

PhD Theses

**SYNTHESIS AND PROPERTIES OF SIMPLE AND
COMPLEX SALTS OF PERMANGANIC ACID**

Kótai László

Institute of Materials and Environmental Chemistry

Chemical Research Center, Hungarian Academy of Sciences

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1. INTRODUCTION AND AIMS

Widespread applicability and the increased quality requirements of permanganate salts require development of new synthetic methods. The transition metal permanganates are precursors of numerous catalytically active metal-manganese oxide composites. Therefore, the exact knowledge of their structure, reactivity and the thermal decomposition characteristics of permanganate compounds is essential to plan the properties of the decomposition products.

The main target of this work was the development of new synthetic methods to prepare simple and complex salts of permanganic acid, including the preparation and the study of ammonium permanganate and some ammine-complex permanganates of transition metals such as Ag, Cu, Ni, Cd, Zn.

2. ANALYTICAL METHODS

Classical inorganic analytical chemistry, IR and Raman spectroscopy, UV-VIS spectroscopy, ESR, XRD, GC-MS, single crystal X-ray and powder neutron diffractometry, TG-gas-titrimetry, TG-MS and DSC methods were used.

3. NEW RESULTS

3.1. SYNTHESSES

3.1.1. Syntheses based on manganese heptoxide

A method has been developed to prepare Ba, Mg, Ca, Ni, Zn, Cd, Cu(II), Al, Fe(III), Y, Ce(IV), Sm, Pr and Gd-permanganates by means of the reaction of KMnO_4 with sulfuric acid monohydrate, followed by extraction of the Mn_2O_7 with CCl_4 and the reaction of the Mn_2O_7 in CCl_4 with catalytic amount of water and the oxide, hydroxide and carbonate of the appropriate metal.

3.1.2. Syntheses based on the metathesis reaction of KMnO_4

Reaction of warm saturated solutions of NH_4Cl and potassium permanganate provided $\text{K}_x(\text{NH}_4)_{1-x}\text{MnO}_4$ ($x=0.2-0.4$) solid solutions instead of NH_4MnO_4 as it has been declared previously. Composition of the solid solutions did not change during recrystallization. In order to prepare pure NH_4MnO_4 , the recrystallizations had to be performed in the presence of NH_4Cl .

Mixing of warm saturated solutions of KMnO_4 and excess of $\text{Al}_2(\text{SO}_4)_3$ provided potassium alum and aluminium sulphate-containing aluminium permanganate solution. This mixture was reacted with $\text{Ba}(\text{OH})_2$, when the traces of potassium could be removed in form of solid $(\text{K,Ba})(\text{SO}_4,\text{MnO}_4)$, and pure barium permanganate solution could be obtained.

3.1.3. Hydrolysis of complex permanganates

[Tetraamminecopper(II)] permanganate could be crystallized from its aqueous solutions below $+5\text{ }^\circ\text{C}$. Above this temperature ammonium permanganate has been formed. The phenomena appears to be due to the hydrolysis of the complex cation, which is then followed by the protonation of the ammonia ligand. This type of reaction could also be observed in the solutions of [diamminesilver(I)]- and [tetraamminezinc(II)] permanganates. Generally, the method can be used for the preparation of onium type permanganates.

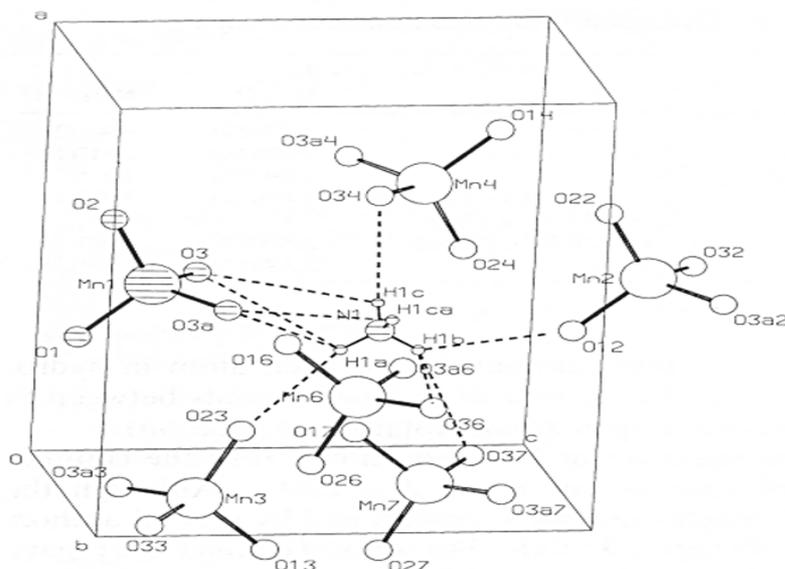
3.1.4. Syntheses based on the disproportionation of barium manganate(VI)

During the preparation of BaMnO_4 by means of the reaction of KMnO_4 and KI (in the presence of BaCl_2 and NaOH) small amount of MnO_2 has also been formed due to the disproportionation of the Na_3MnO_4 by-product. In the presence of KOH , K_3MnO_4 has been precipitated. The pH of the aqueous suspension of BaMnO_4 has been increased from 8.8 to 9.3 during 24 h due to a hydrolysis and a consecutive disproportionation reaction, respectively. Less than 1 % of the BaMnO_4 has been decomposed before reaching equilibrium conditions. Removal of the hydroxide ions shifts the equilibrium. The relative acidity function of the manganic acid has been calculated by using the $\varphi = [-(\delta_{\text{H}})/(\delta_{\text{O}_1})](1 + \delta_{\text{M}})^{0.5}$, relationship. Manganic acid ($\varphi=1.106$) proved to be a weaker acid than the sulfuric or permanganic acid ($\varphi=1.125$ and 1.114 , resp.), but stronger than the carbonic acid ($\varphi=0.965$). Consequently, the carbonic acid cannot liberate manganic acid from their salts, but shifts the hydrolysis-disproportionation equilibrium, therefore the reaction of the barium manganate and the carbonic acid provides barium permanganate. When the $\text{BaMnO}_4:\text{CO}_2$ molar ratio has been less than 1:2, the conversion of the BaMnO_4 could not be completed, because the driving force of the reaction has been the formation of $\text{Ba}(\text{HCO}_3)_2$. Under hydrothermal conditions, from solid BaMnO_4 , ice, and dry ice, (autoclave, $100\text{ }^\circ\text{C}$, autogen pressure, 1.5 h), barium permanganate could be obtained in a yield of 93.8 %.

3.2. STRUCTURE AND PROPERTIES OF PERMANGANATE SALTS

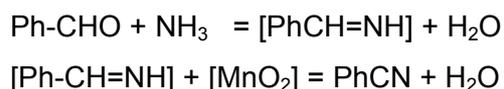
3.2.1. Ammonium permanganate

The structure, hydrogen positions and the presence of N-H...O-Mn hydrogen bonds were determined by single-crystal X-ray studies. The orthorhombic (Pnma, No.61) NH_4MnO_4 is isomorphous with NH_4ClO_4 .



Because of its thermal instability and purple color, Raman studies of ammonium permanganate were performed on rotating sample by far-IR laser excitation. The band splitting of the IR spectra registered by using various matrixes was found to be different which is presumed to be due to changing host-guest interactions between the N-H fragments and the matrix material. During thermal decomposition of the ammonium permanganate (85 °C), besides the classical permanganate decomposition process (NH_3 , MnO_2 and O_2 formation), an intramolecular redox reaction could also be observed with the formation of the oxidation products of ammonia and lower-valence manganese oxides. The heterogeneous oxidation of benzyl alcohol with ammonium permanganate provided benzonitrile via benzaldehyde:

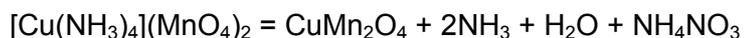




The benzonitrile and the benzaldehyde were formed in a 2:1 molar ratio because the liberated ammonia could transform only 2/3 part of the previously formed aldehyde.

3.2.2. A [tetraamminr ez(II)]-permangan t, $[\text{Cu}(\text{NH}_3)_4](\text{MnO}_4)_2$.

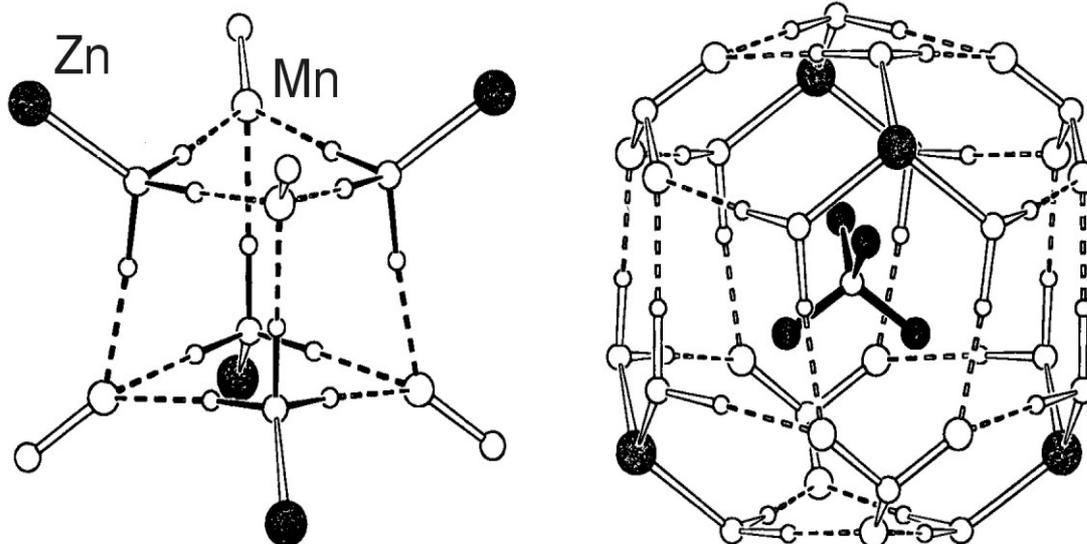
On the basis of factor group analysis, two crystallographically non-equivalent permanganate ion has 9-9 IR and Raman bands, and among the 45-45 IR and Raman bands of the complex cation (C_{4v}) 9-9 bands belong to the CuN_4 (D_{4h}) skeleton. Previously a three-step thermal decomposition with the loss of 2-2 ammonia and O_2 evolution, in addition to the formation of CuMn_2O_4 , has been proposed. Instead of this, the pure compound decomposes in one step at 75 °C-on, with the 308.6 kJ/mol heat evolution and with formaton of Cu, Cu_2O , MnO, Mn_3O_4 , NH_3 , O_2 , N_2 , NO and NO_2 . The Al_2O_3 diluted sample decomposes in two exoterm steps. In the first step 2 mol NH_3 and 1 mol H_2O were formed without O_2 evolution.



The second step is the decomposition of the NH_4NO_3 with the formation of N_2O and H_2O . The reason for the occurrence of this solid phase intramolecular redox reaction is the presence of an N-H...O-Mn hydrogen bond, which acts as a reaction center. This hydrogen bond allows a differentiation between the coordinated ammonia molecules at molecular level.

3.2.3. [Tetraamminezinc(II)] permanganate, $[\text{Zn}(\text{NH}_3)_4](\text{MnO}_4)_2$.

The structure of this complex was determined from the XRD data by using the Rietveld method. The complex has a cubic lattice, ($F4-3m$, No.216, $a=10.335$, $Z=4$, $D_x=2.251$). A polymorph phase transition could be observed at 4.1 °C-on. The structure of the room-temperature modificaton is the following:



In the structure of the complex there are two non-equivalent permanganate-ions. One of them is located in a 3D-hydrogen bonded structure (N-H...O=3.086), the other is located in a cavity built up from the atoms of the 3D-connection H-bonded building blocks. On the basis of the factor group analysis, the splitting and appearing of some IR és Raman bands show the presence of a dynamic lattice distortion phenomenon.

The thermal decomposition characteristics of the complex are very similar to the decomposition of the appropriate Cu-complex. The decomposition (100 °C) process is exothermic, the products are ZnMn_2O_4 , NH_4NO_3 , H_2O and NH_3

3.2.4. $[\text{Cd}(\text{NH}_3)_4](\text{MnO}_4)_2$, $[\text{Ni}(\text{NH}_3)_6](\text{MnO}_4)_2$ and $[\text{Ag}(\text{NH}_3)_2]\text{MnO}_4 \cdot \text{H}_2\text{O}$

[Tetraamminecadmium(II)-, [hexaamminenickel(II)- and [diamminesilver(I)] permanganate monohydrate were also prepared. The cadmium-complex is isomorphous with the zinc compound. The nickel-complex has octahedral cationic structure, the silver complex has an infinite Ag-Ag chain with 2-2 ammonia ligands with the formation of tetrahedral environment. Redox reactions were also detected during thermal decomposition, the reaction products are ammonia, water and ammonium nitrate.

3.2.5. MMn_2O_4 (M=Cu, Zn) compounds

The thermal decomposition of [tetraamminecopper(II)- and [tetraamminezinc(II)] permanganates in an inert organic solvents provided amorphous MMn_2O_4 (M=Zn, Cu) compounds. In case of copper complex CCl_4 (80 °C), in case of zinc compound toluene (100 °C) were used as an inert solvent. The MMn_2O_4 (M=Cu Zn) compounds have defectous

structure, which can be transformed into crystalline spinels at 500 ° via rearrangement of the lattice atoms.

4. USEFULNESS OF THE RESULTS

The new synthetic methods provides processes for the preparation of new, useful and pure permanganate salts. These compounds can be potential oxidants in the organic chemistry, e.g. ammonium permanganate can oxidise the benzyl alcohol into benzonitrile in a one-spot reaction.

The ammine complexes of the transition metal permanganates (Cu, Zn) have hydrogen-bonded structures. This phenomenon is the reason for the appearance of the intramolecular redox reaction in their thermal decomposition. These processes can be performed at low temperature (80-100 °C) with the formation of MMn_2O_4 (M=Zn, Cu) type amorphous and defectous spinell-compounds, which are potential catalysts or catalyst precursors

5. REFERENCES

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