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Heptanuclear zinc carboxylate complex: New supramolecular building unit and unique supramolecular architecture

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel Prize in Chemistry in 1913.

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ABSTRACT

The reaction of the bifunctional ligand (1,8-naphthalimido)propanoate (L_{c2}^{-}), containing a carboxylate group for metal bonding and a 1,8-naphthalimide group for $\pi \cdots \pi$ stacking interactions, with $Zn(O_2CCH_3)_2(H_2O)_2$ yields a novel heptanuclear complex $[Zn_7(O)_2(L_{c2})_{10}(DMF)_2]$. In the solid-state structure, a central zinc(II) cation is linked to six terminal zinc(II) cations by ten bridging carboxylate ligands and two μ_4 -O ions forming a vertex shared bitetrahedron, a new type of secondary building unit (SBU). The heptanuclear units are organized into a complex three-dimensional architecture by $\pi \cdots \pi$ stacking interactions of the 1,8-naphthalimide groups. Eight of the naphthalimide rings on each heptanuclear unit form $\pi \cdots \pi$ stacking interactions with rings on eight adjacent units generating a unique "single linked" three-dimensional architecture. The TGA data indicate this structure is robust and luminescent studies show the solid emits in the green region.

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1. Introduction

The construction of highly organized structures from nodes consisting of metal ions or polynuclear groups of metal ions and multitopic organic ligands that link the metals into three-dimensional networks is an area of considerable interest. The interest stems from the diverse topology of the structures and the possibility of designing solids with particular properties [1–12]. An important development in this chemistry was the use of carboxylate ligands to form robust nodes containing multiple transition metals, known as secondary building units (SBUs), as synthetic modules to direct the formation of specific types of networks. Combining an SBU with a polytopic carboxylate ligand can produce a variety of highly organized structures, generally called metal–organic frameworks (MOFs) [13–16].

We have introduced into related chemistry the 1,8-naphthalimide supramolecular synthon, a π ... π stacking interaction of considerable organizing capability [17–21]. We have prepared bifunctional carboxylate ligands, thus capable of building SBUs, that contain the naphthalimide group (see Scheme 1) for the construction of MOF type structures, but structures that differ significantly from MOFs in that one or more of the dimensions are organized by strong noncovalent interactions. We have termed these solids supramolecular metal–organic frameworks (SMOFs) [17-21], three-dimensional framework solids that are organized partially or completely by robust supramolecular interactions. One of the most important novelties of these solids is the increase in the flexibility of the architecture due to the variable metrics possible in the $\pi \cdots \pi$ stacking interactions, while still retaining significant connections between the SBUs. In our first publications, we incorporated the three ligands pictured in Scheme 1 into paddlewheel Cu₂(O₂CR)₄ type SBUs [17,18]. A series of high dimensional copper(II) coordination architectures were obtained, where all the structures show strong $\pi \cdots \pi$ stacking interactions of the naphthalimide rings. We have also reported the preparation of analogous zinc dimers [19], copper dimers built from similar ligands that also incorporate a chiral center into the ligand [20] and a zinc complex built from the trimetallic Zn₃(O₂CR)₆ SBU core [21]. Reported here are the synthesis, structure and properties of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$, a complex containing the unusual $Zn_7(O)_2(O_2CR)_{10}$ SBU core [22], which has a three-dimensional architecture exclusively organized by the $\pi \cdots \pi$ stacking of the 1,8-naphthalimide rings.

2. Experimental

2.1. General considerations

All reactants were used as purchased from Sigma–Aldrich. Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ). The protonated form of the ligand, 3-(1,8-naphthalimido)propanoic acid (HL_{c2}), was synthesized as previously reported [17].





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Scheme 1. Bifunctional ligands.

2.2. Synthesis of [Zn₇(O)₂(L_{C2})₁₀(DMF)₂]

To a powdered sample of HL_{c2} (0.270 g, 1.0 mmol) suspended in 30 mL water, 1.2 mL of a 1 M methanolic KOH solution and 5 mL of pure methanol was added. The suspension was stirred until it cleared and then the solution was filtered. To this solution was added a solution of $Zn(O_2CCH_3)_2(H_2O)_2$ (0.147 g, 0.67 mmol) in 10 mL water containing 0.12 mL of pyridine. A white precipitate formed immediately. The mixture was stirred for 2 h, the solid was isolated by filtration, washed with 10 mL of water, 10 mL of ethanol and diethyl ether each, and was air-dried. Yield: 0.345 g. Single crystals of the title compound were grown by vapor diffusion from a DMF/Et₂O solvent system. The analytical sample was dried to constant weight. *Anal.* Calc. (Found) for $C_{156}H_{114}N_{12}O_{44}Zn_7$: C 56.46 (55.63); H 3.46 (2.62); N 5.07 (4.66).

2.3. Crystallographic studies

X-ray intensity data from a colorless blocklike crystal were measured at 100(2) K using a Bruker SMART APEX diffractometer (Mo K α radiation, λ = 0.71073 Å) [23]. Raw area detector data frame processing was performed with the sAINT+ and SADABS programs [23]. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL [24]. Details of the data collection are given in Table 1.

The final unit cell parameters were determined by least-squares refinement of 7193 reflections from the data set. The compound crystallizes in the space group $P\bar{1}$ of the triclinic system. There is half of one centrosymmetric complex in the asymmetric unit and a large volume of disordered solvent molecules. The crystallographically identifiable part of the asymmetric unit consists of four independent zinc(II) cations, one μ_4 -oxide anion, five independent ligands and one DMF molecule. The Zn1 is located on an inversion center. The ligands were numbered similarly except for the label suffix A–G. Disorder of two of the five ligands and of the coordinated DMF was observed. Ligands D/E and F/G are disordered over two closely separated positions with refined populations D/E = 0.51(1)/0.49(1) and F/G = 0.40(1)/0.60(1). The disordered DMF

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Selected crystallographic data	and structure refinement	for $[Zn_7(0)_2(L_{C2})]$)10(DMF)2
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Formula	$C_{156}H_{114}N_{12}O_{44}Zn_7$
Formula weight (g mol ⁻¹)	3318.18
Crystal system	triclinic
Space group	ΡĪ
T (K)	100(2)
a (Å)	16.648(2)
b (Å)	17.283(3)
<i>c</i> (Å)	17.895(3)
α (°)	100.322(3)
β(°)	96.187(3)
γ (°)	112.945(3)
V (Å ³)	4574.4(11)
Ζ	1
$R_1 I > 2\sigma(I)$	0.0695
$wR_2 I > 2\sigma(I)$	0.2084

occupies two equally populated sites. The naphthalimide ring geometry of each disordered ligand was restrained to be similar to the well-behaved ligand "C" using the SHELX SAME instruction. The DMF ligands were restrained to be planar. All atoms affected by disorder were refined isotropically: all other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. No chemically reliable disorder model was attained for the interstitial solvent species. Based on trial modeling attempts, they appear to be primarily DMF. The solvent-containing volume was calculated to be 1153.6 Å³ (25.2% of the total unit cell volume). The contribution of these diffusely scattering species (305 electrons per unit cell) was removed from the structure factors with the SQUEEZE program spawned from PLA-TON [25]. The final tabulated F.W., D_{calc}, and F(000) refer to crystallographically identifiable species only.

3. Results

3.1. Synthesis and structure

The reaction of KL_{C2}, generated in situ from the acid form of the ligand and KOH, with $Zn(O_2CCH_3)_2(H_2O)_2$ in the presence of pyridine yielded a white precipitate. Single crystals of $[Zn_7(O)_2(L_{C2})_{10}$ (DMF)₂] were obtained by vapor diffusion of diethyl ether into a dimethylformamide solution of this white solid. Fig. 1 pictures two views of the molecular structure of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ and Tables 2 and 3 contain selected bond lengths and angles.

The heptanuclear zinc complex is centrosymmetric with the zinc centers forming a vertex shared (Zn1 is central) bitetrahedron (Fig. 1b). In the SBU core, a μ_4 -O ion is located in the center of each tetrahedron and each links the central zinc(II) cation with three terminal zinc(II) cations. In addition, the zinc centers are linked by eight bridging κ^2 - and two dibridging κ^3 -carboxylate ligands. Six of these κ^2 -ligands bridge the six terminal zinc centers on the "top" and "bottom" of the bitetrahedron. The other two κ^2 - and the two dibridging κ^3 -carboxylate ligands are located on the "sides" of the bitetrahedron. The bridging κ^2 -pair links the two terminal Zn3 with the central Zn1. One of oxygen donor atoms in each of the dibridging κ^3 -pair of ligands is bonded to one of the two terminal Zn4 while the other oxygen bridges Zn1 and a Zn2 that is located in the other tetrahedron. In addition, one of the two dimethylformamide molecules bonds to each of the two Zn2. This arrangement produces a six-coordinate central Zn1 (distorted octahedral geometry), two five-coordinate Zn2 (square pyramidal geometry, $\tau_5 = 0.08$ [26]) and four, four-coordinate Zn3 and Zn4 (distorted tetrahedral geometry).

The heptanuclear SBUs are organized into a complex threedimensional architecture by $\pi \cdots \pi$ stacking interactions of the naphthalimide groups of the A, B, C and D carboxylate ligands. The naphthalimide rings of the two equivalent G carboxylate ligands are not involved in $\pi \cdots \pi$ stacking interactions. The naphthalimide rings of the A, B and D ligands $\pi \cdots \pi$ stack with equivalent naphthalimide groups on six adjacent SBUs as is illustrated in Fig. 2. These six SBUs are color-coded in the same color type to



Fig. 1. (a) Molecular structure of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$; disordered components of rings D and G (E and F) are not shown for clarity. (b) SBU core of the complex, with the naphthalimide rings removed for clarity.

1.945(4) 1.967(4)

Selected bond lengths Å for $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$.						
Zn(1)-O(1)	1.974(3)	Zn(3) -O(3G)				
Zn(1) -O(4D)	2.146(3)	Zn(3) –O(4B)				
Zn(1) -O(4G)	2.190(5)	Zn(3) -O(4C)				
$7n(1) \cdots 7n(2)$	2 0201(6)	7n(4) = O(1)				

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Zn(1) - O(4G)	2.190(5)	Zn(3) = O(4C)	1.969(3)
Zn(1) $Zn(2)$	2.9291(6)	Zn(4) - O(1)	1.909(3)
Zn(2) -O(21A)	1.947(7)	Zn(4) -O(4A)	1.944(3)
Zn(2) - O(1)	1.967(3)	Zn(4) -O(3D)	1.966(3)
Zn(2) -O(3B)	2.056(3)	Zn(4) -O(3C)	1.976(3)
Zn(2) -O(3A)	2.061(3)		
Zn(2) -O(21B)	2.073(8)		
Zn(2) -O(4Da)	2.265(3)		

represent the three pairs of symmetry equivalent SBUs (these equivalent units are oriented on opposite sides of the blue unit) participating in $\pi \cdots \pi$ stacking interactions with the central blue colored unit.

The B carboxylate ligands on the central blue unit generate strong $\pi \cdots \pi$ stacking interactions with equivalent moieties from the neighboring red/brown SBUs. In these B–B interactions the perpendicular distance between the parallel rings is 3.40 Å and the dipole vectors (which run from the center of the fused aromatic rings through the nitrogen atom) are oriented at 180°, a "head to tail" arrangement (see Table 4). Another important parameter, χ , quantifies the relative slippage of the naphthalimide rings (the degree of overlap) and is the third side of the right triangle formed with the average perpendicular distance between the rings and the line joining the central carbon atoms of the two rings. Although a range of χ values has been previously reported [17–21], those in the range of 0.43–2.40 Å are considered strong interactions. The χ value of the B–B interactions is 0.81 Å.

The napthalimide rings of the two A carboxylate ligands on the central blue SBU $\pi \cdots \pi$ stack with equivalent naphthalimide groups on the two adjacent yellow/orange colored SBUs. In both of these A–A interactions the parallel naphthalimide rings are 3.45 Å apart

Table 3Selected bond angles (deg) for $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2].$

O(1)-Zn(1)-O(4D)	98.97(12)	O(3A)-Zn(2)-Zn(1)	123.46(10)
O(1) - Zn(1) - O(4Da)	81.03(12)	O(21B) - Zn(2) - Zn(1)	120.8(2)
O(1)-Zn(1)-O(4G)	100.02(14)	O(4Da)-Zn(2)-Zn(1)	46.67(8)
O(4D)-Zn(1)-O(4G)	88.13(19)	O(1)-Zn(3)-O(3G)	117.23(15)
O(1)-Zn(1)-O(4Ga)	79.98(14)	O(1)-Zn(3)-O(4B)	114.87(14)
O(4D)-Zn(1)-O(4Ga)	91.87(19)	O(3G)-Zn(3)-O(4B)	97.88(18)
O(21A)-Zn(2)-O(1)	159.7(2)	O(1)-Zn(3)-O(4C)	109.82(13)
O(21A)-Zn(2)-O(3B)	97.1(2)	O(3G)-Zn(3)-O(4C)	112.23(17)
O(1)-Zn(2)-O(3B)	102.35(13)	O(4B)-Zn(3)-O(4C)	103.59(14)
O(21A)-Zn(2)-O(3A)	83.3(3)	O(1)-Zn(4)-O(4A)	117.17(13)
O(1)-Zn(2)-O(3A)	100.56(13)	O(1)-Zn(4)-O(3D)	117.19(13)
O(3B)-Zn(2)-O(3A)	95.57(13)	O(4A)-Zn(4)-O(3D)	102.24(15)
O(1)-Zn(2)-O(21B)	162.6(2)	O(1)-Zn(4)-O(3C)	109.15(13)
O(3B)-Zn(2)-O(21B)	87.1(2)	O(4A)-Zn(4)-O(3C)	106.03(14)
O(3A)-Zn(2)-O(21B)	92.9(2)	O(3D)-Zn(4)-O(3C)	103.74(15)
O(21A)-Zn(2)-O(4Da)	92.8(2)	Zn(4)-O(1)-Zn(3)	113.13(14)
O(1)-Zn(2)-O(4Da)	78.20(11)	Zn(4)-O(1)-Zn(2)	111.87(13)
O(3B)-Zn(2)-O(4Da)	99.54(12)	Zn(3)-O(1)-Zn(2)	111.59(14)
O(3A)-Zn(2)-O(4Da)	164.76(12)	Zn(4)-O(1)-Zn(1)	110.37(13)
O(21B)-Zn(2)-O(4Da)	85.9(2)	Zn(3)-O(1)-Zn(1)	112.70(13)
O(21A) - Zn(2) - Zn(1)	119.6(2)	Zn(2)-O(1)-Zn(1)	96.01(12)
O(1) - Zn(2) - Zn(1)	42.08(7)		
O(3B)-Zn(2)-Zn(1)	127.11(9)		

and have a "head to tail" arrangement. The χ value is 2.93 Å, indicating that the overlap between the two naphthalimide rings is not as substantial as in the B–B interaction. These rings are oriented in Fig. 2 such that the "slippage" can be readily viewed (green circles), although considerable overlap still exists. The D (E) carboxylate ligands (in this case a D always pairs with its disordered counterpart E) are involved in $\pi \cdots \pi$ stacking interactions from the neighboring purple/magenta SBUs. The metric parameters for the D–E interactions are as follows: the parallel naphthalimide rings are 3.40 Å apart, the dipole vector angle is 153° and the slippage value is 1.41 Å.



Fig. 2. Seven heptanuclear SBUs of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ assembled by the $\pi \cdots \pi$ stacking interactions of the naphthalimide rings. The central blue-colored unit overlaps with the *trans*-oriented A-rings of the yellow and orange units (green circles), B-rings of the red and brown units, and D-rings of the purple and magenta units (view down crystallographic axis *a* direction). The green circles emphasize the slippage of the C-rings. (Color online.)

Fig. 3 illustrates the π ··· π stacking interactions of the B and C rings down the crystallographic axis *b*, an orientation approximately perpendicular to that in Fig. 2. The B rings on the central blue-colored unit interact with equivalent moieties from the neighboring red/brown SBUs, interactions also shown in Fig. 2. The C rings on the central blue-colored unit interact with the equivalent moieties from the neighboring light and dark green SBUs. The C-C interactions are strong, with the parallel naphthalimide rings 3.46 Å apart and a χ value of 1.40 Å. The substantial overlap of the C-rings is clearly viewed in the figure, red circles. The naphthalimide rings generating the C-C interactions are perpendicularly oriented with respect to the naphthalimide moieties forming the B interaction.

All of these $\pi \cdots \pi$ stacking interactions build up a complex threedimensional framework. Fig. 4 shows the overall three-dimensional architecture of this compound. In the three-dimensional structure, each SBU is linked to eight adjacent SBUs: six in the *bc* plane and two in the *ac* plane.

3.2. UV-Vis and luminescence spectra

The diffuse reflectance (UV–Vis) spectrum of $[Zn_7(O)_2(L_{C2})_{10}$ (DMF)₂] shows a broad maxima ($\lambda_{max,UV}$) at 364 nm. We also recorded the solid state excitation (Fig. 5a) and emission (Fig. 5b) spectra at room temperature. The compound shows green luminescence with $\lambda_{max,Fl}$ at 444 nm and a large shoulder at 472 nm upon excitation at 288 or 380 nm. This emission maxima is slightly

Table 4 1,8-Naphthalimide interaction parameters for [Zn₇(O)₂(L_{C2})₁₀(DMF)₂].

Interaction type	Central carbon- central carbon distance (Å)	Dipole angle (°)	Plane angle (°)	Avg. perp. distance (Å)	Avg. slippage, χ (Å)
A–A	4.53	180	0	3.45	2.93
B-B	3.50	180	0	3.40	0.81
C-C	3.73	180	0	3.46	1.40
D-E ^a	3.69	153	0.7	3.40	1.41

^a D-rings pairs with its disordered counterpart E-rings on adjacent SBUs.



Fig. 3. Five heptanuclear SBUs of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ assembled by the $\pi \cdots \pi$ stacking interactions of the central blue-colored unit overlapping with the B-rings (red and brown units) and the C-rings of the light and dark green units (view down crystallographic *b* axis). The red circles emphasize the substantial overlap of the C-rings. (Color online.)



Fig. 4. Three-dimensional architecture of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$. Three supramolecular layers are shown: central layer corresponds to Fig. 2, color coded according to this figure; bottom layer is light green and top layer is dark green as in Fig. 3. For the top dark green layer only three SBUs are added, in order to show the color coded central layer. The three supramolecular layers in the *bc* plane are further connected by π ... π stacking interactions in the *ac* direction. (Color online.)

blue shifted in comparison with HL_{C2} ($\lambda_{max,FI}$ at 449 nm). The green emission of the heptamer is due to the large shoulder at 472 nm, a feature not present in the spectrum of the protonated ligand, that can be tentatively assigned as a charge transfer band.

3.3. Thermogravimetric analysis

The DTA–TGA data for $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ (Fig. 6) show a four step decomposition: the loss of unknown solvent of crystallization, followed by loss of the two coordinated DMF molecules at 265 °C, 4.7% (calc. 4.4%). The next two steps, above 290 °C, involve the decomposition of L_{C2} , consequently the collapse of the heptamer. The last step is complete at 558 °C. The remaining 12.8% solid corresponds to ZnO (calc. 15.6%).



Fig. 5. Excitation (a) and emission (b) spectra of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ in the solid state.



Fig. 6. TGA–DTA curves of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$.

4. Discussion

The complex $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ has a unique SBU core. While other compounds have central cores containing seven zinc centers [27,28], only one previously reported example of a complex with a similar formula exists, $[Zn_7(O)_2(pda)_5(H_2O)_2]$ (pda = dicarboxylate from *p*-phenylenediacrylic acid). This compound has a somewhat different structure where each of the four oxygen atoms of the bridging carboxylate ligands bonded to the central Zn1 (those located on the "sides") also bridge to one of the terminal Zn centers in the second tetrahedron; they are all dibridging κ^3 carboxylate ligands [29]. In [Zn₇(O)₂(L_{C2})₁₀(DMF)₂] only half of the analogous four carboxylate ligands bridge in this manner, the other two are bridging κ^2 -ligands. Importantly, the linkages within the extended structure are very different. The biggest difference is that the links with $[Zn_7(O)_2(pda)_5(H_2O)_2]$ are covalent bonds whereas with $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ these links are noncovalent $\pi \cdots \pi$ stacking interactions. Both heptanuclear zinc complexes have potentially 10 points of linkage extensions. As pointed out in a recent review [16], $[Zn_7(O)_2(pda)_5(H_2O)_2]$ links to six other SBUs, with four of the links "double links" between the SBUs with the other two "single linkages," thus using all the linking groups. For $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$, two of the potential linking groups, the naphthalimide "G" groups, do not interact with other SBUs. The other naphthalimide groups in each SBU, form eight single links to eight adjacent SBUs generating a supramolecular metal-organic framework structure. Although held together only by noncovalent interactions, the TGA analysis indicates the structure has considerable stability as it does not break down until approximately 265 $^{\circ}$ C, with the loss of the coordinated solvent.

This study, when taken together with our previous studies on structures organized mainly by $\pi \cdots \pi$ stacked naphthalimide rings [17–21], demonstrate the versatility and importance of the 1,8naphthalimide supramolecular synthon. In the structure of $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$, the variability of the metrics in the $\pi \cdots \pi$ stacking interactions, particularly of the slippage parameter χ , establishes that this supramolecular synthon can support a wide variety of geometric arrangements. That is, this supramolecular synthon is very flexible and can vary its metric parameters without much change in the strength of the interaction to accommodate various structural arrangements and, although not observed here. can also interact on both sides of the rings [18,19]. In addition, $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$ and other naphthalimide complexes [19,21,29] are good candidates for green fluorescent materials due to their thermal stability and insolubility in common organic solvents.

5. Conclusions

A bifunctional ligand containing a carboxylate group for metal bonding and a 1,8-naphthalimide group for π ··· π stacking interactions forms a new type of heptanuclear zinc(II) SBU that has noncovalent "single links" to eight other SBUs forming a complex three-dimensional supramolecular metal–organic framework (SMOF). This structure demonstrates the organizational versatility of the naphthalimide supramolecular synthon and the TGA analysis indicates thermal stability for these SMOF solids.

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Appendix A. Supplementary data

CCDC 857169 contains the supplementary crystallographic data for $[Zn_7(O)_2(L_{C2})_{10}(DMF)_2]$. 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.

References

^[1] S. Qiu, G. Zhu, Coord. Chem. Rev. 253 (2009) 2891.

^[2] A.U. Czaja, N. Trukhan, U. Muller, Chem. Soc. Rev. 38 (2009) 1284.

- [3] L.J. Murray, M. Dinca, J.R. Long, Chem. Soc. Rev. 38 (2009) 1294.
- [4] R.E. Morris, P.S. Wheatley, Angew. Chem., Int. Ed. 47 (2008) 4966.
- [5] U. Muller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, J. Pastre, J. Mater. Chem. 38 (2006) 626.
- [6] A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi, J. Am. Chem. Soc. 128 (2006) 3494.
- [7] (a) J.C. Rowsell, O.M. Yaghi, J. Am. Chem. Soc. 128 (2006) 1304;
 (b) B. Chen, N.W. Ockwig, A.R. Millward, D.S. Contreras, O.M. Yaghi, Angew. Chem., Int. Ed. 44 (2005) 4745.
- [8] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R.V. Belosludov, T.C. Kobayashi,
- H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, Nature 436 (2005) 238. [9] J.C.L. Rowsell, E.C. Spencer, J. Eckert, J.K. Howard, O.M. Yaghi, Science 309
- (2005) 1350. [10] J.L.C. Rowsell, O.M. Yaghi, Microporous Mesoporous Mater. 73 (2004) 3.
- [11] N.L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O.M. Yaghi, CrystEngComm 4 (2002) 401.
- [12] M. Eddaoudi, H. Li, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 1391.
- [13] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi,
- Acc. Chem. Res. 34 (2001) 319. [14] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Nature
- 423 (2003) 705. [15] D.J. Tranchemontagne, J.L. Mendoza-Cortes, M. O'Keeffe, O.M. Yaghi, Chem.
- Soc. Rev. 38 (2009) 1257.
- [16] M. O'Keeffe, O.M. Yaghi, Chem. Rev., 2011. http://dx.doi.org/10.1021/ cr200205.

- [17] D.L. Reger, A. Debreczeni, B. Reinecke, V. Rassolov, M.D. Smith, R.F. Semeniuc, Inorg. Chem. 48 (2009) 8911.
- [18] D.L. Reger, A. Debreczeni, M.D. Smith, J. Jezierska, A. Ozarowski, Inorg. Chem. 50 (2011) 1068.
- [19] D.L. Reger, A. Debreczeni, M.D. Smith, Inorg. Chem. 50 (2011) 11754.
- [20] D.L. Reger, J.J. Horger, A. Debreczeni, M.D. Smith, Inorg. Chem. 50 (2011) 10225.
- [21] D.L. Reger, A. Debreczeni, M.D. Smith, Inorg. Chim. Acta 364 (2010) 10.
- [22] 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.
- [23] SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.10. Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2003.
- [24] G.M. Sheldrick, SHELXTL Version 6.14, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2000.
- [25] SQUEEZE: P.v.d. Sluis, A.L. Spek, Acta Crystallogr., Sect A 46 (1990) 194. PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A.L. Spek (1998).
- [26] A.W. Addison, T.N. Rao, J. Reedijk, J. Van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349. $\tau_s = \frac{(\beta - \alpha)}{60^{-3}}$, where α and β are the two largest angles measured around the metal centers. Perfect square pyramid: $\tau_5 = 0$; perfect trigonal bipyramid: $\tau_5 = 1$.
- [27] M. Bera, G.T. Musie, D.R. Powell, Inorg. Chem. 48 (2009) 4625.
- [28] H.-Y. Liu, B. Zhao, W. Shi, Z.-J. Zhang, P. Cheng, D.-Z. Liao, S.-P. Yan, Eur. J. Inorg. Chem. (2009) 2599.
- [29] D.L. Reger, A. Debreczeni, M.D. Smith, Eur. J. Inorg. Chem. (2012) 712.