Journal of Solid State Chemistry **159**, 239–243 (2001)
doi:10.1006/jssc.2001.9185, available online at http://www.idealibrary.com on IDEAL®

A Novel Phosphovanadate of Co(III) Hexammine: $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$

S. Boudin,*[1] J. Chardon,* M. Daturi,† and B. Raveau*

*Laboratoire CRISMAT, UMR 6508 associée au CNRS; and †Laboratoire de Catalyse et de Spectroscopie, ISMRA et Université de Caen,
6 Bd du Maréchal Juin, 14050 Caen Cedex, France*

Received December 4, 2000; in revised form March 13, 2001; accepted March 26, 2001

The new phosphovanadate $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ has been synthesized by a hydrothermal method at 220°C. It crystallizes in the $P2_1/c$ space group with $a = 9.5206(8)$, $b = 6.9631(6)$, $c = 17.108(1)$, $\beta = 93.028(7)$, and $Z = 4$. The structural resolution using single-crystal X-ray diffraction leads to $R(F_o) = 3.63\%$ and $R_w(F_o^2) = 10.67\%$. This structure consists of $[Co(NH_3)_6]^{3+}$ cations and $[V_{1.5}P_{0.5}O_6OH]^{3-}$ anions assembled in a distorted rock salt arrangement. The presence of the Co(III) hexammine complex $[Co(NH_3)_6]^{3+}$ is particularly original in this structure since no complexes have been isolated up to now in phosphovanadates. The $V_{1.5}P_{0.5}O_6OH$ diphosphovanadate group, with one vanadium tetrahedral site and one tetrahedral site statistically occupied by 0.5 vanadium and 0.5 phosphorus atom, corresponds to the random distribution of V_2O_6OH and VPO_6OH groups as confirmed by the IR spectroscopy study. Magnetic measurements show that the Co(III) cation adopts a low spin configuration.

Key Words: **hydrothermal synthesis; vanadium phosphate; cobalt III hexammine complex; crystal structure.**

INTRODUCTION

The introduction of cobalt (III) complexes in tetrahedral frameworks, as templating agents, has allowed attractive microporous materials to be generated, as shown by the molecular sieve and the silica zeolite discovered by Balkus and Shepelev (1) and by Freyhardt *et al.* (2), respectively. Based on the great inertness and high stability of cobalt (III) complexes, Morgan *et al.* (3) synthesized the Co(III) trisethylenediamine aluminum phosphate $Co(en)_3Al_3P_4O_{16} \cdot 3H_2O$, demonstrating the great ability of such a template to form a layered structure. Then, several new layered aluminum phosphates, involving Co(III) trispropylenediamine and bisdiethylenetriamine complexes, were synthesized by Bruce *et al.* (4, 5). Recently Morgan *et al.* (6) showed the great ability of Co(III) hexammine complex to form a new aluminum phosphate with a layered structure (6). These attractive results suggest the possibility of generating new microporous materials in view of catalytic or separation applications, by associating Co(III) amino complexes with tetrahedral frameworks like phosphates.

Vanadium, owing to its well known ability to form efficient catalysts, is of great interest since, besides its various oxidation states, it also exhibits several types of coordination from octahedral to tetrahedral. Thus, it should be possible to synthesize vanadates with an open framework, using transition metal complexes as templating agents. The synthesis of amino copper and zinc vanadates (7, 8) involving VO_4 tetrahedra supports this viewpoint. Nevertheless, to date, no aminocobalt(III) vanadate has been isolated to our knowledge. We report herein the first phosphovanadate involving complex Co(III) ions, $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$. This diphosphovanadate consists of isolated Co(III) hexammine cations $[Co(NH_3)_6]^{3+}$ and diphosphovanadate anions $[V_{1.5}P_{0.5}O_6OH]^{3-}$, whose cohesion is ensured through ionic and hydrogen bonds.

CRYSTAL GROWTH AND ANALYSIS

Orange crystals of $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ were synthesized by a hydrothermal method. The precursors $Co(NH_3)_6(NO_3)_3$, V_2O_5, and $H(NH_4)_2PO_4$ in ratios 2:1:2 were introduced with 2 cc of water in a 25-ml Teflon container sealed in a steel autoclave and heated at 220°C for 20 h and slowly cooled down to 100°C at a rate of 1°/h for 120 h. By this method orange needles of the new phase were obtained beside pink lamellas of the cobalt phosphate $NH_4CoPO_4 \cdot H_2O$ previously synthesized (9). The presence of Co, V, and P atoms in orange needles was confirmed by EDS analysis. It must be emphasized that this cobalt (III) hexammine phosphovanadate can be obtained as a practically monophasic sample by adding the previous solid precursors to 2 cc of an ammonia solution (28 wt%). In this preparation, large crystals without inclusions were selected for the chemical and physical characterizations. The N/H

---

[1] To whom correspondence should be addressed. Fax: (33)-2-31-95-16-00. E-mail: sophie.boudin@ismra.fr.

0022-4596/01 $35.00

ratios (23.72%/5.52%) measured by the elemental microanalysis are in good agreement with the expected ones (22.96%/5.19%). The thermogravimetric analysis was performed in air between 25 and 800°C on a SETARAM microbalance. A weight loss of 32.5% occurs between 200 and 450°C; it corresponds to the release of six molecules of ammonia and one hydroxyl group per formula unit ($\Delta m = 32.53\%$). According to XRD, the resulting products are V_2O_5 and β $Co_2P_2O_7$.

STRUCTURE DETERMINATION

A $0.068 \times 0.089 \times 0.239$ mm^3 orange needle of $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ was selected for the structure determination. The cell parameters were refined at 20°C using 25 reflections. The data were collected with a CAD Enraf Nonius four circles diffractometer using the Mo$K\alpha$ radiation. The data set was corrected for Lorentz and polarization effects and for absorption using Gaussian integration methods with the JANA98 software (10). The structure resolutions were performed with the SHELX97 programs (11). The extinction conditions, $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, are consistent with the $P2_1/c$ space group. The structure resolution leads to $R(F_o) = 3.63\%$ and $Rw\ (F_o^2) = 10.67\%$ (Table 1) for the atomic coordinates listed in Table 2. The bond valence calculations according to Altermatt and Brown method (12), indicate that vanadium and phosphorus are pentavalent and allow the hydrogen atom of the hydroxyl groups to be located, forming a bond with O(3) (Table 3).

TABLE 1
Crystallographic Parameters of $Co(NH_3)_6(V_{1.5}P_{0.5})O_6(OH)$

Chemical formula	$Co(NH_3)_6(V_{1.5}P_{0.5})O_6(OH)$
Formula weight (g)	366.0
Crystal habit	Orange needle
a (Å)	9.5206(8)
b (Å)	6.9631(6)
c (Å)	17.108(1)
β (°)	93.028(7)
V (Å^3)	1132.6(2)
Space group (No.)	$P2_1/c$ (No. 14)
ρ_{calc} (g cm^{-1})	2.15
T (°C)	20
λ (Mo$K\alpha$) (Å)	0.71073
$h_{min} \rightarrow h_{max}$	$-18 \rightarrow 18$
$k_{min} \rightarrow k_{max}$	$0 \rightarrow 13$
$l_{min} \rightarrow l_{max}$	$0 \rightarrow 33$
Standard reflections	3 every 3000 s
Measured reflections	9296
Independent reflections with $I > 3\sigma(I)$	2906
μ (Mo$K\alpha$) (mm^{-1})	2.79
Absorption correction	Gaussian
T_{min}, T_{max}	0.736, 0.853
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0648 \times P)^2 + 2.84 \times P]$ with $P = (\mathrm{Max}\ (F_o^2, 0) + 2 \times F_c^2)/3$
Parameters refined	146
ρ_{max}, ρ_{min}	0.87, -0.66
$R(F_o)^a$ (%)	3.63
$R_w(F_o^2)^b$ (%)	10.67

[a] $R(F_o) = \sum \|F_o| - |F_c\| / \sum |F_o|$.

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

TABLE 2
Atomic Parameters of $Co(NH_3)_6(V_{1.5}P_{0.5})O_6(OH)$

Atom	x	y	z	U_{eq}	Occ
Co	0.22401(5)	0.12125(7)	0.13822(3)	0.01235(9)	
V(1)	0.27339(7)	0.5553(1)	0.93033(3)	0.0168(1)	
V(2)	0.27721(7)	0.5568(1)	0.34408(4)	0.0145(1)	0.5
P	0.27721(7)	0.5568(1)	0.34408(4)	0.0145(1)	0.5
O(1)	0.1418(3)	0.4945(5)	0.8707(2)	0.0295(7)	
O(2)	0.2155(4)	0.6211(5)	0.0154(2)	0.0269(6)	
HO(3)	0.3912(4)	0.3585(5)	0.9460(2)	0.0284(7)	
O(4)	0.3662(3)	0.7471(5)	0.3834(2)	0.0243(6)	
O(5)	0.1621(3)	0.4978(5)	0.4030(2)	0.0248(6)	
O(6)	0.2078(4)	0.6182(5)	0.2614(2)	0.0282(6)	
O(7)	0.3907(3)	0.3912(5)	0.3339(2)	0.0246(6)	
N(1)	0.1208(3)	$-0.1233(5)$	0.1363(2)	0.0188(5)	
N(2)	0.3493(3)	0.0320(5)	0.2260(2)	0.0207(6)	
N(3)	0.0950(3)	0.2222(5)	0.2145(2)	0.0198(6)	
N(4)	0.3524(3)	0.0234(5)	0.0606(2)	0.0184(6)	
N(5)	0.3309(4)	0.3642(5)	0.1403(2)	0.0199(6)	
N(6)	0.0944(3)	0.2131(5)	0.0523(2)	0.0196(6)	

Note. $U_{eq} = 1/3 \sum U_{ij}$.

STRUCTURE DESCRIPTION AND COMMENTS

The projection of the structure of this new phosphovanadate along b (Fig. 1) and along a (Fig. 2) shows that it consists of isolated cobalt (III) hexammine cations $[Co(NH_3)_6]^{3+}$ and diphosphovanadate anions $[V_{1.5}P_{0.5}O_6OH]^{3-}$. In this very simple structure, the $[Co(NH_3)_6]^{3+}$ cations and $[V_{1.5}P_{0.5}O_6OH]^{3-}$ anions alternate along a and c, forming a distorted rock-salt-type arrangement in the (a, c) plane (Fig. 1). The projection of the structure along a (Fig. 2) shows that the $[V_{1.5}P_{0.5}O_6OH]^{3-}$ ions and the $[Co(NH_3)_6]^{3+}$ cations form rows running along b, one

TABLE 3
Bond Valence Calculations for the Vanadium, Phosphorus, and Oxygen Atoms in $Co(NH_3)_6(V_{1.5}P_{0.5})O_6(OH)$

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	$\sum v$
V(1)	1.600	1.520	1.056	0.898				**5.07**
V(2)/P				1.029	1.381	1.363	1.337	**5.11**
$\sum v$	**1.60**	**1.52**	**1.06**	**1.93**	**1.38**	**1.36**	**1.34**	

Note. The R_{ij} bond valence parameter for the V(2)/P atom is equal to $R_{ij} = (R_{V^{5+}-O} + R_{P^{5+}-O})/2 = 1.7035$.

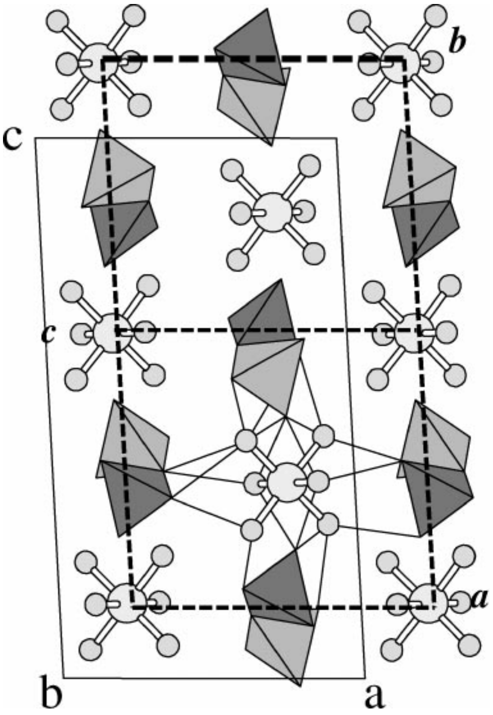

FIG. 1. Projection of the structure of $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ along *b*. The VO_4 and $V_{0.5}P_{0.5}O_4$ tetrahedra are drawn in medium and dark gray polyhedra, respectively. The $[Co(NH_3)_6]^{3+}$ complexes are drawn with balls and sticks. The dashed cell corresponds to the distorted cell of the rock salt arrangement of the $[Co(NH_3)_6]^{3+}$ and $[V_{1.5}P_{0.5}O_6OH]^{3-}$ ions. The N..O bonds shorter than 3.25 Å are drawn with black lines around one $[Co(NH_3)_6]^{3+}$ cation.

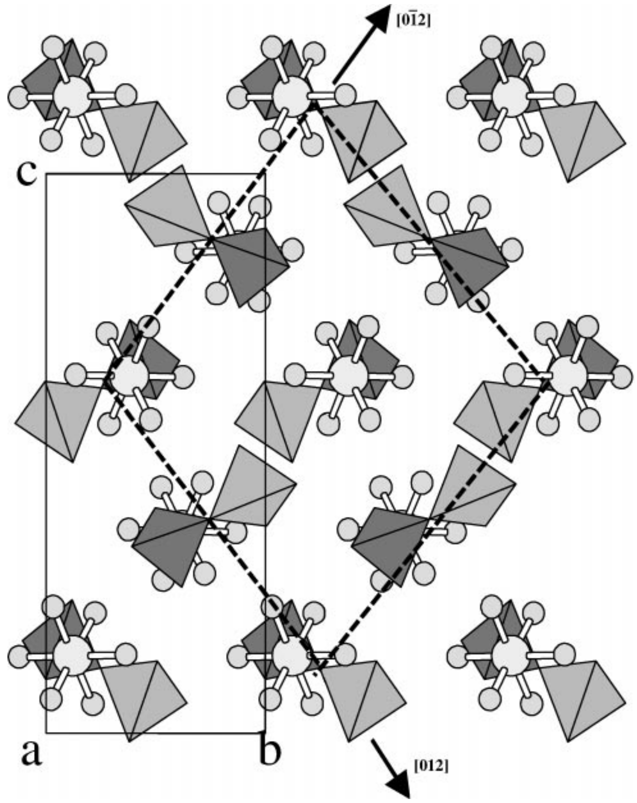

FIG. 2. Projection of the structure of $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ along *a*. The dashed lines indicate the distorted cell of the rock salt arrangement of the $[Co(NH_3)_6]^{3+}$ and $[V_{1.5}P_{0.5}O_6OH]^{3-}$ ions.

$[V_{1.5}P_{0.5}O_6OH]^{3-}$ anions alternating with one $[Co(NH_3)_6]^{3+}$ cation along [0$\bar{1}$2] and [012] directions, so that the arrangement of these two kinds of ions in the (*b*, *c*) plane can be described as derived from a strongly distorted rock salt structure (see the distorted cell of the rock salt arrangement in dashed lines), if one excepts the different orientations of the $[V_{1.5}P_{0.5}O_6OH]^{3-}$ anions.

One specific characteristic of this structure deals with the geometry and chemical composition of the diphosphovanadate anion $[V_{1.5}P_{0.5}O_6OH]^{3-}$. In this ditetrahedral group one tetrahedron V(1) is entirely occupied by vanadium and contains the hydroxyl group. In this VO_3OH tetrahedron, the longest V–O bond (1.843(3) Å), corresponds to the bridging oxygen O(4),[2] as usually observed in diphosphate or divanadate groups. The second tetrahedron is occupied by two kinds of elements simultaneously, V(2) and P, so that in the $(V,P)O_4$ tetrahedron, the average (V,P)–O distances, are significantly smaller than in the first tetrahedron, ranging from 1.582(3) to 1.693(3) Å, the largest distance corresponding to the bridging oxygen O(4). Such a coexistence of V(V) and P(V) on the same crystallographic site has been previously observed in several vanadium phosphates (13–17). It implies a statistical distribution, in the structure of divanadate anions$[V_2O_6OH]^{3-}$ and vanadophosphate anions $[VPO_6OH]^{3-}$. The infrared study of this compound supports this viewpoint, as described below.

The geometry of the Co(III) hexammine cation $[Co(NH_3)_6]^{3+}$ is classical, forming a regular octahedron, with Co–N distances ranging from 1.966(3) to 1.975(3) Å.[2] These results, show that, surprisingly, $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ is rather stable since it could be prepared at 220°C, whereas Morgan *et al.* (6), showed that the cations $[Co(NH_3)_6]^{3+}$ tends to decompose above 150°C and synthesized the aluminum phosphate $(NH_4)_3[Co(NH_3)_6]_3[Al_2(PO_4)_4]_2 \cdot 2H_2O$ at 150°C. In our compound the stability is, as for the latter, ensured through ionic bonds between $[Co(NH_3)_6]^{3+}$ cations and $[V_{1.5}P_{0.5}O_6OH]^{3-}$ anions, but the hydrogen bonding network is denser. Indeed with O(V)..N and O(P,V)..N distances ranging from 2.908(4) to 3.842(5) Å and from 2.868(4) to 3.959(4) Å respectively,[2] we observed an average of 5.4 hydrogen bonds shorter than 4 Å per oxygen atom in $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ against an

---

[2] Structural details, distances, and angles can be obtained free of charge by ordering the crystal structure deposition file 411774 from FIZ Karlsruhe at the e-mail address crysdata@fiz-karlsruhe.de.

average of 4.06 hydrogen bonds per oxygen atom in $(NH_4)_3[Co(NH_3)_6]_3[Al_2(PO_4)_4]_2 \cdot 2H_2O$.

MAGNETIC CHARACTERIZATION

Magnetic susceptibility measurements were performed using a SQUID magnetometer between 4.2 and 300 K. The magnetic susceptibility follows the Curie–Weiss law between 4.2 and 150 K with $C = 0.0174$ emu K mol^{-1} and $\theta = -14.6$ K. The Curie constant which corresponds to an effective moment of 0.38 μ_B per Co^{3+} ions indicates that the Co^{3+} adopts a low-spin configuration. Above 150 K, the deviation from the Curie–Weiss law is due to insignificant and too weak susceptibility values.

INFRARED SPECTROSCOPY STUDY

An FTIR experiment has been performed on a 100-mg KBr pressed disk containing 2% of the analyzed phase accurately dispersed and with a KBr beam splitter. The spectra have been recorded by a Nicolet Magna 750 FT-IR spectrometer (resolution 4 cm^{-1}) and treated by the help of the Nicolet OMNIC software.

The FT-IR spectrum of the new phase is shown in Fig. 3. As reported by Davydov for ammonia in amino complexes (18), the two strong bands at 3272 and 3172 cm^{-1} are assigned to the $\nu_{as}(NH_3)$ and $\nu_s(NH_3)$ stretches, respectively, and the ones located at $\sim$1635 and 1340 cm^{-1} to the corresponding $\delta_{as}(NH_3)$ and the $\delta_s(NH_3)$ bendings. The weaker feature at 3047 cm^{-1} is likely due to the ν[(P)–OH] coupling mode, while other ν(P–OH) vibrations contribute to the broad band extending from 3500 to 2500 cm^{-1}. The corresponding δ_{ip}(POH) and δ_{oop}(POH) bending modes are situated at 1145 and $\sim$633 cm^{-1}. At 1092 and 1047 cm^{-1} we find the bands due to the asymmetric stretch $\nu_{as}(PO_3)$ of the phosphate groups, followed by the corresponding symmetric mode $\nu_s(PO_3)$ at lower wavenumbers (19–22). As already shown (23, 24), the band wavenumbers corresponding to the $\nu_{as}(PO_3)$ mode of the phosphate tetrahedra are low due to long P–O bonds generated by interactions between the oxygen atoms and the $[Co(NH_3)_6]^{3+}$ cations. The $\delta(PO_3)$ bending can be found at 537 cm^{-1}. The band at 935 cm^{-1} could be assigned to a ν[P–(OH)] stretch. The δ_{as}(OPO) and δ_s(OPO) bendings are responsible for the features at 565 and 473 cm^{-1}, respectively (19–22). At 972 cm^{-1} we observe the ν(V=O) stretching mode of the vanadyl species, while the strong and sharp feature at lower wavenumbers (916 cm^{-1}) reasonably assigned to the ν_s(VOV) vibration is in good agreement with the presence of V_2O_6OH groups. The additional bands at 867 and 839 cm^{-1} can be explained by the presence of VPO_6OH groups and can correspond to the ν(VOP) stretching modes of diphosphovanadate group since they occur at intermediate positions between the vibrations ranges usually observed for VOV and POP bonds (25). The shoulder at 795 cm^{-1} by consequence can be explained by the ν[V–(O=V)] couplings in the same units, by analogy with vanadyl diphosphates (21).

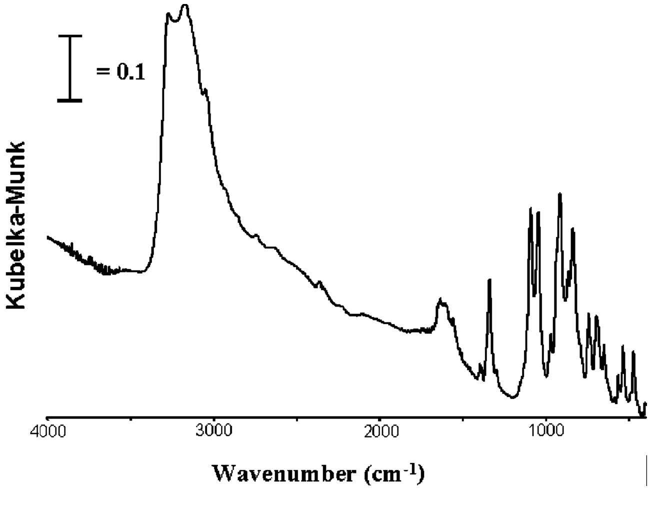

FIG. 3. FT-IR spectrum of $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ single crystals.

CONCLUDING REMARKS

This study of the compound $Co(NH_3)_6(V_{1.5}P_{0.5})O_6OH$ has allowed the first phosphovanadate with complex cobalt (III) cations to be synthesized. Although the $[Co(NH_3)_6]^{3+}$ and $[V_{1.5}P_{0.5}O_6OH]^{3-}$ ions are isolated, this study opens the route to the research of a new family of vanadates and phosphovanadates, whose dimensionality should be increased and tuned by increasing the complex cation/(V + P) ratio or by reducing the charge of the complex cation as suggested by the 2D and 1D vanadates previously studied (7, 8). Further investigations are in progress, using different ammines in order to favor the formation of microporous frameworks.

REFERENCES

1. K. J. Balkus and S. Shepelev, *Microporous Mater.* **1,** 383 (1993).
2. C. C. Freyhardt, M. Tsapatsis, R. F. Lobo, K. J. Balkus, and M. E. Davies, *Nature* **23,** 295 (1996).
3. K. R. Morgan, G. J. Gainsford, and N. B. Milestone, *J. Chem. Soc. Chem. Commun.* 425 (1995).
4. D. A. Bruce, A. P. Wilkinson, M. G. White, and J. A. Bertrand, *J. Chem. Soc. Chem. Commun.* 2059 (1995).
5. D. A. Bruce, A. P. Wilkinson, M. G. White, and J. A. Bertrand, *J. Solid State Chem.* **125,** 228 (1996).
6. K. R. Morgan, G. J. Gainsford, and N. B. Milestone, *J. Chem. Soc. Chem. Commun.* 61 (1997).
7. S. Aschwanden, H. W. Schmalle, A. Reller, and H. Oswald, *Mat. Res. Bull.* **28,** 45 (1993).
8. Y. Zhang, J. Debord, C. O'Connor, R. Haushalter, A. Clearfield, and J. Zubieta, *Angew. Chem.* **35,** 981 (1996).

9. D. Trangui, A. Durif, J. C. Guitel, and M. T. Averbuch-Pouchot, *Bull. Soc. Chim. Fr.* **1968,** 1759 (1968).
10. V. Petricek and M. Dusek, Crystallographic computing system JANA98, Institute of Physics, Academy of Sciences of the Czech Republic, Praha (1998).
11. G. M. Sheldrick, SHELX97, University of Göttingen, Germany (1997).
12. D. Altermatt and I. D. Brown, *Acta Cryst. A* **43,** 125 (1987).
13. K. L. Idler and C. Calvo, *Can. J. Chem.* **53,** 3665 (1975).
14. K. L. Idler, C. Calvo, and H. N. Ng, *J. Solid State Chem.* **25,** 285 (1978).
15. J. M. Kiat, P. Garnier, G. Calvarin, and M. Pirot, *J. Solid State Chem.* **103,** 490 (1993).
16. S. Boudin, A. Grandin, A. Leclaire, M. M. Borel, and B. Raveau, *J. Solid State Chem.* **111,** 365 (1994).
17. C. Ninclaus, R. Retoux, D. Riou, and G. Férey, *J. Solid State Chem.* **122,** 139 (1996).
18. A. A. Davydov, "Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides" (C. H. Rochester, Ed.) Wiley, Chichester, 1984.
19. G. Centi, F. Trifirò, G. Busca, J. Ebner, and J. Gleaves, *Discuss. Faraday Soc.* **87,** 215 (1989).
20. G. T. Stranford and R. A. Condrate, *J. Solid State Chem.* **52,** 248 (1984).
21. L. Lezama, J. M. Rojo, J. L. Pizarro, M. I. Arriortua, and T. Rojo, *Solid State Ionics* **63–65,** 657 (1993).
22. J. Kumamoto, *Spectrochim. Acta* **21,** 345 (1965).
23. M.-M. Borel, A. Leclaire, J. Chardon, M. Daturi, and B. Raveau, *J. Solid State Chem.* **149,** 149 (2000).
24. H. Y. Kang, S. L. Wang, and K. H. Lii, *Acta Crystallogr. C* **48,** 975 (1992).
25. U. Costantino and A. La Ginesta, *Thermochim. Acta* **58,** 179 (1982).