Poster

Structural investigation of fluoridopalladates(IV) by 3D ED

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The chemistry of the XeF_2–MF_4 systems remains a topic of considerable interest due to the ongoing unresolved nature of the first noble-gas compound, $XePtF_6$, which may be a $XeF_2 \cdot PtF_4$ adduct [1]. To date, only a handful of structures of these compounds have been crystallographically characterized, displaying XeF_2 coordination to the metal centres of a fluoridometallate(IV) backbone composed of fluoride-bridged $[MF_6]$ octahedra [2–4]. It has also been observed that fluoridometallate(IV) anions with similar structural motifs can be formed with a variety of both inorganic and organic cations. Among such systems, the fluoridotitanates(IV) are by far the most studied and have been shown to form diverse structures of varying dimensionality, ranging from the discrete $[TiF_6]^{2-}$ to complex 3D framework structures [5]. The structural chemistry of fluoridopalladates(IV), on the other hand, remains much less explored and no crystal structures of oligo- or polyfluoridopalladates(IV) have been reported to date, despite previous work establishing clear parallels between the XeF_2–PdF_4 and XeF_2–PtF_4 systems [6]. This is largely due to the fact that the parent tetrafluoride, PdF_4, is a very strong oxidant that reacts with or is insoluble in many common solvents, rendering the preparation of crystals suitable for single-crystal X-ray diffraction (SCXRD) difficult. Recent developments in 3D electron diffraction (3D ED) have made it the method of choice for structural studies of nanocrystalline compounds, as it can provide structural information consistent with SCXRD [7]. In order to study the highly oxidizing and air-sensitive fluoridopalladates(IV) by 3D ED, a novel method of reactive sample handling and transfer was employed to ensure that the crystals could be transferred into the TEM without decomposition. This allowed for the structural characterization of $XeF_2 \cdot 2PdF_4$ and KPd_2F_9, the first crystallographically characterized fluoridopalladates(IV) with poly- and oligomeric structures, respectively. The structure of $XeF_2 \cdot 2PdF_4$ consists of infinite corrugated double chains, with XeF_2 molecules coordinating to every second Pd^{IV} centre (Figure 1), whereas the structure of KPd_2F_9 features the discrete cube-shaped $[Pd_8F_{36}]^{4-}$ anions. The structural investigations of the aforementioned compounds were also accompanied by low- temperature Raman spectroscopy.

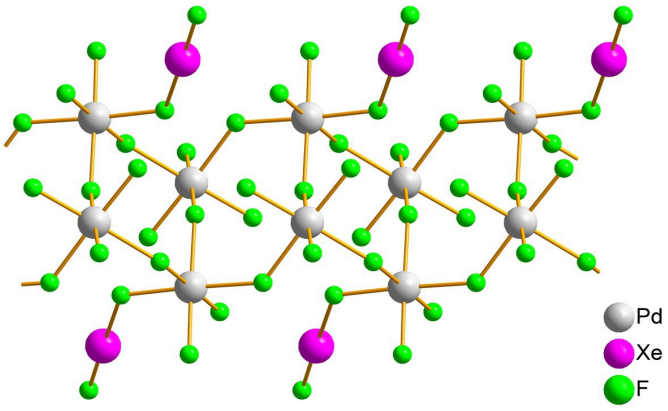

Figure 1. Crystal structure of $XeF_2 \cdot 2PdF_4$ determined from 3D ED data

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