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Inorganic Chemistry Communications 10 (2007) 959–964
INORGANIC CHEMISTRY COMMUNICATIONS
www.elsevier.com/locate/inoche

Role of nitro-substituent in pseudo-polymorphism and in synthesis of metal carboxylato complexes of copper, zinc and manganese

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Received 21 March 2007; accepted 1 April 2007
Available online 10 May 2007

Abstract

The consequence of nitro-group attached to aromatic ring of 2-nitrobenzoato complexes of copper(II) on pseudo-polymorphism and in synthesis of metal carboxylato complexes is demonstrated and the results are compared with analogous first row transition metal carboxylato complexes.

Keywords: 3d-Metal carboxylates; 2-Nitrobenzoato ligand; Polymorphism; Crystal structure; Aqua-bridged complexes; Paddle-wheel structure

Reticular synthesis of metallo-organic framework of carboxylato complexes needs thorough understanding of co-ordination chemistry of simple synthons [1]. Preparation of metallo-organic motif having carboxylato ligands has become increasingly important for storage materials and for molecular recognition [2]. In a recent article it is shown in zinc metallo-organic framework, that multiple number of solvents gets incorporated [3]. In a series of articles we have reported synthetic methodologies to provide varieties in structures of metal carboxylato complexes [4]. In this regard, we had observed a new class of polymorphic compounds from the orientation of nitro-groups in aqua-bridged 2-nitrobenzoato complexes of cobalt(II) [4a]. It is also observed that aqua-bridged dinuclear 2-nitrobenzoato complexes or mononuclear 2-nitrobenzoato complex of nickel(II) and cobalt(II) can be prepared [4b] by variation of reaction conditions. In the cases of nickel [4b] and cobalt [4i] complexes we could obtain pseudo-polymorphs(polymorphs due to solvent of crystallization). Thus, to delineate polymorphism in other transition metal complexes is a challenge and the understanding at basic level will lead to reticular synthesis of different polymorphs in MOF which is emerging as a new area of research. Accordingly, we have taken up structural study and synthesis through solid and solution phase to understand the polymorphism and structural consequences in a series of 2-nitrobenzoato complexes of manganese(II), copper(II) and zinc(II). Preliminary reports are presented in this manuscript.

We have studied various reactions of copper(II) acetate with 2-nitrobenzoic acid in the presence of nitrogen donor ligands [5] as listed in Scheme 1. Copper(II) acetate reacts with 2-nitrobenzoic acid and 3,5-dimethylpyrazole to give a mono-nuclear copper(II) complex (**I**). In this complex the copper has six-cordination geometry with elongated Cu–O bond along the *z*-axis. The bond distances (Å) are Cu1–N, 1.973; Cu1–O1, 1.974 and Cu1–O2, 2.685, respectively. The structure of the complex is shown in Fig. 1a. In this case we could not observe dinuclear compound either through solid state or through solution phase reactions. The two nitro-groups of the rings are oriented *trans* to each other with mirror inversion. When a similar reaction of copper(II) acetate with 2-nitrobenzoic acid was carried out in solid state followed by treatment with pyridine we obtained dinuclear complex having paddle-wheel structure (Fig. 1c). This compound can be obtained in the solvated or unsolvated form. The solvated form or pseudo-polymorphs can be easily crystallized by dissolving **III** in methanol

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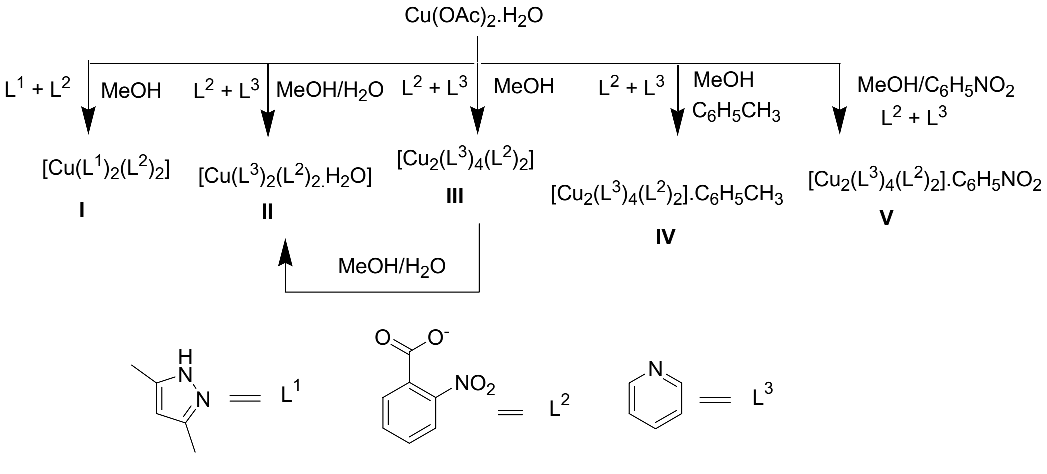
doi:10.1016/j.inoche.2007.04.026



Scheme 1.

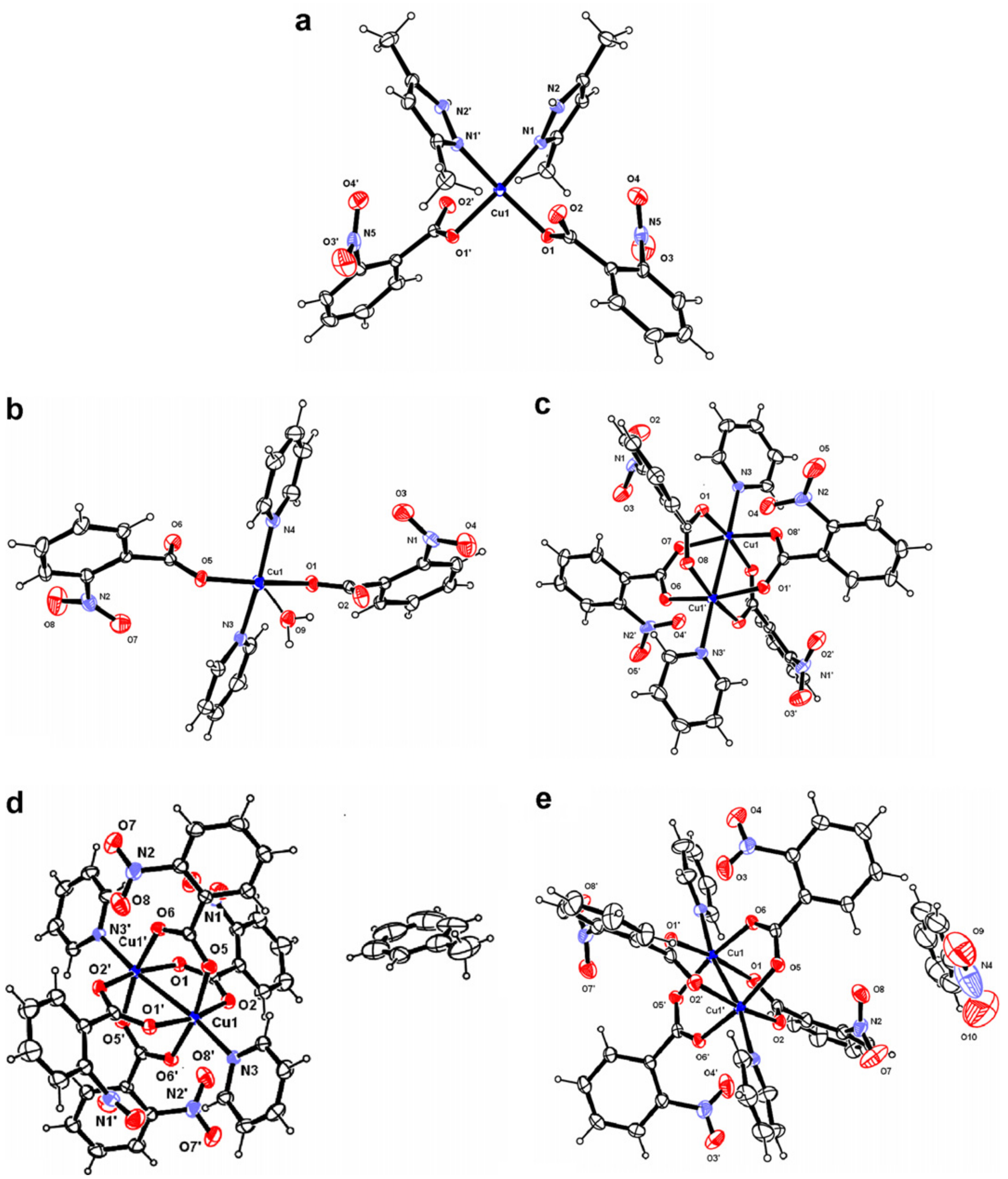


Fig. 1. a–e The crystal structures of **I**–**V** (drawn with 20% thermal ellipsoid).

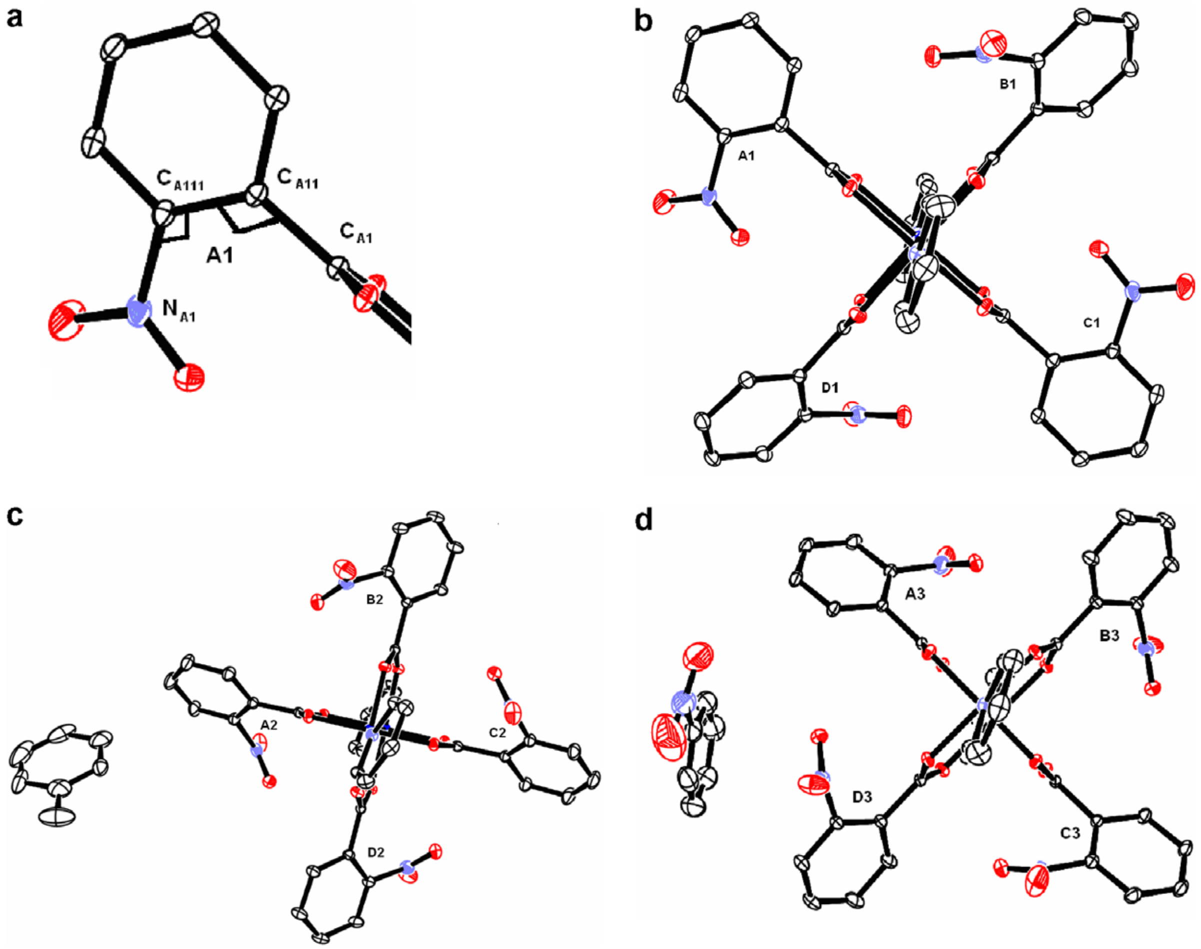


Fig. 2. Representation of torsion angles in complexes **III**–**V**. **A1** is the torsion angle between N_{A1}–C_{A111}–C_{A11}–C_{A1} in complex **III**, analogous definition holds good for torsion angles B1, C1, D1 in **IV**; A2, B2, C2, D2, in **V** and A3, B3, C3, D3 in **V**.

solution with toluene, nitrobenzene etc. The unsolvated form **III** is not stable in aqueous methanol it disproportionate to give mononuclear aqua (bis-2-nitrobenzoato) (bispyridine) copper(II) complex (**II**). The structure of complex **II** is determined by X-ray diffraction and is shown in Fig. 1b. The structure of the toluene and nitrobenzene solvated complexes **IV** and **V** and also the structure of unsolvated dinuclear copper(II) complex **III** are determined. The copper–copper distances in the complexes **III**–**V** are 2.68, 2.71, 2.71 Å, respectively, it suggests that the packing effect of solvent of crystallization plays a role on the structures. The Cu···Cu distance in copper(II) acetate [6] is 2.61 Å, which suggests that the presence of nitro-group at 2-position makes the Cu···Cu contact to slightly elongate due to obvious reason of steric congestion.

Nitro-groups of the complexes are symmetry related to each other through a C_2 axis and their orientations are analysed by looking at the torsion angles between the nitro-plane with that of aromatic ring. For torsion angle analysis we have demarcated the torsion angles by A1, B1, C1, D1 for each nitro-group in a compound by fixing the molecules at particular orientation. The three molecules are then viewed along the *z*-axis passing through the copper(II) atoms. For each pseudo-polymorph such angles are defined as illustrated in Fig. 2. The torsion angles for the three complexes **III**–**V** are listed in Table 1. From the torsion angles it is clear that in each case the orientation of nitro-groups are similar to each other and they are arranged such that the alternate nitro-groups are symmetry related with slight variations of angles for each other. The

Table 1
Different torsion angles in **III**–**V** indicating the orientation of the nitro-group

Complex	Torsion angle (°)	Torsion angle (°)	Torsion angle (°)	Torsion angle (°)
III	A1 = 4.04	B1 = −9.29	C1 = −4.04	D1 = 9.29
IV	A2 = 8.46	B2 = −9.07	C2 = −8.46	D2 = 9.07
V	A3 = −11.0	B3 = −9.08	C3 = 11.06	D3 = 9.08

highest non-planarity among nitro and aromatic ring is obtained in the complex **V** where nitrobenzene is being trapped in the lattice. Thus, the variation of the orientation of the nitro-group is attributed to the packing effect resulting from the co-crystallisation process.

The compound **II** and **III** can be distinguished by IR spectroscopy and the solid state IR spectra of the two compounds are shown in Fig. 3. The complex **II** has an aqua ligand which has the ν_{OH} at 3415 cm^{-1}. In the case of dinuclear the IR has the carboxylato group absorption frequency at 1633 cm^{-1} whereas the mononuclear carboxylato complex has strong absorptions at 1606 and 1568 cm^{-1}. The complex **IV** having toluene as solvent of crystallization has similar IR features as that of **III**, but additional peak for aromatic C=C bond frequency at 1609 cm^{-1} is observed.

We also studied similar complexation reaction with zinc acetate and observed that paddle-wheel type structure can be easily constructed from solid state reactions of zinc(II) acetate with 2-nitrobenzoic acid followed by treatment with pyridine (Scheme 2). Crystal structure of the compound is shown in Fig. 3a. The Zn···Zn separation in this complex is found to be 3.03 Å. This distance in similar dimeric unsubstituted paddle-wheel benzoate complex of zinc [7,4d] is 2.96 Å. In the 2-nitrobenzoate complexes the nitro-groups are symmetry related and the two sets of torsion angle of nitro-group with the aromatic ring are 5.63° and 0.94° suggesting that the nitro-group containing O–N–O plane is nearly perpendicular to the phenyl ring attached to it. This is not the case with copper(II) complexes, suggesting that the size of the metal and longer Zn···Zn separation reduces the steric constrains for nitro-group to twist from most favorable geometry observed in molecules where free C–N bond rotation takes place. Since two axial positions of the paddle-wheel structure are occupied by a mono-dentate pyridine ligand, we felt that use of a chelating ligand would prevent the paddle-wheel structure and give mono-nuclear structure that would serve the basic frame for polymeric structures. In fact we have succeeded in getting five co-ordinated zinc complex from the reaction of zinc acetate with 2-nitrobenzoic acid in the presence of 1,10-phenanthroline. The complex **VII** obtained from this reaction is characterized by

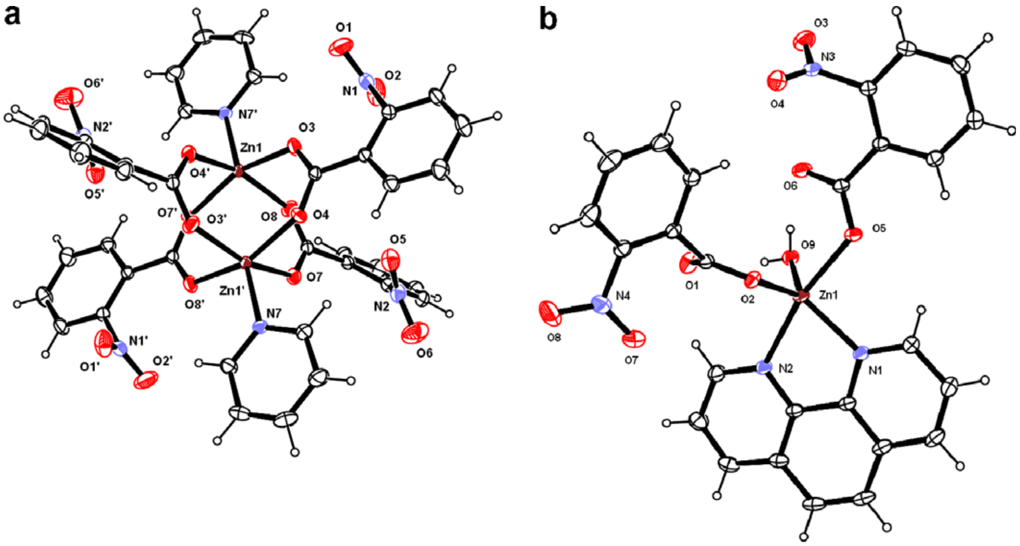
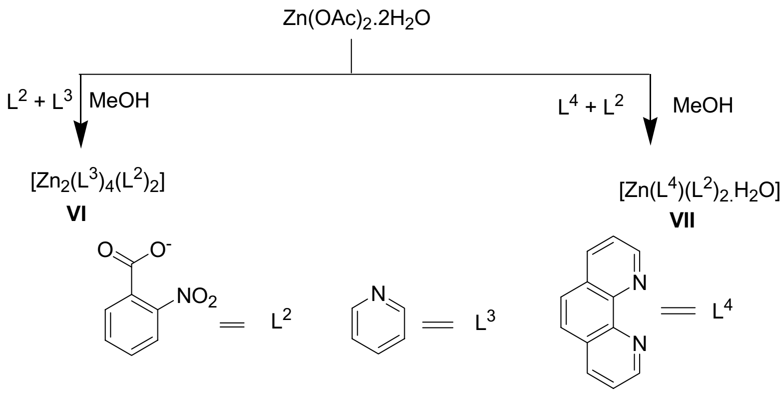


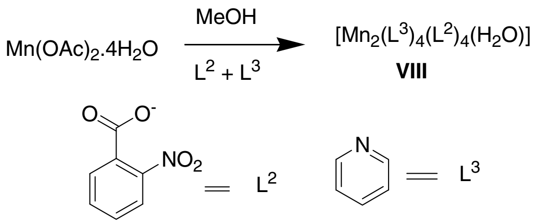
Fig. 3. a and b The crystal structures of **VI** and **VII**, respectively (drawn with 20% thermal ellipsoid).



Scheme 2.

X-ray crystallography and the structure is given in Fig. 3b. The compound has a distorted square pyramidal structure in which two carboxylate groups occupy *cis*-positions. The two nitrogen and the two oxygen atoms complete the dative sites of the basal plane. Selective bond distances in the complex are as follows: Zn1–O5, 1.99; Zn1–O2, 2.08 Zn1–O9$_{\text{(aqua)}}$, 2.04 Zn1–N1, 2.17; Zn1–N2, 2.08 Å.

While carrying out reaction of manganese acetate with 2-nitrobenzoic acid in the presence of pyridine we have observed aqua and carboxylato bridged manganese dinuclear complex having two pyridines per manganese (Scheme 3). This is similar to our observation on reactions of cobalt(II) [4i] and nickel(II) [4b] with 2-nitrobenzoate under solid phase followed by treatment with pyridine; in which we obtained such aqua and carboxylato bridged complexes. The structure of the complex is shown in Fig. 4. In this complex there are both bridging and mono-dentate carboxylato groups are present. The compound is not symmetric and the dihedral angle of the nitro-groups to the phenyl ring attached to it are −0.79° and −5.53° for the bridging pair, whereas for the monodentate pair are 1.56° and 10.75°, respectively. The manganese and manganese separation is 3.65 Å. The analogous trifluoroacetato complex [8] compound has Mn···Mn separation 3.74 Å. However more close structures are the compound of cobalt and nickel with identical environment which shows Co–Co separation [4i] distance is 3.65 Å Ni–Ni [4b] distance is 3.56 Å, respectively. Since ionic radii of $Mn^{2+} > Co^{2+} > Ni^{2+}$, but the M–M separation in the aqua-bridged 2-nitrobenzoato dinuclear complexes are of the order of $Mn^{2+} \sim Co^{2+} > Ni^{2+}$; in addition to the steric factor other factors such as magnetic interactions has a role in deciding these M–M separations, however this needs further experimental evidences.



Scheme 3.

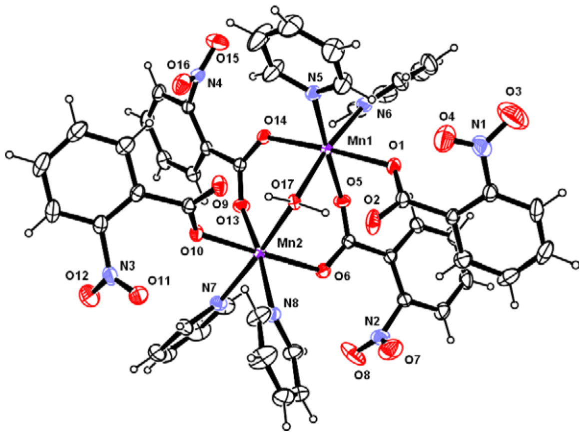


Fig. 4. The crystal structures of **VIII** (drawn with 20% thermal ellipsoid) The select bond distances Mn2–O9, 2.19; Mn2–O13, 2.15; Mn2–N8, 2.27; Mn2–O6 , 2.19; Mn2–O17$_{\text{(aqua)}}$, 2.22; Mn1–O14, 2.17; Mn1–O5, 2.17; Mn1–O17$_{\text{(aqua)}}$, 2.23; Mn1–N5, 2.26; Mn1–N6, 2.27 Å.

In conclusion we have shown here the diverse scope for formation of pseudo-polymorphs in 2-nitrobenzoato complexes of copper(II) and also shown the complexity involved in understanding the basic frameworks that could serve as the guideline for building metallo-organic frameworks. Works are in progress to use these synthons for reticular synthesis of polymorphs of metallo-organic framework.

Acknowledgements

The authors thank Department of Science and Technology, New Delhi, India, for financial assistance and X-ray diffraction facility.

Appendix A. Supplementary materials

CCDC 638265, 638266, 638267, 638268, 639910, 639911, 639912, and 640151 contain the supplementary crystallographic data for I, II, III, IV, V, VI, VII, and VIII. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.04.002.

References

[1] (a) O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature 423 (2003) 705;
(b) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, Acc. Chem. Res. 31 (1998) 474.

[2] (a) F.A. Cotton, C. Lin, C.A. Murillo, Acc. Chem. Res. 34 (2001) 759;
(b) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319;
(c) B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
(d) S.L. James, Chem. Soc. Rev. 32 (2003) 276;
(e) R. Murugavel, M.G. Walawalkar, M. Dan, H.W. Roesky, C.N.R. Rao, Acc. Chem. Res. 37 (2004) 763;
(f) S. Noro, S. Kitagawa, M. Kondo, K. Seki, Angew. Chem., Int. Ed. 39 (2000) 2081.

[3] Q.-R. Fang, G.-S. Zhu, M. Xue, Q.-L. Zhang, J.-Y. Sun, X.-D. Guo, S.-L. Qiu, S.-T. Xu, P. Wang, D.-J. Wang, Y. Wei, Chem. Eur. J. 12 (2006) 3754.

[4] (a) A. Karmakar, R.J. Sarma, J.B. Baruah, Eur. J. Inorg. Chem. (2007) 643;
(b) A. Karmakar, R.J. Sarma, J.B. Baruah, Eur. J. Inorg. Chem. (2006) 4673;
(c) N. Barooah, A. Karmakar, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 1251;
(d) A. Karmakar, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 1169;

(e) K. Deka, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 931;
(f) N. Barooah, R.J. Sarma, J.B. Baruah, Eur. J. Inorg. Chem. (2006) 2942;
(g) A. Karmakar, K. Deka, R.J. Sarma, J.B. Baruah, Inorg. Chem.Commun. 9 (2006) 836;
(h) K. Deka, N. Barooah, R.J. Sarma, J.B. Baruah, J. Mole. Struct. 827 (2007) 44;
(i) A. Karmakar, R.J. Sarma, J.B. Baruah, Polyhedron 26 (2007) 1347.

[5] For the solid phase synthesis as well as solution phase synthesis; the synthetic procedures were identical to the ones reported in Ref. [4], but with appropriate metal salts and ligands are used in each cases.

[6] E.C. Constable, Chem. Ind. (1994) 56.

[7] T. Ohmura, W. Mori, T. Takai, T. Ikeda, A. Maeda, Mater. Sci. Poland 23 (2005) 729.

[8] S.-B. Yu, S.J. Lippard, I. Shweky, A. Bino, Inorg. Chem. 31 (1992) 3502.