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An innovative soft chemical approach has been applied, using an ionic liquid [BMIM]Cl/AlCl3 (BMIM: 1-ethyl-3-methylimidazolium) as an alternative reaction medium for the synthesis of transition metal clusters and main group polycations which have variety of potential applications in electronic devices. X-ray diffraction and Raman spectroscopy has been used for the structural characterization of the isolated compounds. Physical properties of some of the compounds have also been studied. In addition to the synthesis of several known phases, five new compounds; Sn[SnCl][W3Cl13], [Mo2Te12]I6, Bi[Mo5Cl13]I2, [Sb0.6Te0.4][AlCl4], and Te2[Bi12.7Te3Cl14] have been synthesized and isolated from ionic liquids.1-6

This synthetic scheme is based on the extraordinarily high solubility of metal halides in highly polar Lewis acidic systems, which renders pseudo-melt behavior to the saturated solution. Thus, it has been possible to repeat, at room temperature, several of the reactions previously performed in molten AlCl3 at substantially higher temperature. Moreover, performing redox reactions in ionic liquids provides an efficient one-step route to inorganic clusters, which does not require particularly stringent temperature control or gradients. The additional advantages of this synthetic route over other methodologies include:

- Low temperature synthesis eliminates the risk of product decomposition.
- Pure inorganic cluster compounds can be synthesized. Organic components of the ionic liquids are not included in the final products.
- Ionic liquids render stability to the ionic intermediates.
- Unlike for solid-state methods, reactions in ionic liquids are fast; crystal growth requires only few days rather than weeks, and the overall product yields can be high.

The trinuclear complex Sn[SnCl][W3Cl13] was obtained by the reduction of WCl6 with Sn in [BMIM]Cl/AlCl3 at room temperature.1 The structure of Sn[SnCl][W3Cl13] contains a trinuclear [W3Cl13]<sup>-</sup> cluster anion, a tinn(II) cation, and a [SnCl]<sup>+</sup> cation. The cluster anion [W3Cl13]<sup>-</sup> comprises an equilateral triangle of tungsten atoms, which are connected by one µ3-Cl and three µ1-Cl ligands. Each tungsten atom is further coordinated to six terminal Cl ions. Therefore, all tungsten atoms are found in slightly distorted octahedral environment (Fig. 1). The tinn(II) cations, which are in trigonal pyramidal and in distorted trigonal-prismatic coordination by terminal chloride ions, connect the clusters into a layer structure.

Fig. 1 – a) The trinuclear [W3(µ2-Cl)(µ-Cl)3]Cl<sup>+</sup> cluster anion; b) polyhedra representation, emphasising the edge-sharing of coordination octahedra.

The complex salt [Mo2Te12]I6<sup>-</sup> which contains the heteropolycationic [Mo2Te12]<sup>3+</sup> cluster, was obtained by reacting Mo, Te, and I2 in [BMIM]Cl/AlCl3 at room temperature in only three days. In the crystal structure of [Mo2Te12]I6, the cationic complexes [Mo2Te12]<sup>6+</sup> are surrounded by iodide ions, which connect them into a layer structure. In the complex cation [(Mo<sup>5+</sup>)<sub>2</sub>(Te<sup>2-</sup>)<sub>2</sub>(Te<sup>7-</sup>)<sub>2</sub>]<sup>6+</sup>, the two molybdenum atoms are connected by two bridging Te<sup>2-</sup> dumbbells (Fig. 2a). In addition, each molybdenum atom is coordinated by a terminal Te<sup>7-</sup> polyacation in Te<sup>7-</sup> mode. As a result, both molybdenum atoms are in square-antiprismatic environment. Despite the short Mo···Mo distance of 297.16(5) pm, coupling of the magnetic moments is not observed.

The pentanuclear molybdenum cluster compound Bi[Mo5Cl13]Cl was synthesized by the reduction of MoCl5 with Bi in [BMIM]Cl/AlCl3 at room temperature.4 The resulting bismuth(III) cations are included in the final product. In the [Mo5Cl13]<sup>3+</sup> cluster anion, the molybdenum atoms
form a square pyramid, where each metal atom is coordinated by four Cl\(^{-}\) ligands and one Cl\(^{3-}\) ligand. As a result, the Mo\(_{5}\) core is surrounded by eight inner Cl\(^{-}\) ligands in the form of a cube. The bismuth cations are surrounded by the five apical Cl\(^{-}\) and a free chloride ion in a slightly distorted octahedral environment (Fig. 2b).