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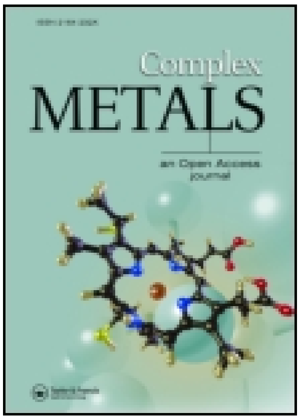

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Synthesis and crystal structure of N-6-[(4-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester zinc complex

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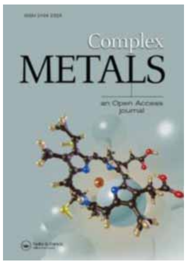

Article

Synthesis and crystal structure of *N*-6-[(4-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester zinc complex

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A reaction between monoamide ligand namely *N*-6-[(4-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L4**) and zinc chloride has been attempted in order to generate a carboxylate complex suitable for anion inclusion. This reaction gives rise to a formation of discrete complex with general formula $[ZnCl_2(\mathbf{L4})_2]$. Complex $[ZnCl_2(\mathbf{L4})_2]$ crystallizes in the monoclinic space group, $P21/c$, with one zinc(II) center, one molecule of ligand **L4**, one coordinated chloride and one methanol molecule in the asymmetric unit. The extended structure of this molecule shows that the zinc atom is coordinated by four donors: two **L4** and two chloride anions. The zinc atom adopts distorted tetrahedral geometry with the angles between the donors in the range 103.62(11)-122.74(8)°. In this study, the amide cavity is bound with methanol through hydrogen-bonding interactions. The methanol molecules is hydrogen bonded to the amide moiety with bond lengths O30-H8· · · O12 and N17-H17· · · O30 of 1.988 and 2.078 Å, respectively.

Keywords: Monoamide; Methyl ester; Zinc complex; Anion binding; Carboxylate

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1. Introduction

The use of unsymmetrical ligands can lead to a broader range of coordination polymers and provides access to novel topologies and architectures. This is because, the unsymmetrical ligands have different coordinating functional groups and different donor ability, and therefore, these ligands are arranged in diverse arrangements around the metal centers. Examples of unsymmetrical linkers with two different functional groups, such as pyridine and carboxylic acid, have been investigated for the synthesis of porous metal–organic frameworks (MOFs) [1]. The employment of carboxylate-containing ligands as efficient donors in the construction of MOFs has also been reported [2]. Most recently, the use of flexible carboxylate ligands has brought to the formation of new MOFs with remarkable luminescence properties [3]. However, it is worth noting that the use of carboxylate donors to synthesize MOFs or coordination polymers for anion inclusion and exchange is more limited. Kitagawa and co-workers [4], for instance, have designed an MOF that could stabilize the anionic guests

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or intermediates in a catalytic reaction through hydrogen-bonding interactions. In other approaches, Custelcean and co-workers have incorporated urea functionalities to generate coordination polymers for binding anions [5]. Along with this interest, our research focused on the incorporation of simple unsymmetrical heterocyclic amide ligands, *N*-6-[(3-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L1**), *N*-6-[(4-pyridylmethylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L2**), *N*-6-[(3-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L3**) and *N*-6-[(4-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L4**) into metallosupramolecular assemblies and coordination polymers. The monoamide ligands were incorporated with 2,6-pyridine dicarboxamide moiety for anion binding and aminomethylpyridine or aminopyridine for metal coordinating sites. Several interesting discrete metallomacrocycles derived from **L1**-**L3** have been published in our previous report [6]. In this account, we outline the synthesis and crystal structure of discrete complex with general formula [$ZnCl_2$(**L4**)$_2$] which was obtained from the reaction of *N*-6-[(4-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L4**) with zinc chloride.

2. Experimental

2.1. Materials and instrumentations

Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Elemental analysis was performed by the Campbell Microanalytical Laboratory at the Universiti Malaysia Terengganu. Infrared (IR) spectra were collected on a Perkin Elmer Spectrum BX IR spectrometer as KBr disks. Unless otherwise stated, all chemicals were obtained from commercial sources and used as received.

2.2. Syntheses

2.2.1. Synthesis of *N*-6-(4-pyridylamino)carbonyl)-pyridine-2-carboxylic acid methyl ester (L4). 6-(Methoxycarbonyl)pyridine-2-carboxylic acid (1.02 g, 5.63 mmol) was suspended in dichloromethane (20 mL). Freshly distilled thionyl chloride (5 mL) and dry dimethylformamide (100 μL) were added and the reaction was heated at reflux for 1 h. After cooling the reaction mixture to room temperature, the solvent was removed in vacuo to give a white solid. The solid was dried under high vacuum for 30 min. The resulting solid was redissolved in dichloromethane (40 mL), 4-aminopyridine (0.55 g, 5.84 mmol) and triethylamine (0.78 mL, 5.94 mmol) were added, and the solution was heated at reflux for 24 h. The mixture was taken to dryness and the residue was dissolved in dichloromethane (100 mL) washed with saturated sodium bicarbonate solution (2 × 100 mL) and dried over magnesium sulfate. The solvent was removed in vacuo to give a sticky brown solid. The solid was washed with diethyl ether, dried and recrystallized from ethanol to give **L4** as a pale brown powder (1.07 g, 75%); m.p. 113–114°C; Anal. Calcd for ($C_{13}H_{14}N_3O_4$) (%): C, 56.51; H, 5.12; N 15.21. Found: C, 56.40; H, 4.76; N, 16.07. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) $\delta = 4.06$ (3H, s, CH_3), 7.76 (2H, m, pyH3′, pyH5′), 8.13 (1H, d, pyH4), 8.31 (1H, dd, pyH3), 8.47 (1H, dd, pyH5), 8.50 (2H, m, pyH2′, pyH6′) and 10.30 (1H, s, NH). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si) $\delta = 92.0$, 152, 164, 166, 178, 183, 185, 188, 189, 198, 203.1, 203.6 m*m*/*z* (ES-MS) 258 (MH^+, 55%). Selected IR bands (KBr disk, cm^{-1}): 3155 (m), N–H *str*. (asym); 1726 (s), C=O *str*.; 1515 (s), N–H *bend*; 1436 (m), C–N *str*.

2.2.2. Synthesis of complex [$ZnCl_2(L4)_2$]. $ZnCl_2$ (0.025 g, 1.98 mmol) was dissolved in methanol (2 mL). This solution was heated for a few minutes before being added dropwise to a solution of **L4** (0.05 g, 1.98 mmol) dissolved in hot methanol (15 mL). A clear solution was obtained rapidly after the addition. The mixture was heated for another 45 min and left to evaporate at room temperature. After a month, the solution afforded [$ZnCl_2$(**L4**)$_2$] as white crystals (yield 85%). Selected IR bands (KBr disk, cm^{-1}): 3225 (s), N–H *str*. (asym); 1632 (m), C=O *str*.; 1416 (m), C–N *str*. Anal. Calcd for ($C_{26}H_{22}Cl_2N_6O_6Zn$)(%): C, 47.49; H, 3.84; Cl, 10.38; N, 12.31; O, 16.40; Zn, 9.58. Found: C, 47.21; H, 3.80; Cl, 10.12; N, 12.22; O, 16.99; Zn, 9.45.

2.3. X-ray crystallography

Crystals were mounted under oil on a plastic loop. X-ray diffraction data were collected with synchrotron radiation ($\lambda = 0.7107$ Å) at 150(2) K using the Protein Micro-crystal and Small Molecule X-ray Diffraction beamline (MX2) at the Australian Synchrotron. All data sets were corrected for absorption using a multi-scan method, and structures were solved by direct methods using SHELXS-97 [7] and refined by full-matrix least squares on F^2 by SHELXL-97 [8], interfaced through the program X-Seed [9]. In general, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. Figures were produced using the program POV-Ray [10] and interfaced through the program X-Seed. Publication materials were prepared using CIFTAB [11].

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Table 1. Crystal data and structure refinement for complex $[ZnCl_2(\mathbf{L4})_2]$.

Empirical formula	C_{28} H_{30} C_{12} N_6 O_8 Zn
Formula weight	714.85
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P21/c$
Unit cell dimensions	$a = 13.348(3)$ Å; $a = 90°$ $b = 6.1610(12)$ Å; $b = 124.00(2)°$ $c = 22.924(7)$ Å; $g = 90°$
Volume	1562.9(7) Å^3
Z	2
Density (calculated)	1.519 Mg/m^3
Absorption coefficient	1.015 mm^{-1}
F(000)	736
Crystal size	$0.25 \times 0.13 \times 0.05$ mm^3
Theta range for data collection	1.84–25.05°
Reflections collected	13978
Completeness to theta = 25.05°	95.9%
Max. and min. transmission	0.9510 and 0.7854
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2657/0/210
Goodness of fit on F^2	1.119
Final R indices [$I > 2\mathrm{sigma}(I)$]	R1 = 0.0827, wR2 = 0.2237
R indices (all data)	R1 = 0.0978, wR2 = 0.2382
Largest diff. peak and hole	1.032 and −1.593 e/Å^3

Details of data collections and structure refinements are attached in Table 1.

3. Results and discussion

In our previous studies, the monoamide ligands derived from 2,6-pyridinedicarboxamide (Figure 1) were found to undergo hydrolysis of the methyl esters to generate ONO chelation site for metal binding sites [6]. This approach has led to the formation of several interesting bowl-shaped structure with the counter anions found located inside the molecules cavity. In addition, all anions are bound to the complexes by weak hydrogen-bonding interactions following our main target. In our effort to synthesize complexes containing carboxylate as precursor for the synthesis of higher coordination frameworks derived from monoamide ligands, reaction of *N*-6-[(4-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L4**) with metal salts is attempted. Ligand **L4** is more rigid compared to its analogue described in Figure 1 by lacking of methylene spacer between amine and pyridine groups.

In contradiction to **L1**-**L3**, ligand **L4** was found decomposed in many reactions but did not undergone hydrolysis when reacted with zinc chloride. This is a surprise because **L4** was found to form anionic ligand namely hydrogen pyridine-2,6-dicarboxylato when reacted with two copper salts (CuX_2, where X = BF_4, ClO_4) while other reactions failed to give isolatable products. The reaction of **L4** with copper salts gave crystals which were obtained as a mixture of products, including single crystals of bis(hydrogen pyridine-2,6-dicarboxylato)copper(II) [12] (Figure 2).

In the case of copper perchlorate, we obtained crystals of bis(hydrogen pyridine-2,6-dicarboxylato)copper(II)

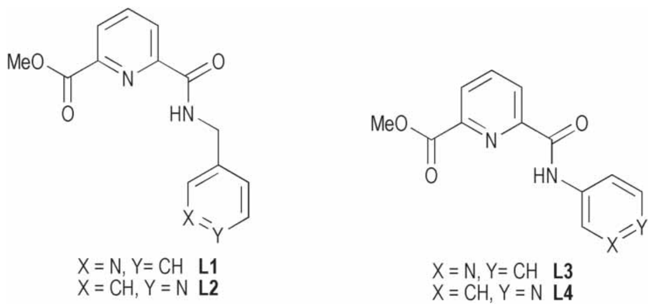

Figure 1. Monoamide ligands derived from 2,6-pyridinedicarboxamide.

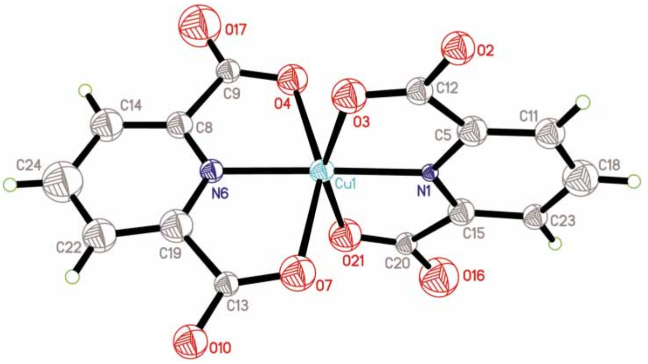

Figure 2. ORTEP diagram of bis(hydrogen pyridine-2,6-dicarboxylato)copper(II) at 50% probability along with atom numbering scheme.

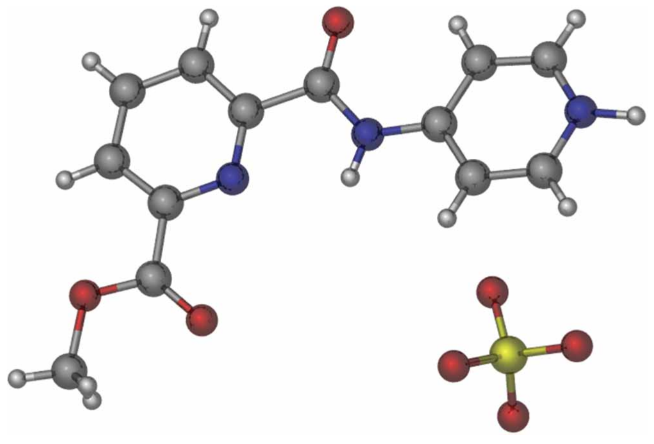

Figure 3. Crystal structure of hydroperchlorate salt of L4.

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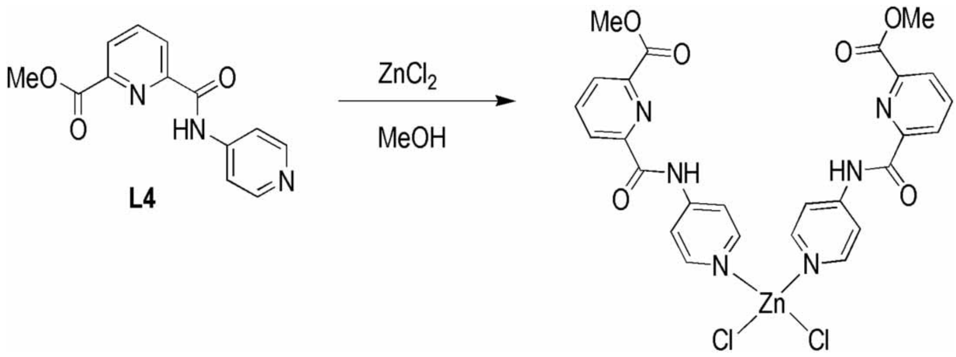
and hydroperchlorate salt of **L4** when reacted with copper perchlorate (Figure 3). Decomposition of related amide ligands has been observed in other work [13] and thus, in this study, it was proposed that amide hydrolysis was responsible for the difficulties involved in obtaining (pure) complexes of either **L4** or **L4**-CH_3.

We are fortunate because our effort to generate a carboxylate complex from (*N*-6-[(4-pyridylamino)carbonyl]-pyridine-2-carboxylic acid methyl ester (**L4**) and $ZnCl_2$ is successful (Scheme 1) where discrete complex with formulation given by elemental analysis as [ZnCl$_2$(**L4**)$_2$] is obtained in high yield. Most importantly, the crystals obtained are suitable for X-ray crystallography analysis.

3.1. Crystal structure of [ZnCl$_2$(L4)$_2$]

X-ray crystallography revealed that the zinc chloride complex crystallizes in the monoclinic space group, $P21/c$, with one zinc(II) center, a molecule of **L4**, one coordinated chloride and one methanol molecule in the asymmetric unit. The extended structure of complex [ZnCl$_2$(**L4**)$_2$] is shown in Figure 4 with two molecules of **L4** coordinated to the Zn atom and methanol located at the amide moieties. In the crystal structure, the zinc atom adopts a highly distorted tetrahedral geometry, with the angles between the donors in the range 103.62(11)–122.74(8)°. The bond lengths and angles around the zinc atom are within 2.049(4)-2.2309(13) and 103.62(11) and 122.74(8), respectively.



Scheme 1. Synthesis of [ZnCl$_2$(**L4**)$_2$].

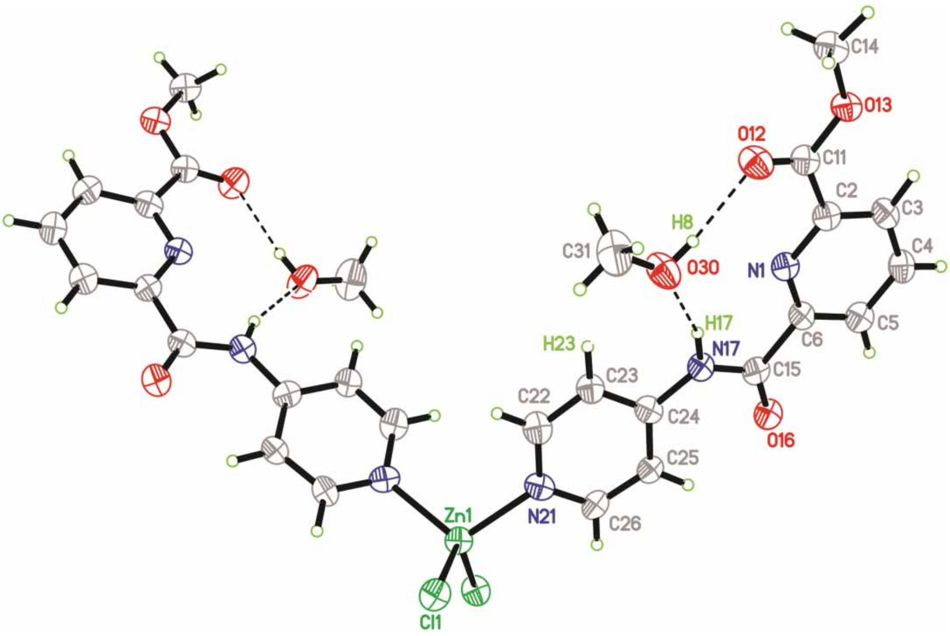


Figure 4. ORTEP diagram of the extended structure of [ZnCl$_2$(**L4**)$_2$] at 50% probability along with atom numbering scheme. Selected bond lengths (Å) and angles (°) around the zinc atom: Zn(1) Cl(1) 2.2309(13), Zn(1) N(21) 2.049(4), N(21) Zn(1) Cl(1) 103.62(11) and N(21) Zn(1) Cl(1A) 122.74(8)°.

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Table 2. Hydrogen-bond geometry (Å, °)

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N17–H17···O30	0.88	2.08	2.921(2)	160
O30–H8···O12	0.87	1.94	2.803(3)	171

In the crystal structure, the methanol molecule is hydrogen bonded to the amide moiety with the bond lengths O-H8···O12 and N-H17···O30 of 1.941 and 2.078 Å, respectively (Table 2). There are no extended hydrogen-bonding interactions or π-stacking interactions occurred within the crystal packing. A perspective view of the crystal packing when viewed along the *ac* axis is shown in Figure 5.

It is interesting to note that the amide NH groups of the ligands are found to face inside the cavity of the molecule. This is common behavior for this type of ligand which pre-organizes the NH functionality of the ligands into a central pocket and acts as hydrogen bond donor [14]. This is similar to the majority of the complexes studied by us, where in many cases, the solvent molecules or counter anions were located inside the molecule cavity and bound through similar interactions [6,15]. The successful in obtaining this compound give us great opportunity to generate extended coordination frameworks suitable for anion inclusion by using the remaining carboxylate groups at both pendant arms of the complex as metal-binding sites.

4. Conclusion

In conclusion, a discrete carboxylate complex with amide binding region can be obtained from reaction between simple monoamide ligand (*N*-6-[(4-pyridylamino) carbonyl]-pyridine-2-carboxylic acid methyl ester (**L4**) and zinc chloride. By having this complex in our hand, further investigation in using this complex as precursor for the synthesis of higher coordination frameworks (e.g. using cadmium salts) will be pursued.

Supplementary materials

CCDC 956616 contains the supplementary crystallographic data for these structures. These data can be

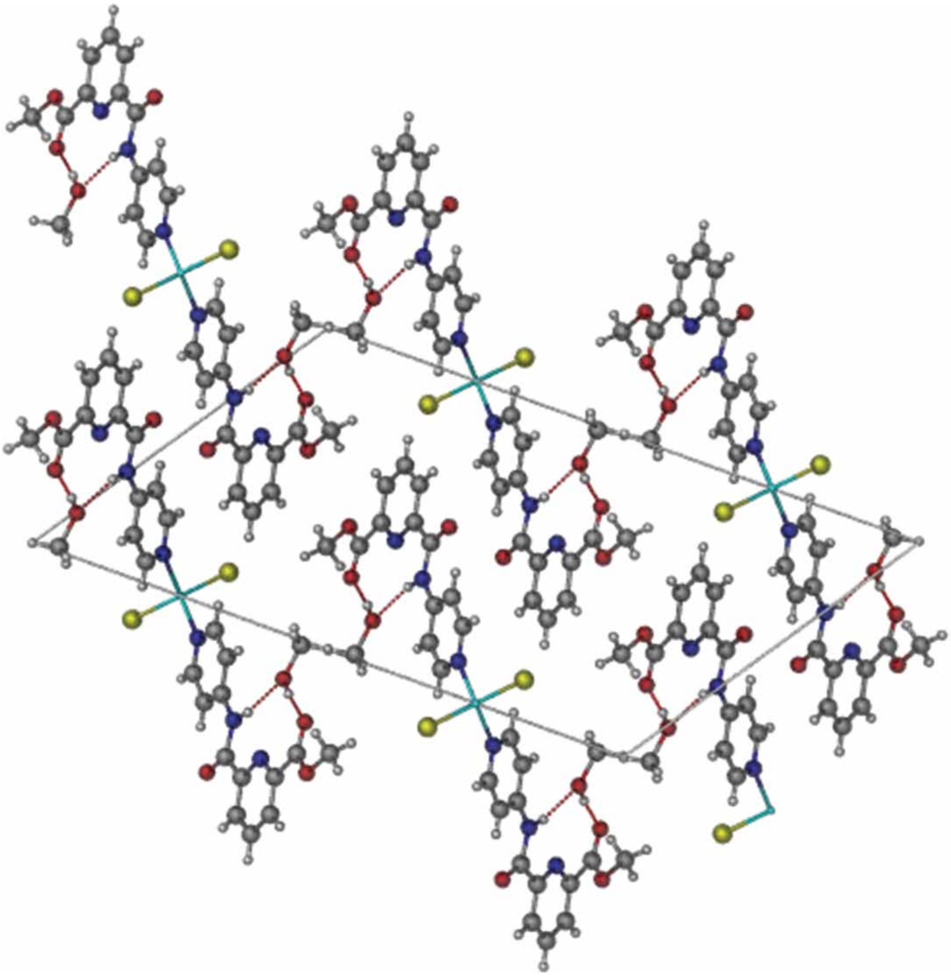

Figure 5. A packing diagram of complex [$ZnCl_2$(**L4**)$_2$] viewed from *ac* axis.

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References

[1] A. Pichon, A.L. Garay, S.L. James. *CrystEngComm.*, **8**, 211 (2006).
[2] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O'Keefe, O.M. Yaghi. *Science*, **300**, 1127 (2003).
[3] Y.H. Huang, T.L. Sheng, Q.L. Zhu, C.H. An, R.B. Fu, S.M. Hu, X.T. Wu. *Chin. J. Struct. Chem.*, **32**, 1572 (2013).
[4] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita, S. Kitagawa. *J. Am. Chem. Soc.*, **129**, 2607 (2007).
[5] (a) R. Custelcean. *Curr. Opinion Solid State Mater. Sci.*, **13**, 68 (2009); (b) R. Custelcean, A. Bock, B.A. Moyer. *J. Am. Chem. Soc.*, **132**, 7177 (2010); (c) R. Custelcean, P. Remy, P.V. Bonnesen, D.E. Jiang, B.A. Moyer. *Angew Chem. Int. Ed. Engl.*, **47**, 1866 (2008); (d) R. Custelcean, V. Sellin, B.A. Moyer. *Chem. Commun.*, **15**, 1541 (2007); (e) R. Custelcean. *Chem. Commun.*, 295 (2008).
[6] L.R. Hanton, A.K. Maisara, C.J. Sumby. *Dalton Trans.*, **40**, 12374 (2011).
[7] G.M. Sheldrick. *SHELXS-97, Programs for Solution of Crystal Structure*, University of Göttingen, Germany (1997).
[8] G.M. Sheldrick. *SHELXL-97, Programs for Solution of Crystal Structure*, University of Göttingen, Germany (1997).
[9] L.J. Barbour. *J. Supramol. Chem.*, **1**, 189 (2001).
[10] Persistence of Vision Raytracer Pty. Ltd, POV-Ray, Williamstown, Australia (2003).
[11] G. M. Sheldrick. *CIFTAB*, University of Göttingen, Göttingen, Germany (1997).
[12] C.M. Biagini, V.A. Chiesi, C. Guastini, M. Nardelli. *Gazz. Chim. Ital.*, **102**, 1026 (1972).
[13] (a) D. Hu, W. Huang, S. Gou, S. Chantrapromma, H.K. Fun, Y. Xu. *Synth. React. Inorg. Met. Org. Chem.*, **32**, 127 (2002); (b) F. Voegtle, W.M. Mueller, E. Buhleier, W. Wehner. *Chem. Ber.*, **112**, 899 (1979).
[14] C.J. Sumby, L.R. Hanton. *Tetrahedron*, **65**, 4681 (2009).
[15] P.R. Clements. A.K. Maisara, L.R. Hanton, C.A. Hollis, C.J. Sumby. *Supramol. Chem.*, **24**, 627 (2012).

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