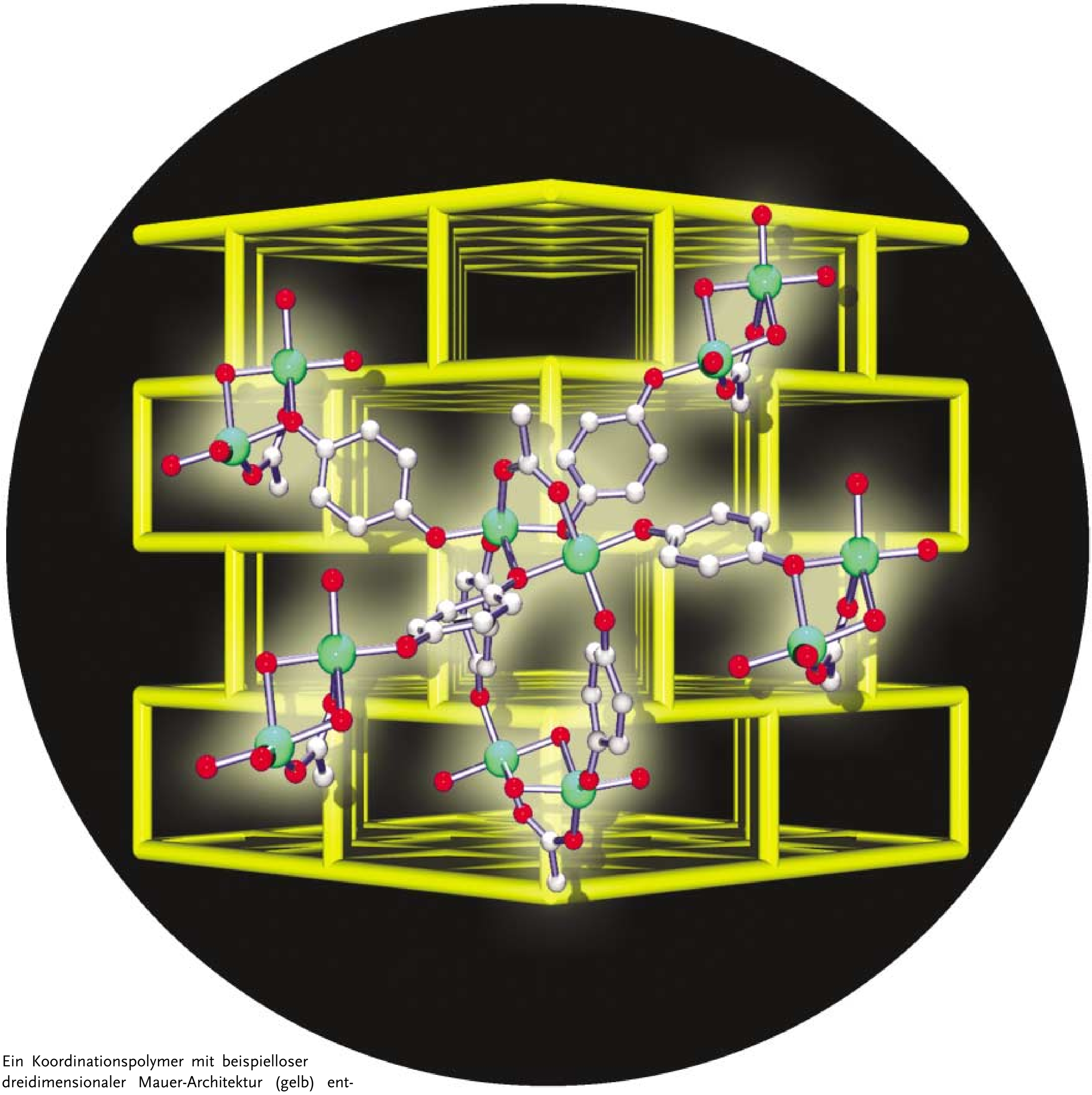
Zuschriften



Ein Koordinationspolymer mit beispielloser dreidimensionaler Mauer-Architektur (gelb) entsteht durch Verbrückung dimerer Kupfer(II)-acetat-Einheiten durch den Organometall-Liganden $[(\eta^4\text{-Benzochinon})\text{Mn(CO)}_3]^-$. Die Kupfer(II)-Zentren sind quadratisch-pyramidal koordiniert. Die Zuschrift von M. Oh, G. B. Carpenter und D. A. Sweigart auf den folgenden Seiten informiert ausführlich über dieses Metall-Organometall-Koordinationspolymer.

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A Metal-Organometallic 3D Network

A Novel 3D Brick-Wall Coordination Network Based on Nodes with Square-Pyramidal Connectivity[**]

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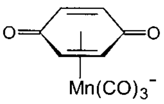
The study of self-assembled finite and infinite metal–organic coordination networks (MONs) is a very active interdisciplinary research area with potential applications in magnetics, optics, electronics, catalysis, and general guest–host interactions.[1] The ability to control or predict the network architectures that obtain from the self-assembly process is a central but elusive goal in this area of supramolecular chemistry. Typically, MONs consist of metal or metal–cluster nodes that are connected by simple organic-spacer molecules that serve as multifunctional ligands. We recently reported the extension of this concept to metal–organometallic networks (MOMNs), in which the spacer is an organometallic complex that functions as a bifunctional ligand ("organometalloligand").[2,3] Specifically, it was shown that the π-complex $[(\eta^4\text{-benzoquinone})Mn(CO)_3]^-$ (QMTC) coordinates to metal ion nodes through the quinonoid oxygen atoms to afford neutral polymeric MOMNs of variable geometry and dimensionality. The resulting materials constitute rare examples of polymers containing both backbone metal sites and pendant metal sites. An impressive range of architectures could be constructed in this manner and, furthermore, it was demonstrated that many of the available architectures could be rationally designed based upon the coordination number, oxidation state, and concentration of the metal ion nodes and based upon the solvent used.[2]



QMTC

A variety of 1D (linear), 2D (planar), and 3D (diamondoid) quinonoid networks have been synthesized by the self-assembly of QMTC spacers and divalent transition-metal ion nodes. Herein, we report the use of these components to generate a simple and highly symmetrical architecture which to our knowledge is unprecedented in the study of coordination polymers—a 3D brick wall. Specifically, QMTC and copper(II) acetate were found to react in methanol to afford a 3D brick wall MOMN with the formula $[Cu_2(\mu\text{-}CH_3CO_2)[(\eta^4\text{-benzoquinone})Mn(CO)_3]_3\cdot MeOH]_\infty$ (**1**). Figure 1 a provides a schematic representation of the 3D brick wall motif viewed edge-on.

To understand the principles behind the construction of a 3D brick wall structure, it is convenient to visualize how the 2D brick wall shown in Figure 1 b can be generated from common "T" shaped building blocks. The 2D brick wall[4] is one of several observed motifs derived from T-shaped nodes; the others include ladder, herringbone, bilayer, and 3D frame structures.[1d,5] In principle, a 3D brick wall structure, as illustrated in Figure 1 c, can be generated from the 2D brick wall by converting the T-shaped nodes to square pyramidal nodes having fivefold connectivity. As documented in more detail below, it was found that such square-pyramidal nodes are formed when QMTC and copper(II) acetate self-assemble in methanol. The resultant 3D MOMN, $[Cu_2(\mu\text{-}CH_3CO_2)[(\eta^4\text{-benzoquinone})Mn(CO)_3]_3\cdot MeOH]_\infty$ (**1**), consists of bimetallic nodes of formula $[Cu_2(\mu\text{-}CH_3CO_2)^{3+}]$ that are linked through linear QMTC spacers in a square-pyramidal geometry. Figure 2 illustrates the fivefold connectivity and square-pyramidal geometry present at each nodal site in **1**. As a consequence of this spatial arrangement, the resultant MOMN has the novel extended 3D brick wall structure shown in Figure 1 a,c.

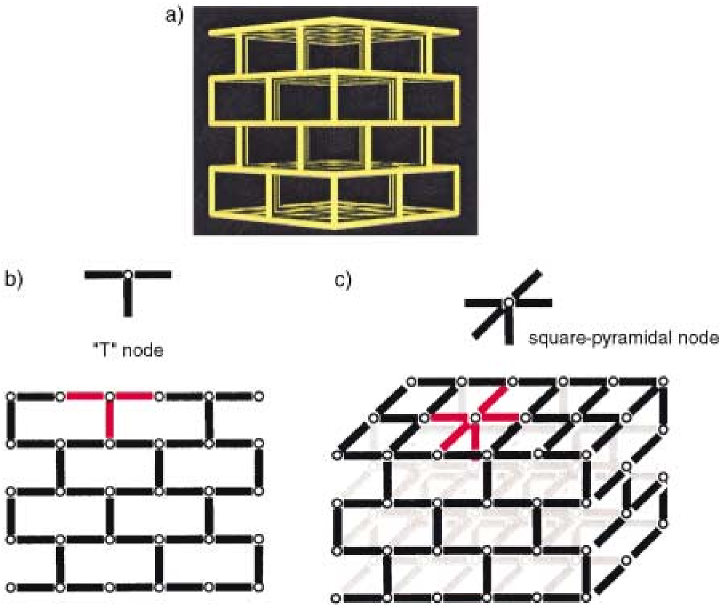


Figure 1. a) A schematic representation of a 3D brick-wall structure viewed edge-on and b,c) how it may be generated from a 2D brick wall by changing the T-shaped nodes to ones with square-pyramidal connectivity.

Green single crystals of MOMN **1** were obtained by the reaction of neutral complex $[(\eta^5\text{-semiquinone})Mn(CO)_3]$ and $Cu(OAc)_2$ at 75 °C in methanol. Figure 3 shows part of the unit cell of **1**. Two uncoordinated molecules of methanol are present in each unit cell as shown. A novel feature of the structure is the arrangement of the copper atoms in the bimetallic units, which are interconnected by QMTC spacers.

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In the context of the 3D structure, the dicopper clusters constitute so-called secondary building units (SBUs).[6] The copper atoms in each SBU are bridged by an acetate anion to give $[Cu_2(\mu\text{-}CH_3CO_2)^{3+}]$ fragments that are positioned as shown in Figure 2. The Cu−Cu distance is 3.14 Å, indicative of little direct metal–metal interaction. Each copper atom is five-coordinate, with one acetate oxygen and four quinone oxygen atoms serving as ligands. There are two types of QMTC spacers present in MOMN **1** (Figure 4). Type 1 QMTC connects to three copper atoms such that one quinone oxygen is monodentate and the other is bidentate. Type 2 QMTC connects to two copper atoms, that is, each quinone oxygen is monodentate. The copper atoms in each SBU are bridged by two oxygen atoms from two type 1 QMTC spacers. The remaining four copper-quinone links are completed in a monodentate fashion, two from type 1 and two from type 2 spacers.

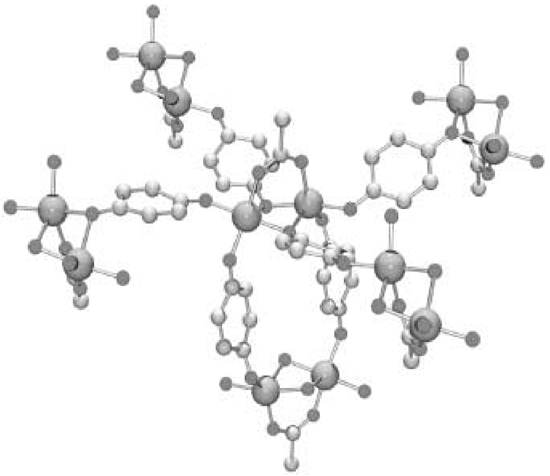

Figure 2. Illustration of a dicopper SBU in MOMN **1,** showing the square-pyramidal connectivity to other dicopper nodes through QMTC spacers. All hydrogen atoms and $Mn(CO)_3$ groups are omitted for clarity.

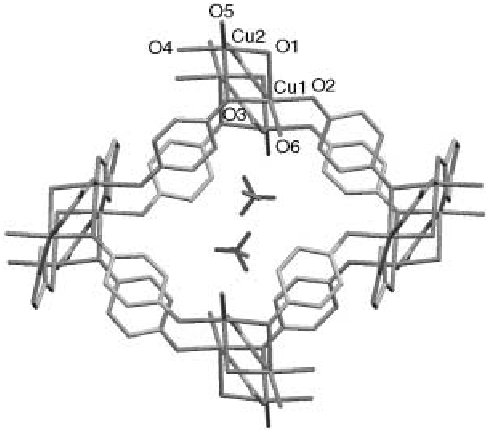

Figure 3. The unit cell contents of MOMN coordination polymer **1**, viewed down the *c* axis. Hydrogen atoms and $Mn(CO)_3$ groups are omitted to facilitate viewing the principle features of the 3D network. Two uncoordinated methanol molecules are present in each unit cell.

The dicopper SBUs in **1** feature fivefold connectivity to adjacent SBUs (Figure 2)and link to the QMTC spacers with a square pyramidal geometry. Four type 1 QMTCs form the base of the pyramid and, along with the SBU, generate the pseudo 2D grid network shown in Figure 5a. The axial direction of the square pyramid is defined by two type 2 QMTCs, which link pairs of SBUs in adjacent planes to generate the 3D brick wall motif shown in Figure 5b (cf. Figure 1a).

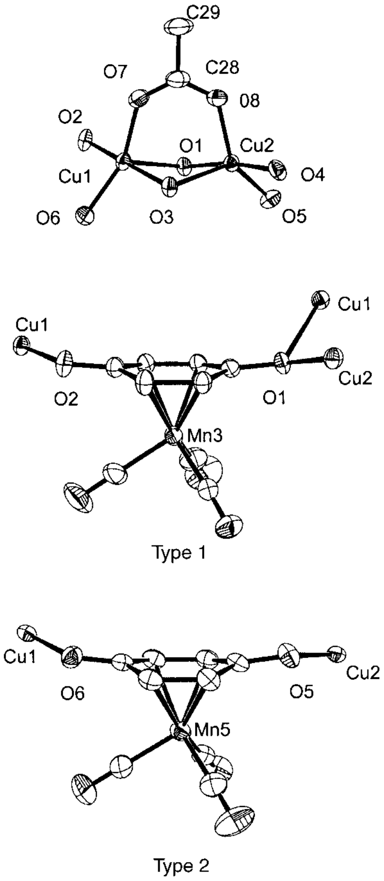

Figure 4. A view of the coordination environment within the dicopper units in **1** and views of the two types of QMTC spacers that connect the dicopper units. Note that type 1 QMTC connects three Cu atoms while type 2 QMTC connects to two Cu atoms. Only one of the two type 1 QMTC spacers present in the asymmetric unit is shown.

In conclusion, this work describes the formation of a novel metal–organometallic network which contains a dicopper cluster as secondary building units and η^4-π-bonded benzoquinone complexes as organometallic spacers. The resulting polymer contains square pyramidal nodes that result in what is the first example of a 3D extended brick-wall network.

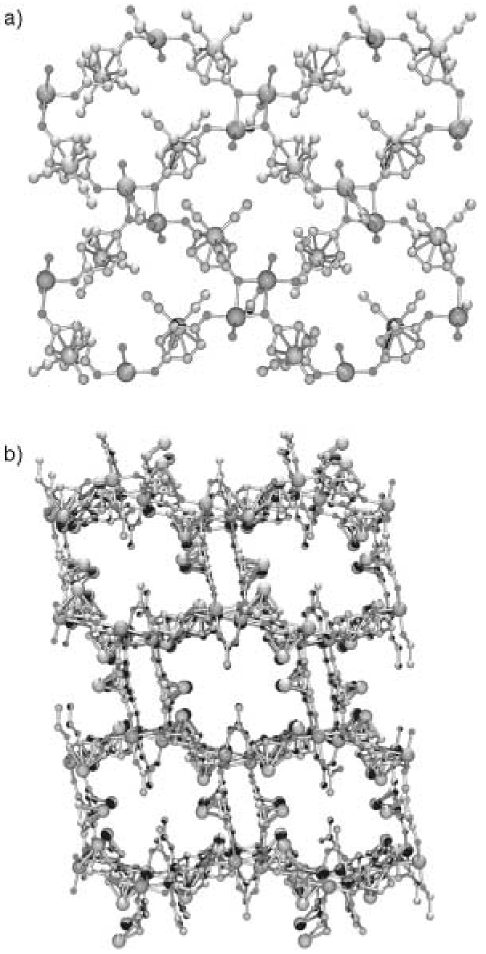

Figure 5. a) A "top" view of the coordination network in **1** showing the base of the square pyramidal SBUs and b) an edge-on view that correlates with the schematic in Figure 1 a. The CO ligands in b) are omitted for clarity.

Experimental Section

The neutral complex [(η^5-semiquinone)Mn(CO)$_3$] (15 mg, 0.060 mmol) and Cu(OAc)$_2$·H$_2$O (6 mg, 0.03 mmol) were heated in CH$_3$OH (0.6 mL) at 75 °C in the dark. After one day, crystals of polymer **1** suitable for X-ray studies were obtained in 82 % yield. IR (KBr) $\tilde{\nu}_{CO} = 2066$ (m), 2038 (s), 2022 (m), 1995 (m), 1978 (s), 1967 (s), 1947 (s), 1930 (m), 1558 (m), 1499 cm^{-1} (s). Elemental analysis calcd (%) for **1**·MeOH, $C_{30}H_{18}Cu_2Mn_3O_{18}$: C 37.60, H 1.89; found: C 37.32, H 1.82. Crystal data for **1**·MeOH: formula $C_{30}H_{19}Cu_2Mn_3O_{18}$, $M_r = 959.35$, monoclinic, space group $P2_1/n$, $a = 14.8202(7)$, $b = 11.8105(6)$, $c = 19.3163(10)$ Å, $\beta = 94.6590(10)°$, $V = 3369.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.891$ g cm^{-3}, $\mu = 2.417$ mm^{-1}, $F(000) = 1904$, θ range 2.02–26.38°, 470 variables refined with 6879 independent reflections to final R indices $[I > 2\sigma(I)]$ of $R_1 = 0.0322$ and $wR_2 = 0.0887$, and $GOF = 1.053$. X-ray data collection with Mo$_{K\alpha}$ radiation was carried out at 298 K using a Bruker Apex diffractometer equipped with a CCD area detector. Structures were determined by direct methods and refined on F squared. CCDC-195906 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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