

An Ionic Nickel(II) Phosphate with Ethylenediamine: $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$. Hydrothermal Synthesis, Crystal Structure, and Spectroscopic Properties

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An ionic nickel(II) phosphate templated by ethylenediamine, $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$, has been prepared by hydrothermal synthesis and characterized by single-crystal diffraction data and spectroscopic techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.226(1)$, $b = 16.241(2)$, and $c = 14.778(2)$ Å, $\beta = 91.28(1)^\circ$, $V = 1493.9(4)$ Å³, and $Z = 4$. The structure consists of isolated $\text{Ni}(\text{H}_2\text{O})_6$ octahedra and HPO_4 tetrahedra, both of them hydrogen-bonded to ethylenediammonium cations. The compound has been characterized by IR spectroscopy, showing the bands characteristic of the $(\text{HPO}_4)^{2-}$ anions and the ethylenediammonium cation. Diffuse reflectance measurements indicate the presence of octahedrally coordinated Ni(II) ions. The D_q (835 cm^{-1}) and Racah ($B = 900$, $C = 4040\text{ cm}^{-1}$) parameters have been calculated for the Ni(II) ions in octahedral sites. © 2000 Academic Press

Key Words: phosphate; crystal structure; UV-visible spectroscopy.

INTRODUCTION

There has been an enormous growth in the chemical diversity of open-framework inorganic during the past few years (1). Most of these compounds are based on oxygen-containing materials with elements of the main block and transition metals. These materials are of great interest from both the industrial and academic points of view due to their catalytic, adsorbent, and ion-exchange properties (2–4). In this way, phosphates of transition metals with open structures represent an interesting group of materials with potential catalytic applications. It has been recently shown that the incorporation of hydrogen-bonded organic molecules, especially diammonium cations, via hydrothermal synthesis is a very general method for the preparation of a large variety of novel organic–inorganic hybrid materials such as

phosphates, phosphonates, and oxides with a large variety of transition metal ions (5–11).

The first metallophosphates were prepared with vanadium and molybdenum (5, 12). Recently, works dealing with organically templated iron phosphates have evidenced a rich structural chemistry in this system (13–16). In this way, some iron(III) and mixed-valence ($\text{Fe}^{2+}/\text{Fe}^{3+}$) iron phosphates with three-dimensional or layered structures together with isolated single chains are known (13–19). An open-framework cobalt phosphate with ethylenediammonium cations containing a tetrahedrally coordinated cobalt(II) center (20) has been synthesized and studied. Recently, we have prepared a layered Mn(II) phosphate templated by ethylenediamine in which the metallic cation exhibits simultaneously trigonal bipyramid and octahedron coordination polyhedra (21). It can be concluded that the choice of organic guest molecules often has a large influence on the final structure of the material. However, no relationship between the crystal structure of the compound and the nature of the organic molecule has been established. In this work we report on the hydrothermal synthesis, crystal structure, and spectroscopic properties of a nickel(II) phosphate templated by ethylenediammonium cations, $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$. As far as we are aware, only an open-framework nickel(II) phosphate has been previously described in the literature (22).

EXPERIMENTAL

Synthesis and Characterization

The title compound was prepared from reaction mixtures of H_3PO_4 (3.75 mmol), ethylenediamine (3.75 mmol), and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.75 mmol) in a mixture of approximately 15 mL of water and 1-butanol (volume ratio 1 : 2). The initial pH of the reaction was approximately 9. The synthesis was carried out in a poly(tetrafluoroethylene)-lined stainless steel container under autogeneous pressure, filled to

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approximately 75% volume capacity, and all reactants were stirred briefly before heating. The reaction mixture was heated at 170°C for 6 days, followed by slow cooling to room temperature. The pH of the reaction decreased to approximately 5. The resulting product was filtered off, washed with ether, and dried in air. Green needle well-formed single crystals appeared in the preparation together with a powdered product, which was identified by X-ray diffraction as the $\text{Ni}_{12+x}\text{H}_{6-2x}(\text{PO}_4)_8(\text{OH})_6$ phase (23). The metal ion and phosphorus contents of the new crystalline compound were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. The content of C, H, and N was determined by elemental analysis. Found: Ni, 13.6; P, 14.4; C, 5.6; H, 5.2; N, 6.5. $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$ requires Ni, 13.9; P, 14.7; C, 5.7; H, 5.7; N, 6.7. The density was measured by flotation in a mixture of $\text{CHBr}_3/\text{C}_4\text{H}_8\text{O}_2$ (ethyl acetate). The obtained value was 1.8(1) $\text{g}\cdot\text{cm}^{-3}$. The decomposition curve obtained from the thermogravimetric study reveals a weight loss of ca. 24% between 100 and 135°C, that might be assigned to the six water molecules present in the compound. At temperatures above ca. 140°C, thermal decomposition of ethylenediamine occurs (ca. 15% of the total mass). The X-ray diffraction pattern of the residue obtained from the thermogravimetric analysis shows the presence of an amorphous product, together with several peaks which can be attributed to the nickel pyrophosphate. The TREOR-4 program (24) was used to obtain the unit cell of the $\text{Ni}_2(\text{P}_2\text{O}_7)$ from the peaks observed in the X-ray diffraction pattern. The results obtained are $a = 5.22(1)$, $b = 9.90(1)$, and $c = 4.50(1)$ Å and $\beta = 97.3(1)^\circ$, in good agreement with those given in the literature (25): $a = 5.212(3)$, $b = 9.913(5)$, and $c = 4.475(3)$ Å and $\beta = 97.5(1)^\circ$.

Single-Crystal X-Ray Diffraction

A suitable single crystal with dimensions $0.3 \times 0.08 \times 0.04$ mm was carefully selected under a polarizing microscope and mounted on a glass fiber. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated $\text{MoK}\alpha$. Details of crystal data, intensity collection, and some features of the structure refinement are reported in Table 1. Lattice constants were obtained by a least-squares refinement of the setting angles of 25 reflections in the range $8^\circ < \theta < 14^\circ$. Intensities and angular positions of two standard reflections were measured every hour and showed no decrease nor misalignment during data collection.

A total of 4481 reflections were measured in the range $1^\circ \leq \theta \leq 30^\circ$. A total of 4334 reflections were independent applying the criterion $I > 2\sigma(I)$. Corrections for Lorentz and polarization effects were done and also for absorption with the empirical ψ scan method (26) by using the XRAYACS program (27). Direct methods (SHELXS 97) (28)

TABLE 1
Crystal Data, Details of Data Collection, and Structure Refinement for the $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$ Phosphate

Formula	$\text{C}_2\text{H}_{24}\text{N}_2\text{O}_{14}\text{P}_2\text{Ni}$
Molecular weight (g mol^{-1})	420.6
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	6.226(1)
b (Å)	16.241(2)
c (Å)	14.778(2)
β ($^\circ$)	91.28(1)
V (Å ³)	1493.9(4)
Z	4
$D_{\text{calc.}}$ (gcm^{-3})	1.871
$D_{\text{obs.}}$ (gcm^{-3})	1.8(1)
Crystal size (mm)	$0.3 \times 0.08 \times 0.04$
$F(000)$	880
μ ($\text{MoK}\alpha$, mm^{-1})	1.586
Measurements	
T (K)	293
Radiation, λ ($\text{MoK}\alpha$) (Å)	0.71073
Scan type	$\omega - 2\theta$
θ Range ($^\circ$)	1–30
No. of measured reflections	4481
Interval h, k, l	$-8 < h < 8, 0 < k < 22,$ $0 < l < 20$
Refinements	
No. of variables	238
No. of unique reflections with $I > 2\sigma(I)$	4334
$R1 = [\sum(F_o - F_c)] / \sum F_o $	0.042
$wR2 = [\sum[w(F_o ^2 - F_c ^2)^2] / \sum[w(F_o ^2)^2]^{1/2}]$	0.100
R , all data	$R1 = 0.080, wR2 = 0.118$
$w = 1/[\sigma^2 F_o ^2 + (xp)^2 + yp]$	$x = 0.0514; y = 0.23$
$p = [\sigma_o ^2 + 2 F_c ^2]/3$	
Goodness of fit	1.045

were employed to solve the structure. The metal ion and the phosphorus atoms were first located. The oxygen, nitrogen, and carbon atoms were found in difference Fourier maps. Both Ni(1) and Ni(2) ions occupy special positions with occupancy factors of 0.5. The structure was refined by the full-matrix least-squares method on the basis of F^2 , using the SHELXL 97 computer program (29). The scattering factors were taken from Ref. (30). Anisotropic thermal parameters were assigned to all nonhydrogen atoms. The coordinates of hydrogen atoms of the water molecules were obtained from difference Fourier maps and those of the ethylenediammonium cation were geometrically placed. The final R factors were $R1 = 0.042$ [$wR2 = 0.100$]. Maximum and minimum peaks in the final difference synthesis were 0.842, $-0.799 \text{ e } \text{Å}^{-3}$. The final atomic positional parameters are listed in Table 2. All drawings were made using PLATON and ATOMS programs (31,32).

TABLE 2
Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$ (e.s.d. in Parentheses)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^a
Ni(1)	0.5	0.5	0.5	16(1)
Ni(2)	0.5	0.0	0.5	17(1)
P(1)	1.0866(1)	0.9196(1)	0.2479(1)	13(1)
P(2)	-0.0849(1)	0.7528(1)	0.4938(1)	15(1)
O(1)	0.2065(4)	0.4636(2)	0.5413(2)	30(1)
O(2)	0.4064(5)	0.4933(3)	0.3680(2)	68(1)
O(3)	0.4090(5)	0.6208(2)	0.5027(4)	81(2)
O(4)	0.2072(4)	0.0290(2)	0.4468(2)	30(1)
O(5)	0.3898(4)	0.0151(2)	0.6280(2)	33(1)
O(6)	0.5921(4)	0.1216(2)	0.4909(2)	41(1)
O(7)	0.9962(4)	0.8386(1)	0.2009(2)	26(1)
O(8)	1.3306(3)	0.9161(2)	0.2497(1)	23(1)
O(9)	1.0037(4)	0.9942(1)	0.1964(1)	20(1)
O(10)	0.9966(3)	0.9145(1)	0.3431(1)	18(1)
O(11)	0.0348(4)	0.7633(1)	0.3997(2)	25(1)
O(12)	-0.0077(3)	0.6695(1)	0.5292(1)	19(1)
O(13)	-0.0148(4)	0.8232(1)	0.5555(2)	22(1)
O(14)	-0.3247(4)	0.7530(1)	0.4716(2)	27(1)
N(1)	0.0981(5)	0.1510(2)	0.2585(2)	29(1)
N(2)	0.4056(5)	0.2890(2)	0.2150(2)	33(1)
C(1)	0.3344(6)	0.1432(2)	0.2514(3)	33(1)
C(2)	0.4559(6)	0.2195(3)	0.2759(3)	36(1)

$$^a U_{\text{eq}} = (8\pi^2/3) [U_{22} + 1/(\sin^2 \beta)(U_{11} + U_{33} + 2U_{13} \cos \beta)].$$

Physicochemical Characterization Techniques

C,H,N elemental analysis was carried out with a Perkin-Elmer model 240 automatic analyzer. Thermogravimetric measurements were performed on a Perkin-Elmer system 7 DSC-TGA instrument. Crucibles containing approximately 20 mg of sample were heated at $5^\circ\text{C}\cdot\text{min}^{-1}$ under dry nitrogen atmosphere in the temperature range 30–800°C. The IR spectrum (KBr pellet) was obtained with a Nicolet FT-IR 740 spectrophotometer in the 400–4000 cm^{-1} range. The diffuse reflectance spectrum was registered at room temperature on a Cary 2415 spectrometer in the 5000–50,000 cm^{-1} range. Magnetic measurements of the powdered sample were performed in the temperature range 4.2–300 K, using a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field was approximately 0.1 T, a value within the range of linear dependence of magnetization vs magnetic field even at 4.2 K.

RESULTS AND DISCUSSION

Crystal Structure

The bond distances and angles of the title compound are given in Table 3.

The structure consists of isolated $\text{Ni}(\text{H}_2\text{O})_6$ octahedra, HPO_4 tetrahedra, and ethylenediammonium cations linked

by hydrogen bonds. Figures 1 and 2 show a view of the crystallographic structural unit and a polyhedral representation. The NiO_6 octahedra are very regular, with a range of Ni–O distances from 2.026(3) to 2.043(3) Å for Ni(1) ions and from 2.025(3) to 2.062(3) Å for Ni(2) ions. The *cis*-O–Ni–O angles range from $88.1(1)^\circ$ to $91.8(1)^\circ$ and from $87.4(1)^\circ$ to $92.6(1)^\circ$ in the $\text{Ni}(1)\text{O}_6$ and $\text{Ni}(2)\text{O}_6$ octahedra, respectively. The *trans*-O–Ni–O angles are, practically, of 180° for both octahedral polyhedra, because the Ni(II) ions are placed on an inversion center. The distortions of these polyhedra, from an octahedron ($\Delta = 0$) to a trigonal prism ($\Delta = 1$), calculated by quantification of the Muetterties and Guggenberger description (33, 34), are $\Delta = 0.004$ and 0.019 for $\text{Ni}(1)\text{O}_6$ and $\text{Ni}(2)\text{O}_6$ polyhedra, respectively, which

TABLE 3
Bond Distances (Å) and Angles ($^\circ$) for $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$ (e.s.d. in Parentheses)

Bond Distances (Å)			
$\text{Ni}(1)\text{O}_6$ octahedron		$\text{Ni}(2)\text{O}_6$ octahedron	
Ni(1)–O(1)/O(1) ⁱ	2.027(3)	Ni(2)–O(4)/O(4) ⁱⁱ	2.025(3)
Ni(1)–O(2)/O(2) ⁱ	2.026(3)	Ni(2)–O(5)/O(5) ⁱⁱ	2.041(3)
Ni(1)–O(3)/O(3) ⁱ	2.043(3)	Ni(2)–O(6)/O(6) ⁱⁱ	2.062(3)
$\text{P}(1)\text{O}_4$ tetrahedron		$\text{P}(2)\text{O}_4$ tetrahedron	
P(1)–O(7)	1.558(2)	P(2)–O(11)	1.601(3)
P(1)–O(8)	1.520(2)	P(2)–O(12)	1.524(2)
P(1)–O(9)	1.515(3)	P(2)–O(13)	1.520(3)
P(1)–O(10)	1.528(2)	P(2)–O(14)	1.521(3)
$(\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3)^{2+}$			
N(1)–C(1)	1.483(5)	N(2)–C(2)	1.473(6)
C(1)–C(2)	1.492(6)		
Bond Angles ($^\circ$)			
$\text{Ni}(1)\text{O}_6$ octahedron		$\text{Ni}(2)\text{O}_6$ octahedron	
O(1)–Ni(1)–O(1) ⁱ	180.0(5)	O(4)–Ni(2)–O(4) ⁱⁱ	180.0(7)
O(2)–Ni(1)–O(2) ⁱ	180.0(9)	O(5)–Ni(2)–O(5) ⁱⁱ	180.0(4)
O(3)–Ni(1)–O(3) ⁱ	180.0(5)	O(6)–Ni(2)–O(6) ⁱⁱ	180.0(9)
O(1)–Ni(1)–O(2)	$91.8(1) \times 2$	O(4)–Ni(2)–O(5)	$90.8(1) \times 2$
O(1)–Ni(1)–O(3)	$91.2(1) \times 2$	O(4)–Ni(2)–O(6)	$90.1(1) \times 2$
O(1)–Ni(1)–O(2) ⁱ	88.1(8)	O(4)–Ni(2)–O(5) ⁱⁱ	89.2(1)
O(1)–Ni(1)–O(3) ⁱ	88.7(1)	O(4)–Ni(2)–O(6) ⁱⁱ	89.9(1)
O(2)–Ni(1)–O(1) ⁱ	88.1(1)	O(5)–Ni(2)–O(4) ⁱⁱ	89.2(1)
O(3)–Ni(1)–O(1) ⁱ	88.7(1)	O(6)–Ni(2)–O(4) ⁱⁱ	89.9(1)
O(2)–Ni(1)–O(3)	$89.8(2) \times 2$	O(5)–Ni(2)–O(6)	$92.6(1) \times 2$
O(2)–Ni(1)–O(3) ⁱ	90.2(2)	O(6)–Ni(2)–O(5) ⁱⁱ	87.4(1)
O(3)–Ni(1)–O(2) ⁱ	90.2(2)	O(5)–Ni(2)–O(6) ⁱⁱ	87.4(1)
$\text{P}(1)\text{O}_4$ tetrahedron		$\text{P}(2)\text{O}_4$ tetrahedron	
O(7)–P(1)–O(8)	108.8(1)	O(11)–P(2)–O(12)	104.1(1)
O(7)–P(1)–O(9)	109.3(1)	O(11)–P(2)–O(13)	107.9(1)
O(7)–P(1)–O(10)	103.0(1)	O(11)–P(2)–O(14)	106.6(2)
O(8)–P(1)–O(9)	111.6(1)	O(12)–P(2)–O(13)	112.2(1)
O(8)–P(1)–O(10)	111.6(1)	O(12)–P(2)–O(14)	112.1(1)
O(9)–P(1)–O(10)	112.2(1)	O(13)–P(2)–O(14)	113.2(1)
$(\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3)^{2+}$			
N(1)–C(1)–C(2)	114.2(3)	C(1)–C(2)–N(2)	112.8(3)

Symmetry code: i = $-x + 1$, $-y + 1$, $-z + 1$; ii = $-x + 1$, $-y$, $-z + 1$.

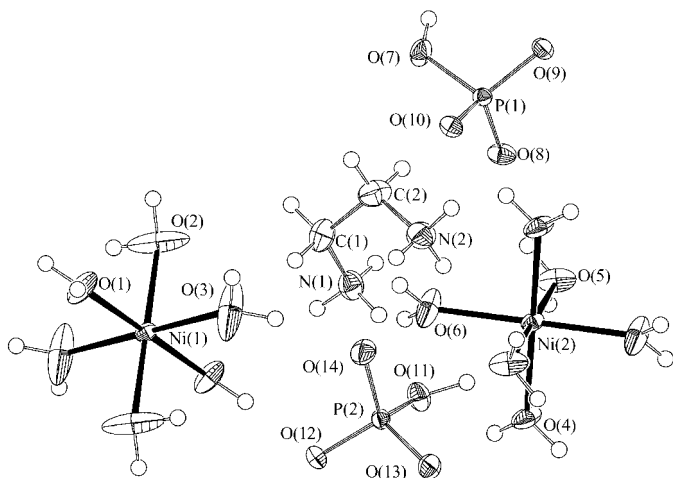


FIG. 1. Structural unit of $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$, with detailed labeling of the atoms. Thermal ellipsoids are shown at 50% probability.

indicate a topology near to an octahedron. The HPO_4 groups can be described as low-distorted tetrahedra, with a mean value for the P–O bond distances of 1.521(5) Å. The P(1)–O(7) and P(2)–O(11) are hydrogen phosphate groups, with bond distances slightly longer than those observed for the other P–O distances. The O–P–O angles are in the range from 103.0(1)° to 113.2(1)°. In the ethylenediammonium cation, the C–C and C–N bond distances are in the range usually found for this molecule (35) and the angles deviate slightly from the ideal value expected for an sp^3 hybridization. The three-dimensional framework of this com-

pound is formed by a complicated scheme of hydrogen bonds established between the water molecules of the NiO_6 octahedra, the hydrogen phosphate anions, and the ethylenediammonium cations. The hydrogen bonds established between the six independent water molecules and the hydrogen phosphate anions range from 2.683(4) to 2.878(4) Å, whereas the hydrogen bonds between the ethylenediammonium cations and the hydrogen phosphate groups are in the range from 2.682(4) to 3.163(4) Å. A related structural arrangement has been found in the $(\text{NH}_4)[\text{M}(\text{H}_2\text{O})_6](\text{PO}_4)$ ($M = \text{Mg}, \text{Ni}$) phases, with *struvite*-type structure, which also show isolated $\text{Ni}(\text{H}_2\text{O})_6$ octahedra and PO_4 tetrahedra linked to the ammonium cations by hydrogen bonds (36, 37).

In addition to the $(\text{NH}_4)[\text{M}(\text{H}_2\text{O})_6](\text{PO}_4)$ phase some other nickel(II) hydrates are reported in the literature (38–42). In Table 4, the ranges of Ni–O bond distances concerning the octahedral $\text{Ni}(\text{H}_2\text{O})_6$ polyhedra, together with the mean value of the *cis*-O–Ni–O and *trans*-O–Ni–O angles and the Δ values, are given. From these results it can be observed that in all the Ni(II) hydrated compounds studied the coordination polyhedra are very regular. So we can conclude that the ethylenediammonium and ammonium cations maintain through hydrogen bonds the structure of the $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$ and $(\text{NH}_4)[\text{Ni}(\text{H}_2\text{O})_6](\text{PO}_4)$ phases.

Infrared and UV-Visible Spectroscopies

The infrared spectrum shows the bands corresponding to the vibrations of the water, ethylenediammonium cations, and hydrogen phosphate anions. The strong band centered at 3395 cm^{-1} corresponds to the stretching mode of the water molecule. The bending mode of this molecule can be observed at about 1650 cm^{-1} . The stretching mode of the $(\text{NH}_3)^+$ group in the ethylenediammonium cation appears at 3240 cm^{-1} . The band near 1575 cm^{-1} can be assigned to the $(\text{NH}_3)^+$ bending vibration. This band is indicative of the presence of the ethylenediamine molecule in its protonated form (35, 43), in good agreement with the structural results. The bending modes of the $-\text{CH}_2-$ groups in the ethylenediammonium appear in the 1400–1200 cm^{-1} range. Four different groups of bands can be attributed to the vibrational modes of the $(\text{HPO}_4)^{2-}$ anions present in the compound (44). The asymmetrical stretching mode [$\nu_{\text{as}}(\text{P}-\text{O})$] appears at frequencies 1075, 1065, and 970 cm^{-1} . The symmetrical stretch [$\nu_{\text{s}}(\text{P}-\text{O})$] is detected at a frequency of 620 cm^{-1} . The asymmetrical deformation vibrations [$\delta_{\text{as}}(\text{O}-\text{P}-\text{O})$] can be observed at 545, 525, and 475 cm^{-1} . Finally, the weak band observed at about 1460 cm^{-1} can be assigned to the bending mode of the H–OP group, in good agreement with the structural data.

The diffuse reflectance spectrum exhibits the essential characteristics of octahedrally coordinated Ni(II) ions.

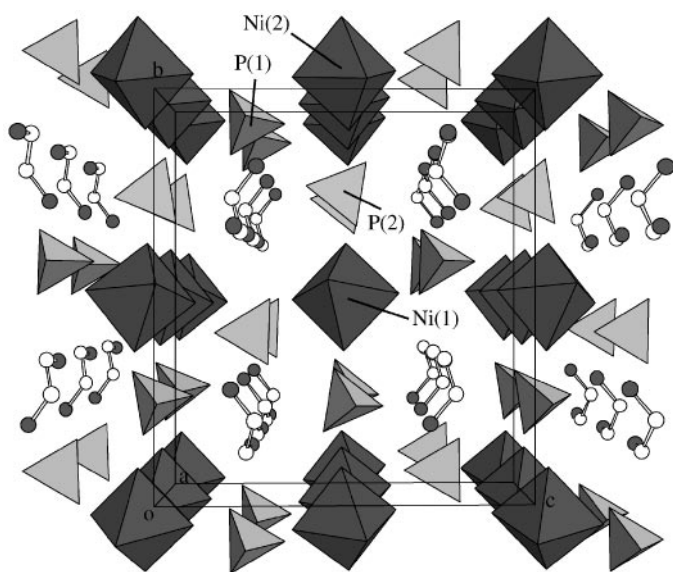


FIG. 2. Polyhedral representation of $(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Ni}(\text{H}_2\text{O})_6](\text{HPO}_4)_2$.

TABLE 4
Selected Crystallographic Data for Some Ni(II) Hydrated Compounds

Compound	Ni–O distances (Å) (min. and max. values)	<i>cis</i> -O–Ni–O angles (°)	<i>trans</i> -O–Ni–O angles (°)	Δ (%)	Ref.
[Ni(H ₂ O) ₆](SO ₄)	2.013(1)–2.099(2)	90(1)	178.6(2)	1.6	38
[Ni(H ₂ O) ₆](SO ₄)(H ₂ O)	1.96–2.14	90(5)	173(1)	1.6	39
[Ni(H ₂ O) ₆](S ₂ O ₃)	2.033(8)–2.097(7)	90(2)	180.0(0)	1.0	40
[Ni(H ₂ O) ₆](SeO ₄)	2.04(2)–2.08(3)	90(2)	176(2)	1.3	41
[Ni(H ₂ O) ₆](NO ₃) ₂	2.022(6)–2.09(1)	90(2)	177(1)	2.1	42
(NH ₄)[Ni(H ₂ O) ₆](PO ₄)	2.040(3)–2.091(5)	90(2)	177(2)	1.3	36
(C ₂ H ₁₀ N ₂)[Ni(H ₂ O) ₆](HPO ₄) ₂	2.026(3)–2.043(3)	90(1)	180(0)	0.4	This work
	2.025(3)–2.062(3)	90(2)	180(0)	1.9	

Note. The Δ values were calculated using the Muetterties and Guggenberger description.

Three absorption bands ascribed to the spin-allowed transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3T_{1g}(F)$, and ${}^3T_{1g}(P)$ are observed at the following values: $\nu_1 = 8335$, $\nu_2 = 12,990$, and $\nu_3 = 24,690 \text{ cm}^{-1}$. The spin-forbidden transitions ${}^3A_{2g} \rightarrow {}^1E_g$ and ${}^1T_{2g}$ can be also observed at $\nu_4 = 14,705$ and $\nu_5 = 22,470 \text{ cm}^{-1}$. The D_q and Racah parameters were calculated by fitting the experimental frequencies to an energy level diagram for octahedral d^8 systems (45). The values obtained are $D_q = 835$, $B = 900$, and $C = 4040 \text{ cm}^{-1}$. The value obtained for the B parameter supposes a reduction of ca. 85% from that of the free Ni(II) ion, which indicates a considerable degree of covalent character in the Ni–O bonds. These results are in the range usually found for octahedrally coordinated Ni(II) compounds (46–48).

Magnetic Properties

The magnetic susceptibility was measured on powdered sample in the range from 4.2 to 300 K. The compound follows a Curie–Weiss law in the entire temperature range studied. The calculated Curie and Weiss constants are $C_m = 1.20 \text{ cm}^3 \text{ K/mol}$ and $\theta = -2 \text{ K}$. This behavior is characteristic of a paramagnetic system, in good agreement with the structural results.

CONCLUDING REMARKS

The first nickel(II) phosphate templated by ethylenediamine with the formula (C₂H₁₀N₂)[Ni(H₂O)₆](HPO₄)₂ has been prepared under hydrothermal conditions. The crystal structure has been resolved by X-ray single-crystal data diffraction. It consists of isolated Ni(H₂O)₆ octahedra, hydrogen phosphate tetrahedra, and ethylenediammonium cations. The three-dimensional framework is formed by hydrogen bonds established between these ions. A comparative structural study of this compound with other related phases shows that the organic cations maintain the crystal-line framework of the compounds through hydrogen bonds.

The D_q and Racah (B and C) parameters have been calculated and they are in the range usually found for Ni(II) ions in octahedral sites. The magnetic susceptibility indicates a paramagnetic behavior for this compound.

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REFERENCES

1. A. K. Cheetham, G. Ferey, and T. Loiseau, *Angew. Chem., Int. Ed.* **38**, 3268 (1999).
2. M. E. Davis and R. F. Lobo, *Chem. Mater.* **4**, 756 (1992).
3. D. W. Breck, "Zeolite Molecule Sieves: Structure, Chemistry and Use." Wiley, New York, 1974.
4. P. B. Venuto, *Microporous Mater.* **2**, 297 (1994).
5. R. Haushalter and L. Mundi, *Chem. Mater.* **4**, 31 (1992).
6. V. Soghomonian, Q. Chen, R. Haushalter, and J. Zubieta, *Chem. Mater.* **5**, 1690 (1993).
7. M. Kahn, Y. Lee, C. O'Connor, R. Haushalter, and J. Zubieta, *J. Am. Chem. Soc.* **116**, 4525 (1994).
8. P. Zapf, D. Rose, R. Haushalter, and J. Zubieta, *J. Solid State Chem.* **125**, 182 (1996).
9. J. DeBord, R. Haushalter, and J. Zubieta, *J. Solid State Chem.* **125**, 270 (1996).
10. S. Dhingra and R. Haushalter, *J. Chem. Soc., Chem. Commun.* **21**, 1665 (1993).
11. Y. Zhang, C. O'Connor, A. Clearfield, and R. Haushalter, *Chem. Mater.* **8**, 595 (1996).
12. M. I. Khan, L. M. Meyer, R. Haushalter, A. L. Schweitzer, J. Zubieta, and J. L. Dye, *Chem. Mater.* **8**, 43 (1996).
13. K.-H. Lii, Y.-F. Huang, V. Zima, C.-Y. Huang, H.-M. Lin, Y.-C. Jiang, F.-L. Liao, and S.-L. Wang, *Chem. Mater.* **10**, 2599 (1998).
14. M. Cavellec, D. Riou, J. M. Greneche, and G. Ferey, *Inorg. Chem.* **36**, 2181 (1997).
15. J. R. D. DeBord, W. M. Reiff, C. J. Warren, R. Haushalter, and J. Zubieta, *Chem. Mater.* **9**, 1994 (1997).
16. K. H. Lii and Y. F. Huang, *J. Chem. Soc., Chem. Commun.* 1311 (1997).

17. V. Zima, K.-H. Lii, N. Nguyen, and A. Ducouret, *Chem. Mater.* **10**, 1914 (1998).
18. J. DeBord, W. Reiff, R. Haushalter, and J. Zubieta, *J. Solid State Chem.* **125**, 186 (1996).
19. K.-H. Lii and Y.-F. Huang, *J. Chem. Soc., Dalton Trans.* 2221 (1997).
20. J. Chen, R. H. Jones, S. Natarajan, M. B. Hursthouse, and J. M. Thomas, *Angew. Chem., Int. Ed. Engl.* **33**, 639 (1994).
21. J. Escobal, J. L. Pizarro, J. L. Mesa, L. Lezama, R. Olazcuaga, M. I. Arriortua, and T. Rojo, *Chem. Mater.* **12**, 376 (2000).
22. N. Guillou, Q. Gao, M. Nogue, R. E. Morris, M. Hervieu, G. Ferey, and A. K. Cheetham, *C. R. Acad. Sci. Paris* **2**, 387 (1999).
23. J. L. Pizarro, M. I. Arriortua, L. Lezama, and T. Rojo, *Solid State Ionics* **63-65**, 71 (1993).
24. P. E. Werner, "TREOR-4 Program." Arrhenius Laboratory, University of Stockholm, Sweden, 1984.
25. R. Masse, J. C. Guitel, and A. Durif, *Mater. Res. Bull.* **14**, 337 (1979).
26. A. C. T. North, D. C. Philips, and F. S. Mathews, *Acta Crystallogr. A* **24**, 351 (1968).
27. A. Chandrasekaran, "XRAYACS: Program for Single Crystal X-ray Data Corrections." Chemistry Department, University of Massachusetts, Amherst, MA, 1998.
28. G. M. Sheldrick, "SHELXS 97: Program for the Solution of Crystal Structures." University of Göttingen, Germany, 1997.
29. G. M. Sheldrick, "SHELXL 97: Program for the Refinement of Crystal Structures." University of Göttingen, Germany, 1997.
30. "International Tables for X-ray Crystallography," Vol. IV, p. 99. Kynoch Press, Birmingham, England, 1974.
31. A. Spek, "PLATON: Program for Molecular Geometry Calculations." University of Utrecht, The Netherlands, 1992.
32. E. Dowty, "ATOMS: A Computer Program for Displaying Atomic Structures." Shape Software, 521 Hidden Valley Rd., Kingsport, TN, 1993.
33. E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.* **96**, 1748 (1974).
34. R. Cortés, M. I. Arriortua, T. Rojo, X. Solans, and D. Beltran, *Polyhedron* **5**, 1987 (1986).
35. A. Gharbi, A. Jouini, M. T. Averbuch-Pouchot, and A. Durif, *J. Solid State Chem.* **111**, 330 (1994).
36. A. Goñi, J. L. Pizarro, L. M. Lezama, G. E. Barberis, M. I. Arriortua, and T. Rojo, *J. Mater. Chem.* **6**(3), 421 (1996).
37. F. Abbona, M. Calleri, and G. Ivaldi, *Acta Crystallogr. B* **40**, 223 (1984).
38. K. Stadnicka, A. M. Glazer, and M. Koralewski, *Acta Crystallogr. B* **43**, 319 (1987).
39. C. A. Beevers and C. M. Schwartz, *Z. Kristallogr.* **91**, 157 (1935).
40. Y. Elerman, A. A. Uraz, and N. Armagan, *Acta Crystallogr. B* **34**, 3330 (1978).
41. H. Fuess, *Z. Anorg. Allgem. Chem.* **379**, 204 (1970).
42. F. Bigoli, A. Braibanti, A. Tiripicchio, and M. Tiripicchio, *Acta Crystallogr. B* **27**, 1427 (1971).
43. D. Dolphin and A. E. Wick, "Tabulation of Infrared Spectral Data." Wiley, New York, 1977.
44. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds." Wiley, New York, 1997.
45. A. B. P. Lever, "Inorganic Electronic Spectroscopy." Elsevier Science Publishers B.V., Amsterdam, The Netherlands, 1984.
46. J. M. Rojo, J. L. Mesa, J. L. Pizarro, L. Lezama, M. I. Arriortua, and T. Rojo, *Mater. Res. Bull.* **31**(8), 925 (1996).
47. J. M. Rojo, J. L. Mesa, J. L. Pizarro, L. Lezama, M. I. Arriortua, and T. Rojo, *J. Solid State Chem.* **132**, 107 (1997).
48. J. L. Mesa, J. L. Pizarro, L. Lezama, J. Escobal, M. I. Arriortua, and T. Rojo, *J. Solid State Chem.* **141**, 508 (1998).