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OH−O and CH−O Hydrogen Bonding in Hydrated Crystals of Paramagnetic $[(\eta^6\text{-}C_6H_6)_2Cr]^+$

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Summary: The hydrated crystalline species $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$ and $[(\eta^6\text{-}C_6H_6)_2Cr][CHD]\cdot 3H_2O$ (CHD = 1,3-cyclohexanedione) have been prepared and structurally characterized, showing that OH−O as well as CH−O hydrogen bonds involving the water molecules are responsible for crystal cohesion.

Organometallic materials are attracting much interest in the field of crystal chemistry and engineering.[1] Organometallic systems combine the intra- and intermolecular bonding features of organic fragments (the ligands) with the variable valence state and magnetic behavior of transition metal atoms. The great structural and chemical variability of organometallic molecules can be utilized to devise solids with predefined physical and chemical properties. This goal can be achieved by choosing appropriate patterns of intermolecular interactions such as those established by hydrogen bond donor and acceptor groups.[2] We are now able to show that water molecules can play an important role in the stabilization of organometallic solids by participating in both OH−O and CH−O interactions. It should be stressed that the hydrogen-bond structure of water and its interactions with the surroundings still represent a key issue in the study of highly hydrated systems.[3] Additional information on water binding can be of some importance in the study of biological macromolecules.[4]

We have recently reported that the organic−organometallic crystalline salt $[(\eta^6\text{-}C_6H_6)_2Cr][(CHD)_4]$ (CHD = 1,3-cyclohexanedione) can be obtained from the oxidation of neutral $[(C_6H_6)_2Cr]$ in the presence of CHD in THF solution. In the solid state, the paramagnetic cation $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ is trapped within a horseshoe-shaped tetrameric monoanion in which the CHD units are linked *via* OH−O hydrogen bonds and interact with the cation *via* CH−O links.[5] This complex structure is reminiscent of Etter's CHD cyclamer encapsulating a benzene molecule.[6]

We now report that when the oxidation reaction is carried out in the presence of water, the hydrated

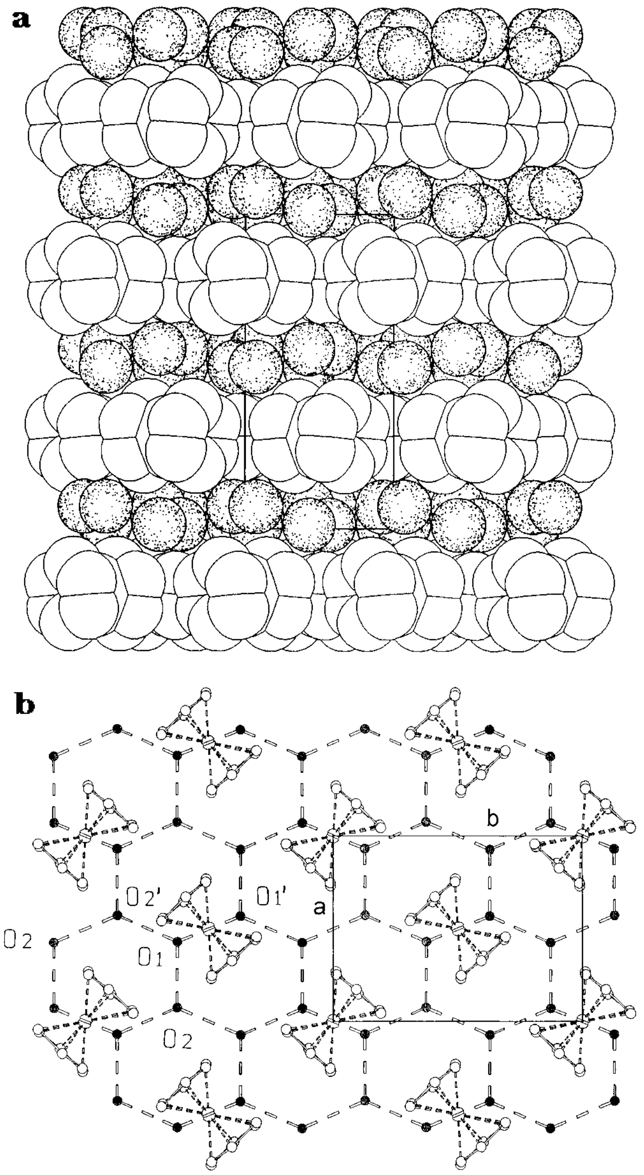

Figure 1. Crystalline $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$: (a) space-filling representation of the stacking along the *c*-axis of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations and $(OH)^-\cdot 3H_2O$; (b) the hexagonal network of hydrogen-bonded O-atoms projected over the underlying $[(C_6H_6)_2Cr]^+$ cations (hydrogen atoms are not shown for clarity). O(water)−O(water) distances are O(1)−O(1′) 2.898, O(1)−O(2) 2.925, O(1)−O(2′) 2.962, and O(2)−O(2′) 2.944 Å; relevant O(water)−H(benzene) hydrogen-bonding interactions are O(1)−H(4′) 2.616, O(2)−H(3) 2.636, and O(2)−H(1′) 2.438 Å and C(4′)−H(4′)−O(1) 142.4, C(3)−H(3)−O(2) 166.1, and C(1′)−H(1′)−O(2) 154.4°. Relevant bonding parameters in $[(\eta^6\text{-}C_6H_6)_2Cr]^+$: mean C−C(benzene) = 1.40(1) and mean Cr−C = 2.137(2) Å.

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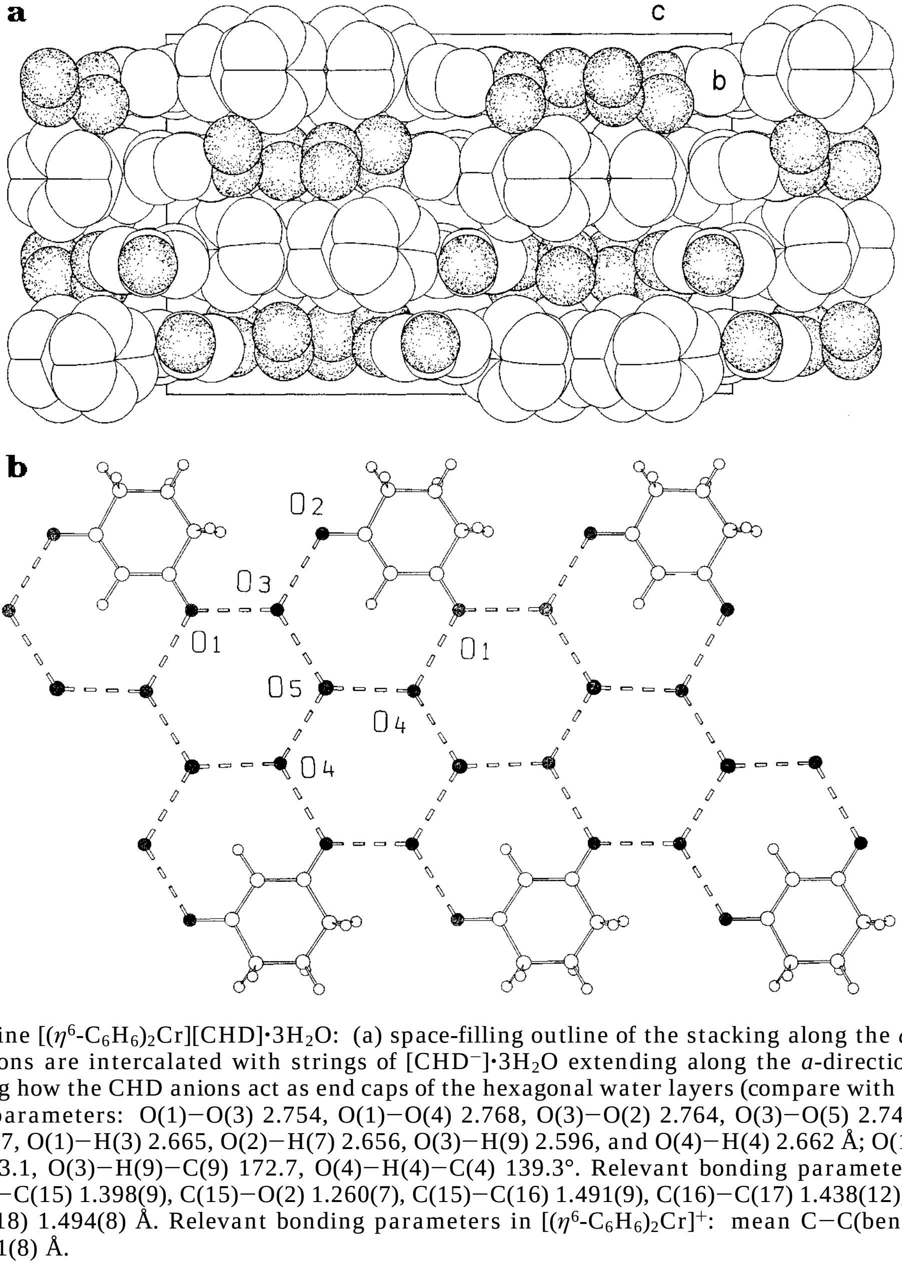

Figure 2. Crystalline $[(\eta^6\text{-}C_6H_6)_2Cr][CHD]\cdot 3H_2O$: (a) space-filling outline of the stacking along the *a*-axis [note how the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations are intercalated with strings of $[CHD^-]\cdot 3H_2O$ extending along the *a*-direction]; (b) projection in the *ac*-plane showing how the CHD anions act as end caps of the hexagonal water layers (compare with Figure 1b). Relevant hydrogen-bonding parameters: O(1)−O(3) 2.754, O(1)−O(4) 2.768, O(3)−O(2) 2.764, O(3)−O(5) 2.740, O(4)−O(5) 2.762, and O(5)−O(4′) 2.777, O(1)−H(3) 2.665, O(2)−H(7) 2.656, O(3)−H(9) 2.596, and O(4)−H(4) 2.662 Å; O(1)−H(3)−C(3) 120.5, O(2)−H(7)−C(7) 123.1, O(3)−H(9)−C(9) 172.7, O(4)−H(4)−C(4) 139.3°. Relevant bonding parameters in CHD: C(13)−O(1) 1.259(7), C(14)−C(15) 1.398(9), C(15)−O(2) 1.260(7), C(15)−C(16) 1.491(9), C(16)−C(17) 1.438(12), C(17)−C(18) 1.430(11), and C(13)−C(18) 1.494(8) Å. Relevant bonding parameters in $[(\eta^6\text{-}C_6H_6)_2Cr]^+$: mean C−C(benzene) = 1.38(1) and mean Cr−C = 2.131(8) Å.

species $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$ (**1**) and $[(\eta^6\text{-}C_6H_6)_2Cr][CHD]\cdot 3H_2O$ (**2**) are obtained.[7] The two systems have been investigated by single-crystal X-ray diffraction.[8]

The hydroxide structure presents some unique features that can be summarized as follows: (i) The crystal is composed of a stacking sequence (ABABAB) of layers containing $[(C_6H_6)_2Cr]^+$ cations intercalated with layers of water molecules and OH^- (see Figure 1a). (ii) This latter layer is formed of a slightly puckered, hexagonal network containing three water molecules and one OH^- group per formula unit, with the O-atoms hydrogen-bonded to three neighbors (see Figure 1b). This type of

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[7] Synthesis of $[(\eta^6\text{-}C_6H_6)_2Cr][CHD]\cdot 3H_2O$: Air is bubbled through a brown solution of $[(\eta^6\text{-}C_6H_6)_2Cr]$ (0.10 g, 0.48 mmol) in 9/1 THF/H_2O (30 mL) and CHD (0.056 g, 0.50 mmol) until the brown color turns to yellow. The reaction mixture is stirred at room temperature for 30 min and then filtered to remove some green material (probably some Cr^{3+} compound coming from overoxidation) and concentrated to dryness *in vacuo*. The solid residue is dissolved in a small amount of THF and transferred to a flask connected to a N_2 line. Slow evaporation of the solvent affords crystals suitable for X-ray diffraction. Synthesis of $[(\eta^6\text{-}C_6H_6)_2Cr][OH]\cdot 3H_2O$: $[(\eta^6\text{-}C_6H_6)_2Cr]$ (0.10 g, 0.48 mmol) is dissolved in benzene (20 mL). Water (19 mL) is added and air is bubbled through the two-layer system until the benzene layer is almost colorless. The yellow water layer is separated and concentrated to dryness. The solid residue is dissolved in a small amount of $CHCl_3$ and transferred to a flask under nitrogen. Slow evaporation of the solvent affords crystals suitable for X-ray diffraction. Both compounds slowly oxidize in air either in solution or in the crystalline state to unidentified green material. Anal. Calcd for $[(C_6H_6)_2Cr][CHD]\cdot 3H_2O$: C, 58.86; H, 6.86. Found: C, 58.50; H, 6.45. Anal. Calcd for $[(C_6H_6)_2Cr][OH]\cdot 3H_2O$: C, 52.38; H, 6.96. Found: C, 52.10; H, 6.60.

[8] Crystal data. $[(C_6H_6)_2Cr][OH]\cdot 3H_2O$ (**1**): $C_{12}H_{15}CrO_4$, $M = 275.18$; orthorhombic, space group *Aba*2; $a = 7.825(3)$, $b = 10.506(4)$, $c = 16.409(3)$ Å; $V = 1349.0(8)$ Å^3; $Z = 4$; $d_c = 1.37$; $F(000) = 588$; $\mu = 0.848$ mm^{-1}; θ-range 3−25°; 613 diffraction reflections measured, 484 with $I > 2\sigma(I)$; refinement on F^2 for 103 parameters; $wR(F^2\text{all}) = 0.17$, R_1(611 refls) = 0.048, $S = 1.099$. $[(\eta^6\text{-}C_6H_6)_2Cr][CHD]\cdot 3H_2O$ (**2**): $C_{18}H_{19}CrO_5$, $M = 367.33$; orthorhombic, space group *Pbca*; $a = 7.948(2)$, $b = 16.919(8)$, $c = 26.547(6)$ Å; $V = 3570(2)$ Å^3; $Z = 8$; $d_c = 1.367$; $F(000) = 1528$; $\mu = 0.664$ mm^{-1}; θ-range 3.0−25°; 3125 diffraction reflections measured, 1525 with $I > 2\sigma(I)$; refinement on F^2 for 3125 parameters; $wR(F^2\text{all}) = 0.24$, R_1(3108 refls) = 0.059, $S = 1.106$. Common to both species: $T = 293(2)$ K, Mo Kα radiation, $\lambda = 0.710\ 69$ Å; monochromator, graphite; the computer program SHELXL93 (ref 14) was used for structure solution and refinement. All atoms except the hydrogens were treated anisotropically. Methylenic hydrogen atoms of CHD were added in calculated positions (C−H = 0.97 Å); all other hydrogen atoms, except for the water hydrogens, were located directly from final low-θ (<20°) Fourier maps. To evaluate the C−H(benzene)−O bonds, the C−H distances were normalized along the experimentally observed direction to the neutron-derived value of 1.08 Å.

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network is present in some inorganic hydroxides, as well as in some forms of ice,[9] whereas, to the best of the authors' knowledge, it is unprecedented in organometallic solids. (iii) Importantly, the interlayer link is provided by three CH−O interactions[10] between each crystallographically independent oxygen atom and the benzene ligands above and below the hydrated layers. In such a way, the "total coordination" around the water (or OH^-) oxygens is given by two donor and one acceptor OH−O bonds and by three CH−O acceptor bonds. The participation of CH−O interactions in satisfying the hydrogen-bond requirements of water molecules has been demonstrated in a survey of neutron diffraction studies carried out on hydrated crystals.[11] The presence of a number of H−O(water) interactions higher than the number of available accepting sites (the O-atom lone pairs) is indicative of the limited directional requirements of the CH−O bonds and of their chiefly electrostatic nature. It has been shown that a key role in the hydrogen bonding of water molecules is played by the repulsions between the oxygen atoms.[12] This is probably the reason why 4-fold coordination is possible when some of the donors are CH groups, while it is extremely rare with only water donors.

The structure of the hydrated $[CHD]^-$ salt is strictly related to that of the hydroxide. The CHD system acts to end cap the hexagonal water layers *via* O(water)H−O-(CHD) links; this results in the formation of strings parallel to the *a*-axis, as shown in Figure 2a. The water molecule arrangement within the strings is similar to that within the hydrated layers of **1**. The CHD moiety possesses idealized *m*-symmetry, which probably arises from delocalization of the charge within the OC−C(H)−CO system, although static $C{=}O/C{-}O^-$ disorder cannot be confidently ruled out. Both CHD and water interact with the $[(C_6H_6)_2Cr]^+$ cations via CH−O interactions of the type discussed earlier. The resulting packing arrangement shown in Figure 2b is reminiscent of that shown in Figure 1a, being composed of a stacking sequence of cations and layers containing water and CHD^- anions. It is worth noting that structure **1** is polar with the layers stacked along the polar *c*-axis of the *Aba*2 space group, whereas structure **2**, in which the extended planes of water molecules are disrupted, is no longer polar.

In summary, this study provides evidence that hydrogen bonds (both of the conventional OH−O and controversial CH−O types) afford a pattern of interactions in common between organics, organometallics,[13] and water that can be utilized to engineer crystalline materials on the basis of the complementarity between donors and acceptors. We plan to investigate in a systematic manner the use of chiral derivatives of CHD, as well as other organometallic cations ($[(\eta^5\text{-}C_5H_5)_2M]^+$, M = Co, Fe; $[(\eta^6\text{-arene})_2Cr]^+$, arene = substituted benzene] to obtain new solid materials.

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Supporting Information Available: Tables of anisotropic thermal parameters and fractional atomic coordinates, complete list of bond lengths and angles, and Ortep drawings (16 pages). Ordering information is given on any current masthead page.

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