Hydrothermal Synthesis and Crystal Structure of [Ni(H₂O)₄][VO(PO₄)]₂, a Nickel(II) Vanadyl(IV) Phosphate

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The new $M^{2+}/V^{4+}/P/O$ phase [Ni(H₂O)₄][VO(PO₄)]₂ was prepared by hydrothermal synthesis and characterized by X-ray crystallography and thermogravimetric analysis. Crystal data: tetragonal space group $I4/mmm$, $a = 6.251(1)$Å, $c = 13.338(3)$Å, $V = 521.2(3)$Å³, $Z = 2$, $D_{calc} = 2.845$ g/cm³; structure solution and refinement based on 176 reflections with $I_0 \geq 3\sigma(I_0)$ (MoKα radiation, $\lambda = 0.71073$Å) converged at $R = 0.0564$. The structure consists of {VO(PO₄)} layers, constructed from VO₅ square pyramids and PO₄ tetrahedra, linked by NiO₆ octahedra. The structure is distinct from that of Ni₀.₅[VO(PO₄)] · 1.5H₂O, which exhibits a three-dimensional network structure with tunnels accommodating the aquo ligands. © 1993 Academic Press, Inc.

Introduction

The vanadium phosphate system offers a rich and complex structural chemistry of significance to the sorptive and catalytic properties of these solid phases (*1–11*). The occurrence of different vanadium coordination geometries and the accessibility of more than one vanadium oxidation state are in part responsible for the varied structural chemistry of these V/P/O phases (*12*). Vanadium sites may adopt tetrahedral, square pyramidal, trigonal bipyramidal, or octahedral geometries (*13*). Aggregation into larger polyhedral units is accomplished by condensation of polyhedra through shared corners, edges, or faces. The three-dimensional structural network of the V/P/O phases is generated by condensing vanadium polyhedra with phosphate tetrahedra. Further structural diversity may be accomplished by introducing a variety of templates which, if incorporated into the solid, require complex patterns of polyhedral connectivities to accommodate the guest molecule. In hydrothermal syntheses, the need to incorporate significant amounts of water of crystallization into the host lattice likewise dictates connectivity patterns which produce lamellar, tunnel, or cage structures (*14*).

While the vanadium phosphate phases of vanadium in the +5 oxidation state have been extensively developed, the phases with vanadium in the +4 oxidation state have only recently received systematic attention, most notably in the development of the alkali metal phases *A*/P/O/V (*A* = K, Cs, Rb) (*15, 16*) and phases with main group metals (*A* = Tl) (*12*).

As part of our studies of the hydrothermal preparation of reduced V/P/O phases (*17*), we have sought to design phases which incorporate potentially catalytically active transition metal centers into these solids.
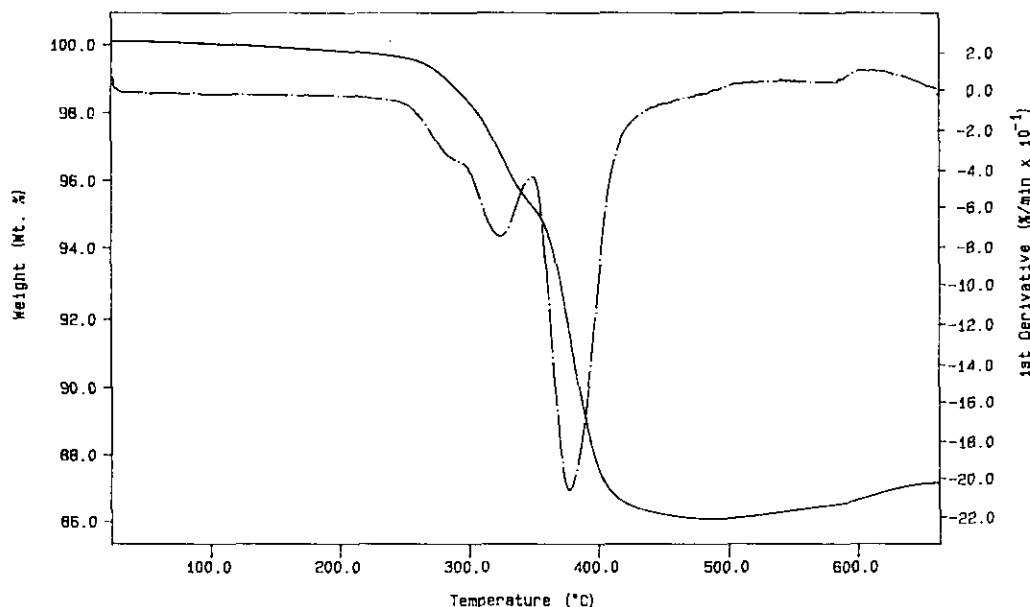
FIG. 1. Thermogravimetric analysis of [Ni(H$_e$O)$_4$][VO(PO$_4$)$_2$] in the temperature range 50 to 500°C.

Such "designer" solids may combine site selectivity, as observed for several vanadium phosphate phases, with reactive sites. The present work describes the hydrothermal synthesis and structural characterization of a member of the A/V/O/P class of solids, where A is a transition metal cation, [Ni(H$_2$O)$_4$][VO(PO$_4$)]$_2$.

Experimental

Synthesis

KVO$_3$ (99.9%) and vanadium metal (325 mesh, 99.5%) were obtained from Cerac Inc. and used as received. A mixture of KVO$_3$, V, CH$_3$PO$_3$H$_2$, H$_3$PO$_4$ (85%), dimethylamine, NiCl$_2$ (Cerac), and H$_2$O in the mole ratio 2.35 : 1 : 3.3 : 8.0 : 10.9 : 10.1 : 1902 was heated for 4 days at 200°C in a 23-ml acid digestion bomb. After the reaction mixture was cooled slowly to room temperature, green crystals of [Ni(H$_2$O)$_4$] [VO(PO$_4$)]$_2$ of tetragonal morphology were collected in 75% yield. The product was washed several times with water, rinsed with acetone and

air dried at ambient temperature. IR(KBr pellet, cm^{-1}): 3295(s), 1120(m), 1026(s), 995(m), 849(w), 679(m), 550(m). The compound was also prepared in quantitative yield by the reaction of V$_2$O$_5$, V, CH$_3$PO$_3$H$_2$, H$_3$PO$_4$, (CH$_3$)$_2$NH, KCl, NiCl$_2$, and H$_2$O in the mole ratio 1.32 : 1 : 3.36 : 8.1 : 4.4 : 2.4 : 11.0 : 1927 at 200°C for 4 days.

Thermal Analysis

Thermogravimetric analysis (TGA) was performed on a crushed sample of manually selected crystals of [Ni(H$_2$O)$_4$][VO(PO$_4$)]$_2$, using a Perkin–Elmer TGA 7 thermogravimetric analyzer. The TGA experiment was performed in an N$_2$ atmosphere using a heating rate of 5°C/min. The results of the TGA are shown in Fig. 1.

Single Crystal X-Ray Diffraction of [Ni(H$_2$O)$_4$][VO(PO$_4$)]$_2$

A green plate of dimensions 0.31 × 0.12 × 0.35 mm was selected for indexing and data collection on a Rigaku AFC5S dif-

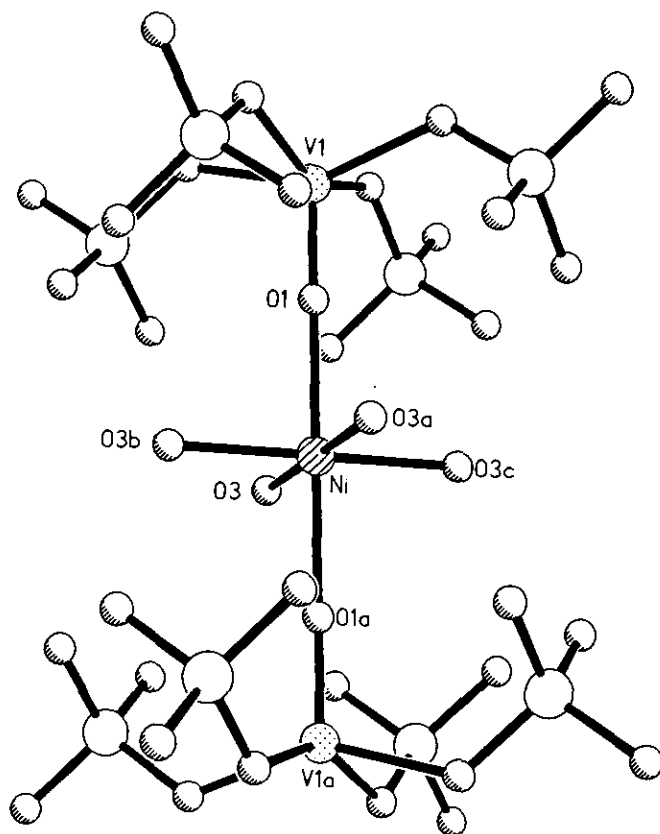FIG. 2. A view of the geometry of the {NiO₂(H₂O)₄} unit and of the neighboring {VO(PO)₄} sites, illustrating the {V=O–Ni–O=V} interconnecting motifs.

fractometer. Table I presents the crystal data and a summary of the details of data collections, structure solution and refinement. *Atomic positional parameters* and isotropic temperature factors are presented in Table II. Selected bond lengths and angles are tabulated in Table III.

Results and Discussion

The hydrothermal reaction for 4 days at 200°C of KVO₃, vanadium metal, CH₃PO₃H₂, H₃PO₄, (CH₃)₂NH, NiCl₂, and H₂O in the mole ratio 8.57 : 1 : 3.34 : 9.07 : 4.12 : 10.18 : 1914.39 yields bright green plates of [Ni(H₂O)₄][VO(PO₄)]₂ in 75% yield. While the organic components of the syn-

thesis do not appear in the product, they are absolutely necessary for the isolation of crystalline products. Such templating influences of organic components have been observed in other hydrothermal preparations. The origin of this effect is not clear to us at this time (*18*). The infrared spectrum of this material exhibits a feature at 996 cm⁻¹ characteristic of *ν*(V=O) and bands at 1120 and 1026 cm⁻¹ associated with the phosphate group.

The thermogravimetric analysis shown in Fig. 1 exhibits water loss in the 325–390°C range, corresponding to the 15.8% loss expected for the removal of the hydration water associated with the Ni²⁺ cation.

As shown in Fig. 2, the structure of [Ni

TABLE I

CRYSTAL DATA AND SUMMARY OF EXPERIMENTAL CONDITIONS FOR THE X-RAY DIFFRACTION STUDY OF [Ni(H$_2$O)$_4$][VO(PO$_4$)]$_2$

	Crystal Data
Empirical formula	Ni$_2$O$_{28}$P$_4$V$_4$
Color, habit	Green plate
Crystal size (mm)	0.31 × 0.12 × 0.35
Crystal system	Tetragonal
Space group	*I4/mmm*
Unit cell dimensions	a = 6.2510(10)Å
	c = 13.338(3)Å
Volume	521.2(3)Å^3
Z	1
Formula weight	893.1
Density (calc.)	2.845 Mg/m^3
Absorption coefficient	3.931 mm^{-1}
F(000)	432
	Data collection
Diffractometer used	Siemens R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	294
Monochromator	Highly oriented graphite crystal
2θ range	2.0° to 45.0°
Scan type	ω
Scan speed	Variable; 2.00° to 29.30°/min in ω
Scan range (ω)	0.06°
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 0.5% of total scan time
Standard reflections	3 measured every 100 reflections
Index ranges	$0 \leq h \leq 8, 0 \leq k \leq 8, 0 \leq l \leq 18$
Reflections collected	404
Independent reflections	260 (R_{int} = 4.21%)
Observed reflections	176 ($F > 6.0\sigma(F)$)
Absorption correction	ψ scans on 5 reflections
	Solution and refinement
System used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Absolute structure	N/A
Extinction correction	N/A
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.00021F^2$
Number of parameters refined	21
Final R indices (obs. data)	R = 5.64%, wR = 6.05%
R indices (all data)	R = 7.96%, wR = 9.32%
Goodness of fit	7.68
Largest and mean Δ/σ	0.000, 0.000
Data-to-parameter ratio	8.4 : 1
Largest difference peak	0.26 e Å^{-3}
Largest difference hole	−0.37 e Å^{-3}

TABLE II

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR [Ni(H$_2$O)$_4$][VO(PO$_4$)]$_2$.

Ni–O(1)	2.101 (12)	Ni–O(3)	2.011 (15)
Ni–O(1A)	2.101 (12)	Ni–O(3A)	2.011 (15)
Ni–O(3B)	2.011 (15)	Ni–O(3C)	2.011 (15)
V(1)–O(1)	1.595 (13)	V(1)–O(2)	1.981 (6)
V(1)–O(2A)	1.981 (6)	V(1)–O(2C)	1.981 (6)
V(1)–O(2E)	1.981 (6)	P–O(2)	1.526 (6)
P–O(2B)	1.526 (6)	P–O(2D)	1.526 (6)
P–O(2F)	1.526 (6)		
O(1)–Ni–O(3)	90.0(1)	O(1)–Ni–O(1A)	180.0(1)
O(3B)–Ni–O(3C)	180.0(1)	O(1)–V(1)–O(2)	106.2(2)
O(1)–V(1)–O(2A)	106.2(2)	O(2)–V(1)–O(2A)	147.7(3)
O(1)–V(1)–O(2C)	106.2(2)	O(2)–V(1)–O(2C)	85.6(1)
O(2A)–V(1)–O(2C)	85.6(1)	O(1)–V(1)–O(2E)	106.2(2)
O(2)–V(1)–O(2E)	85.6(1)	O(2A)–V(1)–O(2E)	85.6(1)
O(2C)–V(1)–O(2E)	147.7(3)	O(2)–P–O(2B)	106.5(4)
O(2)–P–O(2D)	111.0(2)	O(2B)–P–O(2D)	111.0(2)
O(2)–P–O(2F)	111.0(2)	O(2B)–P–O(2F)	111.0(2)
O(2D)–P–O(2F)	106.5(4)	Ni–O(1)–V(1)	180.0(1)
V(1)–O(2)–P	127.1(3)		

(H$_2$O)$_4$][VO(PO$_4$)]$_2$ consists of vanadyl phosphate layers with [Ni(H$_2$O)$_4$]$^{2+}$ units connecting the layers. The layers are constructed from a network of corner-sharing vanadium(IV) square pyramids and phosphate tetrahedra, as shown in Fig. 3. The vanadyl phosphate planes exhibit the {(VO)$_2$(μ_2-PO$_4$)$_2$} unit, which is a characteristic structural motif of the lamellar {VO(PO$_4$)} class of materials (Fig. 4) (*19*).

When viewed down the c-axis, the VO$_5$ square pyramids direct the vertex occupied

TABLE III

ATOMIC POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR [Ni(H$_2$O)$_4$][VO(PO$_4$)]$_2$

	x	y	z	$U(eq)^a$
Ni	0	0	0	9(1)
V(1)	0	0	2771(2)	3(1)
P	5000	0	2500	4(1)
O(1)	0	0	1575(9)	11(3)
O(2)	3044(10)	0	3185(4)	12(2)
O(3)	−2275(17)	−2275(17)	0	66(4)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.
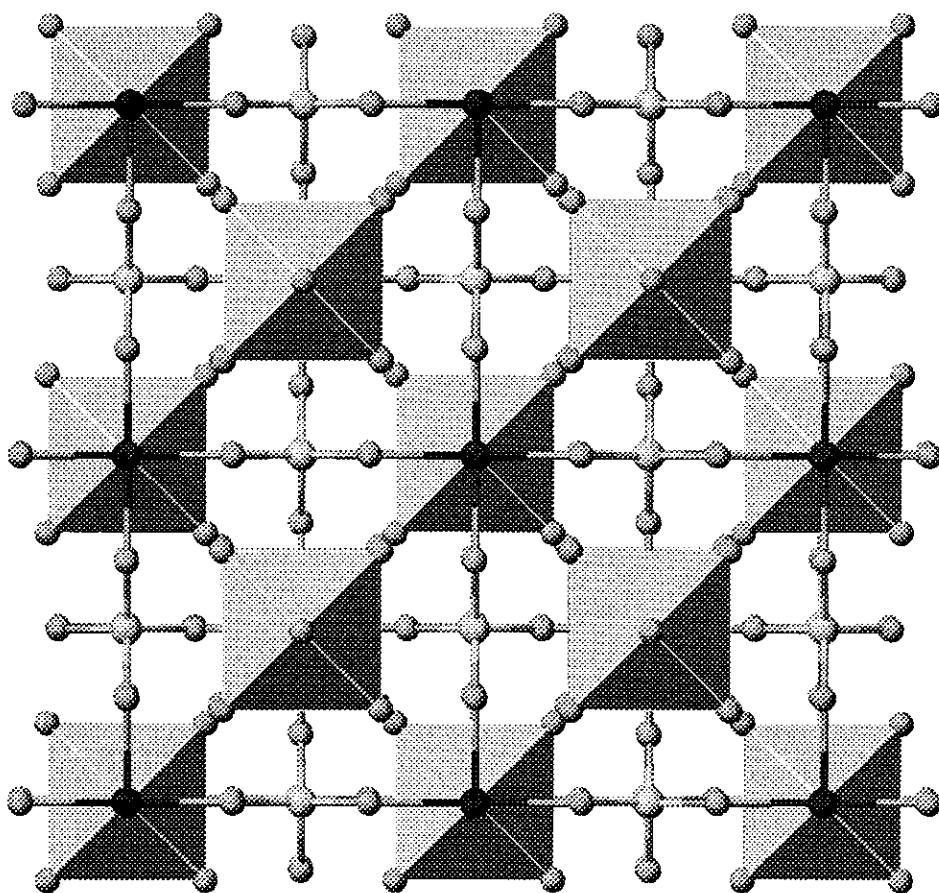
FIG. 3. A polyhedral view of the extended structure of $[Ni(H_2O)_4][VO(PO_4)]_2$.

by the apical oxo-group alternately up and down relative to the layer. Neighboring layers are aligned so as to order the oxo-groups of corresponding vanadyl sites directly toward each other. The Ni^{2+} cations occupy sites at the midpoints of these O1–O1' vectors, with Ni–O1 distances of 2.101(12)Å. The coordination at each Ni^{2+} site is completed by four water molecules with Ni–O3 distances of 2.011(15)Å. The overal structure of $[Ni(H_2O)_4][VO(PO_4)]_2$ may thus be described as layes of corner-sharing vanadium square pyramids and phosphate tetrahedra interconnected through NiO_6 octahedra (see Fig. 5). The distance between the $\{VO(PO_4)\}$ planes, defined by the best planes

through the O2 atoms, is 4.84Å, which may be compared to a distance of 3.91Å in vanadyl orthophosphate $[VO(PO_4)]$ (20). Significantly, the orthovanadate structure consists of $\{VO_6\}$ octahedra and $\{PO_4\}$ tetrahedra arranged in layers held together by long V–O bonds. Thus, in orthophosphate the layers stack so as to orient the V=O vertices of one layer directly in line with the vacant sites of the $\{VO_5\}$ units of the next layer, producing $\{V{=}O \cdots V{=}O \cdots V{=}O\}$ chains of distorted $\{VO_6\}$ octahedra. The registry of $\{VO(PO_4)\}$ layers of $[Ni(H_2O)_4][VO(PO_4)]_2$ is distinct from that of $[VO(PO_4)]$ and related by parallel shearing of length equal to one vanadium polyhe-
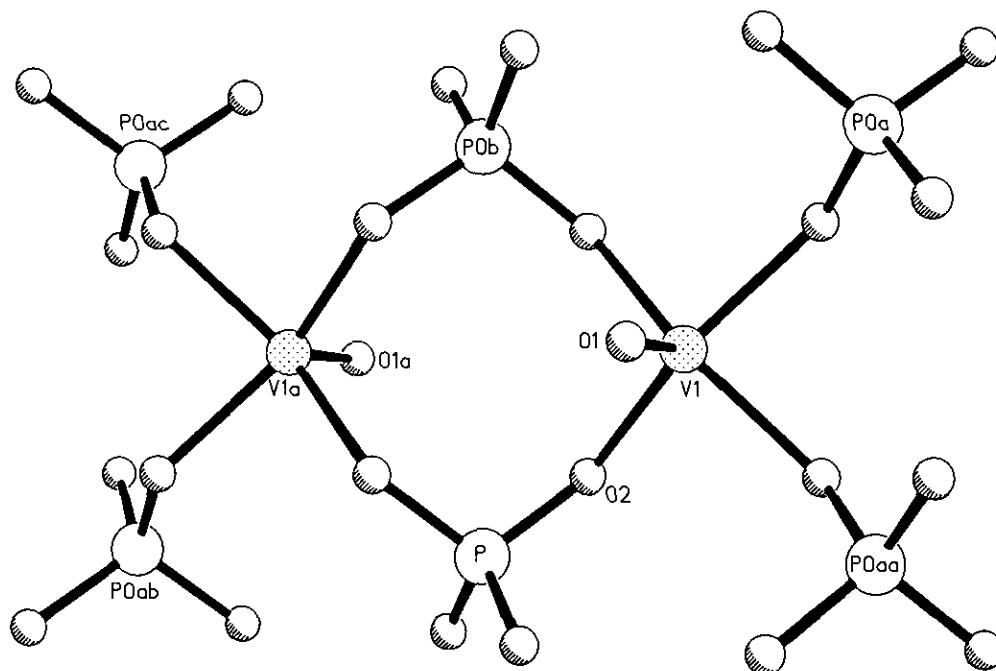
FIG. 4. The $\{(VO)_2(\mu_2\text{-}PO_4)_2\}$ structural motif.

dron so as to point the {V=O} vertices of adjacent layers at one another. The structure of $[Ni(H_2O)_4][VO(PO_4)]_2$ is thus related to that of $[VO(PO_4)]$ by expansion of the interlamellar spacing, translation of the layers relative to each other so as to provide a coordination site for the Ni^{2+} cation, and reduction of the vanadium sites to V(IV). The structural transformation requires only shearing of planes without disruption of any V–O–P bonds and suggests that $[Ni(H_2O)_4]$ $[VO(PO_4)]_2$ may be described as a reduced $VO(PO_4)$ phase with intercalated $\{Ni(H_2O)_4\}^{2+}$ units.

The structure of $[Ni(H_2O)_4][VO(PO_6)]_2$ is quite distinct from that of $Ni_{0.5}[VO(PO)_4] \cdot 1.5H_2O$, a previously reported example of a nickel(II) vanadyl(IV) phosphate phase (21). In contrast to the structure of the title compound, $Ni_{0.5}[VO(PO_4)] \cdot 1.5H_2O$ exhibits a three-dimensional architecture with channels to accommodate the aquo ligands of the {NiO₆} octahedron. Furthermore, the latter features the much more commn octa-

hedral V(IV) coordination sites with a $\{V_2(\mu\text{-}O)(\mu_2\text{-}PO_4)_2\}$ structural motif.

The results described in this work are consistent with the facile formation of numerous crystalline phases of both vanadium(IV) and vanadium(V) in the V/P/O system. The structural diversity of this system may be considerably expanded by the introduction of a variety of cations, including divalent metals of the transition series. The structure of $[Ni(H_2O)_4][VO(PO_4)]$ offers features of both layered structures and three dimensional network structures, as a consequence of the presence of {NiO₆} octahedra interleaving the {VO(PO₄)} layers, and suggests that V/P/O phases exhibiting complex three-dimensional connectivities may be accessible by exploiting the incorporating of a variety of inorganic templating cations.

Acknowledgment
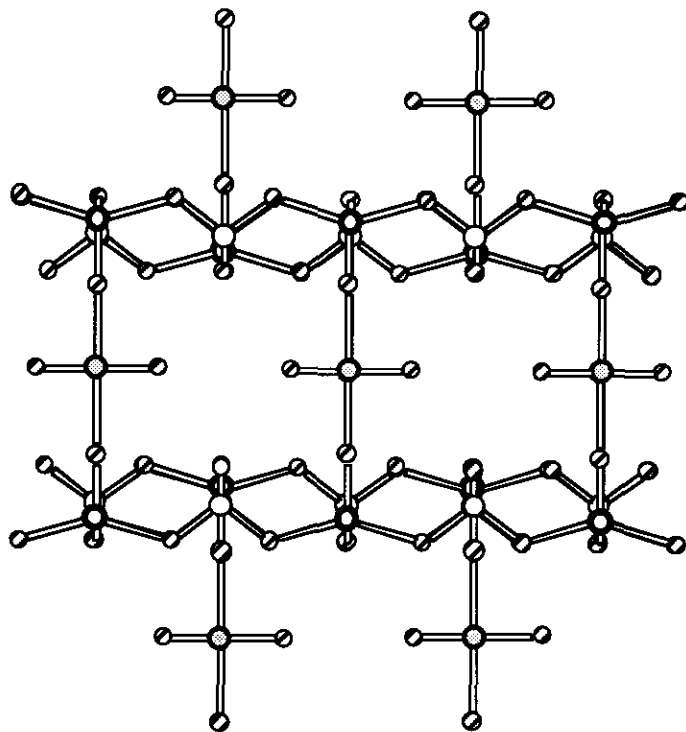
FIG. 5. A view of the structure of $[Ni(H_2O)_4][VO(PO_4)]_2$, showing the $\{VO(PO)_4\}$ layers interconnected by $\{Ni(H_2O)_4\}^{2+}$ groups.

References

1. M. S. WHITTINGHAM AND A.J. JACOBSON (Eds.), "Intercalation Chemistry," Academic Press, New York (1982).
2. A. CLEARFIELD, *Chem. Rev.* **88**, 125 (1991).
3. E. BORDES, P. COURTINE, AND G. PANNETIER *Ann. Chim. (Paris)* **8**, 105 (1973); B. JORDAN AND C. CALVO, *Can. J. Chem.* **51**, 2621 (1973); R. GOPAL AND C. CALVO *J. Solid State Chem.* **5**, 432 (1972).
4. H. R. TIETZE, *Aust. J. Chem.* **34**, 2035 (1981).
5. L. BENES, J. VOTINSKY, J. KALOUSOVA, AND J. KLIKORKA *Inorg. Chim. Acta* **114**, 47 (1986); K. BENEKE AND G. LAGALY, *Inorg. Chem.* **22**, 1503 (1983).
6. J. W. JOHNSON, A. J. JACOBSON, J. F. BRODY, AND S. M. RICH, *Inorg. Chem.* **21**, 3820 (1982).
7. M. MARTINEZ-LARA, L. MORENO-REAL, A. JIMENEZ-LOPEZ, S. BRUQUE-GAMEZ, AND A. RODRIGUEZ-GARCIA, *Mater. Res. Bull.* **21**, 13 (1986).
8. J. W. JOHNSON AND A. J. JACOBSON, *Angew. Chem.* **95**, 422 (1983); M. R. ANTONIO, R. L. BARBOUR, AND P. R. BLUM, *Inorg. Chem.* **26**, 1235 (1987).
9. M. MARTINEZ-LARA, A. JIMENEZ-LOPEZ, L. MORENO-REAL, S. BRUQUE, B. CASAL, AND E. RUIZ-HITZKY, *Mater. Res. Bull.* **20**, 549 (1985).
10. G.-E. MATSUBAZASKI, S. OHTA, AND S. OKIMO *Inorg. Chim. Acta* **184**, 47 (1991).
11. G. CENTI, F. TRIFIRO, J. R. EBNER, AND V. M. FRANCHETTI, *Chem. Rev.* **88**, 55 (1988).
12. G. HUAN, J. W. JOHNSON, A. J. JACOBSON, E. W. CORCORAN, JR., AND D. P. GOSHORN, *J. Solid State Chem.* **93**, 514 (1991).
13. M. T. POPE AND A. MÜLLER, *Angew. Chem. Int. Ed. Engl.* **30**, 34 (1991).
14. R. C. HAUSHALTER AND L. A. MUNDI, *Chem. Mater.* **4**, 31 (1992).
15. $(Zn_2VO(PO_4)_2)$ K. H. LII AND H. J. TSAI, *J. Solid State Chem.* **90**, 291 (1991); $(Cs_2V_3P_4O_{17})$ K. H. LII, Y. P. WANG, AND S. L. WANG, *J. Solid State Chem.* **80**, 127 (1989); $(\beta\text{-}K_2V_3P_4O_{17})$ K. H. LII, H. J. TSAI, AND S. L. WANG, *J. Solid State Chem.* **87**, 396 (1990); $(A_2VOP_2O_7$ $(A = Cs, Rb))$ K. H. LII AND S. L. WANG, *J. Solid State Chem.* **82**, 239 (1989); $(A VP_2O_7$ $(A = Li, Cs))$ K. H. LII, Y. P. WANG, Y. B. CHEN, AND S. L. WANG, *J. Solid State Chem.* **86**, 143 (1990) and references therein; $(NaVOPO_4)$ K. H. LII, C. H. LI, T. M. CHEN, AND S. L. WANG, *Z. Kristallogr.* **197**, 67 (1991); $(RbV_3P_3O_{17+x})$ K. H. LII AND C. S. LEE, *Inorg. Chem.* **29**, 3298 (1990).

16. $(A_{0.5}VOPO_4 \cdot xH_2O$ (A = Na, x = 2.0; A = K, x = 1.5)) S. L. WANG, H. Y. KANG, C. Y. CHENG, AND K. H. LII, *Inorg. Chem.* **30**, 3496 (1991); $(K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O)$ K. H. LII AND H. J. TSAI, *Inorg. Chem.* **30**, 446 (1991); $(K_2(VO)_3(HPO_4)_4)$ K. H. LII AND H. J. TSAI, *Solid State Chem.* **91**, 331 (1991).

17. $((Me_2NH_2)K_4[V_{10}O_{10}(OH)_4(PO_4)_7(H_2O)_2] \cdot 4H_2O)$ V. SOGHOMONIAN, Q. CHEN, R. C. HAUSHALTER, J. ZUBIETA, AND C. J. O'CONNOR, *Science* **259**, 1596 (1993); $(Cs[(V_2O_3)(HPO_4)_2(H_2O)])$ R. C. HAUSHALTER, Z. WANG, M. E. THOMPSON, J. ZUBIETA, AND C. J. O'CONNOR, *Inorg. Chem.*, in press; $(K_2[(VO)_2V(PO_4)_2(HPO_4)(H_2PO_4)(H_2O)_2])$ R. C. HAUSHALTER, Z. WANG, M. E. THOMPSON, J. ZUBIETA, AND C. J. O'CONNOR, *Inorg. Chem.*, in press; $(Cs[V_2(PO_4)(HPO_4)_2(H_2O)_2]$ and $K[(VO)V$ $(HPO_4)_3(H_2O)_2])$ R. C. HAUSHALTER, Z. WANG, M. E. THOMPSON, AND J. ZUBIETA, *Inorg. Chem.*, in press; $((H_3NCH_2CH_2NH_3)(H_3NCH_2CH_2NH_2)$ $[V(H_2O)_2(VO)_8^-(OH)_4(HPO_4)_4(PO_4)_4] \cdot 2H_2O)$ V. SOGHOMONIAN, Q. CHEN, R. C. HAUSHALTER, J. ZUBIETA, *Angew. Chem. Int. Ed. Engl.* **32**, 610 (1993).

18. M. I. KHAN, Q. CHEN, AND J. ZUBIETA, *J. Chem. Soc. Chem. Commun.*, in press.

19. D. BELTRAN-PORTER, P. AMOROS, R. IBANĒZ, E. MARTINEZ, AND A. BELTRAN-PORTER, *Solid State Ionics* **32/33**, 57 (1989).

20. F. CAVANI, G. CENTI, AND F. TRIFIRO, *J. Chem. Soc. Chem. Commun.*, 492 (1985).

21. K. H. LII AND L. F. MAO, *J. Solid State Chem.* **96**, 436 (1992).