

Nanoparticle and nanocluster structures at atomic resolution – even hydrides!

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The structural details which can be validly derived from diffraction experiments underpin the structure-function paradigm which lies at the heart of modern chemistry. In addressing the structures of compounds with significant numbers of heavy atoms (e.g. 374 silver atoms [1] in their core, whether described as clusters, or more popularly, nanoparticles we often encounter significant challenges in elucidating the true structure (or indeed structures) of the molecules contained in these crystals [1, 2 and 3].

The systematic effects which can arise in data dominated by an effectively invariant polynuclear core structure present challenges at all stages including, but not limited to:

- 1) Correct determination of the Unit cell
- 2) Optimal measurement of the bulk of the data which are not dominated by the core
- 3) Recognition of potential alternative interpretations of the data and derivation of and discrimination between competing models and
- 4) Validation of the final model or models – via recourse to both crystallographic and other experimental means.

Analyst directed application of a wide range of tools from the simplest of difference maps through to the application of sophisticated strategies employing myriad restraints in various implementations can be required to yield optimum results[1]. In cases where small but important detail is sought – such as the location of hydride(s) associated with metal cluster cores, optimization of the initial structure has resulted in significant modification to models[2,3] (including their chemical formulation) which were thought to be complete in terms of standard automated checking protocols such as CHECKCIF.

In light of the frequency with which anomalies have been identified in undertaking studies in this area, it is proposed that far greater emphasis needs to be placed on the assessment of the consistency of any proposed crystallographic models with all available supporting spectroscopic data.

In this context, it should also be understood that it is appropriate to report a range of possible formulations which may co-exist in a crystal and to ensure that potential ambiguities in formulation of the nanoparticle, the possible charge states, counter-ions, solvates etc are properly acknowledged.

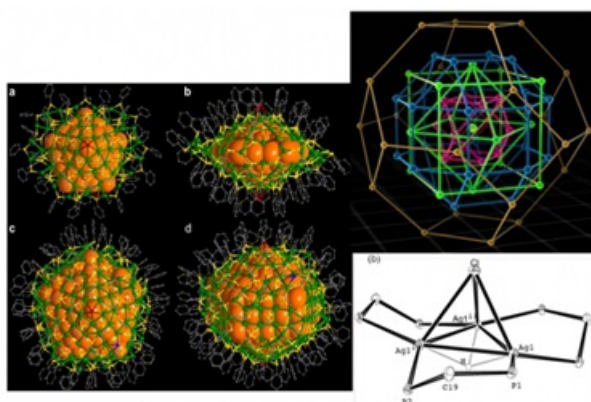
In short, the notion of having determined “the crystal structure” needs to be abandoned in favour of the model oriented concept of “a crystal structure” which can be a source of well determined experimental observation without improperly vesting in it a uniqueness or invariance which is unproven.

If suitable attention to detail is paid when undertaking the initial X-ray studies, then it is even possible to locate hydrogen atoms within the core of such structures using via single-crystal neutron diffraction.

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