Characterization of Manganese(III) Orthophosphate Hydrate

Miguel A. G. Aranda and Sebastian Bruque*

From the IR spectra and the TGA–DTA curves of the manganese(III) phosphate hydrate $MnPO_4\cdot1.3H_2O$, 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 $Mn(OH)(HPO_4)\cdot0.3H_2O$, 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,[6] the McClure parameters were calculated.

Introduction

The most stable compound among the manganese posphates is manganese(III) orthophosphate hydrate. It was synthesized for the first time by Christensen[1] 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, $MnPO_4\cdot xH_2O$. Goloschapov and Martinenko[2] formulated this compound with 1.5 water molecules per formula, and this was later corroborated.[3–5] Narita and Okabe,[6] using thermal decomposition on this phosphate, obtained 1.13 water molecules per formula, but Cudennec et al.[7] 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.,[8] 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, $\beta = 112.3°$, and $Z = 4$. Assuming one water molecule per formula, the structure consists of axially distorted MnO_6 octahedra linked by the water molecule oxygen atom at a common vertex to form zigzag Mn–O–Mn chains. These chains are interconnected by PO_4 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 $MnPO_4\cdot H_2O$ to seek information about its crystal structure and particulary 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 (P:Mn ratio 3:2). The solids were triturated and mixed, and the mixture was then placed in a crucible and heated in a 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.[9] After heating, the gray-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 molybdophosphate 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 $MnPO_4\cdot3H_2O$: Mn_2O_3, 45.6; P_2O_5, 40.9; H_2O, 13.5. Found mass %: Mn_2O_3, 44.5; P_2O_5, 39.7; H_2O, 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 Al_2O_3 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 CaF_2 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 $BaSO_4$ as the reference blank.

Results and Discussion

From its X-ray powder diffraction pattern, this compound is identical with the orthophosphate described earlier[2] as $MnPO_4\cdot1.5H_2O$ and reformulated[8] as $MnPO_4\cdot H_2O$.

The TGA–DTA curves for $MnPO_4$ 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

$$2MnPO_4\cdot1.3H_2O \rightarrow Mn_2P_2O_7 + 2.6H_2O + 0.5O_2$$
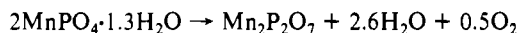
The formal appearance of the curve is essentially analogous to that published by Narita and Okabe,[6] although the quantity of water found by these investigators is slightly less. The manganese(II) pyrophosphate was identified by its powder diffraction pattern.[10]

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 dehydroxylation rather than dehydration. Dehydroxylation could be explained if the water molecules were dissociated, the chemical formula would then be $Mn(OH)(HPO_4)\cdot0.3H_2O$. In this case, the first endotherm would be due to the loss of 0.3 water molecule that was strongly retained

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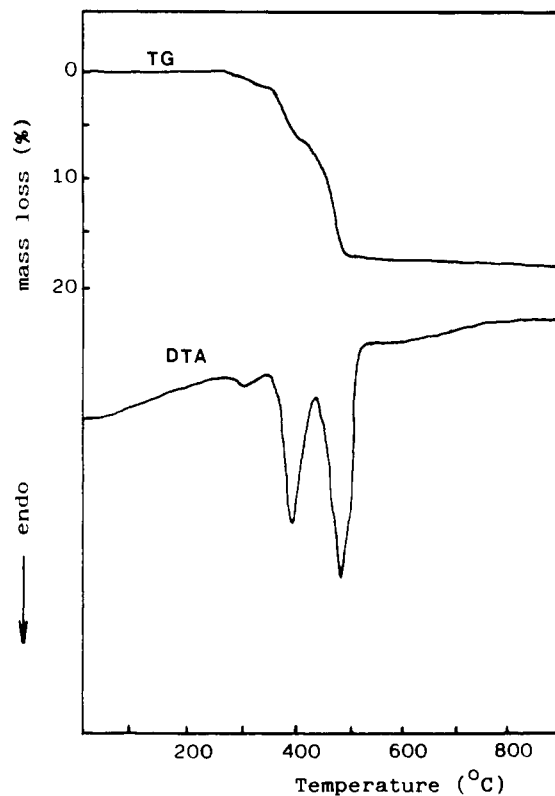
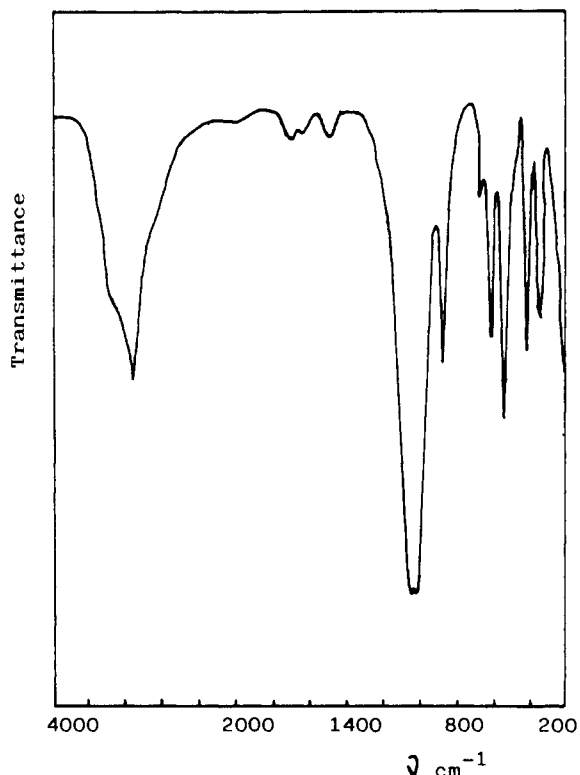**Figure 1.** Thermal analysis (TGA and DTA) of manganese(III) phosphate hydrate.

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

Figure 3. Infrared spectra: CaF_2 crystal (a); $MnPO_4 \cdot 1.3H_2O$ at room temperature (b), 200 °C (c), 300 °C (d), 400 °C (e), and 500 °C (f).

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
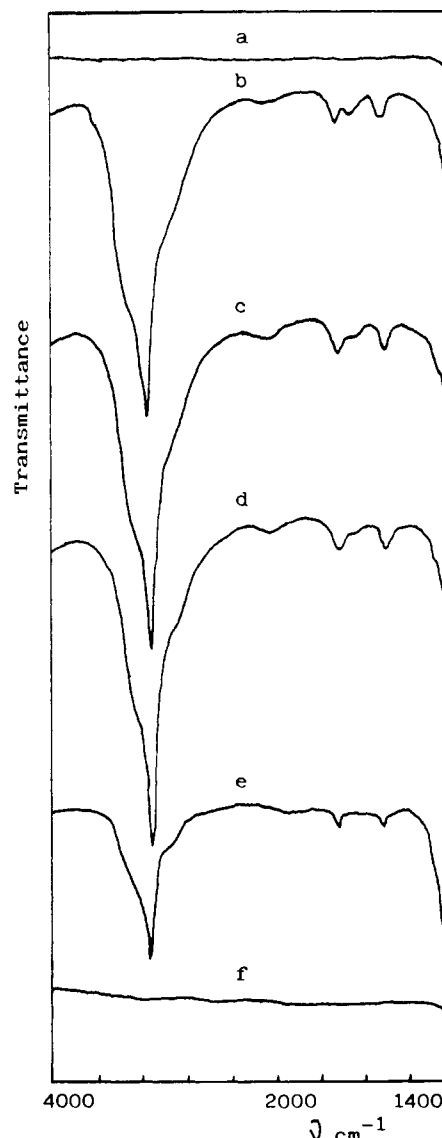
PO–H stretching.[11] The other bands situated at 3300 and 2895 cm^{-1} appear as shoulders: The first band is assigned to ν(HO–H) when the water interacts strongly through the hydrogen bonds. The second band can be assigned to either ν(MnO–H) or ν(H$_3$O$^+$), or both.[12]

The absorption band involving the triply degenerate asymmetric stretching vibrations of the isolated PO$_4$ 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 ν(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), ν_4(PO$_4$), and ν(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

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Scheme I. Mechanism of the Water Molecule Dissociation
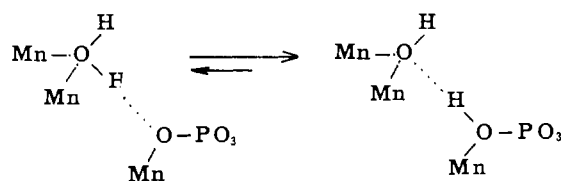
phosphates of tervalent metals ($AlPO_4 \cdot 2H_2O$ and $FePO_4 \cdot 2H_2O$), and this feature can be attributed to the presence of "water of crystallization" as H_3O^+ and OH^-.[14]

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 CaF_2 (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 H_3O^+.[12]

There is no spectroscopic evidence of the chemical entity H_2O, 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 $Mn(OH)[(H_3O)_{0.3}(PO_4)_{0.3}(HPO_4)_{0.7}]$.

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 ν_4 vibration of the NH_4^+ 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 $\nu_3 + \nu_4$ modes of the PO_4 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 PO_4 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-(H_3O^+) band at 500 °C (Figure 3f).

The literature concerning dissociation of water molecules in the first coordination sphere of metal cations in phosphates of transition metals contains precedents[16,17] for the situation described here. For example, Deulin et al.,[16] using the IR spectrum of $NbOPO_4 \cdot 3.25H_2O$, reformulated this compound as $NbO(OH)(HPO_4) \cdot 2.25H_2O$. In the present case, the situation is similar, but moreover the residual water (0.2–0.3 molecule per formula) must be strongly retained and is probably dissociated because it is lost at a high temperature (300 °C); and in addition, no definite H–O–H bending vibration can be detected.

The dissociation of the water molecule (Scheme I) would be consistent with the structure proposed.[8] In this case, however, the MnO_6 octahedra would be joined by the oxygen of the hydroxyl group, instead of the oxygen of a water molecule, to create Mn–O–Mn chains with a μ-hydroxo rather than μ-aquo bridge.

To determine the acidity of $Mn(OH)(HPO_4) \cdot 0.3H_2O$ and the possible ion-exchange capacity of its hydrogen phosphate group, manganese(III) phosphate hydrate was treated with concentrated ammonia fumes. It was observed that, instead of a simple protonation of the ammonia, a chemical reaction occurred in which the manganese(III) phosphate disproportionated to the ammonium manganese(II) phosphate and the manganese(IV) oxide. Figure 4 shows the diffraction patterns of the original compound and the products obtained by reaction with ammonia for periods of 1 and
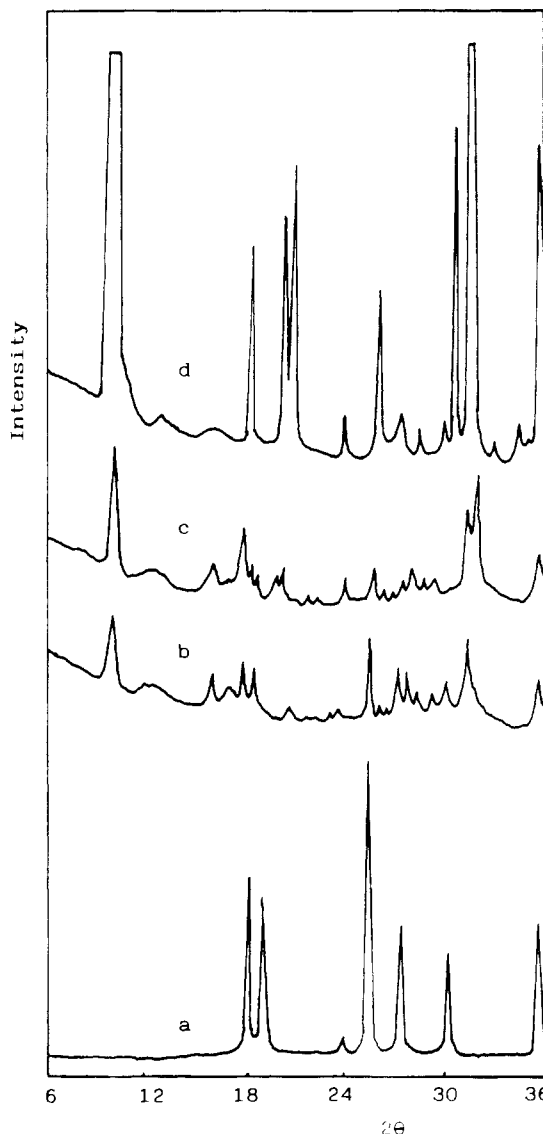
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Figure 4. X-ray diffraction patterns: $MnPO_4 \cdot 1.3H_2O$ (a), treated with NH_3 for 1 week (b) and 3 weeks (c); $MnNH_4PO_4 \cdot H_2O$ (d).

3 weeks. The X-ray powder diffraction pattern $MnNH_4PO_4 \cdot H_2O$, synthesized according to Fraissard and Etienne,[18] is shown at the top. The presence of amorphous manganese dioxide was deduced from the blackish color of the final product and from the its capacity to oxidize chloride at room temperature (this was revealed by the flourescein method).

The acidity of manganese(III) phosphate hydrate was confirmed by treating the sample with benzyl alcohol in a cyclohexane reflux for 6 h: the Mn:alcohol ratio was 1:6. The reaction products were identified by their mass spectra, after separation by gas chromatography. Selectivity was low, but electrophilic reactions such as alcohol condensation and electrophilic attack on the aromatic ring predominate. Of course, for these reactions to occur, there must be acid centers in the original phosphate; these acid centers would be produced by the dissociation of the water molecules, which yields hydrogen phosphate groups.

For testing the exchangeability of the proton in the manganese(III) phosphate hydrate, a solid-state reaction of this compound has been carried out with $LiNO_3$, and a new lithium manganese(III) phosphate has been obtained. This ion-exchange reaction and the possible ionic conductivity will be explained in a forthcoming paper.

Because the crystal structure of this compound showed MnO_6 octahedra highly distorted, it is expected that a Jahn–Teller effect
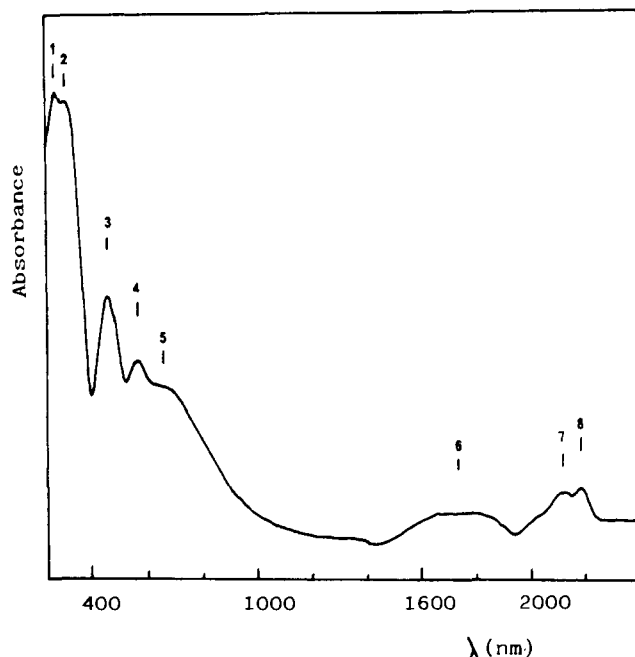
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Figure 5. Diffuse-reflectance spectrum of $MnPO_4 \cdot 1.3H_2O$.

Table I. Diffuse-Reflectance Data for $MnPO_4 \cdot 1.3H_2O$

| band | absorption | | assignment |
	nm	cm^{-1}	
1	255	39 210	charge transfer
2	295	33 900	charge transfer
3	455	21 980	$^5B_{1g} \rightarrow {}^5E_g$
4	565	17 700	$^5B_{1g} \rightarrow {}^5B_{2g}$
5	665	15 040	$^5B_{1g} \rightarrow {}^5A_{1g}$
6	1600–1850	6250–5400	$2\nu(OH)^a$
7	2080	4810	$\nu(OH) + \delta(H_3O^+)$
8	2180	4590	$\nu(OH) + \delta(OHO)$

^{a} Set of bands due to combination and overtones of OH stretching vibrations.

would be seen in its electronic reflectance spectrum. Mn(III) is a d^4 ion and in an octahedral environment one would expect only one absorbance band due to the $^5E_g \rightarrow {}^5T_{2g}$ transition, but in this case, the diffuse-reflectance spectrum (Figure 5) in the UV–vis region is formed by a set of five bands. Two bands near 255 and 295 nm (Table I) are too strong to be d–d transitions, and lying in the ultraviolet, they are assigned as oxygen to Mn(III) charge-transfer bands. The appearance of three bands in the visible region can only be explained by the presence of a strong Jahn–Teller effect. Table I lists the absorption maxima values and their assignments. The Dq parameter for this compound, read directly from the spectrum, has the value 1770 cm^{-1} because $10Dq$ coincides with the fourth transition energy $^5B_{1g} \rightarrow {}^5B_{2g}$. Analogous values are found for other compounds containing Mn(III), for example, 1790 cm^{-1} for Mn(acac)$_3$, 1780 cm^{-1} for [MnF$_6$]$^{3-}$, and 1667 cm^{-1} for Mn(DMSO)$_6{}^{3+}$.[19]

The ground-state splitting (GSS) coincides with the fifth band, and the excited-state splitting (ESS) is the difference between the third and the fourth bands. Thus, the GSS assumes a value of 15 040 cm^{-1}, and the ESS, a value of 4280 cm^{-1}; both these values are of the same order but slightly higher than those found in the literature.[19,20] The assignments lead to fairly large values of McClure[21] parameters, $d\sigma = -5640$ cm^{-1} and $d\pi = -2140$ cm^{-1}. These are consistent with an elongated tetragonal distortion in which the oxygen to manganese π bonding is important. Definitively, the well-resolved splitting of the $^5T_{2g}$ state and the high values of Dq, $d\sigma$, and $d\pi$ picture of Mn(III) environment of tetragonal distorted-octahedral symmetry with a strong degree of covalence in the Mn–O bonding.

On the other hand, the diffuse-reflectance spectrum in the near-infrared region shows two sets of bands: (i) a very wide band (1550–1850 nm) due to the overtones and combinations of the different OH stretchings (ν(PO–H), ν(O–H), ν(MnO–H)) and (ii) two partially overlapping bands centered at 2080 and 2180 nm, which correspond to the ν(PO–H) + δ(H$_3$O$^+$) and ν(PO–H) + δ(OHO) combination vibrations, respectively.

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Contribution from the Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

A Primary Molybdosulfenamide[1]

Mark E. Noble

A sulfide bridge of the Mo(V) dimer anion [Mo$_2$(NC$_7$H$_7$)$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_2$(μ-S)$_2$(μ-O$_2$CCH$_3$)]$^-$ reacted with hydroxylamine-O-sulfonic acid to give the primary molybdosulfenamide [Mo$_2$(NC$_7$H$_7$)$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_2$(μ-S)(μ-O$_2$CCH$_3$)(μ-SNH$_2$)]. This sulfenamide reacted with acetic anhydride to give the imide [Mo$_2$(NC$_7$H$_7$)$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_2$(μ-S)(μ-O$_2$CCH$_3$)(μ-SNHCOCH$_3$)]. Treatment of sulfenamide with (C$_2$H$_5$O)$_2$PS$_2$H or C$_6$H$_5$SH gave reductive S–N cleavage. The disulfide-bridged complex [Mo$_2$(NC$_7$H$_7$)$_2$(S$_2$P(OC$_2$H$_5$)$_2$)$_2$(μ-S)(μ-O$_2$CCH$_3$)(μ-S$_2$PS(OC$_2$H$_5$)$_2$)] was also prepared.

Introduction

The enzyme nitrogenase catalyzes the reduction of atmospheric dinitrogen to ammonia and has generated tremendous interest in agricultural, biological, genetic, and chemical arenas.[2–4] 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.[5–7]

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