

Synthesis of the Bifunctional Ligand *N,N'*-[1,4-Phenylenebis(iminocarbonyl)]di(L-phenylalanine) and Crystal Structure of Its Supramolecular Coordination Polymer with Lead(II)

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The new linker-type ligand **1**, featuring two L-phenylalanine-terminated urea moieties attached to the *para* positions of a central phenylene unit has been synthesized. Its coordination polymer formed with lead(II) and containing DMF and water as solvent molecules has been prepared and structurally studied by X-ray crystallography.

Key words: *N,N'*-[1,4-Phenylenebis(iminocarbonyl)]di(L-phenylalanine), Lead(II) Complex, Synthesis, Crystal Structure, Supramolecular Coordination Polymer

Introduction

Coordination polymers, also known as metal-organic framework materials, are of high current interest [1–3] due to their potential uses in different fields of application including catalysis [4–6], selective gas adsorption [7–9], chromatography [10–12], magnetism [2, 13–15], and non-linear optical behavior [16–18]. Materials of this type owe their properties to a clever choice of the building components, that is the organic linker molecule and the coordinating metal ion. Nevertheless, this is not an easy point because of interpenetration and connectivity problems interfering with the rational design and synthesis of an intended coordination network architecture [2, 19]. Among the great variety of organic linker molecules that have been tested [1, 2, 20], the molecules possessing carboxylic acid functions as coordinating end groups were shown to be particularly efficient. A great many of metal ions have been used for coordination to carboxylic linker molecules including Zn(II), Cu(II), Ni(II) and others [1, 2, 20],

resulting in the formation of specific points of coordinative intersection referred to as SBUs in this context.

Owing to the $6s^2$ lone pair of divalent lead, which can cause distortion of the coordination sphere [21–23] frequently discussed in considering its stereochemical activity [24–26], Pb(II) plays an important role in coordination chemistry since it can lead to either holodirected or hemidirected coordination [27–29] dependent on the nature of the ligand such as containing soft or hard donor atoms or attractive *versus* repulsive interactions among ligands [30]. Hence, Pb(II) complexed to carboxylic ligands, giving rise to both chelating and bridging coordination modes, offers suitable requirements for the construction of polymeric coordination networks [31, 32]. This has been documented in a recent very comprehensive review article showing numerous examples of respective complexes [33]. However, the corresponding complexes of Pb(II) with amino acid ligands [34–40], including phenylalanine [40–42], are still not so common, and related complexes formed of a ditopic linker

molecule based on an amino acid derivative, as far as we know, are not in the literature.

Here we report the coordination polymer of such a new bifunctional amino acid-derived linker molecule featuring two L-phenylalanine-terminated urea moieties attached to the *para* positions of a central phenylene unit with Pb(II). We describe the synthesis of the linker compound as well as the preparation of the coordination polymer and in particular discuss the X-ray crystal structure of the latter species paying – aside from the coordination mode of the metal ion – also attention to the supramolecular behavior of the urea moieties to control the packing.

Experimental Section

General

The melting points were determined with a Melting Point B-540 (Büchi, Switzerland) and are uncorrected. The elemental analyses were determined on a Heraeus CHN rapid analyzer. The IR spectra were obtained with a Nicolet 510 FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance Ultrashield 500 (500 MHz) instrument. The chemical shifts (δ) are reported as ppm relative to SiMe_4 . The mass spectrum (ESI) was recorded with a Varian LCMS-320 spectrometer. Organic solvents were purified by standard procedures. Starting compounds *p*-phenylene diisocyanate, L-phenylalanine and lead(II) nitrate were purchased from commercial suppliers.

Synthesis of *N,N'*-[1,4-phenylenebis(iminocarbonyl)]di(L-phenylalanine), LH_2 (**1**)

L-Phenylalanine (1.65 g, 10 mmol) and NaOH (0.41 g, 10 mmol) were dissolved in water (12.5 mL). A solution of *p*-phenylene diisocyanate (0.79 g, 5 mmol) in toluene (8.5 mL) was added under stirring at 0 °C. After completion of the reaction (4.5 h) the phases were separated. The aqueous phase was acidified with 3 N hydrochloric acid and the precipitate collected. Recrystallization from methanol yielded 1.79 g (73%) of **1** as a colorless powder; m. p. 179–180 °C. – $[\alpha]_{\text{D}}^{20} = +88.1$ ($c = 0.01 \text{ mol L}^{-1}$, MeOH). – IR (KBr): $\nu_{\text{max}} = 3389$ (N-H), 3085, 3060, 3031 (C-H, arom.), 2930 (C-H, alkyl), 1720 (C=O, acid), 1647 (C=O, urea), 1606, 1553, 1511 (C=C, arom.), 1458, 1442, 1404 (C-H, alkyl), 1312 (O-H), 1230 (C-O), 1141, 1081, 834 (C-H, Ar, 1,4-disubst.), 755, 701 (C-H, Ar, monosubst.), 644, 523, 492 cm^{-1} . – ^1H NMR (500.1 MHz, $[\text{D}_6]\text{DMSO}$): $\delta_{\text{H}} = 2.93, 2.96$ (dd, $^2J_{\text{HH}} = 13.8 \text{ Hz}$, $^3J_{\text{HH}} = 7.6 \text{ Hz}$, 2 H, CH_2), 3.05, 3.08 (dd, $^2J_{\text{HH}} = 13.8 \text{ Hz}$, $^3J_{\text{HH}} = 5.2 \text{ Hz}$, 2 H, CH_2), 4.44 (m, $^3J_{\text{HH}} = 5.3 \text{ Hz}$, 2 H, CHCOOH), 6.23 (d, $^3J_{\text{HH}} = 8.0 \text{ Hz}$, 2 H, CHNH), 7.19–7.22 (m, 10 H, Ar-H),

7.30 (s, 4 H, Ar-H), 8.50 (s, 2 H, ArNH), 12.60 (br, 2 H, COOH). – ^{13}C NMR (125.8 MHz, $[\text{D}_6]\text{DMSO}$): $\delta_{\text{C}} = 37.4$ (CH_2), 53.5 (CHCOOH), 118.3, 126.5, 128.2, 129.3, 134.1, 137.2 (Ar-C), 154.7 (NC=O), 173.6 (COOH). – MS (ESI): $m/z = 491.3$ (calcd. 490.49 for $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_6$, $[\text{M}+\text{H}]^+$). – $\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$: calcd. C 59.31, H 5.74, N 10.64; found C 59.79, H 5.85, N 10.83.

Preparation of $\text{PbL} \cdot \text{H}_2\text{O} \cdot \text{DMF}$ (**1a**)

Equimolar amounts of **1** and lead(II) nitrate were dissolved in dimethylformamide. After isothermal evaporation of the solvent, the colorless crystals were collected and dried to yield 74% of **1a**; m. p. 228–230 °C (dec.). – IR (KBr): $\nu_{\text{max}} = 1651$ (C=O, urea), 1559 (COO^-), 1502 (C=C), 1401 (COO^-), 827, 701 (C-H, Ar). – $\text{C}_{29}\text{H}_{33}\text{N}_5\text{O}_8\text{Pb}$: calcd. C 44.27, H 4.23, N 8.90; found C 44.54, H 4.52, N 9.52.

X-Ray structure determination

Intensity data were collected on a Kappa APEX II diffractometer (Bruker AXS) using ω - and ϕ -scans. The collected data were corrected for Lorentz and polarization effects. The structure was solved by Direct Methods (SHELXS-97 [43]) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97 [44]). Empirical absorption correction based on multi-scans was applied by using the program SADABS [45]. The non-hydrogen positions were refined together with their anisotropic displacement parameters; the H atoms were treated isotropically. The hydrogen atoms of the water molecule could not be located from a difference electron density map and thus are not included in the structure model. All other H positions were held riding on the respective parent C and N atoms during the subsequent calculations.

CCDC 885573 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

The ligand LH_2 , **1** (Fig. 1), was synthesized by addition of L-phenylalanine to *p*-phenylene diisocyanate following a related literature procedure [46]. The com-

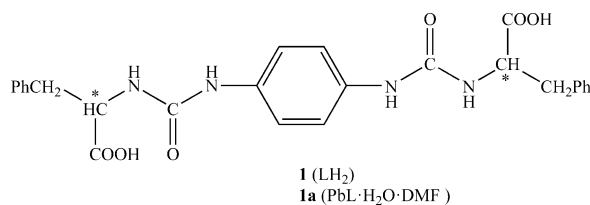


Fig. 1. Compounds studied in this article.

Table 1. Crystallographic data and numbers pertinent to data collection and structure refinement for **1a**.

Empirical formula	C ₂₉ H ₃₃ N ₅ O ₈ Pb
Formula weight	786.79
Crystal system	triclinic
Space group	<i>P</i> 1 (no. 1)
Unit cell dimensions, Å, deg	
<i>a</i>	4.655(1)
<i>b</i>	11.9601(4)
<i>c</i>	15.2256(5)
α	71.960(2)
β	86.700(2)
γ	88.872(2)
<i>V</i> , Å ³	804.67(4)
<i>Z</i>	1
<i>F</i> (000), e	388
<i>D</i> _{calcd.} , Mg m ⁻³	1.62
μ , mm ⁻¹	5.3
Data collection	
Temperature, K	153(2)
θ -range for data collection, deg	1.4–26.1
Index ranges $\pm h$, $\pm k$, $\pm l$	–5/5, –14/14, –18/18
Reflections collected/unique/ <i>R</i> _{int}	12389/5776/0.0209
No. of <i>F</i> values used [<i>I</i> > 2 σ (<i>I</i>)]	5770
No. of refined parameters	390
Final <i>R</i> indices	
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)], <i>R</i> ₁ (all data) ^a	0.0337/0.0363
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^c , <i>wR</i> ₂ (all data) ^b	0.0854/0.1023
Weighting scheme A/B ^b	0.0742/0.0
GoF = <i>S</i> (<i>F</i> ²) ^c	1.246
<i>x</i> (Flack)	0.000(7)
Final $\Delta\rho_{\max}/\min$, e Å ⁻³	2.23/–1.75

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^c $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

plex $\text{PbL}\cdot\text{H}_2\text{O}\cdot\text{DMF}$, **1a**, was prepared analogous to a described procedure [40] by isothermal evaporation of a solution of **1** and Pb(II) nitrate in dimethylformamide (DMF) without the addition of base for neutralization of nitric acid formed during the complexation reaction. Crystals of **1a** of only moderate quality, however suitable for single crystal X-ray diffraction studies, were obtained by slow solvent evaporation. Information concerning the crystallographic data and the structure refinement calculations of the complex is summarized in Table 1. Geometric parameters and possible hydrogen bond interactions are presented in Tables 2 and 3, respectively.

Crystal structure of $\text{PbL}\cdot\text{H}_2\text{O}\cdot\text{DMF}$ (**1a**)

Complex **1a** crystallizes in the space group *P*1 (no. 1) with the unit cell containing one complex unit

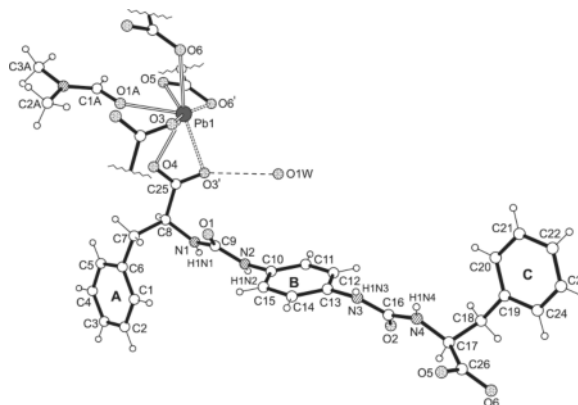


Fig. 2. Relevant structure element of **1a** including atom numbering and ring specification. Oxygen atoms are displayed as dotted, nitrogen atoms as hatched and metal atoms as grey circles.

with the ligand and one molecule of DMF coordinated to the Pb(II) ion (Fig. 2). The proximity of the water oxygen to one of the carboxylate oxygen atoms [$d(\text{O}\cdots\text{O})$ 2.919(9) Å] suggests molecular association via O–H \cdots O bonding. The conformation of the ligand molecule (L) can be expressed by a set of torsion and dihedral angles (Table 2), the latter describing the orientation of the planar molecular elements to each other. The terminal aromatic rings of L adopt approx-

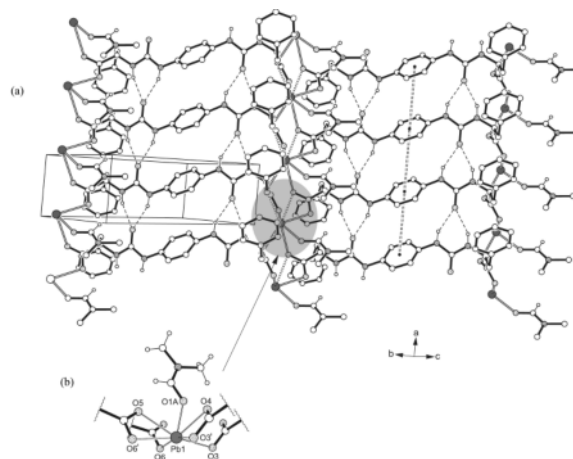


Fig. 3. Excerpt of the two-dimensional network structure of the coordination polymer with detailed specification of the coordination environment around Pb(II). Oxygen atoms are displayed as dotted, nitrogen atoms as hatched and metal atoms as grey circles. Broken lines represent hydrogen bond interactions, double broken lines π stacking contacts.

Dihedral angles (deg) ^a			
mpln(A)-mpln(B)	79.0(3)	mpln(A)-mpln(D)	74.3(3)
mpln(A)-mpln(C)	2.9(6)	mpln(C)-mpln(E)	77.4(3)
mpln(B)-mpln(C)	81.4(3)	mpln(B)-mpln(F)	49.5(3)
		mpln(B)-mpln(G)	49.5(3)
Bond lengths (Å)			
Pb(1)-O(3) ⁱ	2.717(7)	Pb(1)-O(6) ⁱⁱⁱ	2.752(7)
Pb(1)-O(4)	2.373(6)	Pb(1)-O(1A)	2.454(6)
Pb(1)-O(5) ⁱⁱ	2.387(6)	Pb(1)-O(3)	2.824(6)
		Pb(1)-O(6) ^{iv}	2.885(6)
Bond angles (deg)			
O(3)-Pb(1)-O(4)	87.5(2)	O(4)-Pb(1)-O(5)	99.1(2)
O(3)-Pb(1)-O(5)	141.9(2)	O(4)-Pb(1)-O(6)	142.6(2)
O(3)-Pb(1)-O(6)	67.1(2)	O(5)-Pb(1)-O(6)	86.7(2)
O(3)-Pb(1)-O(1A)	71.8(2)		
Torsion angles (deg)			
C(1)-C(6)-C(7)-C(8)	91.9(10)	C(14)-C(13)-N(3)-C(16)	135.1(9)
C(6)-C(7)-C(8)-N(1)	-63.2(9)	C(13)-N(3)-C(16)-N(4)	174.4(8)
C(7)-C(8)-N(1)-C(9)	-77.7(8)	N(3)-C(16)-N(4)-C(17)	169.2(7)
C(8)-N(1)-C(9)-N(2)	-171.3(7)	C(16)-N(4)-C(17)-C(18)	94.4(9)
N(1)-C(9)-N(2)-C(10)	179.8(7)	N(4)-C(17)-C(18)-C(19)	70.8(10)
C(9)-N(2)-C(10)-C(11)	-131.4(9)	C(17)-C(18)-C(19)-C(20)	-93.3(10)

^a Mpln means least-squares plane through the aromatic ring (A-C), the carboxylate (D, E) and urea units (F, G). Ring A: C(1)...C(6); ring B: C(10)...C(15); ring C: C(19)...C(24); D: C(25),O(3),O(4); E: C(26),O(5),O(6); F: C(9),N(1),N(2),O(1); G: C(16),N(3),N(4),O(2). Symmetry codes: (i) 1 + x, y, z; (ii) x, 1 + y, z; (iii) 1 + x, 1 + y, -1 + z; (iv) x, 1 + y, -1 + z.

D-H...A	Symmetry codes	Distances (Å)			Angles (deg)
		D-H	D...A	H...A	D-H...A
N(1)-H(1N1)...O(1)	-1 + x, y, z	0.86	2.933(9)	2.17	147
N(2)-H(1N2)...O(1)	-1 + x, y, z	0.86	2.903(9)	2.11	153
N(3)-H(1N3)...O(2)	1 + x, y, z	0.86	2.871(11)	2.06	157
N(4)-H(1N4)...O(2)	1 + x, y, z	0.86	2.985(9)	2.26	142
C(1A)-H(1A)...O(5)	x, 1 + y, -1 + z	0.93	3.008(12)	2.42	122
C(8)-H(8)...O(4)	-1 + x, y, z	0.98	3.126(10)	2.35	135
C(3A)-H(3A3)...O(1A)	x, y, z	0.96	2.777(15)	2.41	103
C(3A)-H(3A3)...O(4)	1 + x, y, z	0.96	3.490(14)	2.54	172
C(17)-H(17)...O(2)	x, y, z	0.98	2.740(11)	2.41	104
C(17)-H(17)...O(5)	-1 + x, y, z	0.98	3.190(11)	2.32	148
C(15)-H(15)...C(21) ^a	x, 1 + y, z	0.93	3.603(12)	2.81	144
C(12)-H(12)...C(3) ^a	x, -1 + y, z	0.93	3.519(12)	2.75	141

^a To achieve a reasonable hydrogen bond geometry, an individual carbon atom instead of the center of the aromatic ring was chosen as an acceptor.

Table 2. Relevant conformational parameters for **1a**.Table 3. Selected hydrogen bond-type interactions in **1a**.

imate coplanarity [2.9(6)°], but are inclined at angles of 79.0(3) and 81.4(3)° with respect to the plane of the central arene ring. The dihedral angles formed between the planes through the urea fragments and the phenylene ring are 49.5(3)°.

The Pb(II) center adopts a strongly distorted square-bipyramidal coordination environment with the oxygen atom of DMF and the 6s² lone pair on lead occupying the axial positions (Fig. 3). Within the coordination polyhedron, the metal ion is located at a distance

of ca. 0.75 Å from the basal plane which is defined by non-equivalent carboxylate oxygen atoms [O(3)-O(6)] of four different ligand molecules. The Pb-O distances range from 2.373(6) to 2.752(7) Å, the O-Pb-O angles are between 67.1(2) and 142.6(2)°. Two additional weak interactions with Pb-O distances of 2.824(7) and 2.885(7) Å complete the coordination environment of the metal ion. As displayed in Fig. 3(b), the bonds to the ligand molecules are asymmetrically distributed around the metal center and directed to only

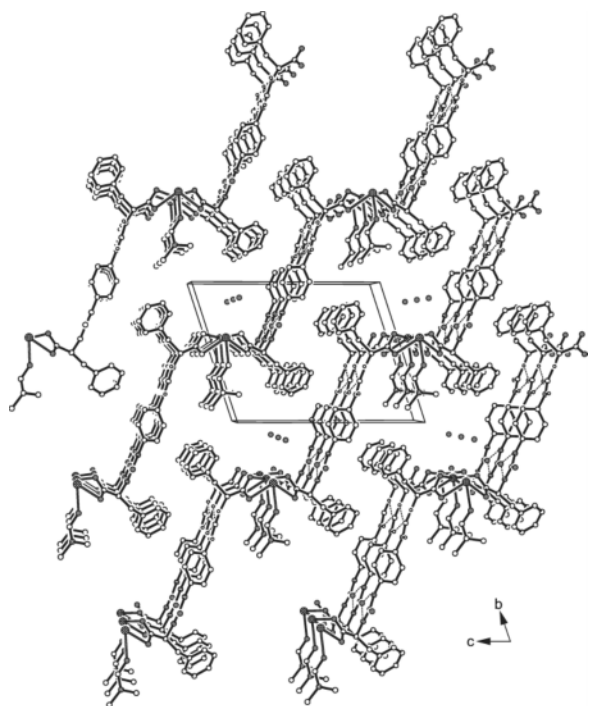


Fig. 4. Packing of the coordination polymer viewed down the crystallographic *a* axis. Oxygen atoms are displayed as grey, nitrogen atoms as hatched and metal atoms as cross-hatched circles. Broken lines represent hydrogen bond interactions.

a part of the coordination sphere. This hemidirected coordination geometry which is induced by the lone pair of electrons [24–26] is found in many Pb(II) complexes [27–29, 33].

According to the given coordination mode, the crystal structure is composed of two-dimensional supramolecular networks extending parallel to the crystallographic [022] plane. In this arrangement, the urea fragments form the well-known α -networks [47] assembled *via* N–H \cdots O=C hydrogen bonds [$d(\text{N}\cdots\text{O})$ 2.871(11)–2.985(9) Å] with the oxygen atoms acting as bifurcated acceptors (Fig. 3). This pattern of hydrogen bonding follows the graph set C(4)[R¹₂(6)] [48] created by both a six-membered hydrogen bonded ring and a C(4) chain. It should be noted at this point that the formation of supramolecular tapes of this kind is observed in the solid-phase structures of a variety of *N,N'*-disubstituted derivatives of urea [48–51], which in many cases have been used as a control element for crystal engineering and template-directed supramolecular synthesis [52–54].

In the present structure, the two sets of α -networks have opposite directions and are assisted by $\pi\cdots\pi$ stacking [55] of the neighboring aromatic rings. The center \cdots center distance of 4.655 Å between interacting rings corresponds with the length of the *a* axis of the unit cell. A view of the packing along this axis reveals a channel-like cavity structure which is partially occupied by solvent molecules (Fig. 4). Moreover, the crystal contains potential solvent-accessible voids of 67.6 Å³ per unit cell, which represents 8.4% of the total cell volume. The 2D networks are associated by weak C–H $\cdots\pi$ arene interactions [56] [C(15)–H(15) \cdots C(21) 2.81 Å, 144°; C(12)–H(12) \cdots C(3) 2.75 Å, 141°].

Conclusions

A new ditopic linker molecule **1**, synthesized from L-phenylalanine and *p*-phenylene diisocyanate, has been found to form a crystalline coordination polymer with Pb(II) containing a hydrogen-bonded supramolecular network structure and getting additional support from $\pi\cdots\pi$ stacking interactions. Induced by its 6s² lone pair, the Pb(II) centers are asymmetrically seven-coordinated including six oxygen atoms of carboxylate groups and the oxygen atom of a DMF solvent molecule, thus giving rise to a hemidirected coordination geometry, rather common in the complexation of Pb(II) [33]. Moreover, the urea subunits show their typical behavior as synthons [57], which is the hydrogen bonded assembly of six-membered rings [58], while $\pi\cdots\pi$ stacking interactions are due to the presence of the central phenylene rings of the linker molecule. This cooperative binding situation, structurally programmed in the linker molecule, finally leads to the formation of the particular two-dimensional coordination polymer which may be seen as a hybrid constellation between coordination polymer and organic framework structure [32, 59–61]. Beyond that, caused by steric effects of the terminal arene groups, channel-like lattice voids are created which are partially filled with solvent molecules, giving the impression of a kind of clathrate formation [62]. As much as 8.4% of the total crystal volume represents empty space so that the crystal also features a porous cavity structure [63].

Based on this property, the present ligand design may arouse interest in the community of re-

searchers dealing with crystal engineering and materials chemistry. Besides, the enantiopure structure of the molecule could open a further direction of development in this field regarding its optical behavior.

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- [1] L. R. MacGillivray (Ed.), *Metal-Organic Frameworks*, Wiley, Hoboken, **2010**.
- [2] S. R. Batten, S. M. Neville, D. R. Turner, *Coordination Polymers*, Royal Society of Chemistry, Cambridge, **2009**.
- [3] P. A. Wright, *Microporous Framework Solids*, Royal Society of Chemistry, Cambridge, **2008**.
- [4] D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem. Int. Ed.* **2009**, *48*, 7502.
- [5] T. Kawamichi, Y. Inokuma, M. Kawano, M. Fujita, *Angew. Chem. Int. Ed.* **2010**, *49*, 2375.
- [6] M. Deng, Y. Ling, B. Xia, Z. Chen, Y. Zhou, X. Liu, B. Yue, H. He, *Chem. Eur. J.* **2011**, *17*, 10323.
- [7] H. Furukawa, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 8875.
- [8] H. J. Park, Y. E. Cheon, M. P. Suh, *Chem. Eur. J.* **2010**, *16*, 11662.
- [9] D. Lässig, J. Lincke, J. Moellmer, C. Reichenbach, A. Moeller, R. Gläser, G. Kalies, K. A. Cychosz, M. Thommes, R. Staudt, H. Krautscheid, *Angew. Chem. Int. Ed.* **2011**, *50*, 10344.
- [10] Z.-Y. Gu, X.-P. Yan, *Angew. Chem. Int. Ed.* **2010**, *49*, 1477.
- [11] A. S. Münch, J. Seidel, A. Obst, E. Weber, F. O. R. L. Mertens, *Chem. Eur. J.* **2011**, *17*, 10958.
- [12] C.-X. Yang, Y.-J. Chen, H.-F. Wang, X.-P. Yan, *Chem. Eur. J.* **2011**, *17*, 11734.
- [13] S. M. Neville, G. J. Halder, K. W. Chapman, M. B. Duriska, B. Moubaraki, K. S. Murray, C. J. Kepert, *J. Am. Chem. Soc.* **2009**, *131*, 12106.
- [14] S. Sato, O. Morohara, D. Fujita, Y. Yamaguchi, K. Kato, M. Fujita, *J. Am. Chem. Soc.* **2010**, *132*, 3670.
- [15] T.-F. Liu, J. Lü, C. Tian, M. Cao, Z. Lin, R. Cao, *Inorg. Chem.* **2011**, *50*, 2264.
- [16] C. Janiak, *Dalton Trans.* **2003**, *14*, 2781.
- [17] W. Lin, S. Wu in *Metal-Organic Frameworks* (Ed.: L. R. MacGillivray), Wiley, Hoboken, **2010**, p. 193.
- [18] X. Duan, Q. Meng, Y. Su, Y. Li, C. Duan, X. Ren, C. Lu, *Chem. Eur. J.* **2011**, *17*, 9936.
- [19] S. R. Batten in *Metal-Organic Frameworks* (Ed.: L. R. MacGillivray), Wiley, Hoboken, **2010**, p. 91.
- [20] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.
- [21] F. Marandi, A. Morsali, A. A. Soudi, *Z. Anorg. Allg. Chem.* **2007**, *633*, 661.
- [22] H. Ahmadzadi, F. Marandi, A. Morsali, *J. Organomet. Chem.* **2009**, *694*, 3565.
- [23] K. L. Zhang, W. Liang, Y. Chang, L. M. Yuan, S. W. Ng, *Polyhedron* **2009**, *28*, 647.
- [24] F. Marandi, B. Mirtamizdoust, A. A. Soudi, V. T. Yilmaz, C. Kazak, *Z. Anorg. Allg. Chem.* **2006**, *632*, 2380.
- [25] J. Abedini, A. Morsali, M. Zeller, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2659.
- [26] A. Aslini, A. Morsali, V. T. Yilmaz, O. Büyükgüngör, *Inorg. Chim. Acta* **2009**, *362*, 1506.
- [27] A. Aslini, A. Morsali, M. Zeller, *Solid State Sci.* **2008**, *10*, 854.
- [28] A. Aslini, A. Morsali, V. T. Yilmaz, C. Kazak, *J. Mol. Struct.* **2009**, *929*, 187.
- [29] A. Aslini, A. Morsali, *Inorg. Chim. Acta* **2009**, *362*, 5012.
- [30] F. Marandi, A. A. Soudi, A. Morsali, R. Kempe, *J. Coord. Chem.* **2005**, *58*, 1233.
- [31] X. Li, R. Cao, Y. Sun, W. Bi, X. Li, Y. Wang, *Eur. J. Inorg. Chem.* **2005**, 321.
- [32] J. Yang, G.-D. Li, J.-J. Cao, Q. Yue, G.-H. Li, J.-S. Chen, *Chem. Eur. J.* **2007**, *13*, 3248.
- [33] M.-L. Hu, A. Morsali, L. Aboutorabi, *Coord. Chem. Rev.* **2011**, *255*, 2821.
- [34] R. Ferrari, S. Bernés, C. R. de Barbarín, G. Mendoza-Díaz, L. Gasque, *Inorg. Chim. Acta* **2002**, *339*, 193.
- [35] A. Morsali, V. T. Yilmaz, C. Kazak, L. G. Zhu, *Helv. Chim. Acta* **2005**, *88*, 2513.
- [36] L. F. Ma, L. Y. Wang, J. G. Wang, Y. F. Wang, X. Feng, *Z. Anorg. Allg. Chem.* **2006**, *632*, 487.
- [37] F. Marandi, N. Shahbakhsh, *J. Coord. Chem.* **2007**, *60*, 2589.
- [38] L. Gasque, M. Verhoeven, S. Bernes, F. Barrios, J. G. Haasnoot, J. Reedijk, *Eur. J. Inorg. Chem.* **2008**, 4395.
- [39] Z. R. Ranjbar, A. Morsali, *J. Mol. Struct.* **2009**, *936*, 206.
- [40] C. D. L. Saunders, L. E. Longobardi, N. Burford, M. D. Lumsden, U. Werner-Zwanziger, B. Chen, R. McDonald, *Inorg. Chem.* **2011**, *50*, 2799.

- [41] F. Marandi, N. Shahbakhsh, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1137.
- [42] S. Bernes, L. Gasque, *Acta Crystallogr.* **2008**, *E64*, m566.
- [43] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.
- [44] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.
- [45] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2004**.
- [46] A. Stankiewicz-Kranc, A. Bielawska, K. Bielawski, E. Skrzydlewska, *Arch. Pharm. Chem. Life Sci.* **2009**, *342*, 632.
- [47] L. S. Reddy, S. K. Chandran, S. George, N. J. Babu, A. Nangia, *Cryst. Growth Des.* **2007**, *7*, 2675.
- [48] C. Capacci-Daniel, S. Dehghan, V. M. Wurster, J. A. Basile, R. Hiremath, A. A. Sarjeant, J. A. Swift, *CrystEngComm* **2008**, *10*, 1875.
- [49] M. C. Etter, J. C. MacDonald, J. Bernstein, *Acta Crystallogr.* **1990**, *B46*, 256.
- [50] L. S. Reddy, S. K. Chandran, S. George, N. J. Babu, A. Nangia, *Cryst. Growth Des.* **2007**, *12*, 2675.
- [51] M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Commun.* **2008**, 2644.
- [52] M. D. Hollingsworth, M. E. Brown, B. D. Santarsiero, J. C. Huffman, C. R. Goss, *Chem. Mater.* **1994**, *6*, 1227.
- [53] J. J. Kane, R.-F. Liao, J. W. Lauher, F. W. Fowler, *J. Am. Chem. Soc.* **1995**, *117*, 12003.
- [54] R. Custelcean, *Chem. Commun.* **2008**, *3*, 295.
- [55] S. L. James in *Encyclopedia of Supramolecular Chemistry* (Eds.: J. L. Atwood, J. W. Steed), CRC Press, Boca Raton, **2004**, p. 1093.
- [56] M. Nishio, Y. Umezawa, K. Honda, S. Tsuboyama, H. Suezawa, *CrystEngComm* **2009**, *11*, 1757.
- [57] G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
- [58] R. E. Meléndez, A. J. Carr, B. R. Linton, A. D. Hamilton in *Molecular Self-Assembly: Organic Versus Inorganic Approaches, Structure and Bonding*, Vol. 96 (Ed.: M. Fujita), Springer, Berlin-Heidelberg, **2000**, p. 31.
- [59] C. L. Schauer, E. Matwey, F. W. Fowler, J. W. Lauher, *Cryst. Eng.* **1998**, *1*, 213.
- [60] M. Du, Z.-H. Zhang, L.-F. Tang, X.-G. Wang, X.-J. Zhao, S. R. Batten, *Chem. Eur. J.* **2007**, *13*, 2578.
- [61] J.-J. Jiang, L. Li, M.-H. Lan, M. Pan, A. Eichhöfer, D. Fenske, C.-Y. Su, *Chem. Eur. J.* **2010**, *16*, 1841.
- [62] E. Weber in *Comprehensive Supramolecular Chemistry*, Vol. 6 (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle), Elsevier, Oxford, **1996**, p. 535.
- [63] T. Hertzsch, J. Hulliger, E. Weber, P. Sozzani in *Encyclopedia of Supramolecular Chemistry* (Eds.: J. L. Atwood, J. W. Steed), Marcel Dekker, New York, **2004**, p. 996.