

Halogenoferrates(II,III) and -manganates(II) with Cations of N-Heterocyclic Bases.

Crystal Structures, Spectroscopic Characterization and Thermal Behaviour

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Numerous fluorometalates with cations of organic amines have been investigated with respect both to the stabilization of unusual metal coordination and to peculiarities of their thermal decomposition. The knowledge about the corresponding chloro- and bromocomplexes, however, is rather limited. As previously shown [1], the thermal behaviour of compounds like Triethylenediammonium tetrachlorocobaltate(II), $(\text{trienH}_2)[\text{CoCl}_4]$, revealed to be as simple as expected. If oxygen is strictly excluded, the mechanism can be described in terms of the liberation of the volatile base hydrochloride accompanied by the formation of CoCl_2 . An analogous behaviour was established for the 1,4-Dimethylpiperazinium, $(\text{dmpipzH}_2)^{2+}$, compounds.

The homologous manganates(II) and ferrates(II) adopt different structures but the thermal behaviour shows certain similarities. The thermal decomposition of $(\text{trienH}_2)[\text{Mn}(\text{H}_2\text{O})_3\text{X}_3]\text{X}\cdot\text{H}_2\text{O}$ ($\text{X}=\text{Cl},\text{Br}$) [2], containing octahedrally coordinated manganese, proceeds via three consecutive steps: the dehydration forming the tetrahalogeno complex, $(\text{trienH}_2)[\text{MnCl}_4]$, an irreversible phase transition of the formed tetrachloromanganate(II), and, finally, its thermal decomposition. $(\text{trienH}_2)[\text{MnCl}_4]$ shows the same behaviour as the isotypic tetrachlorocobaltates(II), *i.e.* an influence of oxidizing or inert gas atmosphere was established.

The variety of compounds which are formed with iron revealed to be unexpectedly wide. Several novel coordination complexes were synthesized and structurally characterized, *e.g.* $(\text{dmpipzH}_2)[\text{Fe}^{\text{II}}\text{Cl}_4(\text{H}_2\text{O})_6]\text{Cl}_2$, $(\text{dmpipzH}_2)[\text{Fe}^{\text{III}}\text{Cl}_4]\text{Cl}$, $(\text{dmpipzH}_2)[\text{Fe}^{\text{III}}\text{Br}_4]_2$, or $(\text{trienH}_2)[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl}_2$ [3].

The most exiting structural features were found in the mixed-valence chloroferrate $(\text{dmpipzH}_2)_6[\text{Fe}^{\text{II}}\text{Cl}_4]_2[\text{Fe}^{\text{III}}\text{Cl}_4]_2[\text{Fe}^{\text{II}}\text{Cl}_5][\text{Fe}^{\text{III}}\text{Cl}_6]$ where six distinct mononuclear chloroferrate anions belonging to four different iron coordination types are arranged on a threefold axis [4]. As yet, only the first stage of the thermal decomposition can be sufficiently understood. Under argon at about 200°C, an almost complete reduction proceeds in a solid state reaction forming Fe^{II} . It is accompanied by the release of HCl and, to a minor degree, carbon containing species. A multi-phase product with at least two chloroferrate species, coke, and C,H,N-containing polymers is formed. A binuclear iron complex, $(\text{dmpipzH}_2)_2[\text{Fe}^{\text{II}}_2\text{Cl}_6]$, and small amounts of $(\text{dmpipzH})[\text{Fe}^{\text{III}}\text{Cl}_4]$ have been proposed to be the major and minor component of the product mixture, respectively [5].

Conventional simultaneous thermal analysis, capillary-coupled TG-MS, *in situ* and *ex situ* Raman and Mössbauer spectroscopy, as well as chemical residue analysis and XRD have been used for the elucidation of the thermal behaviour of the compounds investigated.

[1] M. Feist, R. Kunze, D. Neubert, K. Witke, E. Kemnitz, J. Therm. Anal. **49** (1997) 635.

[2] M. Feist, S. Trojanov, A. Stiewe, E. Kemnitz, R. Kunze, Z. Naturforsch. **52b** (1997) 1094.

[3] S. Trojanov, M. Feist, E. Kemnitz, Z. Anorg. Allg. Chem. **625** (1999) 806.