

# Hydrothermal Synthesis and Structure Determination of 1,4-Diaminobutane Metavanadate

Didier Riou and Gérard Férey

Laboratoire des Fluorures, URA-CNRS 449, Université du Maine, Avenue Olivier Messiaen, 72017 Le Mans Cedex, France

Received March 11, 1996; accepted March 18, 1996

$\text{N}_2\text{C}_4\text{H}_{14}$ ,  $(\text{VO}_3)_2$  is a metavanadate intercalated by organic molecules. It has been hydrothermally prepared (453 K, 24 hr, autogenous pressure) from a mixture of  $\text{V}_2\text{O}_5$ :HF:1,4-diaminobutane: $\text{H}_2\text{O}$  in the molar ratio 1:2:1.5:80. Its structure was solved by single crystal X-ray diffraction. It is monoclinic (space group  $P 2_1/n$  (No. 14)) with lattice parameters  $a = 6.8389(4)$  Å,  $b = 5.5550(3)$  Å,  $c = 14.345(1)$  Å,  $\beta = 99.922(6)^\circ$ ,  $V = 536.82(6)$  Å<sup>3</sup>,  $Z = 2$ . The refinement, led from 2423 unique reflections ( $I > 2\sigma(I)$ ), converges to  $R_1(F) = 0.024$  and  $wR_2(F^2) = 0.071$ .  $\text{N}_2\text{C}_4\text{H}_{14}$ ,  $(\text{VO}_3)_2$  crystallizes in a pyroxene-related structure; the new type of tetrahedral  $(\text{VO}_3)_\infty$  chains is compared to those already described in the literature. © 1996 Academic Press, Inc.

## INTRODUCTION

In the last decade, many works have been devoted to the synthesis of microporous compounds. Nevertheless, two events seem particularly primordial in this course: the discovery in 1982 of a new family of aluminophosphates by Flanigen *et al.* (1) and in 1986 the use of the fluorine route during the hydrothermal synthesis by Guth *et al.* (2). In this way, we have evidenced a new class of oxyfluorinated materials noted ULM-*n* (for University Le Mans) first illustrated by gallophosphate compounds (3 and refs. therein). We recently realized the entire substitution of gallium or aluminum by a 3d transition metal:  $\text{Fe}_4(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_3$ ,  $\text{N}_2\text{C}_6\text{H}_{14}$  (ULM-12) is the first magnetic microporous ferric phosphate (4) whereas  $\text{V}_2^{\text{IV}}\text{PO}_8\text{F}$ ,  $\text{N}_2\text{C}_2\text{H}_{10}$  (ULM-7) is the unique three-dimensional oxyfluorinated vanadophosphate (5). In the meantime, Haushalter *et al.* synthesized a lot of compounds templated by organic molecules in the V–P–O system (6).

The ability of  $\text{V}^{\text{V}}$  for adopting a tetrahedral coordination incited us to substitute  $\text{P}^{\text{V}}$  by  $\text{V}^{\text{V}}$  in our type of compounds. This type of substitution, well known in classical solid state chemistry (7), was obtained with the two-dimensional compounds  $(\text{NH}_4)_2\text{V}^{\text{IV}}\text{O}(\text{V}_{2-x}\text{P}_x\text{O}_7)$  (8) and  $\text{V}^{\text{IV}}\text{O}(\text{V}^{\text{V}}\text{O}_4)$ , 0.5 amine (piperazine, ethylenediamine and 1,3-diaminopropane) (9, 10), vanadyl vanadates that we have recently

synthesized. This possibility of  $\text{P} \leftrightarrow \text{V}$  substitution is now studied as a function of the dimensionality of the structure.

This paper deals with the synthesis and the structure determination of a metavanadate templated by 1,4-diaminobutane. Its  $(\text{VO}_3)_\infty$  chains are compared to those encountered in the pyroxene structure types.

## EXPERIMENTAL

### Synthesis

The title compound was prepared hydrothermally from a mixture of vanadium oxide ( $\text{V}_2\text{O}_5$ , Aldrich 99.6%), hydrofluoric acid (40% HF Prolabo RP Normapur), 1,4-diaminobutane ( $\text{N}_2\text{C}_4\text{H}_{12}$ , Alrich 99%), and  $\text{H}_2\text{O}$  in the molar ratio 1:2:1.5:80. The mixture was placed without stirring in a Teflon lined steel autoclave for 24 hr at 453 K under autogenous pressure. The acidity of the medium decreases from  $\text{pH} \approx 8\text{--}9$  to 5 during the synthesis. The resulting product was washed with water then dried in air at room temperature. The major phase (>75% by visual observation) of light yellow crystals was  $\text{N}_2\text{C}_4\text{H}_{14}$ ,  $(\text{VO}_3)_2$ . The study of the minor component of the reaction, constituted by dark green crystals, is currently in progress. Chemical analysis of  $\text{N}_2\text{C}_4\text{H}_{14}$ ,  $(\text{VO}_3)_2$  proves that it does not contain any  $\text{F}^-$  ions. Its organic content was confirmed by TGA analysis on a SETARAM apparatus operating under oxygen flow (heating rate =  $5^\circ\text{C}/\text{min}$ ). The degradation of the amine occurs between 230 and  $380^\circ\text{C}$ , the weight loss is 32.1 vs 31.25% for the expected value.

### Structure Determination

A suitable crystal with trapezoidal prismatic shape was selected by optical observation. Its quality was checked on Laue photographs. The data collection was performed on a Siemens AED2 four-circle diffractometer equipped with a Stoe goniometer. The intensities were corrected from Lorentz and polarization effects and an absorption correction relative to the crystal morphology was applied. The

TABLE 1  
Crystal Data and Structure Refinement for  $N_2C_4H_{14}, (VO_3)_2$

Empirical formula	$C_2H_7NO_3V$
Formula weight	144
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P 21/n$
Unit cell determination	38 reflections ( $28 \leq 2\theta \leq 32^\circ$ )
Unit cell dimensions	$a = 6.8389(4)$ Å $b = 5.5550(3)$ Å $\beta = 99.922(6)^\circ$ $c = 14.345(1)$ Å
Volume/Z	536.82(6) Å <sup>3</sup> /4
$F(000)$	292
Density (calculated)	1.782 g · cm <sup>-3</sup>
Absorption coefficient	1.851 mm <sup>-1</sup>
Transmission factors	$T_{\min.} = 0.180, T_{\max.} = 0.740$
Crystal size	0.391 × 0.228 × 0.099 mm
Natural faces	{-1 0 1} × {0 -1 0} × {1 0 1}
Theta range for data collection	2.50° to 40.0°
Index ranges	$-12 \leq h \leq 12, 0 \leq k \leq 10, 0 \leq l \leq 25$
Standard measurements (3)	0 2 6; 0 -2 6; -3 0 5
Maximum intensity variations	<1%
Reflections collected	4016
Independent reflections [ $I > 2\sigma(I)$ ]	2423 [ $R(\text{int}) = 0.062$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2423/0/67
Goodness-of-fit on $F^2$	0.343
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0240, wR_2 = 0.0707$
Extinction coefficient	0.026(2)
Largest diff. peak and hole	0.365 and $-0.416 e \cdot \text{Å}^{-3}$

conditions of data measurements are summarized in Table 1.

The structure was solved by direct methods using the TREF option of SHELXS 86 (11). The atoms of the inorganic part were first located. The amine was found by Fourier difference synthesis using SHELXL 93 (12); for the H atoms, some geometrical constraints were considered. An anisotropic thermal motion was applied to each atom except hydrogens which were refined with a common isotropic factor. After the last cycle refinement, the reliability factors  $R_1(F)$  and  $wR_2(F^2)$  (defined in (12)) were, respectively, 0.024 and 0.071 for 67 variables and 2423 unique reflections with  $I > 2\sigma(I)$ . The atomic coordinates and anisotropic displacement parameters are given in Tables 2a and 2b; the principal distances and angles are listed in Table 3.

## DISCUSSION

The structure of  $N_2C_4H_{14}, (VO_3)_2$  consists of single chains of corner-sharing  $VO_4$  tetrahedra running along [010] with the organic molecules intercalated between them (Fig. 1). Inside these chains, one observes two kinds

TABLE 2a  
Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{Å}^2 \times 10^3$ ) for  $N_2C_4H_{14}, (VO_3)_2$

Atoms	$x$	$y$	$z$	$U(\text{eq})$
V	1995(1)	392(1)	3115(1)	18(1)
O(1)	-267(2)	-167(3)	3274(1)	43(1)
O(2)	3357(2)	1293(2)	4105(1)	38(1)
O(3)	3187(2)	-2304(2)	2782(1)	30(1)
N	6892(2)	-2632(2)	4038(1)	25(1)
C(1)	943(2)	5743(3)	5040(1)	29(1)
C(2)	-2459(2)	4801(3)	4077(1)	33(1)
Ha	7818(9)	-1720(4)	3847(10)	44(2)
Hb	6714(20)	-2160(8)	4610(2)	44(2)
Hc	5757(11)	-2484(5)	3632(8)	44(2)
H(1a)	596(2)	7436(3)	5041(1)	44(2)
H(1b)	1547(2)	5449(3)	4486(1)	44(2)
H(2a)	-1884(2)	4435(3)	3521(1)	44(2)
H(2b)	-3608(2)	3771(3)	4068(1)	44(2)

Note.  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

of oxygen atoms: (i) the bridging anions which give long interatomic distances with the vanadium (1.804(2) and 1.808(2) Å), and (ii) the terminal apices which give short V–O distances (1.632(2) and 1.637(2) Å). According to the nomenclature proposed by Hawthorne and Calvo (13) for the pyroxene structures, the bridging oxygen is O(3), the free apex pointing toward the cations between the  $(VO_3)_\infty$  chains is O(2), and the third is O(1). The bond valence analysis calculated from the data of Brese and O'Keeffe (14) unambiguously indicates pentavalent vanadium. Therefore, the chemical formula of the tetrahedral chains is  $(VO_3)_\infty^-$  and the electroneutrality of the structure is ensured by the intercalation of one diprotonated amine between two  $(VO_3)_\infty^-$  files. Moreover, the structure is stabilized by strong interactions (Table 3) between the hydrogens of the ammoniums and the oxygens of the inorganic files.

TABLE 2b  
Anisotropic Displacement Parameters ( $\text{Å}^2 \times 10^3$ ) for  $N_2C_4H_{14}, (VO_3)_2$

Atoms	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
V	19(1)	17(1)	17(1)	1(1)	3(1)	1(1)
O(1)	26(1)	48(1)	58(1)	16(1)	18(1)	1(1)
O(2)	48(1)	40(1)	22(1)	-10(1)	-4(1)	4(1)
O(3)	35(1)	23(1)	30(1)	-9(1)	-1(1)	7(1)
N	20(1)	30(1)	24(1)	3(1)	2(1)	2(1)
C(1)	27(1)	25(1)	31(1)	4(1)	-1(1)	1(1)
C(2)	30(1)	27(1)	35(1)	-4(1)	-9(1)	1(1)

Note. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$ .

TABLE 3  
Principal Bond Lengths (Å) and Angles (°)  
in  $N_2C_4H_{14}, (VO_3)_2$

V	O(1)	[VO <sub>4</sub> ] polyhedron O(2)	O(3)	O(3)
O(1)	1.632(2)	2.684(2)	2.755(2)	2.839(2)
O(2)	110.4(1)	1.637(2)	2.840(2)	2.744(2)
O(3)	106.51(8)	111.16(7)	1.804(2)	2.998(1)
O(3)	111.14(8)	105.51(7)	112.21(8)	1.808(2)
1,4-Diaminobutane				
N–C(2): 1.492(2) (2×)		C(1)–C(1): 1.519(3)		
C(1)–C(2): 1.523(2) (2×)		C(1)–C(1)–C(2): 113.7(2) (2×)		
C(1)–C(1)–C(2): 113.7(2) (2×)		N–C(2)–C(1): 112.1(1) (2×)		
Hydrogen bonds				
O(1)–H(a): 1.87(1)		O(2)–H(b): 1.914(4)		
O(3)–H(c): 1.962(8)				

$N_2C_4H_{14}, (VO_3)_2$  presents a structure closely related to the silicates compounds of the pyroxene type. Their tetrahedral network is well known in the inorganic metavanadate series where the  $(VO_3)_\infty$  chains replace the analogous  $(SiO_3)_\infty$  chains. For the  $A VO_3$  ( $A$  = monovalent cation) compounds, the family is divided into two polymorph classes, only the  $\alpha$  form being of the pyroxene type (13, 15, 16). The same structural type is also encountered for

some compounds where the monovalent cation is substituted by a mono- (17) or divalent (18–20) organic cation. In this last case, the chemical formula becomes diammonium,  $(VO_3)_2$ . All these structures are built up from one unique type of  $(VO_3)_\infty$  chain (Fig. 2a). Its mean direction is given by the O(3) oxygens and all the free apices O(2) point on the same side of the chain. Another kind of zig-zag chain exists in  $Ba(VO_3)_2, H_2O$  (21) (Fig. 2b). The  $VO_4$  tetrahedra are shared by the corners but with a sequence of three tetrahedra (Fig. 2b) instead of two in the chains described above; the central tetrahedra indicate then the mean direction. The two types of tetrahedral files are drawn on Fig. 2.

In the title compound (Fig. 1), the  $(VO_3)_\infty$  chains belong to the first class but with the terminal oxygen O(2) pointing alternatively up and down the chain. We have also to mention 3-aza-1,5-pentamethylenediammonium,  $(VO_3)_2$  (22) which presents a different conformation of the linear chains of corner-sharing  $VO_4$  tetrahedra.

## CONCLUSION

$N_2C_4H_{14}, (VO_3)_2$  presents a metavanadate-like pyroxene framework intercalated by the diprotonated 1,4-diaminobutane. The originality of this one-dimensional structure consists in the hitherto unknown conformation of the tetrahedral  $(VO_3)_\infty$  chains.

By analogy with the recently described  $N_2C_2H_{10}, (VO)_2 (PO_4)_2(H_2PO_4)$  (23) whose inorganic part is constituted by

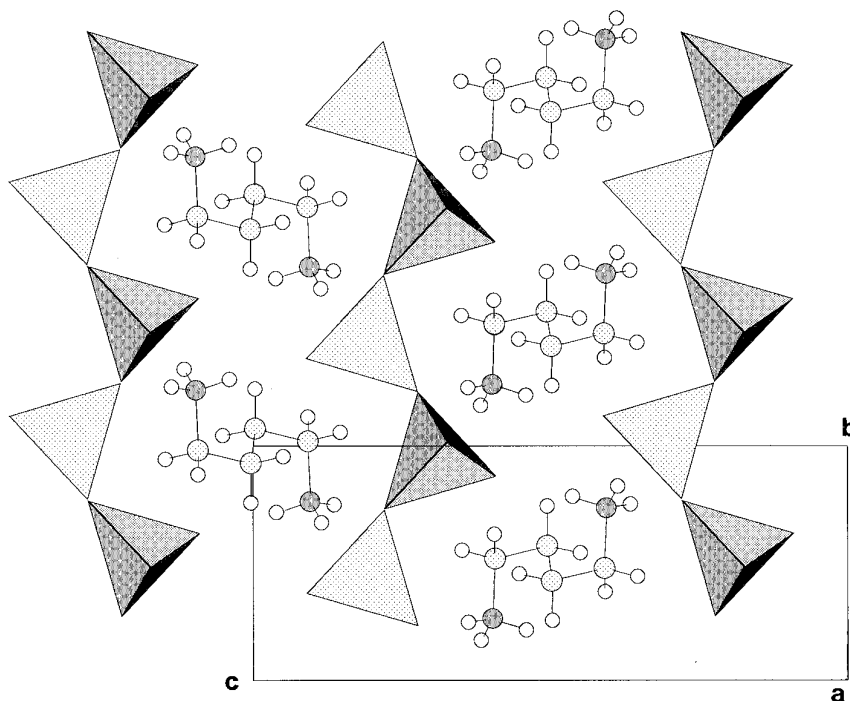


FIG. 1. Projection of  $N_2C_4H_{14}, (VO_3)_2$  along [100].

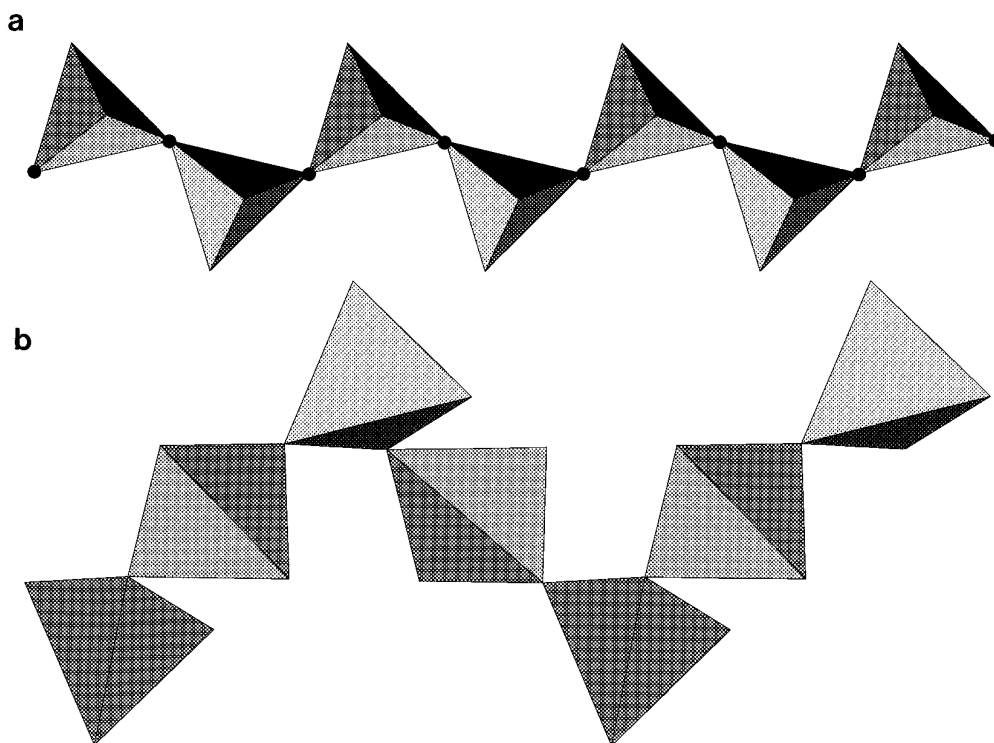


FIG. 2. Polyhedral representations of the  $(VO_3)_\infty$  chains (a) in the metavanadate of the  $\alpha$  form (the circles indicate O(3)), (b) in  $Ba(VO_3)_2 \cdot H_2O$ .

$\alpha$ -VOPO<sub>4</sub> (24) sheets related by one H<sub>2</sub>PO<sub>4</sub> tetrahedron, we are now trying to synthesize three-dimensional vanadyl vanadates.

## REFERENCES

1. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.* **104**, 1146 (1982).
2. J. L. Guth, H. Kessler, and R. Wey, *Stud. Surf. Sci. Catal.* **28**, 121 (1986).
3. G. Férey, *J. Fluorine Chem.* **72**, 187 (1995).
4. M. Cavellec, D. Riou, C. Ninclaus, J. M. Grenèche, and G. Férey, *Zeolites*, in press.
5. D. Riou and G. Férey, *J. Solid State Chem.* **111**, 422 (1994).
6. (a) V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, and J. O'Connor, *Science* **259**, 1596 (1993); (b) R. C. Haushalter, Z. Wang, M. E. Thompson, and J. Zubieta, *Inorg. Chem.* **32**, 3700 (1993); (c) V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, J. O'Connor, and Y. S. Lee, *Chem. Mater.* **5-12**, 1690 (1993).
7. (a) K. L. Idler, C. Calvo, and H. N. Ng, *J. Solid State Chem.* **25**, 285 (1978). (b) K. L. Idler and C. Calvo, *Can. J. Chem.* **53**, 3665 (1975).
8. C. Ninclaus, R. Retoux, D. Riou, and G. Férey, *J. Solid State Chem.* **122**, 139 (1996).
9. D. Riou and G. Férey, *Inorg. Chem.* **34**, 6520 (1995).
10. D. Riou and G. Férey, *J. Solid State Chem.* **120**, 137 (1995).
11. G. M. Sheldrick, *Acta Crystallogr. Sect. A* **46**, 467 (1990).
12. G. M. Sheldrick, "SHELXL-93, A Program for Crystal Structure Determination." University of Göttingen, Germany, 1993.
13. F. C. Hawthorne and C. Calvo, *J. Solid State Chem.* **22**, 157 (1977).
14. N. Brese and M. O'Keeffe, *Acta Crystallogr. Sect. B* **47**, 192 (1991).
15. F. Marumo, M. Isobe, S. Iwai, and Y. Kondo, *Acta Crystallogr. Sect. B* **30**, 1628 (1974).
16. R. D. Shannon and C. Calvo, *Can. J. Chem.* **51**, 265 (1973).
17. P. Roman, A. Aranzabe, A. Luque, and J. M. Gutierrez-Zorrilla, *Mater. Res. Bull.* **26**, 19 (1991).
18. W. Bensch, P. Hug, A. Reller, and H. R. Oswald, *Mater. Res. Bull.* **22**, 577 (1987).
19. J. Tyrseleva and F. Pavelcik, *Acta Crystallogr. Sect. C* **48**, 1207 (1992).
20. J. Tyrseleva, L. Kuchta, and F. Pavelcik, *Acta Crystallogr. Sect. C* **52**, 17 (1996).
21. L. Ulicka, F. Pavelcik, and K. Huml, *Acta Crystallogr. Sect. C* **43**, 2266 (1987).
22. P. Roman, R. Macias, A. Luque, and J. M. Gutierrez-Zorrilla, *Mater. Res. Bull.* **27**, 573 (1992).
23. W. T. A. Harrison, K. Hsu, and A. J. Jacobson, *Chem. Mater.* **7**, 2004 (1995).
24. B. Jordan and C. Calvo, *Can. J. Chem.* **51**, 2621 (1973).