Synthesis, Vibrational Spectra, and Single-Crystal X-ray Structure of the Phosphato-Bridged Dinuclear Peroxovanadate $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$

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Introduction

The role of vanadates as phosphate analogs in biochemistry has generated much interest since it was found that vanadium complexes, even at extremely low concentrations, can inhibit phosphoryl transfer enzymes.[1] A possible participation of vanadium(V)−phosphorus(V) compounds in biochemical processes stimulated several studies on the interaction of vanadates with phosphates in solutions. The formation of mixed phosphate/vanadate anhydrides has been established.[2,3] Although numerous solid heteropoly compounds of V(V) and P(V) are known[4] and polymeric oxovanadium phosphates have been intensively studied owing to their catalytic activity,[5] the stereochemistry of small vanadium−phosphorus molecular systems in the solid state is still very little explored.[6] Surprisingly little is also known about transition metal peroxo phosphato complexes. The crystal structure of a tetranuclear tungsten complex, $[N(C_6H_{13})_4{}^+]_3\{PO_4[WO(O_2)_2]_4\}^{3-}$, was published several years ago.[7] The preparation of peroxophosphatovanadates $M_3[VO(O_2)_2(HPO_4)]\cdot 2H_2O$ (M = NH_4, K) has been reported.[8,9]

As a part of our synthetic studies on peroxo complexes of vanadium(V),[10] we report here the synthesis and characterization of a novel peroxo phosphato complex $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$.

Experimental Section

Chemicals. Chemicals in this work were used as obtained from commercial sources; only NH_4VO_3 was purified by recrystallization. Deuterated chemicals D_2O_2, D_2O, and C_2D_5OD were from Isocommerz (Berlin); $ND_4D_2PO_4$ and ND_4VO_3 were prepared by recrystallization from D_2O.

Instrumentation. Infrared spectra were recorded on a Specord M-80 spectrometer (Zeiss) as Nujol mulls or as KBr pellets. The Raman spectrum was measured with a IFS 55FT-Raman spectrometer (Bruker).

Table 1. Crystallographic Data for $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$

$V_2PO_{15}N_5H_{22}$	fw 465.08
$a = 9.743(5)$ Å	space group $P2_1$ (No. 4)
$b = 6.788(5)$ Å	$T = 20$ °C
$c = 11.685(12)$ Å	$\lambda = 0.710\,69$ Å
$\alpha = 90.00(7)°$	$\varrho_{obsd} = 2.003$ g cm^{-3}
$\beta = 92.97(7)°$	$\varrho_{calcd} = 2.001$ g cm^{-3}
$\gamma = 90.00(5)°$	$\mu = 14.02$ cm^{-1}
$V = 771.8(11)$ Å^3	$R(F_o)^a = 0.0350$
$Z = 2$	$R_w(F_o{}^2)^b = 0.0577$

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

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O^a$

	x	*y*	*z*	*U*(eq)[a]
V(1)	−346(1)	8937(1)	7493(1)	21(1)
V(2)	−3480(1)	7338(1)	8272(1)	24(1)
P(3)	−2837(1)	7751(2)	5651(1)	23(1)
O(4)	458(3)	10733(5)	6977(3)	27(1)
O(5)	923(3)	6880(6)	7207(3)	32(1)
O(6)	1024(3)	7624(6)	8358(3)	32(1)
O(7)	−1994(3)	10120(5)	7997(3)	27(1)
O(8)	−870(3)	10097(5)	8852(3)	28(1)
O(9)	−4510(4)	5522(6)	8215(3)	37(1)
O(10)	−4651(4)	9478(6)	8550(3)	39(1)
O(11)	−3973(4)	8663(7)	9581(3)	41(1)
O(12)	−1729(3)	6241(5)	7951(3)	25(1)
O(13)	−2007(3)	6275(6)	9153(3)	32(1)
O(14)	−1346(3)	8277(5)	6036(3)	28(1)
O(15)	−3760(3)	8100(5)	6645(3)	27(1)
O(16)	−3321(3)	9042(7)	4685(3)	37(1)
O(17)	−2862(3)	5593(6)	5306(3)	33(1)
O(18)	−6871(4)	3185(7)	7639(3)	48(1)
N(19)	729(5)	13527(7)	8953(4)	31(1)
N(20)	−9723(5)	−946(9)	4240(4)	36(1)
N(21)	−3260(4)	12710(8)	9933(4)	32(1)
N(22)	−4119(5)	2456(9)	6209(5)	47(1)
N(23)	3298(4)	8958(11)	6769(4)	53(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Synthesis of $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$. $NH_4H_2PO_4$ (0.575 g, 5 mmol) and NH_4VO_3 (1.17 g, 10 mmol) were dissolved in H_2O_2 (3%, 50 mL). To the clear solution were added aqueous ammonia (25%, 2 mL) and ethanol (50 mL). The reaction mixture was left to crystallize at 5 °C. Prismatic yellow crystals were isolated after several days and washed with ethanol. Anal. Calcd: V, 21.91; $O_2{}^{2-}$, 27.52; N, 15.06; H, 4.77. Found:[11] V, 21.42; $O_2{}^{2-}$, 27.44; N, 15.00; H, 4.62. UV−vis (H_2O): LMCT (L = $O_2{}^{2-}$) band at $\lambda_{max} = 320$ nm (log $\epsilon = 3.14$). The complex is stable at 5 °C. The thermogravimetric curve (20−400 °C, sample mass 50 mg, heating rate 2.5 °C/min; Derivatograph Q 1500 D, MOM, Budapest) of the complex exhibits several not markedly separated steps which correspond to release of O_2, H_2O, and NH_3. Deuterated sample was prepared similarly using $ND_4D_2PO_4$, ND_4VO_3, D_2O_2, D_2O, and C_2D_5OD.

Crystals suitable for X-ray structure analysis were obtained by slow crystallization of a diluted solution containing more than the stoichiometric amount of $NH_4H_2PO_4$.

X-ray Crystallography. Single-crystal diffraction data were collected on Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation and were corrected for Lorentz and polarization effects but not for absorption. Crystal parameters and basic information are summarized in Table 1. The structure was solved via the automated Patterson and Fourier methods using the program XFPS[12] and refined on F^2 by full-matrix least-squares procedure (SHELXL-93),[13] with a

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(1) *Vanadium in Biological Systems*; Chasteen, N. D., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990; p 63.

(2) Gresser, M. J.; Tracey, A. S.; Parkinson, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 6229.

(3) Tracey, A. S.; Gresser, M. J.; Galeffi, B. *Inorg. Chem.* **1988**, *27*, 157.

(4) Evans, H. T., Jr.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501.

(5) Beltran-Porter, D.; Beltran-Porter, A.; Amoros, P.; Ibanez, R.; Martinez, E.; Le Bail, A.; Ferey, G.; Villeneuve, G. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 131.

(6) Chen, Q.; Salta, J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 4485.

(7) Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107.

(8) Bhattacharjee, M.; Chaudhuri, M. K.; Paul, P. C. *Canad. J. Chem.* **1992**, *70*, 2245.

(9) We have not been able to reproduce the results of this work (for M = $NH_4{}^+$). Repeated syntheses led to the mixture of at least two compounds. The spectral data of the mixture did not correspond to the published ones.

(10) (a) Schwendt, P.; Petrovič, P.; Uškert, D. *Z. Anorg. Allg. Chem.* **1980**, *466*, 232. (b) Schwendt, P.; Joniaková, D. *Polyhedron* **1984**, *3*, 287. (c) Lapshin, A. E.; Smolin, Y. I.; Shepelev, Y. F.; Schwendt, P.; Gyepesová, D. *Acta Crystallogr.* **1990**, *C46*, 738. (d) Sivák, M.; Joniaková, D.; Schwendt, P. *Transition Met. Chem.* **1993**, *18*, 304.

(11) Vanadium by titration with $FeSO_4$; $O_2{}^{2-}$ by titration with $KMnO_4$; N, H on a CHN analyser (Carlo Erba).

(12) Pavelčík, F.; Kuchta, L.; Sivý, J. *Acta Crystallogr.* **1992**, *A48*, 791.

(13) Sheldrick, G. M. SHELXL93 program. Dept. Inorg. Chem., University of Göttingen, Germany.

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Table 3. Bond Lengths (Å) and Angles (deg) in the $[V_2O_2(O_2)_4PO_4]^{5-}$ Anion

V(1)−O(4)	1.585(4)	V(2)−O(7)	2.411(4)
V(1)−O(5)	1.906(4)	V(2)−O(9)	1.588(4)
V(1)−O(6)	1.859(4)	V(2)−O(10)	1.886(4)
V(1)−O(7)	1.916(4)	V(2)−O(11)	1.859(4)
V(1)−O(8)	1.867(4)	V(2)−O(12)	1.916(4)
V(1)−O(12)	2.351(4)	V(2)−O(13)	1.867(4)
V(1)−O(14)	1.969(4)	V(2)−O(15)	1.976(4)
P(3)−O(14)	1.540(3)	O(5)−O(6)	1.435(5)
P(3)−O(15)	1.524(4)	O(7)−O(8)	1.444(4)
P(3)−O(16)	1.486(4)	O(10)−O(1)	1.453(5)
P(3)−O(17)	1.519(4)	O(12)−O(1)	1.444(5)
O(4)−V(1)−O(6)	102.7(2)	O(9)−V(2)−O(11)	102.8(2)
O(4)−V(1)−O(8)	99.3(2)	O(9)−V(2)−O(13)	100.9(2)
O(6)−V(1)−O(8)	87.7(2)	O(11)−V(2)−O(13)	87.5(2)
O(4)−V(1)−O(5)	99.1(2)	O(9)−V(2)−O(10)	102.6(2)
O(6)−V(1)−O(5)	44.8(2)	O(11)−V(2)−O(10)	45.7(2)
O(8)−V(1)−O(5)	131.8(2)	O(13)−V(2)−O(10)	131.1(2)
O(4)−V(1)−O(7)	103.5(2)	O(9)−V(2)−O(12)	104.9(2)
O(6)−V(1)−O(7)	128.6(2)	O(11)−V(2)−O(12)	128.3(2)
O(8)−V(1)−O(7)	44.9(2)	O(13)−V(2)−O(12)	44.9(2)
O(5)−V(1)−O(7)	157.3(2)	O(10)−V(2)−O(12)	152.3(2)
O(4)−V(1)−O(14)	94.5(2)	O(9)−V(2)−O(15)	96.1(2)
O(6)−V(1)−O(14)	132.1(2)	O(11)−V(2)−O(15)	129.5(2)
O(8)−V(1)−O(14)	133.3(2)	O(13)−V(2)−O(15)	134.1(2)
O(5)−V(1)−O(14)	88.8(2)	O(10)−V(2)−O(15)	84.8(2)
O(7)−V(1)−O(14)	88.6(2)	O(12)−V(2)−O(15)	89.6(2)
O(4)−V(1)−O(12)	170.3(2)	O(9)−V(2)−O(7)	169.9(2)
O(6)−V(1)−O(12)	84.7(2)	O(11)−V(2)−O(7)	85.0(2)
O(8)−V(1)−O(12)	87.1(2)	O(13)−V(2)−O(7)	85.8(2)
O(5)−V(1)−O(12)	81.6(2)	O(10)−V(2)−O(7)	78.0(2)
O(7)−V(1)−O(12)	75.9(2)	O(12)−V(2)−O(7)	74.4(2)
O(14)−V(1)−O(12)	75.9(2)	O(15)−V(2)−O(7)	73.8(2)
O(16)−P(3)−O(17)	111.5(2)	V(1)−O(7)−V(2)	103.4(2)
O(16)−P(3)−O(15)	108.1(2)	O(7)−O(8)−V(1)	69.4(2)
O(17)−P(3)−O(15)	110.5(2)	O(11)−O(10)−V(2)	66.2(2)
O(16)−P(3)−O(14)	110.0(2)	O(10)−O(11)−V(2)	68.1(2)
O(17)−P(3)−O(14)	107.6(2)	O(13)−O(12)−V(2)	65.8(2)
O(15)−P(3)−O(14)	109.0(2)	O(13)−O(12)−V(1)	110.3(3)
O(6)−O(5)−V(1)	65.9(2)	V(2)−O(12)−V(1)	105.6(2)
O(5)−O(6)−V(1)	69.3(2)	O(12)−O(13)−V(2)	69.4(2)
O(8)−O(7)−V(1)	65.8(2)	P(3)−O(14)−V(1)	136.3(2)
O(8)−O(7)−V(2)	109.8(2)	P(3)−O(15)−V(2)	129.4(2)

weighting scheme which gave acceptable variance analyses. All hydrogen atoms but one were found in a difference synthesis and refined isotropically[14] (U values were constrained to be $1.35U_{eq}$ of bonded N or O, and H-positions were restrained to have similar X−H bond lengths and H−X−H angles (X = N, O)). Positional parameters and equivalent isotropic displacement parameters are listed in Table 2; bond distances in Table 3. All calculation were performed on a 486DX personal computer.

Results and Discussion

The complex $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$ was formed by crystallization from the $NH_4VO_3-NH_4H_2PO_4-NH_3-H_2O_2-H_2O-C_2H_5OH$ system at slightly acidic pH. A necessary condition for crystallization of the complex is a sufficient concentration of ethanol in the solution ($V(C_2H_5OH)/V(H_2O) > 0.7$) otherwise peroxovanadates, mainly $(NH_4)_3[V_2O_2OH(O_2)_4]$, are formed.

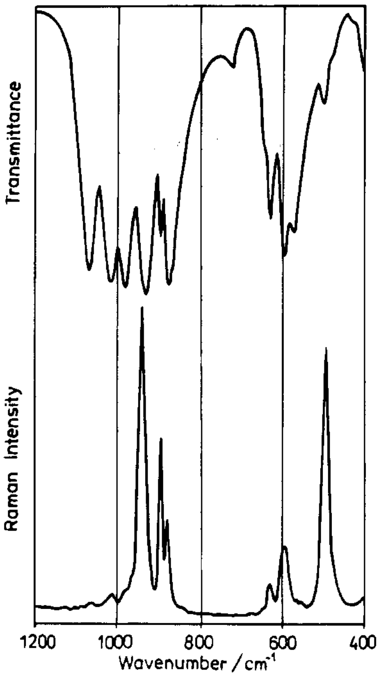

Figure 1. Infrared and Raman spectra of $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$.

Vibrational Spectra. Since the HPO_4 group has been reported in a similar compound,[8] we first investigated whether the PO_4 group is protonated or not. The deuteration of the complex caused a shift of bands assigned to cation and crystal water only. The absence of bands at ca. 2900, 2300, and 1240 cm^{-1} due to ν(P−O−H) and δ(P−O−H),[15] which would be correspondingly shifted on deuteration, is strong evidence for the unprotonated PO_4 group.[16] The splitting of the IR band corresponding to $\nu_3(PO_4)$ into three components (1067, 1015, and 983 cm^{-1}) is indicating C_{2v} or lower symmetry for the PO_4 group which, supported also by the stoichiometry of the complex, is expected to be bound as a bridging ligand ($V-O-PO_2-O-V$).

The vibrational spectra exhibit typical bands of the V=O and O_p-O_p (O_p = peroxo oxygen) groups near 940 and 880 cm^{-1}, respectively (Figure 1). The $V-O_p$ stretching modes, usually observed in the 440−640 cm^{-1} region, are structurally sensitive. For mononuclear diperoxo complexes, the wavenumbers of four $\nu_n(V-O_p)$ vibrations enable the coordination number of vanadium atoms to be ascertained. As the $d(V-Z)$ distance (Figure 2) decreases (i) the $\tilde{\nu}_1(VO_p) - \tilde{\nu}_2(VO_p)$ difference increases and (ii) the very strong Raman band corresponding to $\nu_3(VO_p)$ is shifted to lower wavenumbers.[17] The first rule is not very useful in the case of $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$ because of the overlapping of bands corresponding to the $\nu_1(VO_p)$, $\nu_2(VO_p)$, and $\nu_4(PO_4)$ modes. Assuming that the second rule is valid also for dinuclear complexes containing the $VO(O_2)_2$ moiety, we obtain the correlation between $d(V-Z)$ and the wavenumber of the mentioned characteristic Raman band (Figure 3).[18] At large $d(V-Z)$ values, when the polyhedron can be regarded as a pentagonal pyramide, $\tilde{\nu}_3(V-O_p)$ is approaching a limiting value, approximately 530 cm^{-1}. In $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$, as the characteristic Raman band position at 499 cm^{-1} cor-

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(14) There is either high anisotropic temperature motion or orientational disorder of the N(23) ammonium group. The calculated principal mean-square atomic displacements U are (0.1026, 0.0339, 0.0228). Two hydrogen atoms are fixed by strong hydrogen bonds, and two other H atoms form weak three-centered H-bonds with more freedom to move. One of these atoms was not found in the difference synthesis. Inclusion in refinement at a calculated position caused a small increase of the conventional R_1 factor. The isotropic temperature factor of this hydrogen could only be refined by omitting 300 reflection (one of two strongest).

(15) Berry, E. E. *Spectrochim. Acta* **1968**, *24A*, 1727.

(16) The X-ray structure determination did not answer unequivocally the question of PO_4 group protonation. Some residual electron density peaks near to oxygen atoms, probably due to the lone pairs, were observed.

(17) (a) Schwendt, P.; Volka, K.; Suchánek, M. *Spectrochim. Acta* **1988**, *44A*, 839. (b) Schwendt, P.; Pisárčik, M. *Spectrochim. Acta* **1990**, *46A*, 397.

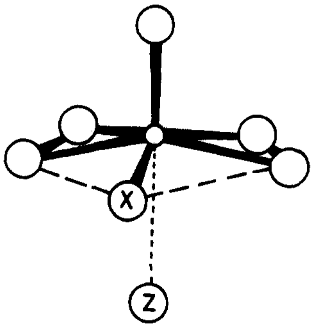

Figure 2. Model of the oxodiperoxovanadate ion. X = atom in the pentagonal plane, and Z = apical atom.

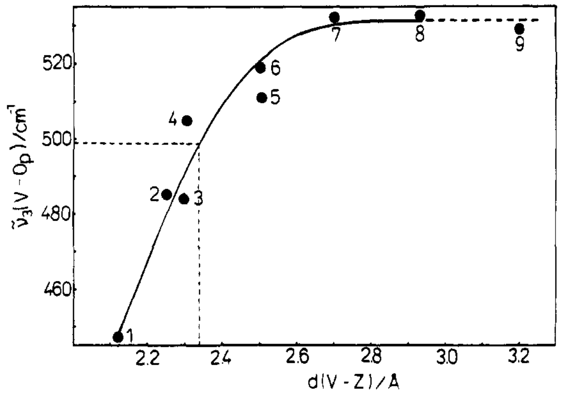

Figure 3. Correlation between the long apical bond length *d*(V−Z) and the wavenumber of the characteristic Raman band $\nu_3(V-O_p)$: (1) $K_3[V_2O_2(O_2)_3F_3]\cdot 2H_2O\cdot HF$;[10b,18a] (2) $K_3[VO(O_2)_2C_2O_4]\cdot H_2O$;[18b,c] (3) $K_3[VO(O_2)_2CO_3]$;[18c,d] (4) $(NH_4)_3[VO(O_2)_2F_2]$;[18c,e] (5) $(NH_4)_2[VO(O_2)_2F]$;[18c,f] (6) $(NH_4)_3[V_2O_2OH(O_2)_4]$;[18c,g] (7) $\{N(CH_3)_4\}_3[V_2O_2(O_2)_4H_2O]\cdot 2H_2O$;[18h,i] (8) $NH_4[VO(O_2)_2NH_3]$;[18c,j] (9) $K_2[VO(O_2)_2F]$, ($d(V-Z) > 3.1$ Å).[18c,k] Dotted lines correspond to $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$.

responds to a V−Z bond length 2.34 Å (Figure 3), a pentagonal bipyramidal arrangement around vanadium atoms with a relatively long apical V−Z bond can be expected.

X-ray Structure of $(NH_4)_5[V_2O_2(O_2)_4PO_4]\cdot H_2O$. All conclusions based on spectroscopic studies were confirmed by the X-ray structure analysis. The crystal structure is built up of $[V_2O_2(O_2)_4PO_4]^{5-}$ anions, NH_4^+ cations, and water molecules held together by extensive hydrogen bonds and electrostatic forces. Almost all hydrogen atoms and oxygen lone pairs are involved in H-bonds [$d(X\cdots Y) < 3.1$ Å]. There are 22 strong H-bonds ($d < 2.9$ Å). The strongest hydrogen bond O17···N23 = 2.681 Å belongs to the phosphate group. The two oxodiperoxovanadium groups are connected by an unprotonated phosphato group thus forming a dinuclear anion (Figure 4). Both vanadium atoms of the anion are seven-coordinated in a pentagonal bipyramidal way. For example, the coordination polyhedron about V1 is formed by a doubly bonded oxygen (O4) in an apical position, two bidentate peroxo groups (O5−O6 and O7−O8), and an oxygen atom O14 from the PO_4 group in the pentagonal plane. The pentagonal bipyramidal environment of the vanadium atom is achieved through the approach of an oxygen atom (O12) from a peroxo group bonded to the other vanadium atom. The seventh ligating atom in an apical position is at a rather large distance, *d*(V1−O12) = 2.351 Å [*d*(V2−O7) = 2.411 Å], in agreement with the distance predicted by the above-mentioned $\tilde{\nu}_3(VO_p)$ vs *d*(V−Z) relationship. The V1 and V2 atoms are displaced from the pentagonal plane by 0.316(2) and 0.371(2) Å, respectively. The anion has only approximate C_2 symmetry because the torsion angles V1−O14−P3−O15 and V2−O15−P3−O14 are 9.4(4) and −45.8(3)°.

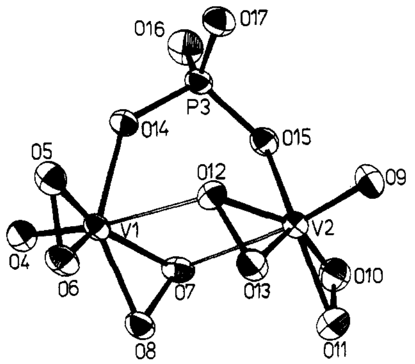

Figure 4. ORTEP drawing of the $[V_2O_2(O_2)_4PO_4]^{5-}$ anion. Ellipsoids of probability 50% are shown.

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Supplementary Material Available: Tables of crystal data, data collection and refinement parameters, thermal parameters, hydrogen positions, and interatomic contacts (4 pages). Ordering information is given on any current masthead page.

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(18) (a) Lapshin, A. E.; Smolin, Y. I.; Shepelev, Y. I.; Schwendt, P.; Gyepesová, D. *Acta Crystallogr.* **1990**, *C46*, 1753. (b) Begin, D.; Einstein, F. W. B.; Field, J. *Inorg. Chem.* **1975**, *14*, 1785. (c) Schwendt, P.; Pisárčik, M. *Chem. Pap.* **1988**, *42*, 305. (d) Stomberg, R. *Acta Chem. Scand.* **1985**, *39A*, 725. (e) Stomberg, R.; Olson, S. *Acta Chem. Scand.* **1984**, *38A*, 801. (f) Campbell, N. J.; Flanagan, J.; Griffith, W. P.; Skapski, A. C. *Transition Met. Chem.* **1985**, *10*, 353. (g) Lapshin, A. E.; Smolin, Y. I.; Shepelev, Y. F.; Gyepesová, D.; Schwendt, P. *Acta Crystallogr.* **1989**, *C45*, 1477. (h) Schwendt, P.; Sýkora, M. *Collect. Czech. Chem. Commun.* **1990**, *55*, 1485. (i) Drew, R. E.; Einstein, F. W. B. *Inorg. Chem.* **1972**, *5*, 1079. (j) Stomberg, R. *Acta Chem. Scand.* **1984**, *38A*, 223.