Synthesis and structural characterization of [Ni(biimidazole)₂(OH)₂] complexes and carboxylate

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Abstract

A vigorous heteromeric hydrogen-bonded synthon $[R^2_2 (9)-Id]$ is abused to drive the measured self-assembly of four coordination complexes $[Ni(H_2biim)_2(OH_2)_2]^{2+}$ and carboxylate counterions. This strategy allowed us to construct atomic structures of 0-, 1-, and 2-dimensions.

Introduction

Hybrid inorganic–organic materials have received muchattention because they incorporate the functionality of both Components¹ Studies related to the design and crystal supramolecularit of these materials are regarded as being within the inorganic crystal engineering field², which has allowed the development and exploitation of rational strategies leading to metal-containing extended supramolecular entities^{1b,1c}. These strategies have been focused on the assembly of organic/metal moieties capable of driving self-recognition or self-assembly, mainly by complementary hydrogen bonds^{1b,1c,3} and/or coordination bonds⁴ In fact, the consideration and utilization of both supramolecular interactions has generated a great diversity of metal-based architectures in solid state⁵. One special case of an unusual harmonisation between both strategies, achieved on the same mesoporous solid, was reported recently⁶ Herein, we are concerned with the family of hybrid materials in which a metal centre provides the orientation ability of its well-known coordination environment, toform inorganic hydrogen-bonded assemblies. It is frequently argued that these hydrogen-bonded networks are less robust than that of inorganic analogues with stronger individually bonds. However, the number and/or the strength of a particular hydrogen bond may act in concert, in principle, in an assembly robust enough to withstand, for instance, guest removal⁷ Recently, Beatty⁸ has reported an extensive revision on the crystal engineering of extended systems based on hydrogenbonded coordination complexes.





A specific natural target for development of hybrid materials is the neutral molecule 2,2'-biimidazole (H₂biim) and its monoanionic subsidiary (Hbiim⁻). Both atomic moieties possess a twofold property, to be specific they can be facilitated to metal centres and can act as a giver in hydrogen bonding interactions⁹ (Plot 1).Fragment Ia, for occasion, has been used to abdicate amplified inorganic supramolecular architectures in the strong state by coordinate interaction between them¹⁰ Both fragments Ia are moreover alluring within the setting of modular assemblies¹¹ in which a moment component with a complementary functional gather may be connected to N–H moieties to abdicate interesting supramolecular frameworks. In this sense, carboxylic units appear to meet with the asked requirement. A carboxylic corrosive utilitarian gather may act as donor– acceptor to associate to the Hbiim⁻ ligand to make Ib. Both oxygen molecules of a carboxylate bunch may too be attached directly to the N–H givers through a charge helped heteromeric synthon of sort R²₂ (9)¹² as portrayed in Id. In this contribution, we report our to begin with comes about in which the R²₂ (9)-Ib synthon is abused as a planning apparatus to lead the measured selfassembly of metal-based structures with diverse dimensionality. Such a technique is come to by the blend and structural characterisation of the four modern coordination complexes [M(H₂biim)₂(OH₂)₂]²⁺ (Xⁿ⁻)_{3-n} [n = 1 or 2; M = Ni²⁺ , X¹⁻ = isonicotinate (1); M = Ni²⁺ , X¹⁻ = 3,4,5-tris-hydroxybenzoate (2)].

Table 1Crystallographic data for compounds 1–2

	1	2
Empirical formula	C24H32N10Ni1O10	C26H34N8Ni1O16
M	679.19	773.20
Crystal system	Triclinic	Monoclinic
Space group	P1 ⁻	P21/c
a/Å	9.424(2)	12.125(5)O
<i>b</i> /Å	10.259(2)	9.255(4)
c/Å	8.699(2)	13.991(4)
α/	100.69(2)	90.01
β/	107.77(2)	98.09(3)
γ/	105.30(1)	90.10
V/Å3	739.0(2)	1557.9(1)
Ζ	1	2
$Dc/g cm_3$	1.518	1.639
μ/mm_	0.731	0.711
Reflections collected	2779	2877
Independent reflections	2606	2739
Goodness of fit	1.01	1.027
<i>R</i> 1 , <i>wR</i> 2 [$I > 2\sigma(I)$]	0.0458, 0.0861	0.0638, 0.1277
<i>R</i> 1 , <i>wR</i> 2 (all data)	0.0769, 0.0942	0.1217, 0.1531

Experimental

Biimidazole was arranged taking after a slightly modified procedure^{13a} of Fieselmann et al^{13b} FT-IR spectra were recorded from KBr pellets within the extend 4000–400 cm 1 on a Magna IR 560 spectrophotometer. Test conditions: 9.5 mg, N₂ atmosphere, heating rate 10 $^{\circ}$ C min⁻¹ and T_{max} 1100 C. Powder X-ray diffraction designs were recorded in a Siemens D5005 diffractometer with Cu-K α radiation ($\lambda = 1.5409$ Å). All diffractograms were recorded with the same test at the same conditions: 0.02⁰ min⁻¹ and 5 s step¹⁻ within the 2 θ run of 5–80⁰

Synthesis of the complexes 1–2

The amalgamations of the compounds were carried out taking after a general method. To a arrangement of metal acetic acid derivation

[Ni(OAc)₂]₄ H₂O(~0.300 mmol) in 50 mL of hot water an amount of H₂biim was included (~0.600 mmol). To the resulting mixture, a arrangement of the comparing carboxylic acid previously broken up in 30 mL of hot water was included. The solution was at that point concentrated to one-third of its initial volume. A metal : acid proportion of 1 : 2 and 1 : 1 were utilized for monocarboxylic and dicarboxylic acids, separately. Crystals of 1-2 were gotten from controlled vanishing of the solution at room temperature, during a period for 2–3 weeks. Compounds 1 is insoluble in common solvent, where as 2 shows a exceptionally destitute dissolvability in DMSO. Anal. calcd. for **1** (yield 97%): C₂₄H₃₂N₁₀NiO₁₀ 42.43; H, 4.75; N, 20.62%. found: C, 42.52; H, 5.19; N, 20.71%. IR (KBr; cm_1): 3390–2740 m; 1586 s, 1552 m; 1391 s; 1138, 994, 846 w; 769, 688 m. Anal calcd. for **2** (yield 47%): C₂₆H₃₄N₈NiO₁₆: C, 42.64; H,4.30; N, 19.89%. found: C, 43.57; H, 4.42; N, 20.65%. IR (KBr;cm_1): 3376–2783 m; 1602 m; 1549 s; 1426 m; 1373 s; 1120, 749,707, 692 w.

X-ray single-crystal determination

Data for both compounds were collected utilizing the ω -scan technique at 2° min⁻¹ room temperature on a Rigaku AFC7Sdiffractometer, prepared with a graphite monochromator and Mo-K α radiation ($\lambda = 0.71073$ Å). Details of crystal data collection and structure refinement are recorded in Table 1. In each case, three reflections were re-measured each 150 reflections to screen instrument and precious stone solidness. Information were corrected for Lp effect and for absorption¹⁴. Structures were solved by coordinate strategies¹⁵ and refined by full-matrix leastsquares on F² with anisotropic uprooting parameters for non-H molecules. Hydrogen molecules on nitrogen were included in their found positions, though those on carbon were calculated in perfect positions. Both were refined with isotropic displacement parameters set to 1.2 × Ueq of the joined molecule. Hydrogen atoms on facilitated water atoms were as found, but those on water of crystallization (but those of disordered molecules)were consider in their ideal position. These hydrogen iotas were refined by employing a riding show with isotropic displacement parameters set to 1.5 × Ueq of the corresponding oxygen molecule.

Theoretical calculations

Both geometry optimizations were performed with the SPARTAN package program¹⁸ at the UHF/PM3 level. Single point ab-initio calculations at the optimized geometries were carried out with the Gaussian-94 program¹⁹ at the DFT level using Becke's Three-Parameter cross breed utilitarian with Lee, Yang and Parr relationship utilitarian²⁰ (B3LYP utilitarian). For N, O, C, H and Li, the allelectron 6-311G(d,p) premise sets were utilized. The interaction energies were calculated utilizing the ab-initio DFT energies and the UHF/PM3 geometries without counting the zero-point energies. This procedure was employed because it has been reported that it provides a good estimation of the dissociation energies²¹. For testing this approach ourselves, we calculated the dissociation energy of the hydrogen-bonded benzoic acid dimer. The theoretical value (16.4 kcal mol_1) resulted in good agreement with the experimental value (16 kcalmol_1)²²

Results and discussion

The interaction R_2^2 (9)-Ib as a supramolecular synthon

The comes about we'll appear in this commitment depend upon the premise that intermolecular interaction Id is strong sufficient that it may truly act as a 'supramolecular glue' to gather coordination complexes and carboxylate in multidimensional arrays. In this setting, Beauchamp et al^{9a} have detailed the synthesis of an octahedral complex [ReCl₂(PPh₃)₂(H₂biim]⁻ (benzoate) (5), in which its gem structure contains benzoate anion connected to both N–H bunches of facilitated biimidazole via N–H ---- O hydrogen bonds (separate N--- O: 2.68 Å). An additional highlight watched within the gem structure is that the carboxylate useful bunch and the biimidazole ligand frame a nearly coplanar (cruel plane deviation: 0.046 Å) arrangement like that expected for Id. The creators moreover carried out a variable- temperature 1H-NMR think about, illustrating that an ion paring complex/carboxylate is held in arrangement. The efficiency of the particle blending arrangement was ascribed to the complementary topology of the H2biim ligand and the carboxylate, which permits two solid N–H---- O hydrogen bonds to act in concert. Two other basic ponders include one ferrous complex²³ [Fe²⁺(H₂biim)₂(CH₃ OH)₂](Ac)₂ (6) and one Zinc complex²⁴ [Zn₂(H₂biim)₂(OH₂)₂](Ac)₂ (7), which contain the acetate as a counterion. In both complexes, the acetic acid derivation, roughly co-planar to the facilitated biimidazole, is connected to both N–H bunches with brief and marginally topsy-turvy N----- O distances of 2.705(2)/2.679(2) Å and 2.756(2)/2.678(2), respectively. Hence, the prove specified so distant bolsters the utilisation of Id as a interfacing device for biimidazole coordination complexes and carboxylate anions by means of measured selfassembly. In the gem designing setting, 5–7 may be seen as zero-dimensional models that permit comparison of the supramolecular parameters of the metal-based congregations sought after in this study.

Energy estimation of the interaction $R^{2}_{2}(9)$ -Id

It is evident that vitality legitimization will eventually gotten to be necessary to get it the vigor proposed for both interactions Ib. As a to begin with step for such an estimation, we have considered the hypothetical calculation of complexes formed from the intermolecular interaction of $R_3CCOOH(R = H, F)$ and atomic parts 'Li¹⁺(Hbiim)' and 'Cu¹⁺(Hbiim)' (Plot 2). These calculations appear that the least vitality is reached in two sorts of structures. Those one with acidic acid (IIa-b), in which the proton was held by the carboxylic unit, and those containing the fluoroacetic moiety whose acidic proton was exchanged to the biimidazolic part (IIc-d). As anticipated, these comes about propose that the arrangement of the hydrogen bond of the sort Ic is encouraged by electron-accepting groups joined to the carboxylic unit. According to the PM3 calculations, in complexes IIa the carboxylic group and the biimidazolic unit are co-planar (mean torsion angle O1–O2–N2–N1=0.4). However, the N--- O distances (mean:N1--- O1=2.71 Å vs. N1--- O1=2.79 Å) indicate an asymmetric intermolecular interaction. This latter result may be justified taking into account that in the coordinated Hbiim the deprotonated imidazole ring maintains a negative net charge, precisely where the OH group is approached, allowing a shorter N--- O distance. In contrast, the torsion angles O1-O2-N2-N1 in complexes IIb appear a deviation from co-planarity (mean: 6.7°) of the carboxylate anion and biimidazole ligand, but suggesting rise to N--- O separations (2.72 Å). In common, the energy calculations appear that quantum chemical interactions are lower in IIa (rise to values: 24.5 kcal mol¹⁻) than in IIb (30.1 kcal mol¹⁻). Hence, the observed misshapening from the planarity shows up to be greater within the case with a more grounded interaction. The magnitude of the interaction too appears to be related to the net charge of the oxygen molecules of the carboxylate; more noteworthy charge on the Oatoms, more noteworthy interaction. As a matter of truth, the oxygens' net charges are O2 = -0.68 and O1 = -0.71 in CH3COOH, whereas the same esteem of -0.75 is embraced for all O-atoms in CF3COO¹. In summary, the evaluated interaction could be described by two factors; an interaction across the H-bridge and one of an electrostatic nature. Calculated energy values for this kind of hydrogen bond II lie in the upper limit of the range invoked for a medium-strong hydrogen bond, with a possible energy interval of 6-20 kcal mol^{1-25} . This H-bonding is thought to be derived by the presence of positive and/or negative charges²⁶



Modular self-assembly strategy

Four metal-containing complexes of common equation $[M(H_2biim)_2(OH_2)_2]^{2+/}(carboxylate)$ have been synthesized and characterised by single-crystal X-ray diffraction. Diverse carboxylate anions have been considered, but as it were those included in this report are delineated in Polt3. Ni²⁺ has been chosen since they may create octahedral environments with the plausibility of planning two biimidazole ligands in trans positions. In this way, carboxylate units may be assembled on both sides of these metal complexes to abdicate the desired models. These cationic complexes permit the additional possibility of changing the counterion i.e. from mono- to dicarboxylate depending on the stoichiometry.



Plot 3

Molecular structures of complexes 1-2

Both the crystal structures consist of a common metal-based building block $[Ni(H_2biim)_2(OH_2)_2]^{2+}$ cation(Fig. 1). Selected bond distance and angles are collected in Table 2. In both cases, the metal centres allow the formation of a distorted octahedral coordination environment with four nitrogen atoms of two H₂ biim ligands arranged *trans* to each other. Two oxygen atoms of water molecules, axial to the metal–biimidazole plane, occupy the remaining coordination sites. The N-M-N bite angles generated by the chelating of the biimidazole in 1 and 2 is 80.8. These angles lie in the ranges registered in the CSD . The M–N lengths and the average angles and distances in the biimidazole ligands also are comparable with those previously reported in the CSD²⁶. The Ni–O(water) bond lengths [average: 2.120(3) Å] of complexes 1 and 2 are similar to each other and to those reported for the cation [Ni(H2biim)2(OH2)2]^{2–}



Fig.1Molecular structure of building block[Ni(H2biim)2(OH)2]²⁺ Cation of1&2.Primed labels are generated by inversion centre

Crystal packing of [Ni₂(H ₂biim)₂(OH₂)₂](isonicotinate)₂ 4H2O,(1)

The asymmetric unit consists of one half of the $[Ni(H2biim)2-(OH2)2]^{2=}$ cation with the Ni²⁺ ion located on a symmetry centre, one isonicotinate anion and two water molecules of crystallisation. The crystal structure contains two isonicotinate anions linked to the N–H groups at both side of the metal complex *via* +a charge assisted hydrogen bond **Ib** (Fig. 2). Both N---- O distances [N21--O1=2.715(3) Å and N31--- O2=2.736(4) Å] show slightly different lengths between them, and are longer than those observed in **5** and **6**. This asymmetry appears, probably, as a consequence of the existence of extra intermolecular interactions of the carboxylate oxygen atoms with water molecules of coordination and crystallisation (see below). In contrast, the C–O bond distances of the carboxylate group [C1-O1=1.258(4) Å and C1-O2=1.254(4) Å] remain statistically equal. In the anion, the plane of the carboxylate group forms dihedral angles of 9.6_ and 8.5_ with the pyridine ring and with the plane formed by the H2biim ligand, respectively.Even then the atoms more directly involved in the hydrogen bonding interaction (O1, C1, O2, N21, N31) lie in a mean plane with a maximum deviation of 0.020 A.

Table 2 Selected bond distances (Å) and angles (_) for compounds 1-2

	1	2
M-N11	2.089(3)	2.072(4)
M-N41	2.098(2)	2.104(4)
M–O1W	2.124(2)	2.115(4)
N11-C2	1 1.369(4)	1.380(6)
C21–C3	1 1.368(4)	1.354(7)
C31–N2	1 1.369(5)	1.369(7)
N21-C1	1 1.334(4)	1.338(6)

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C11–C4	1 1.444(4)	1.454(7)
C41–N3	1 1.343(4)	1.351(6)
N31-C6	1 1.366(4)	1.374(7)
C101	1.258(4)	1.263(6)
C1–O2	1.254(4)	1.247(6)
N11-M-N41	80.51(10)	80.97(16)

The anion--- cation --- anion 0D-arrangement is accommodated beside two water atoms of crystallization to form a hydrogen bonded 2D –assembly in the plane(0 3⁻ 1) (see Fig. 2). The primary water particle is associated to the pyridine nitrogen iota with a N1--- O1c separate of 2.847(4) Å. The second one shapes a hydrogen bond with the coordinated water molecule [O1wi--- O2c = 2.837(3) Å (i: 1 +x, y, 1 +z)]. The water of coordination (O1w) remains over and underneath this 2D-assembly, permitting two extra O–H --O hydrogen bonds with neighboring layers $[O1w^{i}-- O1c^{ii} = 2.830(3) Å$ (i: 1 +x, y, 1+z; ii: 2 - x, 1 - y, 3 - z) and $O1w^{iii}$ --- O2 = 2.779(4) Å (iii: x, y, 1+z)] Therefore coordinated water molecules help to sustain the 2D-assembly and at the same time the final 3D-arrays. A striking feature observed in the packing of **1** is the presence of the isonicotinic moiety acting as an anion. Even though this entity carries a pyridine nitrogen atom with a electron lone pair in the plane of the ring with either coordinating or hydrogen-bonding acceptor properties, the packing prefers to accommodate this unit as a hydrogenbonded counterion. This latter observation could be attributed to the intrinsic robustness of the synthon **Id**.



Fig. 2 Crystal structure of 1 showing two isonicotinate anions to the N-H groups at both sides of the metal complexe via a charge assisted hydrogen bond 1b. Hydrogen atoms on carbon atoms omitted for clarity.Symmetry transformations used to generate equivalent: i=1+x, y, 1+z, ii=2-x, 1-y, 3-z iii=x, y, 1+zCrystal packing of $[Ni^{2+}(H_2biim)_2(OH_2)_2](3,4,5-tris-hydroxybenzoate)_24H2O, (4)$

The asymmetric unit contains one carboxylate anion, two water molecules of crystallisation and one half of the cationic complex with the metal located on a centre of symmetry. The packing consists of $[Ni(H_2biim)_2(OH_2)_2]^{2+}$ joined to the anion through the hydrogenbonded synthon **Ib** (Fig. 5a). In spite of the presence of strong donor/acceptor hydroxyl groups, the synthon evaluated persists in the crystal structure. The C–O bond distances of the carboxylate group [C1-O1=1.263(6) Å and C1-O2=1.247(6) Å] are statistically equal. Once again, the N--- O distances [N21--O1=2.683(6) Å and N31--O2=2.770(6) Å] present a slightly asymmetry, which is higher than that observed in **1**. The carboxylate and the H₂biim form a dihedral angle of 6.9° . The remaining OH moieties on the phenyl ring are utilized to expand the match cation/anion via self-complementary O–H--- O $[O3--- O4^i = 3.087(7) \text{ Å}; O4--- O5^i = 2.823(7) \text{ Å}$ (i: 1- x, 0.5+y, 2.5-z)], in which each hydroxyl acts both as a benefactor and acceptor. The resulting hydrogen-bonded organize permits a 2Darray with cavities occupied by four water particles of crystallization (see Fig 5a). The cruel planes including each sheet include the family of planes (302). The 2D-array stacks within the [101]-direction through hydrogen bonds, including facilitated water molecules, the oxygen particle of the carboxylate and crystallisationwater particles. Cavities of sequential slipped sheets communicate between each other permitting channels (~4 Å × ~6 Å) (Fig. 5b) that run parallel, among others, to the planes (204), (121) and (022) in such a way that these families of planes cut through the channels specifically at positions where water molecules are hosted.

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Fig. 3 View of the crystal structure of 2(a) Hydrogen-bonded 2D- network showing the cavities occupied by water molecules. Symmetry transformation used to generate equivalent atoms: I = 1-x, 0.5+y, 2.5-z (b) Stacking of consecutive sheets.

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