Singly-bonded fullerene dimers: neutral $(C_{60}Cl_5)_2$ and cationic $(C_{70})_2^{2+}$ †

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$C_{60}Br_{24}$ and $C_{70}Br_{10}$ react with $TiCl_4$, splitting out bromine, and, after Br/Cl exchange, forming singly-bonded dimeric structures $(C_{60}Cl_5)_2$ and $[(C_{70})_2](Ti_3Cl_{13})_2$, respectively, the latter consisting of dimeric $[(C_{70})_2]^{2+}$ dications and $(Ti_3Cl_{13})^-$ anions.

Previously, we have developed a method for the selective synthesis of fullerene chlorides by the chlorination of fullerenes with liquid inorganic chlorides or oxychlorides such as $SbCl_5$, VCl_4, PCl_5, $MoCl_5$, $VOCl_3$, $POCl_3$, *etc.*[1] In these reactions, which result in the selective formation of $C_{60}Cl_6$, $C_{60}Cl_{24}$, $C_{60}Cl_{28}$ and $C_{60}Cl_{30}$ (two isomers) for C_{60}, and $C_{70}Cl_{28}$ for C_{70}, the liquid chlorinating agent (a strong Lewis acid) serves simultaneously as the solvent. Non-oxidizing liquid chlorides such as $TiCl_4$, $SnCl_4$, $SiCl_4$, *etc.* form only fullerene solvates, for example $C_{60}\cdot 3TiCl_4$ and $C_{70}\cdot 2TiCl_4$.[2] Recently, it was found that a mixture of $TiCl_4$ and Br_2 also acted as a *chlorinating* agent. The reaction of this mixture with [70]fullerene made the preparation of $C_{70}Cl_{16}$ possible for the first time.[3] Significantly, the reaction of C_{70} with neat Br_2 resulted in a maximum of ten Br atoms being added to the fullerene cage.[4] We were interested in scrutinising this phenomenon, including the influence of the bromine concentration in the fullerene/($TiCl_4$ + Br_2) system on the reaction products. Herein, we report the results for both C_{60} and C_{70}, in particular those concerning the formation of singly-bonded dimeric structures.

The experiments were carried out in glass ampoules to avoid the hydrolysis of $TiCl_4$. [60] or [70]fullerene (36 or 42 mg, 0.05 mmol), $TiCl_4$ (0.5–0.8 mL) and varying amounts of Br_2 were placed in a two-sectioned glass ampoule and cooled with liquid nitrogen. The ampoule was evacuated and sealed off. It was then heated at 50–100 °C for 1–4 weeks; the longer reaction time was used for crystal growth in the same ampoule. The reaction products were separated from the excess $TiCl_4$ and Br_2 by cooling the initially empty section of the ampoule with liquid nitrogen. The isolated products were characterized by IR spectroscopy, X-ray powder diffraction and single-crystal X-ray crystallography.

Reaction products varied significantly depending on the bromine concentration in the system. In the presence of a large bromine excess (*ca.* 0.25 mL, 5 mmol), [60]fullerene reacted to give $C_{60}X_{24}$ derivatives (X = Cl, Br) with a Cl : Br ratio between 1 : 5 and 5 : 1. IR spectra showed broadened bands at intermediate positions between those for pure $C_{60}Br_{24}$[5] and $C_{60}Cl_{24}$.[6] X-Ray crystallography revealed a known T_h structure with a statistical distribution of the Cl and Br atoms over 24 positions.[5,7,8] The experiments at lower Br_2 concentrations (several drops of Br_2; *ca.* 0.05–0.1 mL, 1–2 mmol) resulted in another composition, which was identified by IR spectroscopy and X-ray diffraction as $C_{60}X_6$ (X = Cl, Br) with Cl : Br ratios from 20 : 1 to 100 : 1. The IR spectra were close to that of $C_{60}Cl_6$.[9] X-Ray single-crystal crystallography revealed a layered ABAC packing of the $C_{60}X_6$ molecules, very similar to that of crystalline $C_{60}Cl_6$.[10] The results for the $C_{60}X_{24}$ and $C_{60}X_6$ phases will be published elsewhere in more detail.

Similar experiments in the system C_{70}/($TiCl_4$ + Br_2) showed a reproducible formation of $C_{70}Cl_{16}$ in all runs with an excess of Br_2, whereas the presence of smaller amounts of bromine resulted in the isolation of $C_{70}Cl_{10}$, which is isotypical with $C_{70}Br_{10}$.[4] A detailed description of this phase will be published elsewhere.

More remarkable results were obtained from systems with very low bromine concentrations. In view of the technical difficulties of adding very small amounts of bromine, we prepared $C_{60}Br_{24}$[5,11] and $C_{70}Br_{10}$[4] separately and then carried out ampoule reactions of these fullerene bromides with $TiCl_4$. As established by a single-crystal X-ray crystallographic study,‡ the reaction of $C_{60}Br_{24}$ with $TiCl_4$ resulted in the formation of red crystals of $(C_{60}Cl_5)_2$ in approximately 40% yield based on the starting bromide. The IR spectrum of this product (see ESI†) differed slightly (by 2–5 cm^{-1}) from that of pure $C_{60}Cl_6$.[9] The most evident differences were the absence of the band at 825 cm^{-1} and the presence of some additional bands at 602 and 813 cm^{-1}. The molecular structure of $(C_{60}Cl_5)_2$ contains two $C_{60}Cl_5$ moieties connected by a single C–C bond (Fig. 1). The attachment of five Cl atoms and the C atom from another fullerene cage closely resembles the skewed pyramidal arrangement of the six halogen atoms in the $C_{60}Cl_6$ and $C_{60}Br_6$ molecules.[5,9–11] The relative position of the two $C_{60}Cl_5$

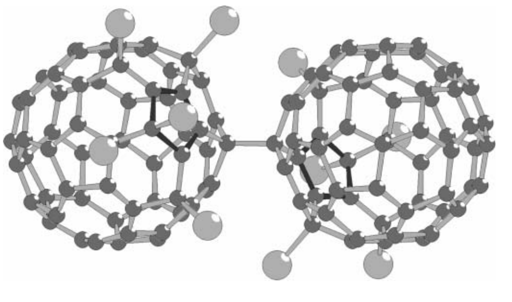

Fig. 1 Molecular structure of $(C_{60}Cl_5)_2$. The two central pentagons in skewed pentagonal pyramids of each [60]fullerene cage are shown black.

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† Electronic supplementary information (ESI) available: IR spectrum of $(C_{60}Cl_5)_2$. See DOI: 10.1039/b702665j

moieties next to each other is approximately centrosymmetric, apparently due to their mutual repulsion.

Owing to the weakness of the C–Br bonds in $C_{60}Br_{24}$, bromine can be removed from the fullerene cage as elemental Br_2 dissolved in $TiCl_4$ or, in an ionized form, as Br^+ and $(TiCl_4Br_2)^{2-}$. This process can result in $C_{60}Br_6$ or, after partial Br–Cl exchange, in $C_{60}X_6$ (note that rearrangement of the remaining addition sites on the fullerene cage is required). Further removal of the X atom, accompanied by Br–Cl exchange, may result in $C_{60}Cl_5^{\bullet}$ radicals, which interact to give dimeric $(C_{60}Cl_5)_2$ molecules.

Similar experimental observations have been made previously for the reaction of C_{60} with ICl in chlorobenzene.[9b] Apart from soluble $C_{60}Cl_6$, a large amount of red insoluble product was formed. Based on its low solubility and the similarity of its IR spectrum to that of $C_{60}Cl_6$, a dimeric or oligomeric structure of this product was tentatively assumed. In fact, such a structure may form in the course of chlorination due to the intermediate generation of $C_{60}Cl_5^{\bullet}$ radicals and their subsequent dimerization. Another stabilization type of a $C_{60}X_5$ moiety was found in $Tl(C_{60}Ph_5)$ due to the formation of pentaaryl[60]fullerene anion with a stable cyclopentadienyl fragment.[12]

In the case of $(C_{60}Cl_5)_2$, the C–C bonding *via* the side (and not the top) site of the skewed pyramid is due to the steric requirements of the five attached chlorine atoms of each $C_{60}Cl_5$ moiety. The intercage C–C bond, 1.66(2) Å, is significantly elongated when compared with other known examples of singly-bonded fullerene dimers, with values of 1.576(6) Å in $[C_{60}CH_2PO_2OEt]_2$,[13] 1.597(7) Å in $(C_{60}–C_{60})^{2-}$ [14] and 1.577(11) Å in $[C_{60}(biphenyl)_5]_2^{4-}$.[15] This elongation may be attributed to the mutual repulsion or electron withdrawing effect of the attached chlorine atoms.

An ampoule reaction of $C_{70}Br_{10}$ with $TiCl_4$ at 60–80 °C for 1–2 d resulted in the quantitative transformation of the orange powder into black crystals. X-Ray crystallography revealed the formation of an ionic compound, $[(C_{70})_2](Ti_3Cl_{13})_2$, containing dimeric $[(C_{70})_2]^{2+}$ dications and $(Ti_3Cl_{13})^-$ anions in a 1 : 2 ratio.‡ Both moieties have been identified for the first time. The compound slowly decomposes in air due to hydrolysis of the chlorotitanate. Upon mixing with KBr, it oxidises Br^- to Br_2, forming a deep brown coloration. The most probable reason for the formation of a dimeric "all-carbon" dication from the brominated C_{70} derivative is due to, on the one hand, weakness of the C–Br bond allowing the splitting-off of Br_2 due to its high solubility in $TiCl_4$ under partial ionization, and, on the other, removal of Br^- anions because of the high Lewis acidity of $TiCl_4$. A similar process of cleaving fullerene–Cl bonds of $C_{60}Ar_5Cl$ in the presence of $AlCl_3$ was shown to result in pentaaryl[60]fullerene carbocations.[16] $C_{70}^{\bullet+}$ radical cations have no steric hindrance to the formation of dimeric dication $[(C_{70})_2]^{2+}$. The corresponding anion is a chlorotitanate, $(Ti_3Cl_{13})^-$, instead of a mixed chlorobromotitanate due to the large excess of $TiCl_4$.

Other known "all-carbon" cations were isolated as radical cations $[C_{60}^{\bullet+}]$ and $[C_{76}^{\bullet+}]$ in salts with carborane anions $[CB_{11}H_6X_6]^-$ (X = Cl, Br) and investigated by means of EPR, IR and NIR spectroscopy.[17] The dimeric $[(C_{70})_2]^{2+}$ cation (Fig. 2) is centrosymmetric with a bridging intercage C–C bond length of 1.616(4) Å; the elongation compared to a C–C single bond may be due to electron deficiency of the dication. A conceivable reason for the intercage bonding between the C atoms from the second row of the C_{70} fullerene cage is a slightly higher C_{70} cage curvature at these sites, *i.e.* a more pronounced tetrahedral geometry (higher deviation from a sp^2 state). A convenient measure of the curvature at a given C atom is the sum of the three bond angles (namely, its deviation from 360°). Theoretical calculations for C_{70} show a slightly higher cage curvature for the C atoms of the second row (347.4°) compared with those of the first (top) row (347.5°).[18] The corresponding average experimental values, 347.4° and 347.7°, for the C_{70} molecule (type A)§ in the structure of $C_{70}\cdot 2TiCl_4$ confirm the difference in curvature,[2] thus providing a plausible explanation for the experimentally found structure of the dimeric dication. Three C_{sp^3}–C_{sp^2} bonds at the tetrahedral carbon atom have average length of 1.521 Å, whereas all other C–C bond lengths of the cationic cage are close to those of parent C_{70}. Averaged values for the eight types of C–C bonds in the dimeric dication are given below (in the order from the cage pole to the cage equator), together with the experimental values (in parentheses) for C_{70} in its solvate with $TiCl_4$ (Å): 1.445 (1.456), 1.390 (1.377), 1.448 (1.461), 1.382 (1.372), 1.441 (1.450), 1.436 (1.437), 1.417 (1.418) and 1.463 (1.476).[2] Noticeably, in the two known examples of singly-bonded $[(C_{70})_2]^{2-}$ dianions, the connection site is from the top pentagons of the C_{70} cages, and the intercage C–C bonds are shorter, 1.584(9) and 1.601(4) Å.[19]

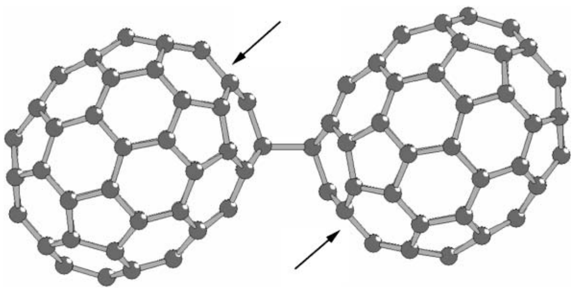

Fig. 2 Structure of the dication $[(C_{70})_2]^{2+}$ viewed perpendicular to the intercage C–C bond and the former D_5 axes of the C_{70} cages (arrows).

A trinuclear chlorotitanate(IV) anion, $(Ti_3Cl_{13})^-$, has been observed for the first time. Dinuclear anions $(Ti_2Cl_9)^-$ and $(Ti_2Cl_{10})^{2-}$ were already known, *e.g.* in the ionic salts $(SCl_3)(Ti_2Cl_9)$ and $(PCl_4)_2(Ti_2Cl_{10})$, respectively.[20] The flattened $(Ti_3Cl_{13})^-$ anion has a molecular C_{3v} symmetry (Fig. 3). Each Ti atom has a distorted octahedral coordination by one μ_3-Cl, two μ_2-Cl and three terminal Cl atoms, the averaged Ti–Cl distances being 2.578, 2.483 and 2.208 Å, respectively. The latter two values can be compared with the bridging and terminal Ti–Cl distances in $(SCl_3)(Ti_2Cl_9)$ of 2.504 and 2.212 Å, respectively.[20a]

The layered packing of the $[(C_{70})_2]^{2+}$ dications and $(Ti_2Cl_9)^-$ anions is shown in Fig. 4. Both positive and negative charges are delocalized on the bulky cation and anion, respectively, thus diminishing their interaction in the structure but contributing to

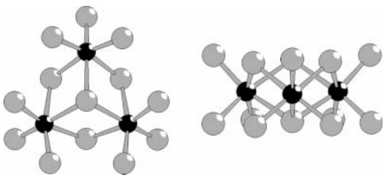

Fig. 3 Top and side views of the $(Ti_3Cl_{13})^-$ anion.

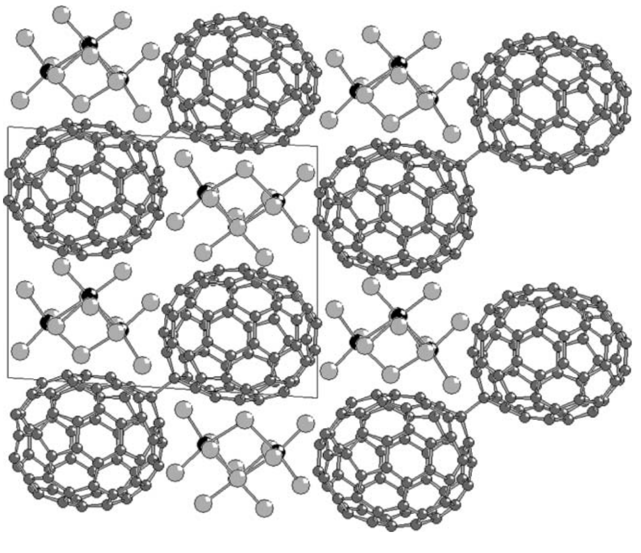

Fig. 4 Projection of the $[(C_{70})_2](Ti_3Cl_{13})_2$ structure along the *a* axis.

the relatively high stability of the compound. The shortest $C\cdots C$ contacts between dimeric molecules within the layer (parallel to (011)) are 3.267–3.367 Å for the equatorial region and 3.298–3.508 Å near the poles. For comparison, $C\cdots C$ contacts in the ordered C_{60} phase are 3.116–3.463 Å long,[21a] whereas the corresponding values for the low temperature phase of C_{70}, 2.97–3.53 Å, are not very reliable due to the many constraints used in the structure refinement.[21b]

In summary, in the system fullerene/($TiCl_4$ + Br_2) with a high bromine concentration, both [60] and [70]fullerenes can be halogenated to high addition levels. When using the fullerene bromides $C_{60}Br_{24}$ and $C_{70}Br_{10}$ as starting compounds in the reaction with $TiCl_4$, removal of Br atoms or Br^- anions results, respectively, in the formation of dimeric chloride $(C_{60}Cl_5)_2$ and the salt $[(C_{70})_2](Ti_3Cl_{13})_2$, containing a dimeric $[(C_{70})_2]^{2+}$ dication.

Further investigations, which are now in progress, will show the applicability of the system $TiCl_4$–Br_2 for obtaining new fullerene chlorides and fullerenium species.

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Notes and references

‡ *Crystal data*: Data collection for crystals was performed on a MAR345 image plate at 100 K using synchrotron radiation at the BESSY storage ring (λ = 0.9100 Å, BL14.2, PSF of the Free University of Berlin, Germany). Structure solution was undertaken with SHELXS-97 and structure refinements with SHELXL-97.

$(C_{60}Cl_5)_2$: orthorhombic, $Pca2_1$, a = 19.579(2), b = 11.2680(8), c = 29.077(3) Å, V = 6415(1) Å^3, Z = 4, R_{int} = 0.099, Flack parameter = 0.13(9), R_1 = 0.113 (for 5696 reflections with $I > 2\sigma(I)$), wR_2 = 0.259 (for 9098 reflections and 1180 parameters). CCDC 635516.

$[(C_{70})_2](Ti_3Cl_{13})_2$: triclinic, $P\bar{1}$, a = 10.1848(2), b = 13.7803(3), c = 16.7018(4) Å, α = 86.242(1), β = 89.054(1), γ = 79.491(1)°, V = 2299.8(1) Å^3, Z = 1, R_{int} = 0.022, R_1 = 0.037 (for 6242 reflections with $I > 2\sigma(I)$), wR_2 = 0.101 (for 6513 reflections and 775 parameters). CCDC 635517.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702665j

§ Of the three crystallographically independent C_{70} molecules (A, B and C) found in the crystal structure of $C_{70}\cdot 2TiCl_4$, molecule A has been determined with a better precision than the other two.

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