C—H···O Hydrogen bonds in the mixed-valence salt $[(\eta^6\text{-}C_6H_6)_2Cr]^+[CrO_3(OCH_3)]^-$ and the breakdown of the length/strength analogy

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The theoretical and experimental study of the ion organisation in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]^+[CrO_3(OCH_3)]^-$ affords a complete picture of the relative contribution to crystal cohesion of Coulombic interactions, π-stacks, and charge assisted C—H···O(−) hydrogen bonds while showing the repulsive nature of short C—H···O contacts between anions.

Crystal engineering is a booming field of research encompassing all traditional chemistry subdivisions.[1] The principal non-covalent interaction in crystal engineering, as well as in supramolecular chemistry, is the hydrogen bond since it combines strength with directionality.[2] We have recently shown that organic–organometallic crystalline materials can be designed and synthesised by exploiting the coexistence of O—H···O and C—H···O hydrogen bonds. These latter weaker bonds can be reinforced ('charge assisted') if the donor groups belong to a cation and the acceptors to an anion.[3]

Here we report the structural characterization,† and theoretical evaluation of the mixed-valence crystalline salt $[(\eta^6\text{-}C_6H_6)_2Cr]^+[CrO_3(OCH_3)]^-$ **1** obtained from the crystallisation of the hydroxide $[(\eta^6\text{-}C_6H_6)_2Cr]^+[OH]^- \cdot 3H_2O$ reported earlier.[5] Compound **1** possesses some peculiar structural features. (*i*) The crystal is formed of columns of methoxychromate anions and of columns of paramagnetic bis-benzene chromium cations [Fig. 1(*a*)]. (*ii*) The cations stack in piles with benzene–benzene distances of *ca.* 3.50 Å. (*iii*) The interaction between cations and anions is based on 'charge-assisted' C—H···O(−) hydrogen bonds [twelve H···O† distances in the range 2.40–2.60 Å, four shorter than 2.45 Å, see Fig. 1(*b*)].[6] (*iv*) The anions are apparently 'linked' along the column *via* a short C—H···O interaction (2.381 Å, C—H···O angle 173°) between a methyl hydrogen and a chromate oxygen [see Fig. 1(*c*)] Such a distance might commonly be taken to be indicative of a relatively strong hydrogen bond.

Besides the intrinsic interest in the isolation of this first example of a mixed-valence methoxychromate salt, the presence *within the same crystal architecture* of C—H···O separations between anions and cations longer than between anions and anions calls for an explanation. To this end we have investigated the crystal packing and ion organisation by means of *ab initio* unrestricted Hartree–Fock (UHF) calculations[7] using a LANL2DZ basis set, of double zeta for the valence electrons, which are core electrons described by the LANL2 effective potentials.[7]

In a first approximation, the crystal interaction energy can be expressed as the sum of pairs [$Ep = \Sigma E(i,j)$] where $E(i,j)$ is the intermolecular interaction energy between the i and j atoms or group of atoms. Clearly, the minimum energy arrangement of the molecules or ions in the crystals is a compromise among all available pair energies, that is, a minimum in *E*p does not necessarily correspond to a minimum for each $E(i,j)$. Hence, repulsive contacts between atoms i and j may be 'tolerated' to some extent if the combined energy of other interactions in the crystal is larger than the repulsive $E(i,j)$ value. This is precisely what happens in **1** as we have been able to demonstrate by means of crystal-packing functional-group analysis[8] which consists in the energetic analysis of the primary packing patterns (PPP).‡ PPP are constituted of two or more nearest neighbour molecules within the crystals and are identified by looking at the molecular arrangements which allow overlap of the positive and negative regions of the molecular electrostatic (MEP) maps.

The MEP of the $[CrO_3(OCH_3)]^-$ anion in **1**, computed at the HF/LANL2DZ level, is shown in Fig. 2(*a*). The potential is negative everywhere in the space around the anion,‡ therefore the anion should not form stable interanionic interactions of the type observed in the crystal. The interaction energy of

† Crystals of **1** were obtained as a minor product (*ca.* 10%) from attempts to crystallise $[(\eta^6\text{-}C_6H_6)_2Cr][OH]$ from MeOH.[4] Crystal data for $[(\eta^6\text{-}C_6H_6)_2Cr]^+[CrO_3(OCH_3)]^-$: $C_{13}H_{15}Cr_2O_4$, $T = 273(2)$ K, $M = 339.25$, triclinic, P$\bar{1}$, $a = 10.060(5)$, $b = 10.510(7)$, $c = 6.818(2)$ Å, $\alpha = 105.82(3)$, $\beta = 109.12(3)$, $\gamma = 82.37(4)°$, $U = 654.6(6)$ Å^3, $Z = 2$, $d_c = 1.721$ g cm^{-3}, $F(000) = 346$, $\mu = 1.665$ mm^{-1}, θ-range 3.0–25°, 2504 reflections measured, 2289 of which independent, refinement on F^2 for 217 parameters, wR (F^2, all refls.) = 0.1597, R_1 $[I > 2\sigma(I)] = 0.0564$. MoKα radiation, $\lambda = 0.71069$ Å, monochromator graphite, psi-scan absorption correction. All non-H atoms were refined anisotropically. All H atoms were directly located from Fourier maps. The computer programs SHELX86[4a] and SHEXL92[4b] were used for structure solution and refinement. The computer program SCHAKAL92 was used for all graphical representations.[4c] In order to evaluate the C—H···O bonds that C—H distances were normalised to the neutron-derived value of 1.08 Å and the program PLATON was used.[4d]

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‡ Stable crystals are associated with stable PPP. These are formed when the orientation of the functional groups present in the molecules allow stable intermolecular contacts (in hydrogen bonds, for instance, this means that the molecules are oriented in such a way that the acid and basic groups are at short distances and at the right orientation). By identifying the stable PPP one can rationalise the crystal, define all major contributions to crystal packing, and pinpoint the origin of crystal stability. The analysis of the overlap of the MEP maps of neighbouring molecules is more powerful than a simple look at the positive and negative regions of charge localisation typically obtained from a Mulliken population analysis, as illustrated here.

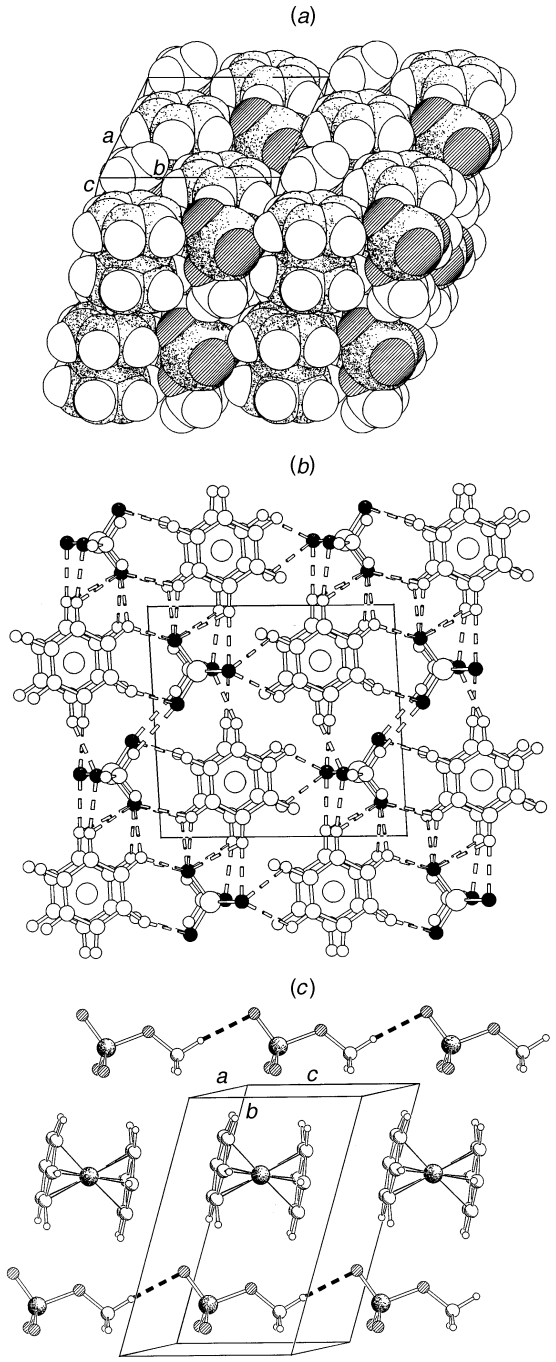

Fig. 1 (*a*) Space filling representation of the ion organization in crystalline $[(\eta^6\text{-}C_6H_6)_2Cr]^+[CrO_3(OCH_3)]^-$: note how cations and anions form parallel columns. (*b*) Network of C—H···O hydrogen bonds between anions and cations (broken lines, oxygen atoms represented as filled spheres). (*c*) Schematic representation of the columns of $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations and of $[CrO_3(OCH_3)]^-$ anions: the filled broken lines mark the short C—H···O contact (2.381 Å), note also the bending of the benzene C—H groups towards the O atoms. Some relevant structural parameters: Cr—OMe 1.795(5), Cr—O 1.596(5), 1.609(5), 1.592(4) O—Me 1.460(8) Cr—C 2.127(6)–2.147(6) Å, Cr—O—Me 120.6(4)°

two $[CrO_3(OCH_3)]^-$ anions computed at the HF/LANL2DZ level with the observed geometry is repulsive by + 58 kcal mol^{-1}. The MEP map in the region of the methyl hydrogens is also negative, even though a Mulliken population analysis indicates positively charged hydrogens (+0.2 e) and a charge of −0.2 e on the methyl carbon. Based on these charges the methyl should be electrostatically attracted by the nearest oxygen of the chromate anion (the charges on chromium, and on the bridging and terminal oxygens are +1.8, −0.9, and −0.8 e, respectively). However, the electrostatic energy computed taking into account these point charges remains repulsive (+40 kcal mol^{-1}) mainly because of the repulsive interaction (+82 kcal mol^{-1}) between the CrO_4 subunits of the two $[CrO_3(OCH_3)]^-$ moieties each bearing a combined charge of −1.4 e. This result warns, *inter alia*, against excessive simplification when dealing with electrostatic interactions.

Thus far we have shown that C—H···O interactions along the $[CrO_3(OCH_3)]^-$ columns are not attractive, and yet why are they so short? The model that best rationalises the observed structure is one in which the crystal is seen as ionic, similar in many ways to the NaCl crystal.§ The $[CrO_3(OCH_3)]^-$ anions and $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cations aggregate in layers [see Fig. 1(*a*)]: as in the NaCl case, one can distinguish $A(-)_2C(+)_2$ repeating units. However in **1**, the layer stack generates A(−)···A(−) and C(+)···C(+) contacts instead of A(−)···C(+), as in the NaCl case. Although A(−)···(−) and C(+)···C(+) interactions, calculated at the HF/LANL2DZ level, are repulsive along the columns (+58 and +52 kcal mol^{-1}, respectively), the $A(-)_2C(+)_2$ unit is stable by −212 kcal mol^{-1}. In fact, the repulsions are largely compensated by A(−)···C(+) attractions between adjacent columns of ions (−128 kcal mol^{-1}). This is an admittedly crude estimate of the energy of the PPP but given the size of the molecules more elaborate computations are not accessible.

The cation MEP map clearly shows that the C − H groups are positively charged [see Fig. 2(*b*)], each with +0.07 e, thus making a grand total of +0.84 e, while the Cr atom has a positive charge of +0.22 e. Therefore the C—H groups may well act as acids against the more basic regions of the anions, located on the oxygens, in particular on the bridge oxygen [dark regions in Fig. 2(*a*)]. The orientation of the A(−)···C(+) units is such as to make as many C—H···O(−) bonds possible. A critical point analysis of the electron density of the $A(-)_2C(+)_2$ unit indicates the presence of six intermolecular C—H···O(−) bonds in one of the A(−)···C(+) dimers and four in the other A(−)···C(+) dimers.

The intriguing case of the mixed-valence crystalline salt **1** can therefore be rationalised as follows. (*i*) The crystal **1** is 'mainly' ionic, *i.e.* the major cohesive contribution results from Coulombic interactions between the methoxychromate anions and bis-benzene cations. (*ii*) The interactions between the bis-benzene chromium cations along the stacks are also repulsive due to a Coulombic component (each benzene has a net charge of + 0.4 e); (*iii*) The relative orientations of anions and cations are controlled by the need to maximise 'charge assisted' C—H···O(−) bonds between cations and anions which contribute largely to crystal stability. (*iv*) On the contrary, the inter-anion C—H···O interaction is repulsive and the short C—H···O distance is not indicative of an attractive interaction.

In summary, in providing theoretical evidence for the relevance of weak C—H···O bonds in crystal packing,[6] we have been able to show that the distance/strength criterion can be misleading when the energetics of the overall intermolecular interactions are not considered or not properly analysed.

§ The same type of calculations discussed here have been performed for the prototypical NaCl crystal. $A(-)_2C(+)_2$ units present one Na(+)···Na(+) and one Cl(−)···Cl(−) contact along the diagonals, and four Na(+)···Cl(−) along the sides. Computing the total energy of the Na(+)···Na(+), Cl(−)···Cl(−) and Na(+)···Cl(−) subunits at the geometry they have in the NaCl crystal multiplied by their occurrence, the $A(-)_2C(+)_2$ unit is found to have a stability of −165 kcal mol^{-1} at the HF/LANL2DZ level, or −41 kcal mol^{-1} per Na(+)—Cl(−) bond. To test if the $A(-)_2C(+)_2$ unit is a good model to evaluate the stability of the NaCl crystal, we computed the stability of a planar Na_8Cl_8 system formed by 12 Na_4Cl_4 units attached by their sides, obtaining a stability of −31 kcal mol^{-1} per each Na(+)—Cl(−) bond.

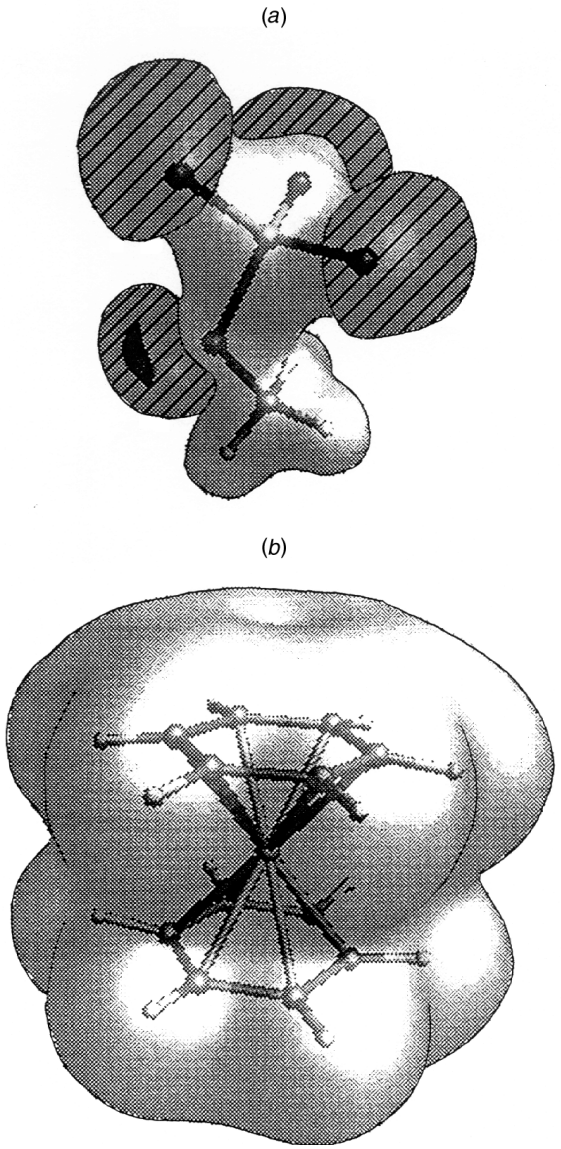

Fig. 2 The MEP maps computed at the HF/LANL2DZ level for the $[CrO_3(OCH_3)]^-$ anion (*a*) and for the $[(\eta^6\text{-}C_6H_6)_2Cr]^+$ cation (*b*). The maps are drawn with energy cuts at -160 (dark), -140 (shaded), 30 (light) for the anion and of $+100$ kcal mol^{-1} for the cation; far from the nuclei the potential is positive everywhere for the cation and negative for the anion

The band structure, charge-transfer properties and spin alignment between Cr^{VI} and Cr^{I} columns and along the paramagnetic Cr^{I} columns will be investigated.

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