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The formation of a single-bonded $(C_{70}^{-})_2$ dimer in a new ionic multicomponent complex of cyclotriveratrylene: $(Cs^{+})_2(C_{70}^{-})_2\cdot CTV\cdot (DMF)_7(C_6H_6)_{0.75}$†

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The molecular structure and properties of a single-bonded $(C_{70}^{-})_2$ dimer in a new ionic complex with cyclotriveratrylene (CTV): $(Cs^{+})_2\cdot(C_{70}^{-})_2\cdot CTV\cdot(DMF)_7\cdot(C_6H_6)_{0.75}$ are presented.

Ionic compounds based on fullerenes are interesting both from their physical properties,[1,2] and a large variety of dimeric and polymeric structures of negatively charged fullerenes.[3,4] Neutral C_{60} forms dimers in the mechano-chemical reaction, under pressure or irradiation.[5] Negatively charged fullerenes are also able to dimerize. For the first time the $(C_{60}^{-})_2$ dimer was found in a metastable phase of $(Rb^{+})\cdot(C_{60}^{\cdot -})$.[6] Recently, dimerization of $C_{60}^{\cdot -}$ was observed in two ionic complexes: $(Tol_2Cr^{\cdot +})$-$(C_{60}^{\cdot -})$ (Tol_2Cr: bis(toluene)chromium and $(Cp^{*}_2Cr^{+})$-$(C_{60}^{\cdot -})(C_6H_4Cl_2)_2$ (Cp^{*}_2Cr: decamethylchromocene; $C_6H_4Cl_2$: *o*-dichlorobenzene) at 250 and 220–200 K, respectively.[7,8] In the latter case the molecular structure of $(C_{60}^{-})_2$ has been determined by X-ray diffraction on a single crystal.[8] Information on the $(C_{70}^{-})_2$ dimer seems to be absent.

Bowl-like shaped hexamethoxycyclotriveratrylene (CTV) (Fig. 1, inset) corresponds well to the spherical shape of fullerenes and is used for the preparation of a complex with the C_{70} fulleride. Neutral CTV complexes with C_{60}: $CTV\cdot C_{60}$ and $CTV\cdot(C_{60})_{1.5}\cdot C_7H_8$ and C_{70}: $CTV\cdot$(*o*-carborane)$\cdot C_{70}\cdot(C_6H_4Cl_2)$ have been characterized.[9] However, ionic complexes of CTV with fullerides are unknown.

The crystals of $(Cs^{+})_2\cdot(C_{70}^{-})_2\cdot CTV\cdot(DMF)_7\cdot(C_6H_6)_{0.75}$ (**1**) were obtained by diffusion, during one month, of hexane in benzene–DMF solution (7 : 1) containing Cs^{+}, $C_{70}^{\cdot -}$ and CTV at a 1 : 1 : 4 molar ratio. The crystals were formed as large black hexagonal plates (up to 2 × 2 mm) with 40% yield. All manipulations were carried out in a glove box. The composition of **1** was determined from the X-ray diffraction data.

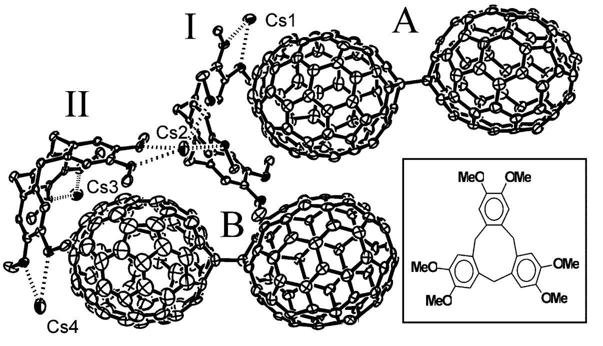

Fig. 1 Mutual arrangement of two crystallographically independent $(C_{70}^{-})_2$ dimers (**A** and **B**), CTV molecules (**I** and **II**) and Cs^{+} cations in **1**. Inset shows molecular structure of CTV molecule. Dotted lines show the shortened O···Cs contacts.

Single crystal X-ray diffraction data for **1**‡ at 120 K show that C_{70}^{-} anions form single-bonded $(C_{70}^{-})_2$ dimers. There are two crystallographically independent dimers (Fig. 1, **A** and **B**). The ordered dimer **A** is refined in anisotropic approximation, whereas the disordered one (**B**) is refined using rigid body constraints.

Here we discuss the molecular structure of the ordered dimer **A**. Symmetry of the $(C_{70}^{-})_2$ configuration is close to C_{2h} (Fig. 1), as in the case of $(C_{60}^{-})_2$ dimer, and is lower than D_{5h} symmetry of parent C_{70}. The average bond angle for sp^3 carbons of 109° is close to tetrahedral geometry. The length of the bridging intercage C–C bonds is 1.584(9) Å and the intermolecular distance between the centers of mass of two fullerenes is 10.417 Å. This length of the intercage C–C bond is longer than that of the normal C–C bond between sp^3 carbons in non-strained molecules (1.541(3) Å)[10] and has an intermediate value between those for the negatively charged $(C_{60}^{-})_2$ and neutral $(C_{60})_2$ dimers: 1.597(7)[8] and 1.575(7) Å,[5] respectively. The change in the length of the intercage C–C bond in the fullerene dimers is qualitatively interpreted by the Coulomb repulsive energy of a dimer. This energy is maximal in the $(C_{60}^{-})_2$ dimer, decreases in the larger $(C_{70}^{-})_2$ dimer and is equal to zero in the neutral $(C_{60})_2$ dimer.

As a whole, **1** has a layered structure (Fig. 2). The layers composed of the CTV molecules coordinating to the Cs^{+} cations alternate with those composed of the $(C_{70}^{-})_2$ dimers along the *c*-axis. Multicomponent complex **1** is an interesting example of a supramolecular array which combines the π–π stacking of bowl-shaped CTV and an elongated sphere of C_{70}^{-} anions with the coordination of oxygen atoms of CTV to the Cs^{+} cations. As a result, the CTV molecules hold together the $(C_{70}^{-})_2$ dimers and Cs^{+} in one ionic multicomponent complex. There are two crystallographycally independent CTV molecules (**I** and **II**). One CTV (**I**) forms shortend van der Waals contacts with the ordered dimer **A**, while the other one (**II**) with the disorderd dimer **B** (Fig. 1). The shortened contacts between the Cs^{+} and $(C_{70}^{-})_2$ dimers are absent (> 3.9 Å). Each CTV molecule coordinates to three Cs^{+} in a crown-like manner (the O···Cs distances are in the range 3.00–3.16 Å) (Figs. 1 and 2). Complex **1** contains also 7 DMF and 0.75 C_6H_6 solvent molecules per formula unit, which occupy the cavities in the packing of CTV and the $(C_{70}^{-})_2$ dimers (Fig. 2). Each DMF molecule coordinates to Cs^{+} by carbonyl oxygen with the O···Cs distances in the range 2.87–3.08 Å.

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† Electronic supplementary information (ESI) available: synthesis and characterisation of **1** including IR, UV–VIS–NIR, EPR and SQUID measuements. See http://www.rsc.org/suppdata/cc/b2/b207035a/

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The IR-spectrum of **1** at room temperature (RT) has numerous bands attributed to the $(C_{70}^{-})_2$ dimer (494, 508, 530, 548, 556, 575, 628, 668, 681, 713, 721, 774, 800, 1175, 1278, 1307, 1323, 1353, 1363, 1393, 1429, 1540 and 1557 cm^{-1}) and the bands of CTV and DMF. As compared with the spectrum of the parent C_{70} (457, 534, 564, 576, 642, 673, 794, 1132, 1413, 1430 cm^{-1}), the position of the bands changed in **1** and numerous new weak bands appeared. These changes can be attributed both to the formation of -1 charged C_{70} and to activation of 'silent' symmetry-forbidden modes due to C_{70}^{-} symmetry lowering in a dimer. For example, the most intense C_{70} bands at 534 and 794 cm^{-1} in **1** shift to 530 and 800 cm^{-1}, respectively. The presence of an intense band at 1393 cm^{-1} in **1** can also be attributed to C_{70} reduction, which is consistent with the position of $F_{1u}(4)$ mode of C_{60} at 1390–1394 cm^{-1} in its radical anion salts.[2]

The characteristic band of isolated $C_{70}^{\cdot-}$ radical anions observed in the solid spectrum of $(Ph_4P^+)_2(C_{70}^{\cdot-})(I^-)$[11] and in the solution spectra of $C_{70}^{\cdot-}$ (1363–1380 nm)[1] in the NIR-range is absent in the spectrum of **1**. Instead, two intense bands centred at 910 and 1240 nm were observed. Thus, dimerization changes absorption of $C_{70}^{\cdot-}$ in the NIR-range. These bands can be attributed to intramolecular transitions in the $(C_{70}^{-})_2$ dimer.

Polycrystalline **1** shows a weak asymmetric EPR signal at RT having three components: $g_1 = 2.0042$ with a line half-width $(\Delta H) = 0.8$ mT, $g_2 = 2.0024$ with $\Delta H = 0.2$ mT, and $g_3 = 1.9923$ with $\Delta H = 2.0$ mT. The estimation of a number of spins from the integral intensity of the signal shows only one spin per 260 formula units. The observed signal cannot be attributed to the $(C_{70}^{-})_2$ dimer but to $C_{70}^{\cdot-}$ since a similar asymmetric signal is known for electro-chemically generated $C_{70}^{\cdot-}$ in solution ($g_1 = 2.007$, $g_2 = 2.003$ and $g_3 = 2.0000$[12]) and for solid $(Ph_4P^+)_2(C_{70}^{\cdot-})(I^-)$ ($g_x = g_y = 1.9996$, g_z (long axis) $= 2.0150$, $g_{av} = 2.0047$[11]). We deduce that the EPR signal attributed to a small amount of $C_{70}^{\cdot-}$ appears in **1** probably due to partial dissociation of the $(C_{70}^{-})_2$ dimer even at RT and that the $(C_{70}^{-})_2$ dimers are EPR silent.

The magnetic susceptibility of **1** was measured in the range 1.9–390 K (Fig. 3). A diamagnetic sample holder contribution and a paramagnetic contribution of the Curie impurities (about 2.4%) were subtracted from the experimental values. Magnetic susceptibility is negative at RT and is temperature independent in the range 1.9–260 K (the temperature independent part of magnetic susceptibility is $\chi_M = -1.7 \times 10^{-3}$ emu $mole^{-1}$). Thus, the $(C_{70}^{-})_2$ dimers are diamagnetic. A small increase in magnetic susceptibility observed in the range 260–360 K can be attributed to partial dissociation of the $(C_{70}^{-})_2$ dimers. This is also the reason for the appearance of the EPR signal from $C_{70}^{\cdot-}$ in **1** at RT. Upon heating **1** above 360 K, the magnetic susceptibility increases abruptly as well as the intensity of the EPR signal attributable to $C_{70}^{\cdot-}$. This indicates that the $(C_{70}^{-})_2$ dimers actually dissociate at this temperature to paramagnetic $C_{70}^{\cdot-}$, and at 390 K about 90% dissociation of the dimer is observed. The dissociation temperature for the $(C_{70}^{-})_2$ dimer (360–390 K) is essentially higher than that for the $(C_{60}^{-})_2$ dimers (200–250 K)[7,8] but lower than for the neutral $(C_{60})_2$ dimer (423–448 K).[5] This correlates with the intermediate length of the intercage C–C bond for $(C_{70}^{-})_2$ dimer between those for $(C_{60}^{-})_2$ and $(C_{60})_2$ ones.

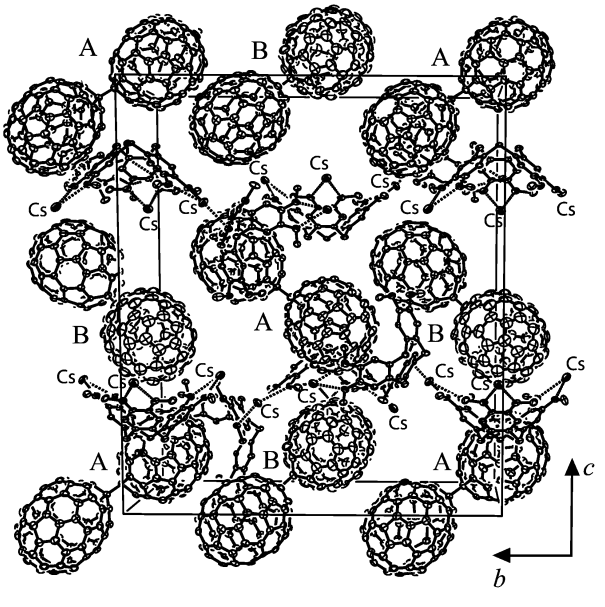

Fig. 2 The projection of the crystal structure of **1** along the *a*-axis. DMF and C_6H_6 molecules are omitted for clarity. Dotted lines indicate the shortened O···Cs contacts.

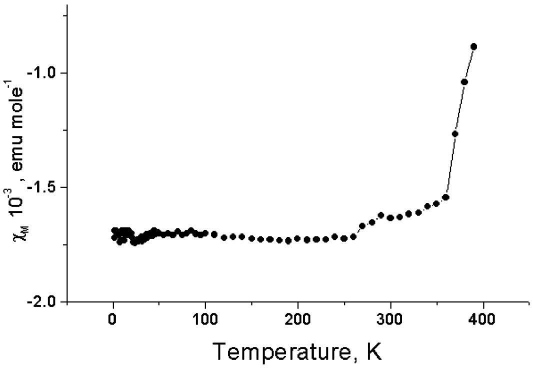

Fig. 3 The temperature dependence of molar magnetic susceptibility of **1** between 390 and 1.9 K by SQUID measurements.

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Notes and references

‡ Crystal data for **1** were collected on a Bruker SMART 1K CCD area detector mounted on a three-circle diffractometer, using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by a direct method and refined by the full-matrix least squares against F^2 of all data using the SHELXTL software. All non-hydrogen atoms of ordered fragments were refined in anisotropic approximation. One $(C_{70}^{-})_2$ dimer (**B**), three DMF molecules and one C_6H_6 molecule are disordered. The positions of carbon atoms in the dimer **B** (except carbons involved in the intercage C–C bond) were refined using rigid body constraints according to the data for the neutral C_{70} molecule.[13] The positions of hydrogen atoms were calculated and included in refinement procedure using rigid model.

Crystal data: $C_{385}H_{167}Cs_4N_{14}O_{26}$, $M_r = 5935.97$, dark red plate, monoclinic, space group $P2_1/n$, $a = 25.937(8)$, $b = 29.113(11)$, $c = 34.221(14)$ Å, $\beta = 103.328(9)°$, $V = 25114(16)$ Å^3, $D_c = 1.568$ g cm^{-3}, $Z = 4$, $T = 120$ K, data/restrains/parameters 42508/1740/2788, final R induces $[I > 2\sigma(I)]$, $R_1 = 0.104$, $wR_2 = 0.262$, GOF = 0.872. CCDC 189653. See http://www.rsc.org/suppdata/CC/b2/b207035a/ for crystallographic data in CIF or other electronic format.

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