Heterobimetallic Mn(II)/Al(III) chalcogenides: Model systems for mixed-valent ferrates(II/III)

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The heterobimetallic Mn/In [1] and Mn/Al (this work) metallates A_3MnAlQ_4 (*A*=K, Rb, Cs; *Q*=S, Se, Te) are model systems for the mixed-valent ferrates(II/III), where the *M*(II):*M*(III) ratio can be specifically adjusted during synthesis. While the pure *p*-block metallates(III) $AAl^{III}Q_2$ are dominated by layered structures of *T*2 supertetrahedra ($KInS_2$-type **22**, i.e., pure corner connections). Both the ferrates(III) $AFe^{III}Q_2$ and the manganates(II) $A_2Mn^{II}Q_2$ exhibit linear chains of *trans*-edge-sharing [$MQ_{4/2}$] tetrahedra $KFeS_2$- **3** and K_2ZnO_2-type **1**, respectively). In contrast, the mixed-valent salts A_xMQ_2, *x*=1-2), show a remarkably diverse crystal chemistry, which in the case of ferrates is accompanied by interesting magnetic properties: The entire series of of the hetero-bimetallic Mn(II):(Al/In)(III)=1:1 model systems $A_3[MnInQ_4]$ (*A*=K-Cs, *Q*=S-Te, [1]) and $A_3[MnAlQ_4]$ (*A*=K, Rb; *Q*=S-Te, this work, e.g. $K_3[MnAlS_4]$: orthorhombic, *Pnma*, *a*=716.5(3), *b*=1144.3(4), *c*=1147.5(2) pm, *R*1=5.06 %), which were obtained from stoichiometric melts, are isotypic to the analogous mixed-valent ferrates of the general composition $A_3Fe_2S_4$ **7** [2,3]. All of these compounds contain strongly corrugated tetrahedral chains, whereby - in the case of the Mn/Al and Mn/In compounds - the tetrahedra centers are statistically occupied by the two metal cations. Attempts to synthesize the analogous cesium Mn/Al metallates were unsuccessful, but in the case of sulfur they yielded the new orthorhombic compound $Cs_{13}Mn_4Al_5S_{18}$ (*x*=1.44, **9,** *Ima*2, *a*=5270.7(5), *b*=1238.2(1), *c*=769.9(1) pm, *R*1=6.08 %) in virtually pure phase. With its complicated bent chains (running along the long *a* axis), this salt represents a model system for those mixed-valent ferrates in which the Fe(II):Fe(III) ratio deviates from 1:1 and which correspondingly exhibit large translation periods along the chains **10,11** [4], up to modulated structures e.g. in $K_{7.15}[FeS_2]_4$ **12** [5]. These similarities between the mixed-valent ferrates and the heterobimetallic Mn/Al and Mn/In metallates show, that only the 'odd' number of A^+ counterions and by no means magnetic effects are responsible for the corrugation of the chains. Until now, 'tetrahedra stars' [M_4Q_8], which serve as model systems for the biologically relevant 4Fe4S clusters, are only observed in mixed-valence ferrates $A_{6-7}[Fe_4Q_8]$ **15-17** with Fe(II):Fe(III) ratios between 1:1 and 3:1 (*x*=1.5-1.75) [6].

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