

Articles

Na₄Mn_{0.5}P_{0.5}O₅: Synthesis of a Novel Mixed-Metal Manganese(VII)/Phosphorus(V) Oxide via Hydroxide Flux

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Received June 25, 1996[⊗]

Vibrant blue crystals of Na₄Mn_{0.5}P_{0.5}O₅ were synthesized via a sodium hydroxide flux. The X-ray structural analysis showed that this sodium manganese(VII) phosphorous oxide crystallizes in an orthorhombic lattice with $a = 8.967(3)$ Å, $b = 7.291(3)$ Å, $c = 8.090(3)$ Å: $Pnma$ (No. 62); $Z = 4$. The manganese and phosphorus cations equally share one crystallographic site and are tetrahedrally coordinated. The (Mn,P)O₄ tetrahedra are held together by sodium cations via Na–O bonds forming an ionic solid, [Na₄O]²⁺[(Mn_{0.5}P_{0.5})O₄]²⁻. The synthesis, structure, thermal property and infrared spectroscopy of the title compound are presented in this paper.

Introduction

Although many low and intermediate oxidation state transition metal compounds are known, high oxidation state compounds, especially VI and VII, are rare. Thus, the effect that these high oxidation state transition metals will have on the structure and bonding of new transition metal compounds has not been thoroughly explored. Additionally, the redox chemistry associated with the instability of high valence metals render them an interesting topic for study.

In an extension our current research into transition metal phosphates and silicates,^{1,2} the Na–Mn–P–O system has been targeted in order to explore the chemistry of a high oxidation state compound. Manganese was chosen because of its multiple oxidation states. Several manganese phosphates of lower oxidation states, Mn(II)^{2,3} and Mn(III),⁴ are already known. No high oxidation states, Mn⁶⁺ or Mn⁷⁺, have been reported in

phosphate, silicate, and related compound families, but are commonly seen in the ionic oxides, such as K₂MnO₄ and KMnO₄, respectively.⁵ High valence states have been shown to be quite stable in basic medium; thus, the sodium hydroxide flux was employed to facilitate the compound formation and crystal growth in our exploratory synthesis. Hydroxide flux, in fact, has been successful in synthesizing high oxidation state Cu(III)⁶ and Bi(V)⁷ compounds. A novel oxide, Na₄Mn_{0.5}P_{0.5}O₅, was discovered during the search. This compound is considered saltlike because of its ionic bonding and extremely hygroscopic nature. In this paper, the infrared spectroscopy, thermal analysis, and chemical reactivity of the title compound are briefly discussed.

Experimental Section

Synthesis. Single crystals of Na₄Mn_{0.5}P_{0.5}O₅ were grown by a two-step process. Initially, Mn(PO₃)₂ was prepared as a precursor by calcining a stoichiometric mixture of (NH₄)₂HPO₄ (Aldrich, 98+%) and MnO (Alfa/Aesar, 99.5%) in air at 400 °C. Four millimoles of this manganese phosphate was ground with 1 mmol of Na₄P₂O₇·10H₂O (Mallinckrodt, 99.49%) and 20 mmol of NaOH (EM Science, 97%). This reaction mixture was placed in an alumina crucible and heated to 600 °C over 2 h, held at 600 °C for 24 h, and then cooled over 3 h to 300 °C. The crucible was then removed and placed in a dry nitrogen atmosphere, in which all manipulations took place. The bright blue crystals formed a thick layer on the surface of the solidified

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

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Table 1. Crystallographic Data for Na₄Mn_{0.5}P_{0.5}O₅

chem formula	Na ₄ Mn _{0.5} P _{0.5} O ₅	fw	214.91
<i>a</i> , Å	8.967 (3)	space group	<i>Pnma</i> (No. 62)
<i>b</i> , Å	7.291 (3)	<i>T</i> , °C	23
<i>c</i> , Å	8.090 (3)	<i>λ</i> , Å	0.710 69
<i>V</i> , Å ³	528.9 (3)	ρ_{calcd} , g cm ⁻³	2.699
<i>Z</i>	4	linear abs coeff, cm ⁻¹	17.065
<i>R^a</i>	0.033	<i>R_w^b</i>	0.047

$${}^a R = \frac{\sum [|F_o| - |F_c|]}{\sum |F_o|}, {}^b R_w = \frac{[\sum w(|F_o| - |F_c|)]^2}{\sum w|F_o|^2}^{1/2}.$$

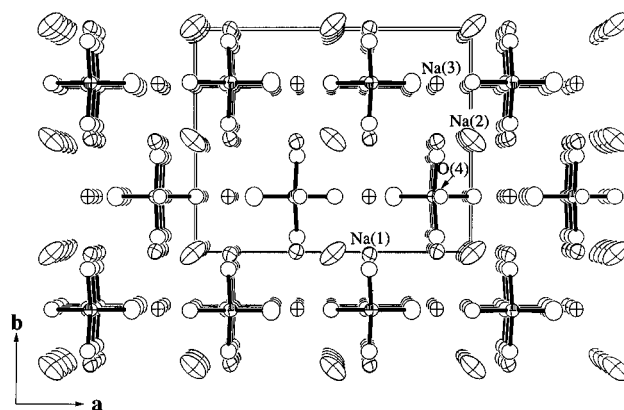
Table 2. Positional and Thermal Parameters^a for Na₄Mn_{0.5}P_{0.5}O₅

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i> , Å ²
Mn ^b	0.36332(4)	1/4	0.35124(5)	1.04(2)
P ^b	0.3633	1/4	0.3512	1.0
Na(1)	0.36932(7)	0.0081(1)	0.65139(8)	1.52(3)
Na(2)	0	0	1/2	2.63(5)
Na(3)	0.12769(9)	1/4	0.7663(1)	1.35(4)
O(1)	0.2179(2)	1/4	0.4631(2)	1.86(7)
O(2)	0.0064(2)	1/4	0.0279(2)	1.32(7)
O(3)	0.3715(1)	0.0707(2)	0.2395(1)	1.46(5)
O(4)	0.3833(2)	1/4	0.8508(2)	1.16(6)

^a Equivalent isotropic thermal parameters defined as $B_{\text{eq}} = (8\pi^2/3)$ trace *U*. ^b The occupancy refinement is based on a fixed value of equal amount of Mn and P.

melt and were isolated mechanically. Qualitative analysis by an energy dispersive spectroscopy using a Cameca SX-50 was performed and showed all three cationic elements.

Structure Determination. A rectangular column crystal (0.25 × 0.50 × 0.20 mm) was mounted and sealed in a 0.3 mm glass capillary tube for single-crystal X-ray diffraction study. The diffraction data were collected at room temperature on a Rigaku AFC5S four-circle diffractometer. Crystallographic data for the title compound are summarized in Table 1. The unit cell parameters and the orientation matrix for data collection were determined by a least-squares fit of 25 peak maxima with $7^\circ < 2\theta < 30^\circ$. There was no detectable decay during data collection, according to the intensities of three standard reflections (1, -1, 0; -1, -1, 0; 1, -2, 0) which were measured every 150 reflections. A total of 1533 reflections ($2\theta_{\text{max}} = 55^\circ$) were collected of which 1153 unique reflections with $I > 3\sigma(I)$ were used for the structure solution and refinement.⁸ Data reduction, intensity analysis, and extinction conditions were determined with the program PROCESS. Lorentz-polarization and empirical absorption corrections based on three computer chosen azimuthal scans ($2\theta = 11.19, 22.49, 29.05^\circ$) were applied to the intensity data. On the basis of extinction conditions and correct structure solution, space group *Pnma* (No. 62) was chosen. The atomic coordinates of Na and Mn were determined using the SHELXS-86 program,⁹ and those of the oxygen atoms were resolved using a difference Fourier map. The refined occupancy of the Mn cation suggested a possible nonstoichiometry due to a cation mixing; the final structure solution was then refined on the basis of an equally populated Mn/P site. (The unconstrained refinement resulted in a phosphorus rich structure solution, which is intuitively impossible based upon the charge neutrality.) The structural and thermal parameters were refined by the full-matrix least-squares method to $R = 0.033$, $R_w = 0.047$, and $\text{GOF} = 2.24$. Table 2 lists the final positional and thermal parameters.

**Figure 1.** Extended structure of Na₄Mn_{0.5}P_{0.5}O₅ viewed along the *c* axis. The unit cell is shown by the box. The (Mn,P)O₄ tetrahedra are outlined by solid lines while the Na-O bonds are omitted for clarity. The anisotropic atoms are presented at 90% probability.

Thermal Analysis. Differential thermal analysis (DTA) was performed on a DuPont 9900 thermal analysis system. The analysis, carried out using single crystals in a fused quartz ampule, was performed from 25 to 425 °C with a heating rate of 10 °C/min. Al₂O₃ powder was employed in the sealed reference tube. The results show that the title compound melts congruently, and the melting point is ca. 290 °C.

Infrared Spectroscopy. The infrared (IR) absorption spectrum of the title compound was studied in the range of 1600–400 cm⁻¹ and recorded on a Perkin-Elmer 1600 Series FTIR spectrometer with 16 scans and 2.0 cm⁻¹ increments. Ground single crystals which were pressed into discs with KBr were used for this study. The O-P-O bending and P-O stretching vibrational frequencies associated with the PO₄ group are seen in multiple bands in the 450–600 and 950–1100 cm⁻¹ ranges, respectively. Additionally, several bands corresponding to the vibrational frequencies of the [MnO₄]⁻ tetrahedra can be seen in the 750–850 cm⁻¹ range.¹⁰

Results and Discussion

Figure 1¹¹ shows that this structure contains the (Mn,P)O₄ tetrahedral unit which is statistically composed of half MnO₄ and half PO₄. The (Mn,P)O₄ tetrahedra are held together by the Na-O bonds (omitted for clarity). To balance the charge in the empirical formula, Mn(VII) and P(V) cations must be present in equal amounts and the structure solution showed that these cations share the same crystallographic site. This site mixing results in a combined oxidation state of 6+, the appropriate number to balance the charge. The (Mn,P)-O bond distances, 1.59–1.61 Å (Table 3), in the tetrahedra are elongated compared to 1.55 Å, the sum of the Shannon crystal radii¹² for 4-coordinated P⁵⁺ (0.31 Å) and O²⁻ (1.24 Å), and are shorter than 1.63 Å, the sum for Mn⁷⁺ (0.39 Å) and O²⁻. This intermediate distance range is consistent with the statistical mixing of the two different sized cations.

The bond valence sum (BVS) analysis¹³ also supports the mixed-cation Mn(VII)/P(V) model. First of all, the BVS calculations suggest the 1+ oxidation state for the sodium cations: 0.96 for Na(1), 1.06 for Na(2), and 1.20 for Na(3). A

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Table 3. Important Bond Distances (Å) and Angles (deg) for Na₄Mn_{0.5}P_{0.5}O₅

(Mn,P)O ₄ Tetrahedra			
(Mn,P) ^a —O(1) ^a	1.587(2)	(Mn,P) ^a —O(3) ^{a,c}	1.591(1) (2×)
(Mn,P) ^a —O(2) ^b	1.613(2)		
O(1) ^a —(Mn,P) ^a —O(2) ^a	107.90(9)	O(2) ^b —(Mn,P) ^a —O(3) ^{a,c}	107.92(5) (2×)
O(1) ^a —(Mn,P) ^a —O(3) ^{a,c}	111.23(5) (2×)	O(3) ^a —(Mn,P) ^a —O(3) ^c	110.48(9)
Na(1)O ₆ Polyhedra			
Na(1) ^a —O(1) ^a	2.697(2)	Na(1) ^a —O(3) ^d	2.346(1)
Na(1) ^a —O(2) ^b	2.593(2)	Na(1) ^a —O(3) ^e	2.552(1)
Na(1) ^a —O(2) ^d	2.405(1)	Na(1) ^a —O(4) ^a	2.393(2)
O(1) ^a —Na(1) ^a —O(2) ^b	58.53(6)	O(2) ^b —Na(1) ^a —O(3) ^e	85.13(5)
O(1) ^a —Na(1) ^a —O(2) ^d	120.70(6)	O(2) ^b —Na(1) ^a —O(4) ^a	81.41(5)
O(1) ^a —Na(1) ^a —O(3) ^d	82.44(5)	O(2) ^d —Na(1) ^a —O(3) ^d	111.18(6)
O(1) ^a —Na(1) ^a —O(3) ^e	143.25(5)	O(2) ^d —Na(1) ^a —O(3) ^e	62.95(5)
O(1) ^a —Na(1) ^a —O(4) ^a	85.70(5)	O(2) ^d —Na(1) ^a —O(4) ^a	146.34(6)
O(2) ^b —Na(1) ^a —O(2) ^d	94.60(3)	O(3) ^d —Na(1) ^a —O(3) ^e	132.70(5)
O(2) ^b —Na(1) ^a —O(3) ^d	140.62(5)	O(3) ^d —Na(1) ^a —O(4) ^a	91.39(5)
O(3) ^e —Na(1) ^a —O(4) ^a	83.40(5)		
Na(2)O ₆ Octahedra			
Na(2) ^a —O(1) ^{a,f}	2.689(1) (2×)	Na(2) ^a —O(3) ^{d,g}	2.312(1) (2×)
Na(2) ^a —O(4) ^{h,i}	2.424(1) (2×)		
O(1) ^a —Na(2) ^a —O(1) ^f	180.0	O(1) ^{a,f} —Na(2) ^a —O(3) ^{d,g}	83.23(5) (2×)
O(1) ^{a,f} —Na(2) ^a —O(3) ^{d,g}	96.77(5) (2×)	O(1) ^{a,f} —Na(2) ^a —O(4) ^{h,i}	81.90(5) (2×)
O(1) ^{a,f} —Na(2) ^a —O(4) ^{h,i}	98.10(5) (2×)	O(3) ^{d,g} —Na(2) ^a —O(3) ^g	180.0
O(3) ^{d,g} —Na(2) ^a —O(4) ^{h,i}	88.02(5) (2×)	O(3) ^{d,g} —Na(2) ^a —O(4) ^{i,h}	91.98(5) (2×)
O(4) ^h —Na(2) ^a —O(4) ⁱ	180.0		
Na(3)O ₆ Octahedra			
Na(3) ^a —O(1) ^a	2.583(2)	Na(3) ^a —O(2) ^j	2.379(2)
Na(3) ^a —O(4) ^a	2.392(2)	Na(3) ^a —O(3) ^{d,k}	2.349(2) (2×)
Na(3) ^a —O(4) ^h	2.387(2)		
O(1) ^a —Na(3) ^a —O(2) ^j	171.05(7)	O(2) ^j —Na(3) ^a —O(4) ^a	86.16(6)
O(1) ^a —Na(3) ^a —O(3) ^{d,k}	84.91(4) (2×)	O(3) ^j —Na(3) ^a —O(3) ^h	169.39(8)
O(2) ^j —Na(3) ^a —O(3) ^{d,k}	94.79(4) (2×)	O(1) ^a —Na(3) ^a —O(4) ^h	84.88(7)
O(3) ^{d,k} —Na(3) ^a —O(4) ^a	91.35(3) (2×)	O(2) ^j —Na(3) ^a —O(4) ^k	100.62(7)
O(3) ^{d,k} —Na(3) ^a —O(4) ^{h,h}	88.05(3) (2×)	O(1) ^a —Na(3) ^a —O(4) ^a	88.34(6)
O(4) ^a —Na(3) ^a —O(4) ^h	173.22(5)		

^a *x*, *y*, *z*. ^b 1/2 + *x*, 1/2 - *y*, 1/2 - *z*. ^c *x*, 1/2 - *y*, *z*. ^d 1/2 - *x*, -*y*, 1/2 + *z*. ^e 1 - *x*, -*y*, 1 - *z*. ^f -*x*, *y* - 1/2, 1 - *z*. ^g *x* - 1/2, *y*, 1/2 - *z*. ^h *x* - 1/2, 1/2 - *y*, 3/2 - *z*. ⁱ 1/2 - *x*, -*y*, *z* - 1/2. ^j *x*, *y*, *z* + 1. ^k 1/2 - *x*, 1/2 + *y*, 1/2 + *z*.

value of 7.43 is calculated for Mn and 4.23 is calculated for P; these values differ slightly from the expected Mn⁷⁺ and P⁵⁺ oxidation states. This deviation is due to the aforementioned compromise between P and Mn as to the bond length, the basis on which the BVS values are calculated, and also to the intrinsic difficulty of achieving accurate values when *r*₀ is calculated using Brown and Altermatt's algorithm.¹⁴

The NaO₆ polyhedra are found in two different geometries. Na(2) forms a nearly perfect octahedral geometry with angles between opposite oxygens atoms of 180.0° and all other angles close to 90°. The bond distances in this octahedron range from 2.31 to 2.69 Å, which are close to 2.42 Å, the sum of the Shannon crystal radii for six-coordinated Na⁺ (1.16 Å) and O²⁻ (1.26 Å). Na(3) adopts a distorted octahedron and has bond distances are in the range 2.35–2.58 Å. Na(1), though, shows no regular geometry, but is also six-coordinated with bond distances ranging from 2.35 to 2.70 Å.

The extended framework can be viewed as formed by the electrostatic interaction between [Na₄O]²⁺ and [(Mn_{0.5}P_{0.5})O₄]²⁻ ion pairs. The Na₄O unit forms a P₄O₆-like Na–O framework, shown in Figure 2, which “captures” the (Mn,P)O₄ tetrahedra. The framework oxygen atom, O(4), which does not have any connection to the (Mn,P)O₄ tetrahedra, bonds to all three sodium cations in a distorted ONa₆ octahedral geometry. The Na–O

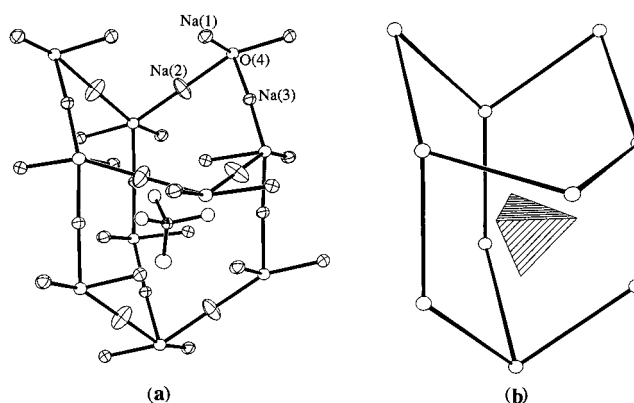


Figure 2. (a) Drawing of the [Na₄O]²⁺ framework with the (Mn,P)O₄ unit captured inside. The cross-hatched circles are Na, the open circles are O(4) and the shaded circle represents (Mn,P). The sodium atoms are all bonded to two oxygens in the extended Na₄O framework; the Na(1) is shown bonded to a single oxygen for clarity. (b) A simplified structure with all the sodiums omitted to show the P₄O₆-like cage, inside which a (Mn,P)O₄ tetrahedron is enclosed.

bond distances (2.39–2.42 Å) are on the short end of the above mentioned ranges and the Na–O–Na bond angles are deviated greatly from those expected for an octahedral coordination (75.95–97.54°, 140.03–155.87°). The Mn–O and P–O bonds are thought to be largely covalent forming a bulky composite anion, [(Mn_{0.5}P_{0.5})O₄]²⁻. The interaction between the two counterions via the Na–O connections, including mostly long

(14) The calculated *r*₀(Mn⁷⁺) is 1.83 for the Mn–O bond. This value is considered to be “not as good” as the experimentally determined values according to ref 13.

bonds (2.31–2.70 Å), is presumably ionic. Thus the saltlike formula of [Na₄O]²⁺[(Mn_{0.5}P_{0.5})O₄]²⁻ is proposed, which is consistent with the observed moisture-sensitive property.

The reactivity of the title compound subject to chemical reduction was also investigated. A few crystals of the title compound were dissolved in acetic acid, the only solvent into which it would dissolve. Upon heating, the solution turned from reddish color to brown, which is an indicative of the reductive disproportionation from MnO₄⁻ to MnO₂ in an acidic solution.¹⁵ A small amount of cholesterol was added to the reddish solution. No sign of conversion with respect to oxidation of cholesterol to cholesterone was observed based on TLC plate analysis. Additionally, the crystal surface changed a brown color in air, and the bulk reacts with water to produce a purple solution and a brown precipitate, MnO₂. (The latter is presumably due to

the decomposition product in air.) The purple color is the result of a charge transfer intrinsic to the MnO₄⁻ ion, which was supported by the UV spectroscopy analysis.

Acknowledgment. Support of this work from the National Science Foundation (Grant DMR-9208529) is gratefully acknowledged. Funds for the Rigaku AFC5S diffractometer by the National Science Foundation are acknowledged. A.S.G. thanks the National Science Foundation for the support of undergraduate summer research. The authors are indebted to Mr. M. L. Pierson and Dr. J. C. Stormer, Jr., for microprobe analysis and to Dr. M. Ciufolini and Ms. K. Dilzer for assistance with reactivity tests.

Supporting Information Available: Tables of detailed crystallographic data and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

IC960752N

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