Hydrogen bonding networks and anion coordination in (η^6-arene)Cr(CO)$_3$ complexes: metal carbonyls as hydrogen bond acceptors

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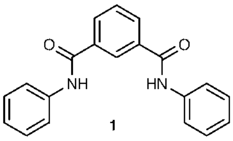
Received (in Cambridge, UK) 15th December 1999, Accepted 12th January 2000

A chloride selective amide cleft molecule 2 containing two $Cr(CO)_3$ moieties has been synthesised by condensation of (η^6-aniline)$Cr(CO)_3$ 3 with isophthaloyl dichloride; the X-ray crystal structure of 2 contains a network of Cr–CO···HN hydrogen bonds giving rise to an extended three-dimensional coordination array; the X-ray crystal structure of (η^6-aniline)$Cr(CO)_3$ 3 has been re-determined and found to contain bifurcated amine NH···OC–Cr hydrogen bonds.

The coordination chemistry of anionic[1–3] and neutral guest species[4] by hydrogen bond donating receptors is an area of supramolecular chemistry that continues to attract the attention of coordination chemists. One strategy that has been used to modulate the affinity or selectivity of a receptor for a particular guest is to alter the electronic environment of the guest-binding site. This may be achieved by synthesising a new receptor containing electron withdrawing or donating functional groups[5] or, alternatively, by coordinating transition metal fragments to a pre-existing receptor. This latter approach has been elegantly employed by Atwood *et al.* to transform calixarenes into anion-binding receptors.[6]

Receptors that contain hydrogen bond donating amide[7,8] or pyrrole[9] moieties have been shown to be effective and selective anion binding agents. Recently, Crabtree and coworkers have shown that simple amide cleft receptors based on compound **1**[10] are capable of binding halide anions.[11,12] As part of our programme of research in anion coordination,[13,14] we decided to synthesise an amide cleft receptor containing two electron withdrawing $Cr(CO)_3$ units that would serve to increase the acidity of the NH protons. However, we found that in addition to binding anions, hydrogen bonds were formed in the solid state between amide NH and chromium carbonyl moieties, leading to the formation of a three-dimensional coordination array.[15,16]

Compound **2** was synthesised by condensation of (η^6-aniline)$Cr(CO)_3$[17] **3** with isophthaloyl dichloride in dichloromethane in the presence of triethylamine and DMAP. The reaction mixture was purified by column chromatography on silica gel and crystallised from CH_2Cl_2–MeOH as yellow needles in 74% yield.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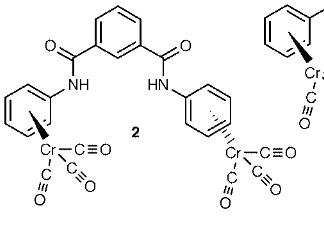
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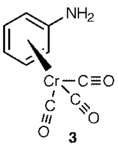
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Crystals of **2** suitable for X-ray analysis† were obtained from CD_3CN solution. The crystal structure and atomic numbering scheme is shown in Fig. 1(a). The centrosymmetric nature of the space group causes the two (η^6-aniline)$Cr(CO)_3$ moieties to adopt orientations at 180° to each other on opposite sides of the molecule, fully enabling these groups to interact with other molecules. The presence of carbonyl and amide groups provide additional hydrogen bond donors and acceptors, facilitating the formation of a supramolecular assembly.[18] Each molecule of **2** donates six hydrogen bonds. These include an intramolecular interaction between H(5) and O(4) (2.22(3) Å), two intermolecular interactions between H(3) and O(4) and H(3′) and O(4′) (2.54(4) Å), and three intermolecular hydrogen bonds to metal carbonyl groups (H(1)··O(2) 2.47(2)Å and H(12) to two O(2) atoms in different adjacent molecules (2.50(3) Å)). This network of hydrogen bonds defines a continuous three-dimensional coordination array, a portion of which is shown in Fig. 1(b).

In light of the formation of this assembly, we decided to re-examine the solid state structure of (η^6-aniline)$Cr(CO)_3$ **3**. The

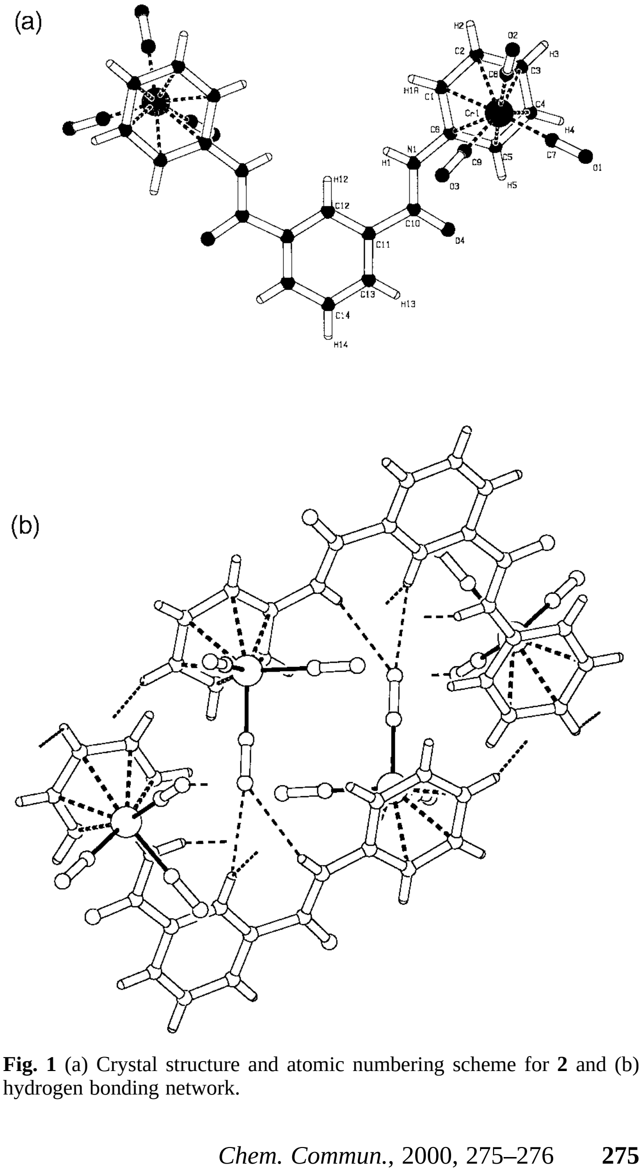

Fig. 1 (a) Crystal structure and atomic numbering scheme for **2** and (b) hydrogen bonding network.

structure of compound **3** was first solved in 1992 by Hunter, Zaworotko and co-workers.[19] In this case, compound **3** crystallised in a monoclinic lattice and contained no hydrogen bonding interactions. We found that if crystallisation occurs under different conditions (*i.e.* at room temperature from dichloromethane) from those used by Hunter *et al.*, a triclinic polymorph, with the same molecular geometry, reproducibly forms a hydrogen bonded network. These hydrogen bonds link molecules together into two-dimensional sheets (shown in Fig. 2). Two bifurcated hydrogen bonds are formed by one NH group to two OC–Cr moieties (H··O 2.55(6) and 2.32(7) Å) and a further hydrogen bond is formed from the other NH hydrogen to a OC–Cr moiety (H··O 2.50(6) Å) (Fig. 2). Each molecule therefore donates and accepts three hydrogen bonds.

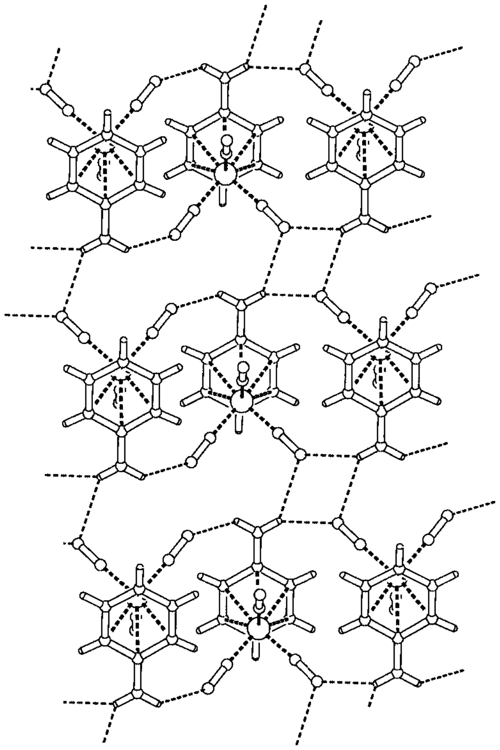

Fig. 2 Crystal structure of **3** emphasizing the hydrogen bonding network.

The anion coordination properties of **2** were studied using ^{1}H NMR titration techniques in CD_3CN by following the NH proton resonance. Stability constants were then calculated using the EQNMR computer program[20] and are presented in Table 1. Receptor **2** shows selectivity for chloride over the other putative anionic guests studied, with a stability constant that is higher than can be reliably measured by this technique (log $K > 4$). Interestingly the selectivity of **2** for chloride over dihydrogen phosphate is high. This may be due to the steric bulk of the $Cr(CO)_3$ moieties hindering the approach of the bulky dihydrogenphosphate anion to the amide cleft. A negative electrospray competititon experiment was run on an acetonitrile solution of **2** containing one equivalent of each of the anions shown in Table 1. Only peaks corresponding to the chloride complex were observed, confirming the chloride selectivity of **2**.

Table 1 Stability constants of compound **2** with a variety of anionic guests in CD_3CN at 298 K. Errors are estimated to be < 16%. All data fitted satisfactorily to a 1 : 1 receptor : anion binding model

Anion	Stability constant/ dm^3 mol^{-1}
F^{-a}	107
Cl^-	> 10^4
Br^-	2910
I^-	102
$H_2PO_4^{-a}$	119

[a] ArH proton used (broadening of the NH proton occurs during the titration).

The coordination of metal carbonyls by activated hydrogen bond donating ligands may lead to new strategies for the modification of the activity of carbonyl containing catalysts.[21] The presence of the hydrogen bonding networks in **2** and **3** leads us to suggest that the $Cr(CO)_3$ fragment in particular, may find future applications in the design of coordination polymers and extended networks in crystals as well as in the activation of NH groups for more effective or selective anion coordination.

P. A. G. thanks the Royal Society for a University Fellowship and the EPSRC for a project studentship (to S. C.).

Notes and references

† *Crystal data*: for $C_{26}H_{16}Cr_2N_2O_8$ **2**, $M_r = 588.41$, monoclinic space group $C2/c$, $a = 17.283(3)$, $b = 11.337(2)$, $c = 14.586(3)$ Å, $\beta = 125.16(3)°$, $U = 2333.6(8)$ Å^3, $Z = 4$, $\mu = 0.989$ mm^{-1}, crystal size 0.15 × 0.025 × 0.025 mm, $T = 150$ K; refinement of 2621 unique reflections ($2\theta \leqslant 27.47°$, $R_{int} = 0.0552$) against 173 parameters gave $R_1 = 0.0418$ and $wR_2 = 0.1100$ [$I > 2\sigma(I)$] ($R_1 = 0.0664$ and $wR_2 = 0.1265$ for all data). For $C_9H_7CrNO_3$ **3**, $M_r = 229.16$, triclinic space group $P\bar{1}$, $a = 7.0198(10)$, $b = 7.3940(11)$, $c = 9.4002(12)$ Å, $\alpha = 86.069(7)$, $\beta = 86.591(8)$, $\gamma = 69.457(7)°$, $U = 455.49(11)$ Å^3, $Z = 2$, $\mu = 1.232$ mm^{-1}, crystal size 0.15 × 0.05 × 0.025 mm, $T = 150$ K; refinement of 1193 unique reflections ($2\theta \leqslant 22.48°$, $R_{int} = 0.0912$) against 127 parameters gave $R_1 = 0.0774$ and $wR_2 = 0.1996$ [$I > 2\sigma(I)$] ($R_1 = 0.0934$ and $wR_2 = 0.2079$ for all data).

Data were collected on a Nonius KappaCCD area detector diffractometer, at the window of a Nonius FR591 rotating anode (λ(Mo-Kα) = 0.71073 Å). Corrections were applied to account for absorption effects by means of comparing multiple and equivalent reflections. Solutions were obtained *via* direct methods and refined by full-matrix least squares on F_0^2, with hydrogens included in idealised positions and refined using the riding model. CCDC 182/1522. See http://www.rsc.org/suppdata/cc/a9/a909861e/ for crystallographic files in .cif format.

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Communication a909861e