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Open-Framework Copper Adeninate Compounds with Three-Dimensional Microchannels Tailored by Aliphatic Monocarboxylic Acids

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S *Supporting Information*

ABSTRACT: A series of isostructural copper(II) coordination polymers containing the nucleobase adenine and different monocarboxylic acids as bridging ligands, $[Cu_2(\mu_3\text{-ade})_2(\mu_2\text{-OOC}(CH_2)_nCH_3)_2]\cdot xH_2O$ (n from 0 to 5), have been prepared. Single-crystal X-ray analysis of acetate ($n = 0$) and butanoate ($n = 2$) compounds shows a covalent three-dimensional network in which the copper(II) centers are bridged by *μ-N3,N7,N9*-adeninato and *μ-O,O′*-carboxylato ligands, with crystallization water molecules trapped in the pores, which are decorated by the Watson–Crick faces of the adenine. The tunable permanent porosity of guest-free compounds was confirmed by gas adsorption measurements.

Coordination polymers offer a means to a novel class of potentially designable materials because their metrics and chemical functionality can be carefully adjusted for specific applications.[1] In recent times, porous metal–organic frameworks (MOFs) have attracted increasing attention because they possess a rich structural chemistry and excellent gas sorption properties. In these types of compounds, we can functionalize the pores to direct their specific recognition capability toward small molecules, and, therefore, the emerging porous MOFs serve as novel functional materials for gas storage, separation, heterogeneous catalysis, and sensing.[2] That is why the judicious choice of the organic ligands is a key step in the design of multidimensional frameworks containing transition-metal complexes as building blocks.[3] In this sense, the unsubstituted adenine nucleobase is a good candidate because it contains at least five donor sites and its versatility as a ligand is well-known.[4] Additionally, it is also known that paddle-wheel cores, with carboxylato and purine derivatives as bridging ligands, are able to build rigid and porous MOFs.[5−8]

We report herein the synthesis and structural and magnetic characterization of a new family of three-dimensional metal–organic compounds, $[Cu_2(\mu_3\text{-ade})_2(\mu_2\text{-OOC}(CH_2)_nCH_3)_2]\cdot xH_2O$ [n from 0 (acetate) to 5 (heptanoate)], whose adsorption measurements have demonstrated that the length of the aliphatic chain of the caboxylate ligands modifies the porosity of the open-framework structures.

Polycrystalline samples of compounds have been prepared by the addition of carboxylic acid to an aqueous solution containing the nucleobase and a copper(II) salt. Good-quality octahedral single crystals of acetate and butanoate compounds have been obtained by the slow diffusion of a methanolic solution of the copper(II) salt into an aqueous solution containing adenine and carboxylic acid (see the Supporting Information). X-ray crystal structure analysis[9] revealed that the basic building unit of the compounds is a centrosymmetric dimer (Figure 1a) in which two copper(II) atoms are bridged by two adenine ligands coordinated by their N3 and N9 nitrogen atoms and two carboxylic ligands with a μ-O,O′ coordination mode. The cluster exhibits a paddle-wheel arrangement with a dihedral angle between the mean plane of the two bridging ligands of ca. 84° and a Cu···Cu distance of around 2.85 Å.

The units are cross-linked (Figure 1b) through the apical coordination of the imidazole N7 atom of the adeninato ligands to four adjacent entities with a Cu···Cu separation across the imidazole N9/N7 bridge of 5.97 Å, so that the purine nucleobase exhibits an unusual tridentate μ-N3,N7,N9 coordination mode.[6,7,10] The linkage is reinforced by a hydrogen-bonding interaction between the coordinated O12 oxygen atom of the carboxylic ligand and the N6–H6A group of the Hoogsteen face of the nucleobase to form a $R_1^1(7)$ ring, implying the copper atom.

The self-assembling process directed by the metal–adeninate linkages generates a 4-connected uninodal net with a **lvt** topology and a $\{4^2.8^4\}$ Schläfli symbol, using as a node the dinuclear building unit.[11] The net exhibits a three-dimensional system of intersecting cavities (Figure 2) whose effective volume comprises 37% and 25% of the unit cell volume for the acetate and butanoate compounds, respectively.[12] It is interesting to note that the free volume is directly related to the length of the aliphatic chain, which is pointing toward the inner portion of the channels, so that a longer chain implies less free volume. The system of microchannels is filled by a variable number of crystallization water molecules, which are engaged themselves and anchored to the inner walls of the pores via hydrogen bonds involving the donor pyrimidinic N1 atom and the acceptor exocyclic N6 amino group of the adeninato ligands. The presence of the Watson–Crick faces of the adenine molecules in the pore walls suggests that these coordination polymers may provide a suitable opportunity for analysis of the host–guest interactions in the solid state.[13] Extended MOFs containing biological moieties (so-called

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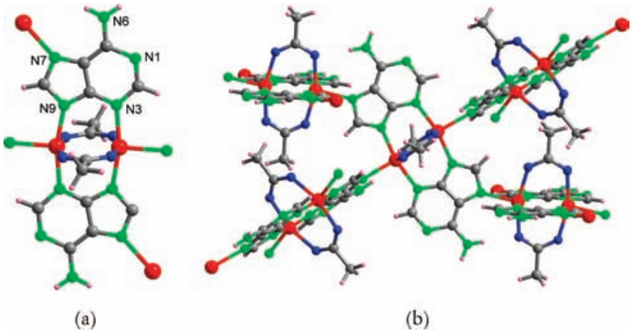

Figure 1. (a) Paddle-wheel core and (b) the cross-linkage between them for an acetate compound.

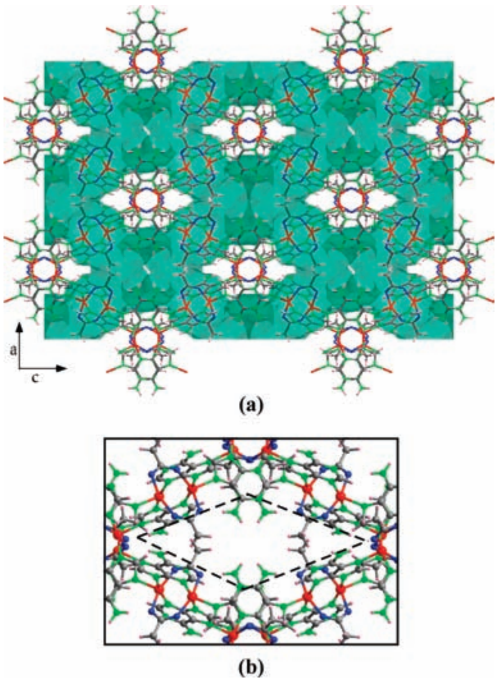

Figure 2. (a) Crystal packing of the acetate compound showing the three-dimensional network of microchannels (backbone blur). (b) Picture showing a cavity with the Watson–Crick face and the aliphatic chains pointing toward it.

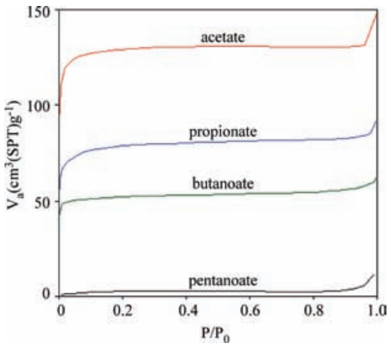

Figure 3. Nitrogen adsorption isotherms at 77 K for degassed compounds.

Table 1. Experimental and Theoretical Adsorption Data

	experimental		theoretical[a]	
compound	area (m^2/g)	V (cm^3/g)	area (m^2/g)	V (cm^3/g)
acetate	505	0.173	654.8	0.286
propionate	301	0.107	393.9	0.232
butanoate	202	0.073	196.0	0.177
pentanoate	8.9	0.004	63.9	0.076

[a] Modeled from the crystal data.

bio-MOFs) are extensively studied to obtain information about a great diversity of biomolecular recognition processes,[14] to analyze their efficiency in selective gas capture,[7,8,15] and to advance in the design of artificial systems suitable for the controllable release of adsorbed bioactive molecules at the cellular level.[16]

Thermal analysis and variable-temperature X-ray diffraction studies (see the Supporting Information) show that the powder diffraction patterns of solvated and desolvated samples do not differ substantially. This fact suggests the stability of the open framework, after removal of the guest molecules, up to around 250 °C.

The permanent porosity of the MOFs was studied by means of measurement of the nitrogen adsorption isotherms at 77 K (Figure 3). All of the samples were dried under vacuum at 150 °C for 8 h to eliminate solvent guest molecules prior to measurement. In the case of acetate, propionate, and butanoate compounds, the adsorption curves resemble a type I isotherm with a sharp knee at low relative pressures ($p/p_0 \sim 0.01$), followed by a plateau, which is characteristic of a crystalline microporous solid with uniform pore-size distribution. On the other hand, the pentanoate compound exhibits an isotherm corresponding to an essentially nonadsorbing solid. The surface area values were obtained by fitting the adsorption data to the Brunauer–Emmett–Teller equation. Table 1 gathers the experimental surface area and micropore volume (t-plot method) along with the corresponding theoretical values extracted from the crystal structures.

Theoretical data of the accessible surface area were calculated by a Monte Carlo integration technique where a probe molecule with a diameter equal to the Lennard-Jones parameter for nitrogen (3.681 Å) is "rolled" over the framework.[17] Generally, the smaller experimental values are attributed to incomplete solvent removal, to partial crystal collapse, or to the presence of impurities. However, discrepancies among the experimental and theoretical values can also arise from the flexibilty of the framework (i.e., the solvent removal, pressure, temperature, and/or adsorbate can affect the disposition of the loose aliphatic chains).[18] The experimental and calculated pore volumes and surface areas are in good accordance with the aforementioned depletion of the effective pore volume caused by the lengthening of the aliphatic chain.

The magnetic behavior of the reported three-dimensional coordination compounds has also been examined. A priori it is dominated by the presence of two magnetic exchange pathways: the interaction involving the dimeric core (resulting from the Cu1–N3–C4–N9–Cu1a and the Cu1–O11–C11–O12–Cu1a bridges) and one pathway through the imidazole bridge that links the dimeric entity with the adjacent ones via the axial N7 positions. Taking into account that the Cu···Cu separation across this last bridge is substantially longer than that involving the dimeric core and that the available data for copper(II) complexes based on bidentate μ-N7,N9-purine nucleobases, to date, indicate very weak antiferromagnetic couplings,[6] the experimental magnetic data of these three-dimensional coordination polymers have been fitted by using the Bleaney−Bowers[19] equation ($H = -JS_1S_2$) for a dinuclear copper(II) complex to give antiferromagnetic interactions with J values ranging from −242 to −212 cm^{-1}. It is well-known that in compounds with the $[Cu_2L_4]$ core (L = purine derivatives) the nonlinear NCN bridges cause antiferromagnetic coupling with J values from −211 to −316 cm^{-1}, which are strongly influenced by the structural parameters of the dimeric entities.[20] Otherwise, experimental and theoretical studies concerning paddle-wheel $[Cu_2(O_2CR)_4X_2]$ species, where X is an apical oxygen or a nitrogen donor ligand, have also shown that a moderate or strong antiferromagnetic coupling is expected in these kinds of compounds.[21] However, the coexistence of two types of bridges in the same exchange magnetic pathway may either add or counterbalance[22] their effects (orbital complementarity and countercomplementarity, respectively). The orbital complementarity of the coordination modes of the adenine and carboxylato ligands within the dimeric unit allows the presence of relatively strong antiferromagnetic couplings in these compounds.

In summary, it has been shown that the adenine nucleobase in combination with aliphatic monocarboxylic acids and a copper(II) salt is an excellent method for the construction of robust open frameworks with interesting adsorptive properties, which are tuned by the length of the aliphatic chains of the organic acids. These MOFs can be good candidates for potential industrial applications because of their high adsorptive capacity, similar to some commercial zeolites, but also because of the method of synthesis, which is easy and reproducible and involves inexpensive starting reagents. Moreover, the presence of the Watson−Crick face of the adenine ligands in the cavity walls suggests that the reported compounds would be suitable for studying supramolecular recognition processes involving molecules of potential biological and medical interest.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of the synthesis, characterization, X-ray analysis, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **1-acetate**: $C_{14}H_{14}Cu_2N_{10}O_4 \cdot xH_2O$, M_r = 513.42 (anhydrous), T = 100(2) K, tetragonal, space group $I4_1/a$, a = 15.298(1) Å, c = 22.517(3) Å, V = 5269.6(8) $Å^3$, Z = 8, ρ_{calcd} = 1.430 g cm^{-3}, μ(Mo Kα) = 1.689 mm^{-1}, θ_{max} = 24°, 5179 reflections collected, and 1978 unique reflections (R_{int} = 0.0633). Final R1 = 0.0723 and wR2 = 0.1931 [$I > 2\sigma(I)$]; R1 = 0.1165 and wR2 = 0.2090 (all data); $\rho_{max/min}$ 0.965/−0.508 $Å^{-3}$. Crystal data for **3-butanoate**: $C_{18}H_{22}Cu_2N_{10}O_4 \cdot xH_2O$, M_r = 569.52 (anhydrous), T = 100(2) K, tetragonal, space group $I4_1/a$, a = 15.348(5) Å, c = 22.702(5) Å, V = 5348(3) $Å^3$, Z = 8, ρ_{calcd} = 1.548 g cm^{-3}, μ(Mo Kα) = 1.657 mm^{-1}, θ_{max} = 24°, 3916 reflections collected, and 2095 unique reflections (R_{int} = 0.1205). Final R1 = 0.0622 and wR2 = 0.0830 [$I > 2\sigma(I)$]; R1 = 0.2080 and wR2 = 0.1014 (all data); $\rho_{max/min}$ 0.438/−0.371 $Å^{-3}$. CCDC 817663 (**1**) and 817664 (**3**) contain the supplementary crystallographic data for this paper.

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