

**Thermochrome Chloro- und Bromocuprate:  $[\text{C}(\text{NH}_2)_3]_2[\text{CuBr}_4]$ ,  
 $(\text{H}_3\text{CC}_2\text{N}_2\text{SNH}_3)_2[\text{Cu}_2\text{Br}_6]$ ,  $(\text{C}_7\text{N}_3\text{H}_{14})_2[\text{CuCl}_4]$ ,  $(\text{C}_7\text{N}_3\text{H}_{14})_2[\text{CuBr}_4]$ ,  
 $[(\text{Cl}, \text{Br})\text{C}_3\text{N}_2\text{H}_6][\text{CuCl}_3\text{OH}_2]$  und  $(\text{BrC}_3\text{N}_2\text{H}_6)_2[\text{CuBr}_4]$**

Thermochromic Chloro- and Bromocuprates:  $[\text{C}(\text{NH}_2)_3]_2\text{CuBr}_4$ ,  
 $(\text{H}_3\text{CC}_2\text{N}_2\text{SNH}_3)_2[\text{Cu}_2\text{Br}_6]$ ,  $(\text{C}_7\text{N}_3\text{H}_{14})_2[\text{CuCl}_4]$ ,  $(\text{C}_7\text{N}_3\text{H}_{14})_2[\text{CuBr}_4]$ ,  
 $[(\text{Cl}, \text{Br})\text{C}_3\text{N}_2\text{H}_6][\text{CuCl}_3\text{OH}_2]$  and  $(\text{BrC}_3\text{N}_2\text{H}_6)_2[\text{CuBr}_4]$

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Chloro Cuprates, Bromo Cuprates, Crystal Structures, Thermochromism

$\text{CuCl}_2$  and  $\text{CuBr}_2$  were reacted in water-ethanol solutions containing HCl or HBr, respectively, with the following organic bases or their chlorides or bromides: guanidine (**1**), 2-amino-5-methyl-1,3,4-thiadiazol (**2**), hexahydro-2*H*-pyrimidine-(1,2*A*)-pyrimidine (**3**), and 2-hydrazino-2-imidazoline (**4**). With **1** and **3** the tetrahalocuprates  $(\text{1H})_2[\text{CuBr}_4]$ ,  $(\text{3H})_2[\text{CuCl}_4]$  and  $(\text{3H})_2[\text{CuBr}_4]$  were obtained having flattened tetrahedral anions. **2** and  $\text{CuBr}_2$  form  $(\text{2H})_2[\text{Cu}_2\text{Br}_6]$ , with nearly planar  $[\text{Cu}_2\text{Br}_6]^{2-}$  ions that are associated to chains with square-pyramidal coordination of Cu. **2** and  $\text{CuCl}_2$  yield the hydrate  $(\text{2H})\text{Cl}\cdot\text{H}_2\text{O}$ . **4** undergoes substitution of the hydrazine group for halogen, yielding the 2-halo-2-imidazolium salts  $(\text{5H})_{0,2}(\text{6H})_{0,8}[\text{CuCl}_3\text{OH}_2]$  and  $(\text{6H})_2[\text{CuBr}_4]$  in addition to  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3][\text{CuCl}_4]$  (**5** = 2-chloro-, **6** = 2-bromo-2-imidazoline). The planar  $[\text{CuCl}_3(\text{OH}_2)]^-$  ions are associated to chains. Crystal structure determinations were performed with  $(\text{1H})_2[\text{CuBr}_4]$ ,  $(\text{2H})_2[\text{Cu}_2\text{Br}_6]$ ,  $(\text{3H})_2[\text{CuCl}_4]$ ,  $(\text{5H})_{0,2}(\text{6H})_{0,8}[\text{CuCl}_3\text{OH}_2]$  and  $(\text{6H})_2[\text{CuBr}_4]$ ; the latter three at 298 K and at 166 K or 173 K. The known crystal structure of  $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3][\text{CuCl}_4]$  was redetermined at 166 K. In all cases small differences of bond lengths and bond angles are observed between room temperature and low temperature. The magnetic properties and electrospray mass spectra were measured. The products show thermochromic behavior.

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