Layered Compounds

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Copper Hydroxide Ethanedisulfonate: A Cationic Inorganic Layered Material for High-Capacity Anion Exchange**

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Many inorganic pollutants in the form of metal oxo-hydroxo anions are listed as EPA (U.S. Environmental Protection Agency) priority pollutants.[1] Recently, EPA set a national limit for perchlorate (ClO_4^-, a widespread anion occurring from rocket fuel, fireworks and other sources) in drinking water.[2] Chromate (CrO_4^{2-}) and pertechnetate (TcO_4^-) are also problematic monomeric oxo anions, in this case upon the vitrification of radioactive waste.[3,4] Meanwhile, pharmaceuticals and their metabolites have gained increasing attention as pollutants, many existing as organic anions at neutral pH. Current treatment processes are insufficient to adsorb them in high capacity and at reasonable cost.[5] Chlorination can lead to even more toxic compounds, such as monohalogenated or oxidized by-products.[6] The typical approach to trap these intrinsically anionic pollutants remains ion exchange resins, though these organic polymers possess limited thermal and chemical stability and thus longevity.[7]

Cationic inorganic layered materials are 2-D extended architectures where the positively charged layers are held together electrostatically by charge-balancing anions. One typical and widely studied example is the layered double hydroxides (LDHs) with general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}\cdot m\,H_2O]$, where M^{2+} and M^{3+} are a range of metals (e.g. Mg^{2+} and Al^{3+}), x is the ratio of $M^{3+}/(M^{2+}+M^{3+})$, and A^{n-} are n-valent interlamellar anions (e.g. CO_3^{2-}).[8,9] Copper-containing LDHs with a second transition or main-group metal are difficult to synthesize but have been shown to catalyze benzene oxidation.[10,11] Also known as hydrotalcites, LDHs are considered plausible alternatives to resins and can exchange many inorganic and organic anions reversibly. Their selectivity towards toxic anions over carbonate and other interfering anions, however, limits adsorption capacities and thus potential application in water purification. Indeed, this class of materials often requires calcination pre-treatment before ion exchange and displays difficulty in recovery and reuse.[12]

Our group has reported a series of cationic layered inorganic materials consisting of lower p-block metal fluoride and oxide-hydroxide layers charge-balanced by nitrate, perchlorate or alkanedisulfonate.[13–16] Attempts to anion exchange the interlamellar anions for toxic pollutants, however, were either unsuccessful or led to decomposition of the host layers. Meanwhile, layered rare earth hydroxides are an emerging class of inorganic materials with halide, nitrate or other anions in the interlayer region.[17–20] In addition, two three-dimensional cationic inorganic extended frameworks were also reported last year. The structures are based on thorium and ytterbium, charge-balanced by borate and chloride, respectively.[21,22] The structures exchange for several smaller anions to 72%, though excess solid was required. Unlike metal-organic frameworks, no investigation has been made on synthesis of cationic inorganic extended materials based on the less toxic, lower cost and more chemically understood first row transition metals.

Herein, we report the successful synthesis and crystallographic characterization of the first example beyond LDHs of a copper based cationic inorganic material. $[Cu_4(OH)_6][O_3SCH_2CH_2SO_3]\cdot 2\,H_2O$ (which we denote SLUG-26, University of California, Santa Cruz, Structure No. 26) possesses high thermal and chemical stability. Infinite M–O–M 2-D inorganic connectivity results in a rare cationic copper hydroxide layer. This first non-LDH copper hydroxide cationic inorganic extended structure displays rich anion intercalation chemistry, with exchange for variable-length α,ω-alkanedicarboxylates and anion pollutant trapping properties.

SLUG-26 was synthesized under hydrothermal conditions with pure phase at optimized conditions (see Experimental Section). Synthesis temperature higher than the ideal 150 °C (160 °C to 180 °C) resulted in CuO (PDF-ICDD #98-000-0429) as the majority phase. Lower temperature (< 125 °C) produced either clear solution or lower yield of the product. Excess 1,2-ethanedisulfonate (EDS) with a molar ratio of 1:4 for copper nitrate to disodium ethanedisulfonate was necessary, since lower molar ratios (1:1 to 1:2) gave no solid product. Presence of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) was also necessary for crystal formation, which is known to facilitate rod-like crystal growth.[23] The high yield and phase purity was supported by experimental powder X-ray diffraction (PXRD) matching well with the theoretical pattern simulated from single-crystal data (Supporting Information, Figure S1).

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SLUG-26 crystallizes with a blue needle-like morphology (Figure S2). Synchrotron single-crystal X-ray diffraction reveals that the structure consists of a cationic copper hydroxide layer with EDS as interlamellar charge-balancing anion (Figure 1 and Figure 2). The $[Cu_4(OH)_6]^{2+}$ layer has two crystallographically independent Cu centers with similar octahedral coordination environments (Figure 1 and Figure 3). Four oxygens in the positively charged layer define a square-plane around Cu1, while one oxygen (O1) of two separate EDS molecules (one above the given layer, one below) weakly bond to complete the octahedral geometry. The other copper atom (Cu2) has the same square-planar connectivity to four intralayer oxygens, with an axial connection to an intralayer hydroxy group and another weak bond to O1 of EDS. All oxygens in the $[Cu_4(OH)_6]^{2+}$ layer are protonated and triply bridge to metal centers as for LDHs, with the proton of each pyramidal OCu_3 center pointing towards the interlamellar region.

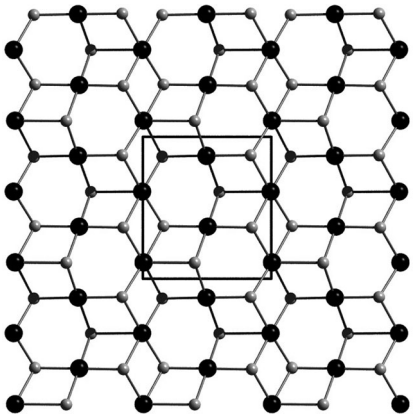

Figure 1. Crystallographic view of one $[Cu_4(OH)_6]^{2+}$ layer of SLUG-26 along the crystallographic *c*-axis (Cu black, O light gray). Hydrogen atoms are omitted for clarity.

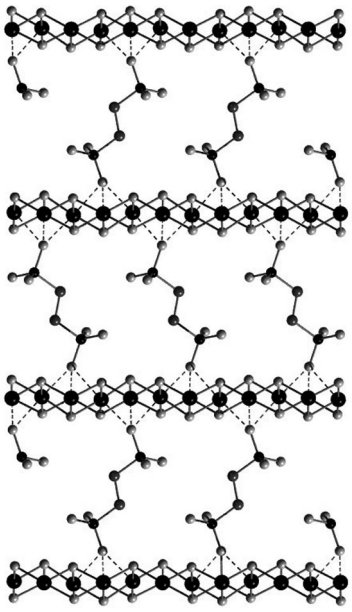

Figure 2. Crystallographic view of SLUG-26 along the *a*-axis (Cu large black, O light gray, S small black, C dark gray). Hydrogen atoms and solvent water molecules are omitted for clarity.

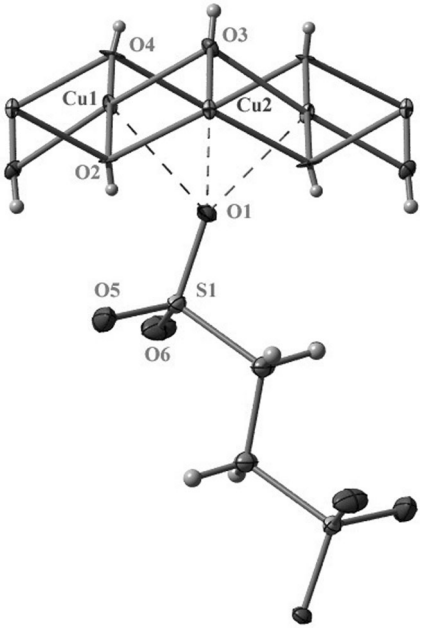

Figure 3. Oak Ridge thermal ellipsoid plot diagrams and atom labeling scheme of the coordination sphere of SLUG-26. Thermal ellipsoids are calculated at 50% probability.

The cationic feature of this new inorganic topology is defined by electrostatic interaction between EDS and positively charged cuprate layers. Only one oxygen (O1) of each sulfonate coordinates to the Cu centers ($O_2SO\cdots Cu$) by weak interaction [2.409(3) Å to 2.488(4) Å]. These contact distances are not only significantly longer than the intralayer square planar Cu–O bonds [1.914(3) Å to 2.001(3) Å] but also longer than the intralayer axial Cu–O bond [2.304(3) Å] which is elongated by a d^9 Jahn–Teller distortion. The Cambridge Crystal Structure Database (CSSD) indicates that 2.4 Å is well outside the accepted distance for a covalent Cu–O bond [2.062 ± 0.204 Å].[24] Indeed, CSSD indicates that 92% of Cu–O bonds are shorter than 2.4 Å, even with the Jahn–Teller effect. Most of the longer bond distances correspond to weakly coordinating monodentate water ligands, which are easily dissociated and thus are not ascribed to covalent bonding.[25–28] The cuprate layers are thus not covalently bonded to the EDS anions, indicating this material is indeed a cationic 2-D layered inorganic structure. Two water molecules are intercalated in the interlamellar regions as for LDHs, and calculations of solvent-accessible void space per unit cell is 36.3 $Å^3$.[29] The resultant 1-D hydrophilic channels along the *c*-axis define 5.6% of the entire structure and are stabilized by hydrogen-bonding to the cuprate–EDS network. This interaction contributes to the chemical stability observed in water, ethanol and other common organic solvents.

This topology is the first example of a 2-D cationic cuprate and a rare non-LDH example based only on a first-row transition metal. There are three similarities between SLUG-26 and LDHs: 1) octahedral coordination around metal centers, which have not been seen with non-LDH type cationic inorganic materials; 2) triply bridging oxygens that are protonated; 3) hydrogen bonding network with the

intercalated anion and water molecules. These structural characteristics likely allow the formation of a cationic structure, for a range of potential applications similar to LDHs such as anion exchange, catalysis and drug delivery.[7] In addition to PXRD, Fourier-transform infrared spectroscopy (FTIR) also confirms the presence of sulfonate ligands [1200m, 1070m (cm^{-1}): RSO_3^- stretch, Figure S3]. Thermogravimetric analysis-mass spectroscopy (TGA-MS) indicates SLUG-26 is thermally stable to ca. 300 °C (Figure S1). Formation of CuO is supported by thermodiffraction at 500 °C under N_2 flow, decomposing to CuO (ICDD PDF#98-000-429).

Since SLUG-26 represents an entirely new transition-metal-based cationic metalate, the intercalation chemistry was investigated by anion exchange, first with various α,ω-alkanedicarboxylate salts. A 3-fold molar excess of malonate, succinate and glutarate in aqueous solution was studied (see detailed in Experimental Section). Low-angle (001) diffraction peaks characteristic of the layer-to-layer distance shifted as expected for anion uptake of malonate [$^-O_2CCH_2CO_2^-$], succinate [$^-O_2C(CH_2)_2CO_2^-$], and glutarate [$^-O_2C(CH_2)_3CO_2^-$] (Figure 4). The exchange gave a decrease of *d*-spacing from 9.6 Å to 7.2 Å for malonate and to 8.6 Å for succinate. The intercalation of glutarate between the $[Cu_4(OH)_6]^{2+}$ layers was also successful and resulted an increase of *d*-spacing from 9.6 Å to 11.1 Å. The completeness of each anion exchange is 100% for malonate, 98.7% for succinate, and 92.4% for glutarate based on the intensity of (001) peak, indicating that shorter dicarboxylate chains more readily intercalate into the positively charged framework. The overall adsorption capacity is 175 $mg\,g^{-1}$ (1.00 $mol\,mol^{-1}$) for malonate, 197 $mg\,g^{-1}$ (0.99 $mol\,mol^{-1}$) for succinate, and 207 $mg\,g^{-1}$ (0.92 $mol\,mol^{-1}$) for glutarate. FTIR before and after anion exchange confirms the exchange process, with sulfonate peaks [1200 m, 1070 m (cm^{-1}): RSO_3^-] completely replaced by carboxylate stretch bands [1570m (cm^{-1}): C=O; 1300s (cm^{-1}): C–O, Figure S3]. The intact crystals, colorless solution and solid and low-angle PXRD diffraction peaks confirm the stability of the cuprate layers. Attempts to exchange EDS for 1,3-propanedisulfonate (PDS) were also successful. The *d*-spacing expanded to 10.2 Å but with only about 60% completeness of exchange and partial loss of crystallinity (Figure S4). Hydrothermal synthesis between various Cu precursors and PDS were unsuccessful in obtaining a stable structure with no solids formed.

In addition to α,ω-alkanedicarboxylates, SLUG-26 displayed anion exchange for metal oxo anion pollutants in far greater capacity than LDHs. Permanganate was employed as a group-7 oxo anion model for pertechnetate, which is a highly problematic radioactive pollutant during the vitrification of nuclear waste.[3,30,31] An equimolar amount of permanganate and as-synthesized SLUG-26 were introduced into aqueous solution under mild stirring (Experimental Section). As monitored by UV/Vis spectroscopy, the permanganate concentration decreased by 36% and 49% with reaction intervals of 8 h and 48 h, respectively (Figure 5). No further decrease in permanganate solution was detected after 48 h, indicating the completion of the process. The overall adsorption capacity of permanganate trapping is therefore 0.51 $mol\,mol^{-1}$ and 201 $mg\,g^{-1}$. These values exceed the majority of LDHs for oxo anions based on a recent review, commonly in the range of 10 $mg\,g^{-1}$ to 150 $mg\,g^{-1}$, even for nitrate- or chloride-containing LDHs or calcined LDH.[12] To verify, we employed both the uncalcined and calcined forms of synthetic hydrotalcite (magnesium aluminum hydroxycarbonate, Aldrich) to perform the anion exchange reactions under the same conditions as SLUG-26. Only 3% and 18% of the permanganate were adsorbed, for adsorption capacity of 6 $mg\,g^{-1}$ and 36 $mg\,g^{-1}$, respectively. These values are less than one-fifth compared to our SLUG-26 material. The lower adsorption capacity of LDHs is likely due to their lower selectivity, which favors carbonate or

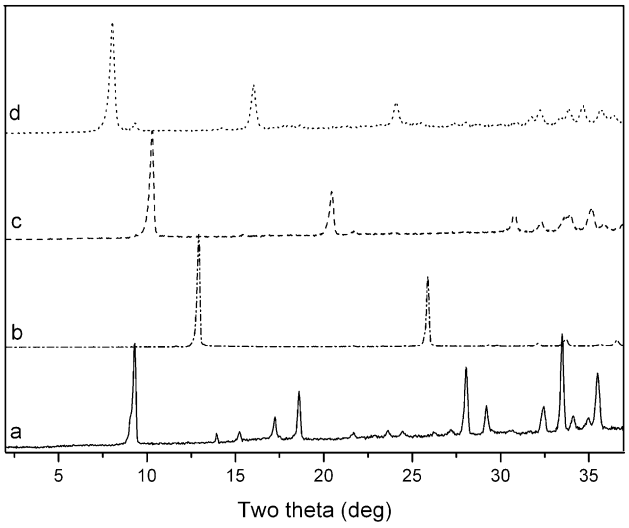

Figure 4. PXRD of SLUG-26: as-synthesized (a, solid line); after exchange with malonate (b, dash-dotted line); after exchange with succinate (c, dashed line); after exchange with glutarate (d, dotted line).

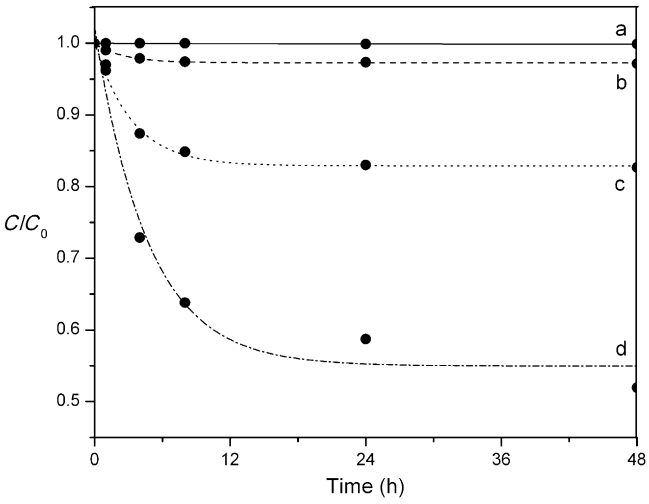

Figure 5. UV/Vis concentration of permanganate vs. time for anion exchange by: blank (no material, a, solid line); uncalcined LDH (b, dashed line); calcined LDHs (c, dotted line); SLUG-26 (d, dash-dotted line).

bicarbonate over all other anions. FTIR does show complete removal of carbonate if calcined LDH is not allowed to re-adsorb CO_2.[8] PXRD before and after anion exchange confirmed that SLUG-26 retains its crystalline layered character after permanganate intercalation, with *d*-spacing decreasing from 9.6 Å to 7.4 Å. The permanganate is permanently trapped, and reusability is in fact undesirable for a highly problematic pollutant such as the radionuclide pertechnetate.

In addition to exceptionally high adsorption capacity, SLUG-26 displays two other advantageous properties over LDHs: 1) SLUG-26 remains heterogeneous throughout anion exchange and can be recovered simply by filtration from the anion solution. LDHs require ca. 30 min centrifugation for total separation; 2) SLUG-26 materials can be used as-synthesized for anion pollutant trapping without pretreatment. LDHs require calcination to partially remove the intercalated water and carbonate in order to achieve its lower capacity anion exchange. Indeed, the memory effect of LDHs necessitates use within 24 h of calcination due to rehydration and reconstruction of the layers.[32–34]

In conclusion, we have synthesized a rare example of a cationic layered inorganic metalate based on a 3d metal, with high thermal stability and excellent anion exchange properties. Despite the structural similarities with LDHs, SLUG-26 demonstrated five time higher adsorption capacity for permanganate with a value over 200 $mg\,g^{-1}$. In addition to metal oxo anion exchange, the material displays flexibility for variable-length α,ω-alkanedicarboxylates, which may be a pathway to adsorbing other problematic anions and/or increasing capacity. Considering the openness of the structure with ordered hydroxyl groups pointing towards the 1D channels, catalysis and exfoliation studies are under investigation.

Experimental Section

Synthesis: copper(II) nitrate hydrate [0.65 g, $Cu(NO_3)_2{\cdot}2.5\,H_2O$, Riedel-de Haen, 98%], 1,2-ethanedisulfonate, disodium salt (2.11 g, $NaO_3SCH_2CH_2SO_3Na$, Acros Organics, 99%), hexadecyltrimethylammonium bromide [0.025 g, $(C_{16}H_{33})N(CH_3)_3Br$, Sigma, 99%], and deionized water (8 mL) were mixed and stirred in a beaker and then introduced into a 15 mL autoclave. The autoclave was sealed and heated statically at 150 °C for 5 days under autogenous pressure, followed by cooling to room temperature at a rate of 6 °C h^{-1}. Blue needle-like crystals were isolated after filtration and rinsed by acetone and deionized water (yield: 0.30 g, 74% based on copper).

Anion exchange: permanganate adsorption capacity experiments were carried out by adding 0.0290 g (1×10^{-4} mol) of as-synthesized SLUG-26 to 0.0158 g (1×10^{-4} mol) $KMnO_4$ (Fisher, 99.8%) in 50 mL aqueous solution. Both calcined and uncalcined LDHs were also studied for comparison. The calcined form of hydrotalcite was prepared by annealing at 450 °C for 2 h and used for anion exchange within 6 h. 0.0603 g (1×10^{-4} mol) of either form of LDH was introduced into the analogous solution as above and studied under the same conditions. For organic anion exchange, 0.0580 g (2×10^{-4} mol) SLUG-26 was added to aqueous solution containing three-fold molar excess (6×10^{-4} mol) of disodium malonate (Sigma, 99%), disodium succinate (TCI America, 99%) or disodium glutarate (TCI America, 99%). For all exchange reactions, the solution was stirred under ambient conditions for 24 to 48 h, followed by filtration to separate and characterize the solids.

Synchrotron X-ray crystallography was collected by the ScRALS program at Beamline 11.3.1 of the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda = 0.77490$ Å. Intensity data were collected on a D8 goniostat equipped with a Bruker APEXII CCD detector. $[Cu_4(OH)_6][O_3SCH_2CH_2SO_3]{\cdot}2\,H_2O$ (SLUG-26): blue needle-like crystal dimensions $0.700\times0.005\times0.005$ mm; monoclinic; space group $P2_1/c$; $a = 5.5798(5)$; $b = 6.1164(6)$; $c = 19.2058(18)$ Å; $\beta = 97.672(5)°$; $V = 649.59(11)$ Å^3; $Z = 4$; $T = 150(2)$ K; μ(synchrotron) = 6.857 mm^{-1}; $d_{calcd} = 2.967$ $g\,cm^{-3}$; 7481 reflections collected; 1274 unique ($R_{int} = 0.0739$); $R_1 = 0.0394$, $wR_2 = 0.1088$ for 1022 data with $I > 2\sigma(I)$ and $R_1 = 0.0483$, $wR_2 = 0.1145$ for all 1274 data. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS. The structure was solved by direct methods with anisotropic refinement of F^2 by full-matrix least-squares. CCDC 830336 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.

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[1] L. H. Keith, W. A. Teillard, *Environ. Sci. Technol.* **1979**, *13*, 416.
[2] C. Hogue, *Chem. Eng. News* **2011**, *89*(6), 6.
[3] Y. Wang, C. Bryan, H. Gao, P. I. Phol, C. J. Brinker, K. Yu, H. Xu, Y. Yang, P. S. Braterman, Z. Xu, *Sandia Report. Potential Applications of Nanostructured Materials in Nuclear Waste Management* **2003**, *SAND2003–3313*, 1.
[4] P. Izak, P. Hrma, B. W. Arey, T. J. Plaisted, *J. Non-Cryst. Solids* **2001**, *289*, 17.
[5] M. Wu, S. Janssen, *Environ. Sci. Technol.* **2011**, *45*, 366.
[6] R. Mark, W. N. Findley, *Polym. Eng. Sci.* **1978**, *18*, 6.
[7] J. B. Quintana, R. Rodil, P. Lopez-Mahia, S. Muniategui-Lorenzo, D. Prada-Rodriguez, *Water Res.* **2010**, *44*, 243.
[8] V. Rives, *LDHs: Layered Double Hydroxides: Present and Future*, Nova Science, Hauppauge, **2001**.
[9] D. G. Evans, R. C. T. Slade, *Layered Double Hydroxides* (Ed.: X. Duan, D. G. Evans), Springer, New York, **2006**.
[10] G. Carja, H. Niiyama, *Mater. Lett.* **2005**, *59*, 24.
[11] C. A. Antonyraj, M. Gandhi, *Ind. Eng. Chem.* **2010**, *49*, 6020.
[12] K. H. Goh, T. T. Lim, Z. Dong, *Water Res.* **2008**, *42*, 1343.
[13] D. T. Tran, P. Y. Zavalij, S. R. J. Oliver, *J. Am. Chem. Soc.* **2002**, *124*, 3966.
[14] C. H. Swanson, H. Shaikh, A. G. Oliver, C. F. Campana, S. R. J. Oliver, *J. Am. Chem. Soc.* **2008**, *130*, 11737.
[15] D. L. Rogow, M. P. Russell, L. M. Wayman, C. H. Swanson, A. G. Oliver, S. R. J. Oliver, *Cryst. Growth Des.* **2010**, *10*, 823.
[16] S. R. J. Oliver, *Chem. Soc. Rev.* **2009**, *38*, 1868.
[17] F. Gándara, J. Perles, N. Snejko, M. Iglesias, B. Gomez-Lor, E. Gutierrez-Puebla, M. A. Monge, *Angew. Chem.* **2006**, *118*, 8166; *Angew. Chem. Int. Ed.* **2006**, *45*, 7998.
[18] L. J. McIntyre, L. K. Jackson, A. M. Fogg, *Chem. Mater.* **2008**, *20*, 335.
[19] F. Geng, Y. Matsushita, R. Ma, H. Xin, M. Tanaka, F. Izumi, N. Iyi, T. Sasaki, *J. Am. Chem. Soc.* **2008**, *130*, 16344.
[20] F. Geng, R. Ma, T. Sasaki, *Acc. Chem. Res.* **2010**, *43*, 1177.
[21] S. Wang, E. V. Alekseev, J. C. Diwu, W. H. Phillips, W. B. L. Depmeier, T. E. Albrecht-Schmitt, *Angew. Chem.* **2010**, *122*, 1075; *Angew. Chem. Int. Ed.* **2010**, *49*, 1057.
[22] H. V. Goulding, S. E. Hulse, W. Clegg, R. W. Harrington, H. Y. Playford, R. I. Walton, A. M. Fogg, *J. Am. Chem. Soc.* **2010**, *132*, 13618.

[23] M. Hu, J.-S. Jiang, X. Li, *Cryst. Growth Des.* **2009**, *9*, 820.
[24] Cambridge Crystal Structure Database: Bond lengths of Cu–O: mean = 2.062 Å, median = 1.958 Å, standard deviation = 0.204 Å. 93.4 % of the bond lengths are shorter than 2.4 Å.
[25] C. K. Prout, J. R. Carruthers, F. J. C. Rossotti, *J. Chem. Soc. A* **1971**, 554.
[26] J. M. Epstein, B. N. Figgis, A. H. White, A. C. Willis, *J. Chem. Soc. Dalton Trans.* **1974**, 1954.
[27] M. Yamanaka, H. Uekusa, S. Ohba, Y. Saito, S. Iwata, M. Kato, T. Tokii, Y. Muto, O. W. Steward, *Acta Crystallogr. Sect. B* **1991**, *47*, 344.
[28] J. H. Miller, J. E. Powell, R. A. Jacobson, S. Kulprathipanja, *Inorg. Chim. Acta* **1976**, *18*, 25.
[29] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht, The Netherlands, **2007**.
[30] J. G. Darab, P. A. Smith, *Chem. Mater.* **1996**, *8*, 1004.
[31] J. G. Darab, A. B. Amonette, D. S. D. Burke, R. D. Orr, S. M. Ponder, B. Schrick, T. M. Mallouk, W. W. Lukens, D. L. Caulder, D. K. Shuh, *Chem. Mater.* **2007**, *19*, 5703.
[32] G. Centi, S. Perathoner, *Microporous Mesoporous Mater.* **2008**, *107*, 3.
[33] P. L. Cardoso, J. Barros, J. Valim, *J. Phys. Chem. Solids* **2006**, *67*, 987.
[34] O. P. Ferreira, O. L. Alves, X. Gouveia, A. G. Souza-Filho, J. A. C. de Pavia, J. M. Filho, *J. Solid State Chem.* **2004**, *177*, 3058.

