118.7 (3);	117.6 (3), 117.9 (2);	118.0 (4)

formulation of the complex as above. Difference map residues were modelled in terms of a mono dmso, hemihydrate solvate: $[Ni(gb)_2] \cdot Me_2SO \cdot 1/2H_2O$, with two formula units, similar but devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. This provides the first structural characterisation of the anionic gb^- ligand in a context that permits comparison of its geometry with that of the free ligand, as well as with it

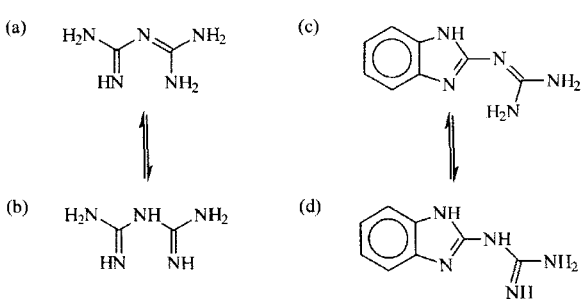
bound in its non-deprotonated form in a nickel complex, coordinating as a chelate. Although we have not been successful in obtaining detailed coordinate data for the previously reported $[Ni(gbH)_2](NO_3)_2$ from any source, its description in the literature is sufficiently detailed to enable some useful comparison to be made, particularly since the same metal, in similar oxidation state and coordination environment, is present in both metal complex structures to be compared.

The geometries of the three species (two independent molecules for the present system) are given in Table I. While the six-membered ring furthest from the guanidine residue is the least affected by the changes of protonation, tautomerisation and coordination, other ramifications of the latter are both significant and varied, although, at times, not totally clearcut because of the influence of conjugation throughout the ligand.

The recent study of the free ligand structure [3] establishes its amino hydrogen distribution to be one at N(3) (in the present numbering scheme), and two each at N(8) and N(9), with N(1) and N(2) devoid of immediately associated hydrogen atoms. However, N(1) is intramolecularly hydrogen bonded to one of the $NH_2(8)$ hydrogen atoms, and N(2) has an intermolecular interaction across an inversion centre with one of the $NH_2(9)$ hydrogens leading to dimerisation. In addition N(3) forms a hydrogen bond with a neighbouring N(1) linking the dimers into a three dimensional network. Within a highly conjugated system N(2)–C(8) is conspicuously short. Some rotation is found about the longer C(2)–N(2) between the benzimidazole and guanidine non-hydrogen planes, which have an interplanar dihedral angle of 13.8°, ascribed to the effects of intermolecular hydrogen bonding.

Coordination of two of the free gbH ligands as chelates about a centrosymmetric 'square planar' nickel atom in the salt $[Ni(gbH)_2](NO_3)_2$ [4] results in transformation of the ligand to an alternative tautomer [(d) in Scheme 1]. In this, the $NH_2(8)$ guanidine hydrogen previously hydrogen-bonded to N(1) has now migrated to N(2), having been displaced by the nickel atom, and C(8)–N(8) and N(2,3)–C(2) are now appreciably shortened while N(2)–C(8) is lengthened. Lacking in detailed description or parametrization, the metallacycle is described "as having a 'boat' shape" [4], presumably a consequence of intramolecular interligand H(8)...H(7) contacts which, in that complex, as in the present one, must be unsustainably close in a completely planar molecule. Ligand angular geometry has changed radically, most notably in that section of the structure which makes up the metallacycle, at C(2) and C(8); at the latter, the lengthening of N(2)–C(8) is accompanied by the opening of the opposed exocyclic angle. Appreciable angular changes are also observed about C(3a), presumably in response to changes in bonding and co-ordination, rather slight in terms of distance, but large in terms of enlargement of the angles opposed to N(3)–C(2,3a). The deprotonation required on passing to the present $[Ni(gb)_2]$ is accomplished by loss of the proton at N(2), in consequence of which the internal ring angles at C(2,8), N(2) revert to values more nearly akin to that of the ligand; changes in bond distances also tend towards those in the ligand.

Further comparison of $[Ni(gbH)_2]^{2+}$ with the present $[Ni(gb)_2] \cdot Me_2SO \cdot 1/2H_2O$ shows some interesting differences in the disposition of the non-hydrogen skeleton about the respective nickel ions. In the dication, the nickel lies at an



SCHEME 1

inversion centre and thus the N_4 core is strictly planar. Close contacts between H(8) and H(7) (other ligand) are avoided in this case by virtue of the 'plane' of the co-ordinated guanidine residue being tilted out of the NiN_4 plane. In the neutral complex the nickel is no longer sited at an inversion centre and the N_4 core is no longer planar, but shows a small tetrahedral distortion (average *trans*-angles N(11)–Ni–N(21) 171(2)° and N(18)–Ni–N(28) 162(2)°), so that the ligands, rather than being 'parallel' as in the dication, are substantially inclined to one another. The dihedral angles between the pair of C_7N_2 benzimidazole planes in each molecule are 57.39(5) (molecule 1), 64.67(5)° (molecule 2). Bonding parameters about the metal atom and within the metallacycle are changed but little, except, as noted, in respect of the angular geometry about and to either side of N(2). This is presumably a response to the fact that the principal difference between the two species is the loss of the hydrogen atom at N(2). Thus, this is an interesting (and somewhat uncommon) example of a metal complex acting as a facile acid/base that does not involve the donor atom sites. Related behaviour to this involving the bis[di(methoxycarbimido)amine]copper(II) species has also been reported recently [6].

The overall form of the present complex appears to be the result of the incipient planarity of the molecule being thwarted by its incompatibility with close contacts of H(8)...H(7) between the two ligands [2.06(4)–2.28(4) Å], though this steric constraint is relieved in a different manner to that observed in the dication. Associated N(8)...C(7) distances in the neutral complex range from 3.043(4) to 3.157(3) Å varying, presumably, in response to perturbations arising from contacts to dimethyl sulfoxide and water oxygen atoms [O(1)...H(129a, 229a)] $(\bar{x}, \bar{y}, 1-z)$ 2.19(3), 2.10(3); O(2)...H(119b) $(1-x, \bar{y}, \bar{z})$, H(219a) 2.00(3), 2.25(3); O(0)(water)...H(219b) $(1-x, \bar{y}, \bar{z})$ 2.27(3) Å). That is, from *all* possible uncoordinated neighbouring groupings. The water hydrogens are linked to the unprotonated N(2) of ligands 1 of each molecule (H(0a)...N(112) 2.0; H(0b)...N(212)$(1+x, y, z)$ 2.1 Å (est.); corresponding O...N 3.010(3), 2.898(4) Å). In their gross conformations, the ligands are similar to those in the free ligand and in $[Ni(gbH)_2]^{2+}$, being made up of effectively planar benzimidazole and guanidine moieties – with the interplanar dihedral angles being 12.2(1), 5.3(1) and 17.1(1), 10.4(1)°, nickel atom deviations from the benzimidazole moieties being 0.219(3), 0.383(3) and 0.169(3), 0.241(3) Å and from the guanidine (N_3C) planes 0.486(4), 0.375(4) and 0.428(5), 0.400(4) Å.

3.2. Supramolecular Aspects

It is of interest to compare the behaviour of biguanide [7] which exists in the solid state in the tautomeric form given by (a) in the Scheme 1. In the crystal each molecule has just one intermolecular hydrogen bond, together with two longer contacts (N–N > 3 Å). When biguanide forms complexes it tautomerises such that all the nitrogen atoms are protonated (see 1b) and so no hydrogen bonding between complex species is expected, nor is it observed [8]. Even on deprotonation, which restores the donor–acceptor–donor motif of the free ligand, no hydrogen bonding occurs in this case between bound biguanide ligands in adjacent complexes [9]. This is also true of neutral dithiobiureto complexes [10].

Free 2-guanidinobenzimidazole, gbH, exists in the tautomeric form (c) shown in Scheme 1 [3]. This is similar to biguanide itself and, also like biguanide, it tautomerises [see (d)] on coordination to transition metal ions to form discrete complex ions with no hydrogen bonding present between individual complex molecules [4]. However, unlike biguanide, free 2-guanidinobenzimidazole forms an extensive three-dimensional hydrogen bonded structure. As mentioned already, in addition to a intramolecular hydrogen bond, the gbH molecules

form dimers by association between molecules. The latter are related by an inversion centre and linked by planar six-membered hydrogen bonded rings. These dimers also form hydrogen bonds to the imidazole N and NH groups of other molecules thus linking the dimers into a three dimensional net such that each donor/acceptor of the individual (NH)(N)(NH) triplet motifs is engaged in hydrogen bonding [1].

While co-ordination of the deprotonated ligand (gb^-) to nickel will obviously prevent the formation of hydrogen bonds involving the imidazole N and NH groups on different ligands (as found in the uncomplexed ligand structure), it will otherwise leave the 'triplet' hydrogen bonding motifs available in a donor–acceptor–donor configuration.

Associated with the molecular distortions and the hydrogen bonding arrays noted above, the crystal packing of $[Ni(gb)_2] \cdot Me_2SO \cdot 1/2H_2O$ presents some features of interest. The unit cell contents shown in projection down *a* (Fig. 2a), show the two molecules of the asymmetric unit with their inversion images, all lying with their planes quasi-parallel to *a*, so as to form four convex walls of a channel, linked at one pair of opposed corners by the hydrogen bonds O(1)...H(129a, 229a) from ligands 2 of the two molecules to the dimethyl sulfoxide (1) oxygen. The other dimethyl sulfoxide moieties (2), together with the water molecule, lie with their inversion images in the channel close to its axis, hydrogen bonding to ligands 1.

There is also hydrogen bonding between complexes in neighbouring unit cells (Fig. 2b) that runs quasi-parallel to *a*. The six-membered ring formed by the hydrogen bonds approximates a chair conformation. The internal angles centred on N(2), the hydrogen bond acceptor, are 111° and 109°, whereas the other four are 119°, 119°, 121° and 122°. The N(2) atoms also act as hydrogen bond acceptors for the hydrogen bound water molecules. The inter-ligand hydrogen bonding geometries are: N(3)–H...N(2) 2.022 Å, 2.079 Å; N...N 2.863 Å, 2.907 Å; angle (N–H...N) 171.2°, 172.4°.

4. CONCLUSION

In this study we have compared the crystal structure of free 2-guanidinobenzimidazole with its structure in corresponding neutral and cationic nickel(II) complexes. The preparation of the neutral complex restored the triplet hydrogen bonding motif of the free ligand which, owing to tautomerisation, is altered on forming the cationic complex. The 'triplet' hydrogen bonding motif is restored by deprotonation of the bound ligand to yield the neutral complex. The latter self-assembles on crystallisation to form channels running parallel to the *a* axis by the formation of six-membered hydrogen bonded rings between adjacent complexes and hydrogen bonding between the amino groups of the ligands and dimethyl sulfoxide molecules, some of which lie within the channels and some outside; water molecules are also found within the channels.

Overall, the results clearly demonstrate the manner by which facile (metal influenced) protonation/deprotonation behaviour may, in a suitable system, act to control a supramolecular assembly process.

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