7. Abstract

The preparation of group 11 cyano-, thiocyanato- and halogenometalates are reported together with the synthesis of mixed-ligand cyanohalogeno- and thiocyanatohalogenocuprates(I) and -argentates(I). In general, the compounds **1** - **22** could be isolated by reaction of CuCN/AgCN or CuSCN/AgSCN with complex halogenides and pseudohalogenides in acetone or acetonitrile and were characterized by X-ray crystallography and vibrational spectroscopy.

The new cuprates {[$(C_4H_9)_4N$] $^{1}_{\infty}$[Cu(CN)Br]} **1**, {[$(C_4H_9)_4N$] $^{1}_{\infty}$[Cu(CN)I]} **2**, {[$((C_6H_5)_3P)_2N$] $^{1}_{\infty}$[$(CuI)_2CN$]} **3**, {[$(CH_3)_4N$] $^{1}_{\infty}$[Cu(SCN)Br]} **4** and {[$(CH_3)_4N$] $^{1}_{\infty}$[Cu_2I_3]} **5** contain infinite one-dimensional chains, whereas in {[$(C_4H_9)_4N$] $^{2}_{\infty}$ [$Cu_3(CN)_4$] · CH_3CN} **6**, {$^{2}_{\infty}$ [Cu(CN)(CH_3CN)]} **7**, {$^{2}_{\infty}$ [Cu(SCN)(CH_3CN)]} **8** the formation of two-dimensional polymeric sheets is observed. In addition, {[$((C_6H_5)_3P)_2N$] [$Cu(SCN)_2$]} **9** and {[$(C_4H_9)_4N$] [$CuBr_2$]} **10** containing isolated dimeric or monomeric anions, respectively, have been obtained. These compounds had been previously reported, the crystal structure determinations, however, could be considerably improved.

For the argentates(I), the formation of pure halogenometalates is clearly prefered as documented by the isolation and characterization of ({[$(CH_3)_4N$] $^{1}_{\infty}$ [$AgBr_2$]} **11**, {[$(C_2H_5)_4N$] $^{1}_{\infty}$ [Ag_2Br_3]} **12**, {[$(C_2H_5)_4N$] $^{1}_{\infty}$ [Ag_2Cl_3]} **13**, {[$(C_4H_9)_4N$] $^{1}_{\infty}$ [Ag_3I_4]} **14** and {[$(CH_3)_3CNH_3$] $^{1}_{\infty}$ [Ag_5I_6]} **15**, in which the anion structure consists of infinite one-dimensional chains. In contrast to the cuprates(I), no compound with an anion layer structure could be observed. Instead, the reaction of AgCN with CsCl in acetonitrile yields {[Cs]$_5$ $^{3}_{\infty}$[$Ag_4(CN)_4Cl]_2$ [$AgCl_4$]} **16** with an intriguing three-dimensional structure. The $[Ag_4(CN)_4Cl]^-$ framework provides two different cylindric channels for the accomodation of cesium cations as well as of previously unknown tetrahedral $[AgCl_4]^{3-}$ anions. Furthermore, several compounds such as {[$(C_2H_5)_4N]_6$ [Ag_6I_{11}][I]} **17**, {[$(C_2H_5)_4N]_5$ [Ag_6Br_{11}]} **18**, {[$((C_6H_5)_3P)_2N$] [$Ag(CN)_2$] · CH_3CN} **19**, {[Cs]$_5$ [$Ag(CN)_2]_4$ [I]} **20**, {[$((C_6H_5)_3P)_2N$] [$Ag(SCN)_2$]} **21** and [$((C_6H_5)_3P)_2N$] [Ag(Cl)I]} **22** containing pure monomeric, dimeric and oligomeric halogeno- or pseudohalogenometalate anions have been characterized. Thereby, the $[Ag(Cl)I]^-$ anion in **22** represents an unusual example of hetero-halogenometalate formation.