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An order–disorder phase transition in the van der Waals based solvate of C_{60} and $CClBrH_2^{\dagger}$

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The co-crystal of C_{60} -2CBrClH₂ possesses a monoclinic (*C*2/*m*) structure at room temperature with both molecular entities, C_{60} and CBrClH₂, orientationally ordered. At 322 K, it transforms reversibly into a hexagonal (*P*6/*mmm*) setting, revealing a rare example of a heteromolecular stator rotator transition in a fullerene co-crystal, which applies to both the fullerene and the coformer analogous to the paradigmatic C_{60} cubane co-crystal. However, in the present case, topological molecular surface matching between the two chemical species is not necessary and the order disorder phase transition reflects simultaneous activation of the orientational disorder of both C_{60} and CBrClH₂.

Introduction

Materials solely consisting of carbon, carbon allotropes, such as fullerenes, carbon nanotubes and graphenes, exhibit extraordinary differences in their properties depending on the synthesis conditions.^{1–3} Among these materials, fullerenes are of interest due to their large number of potential applications.^{4–7} In particular, co-crystals and solvates formed by intercalation of organic or inorganic molecules or even metals into the fullerene structures have attracted renewed interest during the last decade.^{8,9} This is because solvates, or more precisely hexagonal close packed solvates, tend to easily form nanowires not only with high conductivity but also with extraordinary mechanical properties, as has been demonstrated by the discovery of incompressible phases, which are harder than diamond at high pressure.^{3,8,10} In these systems, the superior mechanical properties are related to the 3D network of covalently bonded C atoms between rigid C_{60} molecules together with dopant molecules acting as a spacer between C_{60} units and as a linker between collapsed C_{60} units.

The more fundamentally interesting rotator-stator cocrystals of C_{60} or C_{70} with cubane (C_8H_8) have been discovered recently.^{11,12} The cubic shape and the concave surface of cubane create an almost perfect topological fit with the convex surface of the C_{60} molecules when static (orientationally ordered) cubane molecules occupy octahedral voids of the face-centered-cubic structures of rotating fullerenes. When cooling such co-crystals, a phase transition (around 140 K for co-crystals with C_{60} and 150 K with C_{70}) occurs into an orientationally ordered phase (orthorhombic or tetragonal, respectively). The C_{60} - and C_{70} -cubane co-crystals were reported as the first rotator-stator heteromolecular crystals in which stability is provided due to the perfect match of the molecular surfaces of the involved chemical species.

In this work, we report on C_{60} -CBrClH₂ co-crystals. It will be demonstrated that a low-temperature monoclinic C_{60} ·2CBrClH₂ co-crystal in which both molecular species are orientationally ordered undergoes a phase transition around room temperature to a high-temperature hexagonal phase without a change of stoichiometry, in which CBrClH₂ molecules occupy the prismatic voids of the hexagonal lattice and both C_{60} and CBrClH₂ are orientationally disordered. Its behavior will be compared with the recently studied monoclinic C_{60} ·2CBr₂H₂ co-crystal¹³ in which both molecular species are orientationally ordered. The co-crystal reported here displays

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 $[\]dagger$ Electronic supplementary information (ESI) available: Crystallographic information files for monoclinic C₆₀·2CBrClH₂ at 303 K (C₆₀ 2CBrClH₂ C2M.cif) and hexagonal C₆₀·2CBrClH₂ at 333 K (C₆₀ 2CBrClH₂ P6MMM.cif). See DOI: 10.1039/c8ce00271a

a C2/m lattice symmetry and despite the overall packing it is quite similar to the hexagonal packing of solvates formed between C_{60} and halogen-methane derivatives.^{14–22}

Experimental

Fullerene C_{60} was purchased from TermUSA (purity higher than 99.98%) whereas bromochloro-methane (CBrClH₂) was purchased from Aldrich (purity higher than 99.5%). Cocrystals were prepared at room temperature by mixing C_{60} powder with CBrClH₂ liquid. After a few months, the morphology of the fcc C_{60} crystals disappeared and new crystals appeared.

The structure and phase transitions of the C₆₀·CBrClH₂ cocrystals were studied by means of X-ray powder diffraction (XRPD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). XRPD was conducted by means of a high-resolution horizontally mounted INEL cylindrical position-sensitive detector (CPS-120) using the Debye– Scherrer geometry (angular step *ca.* 0.029°-2 θ over a 2 θ -range from 2 to 115°) equipped with monochromatic Cu K α_1 (λ = 1.5406 Å) radiation (40 kV and 25 mA). The temperature was controlled with a liquid nitrogen 700 series Cryostream Cooler from Oxford Cryosystems (±0.1 K). Samples were held in a 0.5 mm-diameter Lindemann glass capillary and rotated during data acquisition to minimize the effect of preferential orientation.

Pseudo-Voigt fits of the Bragg peaks were used to determine the peak position and lattice parameters with XCELL. For the disordered structures, Rietveld refinement was carried out using the FullProf Suite²³ while the C₆₀ molecule was described with spherical harmonics as a homogeneous distribution of 60 C-atoms positioned on a sphere with a radius of 3.59 Å. For the ordered structures, the Materials Studio²⁴ package was used. In both cases, the CBrClH₂ molecule was described as a rigid body (C–Cl: 1.76 Å, C–Br: 1.93 Å, C– H: 1.09 Å).

DSC measurements were performed using a Q100 analyzer from TA Instruments (New Castle, DE, USA) with masses from 5 to 20 mg and heating rates typically of 2 K min ¹ in hermetically sealed high-pressure stainless steel pans from Perkin-Elmer to resist the vapor pressure of the solvent. TG experiments were conducted under a nitrogen flow using a Q50 thermobalance from TA Instruments (New Castle, DE, USA) at a 2 K min ¹ rate with masses ranging between 2 and 10 mg.

Results and discussion

Due to the fast decomposition of the C_{60} -CBrClH₂ co-crystals outside of the mother liquor at room temperature, both were introduced into a Lindeman capillary to obtain XRPD patterns at 303 K (Fig. 1).

The XRPD pattern obtained at 303 K was indexed using XCELL. It resulted in a monoclinic unit cell with lattice parameters (after Rietveld refinement) a = 9.9153(6) Å, b =



Fig. 1 Experimental (red circles) and calculated (black line) X ray pow der diffraction patterns at 303 K along with the difference profile (blue line) and Bragg reflections (vertical bars) of the monoclinic C2/m space group of the C₆₀·2CBrClH₂ co crystal. The inset provides the data be tween 50 and 70° (2 θ) at an increased scale.

17.412(2) Å, c = 10.0478(6) Å, $\beta = 101.966(3)^{\circ}$, and V = 1697.0(5) Å³, and the systematic absences are compatible with the space group C2/m (isostructural to the C₆₀·2CBr₂H₂ co-crystals).

Monoclinic co-crystals together with a small quantity of the mother liquor were taken from the beaker for TG analyses. The sample mass was in the first instance recorded at a constant temperature (303 K) leading to the inflection point "a" (in Fig. 2) indicating the complete depletion of the mother liquor. The sample mass continued to decrease, while the temperature remained constant, indicating that the cocrystals are unstable under nitrogen gas. On heating, the sample subsequently lost more mass with a total decrease



Fig. 2 Thermogravimetric analysis of a heterogeneous sample consisting of C_{60} -2CBrClH₂ co crystals and an excess of mother liquor (vertical axis: sample mass). From t = 0 to t = 60 min under isothermal conditions (303 K) (shaded area) followed by heating with a scanning rate of 5 K min⁻¹. Evaporation rate: -0.38 mg min⁻¹ in the first part (t = 0 to $t = t_a$). Inset: Details of the curve following the inflection point "a" (mass loss is expressed in % of the weight of the sample defined by point "a").

from the inflection point "*a*" of 26%, *i.e.* close to the 27% calculated for a C_{60} : 2CBrClH₂ molar ratio.

With the 1C₆₀: 2CBrClH₂ stoichiometry, Rietveld refinement was carried out using Materials Studio and applying the rigid-body constraint for CBrClH₂ (the molecular structure was based on the data of Podsiadło et al.).²⁵ The positions and orientations of the molecules were refined with a single overall isotropic displacement parameter and a preferred orientation correction using the March-Dollase formula.²⁶ The refinement result is presented in Fig. 1, together with the experimental pattern. Surprisingly, both C₆₀ and CBrClH₂ are orientationally ordered within the co-crystals. The C₆₀ molecule is located at the 2a Wyckoff position for 2/m symmetry, whereas the solvent molecule is located at the 4h Wyckoff position (0, y = 0.2768(2), 1/2). The two halogen atoms (Cl and Br) are statistically disordered with a 50/50% distribution over their respective sites. For the lowtemperature phase of CBrClH₂, the halogen atoms, Cl and Br, are also disordered with similar 0.5 occupancies to what was reported for the low-temperature phase of CBrClH₂. The final Rietveld refinement yielded profile factors of $R_{wp} = 5.26\%$ and $R_p = 3.83\%$, an overall isotropic temperature factor of 0.064 ± 0.001 and March-Dollase preferred orientation parameters of $a^* = 0.199(19)$, $b^* = 0.746(24)$, $c^* = 0.636(26)$, and $R_0 = 0.917(6)$.

The stacking of alternating C_{60} and $CBrClH_2$ molecules is presented in Fig. 3. The solvent molecules have their 2-fold axis along the monoclinic *b* axis and the halogen ligands pointing along the longer diagonal of the *a*-*c* plane.

To examine possible phase transitions, mixtures of cocrystals and their mother liquor were placed in stainless steel high-pressure pans for DSC studies and in Lindemann capillaries to identify structural changes. The resulting DSC curve can be seen in Fig. 4. The endothermic peak P1 corresponds to the melting of excess monoclinic (C2/c) CBrClH₂ at virtually the same temperature as the pure solvent.²⁷ It corresponds to a degenerate eutectic equilibrium in the C₆₀– CBrClH₂ binary system. Peak P2, at 322 K, corresponds to a



Fig. 3 The (001) plane (left panel) and the (010) plane (right panel) of the crystal structure of monoclinic C_{60} ·2CBrClH₂ at 303 K. The overlap of the red (Br) and green (Cl) colored halogens highlights the occupational disorder.



Fig. 4 (a) DSC curve of C_{60} ·2CBrClH₂ in the presence of the mother liquor obtained in a sealed pan. Peak P1 corresponds to the melting of CBrClH₂, peak P2 to the reversible order disorder phase transition of C_{60} ·2CBrClH₂ and peak P3 to the peritectic invariant (hexagonal C_{60} ·2CBrClH₂ \leftrightarrow L + FCC C_{60}). (b) XRPD patterns for C_{60} ·2CBrClH₂ in the presence of the mother liquor in a closed capillary as a function of temperature: 303 K, monoclinic solvate C_{60} ·2CBrClH₂; 333 K, hexagonal solvate C_{60} ·2CBrClH₂; 393 K, FCC C_{60} + liquid. The pattern at the top of the figure is that of fcc C_{60} and is provided for reference. For the pattern at 333 K, the refinement results have been indicated as well: calculated pattern (black line), difference between calculated and experimental pattern (blue line) and the Bragg reflections (vertical red bars) of the hexagonal *P6/mmm* space group of the C_{60} ·2CBrClH₂ co crystal obtained from the low temperature monoclinic co crystal by heating.

reversible solid-solid phase transition (see the inset in Fig. 4a) without a stoichiometric change of the co-crystal. As highlighted in Fig. 4b, the XRPD pattern at 333 K reveals a different structure for the co-crystal in relation to the one at 300 K. Preliminary DICVOL analysis revealed a hexagonal lattice with systematic absences compatible with the P6/mmm space group, isostructural to many other co-crystals of C₆₀ with halogenated methane derivatives^{14,16} and to the hexagonal phase of C₆₀.²⁸ The structure was analyzed using the FullProf Suite.²³ The C₆₀ molecule was modeled with spherical harmonics describing a homogeneous distribution of 60 C-atoms located on a sphere with an overall radius of 3.59 Å. The center of C₆₀ was positioned at the 1a Wyckoff position and the carbon of the tetrahedral CBrClH₂ molecule at the (1/3, 2/3, 1/2) position. The CBrClH₂ molecule was again described using a rigid body as for the low-temperature monoclinic structure. The C-atom position and orientation of the molecule were refined, obtaining a position of (0.329(6), 0.711(3), and 0. 544(5)). The final Rietveld refinement yields profile factors of R_{wp} = 4.02% and R_p = 3.09%. Due to the fact that CBrClH₂ has a lower symmetry than the 2d site, the resulting orientation of the molecule is in no special relation to the rotation axis and is therefore orientationally disordered. The refined and experimental patterns are depicted in Fig. 4b.

Finally, the DSC peak P3 at around 390 K in Fig. 4a shows the peritectic invariant (hexagonal C_{60} ·2CBrClH₂ \leftrightarrow liquid L + FCC C_{60}), *i.e.* the desolvation process of the hexagonal cocrystal. The phase diagram of C_{60} :CBrClH₂ is shown in Fig. S1 (see the ESI[†]).

The order–disorder phase transition of the C_{60} ·2CBrClH₂ cocrystal at around 322 K is accompanied by an enthalpy change of 4.85 J g¹ (4.75(20) kJ mol¹), as determined from the Tammann diagram of the solvent-rich side of the equilibrium involving the monoclinic and hexagonal forms of the solvate (see Fig. S2, ESI[†]). This enthalpy change involves an entropy change of 14.7(6) J mol¹ K¹ which is of the same order as that involved in the order–disorder phase transition for the C₆₀-cubane co-crystal, in which similarly both C₆₀ and cubane are orientationally frozen at low temperature.^{11,12} For C₆₀ co-crystals with an order–disorder phase transition involving exclusively the solvent molecule, while C₆₀ displays orientational disorder in both phases, the entropy change is about twice as small, 6.1 kJ mol¹ K¹ for C₆₀·2C(CH₃)Cl₃ (at 212 K)²² and 7.8 kJ mol¹ K¹ for C60·2CCl₄ (at 223 K).²⁹ These thermodynamic values support the structural results reported.

Conclusions

The room temperature co-crystals C_{60} ·2CBrClH₂ exhibit a monoclinic structure (space group C2/m), as revealed by X-ray powder diffraction, with both C_{60} and CBrClH₂ molecules orientationally ordered, the only disorder being that of the halogen atoms, Cl and Br, distributed over two sites with 0.5 occupancies. The structure displays stacking of alternating C_{60} and CBrClH₂ molecules with the solvent molecules having their 2-fold axis along the monoclinic *b* axis and the halogen ligands pointing along the longer diagonal of the *a*-*c* plane.

Without a change in stoichiometry, the co-crystal transforms at 322 K into a high-temperature hexagonal structure (space group P6/mmm) with a similar packing to previously reported hexagonal co-crystals with halogen-methane derivatives.

Conflicts of interest

The authors declare no competing financial interests.

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