COMMUNICATION

ChemComm www.rsc.org/chemcomm

Physical stability *vs.* chemical lability in microporous metal coordination polymers: a comparison of $[Cu(OH)(INA)]_n$ and $[Cu(INA)_2]_n$: INA = 1,4-$(NC_5H_4CO_2)$†

Candy Z-J. Lin,[a] Stephen S-Y. Chui,[a] Samuel M-F. Lo,[a] Fanny L-Y. Shek,[a] Mingmei Wu,[a] Kinga Suwinska,[b] Janusz Lipkowski[b] and Ian D. Williams*[a]

[a] *Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: chwill@ust.hk*

[b] *Institute of Physical Chemistry (PAN), Polish Academy of Sciences, Kasprzaca 44/52, Warszawa, PL-01224 Poland*

Received (in Columbia, MO, USA) 11th February 2002, Accepted 8th May 2002

First published as an Advance Article on the web 2nd July 2002

Two microporous copper isonicotinate polymers [Cu(OH)(INA)] and $[Cu(INA)_2]$ have been formed hydrothermally in good yield and purity; each have 1D channels of *ca.* 4 × 6 Å dimension, but with quite different hydrophilicities; both frameworks retain structural integrity to above 200 °C, however whilst [Cu(OH)(INA)] is also chemically stable, $[Cu(INA)_2]$ is highly labile and readily transforms to the molecular complex $[Cu(INA)_2(H_2O)_4]$ in water at room temperature.

The current interest in metal coordination polymer zeolite analogues or zeotypes is driven by the goal of forming new materials which have complementary properties to zeolites.[1] One potential advantage is that the framework and channel linings will be more chemically active than inorganic oxide frameworks, however the chemical lability may also render the material unstable. Herein we report the synthesis of two related microporous phases $[Cu(OH)(INA)]\cdot H_2O$ **1** and $[Cu(INA)_2]\cdot 2H_2O$ **2** (INA = $NC_5H_4CO_2$ isonicotinate or pyridine-4-carboxylate). These both have open 3D frameworks with rectangular 1D channels of approximately 4 × 6 Å dimension, and have comparable framework thermal stabilities of >200 °C, but show dramatically different chemical stabilities.

The variation of synthesis conditions is critical for successful isolation of 3D open framework metal polymer zeotypes in a particular system, since many non-polymeric complexes, low dimensional polymeric phases and interpenetrated products can also be formed. In the copper–isonicotinate system a simple metal complex $[Cu(INA)_2(H_2O)_4]$ **3** is formed from aqueous-ethanolic solutions at room temperature.[2] Recently a novel phase $[Cu_2(INA)_4(H_2O)_3][Cu_2(INA)_4(H_2O)_2]\cdot 3H_2O$ possessing interpenetrating 2D and 3D frameworks was reported from hydrothermal reaction of copper nitrate, nicotinic acid and *trans*-1,2-bis(4-pyridyl)ethylene at 140 °C.[3] A rearrangement of nicotinic acid was proposed to account for this, though oxidative cleavage of *trans*-1,2-bis(4-pyridyl)ethylene appears a more likely source for the INA. We have investigated the products of hydrothermal synthesis at higher temperatures in this system, to promote further reduction in ancillary ligation and so allow control of polymer dimensionality.[4,5] Hydrothermal reaction for 2 days at 180 °C of $Cu(NO_3)_2\cdot xH_2O$ and H-INA in 1 : 1 and 1 : 3 ratios give the polymer phases $[Cu(OH)(INA)]\cdot H_2O$ **1** and $[Cu(INA)_2]\cdot 2H_2O$ **2**, respectively.‡§ Single crystal structure determinations revealed both compounds had 3D open frameworks with 1D channels. These are shown in the packing diagrams in Fig. 1.

The frameworks of **1** and **2** offer only modestly sized micropores, however the compositional and structural differences made it of interest to test and compare their structural integrity. Accordingly polycrystalline samples of each were heated at successively higher temperatures for 1 day and the powder diffractograms recorded upon cooling. Assuming no 'recrystallization' takes place upon cooling as recently reported by Wood and coworkers[6] the diffraction patterns indicate structural integrity of **1** is retained up to 225 °C and for **2** up to 250 °C. These temperatures represent excellent thermal stabilities within the class of open framework coordination polymers, with very few examples having higher thermal limits for their structural integrity.[4,7] Having demonstrated that the framework structure is not lost upon removal of the channel water molecules, programmed thermal gravimetric analyses were

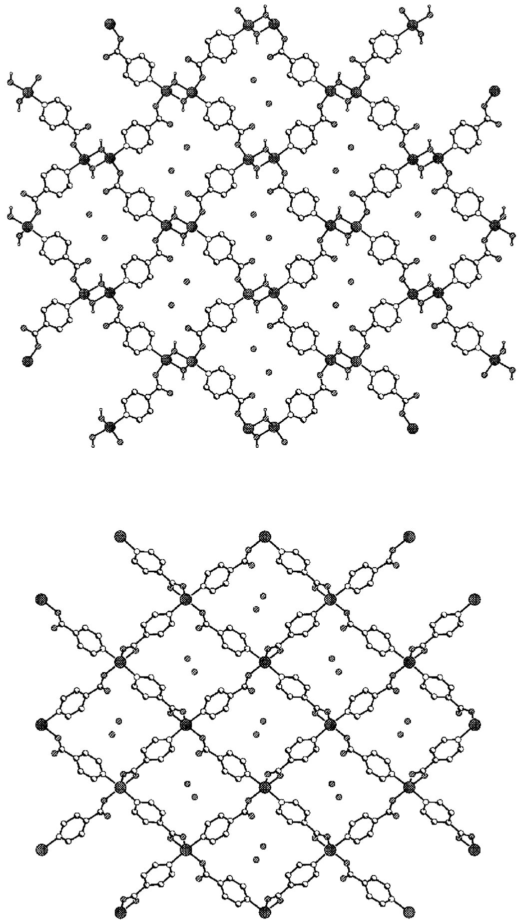

Fig. 1 (a) Packing diagram for $[Cu(OH)(INA)]\cdot H_2O$ **1** and (b) packing diagram for $[Cu(INA)_2(H_2O)]\cdot 2H_2O$ **2**, both viewed along their *a*-axis.

---

† Electronic supplementary information (ESI) available: 1. Structure determination summaries for compounds **1**–**3**. 2. Powder X-ray diffraction patterns: (a) for **1** and (b) for **2** after prolonged heating at different temperatures, establishing framework stabilities and (c) showing transformation of polymer **2** to the molecular compound **3**, after 12 h in H_2O. Fig. S1: copper coordination environments in compounds **1**–**3**. See http://www.rsc.org/suppdata/cc/b2/b201501n/

DOI: 10.1039/b201501n

carried out on **1** and **2** to investigate their desorption–re-sorption properties (Fig. 2). This shows that while the isonicotinate–hydroxide polymer **1** has almost completely reversible sorption characteristics and serves as a drying agent of house-nitrogen, the pure isonicotinate polymer **2** resorbs only a fraction (*ca.* 10%) of the original guest aqua molecules from such gas, implying a much reduced channel hydrophilicity. The limited resorption of water by **3** is consistent with the fact that the previously reported iron(II) analogue [Fe(INA)$_2$] was found to be completely anhydrous. This has octahedral metal centres and all carboxylate oxygens coordinated which presumably renders the channels more hydrophobic than for **2**.[8] The relative hydrophilicities of **1** and **2** may be explained in that for **2** only half of the channel waters form a hydrogen bond to the channel oxygens, whilst in **1** all channel waters are H-bonded to the framework.

In further investigation of the resorption of water by **2** we have unexpectedly discovered that its framework has exceptionally high chemical lability. Hence stirring polymer **2** in water for 1 day, results in clean transformation back to the molecular complex **3**, as demonstrated by powder X-ray diffraction and a colour change from blue to pale-green. This result was quite unexpected, since the physical stability of the framework of **2** was already established to be remarkably high, and furthermore since the initial *formation* of compound **2** occurs in aqueous solution at high temperature and pressure over several days. At first these findings appear contradictory and a satisfactory explanation for them must be sought. The answer may lie in the fact that the thermodynamic equilibrium involving solids **2** and **3** is temperature dependent.

$$\underset{\mathbf{3}}{[Cu(INA)_2(H_2O)_4]} \underset{LT}{\overset{HT}{\rightleftharpoons}} \underset{\mathbf{2}}{[Cu(INA)_2]\bullet 2H_2O} + 2H_2O \tag{1}$$

We have already mentioned that use of hydrothermal conditions promotes the reduction of ancillary ligation. This is partly due to the higher enthalpy of ligating carboxylate anions rather than neutral aqua groups, but is also favored by the increased entropy of releasing free water molecules from the polymer. The thermal dependence of the equilibrium between phases **2** and **3** is further demonstrated by the fact that when crystals of pure **3** are heated as a dry solid in a hydrothermal bomb at 110 °C they smoothly convert to crystalline **2** after 1 day.

The synthesis of mixed hydroxide species in hydrothermal syntheses of coordination polymers has been seen frequently, especially at higher temperatures and pH.[5,6,9] In the case of the hybrid hydroxide polymer **1**, it is synthesized with limiting amounts of INA at pH 4, whilst **2** is formed with excess of the INA ligand at pH 3. The formation of the copper–hydroxide component in **1** is effectively irreversible and incorporation of (μ_3-OH) renders the polymer more chemically inert and it is stable in the pH range 2–9. In stronger bases it gradually decomposes with formation of copper(II) oxide. Regarding organic solvents and reagents, both **1** and **2** are insoluble and indefinitely stable in ethanol, but in dry pyridine **1** dissolves slightly over 1 day giving a light green solution, whilst **2** dissolves fully to give a deep blue colour.

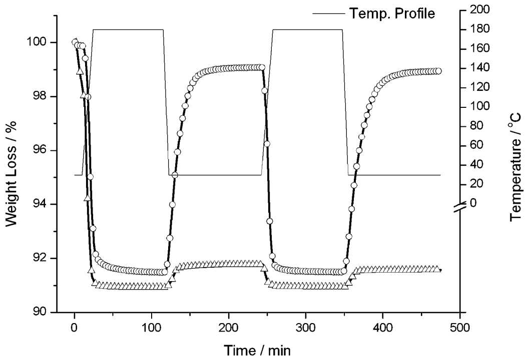

Fig. 2 Thermal gravimetric profiles of **1** (-○-) and **2** (-Δ-) for repeated heating and cooling cycles, showing selective re-sorption of H_2O for **1**.

A comparison of the hydroxide polymer **1** with the pure metal–organic polymer **2** for three key properties may be summarized; first no major improvement is found in framework thermal stability. This may be due to the fact that in both cases crystallinity is lost when the mono-dentate binding of INA ligands becomes unstable. Secondly although the channels in both **1** and **2** have similar size and both initially contain channel aqua groups, the rehydration of the channels in **1** is more rapid and complete than for polymer **2**. The enhancement in channel hydrophilicity is not a direct effect of the hydroxide function, but is supra-molecular in nature. Finally the extreme chemical lability of the coordination polymer **2** is not found for the hybrid solid **1**, albeit the chemical functionalities present should still allow it to play an active role in catalytic applications.

In conclusion the current study shows the importance of synthetic variations in forming open framework coordination polymers,[5,10] and the possible advantage of incorporating ceramic hybrid functionalities such as hydroxide for their stabilization. Furthermore the need for critical examination of both the physical *and* chemical stabilities is highlighted, which also holds for chemically stable yet physically active framework materials that are also of current interest.[11]

We wish to thank the Research Grants Council of Hong Kong for financial support (grants 6061/98P and 6128/01P).

Notes and references

‡ *Synthesis and data*: for **1**: 140 mg (0.6 mmol) $Cu(NO_3)_2\cdot 2.5H_2O$, 65 mg (0.5 mmol) H-INA in 5 mL (275 mmol) H_2O heated in a 23 mL Teflon cup at 180 °C for 1 day (pH 4) gives 60 mg $[Cu(OH)(INA)]\cdot H_2O$ **1**, 55% yield. $C_6H_5CuNO_3\cdot H_2O$, $M = 220.7$, Calc. (found): C, 32.65(32.55); H, 3.17 (2.94); N, 6.35 (6.41%). TGA: Δw −8.2% (100–150 °C); −44.8% (270–300 °C). Powder XRD: *d*/Å, *hkl* (intensity): 9.99, 0 1 1 (100); 4.99, 0 2 2 (50); 4.15, 0 1 3 (20); 3.22, 1 1 1 (90); 3.21, 1 2 0 (40). For **2**: 120 mg (0.5 mmol) $Cu(NO_3)_2\cdot 2.5H_2O$, 190 mg (1.5 mmol) H-INA in 5 mL (275 mmol) H_2O heated in a 23 mL Teflon cup at 180 °C for 3 days (pH 3) gives 110 mg $[Cu(INA)_2]\cdot 2H_2O$ **1**, 65% yield. $C_{12}H_{12}CuN_2O_6$, $M = 343.8$, Calc. (found): C, 41.90 (42.26); H, 3.49 (3.33); N, 8.15 (8.36). TGA: Δw −7.0% (100–150 °C); −53.5% (290–320 °C). Powder XRD: *d*/Å, *hkl*, (intensity): 8.20, 0 2 1 (100); 4.63, 1 1 −1 (55); 4.22, 1 3 0 (65); 4.10, 0 4 2 (65); 3.86, 1 1 −2 (95). For **3**: powder XRD: *d*/Å, *hkl* (intensity): 8.56, 0 0 1 (5); 6.34, 0 1 0 (5); 5.71, 1 0 −1 (100); 3.35, 1 −2 0 (15); 3.27, 0 2 −1 (10).

§ Crystal data for **1–3** provided as ESI. CCDC reference numbers 179661–179663. See http://www.rsc.org/suppdata/cc/b2/b201501n/ for crystallographic data in CIF or other electronic format.

1 S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1739; O. M. Yaghi, H. Li, C. Davis, D. Richardson and R. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268; M. J. Zaworotko, *Chem Commun.*, 2001, 1.

2 K. Waizumi, M. Takuno, N. Fukushima and H. Masuda, *J. Coord. Chem.*, 1998, **44**, 269.

3 J. Y. Lu and A. M. Babb, *Chem. Commun.*, 2001, 821.

4 S. S-Y. Chui, S. M-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148.

5 I. D. Williams, S. S-Y. Chui, S. M-F. Lo, M. Wu, J. A. Cha, T. S-C. Law, H. H-Y. Sung, F. L-Y. Shek, J. L. Gao and T. M. Fasina, *Stud. Surf. Sci. Catal.*, 2000, **129**, 459; S. S-Y. Chui, A. Siu, X. Feng, Z. Y. Zhang, T. C. W. Mak and I. D. Williams, *Inorg. Chem. Commun.*, 2001, **4**, 467.

6 S. O. H. Gutschke, D. J. Price, A. K. Powell and P. T. Wood, *Eur. J. Inorg. Chem.*, 2001, 2739.

7 H. Li, M. Eddouadi, M. O'Keefe and O. M. Yaghi, *Nature*, 1999, **402**, 276.

8 R-G. Xiong, S. R. Wilson and W. Lin, *J. Chem. Soc., Dalton Trans.*, 1998, 4089.

9 L. A. Gerrard and P. T. Wood, *Chem. Commun,*, 2000, 2107; S. O. H. Gutschke, M. Molinier, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed.*, 2001, **40**, 1920.

10 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.

11 S. K. Makinen, N. J. Melcer, M. Parvez and G. K. H. Shimizu, *Chem. Euro. J.*, 2001, **7**, 5176.