

Rapid communication

Room temperature synthesis and solid-state structure of $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$

J.M. Haag^a, G.C. LeBret^a, D.A. Cleary^{a,*}, B. Twamley^b

^aDepartment of Chemistry, Gonzaga University, 502 East Boone, Spokane, WA 99258-0013, USA

^bUniversity Research Office, University of Idaho, Moscow, ID 83844, USA

Received 3 November 2004; received in revised form 30 November 2004; accepted 2 December 2004

Abstract

The synthesis and crystal structure of $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ are reported. The compound was synthesized from aqueous solutions of nickel chloride and sodium hypodiphosphate at room temperature. The space group is orthorhombic, *Pnmm*. Unit cell dimensions are $a = 11.2418(5)$ Å, $b = 18.5245(8)$ Å, and $c = 7.3188(3)$ Å, $Z = 4$. The product is unstable with respect to dehydration above room temperature.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Metal hypodiphosphate; Room temperature synthesis

1. Introduction

The transition metal hypodithiophosphates, $M_2\text{P}_2\text{S}_6$ (e.g. $M = \text{Mn}$ [1], Fe [1], Co [1], Ni [1], Cd [1], Sn [2]) have received considerable attention because of the interesting structural, chemical, and magnetic behavior demonstrated by this class of compounds [3]. Several reports of the room temperature preparation of transition metal hypodithiophosphates have been published. Bourdon et al. [4] reported the room temperature synthesis of $\text{Sn}_2\text{P}_2\text{S}_6$, with an estimated particle size of ca. 20 nm. Fragnaud et al. [5] reported the synthesis of a highly disordered $\text{Ni}_2\text{P}_2\text{S}_6$. Huang et al. [6] also reported the room temperature synthesis of $\text{Ni}_2\text{P}_2\text{S}_6$, but their product appears to be non-crystalline.

The corresponding hypodiphosphates, $M_2\text{P}_2\text{O}_6$, have received considerably less attention, in spite of their useful properties (e.g. in situ Ni metal deposition) [7]. One reason may be the difficulty in preparing metal hypodiphosphates. In both of these classes of compounds, the phosphorus assumes the unusual oxidation

state of IV and is susceptible to disproportionation (vide infra) [8].

In this communication, we report the synthesis and solid-state structure of high quality crystalline $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ grown from aqueous solution.

2. Experimental section

2.1. Synthesis

Single crystals of $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ were prepared by mixing two aqueous solutions: nickel chloride and sodium hypodiphosphate. The nickel chloride solution was prepared with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.37 g, 9.97 mmol) and deionized (DI) water (10 mL, 17 MΩ) forming a clear green solution. Sodium hypodiphosphate was prepared using a modified procedure reported by Leininger and Chulski [9]. Sodium chlorite (8.19 g, 90.6 mmol) was mixed with DI water (12 mL) for 15 min resulting in a light yellow creamy colored mixture. Red phosphorus (1.84 g, 59.4 mmol) was mixed with DI water (~20 mL) in a separate beaker forming a reddish brown mixture. The sodium chlorite solution was then slowly added to

*Corresponding author. Fax: +1 509 323 5804

E-mail address: cleary@gonzaga.edu (D.A. Cleary).

the red phosphorous mixture. The reaction between the two mixtures was violent and exothermic, resulting in the evolution of a yellow gas and the solvent boiling. The color of the mixture changed from reddish brown to a bright yellow as the sodium chlorite was added. After all of the sodium chlorite was added, the mixture was filtered (medium) yielding a bright yellow solution with a pH near 0. The pH was raised to 10 by the addition of 3 M NaOH(aq). At a pH of ca. 8, crystals of $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ began falling out of solution. After all of the NaOH(aq) was added, the crystals were isolated with a Buchner funnel and allowed to air dry. The crystals were redissolved in $\text{H}_2\text{O}/\text{D}_2\text{O}$ and the resulting solution analyzed using ^{31}P NMR spectroscopy. The solution showed a single ^{31}P resonance peak between 10 and 14.5 ppm (relative to 85% $\text{H}_3\text{PO}_4(\text{aq})$) depending on the pH of the solution [10]. The crystals were also analyzed with thermogravimetric analysis (TGA), which showed a weight loss consistent with the dehydration of ten water molecules per formula unit.

Nickel chloride hexahydrate (99%) and sodium chlorite (80%) were purchased from Aldrich. The amorphous red phosphorous (99%, 100 mesh) was purchased from Alfa Aesar. All reagents were used as received.

$\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ (0.066 g, 0.154 mmol) was dissolved in DI water (20 mL) forming a clear and colorless solution. This solution was poured into a vial containing the NiCl_2 solution. The combined solutions were a slightly lighter green than the initial nickel solution and no visible reaction had occurred. After 3 h, crystals could be seen at the bottom of the vial and below the meniscus. After 24 h, a large quantity of light green $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ crystals were produced and isolated. When the reaction was allowed to proceed for one week, a yield of 60.1% (based on $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$) was realized.

2.2. Single crystal X-ray diffraction

Crystals of compound 1 were removed from the flask, a suitable crystal was selected, attached to a glass fiber and data were collected at 292(2) K using a Bruker/Siemens SMART APEX instrument (MoK α radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3° per frame for 20 s, and a full sphere of data was collected. A total of 2450 frames were collected with a final resolution of 0.77 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART [11] software and refined using SAINTplus [12] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTplus software. Absorption corrections were applied using SADABS [13]. The structure was solved by direct

Table 1
Crystal data and structure refinement for $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$

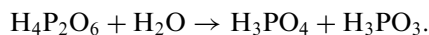
Empirical formula	$\text{H}_{24}\text{Ni}_2\text{O}_{18}\text{P}_2$
Formula weight	491.55
Temperature (K)	292(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pnmm</i>
<i>a</i> (Å)	11.2418(5)
<i>b</i> (Å)	18.5245(8)
<i>c</i> (Å)	7.3188(3)
Volume (Å ³)	1524.13(11)
<i>Z</i>	4
Density calc. (mg/m ³)	2.142
μ (mm ⁻¹)	2.771
Crystal color and habit	Light green needle
Index ranges	$-14 \leq h \leq 14$, $-24 \leq k \leq 24$, $-9 \leq l \leq 9$
Reflns (collected/independent)	22951/1891 ($R_{\text{int}} = 0.0378$)
Data/restraints/parameters	1891/0/117
GOF	1.153
<i>R</i> indices ($I > 2\sigma(I)$)	$R_1 = 0.0358$, $wR_2 = 0.0793$

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

methods and refined by least-squares method on F^2 using the SHELXTL program package [14]. The structure was solved in the space group *Pnmm* (# 58) by analysis of systematic absences. All atoms were refined anisotropically. Hydrogen atoms were located on the difference map and their positions were fixed, in spite of some close intermolecular distances. Hydrogen thermal parameters were refined with a riding model with $U_{\text{iso}} = 1.5U_{\text{eq}}$ of the parent atom. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1 [15].

3. Results and discussion

One reason for the paucity of hypodiphosphate materials is the instability of the $\text{P}_2\text{O}_6^{4-}$ species. Under acidic conditions, it is thermodynamically unstable with respect to disproportionation [8]



Nevertheless, in our experiments, the $\text{P}_2\text{O}_6^{4-}(\text{aq})$ moiety remained intact long enough (several hours) to react with $\text{Ni}^{2+}(\text{aq})$ to produce $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}(\text{s})$. In similar experiments with hypodithiophosphate, $\text{P}_2\text{S}_6^{4-}(\text{aq})$, we have been unable to obtain a crystalline material that can be characterized by single crystal X-ray diffraction.

The structure of $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ is shown in Figs. 1a and b. There is considerable strong hydrogen bonding between the cations and the anions ranging from 2.606(2) Å (O5–H5b...O10) at the closet to 2.837(2) Å (O1–H1a...O11). This links the whole structure into a

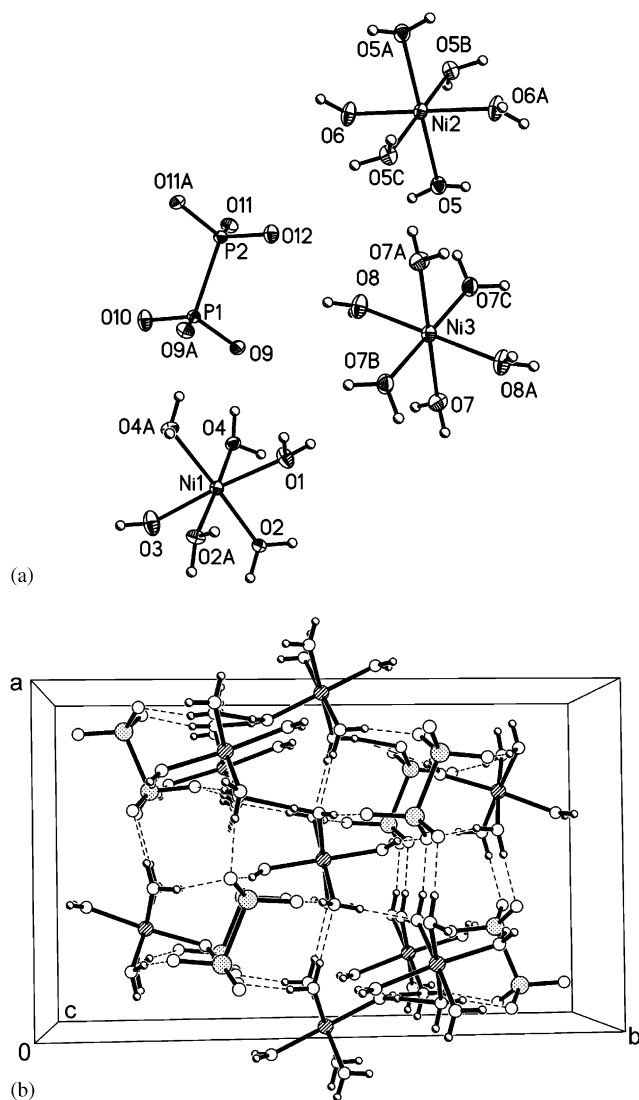


Fig. 1.

Table 2
Selected bond lengths (Å) and angles (deg) for $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$

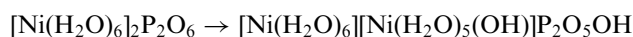
Ni1–O1	2.069(3)	O1–Ni1–O2	92.13(7)
Ni1–O2 ^{+O2i}	2.0532(18)	O1–Ni1–O4	90.41(8)
Ni1–O3	2.095(3)	O2–Ni1–O3	85.02(8)
Ni1–O4 ^{+O4i}	2.0572(18)	O3–Ni1–O4	92.48(8)
Ni2–O5 ^{+O5i, ii, iii}	2.0886(19)	O1–Ni1–O3	175.78(12)
Ni2–O6 ^{+O6ii}	2.013(3)		
Ni3–O7 ^{+O7i, iv}	2.0854(19)	O10–P1–O9 ^{+O9i}	112.39(9)
Ni3–O8 ^{+O8iv}	2.050(3)	O9–P1–O9 ⁱ	111.35(15)
P1–P2	2.1700(13)	O12–P2–O11 ^{+O11i}	111.60(9)
P1–O9 ^{+O9i}	1.5310(19)	O11–P2–O11 ⁱ	112.07(15)
P1–O10	1.516(3)		
P2–O11 ^{+O11i}	1.5371(19)		
P2–O12	1.514(3)		

Symmetry transformations used to generate equivalent atoms: (i) $x, y, -z$; (ii) $-x, y, -z$; (iii) $-x, -y, z$; (iv) $-x + 1, -y, -z$.

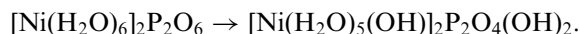
complex 3D network (Fig. 1b). In the asymmetric unit, there are three unique Ni sites and both phosphorus atoms of the $\text{P}_2\text{O}_6^{4-}$ unit are on special positions. The complete coordination around each of these moieties is generated by symmetry (see Fig. 1a). This results in each Ni^{2+} cation being octahedrally coordinated by waters of hydration. There is some distortion of the NiO_6 polyhedra from true octahedra with Ni–O bond lengths ranging from 2.013 to 2.089 Å, and the greatest distortion is seen around Ni2 (Table 2). The anion $\text{P}_2\text{O}_6^{4-}$ is an unusual moiety, and has a P–P distance of 2.1700(13) Å. This is similar to the P–P distances in other hypodiphosphates: $\text{Co}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ (2.179(4) Å) [16], $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ (2.190(2) Å) [17], and $(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_6$ (2.170(3) Å) [18]. This distance is also similar to the P–P distance in hypodithiophosphates, $\text{P}_2\text{S}_6^{4-}$, e.g. $\text{Co}_2\text{P}_2\text{S}_6$, (2.165(3) Å) and $\text{Fe}_2\text{P}_2\text{S}_6$ (2.174(3) Å) [1]. The $\text{P}_2\text{O}_6^{4-}$ moiety has one P–O bond ca. 1.51 Å and two slightly longer P–O bonds ca. 1.53 Å on each phosphorus atom (see Table 2). Similar bond lengths and angles are seen in $\text{Co}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ (av. 1.535 Å) and $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ (av. 1.504 and 1.583 Å for the P–OH bond). In this case the differences in the P–O bond lengths could be attributed to the extensive hydrogen bonding between the water molecules and the $\text{P}_2\text{O}_6^{4-}$ anion. Unlike other hypodiphosphate structures, the $\text{P}_2\text{O}_6^{4-}$ moiety in $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ is not directly bonded to the Ni cation. Hence, the $\text{P}_2\text{O}_6^{4-}$ anion is not required to stretch or compress in order to accommodate the geometry around the Ni atoms. The structure is best considered as an ionic compound consisting of discrete $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ cations and $\text{P}_2\text{O}_6^{4-}$ anions.

Our TGA of $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ is incomplete, but it is clear that the slightest increase in temperature above room temperature causes $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ to dehydrate. Our samples were stored in water at room temperature.

The oxygen–oxygen distances between the waters of hydration and the hypodiphosphate are short enough that the possibility exists that the hydrogen formally assigned to the water is transferred to the highly charged Brønsted–Lowry base, $\text{P}_2\text{O}_6^{4-}$. This would result in a rewriting of the formula such as



or



This internal hydrolysis may be the reason for the lack of a clear loss of 12 waters of hydration upon heating in TGA. In addition, as the temperature of $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ is raised in TGA, the dodecahydrate is not necessarily the appropriate formula to consider for dehydration.

4. Conclusions

We have shown that crystalline $\text{Ni}_2\text{P}_2\text{O}_6 \cdot 12\text{H}_2\text{O}$ can be produced easily and in high yield and that the hypodiphosphate moiety is stable enough to react with simple metal salts. As long as water is present the complex is stable at room temperature. The complex consists of charge separate ions which are stabilized with significant hydrogen bonding. We are trying to extend this study to other transition metal hypodiphosphates which will be reported in the near future.

Acknowledgments

The authors gratefully acknowledge the National Science Foundation (DMR-0102149) for its support of this research. The Bruker (Siemens) SMART CCD diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M.J. Murdock Charitable Trust, Vancouver, WA.

References

- [1] G. Ourvard, R. Brec, J. Rouxel, *Mater. Res. Bull.* 20 (1985) 1181.
- [2] Z. Wang, R.D. Willett, R.A. Laitinen, D.A. Cleary, *Chem. Mater.* 7 (1995) 856.
- [3] R. Brec, *Solid State Ionics* 22 (1986) 3.
- [4] X. Bourdon, E. Prouzet, V.B. Cajipe, *J. Solid State Chem.* 129 (1997) 157.
- [5] P. Fragnaud, E. Prouzet, G. Ouvrard, J.L. Mansot, C. Payen, R. Brec, H. Dexpert, *J. Non-Cryst. Solids* 160 (1993) 1.
- [6] Z.-L. Huang, J.-G. Chen, S.-Y. Mao, J.-T. Zhao, M.-X. Zhan, L.-S. Zheng, *Gaodeng Xuexiao Huaxue Xuebao* 20 (1999) 499.
- [7]
 - (a) R.G. Rozenblyum, A.A. D'yakov, *Zashchita Metall.* 6 (1) (1970) 72;
 - (b) V.K. Gouda, S. Shawki, H. El-Tawil, *Metal Finishing* 70 (5) (1972) 77;
 - (c) P. Cavallotti, G. Salvago, *Electrochim. Metall.* 3 (1) (1968) 23.
- [8] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, UK, 1984, p. 590.
- [9] E. Leininger, T. Chulski, *Inorg. Synth.* 4 (1953) 68.
- [10] N. Yoza, N. Ueda, Nakashima, S. Fresenius, *J. Anal. Chem.* 348 (1994) 633.
- [11] SMART: v.5.626, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, 2002.
- [12] SAINTPlus: v. 6.36a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, 2001.
- [13] SADABS: v.2.01, an empirical absorption correction program, Bruker AXS Inc., Madison, WI, 2001.
- [14] SHELXTL: v. 6.10, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, 2001.
- [15] Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-414634.
- [16] S. Hagen, M. Jansen, *Z. Anorg. Allg. Chem.* 621 (1995) 149.
- [17] R.L. Collin, M. Willis, *Acta Crystallogr. B* 27 (1971) 291.
- [18] A. Wilson, H. McD. McGeachin, *Acta Crystallogr.* 17 (1964) 1352.