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Organic–Organometallic Crystal Engineering: Novel Formation of a Honeycomb Supramolecular Architecture of $[\mathrm{Re_2}(\mu\text{-}\mathrm{OMe})_3(\mathrm{CO})_6]^-$ Anions Encapsulating a Linear H-Bonded Chain of $[\mathrm{DABCO\text{-}H}]^+$ Cations

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The title salt $[\mathrm{Re_2}(\mu\text{-}\mathrm{OMe})_3(\mathrm{CO})_6]^-[\mathrm{DABCO\text{-}H}]^+$ (**1**) was prepared as colorless prismatic crystals by the reaction of DABCO with $\mathrm{Re(CO)_5(OTf)}$ in refluxing methanol solution and was characterized by spectroscopic means including single-crystal X-ray diffraction techniques. The molecular structure of **1** revealed that a novel honeycomb supramolecular architecture of the anionic organometallic complex created a cavity with an effective diameter of 7.450(3) Å that houses a linear H-bonded chain of $[\mathrm{DABCO\text{-}H}]^+$ in its center. This structure also represents the first example of the use of a linear chain of $[\mathrm{DABCO\text{-}H}]^+$ species as a countercation for a coordination compound.

The design and construction of supramolecular architectures has been extensively studied in recent years,[1] and a variety of one-, two-, and three-dimensional supramolecular frameworks including diamondoids,[2] ladders,[3] helices,[4] and honeycombs[5] have emerged via self-assembly processes. These processes have involved directional forces such as hydrogen bonding, $\pi-\pi$ stacking, and van der Waals interactions. Most common among these processes is H-bonding between supramolecular framework building blocks, and strong directional interactions of this type have been developed that are capable of arranging building blocks in rigid skeletons possessing channels and cavities.[6] Recently, Braga et al. declared that organic–organometallic crystal engineering could serve as a bridge between supramolecular chemistry and materials chemistry.[7] These authors demonstrated that cationic organometallic species, such as the cobalticenium cation, could be encapsulated within an anionic organic honeycomb framework via charge assistance from H-bonds,[8] and they also showed that small cations such as simple ammonium or phosphonium cations (e.g., $\mathrm{NMe_4}^+$ or $\mathrm{PPh_4}^+$) favor 1-D or 2-D aggregation of anions when anionic hexanuclear carbonyl clusters are crystallized with such organic counterions.[9] Thus the crystal structures of 28 hexanuclear carbonyl cluster anions of the type $[\mathrm{M_6X(CO)_{15}}]^{n-}$ [$\mathrm{M} = \mathrm{Co, Rh}$; $\mathrm{X} = \mathrm{N}$, $n = 1$; $\mathrm{X} = \mathrm{C}$, $n = 2$] and $[\mathrm{M_6(CO)}_x]^{n-}$ [$\mathrm{M} = \mathrm{Ni, Pt}$, $x = 12$, $n = 2$; $\mathrm{M} = \mathrm{Co}$, $x = 15$, $n = 2$; $\mathrm{M} = \mathrm{Co}$, $x = 14$, $n = 4$; etc.] were examined, and the relationship among shape, size, and charge of the component ions and the formation of preferential aggregates in the crystal lattice were analyzed. It was demonstrated that, with large organic cations, the packing pattern is essentially that of molecular mixed crystals, while small cations tend to cause monodimensional aggregation of the anions.

Braga's pioneering work notwithstanding, examples of anionic organometallic supramolecular frameworks that

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encapsulate organic cations remain very rare.[9] Moreover, examples featuring linear H-bonded chains of the monoprotonated 1,4-diazabicyclo[2.2.2]octane (DABCO) as a countercation in coordination chemistry in place of the more commonly encountered isolated NMe_4^+ or NEt_4^+ ions have to our knowledge not been reported. Although our original intent was to synthesize a self-assembled polygon consisting of $Re(CO)_4^+$ corners connected by DABCO ligands, our path led to a novel compound in which $[DABCO\text{-}H]^+$ functions as a replacement for $[NMe_4]^+$ in the solid-state structure of $[NMe_4]^+[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$,[10] but not in the expected manner.

Here we report that a molecular honeycomb structure of $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$ anions self-assembles in the presence of $[DABCO\text{-}H]^+$ cations in a novel reaction. Initially, we employed $[NMe_4][Re_2(\mu\text{-}OMe)_3(CO)_6]$ in a reaction with $[DABCO\text{-}H]^+$ in MeOH solution, and also a reaction of $Re(CO)_5Br$ with DABCO in a sodium/methanol solution. (The reaction of $ReBr(CO)_5$ with NaOMe is known to form $[Re_2(\mu\text{-}OMe)_3(CO)_6]^-$.[10]) Unfortunately only mixtures were obtained in both of our aforementioned attempts. However, $[DABCO\text{-}H][Re_2(\mu\text{-}OMe)_3(CO)_6]$ (**1**) was obtained as colorless prismatic crystals in a reaction of DABCO with $Re(CO)_5(OTf)$ in refluxing methanol solution,[11] a synthetic approach quite different from that reported by others to be successful for the synthesis of ammonium salts of $[Re_2(\mu\text{-}OR)_3(CO)_6]^-$.[10,12] Compound **1** was characterized by IR and NMR spectroscopies[11] and an X-ray study.[13]

The fundamental building units of **1** are depicted in Figure 1a, and in Figure 1b are shown the coordination environment around the Re centers and also the H-bonded network. The $[DABCO\text{-}H]^+$ cations form linear polymeric chains via N−H···N hydrogen bonds along the *c*-axis in which the N−H···N distance is ca. 2.794(6) Å in Figure 1b. It should be mentioned, however, that the hydrogens were not located in the X-ray structure. Although evidence for the ability of the N−H groups in DABCO-H to participate in H-bonding with a neighboring DABCO molecule was put forth previously,[14] this type of interaction was established structurally only in recent years.[15a,c,e] Previous related work in which DABCO was shown to function as a metal ligand was focused on its direct ligation to a metal ion or its indirect linkage to such an ion via a proton hydrogen bonded to an electron pair located on a donor ligated to a metal.[15b,d,f−h] However, compound **1** is the first reported example of an anionic coordination complex associated with a linear chain of $DABCO\text{-}H^+$ countercations.

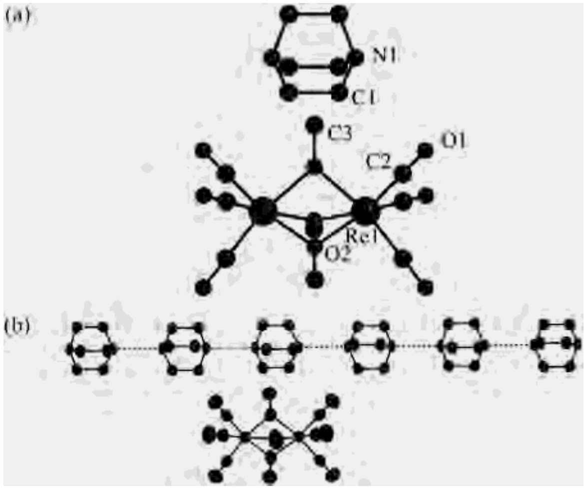

Figure 1. (a) Ball and stick drawing of **1** with the atomic numbering scheme. (b) Local coordination in the structure of **1** along the *c*-axis showing how protonated $[DABCO\text{-}H]^+$ forms a 1-dimensional H-bonded rod. The H atoms are omitted for clarity.

The rhenium centers possess a distorted octahedral geometry in which the two $Re(CO)_3$ fragments are bridged by three OMe ligands, creating two mutually perpendicular mirror planes, as has been found for the monomeric form of this anion in previous structures. One mirror plane is generated by the three oxygen atoms of the OMe bridges, and the second is in the Re−Re axis. Interestingly, the Re−Re distance of 3.0919(8) Å in **1** falls near the short end of the range of 3.104(4)−3.154(1) Å found in previously structurally characterized $[NR'_4][Re_2(\mu\text{-}OR)_3(CO)_6]$ salts.[10,12] However, the average Re−C, Re−O, and C−O bond distances and the Re−(μ-O)−Re bond angle in **1** are similar to the average values for these metrics found in the literature for these ammonium salts.[10,15]

Unlike $[NMe_4][Re_2(\mu\text{-}OMe)_3(CO)_6]$, which possesses no 3-dimensional supramolecular framework,[10] the structure of **1** consists of close-packed channels in a honeycomb array oriented parallel to the *c*-axis (Figure 2). Six dirhenium

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(11) A solution of $Re(CO)_5(OTf)$ (2 mmol, 0.95 g) in methanol (40 mL) was added dropwise via cannula to a solution of DABCO (6 mmol, 0.34 g) in methanol (30 mL) with stirring at room temperature over a period of 10 min. The solution was refluxed overnight, and all volatiles were removed in vacuo, leaving a colorless solid, to which was added 15 mL of toluene. The clear solution was filtered, and fractional recrystallization was carried out. The product **1** was isolated as colorless prismatic crystals after the solution remained at −15 °C in a refrigerator for a few days (0.45 g, yield, 60%). IR (Nujol mull): 3981 w, 3839 w, 3818 w, 3698 w, 2926 s, 2855 s, 2815s, 1985 m, 1877 m, 1465 m, 1365 w, 1330 w, 1292 w, 1202 w, 1183 w, 1148 w, 1070 s, 1051 s, 1008 m, 901 w, 842 s, 800 s, 776 m, 722 w, 698 w, 667 w. ^1H NMR (400.147 MHz, acetone-d_6, ppm): δ 4.20 (s, 1H, N*H*), 3.30 (s, 9H, O*Me*), 3.09 (br s, 12H, NC*H*$_2$). Elemental anal. Calcd for $C_{15}H_{22}N_2O_9Re_2$: C, 24.13; H, 2.97; N, 3.75. Found: C, 24.21; H, 3.11; N, 3.82.

(12) $[NEt_4][Re_2(\mu\text{-}OR)_3(CO)_6]$. (a) R = H: Alberto, R.; Egli, A.; Abram, U.; Hegetschweiler, K.; Gramlich, V.; Schubiger, P. A. *J. Chem. Soc., Dalton Trans.* **1994**, 2815. (b) R = Ph: Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Chem. Soc., Dalton Trans*. **1985**, 1507.

(13) Crystal data for **1** (298 K): space group $P6_3/mmc$ with $a = 10.6721(15)$ Å, $b = 10.6721(15)$ Å, $c = 10.617(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 1047.2(3)$ Å^3, $Z = 2$, $d_{calc} = 2.368$ Mg/m^3, $\mu = 11.596$ mm^{-1}, 9048 reflections measured (531 unique). R (based on F^2 for $I \geq 2\sigma$) = 0.0179, R_w (based on F^2 for $I \geq 2\sigma$) = 0.0391, and GOF = 1.043.

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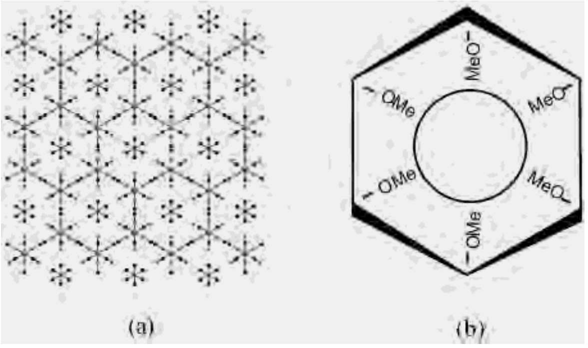

Figure 2. (a) View of the structure of **1** down the *c*-axis, showing a nanochannel containing the 1-dimensional rods. H atoms are omitted for clarity. (b) Depiction of a cylindrical cavity whose diameter is limited by the inwardly protruding OMe hydrogens.

carbonyl anions aggregate so that the rhenium atoms form a six-membered ring containing a rhenium atom at each corner. Each ring adopts a chair conformation in which alternate rhenium atoms are in the same plane, and the edges of the rings are 8.132(1) Å in length. In addition, each layer of six-membered rhenium rings is superimposed above the layer below in perfect register with an interlayer distance of 10.672(2) Å between planes of terminal oxygen atoms on the anions. The effective diameter of the cavities paralleling the *c*-axis is 7.450(3) Å as measured by the diameter of a cylinder that circumscribes a hexagonal column whose apexes contact the van der Waals radii of the hydrogens of the methyl groups as depicted in Figure 2b. (These methyl groups penetrate further into the cavity than do the terminal CO oxygens as can be seen from Figure 1.) The cylindrical cavity comfortably accommodates the H-bonded DABCO chain whose diameter (as defined by the van der Waals radii of the hydrogens on their methylene groups) is 5.991(6) Å.

The closest distance between any oxygens and methyl hydrogens on adjacent anions in a layer of rhenium six-membered rings is 3.626(5) Å, a distance that militates against hydrogen bonding from such interactions as a stabilizing force in these ring systems. It appears rather that the honeycomb structure composed of bundles of parallel anionic nanotubes is stabilized by anion−cation crystal packing forces and hydrogen bonds of the type C(1)−H···O(1) [C(1)−O(1) distance = 3.477 and 3.488 Å] between CO oxygens on the walls of the nanotube and methylene hydrogens protruding from the cationic rods.

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Supporting Information Available: X-ray data for compound **1** (PDF) and details of the refinement procedure in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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