Characterization of Manganese(III) Orthophosphate Hydrate

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Received June 19, 1989

From the IR spectra and the TGA–DTA curves of the manganese(III) phosphate hydrate MnPO₄·1.3H₂O, it has been deduced that the water molecule must be dissociated to produce a hydroxy cation. The proton is transferred to a phosphate group to form a hydrogen phosphate, with the chemical formula MnOH(HPO₄)·0.3H₂O, in which the 0.3 water molecule is strongly retained within the structure. The diffuse-reflectance spectrum revealed that this compound presents a strong Jahn–Teller effect, in agreement with the crystal structure, with three bands in the visible region. After the transitions were assigned, the McClure parameters were calculated.

Introduction

The most stable compound among the manganese phosphates is manganese(III) orthophosphate hydrate. It was synthesized for the first time by Christensen from manganese(III) acetate and phosphoric acid and also by the oxidation of manganese(II) nitrate by nitric acid in the presence of phosphoric acid.

There are several reports about the hydration of manganese(III) phosphate, MnPO₄·xH₂O. Goloschapov and Martinenko formulated this compound with 1.5 water molecules per formula, and this was later corroborated by Narita and Okabe, using thermal decomposition on this phosphate, obtained 1.13 water molecules per formula, but Cudennec et al. established that the number of water molecules in this compound could vary from 1 to 1.7 without appreciably modifying the X-ray diffraction pattern.

The structure of manganese(III) phosphate was resolved by Lightfoot et al. using synchrotron X-ray powder diffraction. This compound crystallizes in the monoclinic space group, C2/c, and the lattice parameters are a = 6.912 Å, b = 7.470 Å, c = 7.357 Å, β = 112.3°, and γ = 4. Assuming one water molecule per formula, the structure consists of axially distorted MnO₆ octahedra linked by the water molecule oxygen atom at a common vertex to form zigzag Mn-O-Mn chains. These chains are interconnected by PO₄ tetrahedra to form a continuous three-dimensional network with small channels running parallel to the c axis, into which the hydrogen atoms of the water molecules would be situated.

As the literature contains no detailed spectroscopic characterization of this compound, this present work used thermal analysis and infrared and diffuse-reflectance spectra to analyze MnPO₄·H₂O to seek information about its crystal structure and particularity to determine the nature of the water.

Experimental Section

Manganese phosphate(III) hydrate was prepared by reacting 20 g of activated manganese dioxide with 31.3 g of pure solid phosphoric acid (P₂O₅ ratio 3:2). The solids were triturated and mixed, and the mixture was then placed in a crucible and heated in an oven at 150 °C for 1 day. All the reactants were of reagent grade. The highly reactive activated manganese dioxide was synthesized according to Heiba et al. After heating, the grey-green solid product was washed thoroughly with deionized water and then air-dried.

The chemical composition was determined by dissolving the solid in boiling concentrated hydrochloric acid. Under these conditions, the reduction of manganese(III) to manganese(II) and the consequent oxidation of chloride to chlorine resulted in the dissolution of the solid. Phosphorus content was determined by colorimetric analysis of the molybdenum complex. Manganese content was determined by atomic absorption spectrophotometry. Water content was measured by heating at 600 °C and took into account that the complete weight loss is due not only to the loss of water but also to the release of oxygen when manganese(III) is reduced to manganese(II). The results of the chemical analysis of the compound synthesized are compared with the calculated data.

Calculated mass % for MnPO₄·1.3H₂O: Mn₂O₃, 45.6; P₂O₅, 40.9; H₂O, 13.5. Found mass %: Mn₂O₃, 44.5; P₂O₅, 39.7; H₂O, 13.7.

Thermal analysis (TGA and DTA) was carried out in air on a Rigaku Thermoflex apparatus at a heating rate of 10 K·min⁻¹ with calcined Al₂O₃ as the standard reference. X-ray powder diffraction patterns were obtained with a Siemens D-501 automated diffractometer using graphite-monochromated Cu Kα radiation. Infrared spectra were recorded on a Perkin-Elmer 883 spectrometer in a spectral range of 4000–200 cm⁻¹ using either a dry KBr pellet containing 2% of the sample or an air-dried deposit of a 0.1% aqueous suspension onto a CaF₂ crystal, which is transparent to infrared radiation within the range 4000–1100 cm⁻¹. The diffuse-reflectance spectra (UV–vis–near-IR) were obtained on a Shimadzu UV-3100 spectrophotometer using an integrating sphere and BaSO₄ as the reference blank.

Results and Discussion

From its X-ray powder diffraction pattern, this compound is identical with the orthophosphate described earlier as MnPO₄·1.5H₂O and reformulated as MnPO₄·H₂O. The TGA–DTA curves for MnPO₄ hydrate are shown in Figure 1. The DTA curve shows three endothermic effects centered at 300, 383, and 478 °C. The small first endothermic effect is associated with a loss of weight that corresponds to ≈0.2–0.3 water molecule; the second is due to the reduction of manganese(III) to manganese(II) and the consequent release of oxygen; the third is associated with the weight loss that corresponds to ≈1 water molecule. The overall reaction is

$$2\text{MnPO}_4\cdot1.3\text{H}_2\text{O} \rightarrow \text{Mn}_2\text{P}_2\text{O}_7 + 2.6\text{H}_2\text{O} + 0.5\text{O}_2$$

The formal appearance of the curve is essentially analogous to that published by Narita and Okabe, although the quantity of water found by these investigators is slightly less. The manganese(II) pyrophosphate was identified by its powder diffraction pattern.

Unusual for a compound containing water of hydration is the observation that no weight loss was observed until 270 °C. The behavior is, perhaps, more appropriate for a hydrogen phosphate rather than a hydrate because the loss of the water molecule, between 450 and 500 °C, suggests dehydration rather than dehydroxylation. Dehydroxylation could be explained if the water molecules were dissociated, the chemical formula would then be Mn(OH)(HPO₄)·0.3H₂O. In this case, the first endotherm would be due to the loss of 0.3 water molecule that was strongly retained.

(1) Christensen, O. T. J. Prakt. Chem. 1883, 28, 1.
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Figure 1. Thermal analysis (TGA and DTA) of manganese(III) phosphate hydrate.

Figure 2. Infrared spectrum of manganese(III) phosphate hydrate.

within the structure, and the third, to dehydroxylation.

Several preparation methods of manganese(III) phosphate hydrate have been tested; the water content was determined, and the values range between 1.2 and 1.4 water molecules per unit formula of manganese phosphate.

The IR spectrum of the sample (Figure 2) confirmed this reformulation. Three bands appear in the region of hydroxyl stretching. The main absorption band centered at 3110 cm⁻¹ is typical of the hydrogen phosphates and has been attributed to the

Figure 3. Infrared spectra: CaF₂ crystal (a); MnPO₄·1.3H₂O at room temperature (b), 200 °C (c), 300 °C (d), 400 °C (e), and 500 °C (f).

PO–H stretching.¹¹ The other bands situated at 3300 and 2895 cm⁻¹ appear as shoulders: The first band is assigned to υ(HO–H) when the water interacts strongly through the hydrogen bonds. The second band can be assigned to either υ(MnO–H) or υ(H₃O⁺), or both.¹²

The absorption band involving the triply degenerate asymmetric stretching vibrations of the isolated PO₄ tetrahedra is split into two bands, a doubly degenerated band at 1058 cm⁻¹ and a non-degenerated band at 1020 cm⁻¹. The bands centered at 871 and 666 cm⁻¹ were assigned to the υ(P–OH) stretching and the δ-(Mn–O–H) bending, respectively, due to the fact that they disappear in the heating process when the compound changes to anhydrous manganese(II) pyrophosphate; they are consistent with the different assignments for hydrogen phosphates given by Farmer.¹³ The bands at 610, 544, and 412 cm⁻¹ were assigned to δ(P–O–Mn), υ₄(PO₄), and υ(Mn–OP), respectively, according to the literature.¹¹,¹³ Below 400 cm⁻¹, the observed bands involve strong couplings between the different bending vibrations.

No definite band can be seen in the H–O–H bending region around 1600 cm⁻¹. Similar behavior has been observed for other

Scheme I. Mechanism of the Water Molecule Dissociation


phosphates of tervalent metals (AlPO4·2H2O and FePO4·2H2O), and this feature can be attributed to the presence of "water of crystallization" as H3O+ and OH-.

To avoid the possible interference from water, which sometimes accompanies KBr, an IR spectrum of manganese(III) phosphate hydrate was obtained from an air-dried aqueous deposit on a crystal of CaF2 (Figure 3). The water bending vibration δ(H–O–H) appears at 1640 cm⁻¹ as a very weak satellite band, and another, more conspicuous band can be observed at 1715 cm⁻¹, which is attributed to the deformation vibration of the species H2O+.

There is no spectroscopic evidence of the chemical entity H2O, except for the very weak band at 1640 cm⁻¹, and assuming that the band at 1715 cm⁻¹ is much stronger, the limit formula could be established as Mn(0H)4[(H3O)O8(P04)10(HPO4)17].

A small band of intensity similar to that at 1715 cm⁻¹ can be seen at 1495 cm⁻¹; its assignment is difficult, because it is situated within the zone of the ν4 vibration of the NH4+ ion, and careful experiments rule out the possibility that the sample was contaminated by this compound. It could be attributed to the combination vibration of the ν1 + ν4 modes of the PO4 group at 1080 and 580 cm⁻¹, but perhaps it would be more correct to associate it with the in-plane deformation of the O–H–O group, δ(O–H–O), shown in Scheme I. This assignment implies that there is an interaction between the OH group of the manganese octahedron vertex and the apical oxygen of the PO4 group. This is consistent with the fact that this band persists at temperatures as high as 300 °C (Figure 3d) and only decreases in intensity as the structural water is leaving (400 °C, Figure 3e) and then disappears like the δ-(H2O+) band at 500 °C (Figure 3f).

The literature concerning dissociation of water molecules in the first coordination sphere of metal cations in phosphates of tervalent metals (AlPO4·2H2O and FePO4·2H2O), and this feature can be attributed to the presence of "water of crystallization" as H3O+ and OH-.
A Primary Molybdosulfenamide

Mark E. Noble

Received July 3, 1989

A sulfide bridge of the Mo(V) dimer anion \([\text{Mo}_2(\text{NC}_3\text{H}_2)_2\text{S}_2\text{P}((\text{OC})\text{H}_2)_2\text{S}\text{S}])^{2+}\) reacted with hydroxylamine-G-sulfonic acid to give the primary molybdosulfenamide \([\text{Mo}_2(\text{NC}_3\text{H}_2)_2\text{S}_2\text{P}((\text{OC})\text{H}_2)_2\text{S}\text{S}])^{2+}\). This sulfenamide reacted with acetic anhydride to give the imide \([\text{Mo}_2(\text{NC}_3\text{H}_2)_2\text{S}_2\text{P}((\text{OC})\text{H}_2)_2\text{S}\text{S}])^{2+}\). Treatment of sulfenamide with \((\text{C}_2\text{H}_5\text{O})_2\text{PS}_2\text{H}\) or \(\text{C}_6\text{H}_5\text{SH}\) gave reductive S-N cleavage. The disulfide-bridged complex \([\text{Mo}_2(\text{NC}_3\text{H}_2)_2\text{S}_2\text{P}((\text{OC})\text{H}_2)_2\text{S}\text{S}])^{2+}\) was also prepared.

Introduction

The enzyme nitorgenase catalyzes the reduction of atmospheric dinitrogen to ammonia and has generated tremendous interest in agricultural, biological, genetic, and chemical arenas. Much effort and emphasis have been placed on understanding the chemical structure and mechanism of action at the active binding site, but these yet remain unknown. The binding site is believed to be a Mo-Fe-S cluster, of which there are two per protein.

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