

Priority Programme

“Material Synthesis near Room Temperature”



Project Description – Project Proposal

New Early Transition Metal Atom Cluster Materials: In and with Ionic Liquids

Applicant	Prof. Dr. Martin Köckerling
Institution	Universität Rostock Institut für Chemie Abteilung Anorganische Chemie - Festkörperchemie Albert-Einstein-Straße 3a 18059 Rostock Tel.: 0381/498-6390 E-Mail: martin.koeckerling@uni-rostock.de

Summary of proposal

Polynuclear transition metal coordination compounds with direct metal-metal bonds, especially hexanuclear, octahedral units of early transition metal atoms (M₆-clusters) have attracted scientific and industrial interest for decades already. With the recently started eruption of activities with ionic liquids (ILs) this field seems to be jump-started again, because preliminary experiments indicate, that a multitude of novel compounds is available through the use of ILs in respective chemical reactions. Within the first funding period we succeeded in the synthesis and characterization of a number of new unprecedented hexanuclear niobium cluster compounds using ionic liquids for the preparations. These comprise the first characterized octahedral M₆ cluster compounds with intra-chelate ligands. Also, the preparative reaction is the first example of a 6-8 to 6-12 cluster type transformation. Another unprecedented new compound is (BMIm)₂[Nb₆Cl₁₂(NCS)₆{Ag₂Cl}]. This contains uncommon [Ag₂Cl]⁺ cations, which form inorganic chelate ligands NCS-Ag-Cl-Ag-SCN, which also connect neighbouring cluster units three-dimensionally. For the synthesis of this compound a diffusion technique was developed, which requires viscous ionic liquids. Using different polar organic solvents is not successful. Using this ionic liquid diffusion technique, a larger number of cluster network compounds was synthesized, which consist of iso-thiocyanato ligated cluster units, which are interconnected through the thiophilic late transition metal cations Ag(I), Cu(I), or Hg(I) or cationic complexes of the same metals. In the research direction of Nb₆ cluster compounds with perfluorinated ligands, aiming for weakly coordinating 'cluster ionic liquids', three compounds with trifluoroacetato ligands on the octahedral exo sites were synthesized and characterized. The research in these three fields, WP1: network structures; WP2: chelate ligands; WP3: perfluorinated ligands, is proposed to be continued. The chemistry of the new cluster network structures shall be extended onto EMIm containing ionic liquids, as well as towards attempts to prepare void containing cluster-MOFs. A third extension is directed onto different interconnecting metal ions, i.e. Au(I), Ni(II), Co(II), and Zn(II). Within WP2 a thorough characterization of the cluster compound with intra-cluster 2-aminoethanolato ligands is planned to be done, especially with respect to thermal stability in air. Furthermore, preparative attempts in ionic liquids using o-aminophenolate as

ligand are intended. New Nb₆ cluster compounds with low melting points and perfluorinated carboxylato ligands are intended to be obtained using hexamethylguanidinium cations instead of tetramethylguanidinium, thereby avoiding hydrogen bonding. Also, further reactions using perfluorinated alcoholato ligands shall be done. In the last working package, WP4, niobium cluster units shall be obtained through electrochemical synthesis in ionic liquids.