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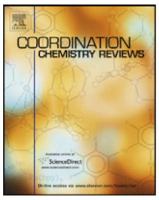

Organically directed heterometallic chalcogenidometalates containing group 12(II)/13(III)/14(IV) metal ions and antimony(III)

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Abbreviations: AEP, *N*-(2-aminoethyl)piperazine; AFM, atomic force microscopy; api, *N*-(3-aminopropyl)imidazole; bapen, *N,N′*-bis(3-aminopropyl)ethylenediamine; BET, Brunauer–Emmett–Teller; BU, building unit; bipy, 2,2′-bipyridine; chxn, *trans*-1,2-diaminocyclohexane; D, dimensional; 1,2-dap, 1,2-diaminopropane; 1,3-dap, 1,3-diaminopropane; 1,4-dab, 1,4-diaminobutane; 1,6-dah, 1,6-diaminohexane; Dabco, 1,4-diazabicyclo[2.2.2]octane; DEA, diethylamine; DMA, dimethylamine; DMF, *N,N*-dimethylformamide; DFT, density-functional theory; dien, diethylenetriamine; DPA, dipropylamine; EA, ethylamine; en, ethylenediamine; EPR, electron paramagnetic resonance; Et, ethyl; LEP, lone electron pair; FTIR, Fourier transform infrared; Ln, lanthanide; MA, methylamine; Me, methyl; MO, methyl orange; MOF, metal-organic framework; *N,N*-dmen, *N,N*-dimethylethylenediamine; *n*-MR, *n*-membered ring; NTE, negative thermal expansion; PA, *n*-propylamine; PBU, primary building unit; Ph, phenyl; phen, 1,10-phenanthroline; PTE, positive thermal expansion; pu, propyleneurea; RhB, rhodamine B; SAED, selected-area electron diffraction; SBU, secondary building unit; SDA, structure-directing agent; SEM, scanning electron microscopy; TBU, tertiary building unit; TEM, transmission electron microscopy; teta, triethylenetetramine; tepa, tetraethylenepentamine; TM, transition metal; tren, tris(2-aminoethyl)amine; XRD, X-ray diffraction; ZTE, zero thermal expansion.

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ABSTRACT

Crystalline chalcogenidometalates are a class of solid-state materials with great significance for both basic science and technological applications. The strong dependence of their functionalities on the crystal structures has led to increasing efforts in preparing new compounds with targeted structural features. It has proven to be a powerful structure-construction strategy to combine the elements with different coordination behaviors into one single crystal lattice. This review focuses on an emerging and effective method to construct chalcogenidometalates, namely combining the regular-polyhedral {M(Q/N)$_x$} (M = 12(II) of Zn, Cd, Hg; 13(III) of Ga, In; 14(IV) of Ge, Sn; Q = S, Se; N = N donor atom of ligand; x = 2, 3, 4, 5, 6) and the pseudo-polyhedral ψ-{SbQ$_x$} (Q = S, Se; x = 3, 4) in the presence of neutral/protonated amine molecules and metal–amine complexes. We analyze systematically the coordination characteristics of PBUs and the condensation of PBUs to form SBUs or even TBUs. Based on the structural survey and comparison, the significant contributions of intrinsic coordination behavior of metal centers to the novelty of the overall solid-state structures are revealed. In addition, the crucial structure-directing roles of amines in the formation of these chalcogenidometalates are discussed in detail. Finally, the advances in the functionalization of these materials for heavy metal ion-exchange, photocatalysis, and NTE are presented, as well as structure- and composition-property relationships.

1. Introduction

Solid-state chalcogenidometalates have received enormous attention for their interesting chemical, optical, electrical, and mechanical properties [1,2]. Extensive studies, from synthesis to structural examination, have revealed a versatile structural evolution and its relevance to the technological applications of these materials in ion-exchange [3–7], nonlinear optics [8–11], superionic conductivity [12–15], thermoelectrics [16–20], photocatalysis [21–23], photoluminescence [24,25], to name several. An enthusiasm for the generation of new crystalline chalcogenidometalates with targeted functionality has greatly facilitated the development of structure-construction strategies based on the combination of different elements.

For an easy structural description, the concept of BU has been widely used to analyze the solids [26–31]. Metal chalcogenide coordination polyhedra, the minimum assemblies of atoms in chalcogenidometalates, are usually viewed as the PBUs. Oligomerization of such "brick"-like PBUs by sharing vertices and/or edges can lead to SBUs. In special cases, further interconnections of SBUs or mixed PBUs/SBUs lead to more complicated assemblies that can be termed here as TBUs. All the types of BUs mentioned above, varying from clusters to chain-like or even layered motifs, can undergo condensation with other groups (identical or different) in various modes to generate the solid chalcogenidometalates with a highly structural diversity. Such an increasing diversity stems essentially from the chemical nature of the metal centers, in terms of their coordination numbers as well as their geometries.

Metal ions with d^{10} electronic configuration can accommodate different coordination geometries due to the lack of crystal field stabilization [2]. Group 12(II) metal ions Zn^{2+} and Cd^{2+} favor adopting the tetrahedral geometry when they are coordinated by chalcogen Q (Q = S, Se, Te) atoms. As a result, a great deal of group 12(II) metal chalcogenides crystallize in either zinc blende or wurtzite structural types. Moreover, steric requirements of organic ligands would lead to other geometries with higher coordination numbers of 5 or 6. In comparison, the larger Hg^{2+} ion adopts a flexible coordination geometry, ranging from the low-coordinate linear pattern to the high-coordinate octahedron, which may be regarded as a consequence of the larger size and greater polarizability of the Hg^{2+} [32–34]. The group 13(III) and 14(IV) chalcogenidometalates are dominated by the heavier metal ions Ga^{3+}, In^{3+}, Ge^{4+}, and Sn^{4+} due to their greater affinity for Q (in most known cases, Q = S, Se) atoms compared to the lighter elements (B^{3+}, Al^{3+}, C^{4+}, Si^{4+}). These four metal ions, especially Ga^{3+} and Ge^{4+}, are inclined to adopt tetrahedral coordination to form either discrete ortho-anion or oligomeric or polymeric entities, as was well illustrated in several crucial reviews [35–39]. On the other hand, the larger size of Q atoms compared to that of oxygen can easily extend its coordination number up to 4. This makes it possible to connect such {MQ_4} (M = Zn, Cd, Ga, In, Ge, Sn; Q = S, Se, Te) tetrahedra in a similar arrangement of a cubic ZnS lattice, resulting in supertetrahedral clusters (T*n*, P*n*, C*n*) with diverse sizes and compositions [35,40,41]. Significant development on the further assembly of such supertetrahedral clusters as SBUs to fabricate microporous chalcogenides has been made in the last two decades [12,42–51]. In addition, higher coordination numbers of 5 and 6 have also become possible for In^{3+} and Sn^{4+} due to their larger ionic radius. For example, {SnQ_5} (Q = S, Se) trigonal bipyramid and {SnS_6} octahedron have proven to be critical BUs for the construction of two- and three-dimensional (2D and 3D) Sn-Q anionic structures [37,38]. Overall, the group 12(II) (Zn^{2+}, Cd^{2+}, Hg^{2+}), 13(III) (Ga^{3+}, In^{3+}), and 14(IV) (Ge^{4+}, Sn^{4+}) chalcogenidometalates exhibit a wide range of polyhedral geometries (see Fig. 1 for some

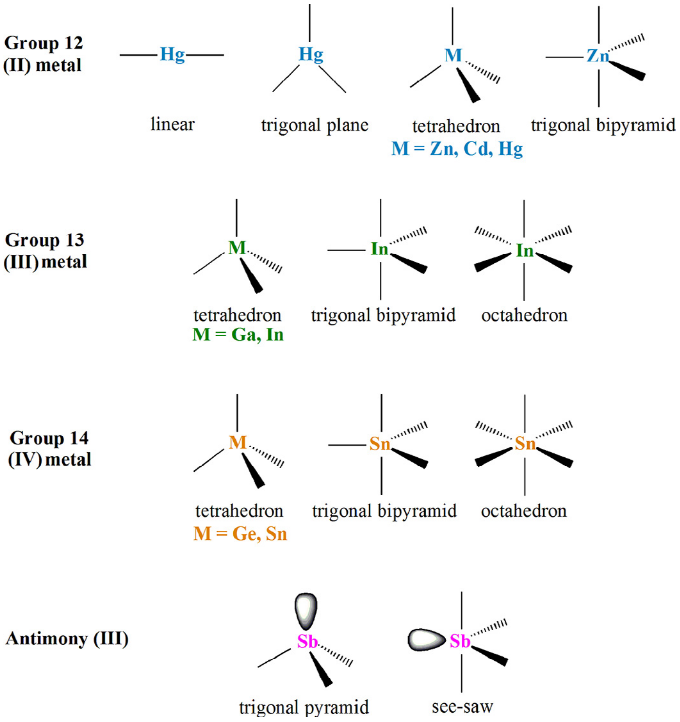

Fig. 1. Common coordination geometries of the group 12(II), 13(III), and 14(IV) metal ions and antimony(III) in the solid-state structures of the chalcogenidometalates.