

Abstract

The subject of the presented work is the development of new synthetic routes towards $[\text{Fe}_4\text{S}_4]$ cubane-like clusters with terminal halide ligands which are bio-inspired by naturally occurring, ubiquitous iron sulphur proteins and have recently been shown to be good precursors for material synthesis. Compared to well-known procedures the investigated methods are less complicated and achieve high conversion rates. Additionally, these methods are excellent tools for the preparation of new $[\text{Fe}_4\text{S}_4\text{X}_2\text{Y}_2]^{2-}$ clusters with chloride, bromide and iodide as heteroleptic ligand sets. The spectroscopic, electronic and structural characteristics of these compounds are examined in detail. The literature-known pathway for the synthesis of $[\text{Fe}_4\text{S}_4\text{I}_4]^{2-}$ with BTMA^+ (benzyltrimethylammonium) and Ph_4P^+ as counter ions starting from $[\text{Fe}(\text{CO})_5]$, elemental sulphur, iodine and iodide could be improved. The analysis of the resulting clusters showed negative ESI mass spectrometry and X-ray powder diffraction especially with synchrotron radiation to be strong tools for product identification. By introducing ferrous iron halides or tetrahalidoferrates(II) instead of elemental halogens the homoleptic clusters $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$ have been prepared. Using different halides sources FeX_2 and Y^- leads to formation of the new clusters $[\text{Fe}_4\text{S}_4\text{Cl}_2\text{I}_2]^{2-}$, $[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]^{2-}$ in solution the properties of which have been recorded by UV/vis absorption spectroscopy. Salts of $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$, $[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]^{2-}$, $[\text{Fe}_4\text{S}_4\text{Br}_2\text{Cl}_2]^{2-}$ and $[\text{Fe}_4\text{S}_4\text{Br}_2\text{I}_2]^{2-}$ could be obtained with the BTMA cation. Furthermore, the prisman clusters $[\text{Fe}_6\text{S}_6\text{Cl}_6]^{3-}$ and the novel prisman cluster $[\text{Fe}_4\text{S}_4\text{Cl}_3\text{I}_3]^{3-}$ being intermediates of $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ cluster rearrangement-degradation process could be crystalized. The molecular structure of these compounds in single crystal and in bulk material has been compared. By using interhalide compounds instead of iodine formation of $[\text{Fe}_4\text{S}_4\text{X}_{4-n}\text{Y}_n]^{2-}$ mixtures can be achieved due to a ligand exchange equilibrium that is well-known for thiolate coordinated cluster. The utilisation of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$ as a precursor for the preparation of thiolate ligated clusters by ligand exchange reactions was tested as well. Conversions of $(\text{BTMA})_2[\text{Fe}_4\text{S}_4\text{I}_4]$ with potassium 2-thionaphtholate lead to the formation of the dianion $[\text{Fe}_4\text{S}_4(2\text{-NaphS})_4]^{2-}$ which was characterised in detail by spectroscopic methods. Furthermore, various tetrahalidometallates(II) with iron and cobalt have been synthesised with different counter ions to be utilised as precursors for cluster preparation. It could also be shown that the stability of the tetrahalidometallate(II) dianion varies depending on the counter ion in solid state. Crystal structure analysis reveals that bulky, weakly coordinating cations like PNP^+ (bis(triphenylphosphin)iminium) leads to crystallisation of $(\text{PNP})[\text{Fe}(\text{EtOH})\text{X}_3]$ with $\text{X} = \text{Cl}$ or Br instead of forming $[\text{FeX}_4]^{2-}$ anions.