MS31-P02 | TRIETHYLPHOSPHINE AS A MOLECULAR GEAR — PHASE TRANSITIONS IN FERROCENYL–ACETYLIDE–GOLD(I)

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Molecular materials undergoing single-crystal-to-single-crystal (SCSC) phase transitions are of great interest to science and industry. Their spectroscopic, photoelectric, mechanic or gas-storage properties can be switched by controlled pressure or temperature changes without destroying crystallinity, while their the mechanisms, vital for understanding the processes and for materials design, can be probed by means of systematic structural studies.

A sequence of two such discontinuous phase transitions has been observed for a ferrocenyl–acetylide–gold(I) complex with triethylphosphine, by means of a multi-temperature single-crystal X-ray diffraction. Three distinct phases have been identified. The high-temperature and low-temperature phases share the same space group Pbca, whereas the intermediate phase is in the Pb21a subgroup of Pbca.

In all phases molecules of form well defined double layers, with PEt_3 groups interlocking in planes perpendicular to [001]. On the molecular level, both phase transitions involve almost uniquely a conformational change of triethylpho-sphine: a gear-like rotation around the P—Au axis.

The mechanism of these transitions may be imagined as initiated by a rotation of a single PEt_3 group in a double layer (a single gear movement), followed by adjacent phosphines adjusting their conformations as a result of steric strain. These structural changes are sequential, occurring layer-wise and involving approximately every other layer in the crystal lattice.

The sequence of phase transitions results in a noticeable contraction of the crystal cell volume with temperature. The mechanism resembles the concerted rotation of the rigid $Fe(CN)_6$ octahedra underlying extreme compressibility of $LnFe(CN)_6$ under pressure.