Crucial Influence of Solvent and Chirality—The Formation of Helices and Three-Dimensional Nets by Hydrogen-Bonded Biimidazolate Complexes

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Abstract: Deprotonation and recrystallisation of racemic [Co(2,2′-biimidazole)$_3$][NO$_3$]$_3$ by ammonia in water/dimethylformamide solutions gave crystals of [Co(Hbiim)$_3$]$\cdot$0.8H$_2$O$\cdot$0.5DMF (**2**: Hbiim = monoanion of 2,2′-biimidazole, DMF = dimethylformamide), a porous material that contains fourfold interpenetrating (10,3) three-dimensional nets formed by neutral, hydrogen-bonded [Co(Hbiim)$_3$] units, with DMF molecules in the narrow channels. Recrystallisation of [Δ-Co(2,2′-biimidazolate)$_3$] gave helices instead of the expected (10,3)-a net. These results are discussed in the light of additional density functional theory and molecular mechanics calculations and the X-ray structure of [Co(H$_2$biim)$_3$][NO$_3$]$_3$.

Keywords: cobalt · crystal engineering · hydrogen bonds · N ligands · supramolecular chemistry

Introduction

For a century or so, synthetic chemistry has been directed at the rational preparation of either discrete molecules or solid phases. However, lately another goal has been set: the rational synthesis of assemblies of molecular units forming predictively designed, infinite three-dimensional networks, preferably with built-in features like porosity[1] or magnetism,[2] so-called molecular-based materials.[3]

An attractive goal is the synthesis of (10,3)-a nets (Figure 1b),[4] which are chiral and form structures with large channels. The quest for such new porous materials is currently a very active area, incorporating classical zeolite-type materials,[5] inorganic[6] and organic chemistry,[1, 7] and even proteins.[8] Recent examples of molecular-based porous materials are interconnected Zn^{II} and Cu^{II} carboxylate clusters, achiral[9, 10] and chiral,[11] chiral (4,4) or (10,3) nets,[12, 13] axially interconnected metalloporphyrins,[14] and three-dimensional-interpenetrating Cu^{II}–bis(pyridyl) two-dimensional nets.[15] It is significant that all these examples are based on transition metal chemistry with its richness of coordination geometries; lanthanides have also lately been used for this purpose.[16]

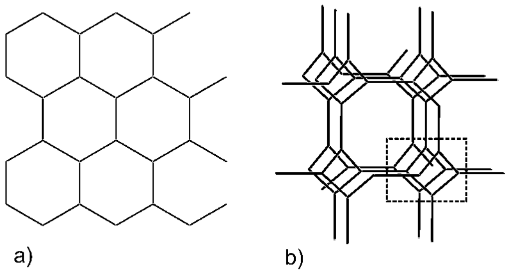
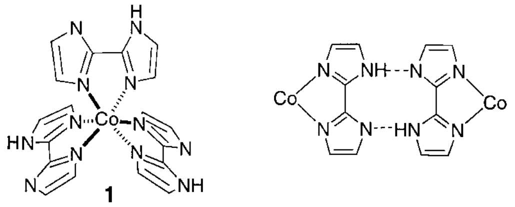


Figure 1. Ideal network topologies: a) the honeycomb net and b) the chiral (10,3)-a net. If the repeating unit is [Co(Hbiim)$_3$] then in b) all centres have the same chirality, and in a) the centres have alternating chirality, Δ or Λ. The dotted box in b) shows a single helix corresponding to compound **4**.

The ligand 2,2′-biimidazole, in its various stages of deprotonation, has been used to create many different types of networks with Ni^{II}, Cu^{II}, Co^{III} and Fe^{III}.[17] When monodeprotonated it has the attractive feature of being able to form autocomplimentary hydrogen bonds; hence, molecules like [Co(Hbiim)$_3$] (Hbiim = the monoanion of 2,2′-biimidazole) have the possibility to "self-assemble" into extended structures (Scheme 1). A consideration of the topology would predict the formation of (10,3)-a nets (Figure 1b) from enantiomerically pure [Co(Hbiim)$_3$] (**1**),[18] possibly with one or more nets interpenetrating.[13] On the other hand, racemic material should give either stacked[19] or interpenetrating[20] honeycomb two-dimensional nets with alternating Δ and Λ



Scheme 1.

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chirality at the branching points (Figure 1a). In this study, we report two new extended networks based on the [Co(Hbiim)$_3$] molecule and show that this simplistic approach is far from reliable.

Results and Discussion

A three-dimensional net and [Co(H$_2$biim)$_3$][NO$_3$]$_3$: In agreement with the argument above, Tadokoro et al. reported that crystals of [Co(Hbiim)$_3$] grown in methanol/ethyl acetate mixtures form stacked hydrogen-bonded honeycomb nets with large porosity.[21] However, we found that the deprotonation of racemic [Co(H$_2$biim)$_3$][NO$_3$]$_3$ by ammonia in water/DMF instead gave crystals of the compound **2**. The basic structural unit is a (10,3) net with interconnected helices formed by the sequence -Δ-Δ-Λ-Λ- along the *a* and *c* axis and -Λ-Δ-Λ-Δ- helices along the *b* axis giving slightly oval pores 23 × 11 Å wide, see Figure 2. The Hbiim–Hbiim bridges are essentially planar (average deviation 7°) except for two in each ten-membered ring that are twisted 40° although the hydrogen bond lengths remain the same (2.78 Å compared to the average 2.80 Å for the other bridges).

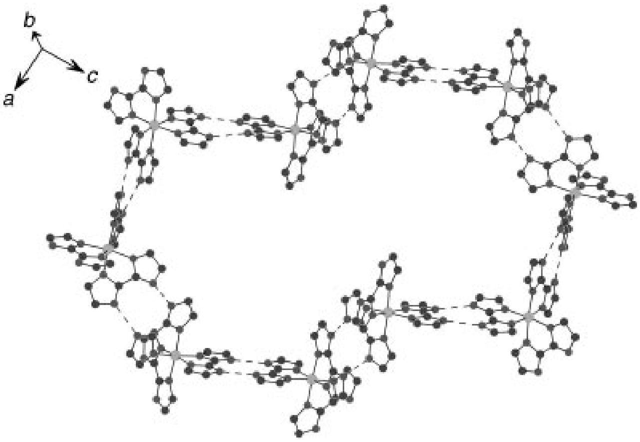

Figure 2. The 10-membered rings formed by hydrogen bonding (dashed lines) of [Co(Hbiim)$_3$] in **2**. Hydrogen atoms omitted for clarity.

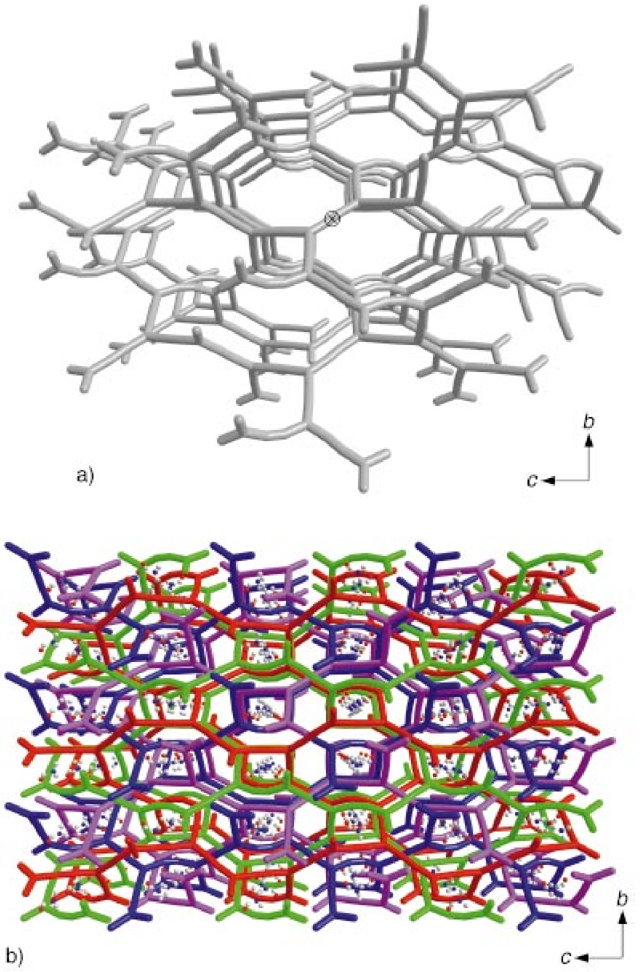

Figure 3. Schematic view along the *a* axis of a) a single net (the ⊗ indicates an inversion centre), and b) the four entangled (10,3) nets showing the 9 × 3 Å wide channels with solvent molecules. Cobalt atoms are at the intersections and the tilted hydrogen bonds can be seen as nicks on the otherwise straight tubes connecting the metal centres.

These nets (Figure 3a), as opposed to the (10,3)-a nets, are not chiral and are instead of the ThSi$_2$-type.[4] This may seem self-evident since they contain a racemate, but this is not a sufficient argument, the whole topology has to be considered. There are no mirror planes in the net, since such a plane would have to pass through at least one type of helix, and a helix, of course, has no mirror plane. However, parallel helices with opposed chirality are related by an inversion centre (and thus an S_2 axis, indicated in Figure 3a); hence the achirality of the net.

Four interpenetrating nets fill these large pores and occupy together 86% of the unit cell volume (PLATO[22] analysis). The total entangled structure is shown in Figure 3b; the solvent molecules that occupy the resulting narrow channels are also shown. Each channel is formed by two nets and is 9 × 3 Å wide in the narrowest region (shortest atom–atom distance excluding the van der Waals radii). In Figure 4 a stereo view of the limiting surfaces of one such channel have been plotted (SURFNET[23] analysis). DMF molecules located within are disordered and in pairs (distance 3.4 Å) occupy larger voids within the channels separated (8.0 Å) by narrower sections. Water molecules could not be located by X-ray diffraction, but elemental analysis indicates equal amounts of DMF and water in the pores. Thermogravimetric analysis shows gradual loss of first water and then DMF.

In order to analyse strains within this network we also determined the structure of racemic [Co(H$_2$biim)$_3$][NO$_3$]$_3$ (**3**). This compound contains hydrogen-bonded ion clusters (Figure 5a) with an N–H···O hydrogen bond length of 2.770(4) Å. The thermal parameters for the nitrate ion indicate that the two hydrogen-bound oxygens can swop amines. The third oxygen has only weak interaction with its neighbours (a nonclassical hydrogen bond to two Hbiim C–H groups, O···H–C distance 3.232 Å) and the remaining intermolecular distances are also long. Nevertheless, these weak interactions "glue" the clusters together in the *a* and *b* directions, while in the *c* direction [Co(H$_2$biim)$_3$][NO$_3$]$_3$ units of different chirality are stacked on top of each other, see the

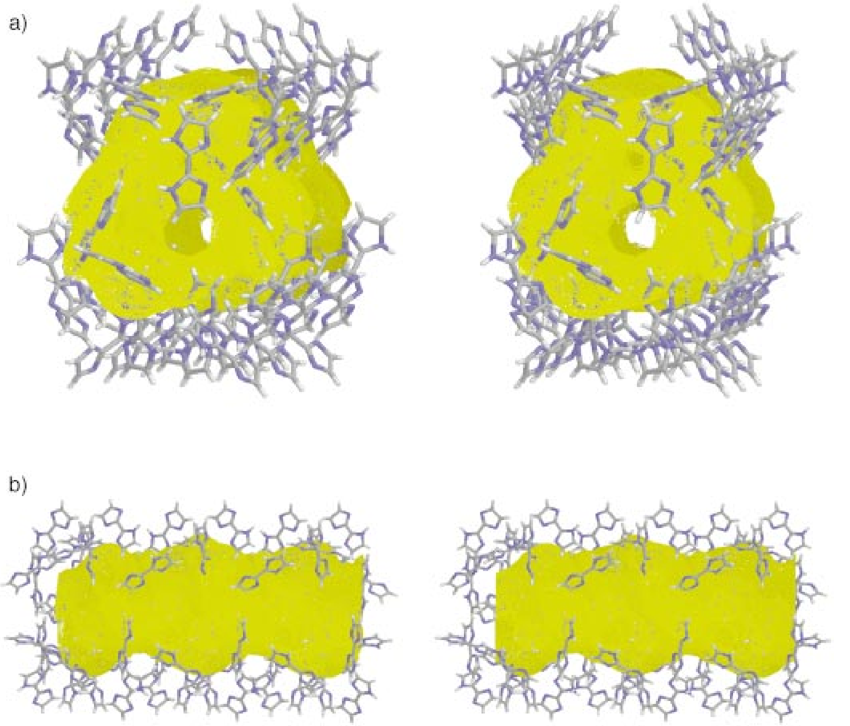

Figure 4. SURFNET[23] stereo view of the limiting surface of a channel section. a) View along the *a* axis and b) view along the *c* axis.

eleven neutral H_2biim molecules (Co replaced by H) was created. Two DMF molecules were allowed to relax from the approximate atom positions suggested by X-ray diffraction. The optimised DMF atoms came close to the approximate positions suggested by the X-ray data (average deviation 0.8 Å), and the strain in the so-obtained geometries were calculated by a reoptimisation of the two DMF molecules, this time without the channel. The energy cost to obtain the channel-adapted structures from a completely relaxed structure was computed to be 7 kJ mol^{-1}. In the same way, two ethyl acetate molecules were placed in the channel. In this case more than ten different original orientations were tested, but in no case was the computed strain of EtOAc in the channels less than 28 kJ mol^{-1}. Thus, in order to fit into the channels, the ethyl acetate molecules have to twist and bend at a cost of 28 kJ mol^{-1}. While not definitive proof, this does support the size argument.

packing diagram in Figure 5b. The compound can therefore be regarded as a packing of neutral discrete species and should contain an "ideal" $[Co(H_2biim)_3]^{3+}$ octahedron.

However, comparison of the bond lengths and angles for the two crystallographically different [Co(Hbiim)$_3$] molecules in **2** with the $[Co(H_2biim)_3]^{3+}$ ion do not indicate twisting or other distortions in the coordination sphere. Thus, the non-planarity of the hydrogen-bond bridges are the only deviations from ideality for **2**.

While this tilting certainly is unfavourable, the maintenance of the same N···H–N distances suggests that the loss in binding energy may not be so large. This was investigated by density functional theory (DFT) calculations. Single-point calculations on the three different Hbiim–Hbiim geometries found in the structure were compared to an ideal flat Hbiim–Hbiim unit that retained the essential intra- and intermolecular distances. The lost stabilisation is calculated to be 5 kJ mol^{-1} per N···H–N bond and the ideal strength of the hydrogen bond to be 36 kJ mol^{-1}. The latter value is in the expected range for such hydrogen bonds.[24] Thus, the calculations indicate that only 14 % of the bond energy is lost.

Why does the change of solvents, from the MeOH/EtOAc of Tadokor et al. to water/DMF in our case, cause such a major change in structure? This is yet another example of the unpredictability that continues to plague or fascinate (depending on your point of view) crystal engineering, even when the building blocks are deceivingly simple and rigid.

A possible explanation is that ethyl acetate, being approximately one methyl group larger than DMF, will not fit into the channels. This hypothesis was tested by molecular mechanics calculations. A part of the channel containing

Even so, this does not explain why crystals grown from DMF/H_2O do not have the much likelier, as it seems from the number of examples in the literature, honeycomb structure (Figure 1a). That the six-membered rings of the honeycomb structure should be more probable can also be motivated by considering that only three points have to be added before a new ring is complete, the probability of the correct order of chirality is thus 1/8. The (10,3) nets require six points and the probability drops to 1/64.

We can consider the DMF inclusion as a template effect. However, one usually thinks of a template as a single molecule and, moreover, the disorder indicates that DMF is mobile. The solvent forms pairs within the larger cavities in which one of the approximately planar DMF molecules is rotated 180°. This allows for a favourable dipole–dipole interaction with a DMF–DMF distance of about 3.4 Å. A search in the Cambridge Crystallographic Database reveals a number of similar arrangements with two or more DMF molecules stacked with intermolecular distances in this range.[25] Although the main interaction in DMF ought be a hydrogen-bonded dimer,[26] the formation of "dipolar" dimers may be a crucial step during the crystallisation process. We note that several porous structures with DMF have been reported,[9, 27] and suggest that the use of DMF or similar molecules is a good way of generating such materials.

A helix: Recrystallisation in ethanol of the solid compound obtained by deprotonation of [Δ-Co(2,2′-biimidazole)$_3$][NO$_3$]$_3$ by ammonia in water,[28] gave air-sensitive orange

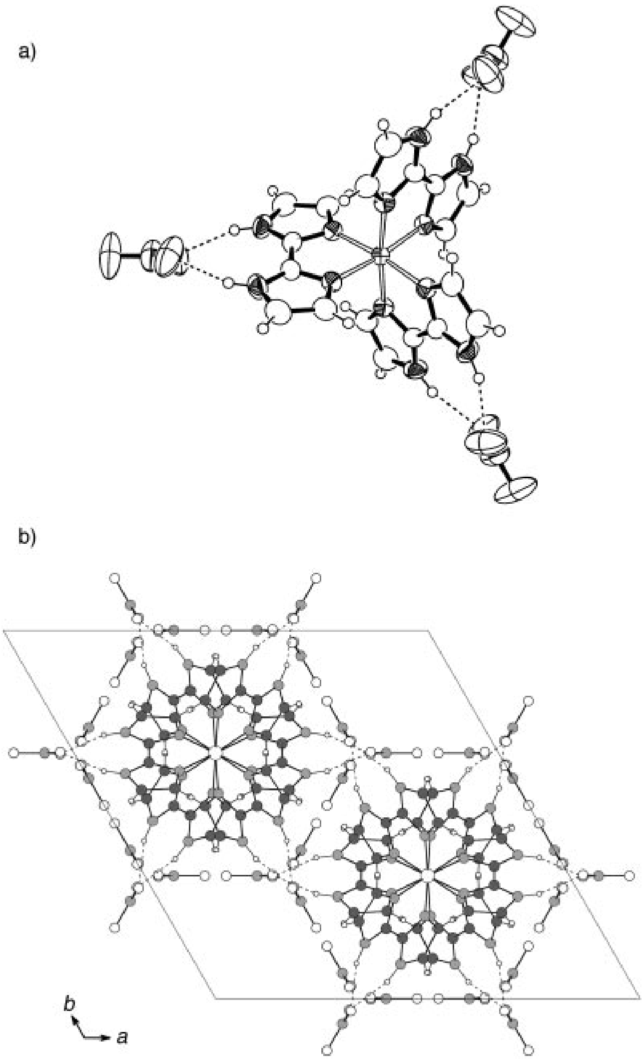

Figure 5. a) Thermal ellipsoid plot of racemic [Co(H$_2$biim)$_3$][NO$_3$]$_3$, compound **3** (only the Δ isomer is shown). Atoms are drawn at the 50% probability level. b) Packing of the unit cell showing four complete [Co(H$_2$biim)$_3$]$^{3+}$ ions with all the surrounding nitrate groups. The [Co(H$_2$biim)$_3$]$^{3+}$ ions are stacked on top of each other with alternating chirality and no intervening nitrates.

crystals of compound **4**. However, the highly porous chiral (10,3)-a net was not formed, instead each cobalt complex hydrogen bonds with only two of the three biimidazoles giving a helix structure (Figure 6).

While not the desired chiral (10,3)-a net, structure **4** is interesting in its own right. Such helical motifs have been popular synthetic goals during the last 20 years[29] and have been successfully prepared by means of coordination chemistry by using suitable ligands or from enantiomerically pure organic hydrogen-bonding donors and acceptors, frequently by "self-assembly".[30]

The structure consists of helices packed along the *c* axis. Each helix is surrounded by four other helices interlocking with "π interactions" between the four biimidazoles (at each turn of the helix), which stick out horizontally from the spirals. Four additional helices are positioned in-between the nearest neighbour helices completing the set of eight. Thus, the helices are not intertwined and no "double helices" are formed. Disordered ethanol and water molecules occupy voids in the structure.

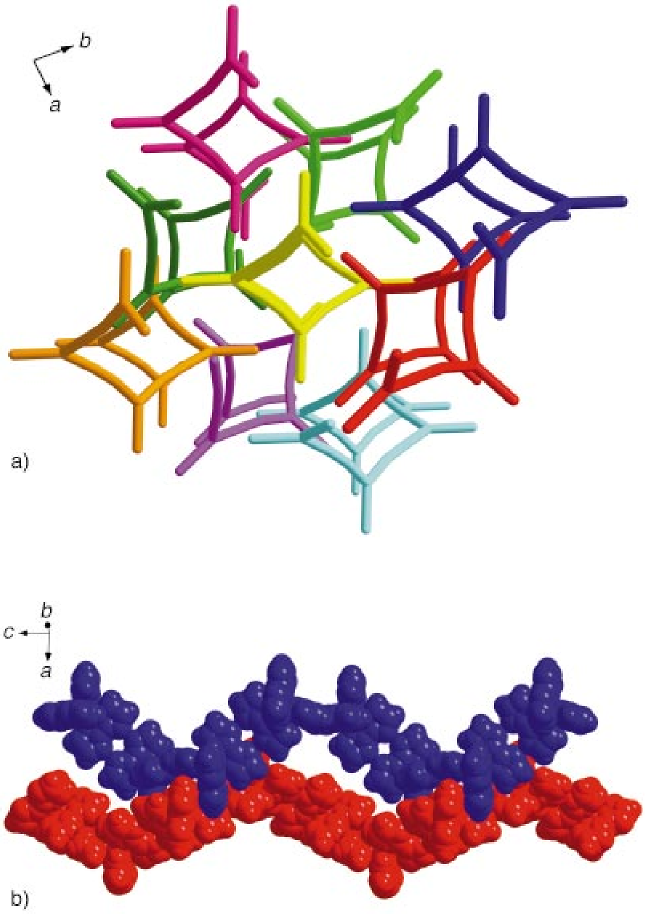

Figure 6. a) Schematic view along the *c* axis showing the packing of the helices formed by [Δ-Co(Hbiim)$_3$] recrystallised from ethanol (**4**). Cobalt atoms are at the intersections. b) Packing of two of the helices (view along the *b* axis).

Note that these helices are a part of the desired chiral (10,3)-a nets; the hydrogen bonding to the next spiral being replaced by interactions with the solvent (see dotted box in Figure 1b). A fourfold interpenetrating net, similar to that of **2**, could be envisaged as an alternative way of close-packing the (10,3)-a net. We attribute the fact that this does not happen to the stronger hydrogen bonds between ethanol and Hbiim relative to the hydrogen bonds between DMF and Hbiim. In the former case ethanol can compete with the Hbiim–Hbiim interaction and interrupt the building up of a three-dimensional net, whereas in the latter case the much weaker DMF–Hbiim interaction cannot. As stated above, we also believe the dipolar interaction between the flat DMF molecules to be important. However, so far recrystallisation of **4** in DMF or similar solvents has not yielded crystals suitable for X-ray structure analysis.

Conclusion

We have demonstrated that a change of (non-coordinating) solvent may induce structural changes in the net ("network polymorphism") and that chirality is an important issue for the formation of extended structures. Ligand control over network chirality has been demonstrated by Kepert et al.,[13] and enantiomerically pure transition metal complexes have been used in the synthesis of "molecular hexagons",[31] but the use of metal racemates have been the rule for extended structures (although spontaneous resolution sometimes occur[18, 32]). Moreover, the channels, albeit narrow, in compound **2** show that interpenetration does not always exclude the formation of porous networks. Indeed, the additional net–net van der Waals and "π–π" interactions may in fact stabilise the otherwise less rigid (10,3) nets towards collapse on solvent removal.

Experimental Section

General: All reagents were purchased from commercial sources and used without further purification. [Co(2,2′-biimidazole)$_3$][NO$_3$]$_3$ (**3**) and the precursor [Δ-Co(Hbiim)$_3$]·2H$_2$O were prepared according to the literature.[28] IR spectra were recorded in the range 4000–200 cm^{-1} with a Nicolet Magna IR560 spectrometer. Thermogravimetry measurements were made on a Mettler instrument.

Synthesis of 2: [Co(2,2′-biimidazole)$_3$][NO$_3$]$_3$ (0.0376 g 0.06 mmol) was dissolved in a mixture of DMF (8 mL) and H$_2$O (5 mL). Then, aqueous NH$_3$ (0.25 mL, 25 %) was added, and the resulting suspension was heated to 100 °C and filtered. After cooling to room temperature the clear solution was stored at 4 °C, and after several weeks crystals of [Co(Hbiim)$_3$]·0.8H$_2$O·0.5DMF were obtained. Elemental analysis calcd (%) for $C_{19.5}H_{20.1}CoN_{12.5}O_{1.3}$ (509.3): C 45.98, H 3.98, N 34.38; found: C 45.85, H 3.7, N 33.95; IR (KBr): $\tilde{\nu}$ = 1670 cm^{-1} (DMF, C=O); thermogravimetry on a 13.53 mg sample: 50 °C–100 °C: −0.4 mg (water); 110 °C–200 °C: −0.6 mg (DMF); 300 °C: −3.5 mg (biimidazole). The melting point is above 250 °C and up to this temperature no visible change of the crystals occurred.

Synthesis of 4: Recrystallisation of the precursor [Δ-Co(Hbiim)$_3$]·2H$_2$O from ethanol yielded brilliant orange octhahedra of **4** that decompose rapidly in air.

X-ray crystallography: For data collection from the crystals of **2** and **4** SMART CCD diffractometers were used, data were extracted with the SAINT+ package and intensity data were prepared with XPREP.[33] SADABS was used for the empirical absorption correction.[33] For **3** an Enraf-Nonius CAD4 diffractometer was used and data processing and absorption correction were made with XCAD[35] and PLATO,[22] respectively.

The structures were solved by direct methods and subsequent full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and not refined. Structure solution and refinement were carried out with the SHELXS-97 and SHELXL-97 program packages and refined against $|F^2|$.[34] All data were collected at ambient temperature.

Crystallographic data for [Co(Hbiim)$_3$]·0.8H$_2$O·0.5DMF (2): Formula: $C_{19.5}H_{18.5}CoN_{12.5}O_{0.5}$, crystal dimensions: 0.03 × 0.02 × 0.01 mm, Bruker Smart 1000CCD diffractometer with synchrotron radiation (MAXLAB II, Lund, Sweden), ω scan, $\lambda = 0.8522$ Å. $M_r = 494.88$, orthorhombic, space group: *Pbcn* (no. 60), $a = 12.600(3)$, $b = 20.900(4)$, $c = 32.790(7)$ Å, $V = 8635(3)$ Å^3, $Z = 16$, $\rho_{\text{calcd}} = 1.523$ g cm^{-3}, $F(000) = 4208$, 707 parameters; $R = 0.0650$, $wR = 0.1650$, GOF = 1.043 for all 4976 data [$I > 2\sigma(I)$]; min./max. residual electron density: −0.628/0.788 e Å^{-3}; $\mu = 1.192$ cm^{-1}; 33237 reflections collected. $2\theta_{\max} = 56°$, min/max transmission = 0.75169/0.97715 (SADABS). Electron density peaks (>2 e Å^{-3}) in the channels were treated as disordered DMF.

Crystallographic data for [Co(H$_2$biim)$_3$][NO$_3$]$_3$ (3): Formula: $C_{18}H_{18}CoN_{15}O_9$; crystal dimensions: 0.24 × 0.15 × 0.11 mm Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo$_{K\alpha}$ radiation. $\omega/2\theta$-scan, $\lambda = 0.71073$ Å. $M_r = 647.40$, trigonal, space group $R\bar{3}c$ (hexagonal setting) (no. 167), $a = 16.9262(5)$, $b = 16.9262(5)$, $c = 15.8376(6)$ Å, $V = 3929.5(2)$ Å^3, $Z = 6$, $\rho_{\text{calcd}} = 1.641$ g cm^{-3}, $F(000) = 1980$, 67 parameters; $R = 0.0375$, $wR = 0.0850$, GOF = 0.998 for all 588 data [$I > 2\sigma(I)$]; min/max residual electron density: −0.213/0.284 e Å^{-3}; $\mu = 0.7400$ cm^{-1}; 948 reflections collected. $2\theta_{\max} = 54°$; min/max transmission: 0.8952/0.9328 (Gaussian).

Crystallographic data for [Δ-Co(Hbiim)$_3$]·0.8EtOH·0.4H$_2$O (4): Formula: $C_{20.1}H_{21.3}CoN_{12}O_{1.5}$; crystal dimensions: 0.5 × 0.3 × 0.2 mm Siemens SMART CCD diffractometer with graphite monochromated Mo$_{K\alpha}$ radiation, ω scan, $\lambda = 0.71073$ Å. $M_r = 506.71$, orthorhombic, space group: $P2_12_12_1$ (no. 19), $a = 12.8963(2)$, $b = 13.8974(3)$, $c = 30.2627(7)$ Å, $V = 5423.83(19)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.250$ g cm^{-3}, $F(000) = 2044$, 612 parameters; $R = 0.088$, $wR = 0.238$, GOF = 0.972 for all 7249 data [$I > 2\sigma(I)$]; min/max residual electron density: −0.396/0.859 e Å^{-3}; $\mu = 0.665$ cm^{-1}; 52379 reflections collected; $2\theta_{\max} = 51°$; Flack parameter = 0.04(3). Electron density peaks (>2 e Å^{-3}) in the cavities were treated as disordered EtOH and water.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155315, CCDC-155316 and CCDC-155317. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational details: DFT calculations were performed with the DFT module in Spartan 5.1.3a1.[36] by employing the exchange and correlation functionals of Becke[37] and Perdew,[38] respectively (BP86). A numerical basis set, DN*, which included polarisation and d functions for C and N, was used. This basis set is roughly equivalent in "size" to the 6–31G* basis set, but is claimed to yield results closer to much larger Gaussian basis sets.[39] The molecular mechanics calculations were performed with the MM force field[40] implemented in Chem3D 3.5.1.[41] The MMFF94 force field[42] as implemented in Spartan 5.1.3a1[36] gave consistent results.

Acknowledgement

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