MS20-P12 I_7^-: from stoichiometry to structural unit

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High pressure studies of metal coordination complexes have been reported for almost 30 years, but it is only recently these have appeared in significant numbers: in fact, of a total of around 50 studies, approximately two-thirds have appeared in the last five years [1]. One consequence of this limited number is that much of the coverage comprises isolated studies of very different materials and properties, with systematic comparative studies such as [2] being rare.

As part of a broader programme searching for new phenomena in metal coordination complexes, we turned our attention to the iodide salt of the complex cation $[Ag([18]aneS_6)]^+$: this crystallises with the stoichiometry $[Ag([18]aneS_6)]I_7$ and adopts a highly unusual and visually striking structure (see Figure 1) whereby the cation templates the formation of a distorted cubic cage consisting of iodine molecules (I2) and iodide ions (I^-) with iodine-iodine separations of 2.7519(14) Å for I–I and 3.3564(15) Å for I···I [3]. The iodines and iodides form an extended polymeric matrix in which the cations reside.

In response to compression to a maximum pressure of 46 kbar, $[Ag([18]aneS_6)]I_7$ undergoes two distinct phase changes and increasing desymmetrisation of the cubic cage, the details and consequences of which will be explored.

References:

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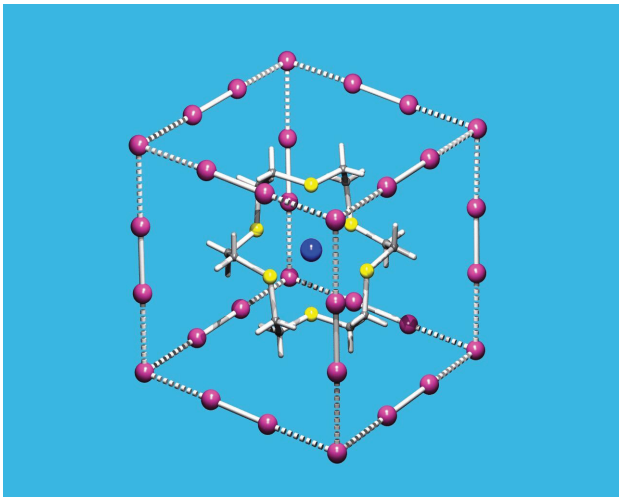

Figure 1. A section of the extended structure of $\{[Ag([18]aneS_6)]I_7\}_n$.

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