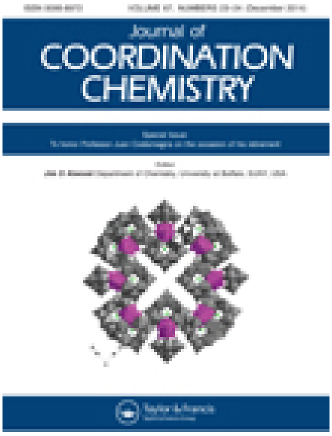
This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:30
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Click for updates

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

The quest for hydrogen bond-based metal organic nanotubes (MONT)

Andrea Ienco[a], Maria Caporali[a], Ferdinando Costantino[ab], Annalisa Guerri[c], Gabriele Manca[a], Simonetta Moneti[a] & Maurizio Peruzzini[a]
[a] Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, Firenze, Italy
[b] Dipartimento di Chimica and CEMIN, Università di Perugia, Perugia, Italy
[c] Dipartimento di Chimica, Università di Firenze, Firenze, Italy

Accepted author version posted online: 23 Sep 2014.Published online: 03 Oct 2014.

To cite this article: Andrea Ienco, Maria Caporali, Ferdinando Costantino, Annalisa Guerri, Gabriele Manca, Simonetta Moneti & Maurizio Peruzzini (2014) The quest for hydrogen bond-based metal organic nanotubes (MONT), Journal of Coordination Chemistry, 67:23-24, 3863-3872, DOI: 10.1080/00958972.2014.964698

To link to this article: http://dx.doi.org/10.1080/00958972.2014.964698

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

Journal of Coordination Chemistry, 2014
Vol. 67, Nos. 23–24, 3863–3872, http://dx.doi.org/10.1080/00958972.2014.964698

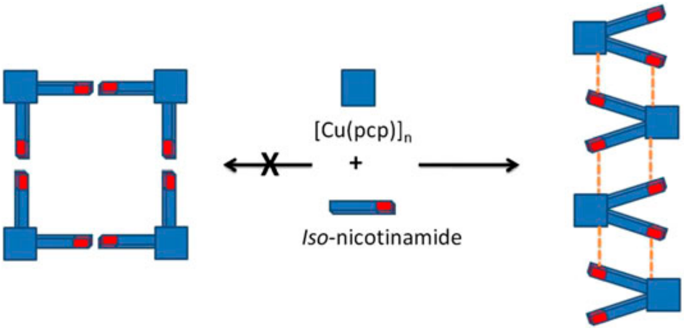
Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

The quest for hydrogen bond-based metal organic nanotubes (MONT)

ANDREA IENCO*†, MARIA CAPORALI†, FERDINANDO COSTANTINO†‡,
ANNALISA GUERRI§, GABRIELE MANCA†, SIMONETTA MONETI† and
MAURIZIO PERUZZINI*†

†Istituto di Chimica dei Composti Organometallici, Consiglio Nazionale delle Ricerche, Firenze, Italy
‡Dipartimento di Chimica and CEMIN, Università di Perugia, Perugia, Italy
§Dipartimento di Chimica, Università di Firenze, Firenze, Italy

(*Received 7 July 2014; accepted 28 August 2014*)



Given the ability of forming homomeric amide···amide dimer by *iso*-nicotinamide (*nda*), we postulate the existence of a hydrogen bond equivalent of the iso-reticular metal organic nanotubes (MONT) built by using copper, p,p′-diphenylmethylene-diphosphinate (pcp), and bipyridine. We obtained the desired primary arrangement of Cu/pcp/nda consisting of a 1-D chain. Instead of the expected amide/amide dimer, the NH_2 groups were engaged in H-bonding networks with the phosphinate ligands in a series of 2-D slabs. The differences and the similarities of the Cu/pcp chains in known MONTs and in the reported structure are also highlighted.

Keywords: Coordination polymers; MONT; Phosphinates; X-ray structure; Copper

1. Introduction

Metal organic nanotubes (MONTs) are single nanoobjects constituted by a hollow cylinder with solid metal organic walls surrounding a free space [1]. They are rare and constitute a very narrow class among known metal organic frameworks [1–20]. We have described the

---

*Corresponding authors. Email: andrea.ienco@iccom.cnr.it (A. Ienco); maurizio.peruzzini@iccom.cnr.it (M. Peruzzini)
This contribution is dedicated to our friend, Professor Juan Costamagna, on the occasion of his retirement.

© 2014 Taylor & Francis

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

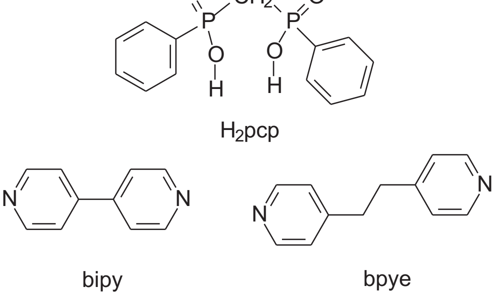
first two chemically equivalent and iso-reticular but not iso-structural MONTs, $[Cu_2(pcp)_2\text{-}bipy] \cdot 5H_2O]_n$, **1**, [18] and $[[Cu_2(pcp)_2bpye]{\cdot}2.5H_2O]_n$, **2**, [19] where pcp = p,p′-diphenylmethylene-diphosphinate, bipy = 4,4′-bipyridine, and bpye = 1,2-bis(4-pyridyl)ethane as shown in scheme 1. Although bidentate phosphinate-based ligands have been rarely used for coordination polymers, the obtained networks present a large variety of structural architectures with dimensionality ranges from 1-D to 3-D [21].

Our MONTs consist of single-walled tubules packed together along the crystallographic *c* axis by a soft network of van der Waals interactions. As highlighted in figure 1, each tube is formed by four columns of the 1-D $[Cu(pcp)]_n$ connected by the bipyridine ligands. The MONTs are self-assembled in water by mixing in appropriate ratio of copper salt, the pcp ligand, and a bipyridine ligand. Varying the synthetic conditions, it was possible to prepare nanosized rods with a small number of aggregated nanotubes [19].

A different behavior in gas up-taking was noticed for the bulk crystalline phase in comparison to the nanostructured material. We also found that **1** has remarkable stability in water [22]. This is a very important property for materials that may be used in industrial applications such as CO_2 separation or storage as well as in reactions performed in water [23]. It has been observed that in water, **2** progressively transforms in a non-porous more dense pseudo-polymorphic phase after a few days. We found out that this process has to be correlated with the existence of a thermodynamic more stable phase for **2** whereas for **1** the corresponding phase has a predicted unfavorable crystal packing [22].

Amide moieties form a homomeric amide···amide dimer thanks to the self-complementarity nature of its hydrogen bond donor/acceptor forming a $R_2^2(8)$ hydrogen bond cycle as shown in scheme 2. In particular, *iso*-nicotinamide (*nda*) could be used as a supramolecular replacement of a 4,4′-bipyridine [24].

Therefore, in this manuscript we planned to replace the bipy and bpye with *iso*-nicotinamide dimer to obtain an iso-reticular and amide-amide hydrogen-bonded MONT. In principle, we were confident that the copper and pcp have a very strong tendency to form a 1-D chain and that the pyridine nitrogen could be easily involved in coordination to copper. There are other hydrogen bonding acceptors for the NH_2 groups that can disrupt the *iso*-nicotinamide dimer. Thus, we decided to explore this chemistry and herein report our attempts to form a hydrogen-bonded MONT using the *iso*-nicotinamide (*nda*). Although we failed to obtain the desired material, thanks to the unexpected results, we learned something new on the structures of MONT **1** and **2** as well as on the way the $[Cu(pcp)]_n$ columns self assembled.



Scheme 1. Ligands used for building MONT **1** and **2**.

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

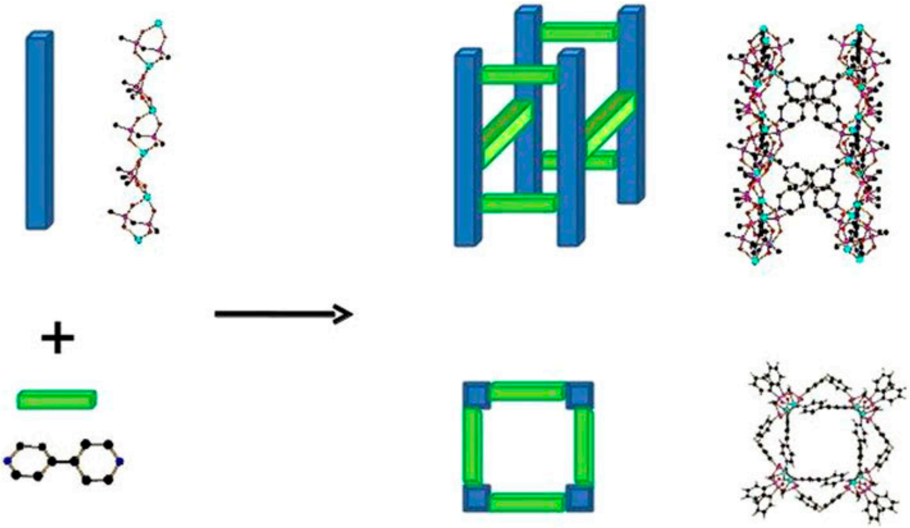
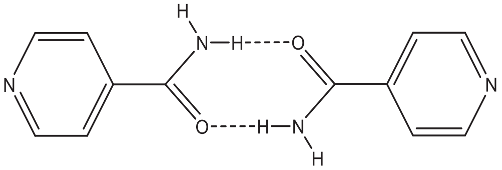


Figure 1. Schematic representation of the building of a diphosphinate MONT. Four $[Cu(pcp)]_n$ chains are connected by bipyridine. A lateral and a top view of MONT are shown on the upper right and lower right, respectively.



Scheme 2. Homomeric *iso*-nicotinamide dimer.

2. Experimental

2.1. *Materials and methods*

All reagents were analytical-grade commercial products and were used without purification. The p,p′-diphenylmethylene-diphosphinic acid (H_2pcp) was prepared as previously described [25]. Elemental analyses (C, H, N) were performed with an EA 1108 CHNS-O automatic analyzer.

2.2. *Synthesis of [Cu(pcp)nda]$_n$, 3*

A solution of $Cu(CH_3COO)_2{\cdot}H_2O$ (0.020 g, 0.1 mM) in 6 mL of H_2O was added to a solution of H_2pcp (0.030 g, 0.1 mM) and *nda* (0.025 g, 0.2 mM) in 50 mL of H_2O at 90 °C. The resulting reaction mixture was allowed to stand at 90 °C, exposed to air, for ca. 2 h. After this time, the light blue needles which formed were separated by filtration, washed with water, and dried in air at room temperature. Yield: 75% (based on H_2pcp). Anal. Calcd for $C_{19}H_{18}CuN_2O_5P_2$ (%): C, 47.56; H, 3.78; N, 5.84. Found (%): C, 47.51; H, 3.83; N, 5.90.

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

2.3. *X-ray structure determination*

A summary of the crystal data are given in table 1. The data collection was performed at room temperature on an Oxford Diffraction Excalibur 3 diffractometer equipped with Mo-Kα radiation and a CCD area detector. Data collections were performed with CrysAlis CCD [26] and data reductions were carried out with CrysAlis RED [27]. Absorption correction was applied through the program ABSPACK [27]. The structure was solved using direct methods using Sir97 [28] and refined on F^2 by full-matrix least squares techniques with SHELXL [29]. All non-hydrogen atoms were refined anisotropically. Hydrogens of the coordinated water were found in the Fourier map and refined with distance restraints. The hydrogens bonded to carbons were introduced in calculated positions.

3. Results and discussion

The reaction between H_2pcp, *nda* and copper acetate in boiling water afforded light blue crystals of $[Cu(nda)(pcp)]_n$, **3**. Single-crystal X-ray analysis of **3** revealed a 1-D structure. As expected, we isolated a polymeric structure that exactly corresponds at one fourth of the MONT **1** and **2**. The asymmetric unit, shown in figure 2, contains one copper, one pcp, and one *nda*. Table 2 reports selected distances and angles. The copper is surrounded by four oxygens of two different pcp ligands and by one nitrogen of the *nda*. The overall coordination around copper can be described as almost square pyramidal geometry ($\tau = 0.29$) [30]. The apical position is occupied by O4 and Cu1–O4 distance is slightly longer than other

Table 1. Crystal data and structure refinement for **3**.

Empirical formula	$C_{19}H_{18}CuN_2O_5P_2$
Formula weight	479.83
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P\,2_1/c$
Unit cell dimensions	$a = 14.9144(11)$ Å $b = 14.3798(8)$ Å $c = 9.6643(4)$ Å $\beta = 99.551(6)°$
Volume	2043.9(2) $Å^3$
Z	4
Density (calculated)	1.559 mg m^{-3}
Absorption coefficient	1.259 mm^{-1}
F (0 0 0)	980
Crystal size	0.2 × 0.1 × 0.05 mm^3
θ Range for data collection	4.16°–29.06°
Index ranges	$-20 \le h \le 19$, $-13 \le k \le 19$, $-12 \le l \le 12$
Reflections collected	15,048
Independent reflections	4765 [R(int) = 0.0804]
Completeness to $\theta = 26.5°$	99.6%
Absorption correction	Semi-empirical from equivalents
Max and min transmission	1 and 0.70137
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4765/0/268
Goodness-of-fit on F^2	0.793
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0397$, $wR_2 = 0.0438$
R indices (all data)	$R_1 = 0.1093$, $wR_2 = 0.0483$
Largest diff. peak and hole	0.362 and −0.39 e $Å^{-3}$

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

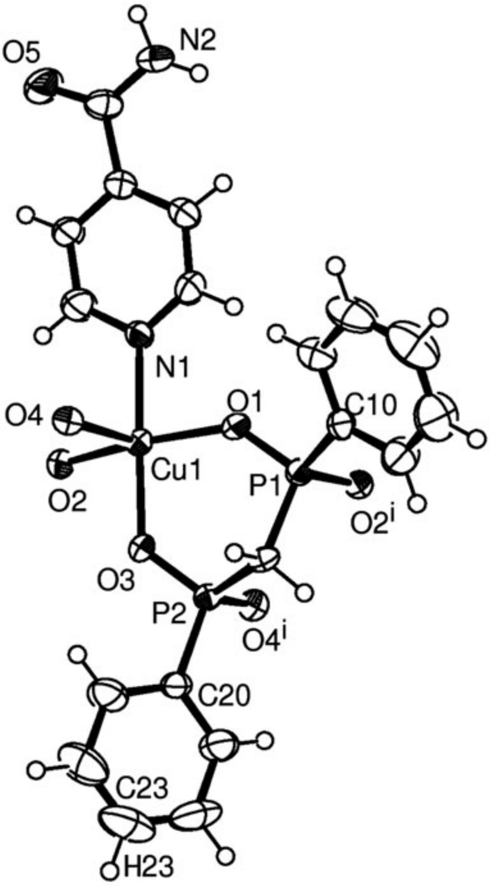


Figure 2. ORTEP drawings of the asymmetric units of **3**. For sake of clarity O2^{i} and O4^{i} are added to complete the pcp ligand (symmetry transformations: #i x, $-y + 1/2$, $z + 1/2$).

Table 2. Selected bond lengths (Å) and angles (°) for **3**.

	Bond distance		Angle
Cu(1)–O(1)	1.9468(16)	O(1)–Cu(1)–O(3)	93.19(8)
Cu(1)–O(2)	1.9989(17)	O(1)–Cu(1)–O(2)	162.34(8)
Cu(1)–O(3)	1.974(2)	O(3)–Cu(1)–O(2)	86.12(8)
Cu(1)–O(4)	2.1697(19)	O(1)–Cu(1)–N(1)	87.80(9)
Cu(1)–N(1)	2.065(3)	O(3)–Cu(1)–N(1)	174.51(9)
P(1)–O(1)	1.5092(18)	O(2)–Cu(1)–N(1)	91.30(9)
P(1)–O(2)#1	1.512(2)	O(1)–Cu(1)–O(4)	101.43(7)
P(1)–C(10)	1.790(3)	O(3)–Cu(1)–O(4)	92.79(8)
P(1)–C(1)	1.799(3)	O(2)–Cu(1)–O(4)	96.23(7)
P(2)–O(3)	1.5082(17)	N(1)–Cu(1)–O(4)	92.31(9)
P(2)–O(4)#1	1.4967(19)		
P(2)–C(1)	1.815(2)		
P(2)–C(20)	1.785(3)		

Note: Symmetry transformations used to generate equivalent atoms: #1 x, $-y + 1/2$, $z + 1/2$.

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

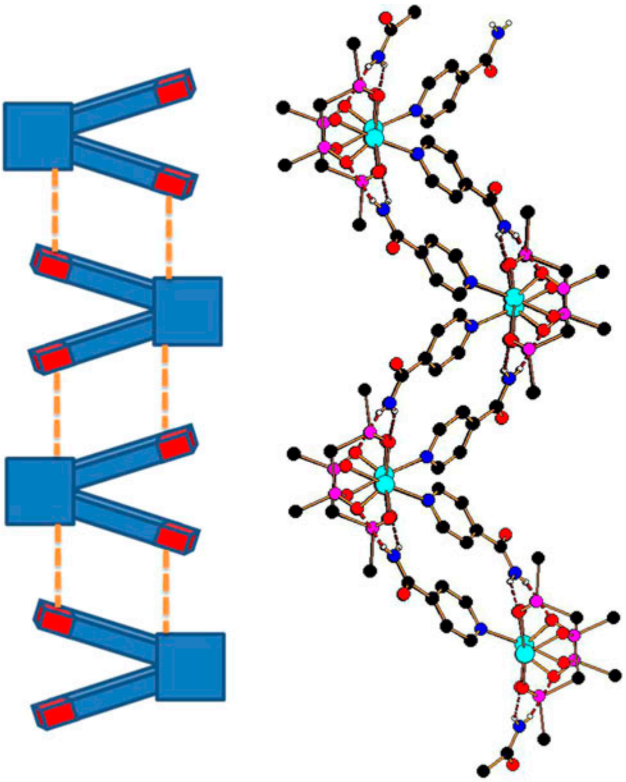


Figure 3. Schematic (left side) and ball and stick drawing of the 2-D sheet of **3**, for which the 1-D chains are bonded through the hydrogen bond between the amide hydrogen and phosphinate oxygens. The phenyl rings except the *ipso* carbon were removed for clarity.

Cu1–O bonds (2.170(2) Å *versus* 1.973(2) Å as average). The Cu1–N1 distance is 2.065 (3) Å. These linkages are in good agreement with those found for **1** and **2**. The pcp connects two coppers in a bridging mode, forming the 1-D $[Cu(pcp)]_n$ chain running along the crystallographic *c* axis. The overall conformation of the chain is the same as in **1** and **2**.

The *nda* coordinates through the pyridine nitrogen. Unfortunately, the amide does not form the expected hydrogen bond dimer. The amidic N2 were instead engaged in hydrogen bonds with O2 and O4 oxygen atoms of adjacent 1-D chains ($N2\cdots O2^{i} = 3.126(3)$ Å and $N2\cdots O4^{ii} = 2.936(4)$ Å with $i = -x + 1,\ y + 1/2,\ -z + 1/2$ and $ii = -x + 1,\ -y + 1/2,\ -z$). As shown in figure 3, the 1-D chains pack in a head/tail motif to form 2-D hydrogen bond slabs parallel to the *b* and *c* crystallographic directions. Eventually, the 2-D planes extended in the third dimension thanks to the $C–H\cdots\pi$ (see for instance the distance $H23\cdots C15^{i}$ is 3.409(3) Å with $i = -x,\ -y + 1,\ -z + 1$) and $\pi\cdots\pi$ interactions among the phenyl rings bonded to P2 where the ring centroid distance is 4.029(4) Å as shown in figure 4.

While we failed in obtaining the desired hydrogen bond MONT, we still can learn something from the comparison of the MONTs with **3**. The $[Cu(pcp)]_n$ chain is a secondary building unit (SBU). In **1** and **2**, the column is built using two independent copper ions and pcp ligands while in **3** just one copper and one pcp are repeated thanks to a glide plane. An analytical comparison could be done using the geometric parameters of table 3 and

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

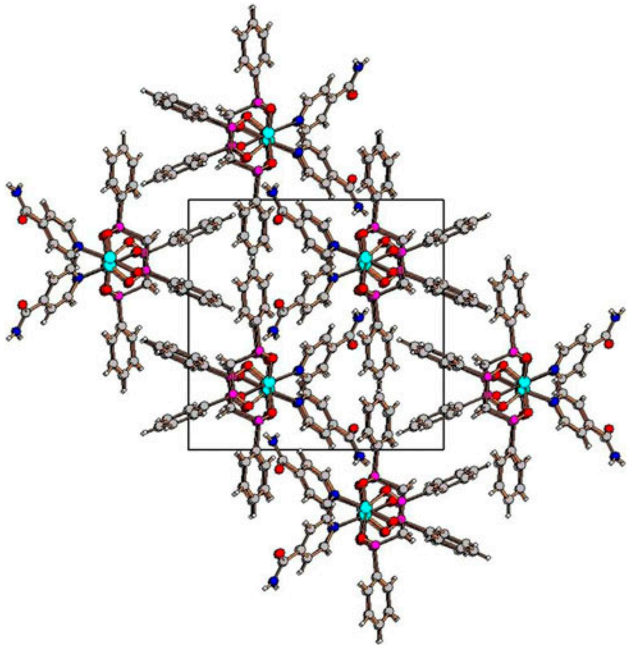


Figure 4. Packing diagram of **3** showing the C–H···π and π···π interactions among the phenyl rings.

Table 3. Selected geometrical parameters for the Cu/pcp SBU [distances (Å) and angles (°)].

	d_a	d_{11}	d_{12}	d_{21}	w
MONT **1**	0.72	9.64	5.34	4.30	104
MONT **2**	0.31	9.77	4.91	4.86	94
3	0.20	9.66	4.83	4.83	54

illustrated in figure 5. In particular, table 3 reports the different distances between copper ions and the line equidistant from the copper ions in the middle of the $[Cu(pcp)]_n$ chain. The angle *w* is defined between the planes of the nitrogens of the pyridines and the axis of the [Cu(pcp)] chain. As it can be visually considered looking at figures 1 and 3, the value of *w* goes from 54.2° to 104.4° for **3** and **1**, respectively. On this basis, the Cu/pcp SBU is flexible and it can easily assume different conformations. The chain is found to be deformed also when bonded in the solid state. The dynamic behavior found for MONT **2** [22] is in line with this kind of analysis.

We also tried to obtain a [Cu(pcp)] column without interference of the hydrogen bond using pyridine instead of the *iso*-nicotinamide. After several days, instead of the expected product, we obtained the already reported $[Cu(pcp)(H_2O)_2 \cdot H_2O]_n$ [31]. These results highlight the importance of hydrogen bonds for the stability of **3** and show that the Cu–pcp interactions are more efficient than the Cu–pyridine interaction. Also water molecules are able to compete with the nitrogen donor more effectively than the oxygens of the phosphinate. This

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

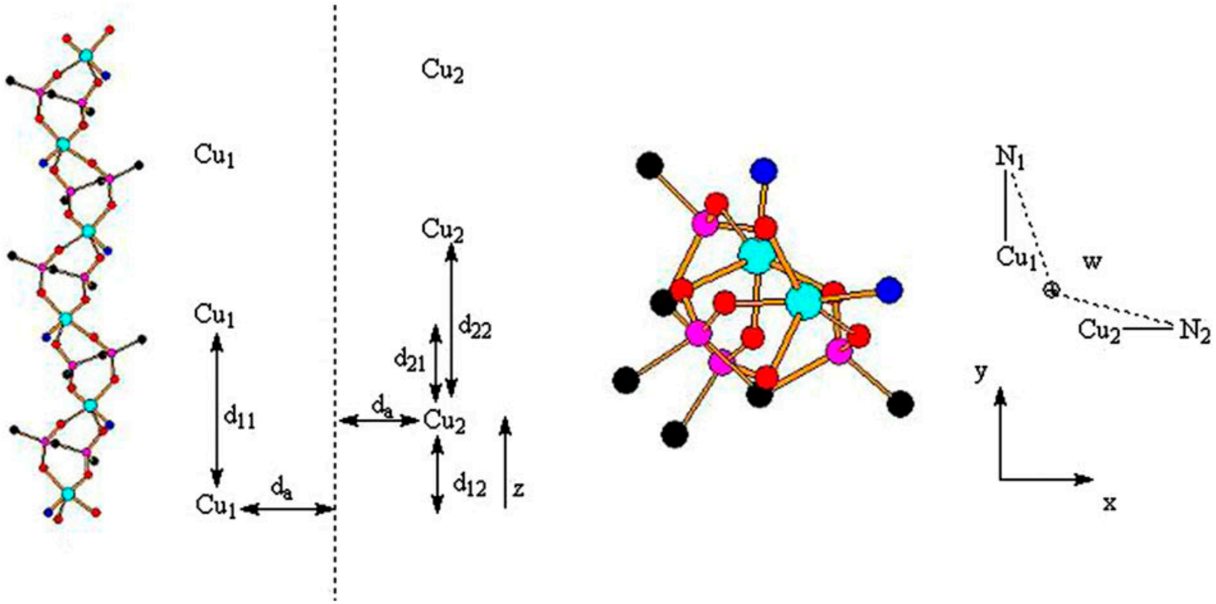


Figure 5. Schematic representation of the geometric parameters reported in table 3.

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014

is indirect confirmation of the assumed mechanism for the solid state transformation of MONT **2** where the breaking of Cu–N bond has to occur together with the hydrolysis of the Cu–O bond by a water molecule [22].

4. Conclusion

With the aim of obtaining a hydrogen bond equivalent of the copper diphosphinate **1** and **2** MONTs, we replaced the bipyridine with *iso*-nicotinamide (*nda*), a potential supramolecular equivalent ligand for the building of the tubular structures. We succeeded in obtaining the desired arrangement for the Cu/pcp skeleton but the amide groups of *iso*-nicotinamide did not behave as expected. Instead of amide-amide hydrogen bonds, the 1-D chains pack in a head-to-tail motif forming 2-D hydrogen bond slabs with the amide hydrogens interacting with the oxygens of diphosphinate groups. Comparison of the obtained structure with the Cu/pcp chains of MONTs **1** and **2** allowed us to stress the importance of the hydrogen bonds in the packing of **3** and to highlight the capacity of the chain to assume a variety of conformations in different supramolecular environment.

Supplementary material

CCDC-1010392 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

This work and the grant of G.M. were financially supported by Ente Cassa di Risparmio di Firenze project “Firenze Hydrolab^2” which is gratefully acknowledged.

References

[1] P. Thanasekaran, T.-T. Luo, C.-H. Lee, K.-L. Lu. *J. Mater. Chem.*, **21**, 13140 (2011).

[2] M.A.G. Aranda, A. Cabeza, S. Bruque, D.M. Poojary, A. Clearfield. *Inorg. Chem.*, **37**, 1827 (1998).

[3] M. Hong, Y. Zhao, W. Su, R. Cao, M. Fujita, Z. Zhou, A.S.C. Chan. *Angew. Chem. Int. Ed.*, **39**, 2468 (2000).

[4] R. Wang, M. Hong, J. Luo, R. Cao, J. Weng. *Chem. Commun.*, 1018 (2003).

[5] A.L. Pickering, G. Seeber, D.L. Long, L. Cronin. *Chem. Commun.*, 136 (2004).

[6] Z. Fei, D. Zhao, T.J. Geldbach, R. Scopelliti, P.J. Dyson, S. Antonijevic, G. Bodenhausen. *Angew. Chem. Int. Ed.*, **44**, 5720 (2005).

[7] H.-T. Zhang, Y.-Z. Li, T.-W. Wang, E.N. Nfor, H.-Q. Wang, X.-Z. You. *Eur. J. Inorg. Chem.*, **2006**, 3532 (2006).

[8] J. Xia, W. Shi, X.-Y. Chen, H.-S. Wang, P. Cheng, D.-Z. Liao, S.-P. Yan. *Dalton Trans.*, 2373 (2007).

[9] M.N. Kozlova, S. Ferlay, S.E. Solovieva, I.S. Antipin, A.I. Konovalov, N. Kyritsakas, M.W. Hosseini. *Dalton Trans.*, 5126 (2007).

[10] X.C. Huang, W. Luo, Y.F. Chen, X.J. Lin, D. Li. *Chem. Commun.*, 3995 (2008).

[11] F. Dai, H. He, D. Sun. *J. Am. Chem. Soc.*, **130**, 14064 (2008).

[12] F. Dai, H. He, D. Sun. *Inorg. Chem.*, **48**, 4613 (2009).

[13] T.-T. Luo, H.-C. Wu, Y.-C. Jao, S.-M. Huang, T.-W. Tseng, Y.S. Wen, G.-H. Lee, S.-M. Peng, K.-L. Lu. *Angew. Chem. Int. Ed.*, **48**, 9461 (2009).
[14] S. Kennedy, G. Karotsis, C.M. Beavers, S.J. Teat, E.K. Brechin, S.J. Dalgarno. *Angew. Chem. Int. Ed.*, **49**, 4205 (2010).
[15] T. Panda, T. Kundi, R. Banarjee. *Chem. Commun.*, **48**, 136 (2012).
[16] S. Wu, S. Wang, J. Diwu, W. Depmeier, T. Malcherek, E.V. Alekseev, T.E. Albrecht-Schmitt. *Chem. Commun.*, **48**, 3479 (2012).
[17] C. Fang, Q.-K. Liu, J.-P. Ma, Y.-B. Dong. *Inorg. Chem.*, **51**, 3923 (2012).
[18] T. Bataille, F. Costantino, P. Lorenzo-Luis, S. Midollini, A. Orlandini. *Inorg. Chim. Acta*, **361**, 327 (2008).
[19] T. Bataille, S. Bracco, A. Comotti, F. Costantino, A. Guerri, A. Ienco, F. Marmottini. *CrystEngComm*, **14**, 7170 (2012).
[20] C.R. Murdock, D.M. Jenkins. *J. Am. Chem. Soc.*, **136**, 10983 (2014).
[21] (a) J. Beckmann, F. Costantino, D. Dakternieks, A. Duthie, A. Ienco, S. Midollini, C. Mitchell, A. Orlandini, L. Sorace. *Inorg. Chem.*, **44**, 9416 (2005); (b) F. Costantino, S. Midollini, A. Orlandini, L. Sorace. *Inorg. Chem. Commun.*, **9**, 591 (2006); (c) T. Bataille, F. Costantino, A. Ienco, A. Guerri, F. Marmottini, S. Midollini. *Chem. Commun.*, 6381 (2008); (d) F. Costantino, A. Ienco, S. Midollini. *Cryst. Growth Des.*, **10**, 7 (2010); (e) F. Costantino, A. Ienco, S. Midollini, A. Orlandini, A. Rossin, L. Sorace. *Eur. J. Inorg. Chem.*, **2006**, 3179 (2010); (f) L.-J. Dong, C.-C. Zhao, X. Xu, Z.-Y. Du, Y.-R. Xie, J. Zhang. *Cryst. Growth Des.*, **12**, 2052 (2012).
[22] M. Taddei, A. Ienco, F. Costantino, A. Guerri. *RSC Adv.*, **3**, 26177 (2013).
[23] (a) P.M. Schoenecker, C.G. Carson, H. Jasuja, C.J.J. Flemming, K.S. Walton. *Ind. Eng. Chem. Res.*, **51**, 6513 (2012); (b) J.A. Greathouse, M.D. Allendorf. *J. Am. Chem. Soc.*, **128**, 10678 (2006); (c) S.S. Kaye, A. Dailly, O.M. Yaghi, J.R. Long. *J. Am. Chem. Soc.*, **129**, 14176 (2007); (d) T.J. Wu, L.J. Shen, M. Luebbers, C.H. Hu, Q.M. Chen, Z. Ni, R.I. Masel. *Chem. Commun.*, **46**, 6120 (2010).
[24] C.B. Aakeröy, A.M. Beatty, B.A. Helfrich. *J. Am. Chem. Soc.*, **124**, 14425 (2002).
[25] (a) S. Midollini, P. Lorenzo-Luis, A. Orlandini. *Inorg. Chim. Acta*, **359**, 3275 (2006); (b) M.E. Garst. *Synth. Commun.*, **9**, 261 (1979).
[26] CrysAlis CCD. *Version 1.171.33.41 (release 06-05-2009 CrysAlis171 .NET)*, Oxford Diffraction Ltd, Abingdon, UK (2009).
[27] CrysAlis RED. *Version 1.171.33.41 (release 06-05-2009 CrysAlis171 .NET)*, Oxford Diffraction Ltd, Abingdon, UK (2009).
[28] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Crystallogr.*, **32**, 115 (1999).
[29] G.M. Sheldrick. *Acta Crystallogr.*, **A64**, 112 (2008).
[30] A.W. Addison, T.N. Rao, J. Reedijk, J. Van Rijn, G.C.J. Vershcoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).
[31] S. Ciattini, F. Costantino, P. Lorenzo-Luis, S. Midollini, A. Orlandini, A. Vacca. *Inorg. Chem.*, **44**, 4008 (2005).

Downloaded by [Institute Of Atmospheric Physics] at 15:30 09 December 2014