

Hosting Paramagnetic $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+$ in an Organic Anion Framework via $\text{CH}\cdots\text{O}$ Hydrogen Bonds

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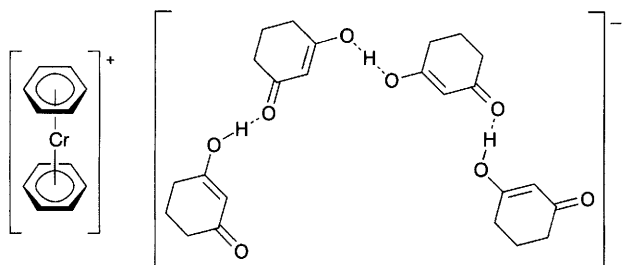
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The hydrogen bond based construction of a crystalline salt in which paramagnetic $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+$ is encapsulated within an organic anion framework derived from cyclohexane-1,3-dione is reported.

Organic crystal engineering is a well established field of research¹ that is attracting much interest in the area of supramolecular chemistry.² The design and construction of molecular ferromagnets^{3a} and of molecular aggregates for non-linear optics is also being intensively investigated.^{3b} Crystalline materials with predefined molecular arrangements can be constructed by choosing appropriate patterns of intermolecular interactions such as those established by hydrogen bond donor and acceptor groups.⁴ Recently, a systematic study of hydrogen bonding in organometallic systems has been undertaken.⁵

In this paper we report our first success in using 'strong' $\text{OH}\cdots\text{O}$ as well as 'weak' $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding interactions^{5a} to construct a crystalline salt in which paramagnetic $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+$ interacts with a complex monoanion aggregate formed by four cyclohexane-1,3-dione (CHD) molecules in the solid state.

CHD is known to exist in two crystalline forms:⁶ one which contains chains of molecules linked head-to-tail via $\text{C}=\text{O}\cdots\text{HO}$ hydrogen bonds [$\text{O}\cdots\text{O}$ 2.561(4) Å] and one in which six CHD molecules form a ring (a cyclamer) which encloses an ordered benzene molecule. In this latter crystal form the CHD molecules adopt a *syn-anti* configuration with the carbonyl groups pointing towards the encapsulated benzene molecule. The $\text{O}\cdots\text{O}$ separation is slightly longer than in the chain form [2.579(1) Å].



If CHD is treated with $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ in *thf* solution† a redox process occurs yielding the paramagnetic cation $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$.‡ A single-crystal X-ray diffraction study§ showed that $[\text{Cr}(\text{C}_6\text{H}_6)_2]^+$ is encapsulated within an organic anion framework derived from cyclohexane-1,3-dione. The monoanion aggregate wraps around a single $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ ion, as shown in Fig. 1. The interaction between the tetramer and $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ is based on $\text{C}-\text{H}\cdots\text{O}=\text{C}$ bonds. The key features of this novel complex can be summarized as follows. (i) The crystal contains a fully independent $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ cation⁷ with the benzene ligands adopting an eclipsed conformation; Cr-C and C-C bond lengths are comparable to those known for $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ in the solid state and do not show any significant pattern of C-C long-short alternation.⁸

(ii) The benzene hydrogen atoms are found to bend towards the metal atom with an average deviation from the planes of the two rings of 0.10 and 0.07 Å, respectively.

(iii) The CHD molecules form a 'horse-shoe' shaped tetrameric anion in which four units are linked via $\text{C}=\text{O}\cdots\text{HO}$ hydrogen bonds: $\text{O}(1)\cdots\text{O}(4)$ 2.55, $\text{O}(6)\cdots\text{O}(7)$ 2.58, $\text{O}(2)\cdots\text{O}(5)$ 2.47 Å. The two outer CHD molecules are in the keto-enol form with the enol oxygens [O(4) and O(7)] acting as hydrogen bonding donors towards the inner tautomeric anion composed

of one CHD molecule and one enolate group dynamically disordered. The tautomeric pair is linked via O(2) and O(5).

(iv) Each $[(\text{CHD})_4]^-$ anion interacts with one $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ cation via short $\text{C}-\text{H}\cdots\text{OC}$ hydrogen bonds, seven benzene hydrogens are involved in interactions in the range 2.29–2.60 Å.⁸ Since hydrogen bonds are essentially electrostatic interactions the ion pairing accounts for these short $\text{C}-\text{H}\cdots\text{O}$ interactions as well as for the short inner $\text{O}\cdots\text{O}$ separation.

(v) Two $[(\text{CHD})_4]^-$ – $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ systems are related by a centre of inversion so that the C=O terminus [O(8)] links two $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ cations via a bifurcated interaction. The resulting structural unit contains a large nearly planar system formed by two $[(\text{CHD})_4]^-$ systems and two benzene ligands as shown in Fig. 2.

The main outcome of this study is the design of an organic-organometallic crystalline salt of paramagnetic $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ based on the *shape analogy* between benzene and dibenzene-

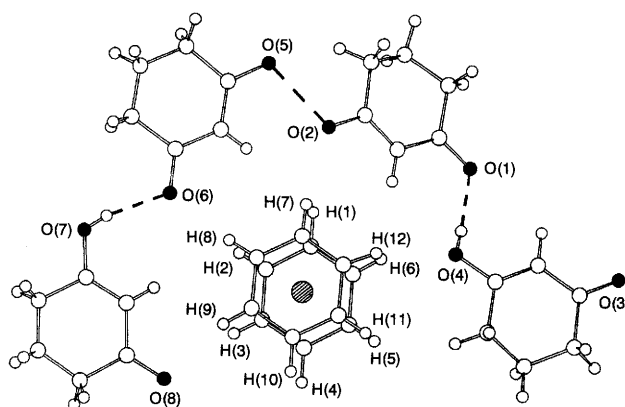


Fig. 1 The tetrameric monoanion $[(\text{CHD})_4]^-$ formed by two outer CHD molecules in the keto-enol form and one inner tautomeric pair wrapped around a single $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ ion. Relevant hydrogen bonding parameters (Å) are $\text{O}(1)\cdots\text{O}(4)$ 2.55, $\text{O}(6)\cdots\text{O}(7)$ 2.55, $\text{O}(2)\cdots\text{O}(5)$ 2.47; § short (<2.60 Å) (benzene) $\text{CH}\cdots\text{O}$ distances (Å) are: $\text{C}(1)\text{H}(1)\cdots\text{O}(2)$ 2.37, $\text{C}(2)\text{H}(2)\cdots\text{O}(6)$ 2.59, $\text{C}(3)\text{H}(3)\cdots\text{O}(8)$ 2.42, $\text{C}(4)\text{H}(4)\cdots\text{O}(8)$ 2.42, $\text{C}(7)\text{H}(7)\cdots\text{O}(5)$ 2.29, $\text{C}(10)\text{H}(10)\cdots\text{O}(3)$ 2.60, $\text{C}(11)\text{H}(11)\cdots\text{O}(3)$ 2.42; relevant bonding parameters (Å) in $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$: mean C-C (benzene) 1.40(1), mean Cr-C 2.137(7); within the $[(\text{CHD})_4]^-$ system C(13)–O(1) 1.254(6), C(15)–O(2) 1.279(6), C(19)–O(3) 1.224(7), C(21)–O(4) 1.328(6), C(25)–O(5) 1.291(6), C(27)–O(6) 1.252(6), C(31)–O(7) 1.321(7), C(33)–O(8) 1.219(7).

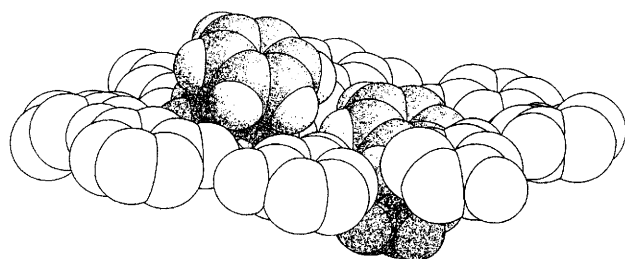


Fig. 2 Space-filling outline of a centrosymmetric pair of $[(\text{CHD})_4]^-$ – $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ ion pairs. Note how two tetramers and two benzene rings belonging to different $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ ions are roughly coplanar.

chromium.⁹ Our study provides evidence that not only 'strong' C=O...HO but also 'weak' CH...O= hydrogen bonds can be used to engineer crystalline materials starting from a knowledge of the intermolecular functions of given atomic groups. Work is in progress to isolate and characterize other crystalline salts of $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ with a varying number of CHD partners in the crystal structure and to explore the use of different templates for shape control on the aggregational process (*e.g.* ferrocenium ions, *etc.*). The magnetic behaviour³ as well as solid-state dynamics of $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ in the crystal will be studied.¹⁰

The work reported in this communication was inspired by the late Professor Margaret Etter. The paper is dedicated to her memory. The ERASMUS exchange program 'Crystallography' is acknowledged for financing J. B.; the Deutscher Akademischer Austauschdienst, Bonn, and the Conferenza Nazionale dei Rettori, Roma, are thanked for a scientific exchange grant within the Programme Vigoni (A. W.). The help of Carmen Paradisi, Alessandro Bongini and Douglas Shepherd is gratefully acknowledged.

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Footnotes

† Yellow powder of CHD (400 mg, 0.036 mol) and brown crystalline $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$ (125 mg, 0.006 mol) were added to a dry Schlenk tube and ground with a glass rod under an argon atmosphere. The finely ground mixture was then dried *in vacuo* (1 h) to remove any water present in solid CHD. Tetrahydrofuran (30 ml) was then added to the mixture. The mixture was stirred until complete dissolution. The insoluble NaCl (present as stabilizer) was removed by filtration. Deep yellow crystals which were stable in the air were obtained by slow evaporation of the solvent at 0 °C.

‡ Unambiguous characterization of the chromium complex as the paramagnetic cation $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ was obtained from the solution ¹H NMR spectrum which revealed four very broad resonances (δ 5.86, 3.44, 2.41, 2.00 relative to CDCl₃ as internal standard at δ 7.2716) indicating its paramagnetic nature and consistent with the formulation as a Cr^I salt.

§ *Crystal data*: C₃₆H₄₃CrO₈, *M* = 655.71, triclinic, space group $P\bar{1}$; *a* = 8.113(2), *b* = 13.000(7), *c* = 17.121(3) Å, α = 109.63(3), β = 99.89(10), γ = 98.16(2)°, *V* = 1636(1) Å³, *Z* = 2, *T* = 293(2) K, *D_c* = 1.333 g cm⁻³, *F*(000) = 694, μ = 0.401 mm⁻¹, Mo-K α radiation, λ = 0.7169 Å, graphite monochromator, 9495 diffraction reflections measured; θ -range 3.0–30°; 3961 of which with *I* > 2 σ (*I*), refinement on *F*² for 470 parameters; *wR*(*F*² all) = 0.169, *R*₁(3961 reflections) = 0.053. The computer program SHELXL93¹¹ was used for structure solution and refinement. All atoms

except the hydrogen atoms were treated anisotropically. Methylene hydrogen atoms of the CHD molecules were added in calculated positions (C–H 1.08 Å), all other hydrogen atoms were located directly from final low- θ (<20°) Fourier maps. In order 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. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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