

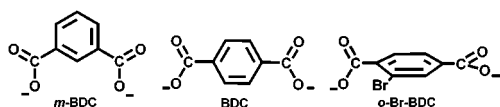
Cu₂[*o*-Br-C₆H₃(CO₂)₂]₂(H₂O)₂·(DMF)₈(H₂O)₂: A Framework Deliberately Designed To Have the NbO Structure Type

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The concept of design in solid-state synthesis has thus far been largely practiced in a retrospective rather than in a truly deliberate manner. This is mainly due to lack of control over the coordination modes of single atoms and ions during assembly of extended structures. To address this issue, we and others have focused on the use of clusters as molecular building blocks since they provide specific rigid molecular geometries that aid in directing the construction of a given structure.^{1–3} Recently, we have developed the use of metal carboxylate clusters for the design of porous metal–organic frameworks (MOFs), in which chelating functional groups lock the metal ions in their position and produce M–O–C clusters referred to as secondary building units (SBUs).⁴ The rigidity of such entities allows their reticulation with the appropriate links into predetermined networks. For example, the bent *m*-BDC and the linear BDC direct the reticulation of the paddle wheel M₂(CO₂)₄ (M = Cu, Zn) cluster into a large discrete truncated cuboctahedron and an extended square grid, respectively.⁵ In this report we show that *o*-Br-BDC, a 90° link, can be used to successfully reticulate the square SBU into Cu₂[*o*-Br-BDC]₂(H₂O)₂·(DMF)₈(H₂O)₂ (termed MOF-101), which has the expected target structure of the NbO network.^{4d} We also use the concept of dual structures to assist in interpreting the lack of intergrowth (catenation) in MOF-101 despite its large openings and voids.



Our synthetic approach began by focusing on the NbO network (Figure 1a) as a target for synthesis. The essential features of this network include its square planar vertexes and their connectivity at right angles to each other.⁶ Having previously identified the synthetic conditions that yield the paddle wheel cluster,^{4a,c,5,7} in which the carboxylate C atoms represent the corners of a square SBU (Figure 1b), it was clear that a rodlike link with carboxylates predisposed at right angles would reticulate the squares as desired for producing a MOF with an NbO-type structure. Since the angle that two carboxylates make within 1,4-benzenedicarboxylates is known to be directly related to the size and nature of substituents on the *ortho* position, we considered and chose *o*-Br-BDC as it was expected to provide the ideal right angle at room temperature.⁸ Indeed, reaction of equimolar amounts of *o*-Br-BDC acid (0.020 g, 0.082 mmol) and Cu(NO₃)₂·2.5H₂O (0.019 g, 0.082 mmol) in DMF (2.0 mL) in a capped vial at room temperature gave blue cubic crystals of the expected framework in 67% yield. The compound was formulated as Cu₂[*o*-Br-BDC]₂(H₂O)₂·(DMF)₈·

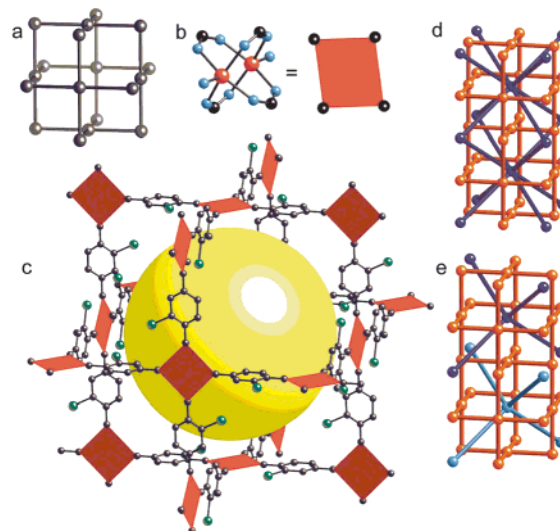


Figure 1. The crystal structure of Cu₂[*o*-Br-C₆H₃(CO₂)₂]₂(H₂O)₂·(DMF)₈·(H₂O)₂ (MOF-101) that was deliberately designed to have an NbO framework (a) by using reaction conditions that produce the paddle wheel unit, a square secondary building unit (SBU). (b) The right angles between carboxylate groups in *o*-Br-BDC ensure the reticulation of the square SBUs into the expected framework (c) having large apertures and voids. This NbO-type structure is noninterpenetrating due to the fact that the body centered cubic network is its dual. (d) Partial interpenetration by diamond is potentially possible (e). [Color scheme for parts b and c: O, blue; C, black; Cu, red spheres; Br, green. NbO network is orange in parts d and e, and its dual, the body centered cubic network is blue in part d, and partial interpenetrating diamond networks are light and dark blue in part e.] Note: The linkers are rotationally disordered so that each Br was in one of four possible positions and just one was selected in making the illustration. There is no disorder in paddle-wheel orientation.

(H₂O)₂ (MOF-101) by elemental microanalysis and single-crystal X-ray diffraction studies.^{9,10} We observed that the crystals are sensitive to water as a solvent but are unaffected for an indefinite period in common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, chloroform, ethanol, methanol, *n*-propanol, dichloromethane, acetone, and DMF.

The crystal structure of MOF-101 (Figure 1c) confirms that the link caused the reticulation of the paddle wheel square SBUs at right angles to each other and ultimately into an NbO-like extended network. Each square planar vertex in NbO has been replaced by a square SBU (decoration) and spaced away from other vertexes by the *o*-Br-C₆H₃ link (expansion) to produce a very open MOF structure. In addition to two axially bound water ligands, at least eight DMF and one water molecule per formula unit are found to fill a 3-D body centered channel system. The remarkable openness of the MOF-101 structure is indicated by the presence of wide hexagonal apertures of 12–14 Å cross-section diameter, and spherical internal voids of diameter 19–21 Å. The volume of a

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van der Waals sphere that would just fit inside the voids is 2309 \AA^3 ,¹¹ a value which exceeds that observed for the most open zeolites, such as faujasite in which the supercage has a volume of 720 \AA^3 .¹²

To evaluate the mobility of the guests within the framework, we examined the as-synthesized crystals by thermal gravimetric techniques: A crystalline sample was heated at a constant rate of $5 \text{ }^\circ\text{C}/\text{min}$. A rapid weight loss of 52.38% was observed below $100 \text{ }^\circ\text{C}$ corresponding to the liberation of all eight DMF and two water guests per formula unit (Calcd: 50.70%). Beyond this temperature, two weight loss steps between $100\text{--}300$ and $300\text{--}400 \text{ }^\circ\text{C}$ were observed and are attributed to loss of water ligands and decomposition of the framework. We have not succeeded yet in our attempts to measure the gas sorption isotherms for the evacuated form of MOF-101, evidence that points to the likelihood that its evacuated framework may not be sufficiently rigid to remain open in the absence of guest. We do not believe that the unusually large space (79% of the total crystal volume) that would be left unoccupied by the framework in MOF-101 upon its evacuation is necessarily the cause of its architectural instability. It is possible that evacuation of the framework causes detrimental shear forces within the paddle wheel unit that are enhanced by the presence of long linear links (*o*-Br-BDC), but can be minimized by tetrahedral and trigonal links as demonstrated for MOF-11 and MOF-14.^{4c,7} Octahedral SBUs as in MOF-5 can also be used with long linear links to generate structurally stable architectures.^{4b} Indeed, these frameworks were determined to have thermal and structural stability up to at least $300 \text{ }^\circ\text{C}$, and to have permanent porosity in the absence of guests.

Nevertheless, it is possible to exchange the guests in solution without destruction of the framework. Immersion of the as-synthesized crystals into chloroform, benzene, acetonitrile, methanol, ethanol, tetrahydrofuran, and dimethyl sulfoxide solvents results in significant decrease in the amount of DMF in the pores as evidenced by elemental microanalysis of the solid produced after exchange.¹³ The X-ray powder diffraction patterns for the exchanged products show the same pattern of intense diffraction lines as that of the as-synthesized MOF-101 material, indicating stability of the framework to solvent exchange.

The fact that MOF-101 is a rare example of an NbO-type network coupled to the observation that it is *not* interpenetrating, despite of the large voids and apertures within its framework, led us to consider the concept of dual structures. In general terms, the *dual* of a network is obtained by placing a vertex inside each repeat unit (*tile*) and linking these new vertexes together through the rings of the original network.¹⁴ This concept is useful in the context of catenation in MOFs, since networks that are self-dual such as diamond, SrSi₂, and primitive cubic are known to readily form interpenetrating MOF structures in which all the frameworks in the crystal are identical.¹⁴ However, NbO is not self-dual; its dual is the body centered cubic network, which would require 8-coordinated atoms, ions, or SBUs in order to form an interpenetrating structure (Figure 1d). It should be noted that if partial interpenetration (in which a link does not pass through every ring of the original network) is considered in NbO, it is conceivable to have it interpenetrated by two mutually interpenetrating diamond networks (Figure 1 e) because body centered cubic can be decomposed into two interpenetrating diamond networks as in the familiar NaTi structure.¹⁵ The design of suitable diamond networks of commensurate dimensions for possible interpenetration with MOF-101 is an interesting challenge that we are actively considering.

This study demonstrates that molecular building blocks can be directed by the geometry of links to reticulate into target frameworks *by design*. The example of MOF-101 having the NbO-type network

is a particularly instructive one since it illustrates the importance of considering duals in MOF structures.

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Supporting Information Available: Crystallographic data (CIF) and bond lengths and bond angles of MOF-101, including the X-ray powder diffraction patterns for the exchange products (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) A blue block crystal of MOF-101 was analyzed: cubic, space group *Im* $\bar{3}m$ (No. 229) with $a = 21.607(3) \text{ \AA}$, $V = 10088(2) \text{ \AA}^3$, $Z = 6$, $d_{\text{calc}} = 1.254 \text{ g/cm}^3$, $T = 295(2) \text{ K}$, and $\mu(\text{Mo K}\alpha) = 1.884 \text{ mm}^{-1}$. All measurements were made on a SMART CCD area detector with graphite-monochromated Mo K α radiation. The structure was solved by direct methods and subsequent difference Fourier syntheses by using the SHELX-TL program package. Both Cu(II) and axial water oxygen (O(2)) sit on the Wyckoff position, e, respectively. The whole *o*-Br-BDC link was located on the mirror plane and the phenyl ring was disordered over two sites on two perpendicular mirror planes. Although the fact that the thermal ellipsoid of disordered Br showed an elongation perpendicular to the phenyl ring implied another disorder around a mirror plane, further resolving was not applied. The guest DMF molecule on a general position was disordered around the coordinated water (O(2)) over four sites. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were not included in the refinement process. R_1 ($I > 2\sigma(I)$) = 0.0788 and wR_2 (all data) = 0.2840. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.327 and $-0.420 \text{ e}^-/\text{\AA}^3$, respectively.
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