DOI: 10.1002/ejic.200500652

A New Coordination Polymer Architecture with (10,3)-a Network Containing Chiral Hydrophilic 3-D Channels

Aksana Zharkouskaya,[a] Axel Buchholz,[a] and Winfried Plass*[a]

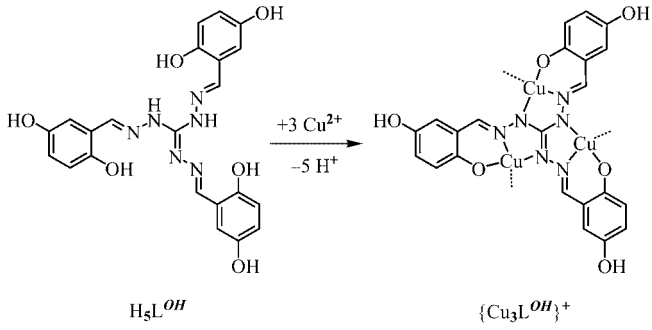
Keywords: Coordination polymer / Copper / Magnetic properties / N,O ligands

The triaminoguanidine-based Schiff-base ligand H_5L^{OH} reacts with copper(II) ions to afford a three-dimensional coordination polymer with (10,3)-a topology which is solely assembled by a single trigonal molecular building block $\{Cu_3L^{OH}\}^+$. The unusual bridging mode of the phenolate oxygen atoms between the trigonal building blocks leads to a dihedral angle between the interlinked $\{Cu_3L^{OH}\}^+$ units of 71°. The (10,3)-a topology of the singular network results in a rather large void space of about 56 % that is established by interpenetrated chiral channels with a diameter limited by pseudo-tetrahedral cavities defined by non-coordinating phenolate hydroxy groups of the ligand. Additional information to establish the composition is derived from elemental analysis and TGA measurements. For the coordination polymer an overall antiferromagnetic behavior is observed. The spin-frustrated trinuclear building blocks $\{Cu_3L^{OH}\}^+$ are antiferromagnetically coupled via the bis(phenoxide)-bridged dinuclear copper(II) moieties for which a dihedral angle of 132° is observed.

Over the last decade the design of porous coordination polymers has become one of the most rapidly developing areas because of their potential applications as rationally designed functional solids with interesting optical, electrical and magnetic properties.[1,2] Of great interest is the architecture and the topological variety of frameworks.[3] Particularly challenging is the design of crystalline material combining different properties like porosity and chirality.[4] Because of specific pore size, type and function of cavities such materials can be applied in ion exchange, catalysis, enantioselective sorption, and gas separation.[1,5] Coordination polymers with (10,3)-a topology are particularly interesting, since they are known to form homochiral porous frameworks which at the same time can show considerable structural stability towards the exchange of guest molecules. These properties make such materials important subjects of research for the development of enantioselective sorption and chiral catalysis.[6]

The interaction of transition metal ions with multifunctional ligands by self-assembly processes is a basic strategy to afford a broad variety of coordination polymers.[1] In particular, the assembly of (10,3)-a nets is generally based on trigonal molecular building blocks that are linked by additional connecting units; both can be either appropriate ligands or metal fragments.[3] Triaminoguanidine-based ligand systems have recently been employed by Robson and Müller et al. in the synthesis of a variety of interesting discrete cage molecules with different topologies.[7]

Here, we report a novel three-dimensional coordination polymer with (10,3)-a topology assembled from a single trigonal molecular building block leading to a homochiral three-dimensional channel system. The utilized trigonal building block is derived from tris[(2,5-dihydroxybenzylidene)amino]guanidine (H_5L^{OH}) chelating copper(II) ions as depicted in Scheme 1. Dark brown cube-shaped single crystals of $[Cu_6(L^{OH})_2(HCOO)_2(H_2O)_{0.5}(DMF)_{0.5}]\cdot xH_2O\cdot y$DMF (**1**) were obtained by slow diffusion of a solution of Bu_4NOH in methanol into a DMF solution containing $(H_6L^{OH})Cl$ and $Cu(BF_4)_2\cdot 6H_2O$ in a 1:3 molar ratio at room temperature.



Scheme 1.

Single-crystal X-ray diffraction reveals a three-dimensional porous framework that is composed of trigonal $\{Cu_3L^{OH}\}^+$ units which are interlocked by the formation of bis(phenoxide)-bridged dinuclear copper(II) moieties as

[a] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena,
Carl-Zeiss-Promenade 10, 07745 Jena, Germany
Fax: +49-3641-948132
E-mail: Sekr.Plass@uni-jena.de

depicted in Figure 1. In contrast to the generally observed planar coordination motif for the bis(phenoxide)-bridged dinuclear copper(II) moieties a dihedral angle of 132° is observed for compound **1**. The typically observed symmetric planar bridging mode is prevented by the steric requirements of the given ligand. As a consequence, an asymmetric bridging moiety is obtained, with the bridging oxygen atoms O11 and O21 in an equatorial position at Cu1, whereas for Cu2 they occupy axial and equatorial positions, respectively. As a result, the copper ions of the two crystallographically distinct $\{Cu_3L^{OH}\}^+$ units exhibit different coordination environments, which are tetracoordinate square-planar for Cu1 and pentacoordinate square-pyramidal for Cu2. In the latter case the bridging oxygen atom O11 is in the apical position at a distance of 232.5 pm and the fourth equatorial position, not occupied by the ligand L^{OH}, is filled by an oxygen atom from the formate counterion or a solvent molecule (see Exp. Sect.). This leads to distinct conformational variations of the two crystallographically independent $\{Cu_3L^{OH}\}^+$ units as depicted in Figure 2. Within the two trinuclear units the distance between the copper ions is about 475 pm, whereas a distance of 290 pm is found along the bridging dinuclear moiety. The resulting dihedral angle between the interlinked $\{Cu_3L^{OH}\}^+$ units is about 71°.

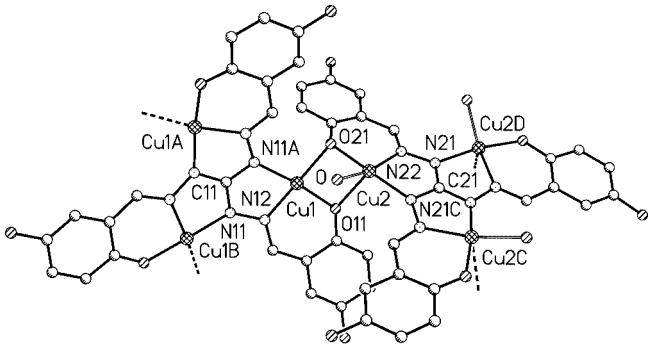


Figure 1. Molecular structure of the $\{Cu_6(L^{OH})_2\}$ building unit of the 3-D coordination polymer **1**. Hydrogen atoms are omitted for clarity; formate anion and solvent molecules are represented by the coordinating oxygen atom; symmetry-equivalent atoms are denoted by A–D. Selected bond lengths [pm] and angles [°]: Cu1–O11 188.9(6), Cu1–O21 200.6(5), Cu1–N12 192.9(6), Cu1–N11A 194.8(6), N11–N12 138.4(9), Cu2–O11 232.5(6), Cu2–O21 195.1(5), Cu2–N22 194.8(6), Cu2–N21C 1.952(6), N21–N22 139.3(9); O11–Cu1–O21 82.9(2), N12–Cu1–N11A 80.5(3), O21–Cu2–O11 73.6(2), N22–Cu2–N21C 80.7(3), Cu1–O11–Cu2 86.4(2), Cu2–O21–Cu1 94.3(2).

The three-dimensional coordination polymer **1** possesses a (10,3)-a network as shown using a simplified view in Figure 3. The fact that two different $\{Cu_3L^{OH}\}^+$ trigonal building blocks assemble the framework leads to a considerable distortion of the archetype (10,3)-a network. The distortion arises from the intercentroid vectors no longer being coplanar, with the angles between the vectors centered at the trigonal building blocks $\{Cu1_3L^{OH}\}^+$ and $\{Cu2_3L^{OH}\}^+$ changing from 120° in an ideal (10,3)-a net to 114.9 and 118.7°, respectively. The chirality of the present (10,3)-a network arises form the [100] pseudo-fourfold and [111] pseudo-

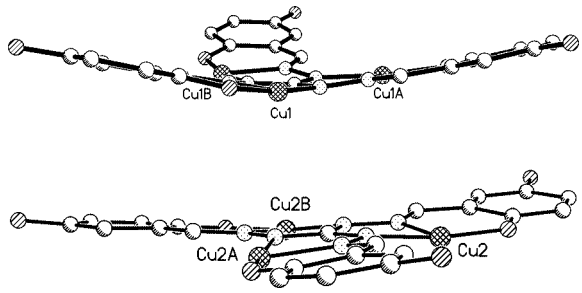


Figure 2. Molecular conformations of the trinuclear building units of **1**: Bowl-shaped $\{Cu1_3L^{OH}\}^+$ (top) and propeller-shaped $\{Cu2_3L^{OH}\}^+$ (bottom).

threefold coordination helices running along the crystallographic 2_1 and 3_2 axes which are of the same handedness propagating in all crystallographic equivalent directions. The packing diagram of compound **1** depicted in Figure 4 shows pseudotetragonal channels along the [100] direction. The size-limiting feature of these channels are the pseudotetrahedral cavities centered at 0,0,1/4 which are defined by the noncoordinating phenol hydroxy groups of the ligand with a diameter of 800 pm for an inscribed sphere. Along the [111] direction this leads to pseudohexagonal zigzag channels passing through these cavities (see Figure 4). The noncoordinating hydroxy groups lead to a hydrophilic character of the solvent-accessible free volume of compound **1**. As a consequence, the resulting void space of **1** is occupied by disordered DMF and H_2O guest molecules.[8] The effective free volume of **1** was calculated with PLATON[9] as 56.4% of the crystal volume (6327 nm^3 out of the 11220 nm^3 unit cell volume). A representation of the void space of **1**, based on the pseudotetragonal channels, is given in Figure 5.

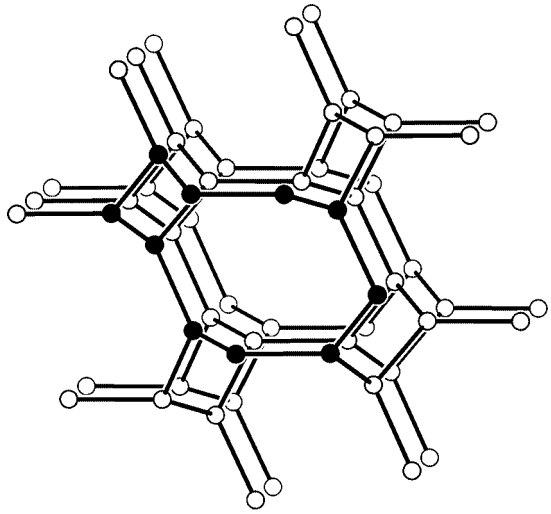


Figure 3. Topology of the 3-D porous framework of **1** shown along [010] with one of the 10-membered rings of the (10,3)-a network highlighted; the nodes represent the central carbon atoms C11 and C21 of the building units.

The thermal behavior of **1** was studied in the range 298–573 K under a flow of nitrogen. The TGA analysis indicates, that the guest molecules can be removed over the tem-

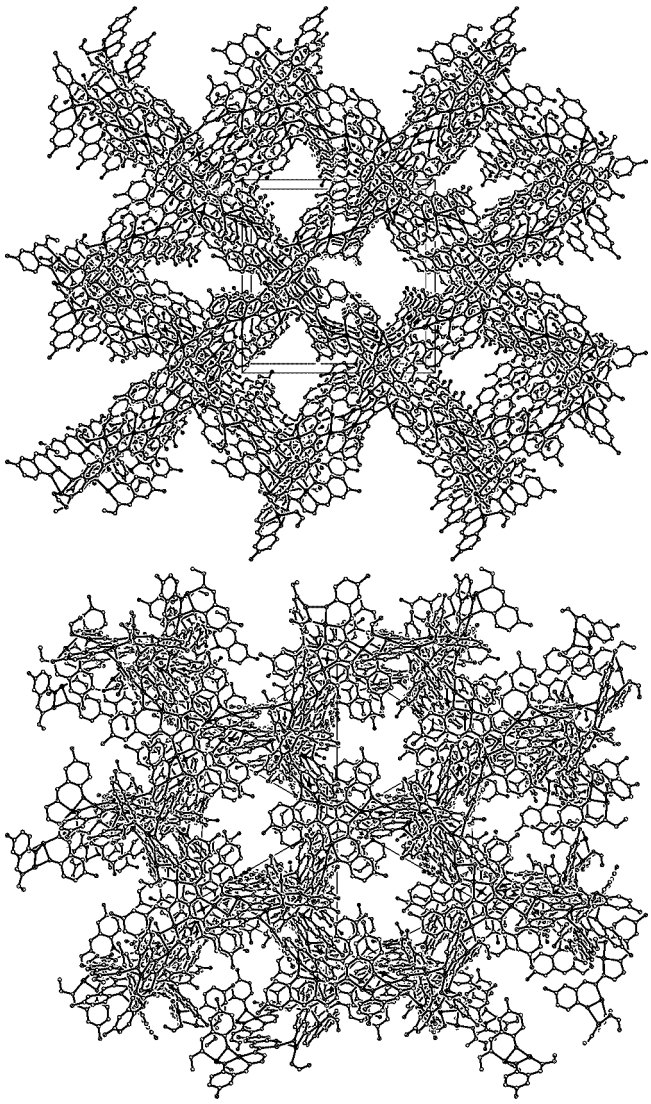


Figure 4. Representation of the network structure of **1** showing the channels along [100] (top) and [111] (bottom).

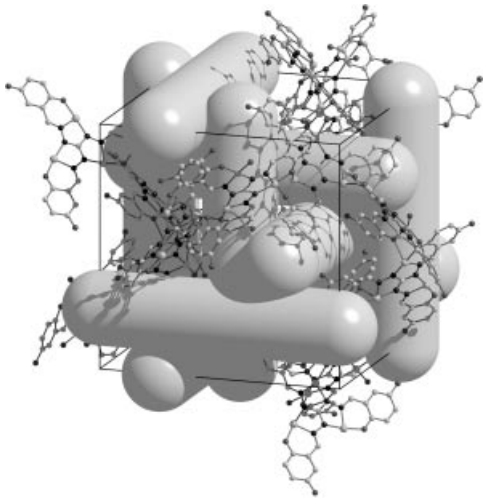


Figure 5. Unit cell of **1** with the pseudo-tetragonal channels represented by cylinders with a diameter of 0.8 nm; all building units originating within the cell are generated.

perature range 313–453 K with an observed weight loss of about 25%. Together with the data from the elemental analyses for samples after prolonged storage under ambient conditions (temperature and atmosphere) this gives a number of three DMF and six H_2O guest molecules per formula unit of **1** filled in the void space.[10] X-ray powder diffraction studies of samples heated to 453 K indicate that the long-range order of the framework structure of **1** is retained upon removal of the guest molecules. If samples of **1** are evacuated at room temperature, a weight loss of about 9% is observed within the first 5.5 h. After 36 h in vacuo, the final weight was constant with an observed loss of about 12%.

The magnetic susceptibility of **1** was measured with a SQUID susceptometer for polycrystalline samples in the temperature range of 2–300 K at a field of 1000 Oe. The temperature dependence of the susceptibility χ and the product χT is shown in Figure 6. For practical reasons the mass susceptibility χ_g was used here, as the actual solvent content can vary considerably.[10] Within the measured range the high-temperature limit expected for a spin-only value of independent copper(II) centers is not reached. In fact, the room-temperature value of χT, based on a molecular mass as derived form TGA and elemental analysis, corresponds to less than 80% of the expected spin-only value. Together with the observed decrease of χT upon cooling, this is indicative for rather strong antiferromagnetic interactions within the system. Nevertheless, within the low-temperature limit of the measurement at 2 K the χT product does not vanish completely with a value that corresponds approximately to the spin-only value of one copper(II) center. The X-band ESR spectrum of **1** recorded on a powdered sample at 77 K exhibits one unstructured broad band at g = 2.072 with a peak-to-peak separation of 29 mT.

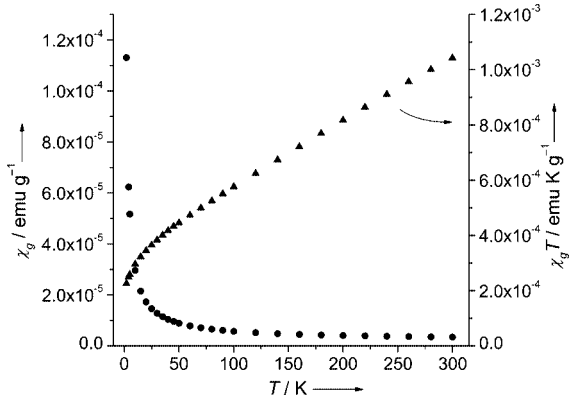


Figure 6. Temperature dependence of χ_g (•) and $\chi_g T$ (▲) for **1**.

Given the structural topology, two basic exchange pathways between the copper(II) centers are possible. One across the trinuclear $\{Cu_3L^{OH}\}^+$ units and the other within the bis(phenoxide)-bridged dinuclear copper(II) moieties. Consequently, two simplified exchange models could be anticipated if either of the two coupling constants prevails the

overall system. Attempts to fit the experimental data with either isotropic spin Hamiltonian model did not yield satisfactory results, suggesting that both exchange pathways are important. For the interaction of the two bis(phenoxide)-bridged dinuclear copper(II) centers Thompson's linear relationship between the Cu–O(Ph)–Cu angle and the coupling constant J (J = 2462 – 31.95a)[11] gives an estimate of about –400 cm^{-1}, based on an average angle of 90°. Nevertheless, this value probably overestimates the actual exchange coupling constant, since for compound **1** with a dihedral angle of 71° a considerable distortion from the coplanarity of the two square planes is observed (cf. Figure 1). On the other hand for isolated trinuclear $\{Cu_3L^{OH}\}^+$ units as part of complexes with appropriate capping ligands at the copper(II) centers a spin-frustrated system with antiferromagnetic coupling parameters in the order of –320 cm^{-1} is observed.[12] The fact that no plateau in the χT diagram corresponding to the spin-frustrated triangular units is evident, indicates the equal importance of the exchange coupling along the dinuclear copper(II) interlocking moieties.

In summary, a novel magnetic 3-D coordination polymer with distorted (10,3)-a network has been synthesized. The size limit and character of the void space of the polymer is defined by the *para* substituent on the coordinating phenolate moiety of the ligand. Both the variation of the ligand substitution and the metal ion are expected to yield materials with interesting new properties.

Experimental Section

General: $Cu(BF_4)_2{\cdot}6H_2O$ and Bu_4NOH were purchased from commercial sources and used as received. (H_6L^{OH})Cl was prepared analogous to procedures reported in the literature.[13] Yield: 79%. (H_6L^{OH})Cl·3H$_2$O ($C_{22}H_{27}ClN_6O_9$, 554.9): calcd. C 47.62, H 4.90, N 15.14; found C 48.01, H 4.79, N 15.38. ^{1}H NMR (200 MHz, CD_3OD, 298 K): δ = 8.80 (s, 3 H, N=CH), 7.39 (d, J = 2.72 Hz, 3 H, C6-H), 6.73–6.85 (m, 6 H, aromatic CH) ppm. ^{13}C NMR (50 MHz, CD_3OD, 298 K): δ = 114.0, 118.0, 120.9, 121.4, 150.2, 150.5, 151.4, 152.2 ppm.

[$Cu_6(L^{OH})_2(HCOO)_2(H_2O)_{0.5}(DMF)_{0.5}$]·$xH_2$O·$y$DMF (1): A solution of ($H_6L^{OH}$)Cl·3H$_2$O (278 mg, 0.5 mmol) in DMF (5 mL) was added to a solution of $Cu(BF_4)_2{\cdot}6H_2O$ (518 mg, 1.5 mmol) in DMF (5 mL). The resulting dark green-brown solution was carefully layered in a glass tube with DMF (3 mL) and with a 1 M methanolic solution of Bu_4NOH (2.5 mL). The glass tube was sealed and left at room temperature. Slow diffusion afforded dark brown crystals of **1** within 3 weeks. The crystals were isolated, washed with MeOH and dried in air. Yield: 30 mg. **1** with x = 6 and y = 3 (prolonged storage at room temperature, $C_{56.5}H_{69.5}Cu_6N_{15.5}O_{26}$, 1763.0): calcd. C 38.49, H 3.97, N 12.31; found C 38.56, H 3.77, N 12.66. Elemental analyses for freshly prepared samples shown higher C and H values due to a higher content of disordered solvent molecules.

Crystal Data for 1: $C_{47.5}H_{36.5}Cu_6N_{12.5}O_{17}$·guests, M = 1435.7, 0.03 × 0.03 × 0.02 mm, cubic, space group $P2_13$, a = 2238.69(5) pm, V = 11.2197(4) nm^3, Z = 4, $\rho_{calcd.}$ = 0.917 g cm^{-3}, T = 183 K, λ = 71.073 pm, μ(Mo-K_α) = 1.164 mm^{-1}, Θ range 3.28–27.46°, 7530 measured and 5231 independent reflections (R_{int} = 0.0415), 285 parameters with no restraints, R_1 = 0.0746, wR_2 = 0.1799 for 5231 reflections with $I > 2\sigma(I)$, GOF = 1.089, Flack parameter = –0.02(4). The data were collected with a Nonius KappaCCD diffractometer. The structure was solved by direct methods (SHELXS) and subsequent full-matrix least-squares refinement against F^2 (SHELXL). The fourth equatorial position at Cu2 (not occupied by the ligand L^{OH}) is occupied by an oxygen atom from either a formate counterion or a solvent molecule of DMF or H_2O, leading to a partial occupation of the corresponding positions in the ratio of 2:3, 1:6 and 1:6, respectively. CCDC-268709 (**1**) 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.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

[1] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388–2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334–2475.

[2] a) D. Maspoch, D. Ruiz-Molina, J. Veciana, in: *Magnetism: Molecules to Materials, V* (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, **2005**, pp. 261–282; b) B. Kesanli, W. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305–326; c) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511–522; d) G. Ferey, *Science* **2001**, *291*, 994–995; e) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; f) B. Moulton, M. J. Zawarotko, *Chem. Rev.* **2001**, *101*, 1629–1658; g) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.

[3] a) L. Öhrström, K. Larsson, *Dalton Trans.* **2004**, 347–353; b) A. F. Wells, *Three-Dimensional Nets and Polyhedra*, Wiley, New York **1977**.

[4] M. E. Davis, *Nature* **2002**, *417*, 813–821.

[5] a) B. Kesanli, Y. Cui, M. R. Smith, E. W. Bittner, B. C. Bockrath, W. Lin, *Angew. Chem.* **2005**, *117*, 74–77; *Angew. Chem. Int. Ed.* **2005**, *44*, 72–75; b) Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kato, M. Sakata, T. C. Kobayashi, *Angew. Chem.* **2005**, *117*, 942–945; *Angew. Chem. Int. Ed.* **2005**, *44*, 920–923; c) P. M. Forster, A. K. Cheetham, *Top. Catal.* **2003**, *24*, 79–86; d) A. Vishnyakov, P. I. Ravikovitch, A. V. Neimark, M. Bülow, Q. M. Wang, *Nano Lett.* **2003**, *3*, 713–718; e) L. Pan, M. B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J. K. Johnson, *J. Am. Chem. Soc.* **2004**, *126*, 1308–1309.

[6] a) D. Bradshaw, T. J. Prior, E. J. Cussen, J. B. Claridge, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2004**, *126*, 6106–6114; b) E. Tynan, P. Jensen, N. R. Kelly, P. E. Kruger, A. C. Lees, B. Moubaraki, K. S. Murray, *Dalton Trans.* **2004**, 3440–3447; c) C. J. Kepert, T. J. Prior, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2000**, *122*, 5158–5168; d) B. F. Abrahams, P. A. Jackson, R. Robson, *Angew. Chem.* **1998**, *110*, 2801–2804; *Angew. Chem. Int. Ed.* **1998**, *37*, 2656–2659; e) O. M. Yaghi, C. E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.* **1997**, *119*, 2861–2868; f) O. M. Yaghi, H. Li, *J. Am. Chem. Soc.* **1995**, *117*, 10401–10402.

[7] a) I. M. Müller, D. Möller, *Angew. Chem.* **2005**, *117*, 3029–3033; *Angew. Chem. Int. Ed.* **2005**, *44*, 2969–2973; b) I. M. Müller, D. Möller, C. A. Schalley, *Angew. Chem.* **2005**, *117*, 485–488; *Angew. Chem. Int. Ed.* **2005**, *44*, 480–484; c) I. M. Müller, S. Spillmann, H. Franck, R. Pietschnig, *Chem. Eur. J.* **2004**, *10*, 2207–2213; d) I. M. Müller, R. Robson, F. Separovic, *Angew. Chem.* **2001**, *113*, 4519–4520; *Angew. Chem. Int. Ed.* **2001**, *40*, 4385–4386; e) I. M. Müller, R. Robson, *Angew. Chem.* **2000**, *112*, 4527–4530; *Angew. Chem. Int. Ed.* **2000**, *39*, 4357–4359.

[8] Although the exact location of the included solvent molecules cannot be unambiguously determined from the single-crystal X-ray diffraction studies due to their high disorder, the formu-

lation of **1** has been established based on TGA and elemental analyses.
[9] A. L. Spek, *Acta Crystallogr., Sect. A* **1990**, *46*, C34.
[10] Repeated elemental analyses for different samples indicate a considerable variation in the actual solvent content with an estimated range of ±1 for *x* and *y*. Analyses performed on freshly prepared samples gave considerably higher values for carbon and hydrogen, which decrease upon storage or drying in vacuo.
[11] L. K. Thompson, S. K. Mandal, S. S. Tandon, J. N. Bridson, M. K. Park, *Inorg. Chem.* **1996**, *35*, 3117–3125.
[12] A. Zharkouskaya, W. Plass, unpublished results.
[13] a) I. M. Müller, D. Möller, *Eur. J. Inorg. Chem.* **2005**, 257–263; b) E. Winkelmann, W. Raether (Farbwerke Hoechst AG, Deutschland), DE-B 2104346, **1972**; *Chem. Abstr.* **1972**, *77*, 126264.

Received: July 22, 2005
Published Online: November 7, 2005

