

COMBINED X-RAY & NEUTRON POWDER DIFFRACTION STUDY OF A DIMORPHIC C₆₀ SOLVATE: C₆₀ · 1.5 CH₂Cl₂

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Fullerenes and derivative compounds have been around for 20 years and still remain an open field with unsolved mysteries. Among those, the characterization of C₆₀ solvates and the possible polymorphism of the latter still attract unrelenting attention [1,2]. Our primary focus rests with the structural determination of such compounds using laboratory X-rays and neutrons complemented

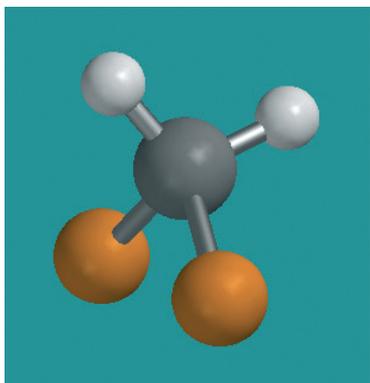


Figure 1a. The solvent molecule CH₂Cl₂ is optimized using Molecular Modeling in order to provide suitable bond lengths and angles to be used as restraints in GSAS.

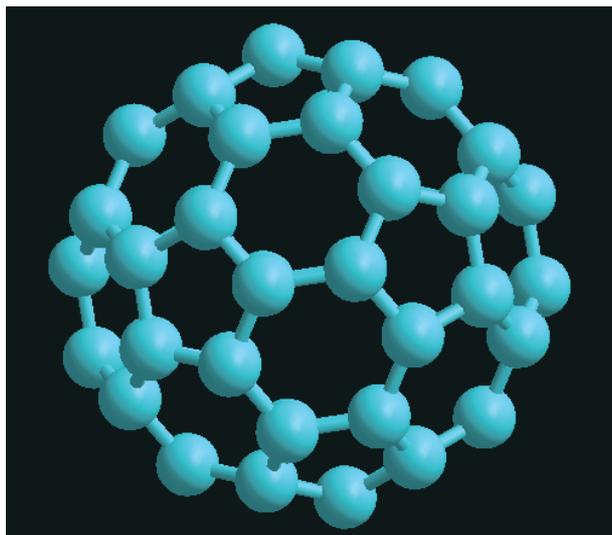


Figure 1b. The C₆₀ molecule is geometrically modeled using 6 independent atoms to allow Rigid Body refinement within any site symmetry using GSAS.

with macroscopic thermodynamic measurements. Structure determinations of C₆₀ solvates from

powder diffraction remain extremely rare and are usually borne from synchrotron measurements [3]. The stoichiometry and symmetry of the title compound have remained a puzzle until now [4,5], although the latter was first synthesized about 10 years ago. The present work resolves this dilemma.

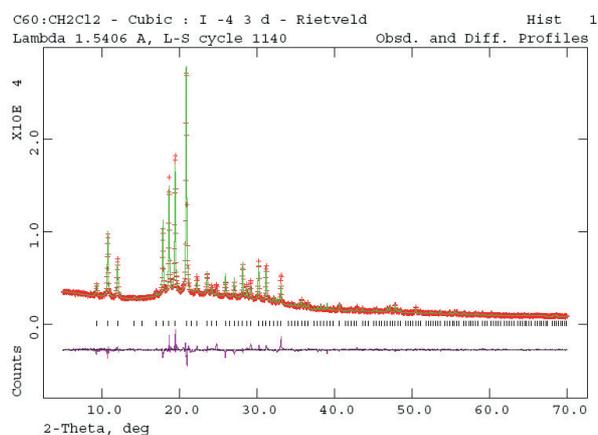


Figure 2a. A lab monochromatic X-ray experiment is carried out using an INEL CPS120 multidetector. It provides an acceptable space group I-4 3 d and the right stoichiometry [1.5 CH₂Cl₂ molecule per C₆₀]. The latter was subsequently confirmed via a most careful TGA (ThermoGravimetricAnalysis) experiment.

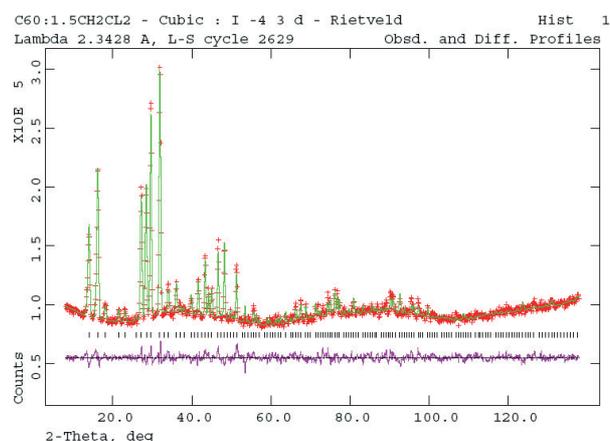


Figure 2b. A monochromatic neutron experiment is carried at the Orphée reactor on the G4.2 spectrometer using an hydrogenated sample. Protons are found and shown to belong to an ordered solvent molecule at T=250 K.

The limited number of experimentally available diffraction peaks makes it mandatory to use available chemical information as much as possible: eg, number of C_{60} buckyballs per unit cell, approximate geometry of solvent and C_{60} molecules. A reasonable geometry of the former is readily obtained using the widespread Molecular Modeling software Spartan'04 [6] (Fig.1a). Whereas the latter (Fig. 1b) is usually documented for specific cases only [7], we have worked out a general description valid for any site symmetry. We have eventually solved our compound structure from our lab X-ray data [Université de Tours] using an acentric space group (I-43d), and a cubic unit cell with a ca. 23 Å (Fig. 2b). Stoichiometry

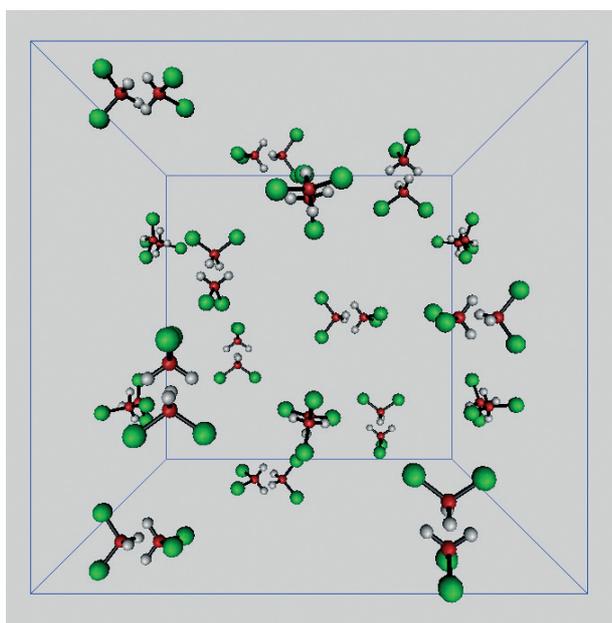


Figure 3. Detailed arrangement of the CH_2Cl_2 solvent molecules in the crystal unit cell, as refined from the neutron data at $T = 250K$. The C_{60} molecules, not shown for clarity, occupy off-centered x,x,x and related sites.

is found to be 1.5 CH_2Cl_2 per C_{60} , i.e. half-way between previously published results [4,5], and as

confirmed by recent most careful TGA experiments carried out by us at Université Paris 5. Neutrons provide the last but not least piece to the puzzle (Fig.2b), namely the detailed **ordered** arrangement of the solvent molecule within the unit-cell (Fig.3). In spite of incoherent scattering an hydrogenated sample does the trick due to an increased contrast between C, Cl and H atoms, due to the negative scattering length of Hydrogen, a unique feature of the neutron. A spherically disordered solvent molecule yields a much poorer fit, and must thus be discarded.

Finally, the low-temperature cryostat available on G4.2 was used to obtain data down to 1.5 K, evidencing at least one phase transition above $T=100$ K and possibly a second one between 100 K and 1.5 K (Fig. 4). The resulting structural modifications are currently being investigated.

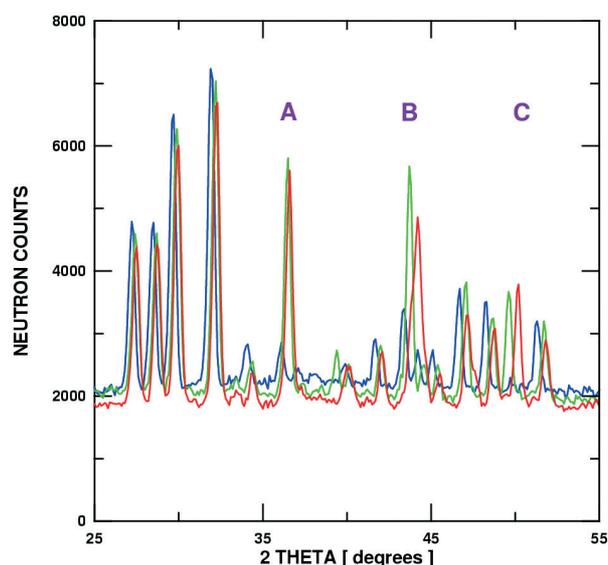


Figure 4. Zoomed part of the neutron data at $T = 250$ K (blue), 100 K (green) and 1.5 K (red), indicating a likely phase transition between 250 K and 100 K (peaks A & C). Distorted lineshapes (eg, peak B, red) may suggest a second phase transition between $T = 100$ K and $T = 1.5$ K.

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