Halogen bonding between metal centers and halocarbons†

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Metal-involving halogen bonding was detected in a series of associates of CH$_3$ with trans-[PtX$_2$(NCNAlk)$_2$] (X = Cl, Br). The H$_3$I$^-$⋯Cl$^{-}$ halogen bonding and the bifurcated H$_2$I⋯Cl$^{-}$⋯Cl bonds were observed and confirmed theoretically. Halogen bonding (XB), among various non-covalent weak interactions, is one of the most intensively studied systems in modern science. Together with hydrogen bonding, π⋯π-, and metalophilic interactions, it is successfully applied in crystal engineering and design of compounds exhibiting pharmacological significance. Recent applications of XB include stabilization of explosives and molecular design of materials with tunable photophysical properties.

In accord with the IUPAC definition, XB is the real R−X⋯Y (X = halogen) contact, when, firstly, the intratomeric distance between X and an appropriate nucleophilic atom of Y (Y = F, O, N, Cl, etc.) is less than the sum of their van der Waals radii and, secondly, the \( \angle (\mathrm{R−X⋯Y}) \) angle is close to 180° (exceptions from the linearity have been reviewed). These geometrical parameters are usually easily obtained using single-crystal X-ray diffraction (XRD), which is the most common method for the detection of XB. When application of the two criteria in XRD data fails, some other criteria (lengthening of R−X covalent bonds due to XB and also changes in the appropriate spectroscopic parameters), or application of some other indirect methods, e.g. UV-vis, IR and Raman spectroscopy, differential anomalous X-ray scattering studies, NMR, and phosphorescence spectroscopy, were also applied for XB recognition.

In the majority of the reported cases when XB was reliably identified, only typical Lewis basic non-metal atoms bearing lone pairs (viz. O, N, S, halogens etc.) behave as XB acceptors, whereas possible XB donors with metal centers was found only for I$_2$. Our inspection of the relevant literature indicates few experimental studies describing X⋯M short contacts, which were either not considered as halogen bonds, or their geometrical parameters fulfill only one of the two aforementioned structural IUPAC criteria. Therefore definitive attribution of these weak interactions to XB was not provided and the other IUPAC criteria should be applied for their identification. Indeed, Chen et al. Wölper et al., and Laguna et al. observed X⋯Au and X⋯Ag contacts, which fulfilled only the “van der Waals criterion”, but in all the three cases the corresponding R−X⋯M angles strongly deviate from 180° (by 30−90, 60−70, and 85−22) thus contrasting with the second structural IUPAC criterion. Yamamoto et al. and Liu et al. reported, respectively, the I⋯Au and Cl⋯Au contacts, which can be interpreted as X⋯Au halogen bonds, but the nature of these contacts was not verified. Finally, Blakey et al. observed contacts between the typical XB donors such as iodoperfluorobenzenes and gold nanoparticles in water solutions, but these halogen bonds were confirmed only by indirect methods such as UV-vis difference spectroscopy, SERS, and XPS and the geometrical parameters were not obtained.

It is important that a metal atom can be an XB acceptor if it contains at least one lone pair, which could interact with empty σ*−orbitals of an XB donor. In particular, some d$^3$-Pt and d$^8$-Rh centers may behave similarly to d$^{10}$-Au ones as these centers feature lone pairs on 4d$_z^2$ or 5d$_z^2$ orbitals. In particular, weak contacts were observed between some d$^8$-Pt and d$^8$-Rh species and iodine. These two were the only reports on unambiguous recognition of metal-involving XB.

Taking into account that no data for XB between metal centers and halocarbons were published, we focused our efforts...
on the search of metal-involving XB and we applied platinum(II) species as potential XB donors and iodoform as an XB acceptor.

In the current work, we report that the dialkyldicyanamide d8-Pt(I) complexes trans-[PtX2(NCNR2)]2+ (R2 = Me2, X = Cl 1a, Br 1b; Et2 2, (CH2)3 3, (CH2)4 4) easily co-crystallize with iodoform taken as the XB donor. We observed that CHI3 tends to co-crystallize with 1a-b and 4 forming HI2C–I···Pt metal-involving halogen bonds (Chart 1, B) that fulfill both structural IUPAC criteria for halogen bonding. The existence of metal-involving halogen bonding has also been confirmed theoretically by the combination of DFT and AIM methods. Within the AIM theory, the (3, −1) critical points (bond critical points, BCPs) on the surface of the theoretical electron density function ρ(r) unambiguously reveal all bonding intermolecular interactions, including non-covalent interactions. Energies for the corresponding contacts Eint can be determined using semi-empirical correlations between local energy densities in BCPs and interaction strength.27,28 Moreover, we found and confirmed theoretically by combination of DFT and AIM methods the unique bifurcated HI2C–I···I(C–I) xb that undergoes thermally induced reversible HI2C–I···I(C–I) ⇌ HI2C–I···I(C–I) † transformation.

Complexes 1a and 1b form isostructural associates 1a·2CHCl3, 1a·CHI3, 1a·2CHI3, and 1b·2CHI3 upon crystallization from 1a: CHI3 = 1 : 2 (molar ratio) solutions in chloroform or dichloromethane, or from 1b·CHI3 = 1 : 2 (molar ratio) solution in dichloromethane, respectively. Apart from numerous HI2C–I···X–Pt halogen bonds (Chart 1, A), they exhibit the HI2C–I···Pt short contacts, which can be interpreted as metal-involving XB according to both structural IUPAC criteria as the distances d(I···Pt) = 3.4276(5), 3.4389(5), and 3.4023(5) Å are less than sums of Bondi’s vdW radii (vdW(Pt) + vdw(I) = 3.73 Å) and the corresponding angles (164.84(17), 169.8(3), and 172.7(2)) are close to 180° (for more details see Section XR2 of the ESI†). We also confirmed the formation of the 1a·Pt non-covalent interaction in 1a·2CHCl3, 1a·CHI3, and 1b·2CHI3 systems theoretically for the 1a·(CHI3)6 and 1b·(CHI3)6 model structures by using Bader’s AIM analysis (Fig. 1 and 2; for details see Section TH1 in the ESI†). The estimated energies (Eint) of these contacts are in the ranges of 2.4–2.8 kcal mol−1 and 2.7–3.1 kcal mol−1, respectively. The strength of these weak interactions has been defined according to the procedures proposed by Espinosa et al.27 and Vener et al.,28 these approaches considered explore linear relationships between the local electronic potential V(r) and kinetic G(r) densities at the bond critical points and energies of appropriate contacts.
Variable temperature XRD experiments for the same single-crystal of 2CHI₃ were performed at 100, 150, 200, 250, and 300 K. An inspection of the obtained data indicates that the heating leads only to the elongation of the intermolecular distances, whereas the covalent bond lengths remain almost the same. The most significant changes were detected for the bifurcated HI₂C–I⁻ · · · η²(Pt–Cl) contacts (by 0.08 Å upon an increase in temperature from 100 to 300 K), whereas the HI₂C–I⁻ · · · Cl⁻–Pt halogen bonds were lengthened by only 0.05 and 0.03 Å, correspondingly (see also XR3 of the ESI†). Bader’s AIM analysis (TH2 of ESI†) for the 4(CHI₃)₆ model systems at each temperature indicated above showed the gradual reduction of the estimated energies of all halogen bonds. Apart from that one of the bond critical points (between Cl and I) in the bifurcated XB disappeared on going from 250 to 300 K. The reversibility of the thermal transformation was proved by three consecutive XRD experiments for the same single-crystal at 100 K, 300 K, and again at 100 K. This experiment gives evidence supporting the thermally induced reversible HI₂C–I⁻ · · · η²(Pt–Cl) ⇌ HI₂C–I⁻ · · · η¹(Pt) transformation.

Complexes 2 and 3 were co-crystallized with CHI₃ in a 1:2 molar ratio from chloroform solutions forming 2·2CHI₃ and 3·2CHI₃, respectively. These associates were found to form only three types of HI₂C–I⁻ · · · Cl⁻–Pt XB in each case (Fig. 4 and 5). In all cases (1a·2CHCl₃, 1b·CHCl₃, 2b·2CHI₃, 2·2CHI₃, 3·2CHI₃, and 4·2CHI₃), the formation of halogen bonds with the halide ligands was confirmed theoretically by using Bader’s AIM analysis (XR2 and TH1 of the ESI†). The estimated energies (Eint) of this type of weak interaction are in the range of 1.9–3.5 kcal mol⁻¹. Only the HI₂C–I⁻ · · · Cl⁻ and the HI₂C–I⁻ · · · Br⁻ weak interactions were previously described,31 but no single example of the XB between metal-coordinated chloride or bromide and CHI₃ has been previously reported.

The elongation of the Pt-X (X = Cl, Br) bonds in the CHI₃-associates was detected when XRD data of the associates were compared with those of CHI₃-free 1a,32 1b, and 433 (see XR1 in the ESI†). The Pt-Cl distances in 2·2CHI₃ and 3·2CHI₃ are longer than in CHI₃-free complexes 1a and 4. Although these differences are not too large (0.01–0.03 Å), the observed elongation indirectly point out (Chart 2) to the presence of the HI₂C–I⁻ · · · X–Pt and HI₂C–I⁻ · · · Pt contacts (see XR2 and TH1 in the ESI†) additionally supporting our conclusions.
In this communication, we reported the first examples of definite and unambiguous identification of metal-involving XB with halocarbons, viz. between PtII and CHI3. Various PtII centers are known to participate in donor–acceptor interactions with Lewis acids (BIII and SIV compounds)34,35, but in all cases these donor–acceptor bonds are too strong to be treated as non-covalent bonds. The most relevant example of XB is weak contacts between the PtIII and RhI centers and iodine.16–19 Examples of the X–Pt and X–Rh interactions given in the Introduction have not been clearly identified as metal-involving XB. We plan to continue our studies in the area of metal-involving XB and to expand the range of studied systems to other X’s and X-containing species (e.g. Br) and metal centers (e.g. PtIII) and studies in these directions are underway in our group.

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