

pH-Specific Structural Speciation of the Ternary V(V)–Peroxi–Betaine System: A Chemical Reactivity–Structure Correlation

C. Gabriel,[†] E. Kioseoglou,[†] J. Venetis,[†] V. Psycharis,[‡] C. P. Raptopoulou,[‡] A. Terzis,[‡] G. Voyiatzis,[§] M. Bertmer,^{||} C. Mateescu,[⊥] and A. Salifoglou^{*,†}

[†]Laboratory of Inorganic Chemistry, Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece

[‡]Institute of Materials Science, NCSR “Demokritos”, Aghia Paraskevi, Attiki 15310, Greece

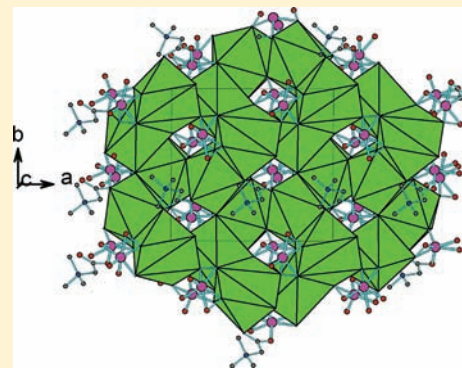
[§]Foundation for Research and Technology Hellas (FORTH), Institute of Chemical Engineering and High Temperature Chemical Processes (ICE/HT), Patras 26500, Greece

^{||}Institut für Experimentelle Physik II, Universität Leipzig, Leipzig 04103, Germany

[⊥]Banat's University of Agricultural Sciences and Veterinary Medicine, Timisoara 300645, Romania

Supporting Information

ABSTRACT: Vanadium involvement in cellular processes requires deep understanding of the nature and properties of its soluble and bioavailable forms arising in aqueous speciations of binary and ternary systems. In an effort to understand the ternary vanadium–H₂O₂–ligand interactions relevant to that metal ion's biological role, synthetic efforts were launched involving the physiological ligands betaine (Me₃N⁺CH₂CO₂[−]) and H₂O₂. In a pH-specific fashion, V₂O₅, betaine, and H₂O₂ reacted and afforded three new, unusual, and unique compounds, consistent with the molecular formulation K₂[V₂O₂(O₂)₄{(CH₃)₃NCH₂CO₂}]·H₂O (1), (NH₄)₂[V₂O₂(O₂)₄{(CH₃)₃NCH₂CO₂}]·0.75H₂O (2), and {Na₂[V₂O₂(O₂)₄{(CH₃)₃NCH₂CO₂}]·4nH₂O} (3). All complexes 1–3 were characterized by elemental analysis; UV/visible, FT-IR, Raman, and NMR spectroscopy in solution and the solid state; cyclic voltammetry; TGA-DTG; and X-ray crystallography. The structures of 1 and 2 reveal the presence of unusual ternary dinuclear vanadium–tetraperoxi–betaine complexes containing [(V^V=O)(O₂)₂] units interacting through long V–O bonds. The two V(V) ions are bridged through the oxygen terminal of one of the peroxide groups bound to the vanadium centers. The betaine ligand binds only one of the two V(V) ions. In the case of the third complex 3, the two vanadium centers are not immediate neighbors, with Na⁺ ions (a) acting as efficient oxygen anchors and through Na–O bonds holding the two vanadium ions in place and (b) providing for oxygen-containing ligand binding leading to a polymeric lattice. In 1 and 3, interesting 2D (honeycomb) and 1D (zigzag chains) topologies of potassium nine-coordinate polyhedra (1) and sodium octahedra (3), respectively, form. The collective physicochemical properties of the three ternary species 1–3 project the chemical role of the low molecular mass biosubstrate betaine in binding V(V)–diperoxi units, thereby stabilizing a dinuclear V(V)–tetraperoxi dianion. Structural comparisons of the anions in 1–3 with other known dinuclear V(V)–tetraperoxi binary anionic species provide insight into the chemical reactivity of V(V)–diperoxi systems and their potential link to cellular events such as insulin mimesis and antitumorogenicity modulated by the presence of betaine.



INTRODUCTION

Vanadium participation in numerous abiotic applications and biological systems has been widely shown in past years and has triggered research efforts toward delineating its role and biological action.¹ To this end, vanadium metallobiochemistry has been at the forefront of attention, featuring the nature of the active sites and their incipient biochemical activity in metalloenzyme systems,² such as nitrogenases³ and haloperoxidases.^{4–8} Beyond its direct participation in metalloenzyme active sites, vanadium has been shown to act as an inorganic cofactor possessing and promoting bioactivities extending from antitumorogenicity⁹ to mitogenicity,¹⁰ the inhibition of

metabolic enzymes (i.e., phosphoglucomutases), and others.¹¹ Among a number of such actions, outstanding was the ability of vanadium to influence glucose catabolizing processes linked to the heterogeneous syndrome of diabetes mellitus.^{12,13} To this end, a number of binary and ternary vanadium compounds have been shown to trigger biochemical responses,¹⁴ acting as antitumorogenic agents and potential insulin-mimetics in the treatment of diabetes.¹⁵

Received: December 1, 2011

Published: May 23, 2012

Betaine, i.e., trimethylammonium acetate ($\text{Me}_3\text{N}^+\text{CH}_2\text{CO}_2^-$),¹⁶ is a biological base and a methyl-transfer agent in amino acid synthesis.^{17,18} It is widely distributed in plants and animals. It and its derivative trimethylammonium propionate ($\text{Me}_3\text{N}^+\text{CH}_2\text{CH}_2\text{CO}_2^-$) can be considered as amino acid derivatives with an avid propensity for metal ion coordination. Amino acids, such as proline¹⁹ and its derivatives,²⁰ commonly act as zwitterionic species in ligation reactions with metal centers. Likewise, betaine and its analogues, existing solely in the zwitterionic form, are found to coordinate metal centers at different molar ratios *via* their carboxylate moiety.^{21,22}

Over the past several decades, metal–pseudohalide complexes have been extensively studied with respect to the incorporation of neutral nitrogen-donor ligands, such as pyridine derivatives^{23–27} and polyamines, in the coordination sphere of a metal ion.^{28,29} In view of the negative charge that accompanies the binding of pseudohalides to a metal ion, it is difficult to attach one or more anionic carboxylate groups into the assembly of a metal carboxylate pseudohalide system. Mixed-ligand complexes of this type may conceivably be achieved by using neutral zwitterionic ligands containing carboxylate oxygen donors, such as amino acids and betaine derivatives, instead of anionic carboxylates.

Given that low molecular mass substrates available in biofluids are potential vanadium targets, amino acid derivatives, such as betaine, (a) present themselves as primary ligands dictating interactions with metal ions either in their free or bound form and (b) influence the activity of ternary V(V)–peroxido–betaine species as a function of pH and participant molecular stoichiometry. In view of the paucity of ternary V(V) species bearing more than one peroxido moiety, research efforts were launched in our lab concentrating on chemical reactivity in the ternary V(V)– H_2O_2 –betaine system. Herein, we describe the synthesis, isolation, and spectroscopic and structural characterization of unusual ternary V(V)–peroxido species bearing betaine. The properties of such species are discussed in terms of their structural features, potentially affecting the chemical reactivity of V(V) in a biologically relevant setting.

■ EXPERIMENTAL SECTION

Materials and Methods. All experiments were carried out under aerobic conditions. Nanopure quality water was used for all reactions. V_2O_5 , betaine, and 30% H_2O_2 were purchased from Aldrich. Ammonia, potassium hydroxide, and sodium hydroxide were supplied by Fluka.

Physical Measurements. FT-IR spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer. UV/visible measurements were carried out on a Hitachi U2001 spectrophotometer in the range from 190 to 1000 nm. A ThermoFinnigan Flash EA 1112 CHNS elemental analyzer was used for the simultaneous determination of carbon, hydrogen, and nitrogen (%). The analyzer operation is based on the dynamic flash combustion of the sample (at 1800 °C) followed by reduction, trapping, complete GC separation, and detection of the products. The instrument is (a) fully automated and controlled by PC via the Eager 300 dedicated software and (b) capable of handling solid, liquid, or gaseous substances.

Solid-State NMR Spectroscopy. Solid-state CP-MAS ^{13}C NMR spectra for **1** were obtained on a Varian 400 MHz spectrometer operating at 100.53 MHz. In each case, a sufficient sample quantity was placed in a 3.2 mm rotor. A double resonance HX probe was used. The spinning rate was set at 12 kHz. A RAMP-CP pulse sequence of the Vnmrj library was applied, whereby the ^{13}C spin-lock amplitude varied linearly during CP, while the ^1H spin-lock amplitude was kept constant. RAMP-CP eliminates the Hartmann–Hahn matching profile

dependence from the MAS spinning rate and optimizes signal intensity.³⁰ The spectra were recorded with 1000 scans, a contact pulse of 2.0 μs , and a pulse repetition time of 8 s. Adamantane ($\text{C}_{10}\text{H}_{16}$) was used as an external reference to report the chemical shifts of ^{13}C resonance peaks.

The solid state CP-MAS ^{13}C NMR spectra for **3** were obtained on a Bruker MSL400 NMR spectrometer. The high resolution solid-state cross polarized ^{13}C magic angle spinning (MAS) NMR spectra were measured at 100.61 MHz. The spinning rate used was 10.0 kHz at 0 °C. The solid-state spectrum was a result of the accumulation of 512 scans. The recycle delay used was 1 s. The 90° pulse was 2.4 μs , and the contact time was 1 ms. The spectra were referenced to adamantane, which showed two peaks at 26.5 and 37.6 ppm, respectively, and to the external reference of TMS.

The high resolution solid state ^{51}V magic angle spinning (MAS) NMR spectra of **3** were measured at 105.25 MHz. The spinning rate used was 11.77 kHz at 0 °C. High power decoupling was used with a 90° pulse of 1.5 μs . Each solid-state spectrum was a result of the accumulation of 512 scans, and the recycle delay used was 1 s. All solid-state spectra were referenced to NaVO_3 , which showed a resonance at -513 ppm with respect to liquid VOCl_3 .

Solution NMR Spectroscopy. Solution ^1H and ^{13}C NMR experiments for **1** and **3** were carried out on Varian 600 and 300 MHz spectrometers. The sample concentration was ~ 5 mM. The compounds were dissolved in D_2O . Carbon spectra were acquired with 5000 transients, a spectral width of 37 000 Hz and a relaxation delay of 2 s. Proton spectra were acquired with 16 transients and a spectral width of 5000 Hz. Experimental data were processed using VNMR routines. Spectra were zero-filled and subjected to exponential apodization prior to FT. Chemical shifts (δ) are reported in parts per million, while spectra were referenced by the standard experimental setup.

Micro-Raman Spectroscopy. Micro-Raman measurements were obtained with a T-64000 triple spectrometer from Jobin Yvon (F)–Horiba. The Raman spectra were excited with a He–Ne laser (Optronics Technologies S.A. model HLA-20P, 20 mW) operating at 632.8 nm. A narrow-band-pass interference filter was used for the elimination of the laser plasma lines. The excitation beam was directed to the sample compartment of a properly modulated metallurgical microscope (Olympus BHSM-BH2). The microscope was used for the delivery of the excitation laser beam onto the sample. The collection of the backscattered light through a beam splitter and the objective lens were adapted to the aperture of the microscope. The focusing objective was a long working distance (8 mm) 50 \times /0.55 Olympus lens. The spectra were obtained using a 0.8 mW laser power on the specimen for a total integration time of 120 s. A viewing screen connected to the microscope offered good sample positioning and beam focus as well as direct surface inspection before and after laser delivery. For the rejection of the elastic Rayleigh scattering, an edge filter (LP02-633RU-25, Laser 2000 (UK) Ltd.) was used. The Raman photons were directed to the spectrograph, where they were dispersed by a 600-grooves/mm (76 mm \times 76 mm) 500 nm blazed holographic diffraction grating and detected by a standard LN₂ cooled (at 140 K) front illuminated CCD (Spectraview-2D, 1024 \times 256–1) detector. The spectral slit width was approximately 4 cm^{-1} .

FT-Raman Spectroscopy. Fourier transform Raman (FT-Raman) measurements were obtained using a Bruker (D) FRA-106/S component attached to an EQUINOX 55 spectrometer. A R510 diode pumped Nd:YAG polarized laser at 1064 nm (with a maximum output power of 500 mW) was used for Raman excitation in a 180° scattering sample illumination mode. Optical filtration reduced the Rayleigh elastic scattering and in combination with a CaF_2 beam splitter as well as a high sensitivity liquid N₂ cooled Ge-detector allowed Raman intensities to be recorded from 50 to 3300 cm^{-1} in the Stokes-shifted Raman region, all in one scan. The resulting spectra were an average of 300 scans recorded at a resolution of 2 cm^{-1} . The laser was focused onto the sample on a circular area of ~ 100 μm in diameter with an output power of ~ 100 mW. Similar results were obtained utilizing 100 scans recorded at a resolution of 4 cm^{-1} with an output laser power of 300 mW on the sample. The FT-spectra were

Table 1. Summary of Crystal, Intensity Collection, and Refinement Data for $K_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}]\cdot H_2O$ (1), $(NH_4)_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}]\cdot 0.75H_2O$ (2), and $\{Na_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}_2]\}_n\cdot 4nH_2O$ (3)

	1	2	3
formula	$C_5H_{13}K_2NO_{13}V_2$	$C_5H_{20.5}N_3O_{12.75}V_2$	$C_{10}H_{30}N_2Na_2O_{18}V_2$
formula molecular mass	475.25	428.62	614.22
<i>T</i> , K	293(2)	160(2)	160(2)
wavelength, λ (Å)	0.71073	1.54178	1.54178
space group	Pcab	$P2_1/n$	$P\bar{1}$
<i>a</i> (Å)	12.211(5)	12.0809(2)	10.8295(2)
<i>b</i> (Å)	11.481(4)	14.8646(2)	10.8893(2)
<i>c</i> (Å)	22.266(9)	17.5309(2)	11.5148(2)
α , deg	90	90	111.912(1)
β , deg	90	94.908(1)	108.499(1)
γ , deg	90	90	94.355(1)
<i>V</i> , (Å ³)	3122(2)	3136.62(8)	1165.19(4)
<i>Z</i>	8	8	2
<i>D</i> _{calcd} (Mg m ⁻³)	2.022	1.815	1.751
abs. coeff. (μ), mm ⁻¹	1.796	10.676	7.899
range of <i>h</i> , <i>k</i> , <i>l</i>	0 → 14, 0 → 13, 0 → 26	-14 → 11, -16 → 17, -18 → 20	-10 → 12, -12 → 13, -13 → 13
goodness-of-fit on <i>F</i> ²	1.061	1.044	1.024
no. of params	246	470	431
<i>R</i> ^a	0.0395 ^b	0.0487 ^b	0.0296 ^b
<i>R</i> _w ^a	0.1013 ^b	0.1217 ^b	0.0785 ^b

^a*R* values are based on *F* values. *R*_w values are based on *F*². $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$, $R = (\sum \|F_o\| - \|F_c\|) / (\sum (F_o))$, $R_w = (\sum [w(F_o^2 - F_c^2)^2]) / (\sum [w(F_o^2)^2])^{1/2}$. ^bFor 2278 (1), 4108 (2), and 3581 (3) reflections with $I > 2\sigma(I)$.

corrected for scattering as Rayleigh's ν^{-4} -law provides the scattering as a function of the wavenumber. The Raman calibration test utilizing cyclohexane gave in both cases a peak frequency uncertainty of ± 1 cm⁻¹ at around 1029 cm⁻¹.

Electrochemical Measurements. Cyclic voltammetric measurements were carried out with an Autolab model PGSTAT100 potentiostat-galvanostat. The entire system was under computer control and supported by the appropriate computer software, Autolab GPES, running on Windows XP. The electrochemical cell used had platinum (disk) working and auxiliary (wire) electrodes. A saturated Ag/AgCl electrode was used as a reference electrode. The water used in the electrochemical measurements was of nanopure quality. KNO₃ was used as a supporting electrolyte. Normal concentrations used were 1–6 mM in the electroanalyte and 0.1 M in the supporting electrolyte. Purified argon was used to purge the solutions prior to the electrochemical measurements. Derived *E*_{1/2} values are reported vs the Ag/AgCl electrode.

Preparation of Complex $K_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}]\cdot H_2O$ (1). A sample of V₂O₅ (0.20 g, 1.1 mmol) was placed in 3.0 mL of H₂O, and a solution of potassium hydroxide (1 N) was added slowly under stirring. The resulting solution was heated and stirred at 50 °C. After 2 h, betaine (0.52 g, 4.4 mmol) was added under continuous stirring. The resulting slurry was yellow in color. Stirring continued for an additional hour at room temperature. Subsequently, HCl was added dropwise until the solution turned clear. The final pH of the solution was 4.5, and the color was yellow-orange. The reaction flask was then placed on an ice bath, and 30% hydrogen peroxide (0.60 g, 18 mmol) was added slowly and under continuous stirring. The solution was still clear yellow-orange and stayed on as such. The reaction flask was placed at 4 °C, and ethanol was added. A few days later, yellow crystalline material precipitated and was isolated by filtration and dried in vacuo. Yield: 0.40 g (77%). Anal. Calcd for 1, $K_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}]\cdot H_2O$ (1; C₅H₁₃NK₂O₁₃V₂, *M*_r = 475.25): C, 12.62; H, 2.73; N 2.94. Found: C, 12.78; H, 2.73; N 2.84.

Preparation of Complex $(NH_4)_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}]\cdot 0.75H_2O$ (2). A sample of V₂O₅ (0.20 g, 1.1 mmol) was placed in 3.0 mL of H₂O, and a solution of ammonia/water (1:1) was added slowly under stirring. The resulting white slurry was heated and stirred at 100 °C for 30 min (pH 13). Finally, the reaction mixture

turned into a milky emulsion. The mixture was stirred for 1 h at 25 °C. Subsequently, betaine (0.66 g, 5.6 mmol) was added under continuous stirring. Stirring continued for an additional hour at room temperature (pH 11). In addition to this, 2.0 mL HCl/H₂O (1:1) was added. The final pH of the solution was 7, and the color was orange. The reaction flask was then placed on an ice bath, and 30% hydrogen peroxide (0.60 g, 18 mmol) was added slowly (in 2.0 mL aliquots and under continuous stirring) for 2 h. The solution ultimately turned yellow-orange and stayed on as such. Subsequently, the reaction flask was placed at 4 °C, and ethanol was added. A month later, yellow crystalline material precipitated at the bottom of the flask. The product was isolated by filtration and dried in vacuo. Yield: 0.30 g (64%). Anal. Calcd for 2, $(NH_4)_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}]\cdot 0.75H_2O$ (2; C₅H_{20.5}N₃O_{12.75}V₂, *M*_r = 428.62): C, 14.00; H, 4.78; N, 9.80. Found: C, 14.05; H, 4.83; N, 9.71.

Preparation of Complex $\{Na_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}_2]\}_n\cdot 4nH_2O$ (3). A sample of V₂O₅ (0.20 g, 1.1 mmol) was placed in 5.0 mL of H₂O, and a solution of NaOH (1 N) was added slowly under continuous stirring. The resulting slurry was heated and stirred at 50 °C for 1 h. Subsequently, betaine (0.66 g, 5.6 mmol) was added under continuous stirring at 25 °C. Stirring continued for 2 h at room temperature. Subsequently, HCl was added until the solution turned clear. The final pH of the solution was 6.0, and the color was orange. The reaction flask was then placed on an ice bath, and 30% hydrogen peroxide (0.60 g, 18 mmol) was added slowly and under continuous stirring for 2 h. The solution turned yellow orange and stayed on as such. The reaction flask was placed at 4 °C, and ethanol was added. A few weeks later, yellow crystalline material precipitated at the bottom of the flask. It was isolated by filtration and dried in vacuo. Yield: 0.60 g (65%). Anal. Calcd for 3, $Na_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}_2]\cdot 4H_2O$ (3; C₁₀H₃₀N₂O₁₈Na₂V₂, *M*_r = 614.22): C, 19.54; H, 4.88; N, 4.56. Found: C, 19.58; H, 4.88; N, 4.58.

X-ray Crystal Structure Determination. X-ray quality crystals of compounds 1, 2, and 3 were grown from mixtures of water–ethanol solutions. A crystal of 1 (0.20 × 0.20 × 0.40 mm) was mounted in the air and covered with epoxy glue. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered

Table 2. Bond lengths [\AA] and Angles [deg] for $\text{K}_2[\text{V}_2\text{O}_2(\text{O}_2)_4\{(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\}]\cdot\text{H}_2\text{O}$ (1), $(\text{NH}_4)_2[\text{V}_2\text{O}_2(\text{O}_2)_4\{(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\}]\cdot 0.75\text{H}_2\text{O}$ (2), and $\{\text{Na}_2[\text{V}_2\text{O}_2(\text{O}_2)_4\{(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\}_2]\}_n\cdot 4n\text{H}_2\text{O}$ (3)

1		2		3	
Distances					
V(1)—O(7)	1.600(2)	V(1)—O(1)	1.590(3)	V(1)—O(7)	1.607(2)
V(1)—O(5)	1.878(2)	V(1)—O(4)	1.861(3)	V(1)—O(5)	1.854(2)
V(1)—O(3)	1.888(3)	V(1)—O(5)	1.871(3)	V(1)—O(3)	1.874(2)
V(1)—O(6)	1.890(3)	V(1)—O(6)	1.879(3)	V(1)—O(4)	1.880(2)
V(1)—O(4)	1.943(3)	V(1)—O(3)	1.891(2)	V(1)—O(6)	1.881(2)
V(1)—O(1)	2.019(3)	V(1)—O(7)	2.030(2)	V(1)—O(1)	2.030(1)
V(2)—O(12)	1.594(3)	V(2)—O(2)	1.588(2)	V(2)—O(17)	1.607(2)
V(2)—O(9)	1.869(3)	V(2)—O(9)	1.867(2)	V(2)—O(15)	1.866(2)
V(2)—O(8)	1.877(3)	V(2)—O(8)	1.887(3)	V(2)—O(14)	1.878(2)
V(2)—O(10)	1.883(2)	V(2)—O(10)	1.891(2)	V(2)—O(13)	1.886(2)
V(2)—O(11)	1.892(3)	V(2)—O(7)	1.931(2)	V(2)—O(16)	1.890(2)
V(2)—O(4)	2.057(3)	V(2)—O(11)	2.002(2)	V(2)—O(12)	2.041(1)
Angles					
O(7)—V(1)—O(5)	104.2(1)	O(1)—V(1)—O(4)	107.6(1)	O(7)—V(1)—O(5)	109.5(1)
O(7)—V(1)—O(3)	106.5(1)	O(1)—V(1)—O(5)	104.3(1)	O(7)—V(1)—O(3)	110.4(1)
O(5)—V(1)—O(3)	126.6(1)	O(4)—V(1)—O(5)	90.1(1)	O(5)—V(1)—O(3)	139.3(1)
O(7)—V(1)—O(4)	103.3(1)	O(1)—V(1)—O(6)	106.3(1)	O(7)—V(1)—O(4)	106.8(1)
O(5)—V(1)—O(4)	86.1(1)	O(4)—V(1)—O(6)	129.9(1)	O(5)—V(1)—O(4)	126.4(1)
O(3)—V(1)—O(4)	44.9(1)	O(5)—V(1)—O(6)	46.1(1)	O(3)—V(1)—O(4)	46.1(1)
O(7)—V(1)—O(6)	106.5(1)	O(1)—V(1)—O(3)	105.9(1)	O(7)—V(1)—O(6)	106.1(1)
O(5)—V(1)—O(6)	45.7(1)	O(4)—V(1)—O(3)	46.1(1)	O(5)—V(1)—O(6)	45.9(1)
O(3)—V(1)—O(6)	146.8(1)	O(5)—V(1)—O(3)	132.6(1)	O(3)—V(1)—O(6)	126.6(1)
O(4)—V(1)—O(6)	127.8(1)	O(6)—V(1)—O(3)	146.1(1)	O(4)—V(1)—O(6)	86.9(1)
O(7)—V(1)—O(1)	99.0(1)	O(1)—V(1)—O(7)	101.6(1)	O(7)—V(1)—O(1)	95.8(1)
O(5)—V(1)—O(1)	125.8(1)	O(4)—V(1)—O(7)	125.7(1)	O(5)—V(1)—O(1)	83.8(1)
O(3)—V(1)—O(1)	90.9(1)	O(5)—V(1)—O(7)	125.5(1)	O(3)—V(1)—O(1)	84.2(1)
O(4)—V(1)—O(1)	134.5(1)	O(6)—V(1)—O(7)	80.8(1)	O(4)—V(1)—O(1)	129.8(1)
O(6)—V(1)—O(1)	80.9(1)	O(3)—V(1)—O(7)	82.6(1)	O(6)—V(1)—O(1)	129.2(1)
O(12)—V(2)—O(9)	107.1(1)	O(2)—V(2)—O(9)	106.5(1)	O(17)—V(2)—O(15)	110.5(1)
O(2)—V(2)—O(8)	105.7(2)	O(2)—V(2)—O(8)	103.8(1)	O(17)—V(2)—O(14)	108.0(1)
O(9)—V(2)—O(8)	45.7(1)	O(9)—V(2)—O(8)	126.8(1)	O(15)—V(2)—O(14)	124.5(1)
O(12)—V(2)—O(10)	105.0(1)	O(2)—V(2)—O(10)	106.5(1)	O(17)—V(2)—O(13)	110.6(1)
O(9)—V(2)—O(12)	131.4(1)	O(9)—V(2)—O(10)	45.7(1)	O(15)—V(2)—O(13)	138.1(1)
O(8)—V(2)—O(10)	147.6(1)	O(8)—V(2)—O(10)	149.5(1)	O(14)—V(2)—O(13)	46.1(1)
O(12)—V(2)—O(11)	106.1(2)	O(2)—V(2)—O(7)	103.8(1)	O(17)—V(2)—O(16)	105.6(1)
O(9)—V(2)—O(11)	90.1(1)	O(9)—V(2)—O(7)	85.6(1)	O(15)—V(2)—O(16)	46.3(1)
O(8)—V(2)—O(11)	131.6(1)	O(8)—V(2)—O(7)	44.8(1)	O(14)—V(2)—O(16)	86.0(1)
O(10)—V(2)—O(11)	45.9(1)	O(10)—V(2)—O(7)	127.9(1)	O(13)—V(2)—O(16)	126.4(1)
O(12)—V(2)—O(4)	102.0(1)	O(2)—V(2)—O(11)	100.3(1)	O(17)—V(2)—O(12)	94.7(1)
O(9)—V(2)—O(4)	125.2(1)	O(9)—V(2)—O(11)	126.4(1)	O(15)—V(2)—O(12)	84.4(1)
O(8)—V(2)—O(4)	82.3(1)	O(8)—V(2)—O(11)	88.8(1)	O(14)—V(2)—O(12)	130.0(1)
O(10)—V(2)—O(4)	81.3(1)	O(10)—V(2)—O(11)	82.7(1)	O(13)—V(2)—O(12)	84.5(1)
O(10)—V(2)—O(4)	124.6(1)	O(7)—V(2)—O(11)	131.5(1)	O(16)—V(2)—O(12)	130.4(1)

reflections in the range $11 < 2\theta < 23^\circ$. Intensity data were recorded using a θ - 2θ scan. Three standard reflections, monitored every 97 reflections, showed less than 3% variation and no decay. Lorentz and polarization corrections were applied using Crystal Logic software. A crystal of **2** ($0.12 \times 0.12 \times 0.30$ mm) and a crystal of **3** ($0.19 \times 0.22 \times 0.49$ mm) were taken from the mother liquor and immediately cooled to -113°C . Diffraction measurements were made on a Rigaku R-Axis SPIDER Image Plate diffractometer using graphite monochromated Cu $K\alpha$ radiation. Data collection (ω -scans) and processing (cell refinement, data reduction, and empirical absorption correction) were performed using the CrystalClear program package.³¹ The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 .³² In all three structures (1–3), all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were either located by difference maps or were introduced at calculated positions as riding on bonded atoms. Crystallographic details for **1**, **2**, and **3** are

summarized in Table 1. Further details on the crystallographic studies as well as atomic displacement parameters are given as Supporting Information in the form of CIF files. Further experimental crystallographic details for **1**: $2\theta_{\text{max}} = 50.0^\circ$; number of reflections collected/unique/used, 2747/2747 [$R(\text{int}) = 0.0$]/2747; $(\Delta\rho)_{\text{max}}/(\Delta\rho)_{\text{min}} = 0.552/-0.524$ e/ \AA^3 ; R/R_w (for all data), 0.0507/0.1086. Further experimental crystallographic details for **2**: $2\theta_{\text{max}} = 130^\circ$; number of reflections collected/unique/used, 17763/5181 [$R(\text{int}) = 0.0632$]/5181; $(\Delta\rho)_{\text{max}}/(\Delta\rho)_{\text{min}} = 0.818/-0.696$ e/ \AA^3 ; R/R_w (for all data), 0.0609/0.1324. Further experimental crystallographic details for **3**: $2\theta_{\text{max}} = 130^\circ$; number of reflections collected/unique/used, 15676/3737 [$R(\text{int}) = 0.0431$]/3737; $(\Delta\rho)_{\text{max}}/(\Delta\rho)_{\text{min}} = 0.386/-0.436$ e/ \AA^3 ; R/R_w (for all data), 0.0307/0.0791.

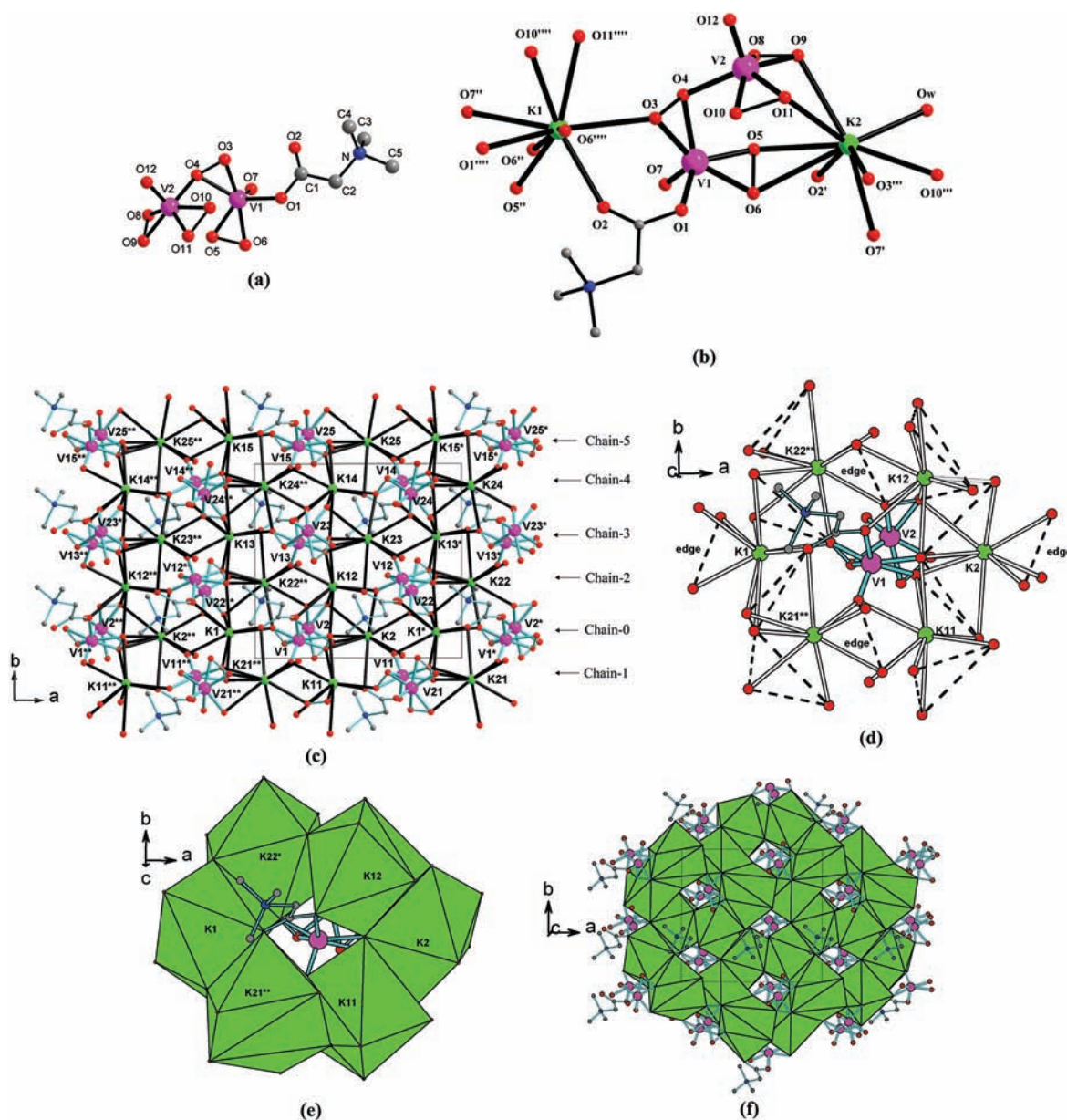
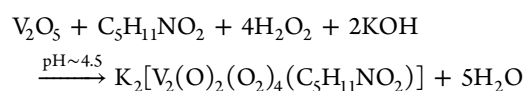


Figure 1. (a) Labeled plot of the dinuclear anions in **1** with thermal ellipsoids at the 30% probability level. Hydrogen atoms were omitted for clarity. (b) Labeled plot showing the linkage of the V(V) dinuclear anions with the K^+ through K–O interactions. Primed atoms are generated by symmetry: (') $0.5 + x, -y, 0.5 - z$; (") $-0.5 + x, -y, 0.5 - z$; (""') $0.5 + x, 0.5 - y, z$; (""") $-0.5 + x, 0.5 - y, z$. (c) Plot of the 2D network in **1**, due to K...O interactions, which extends parallel to the crystallographic *ab* plane. [K11–V11–V21–K21], [K12–V12–V22–K22], [K13–V13–V23–K23], [K14–V14–V24–K24], and [K15–V15–V25–K25] units are related to the K1–V1–V2–K2 unit by the following symmetry operations: $(0.5 + x, -y, 0.5 - z)$, $(0.5 + x, 0.5 - y, z)$, $(x, 0.5 + y, 0.5 - z)$, $(0.5 + x, 1 - y, 0.5 - z)$, and $(x, 1 + y, z)$, respectively. Symbols with one star indicate translation along the positive *a*-axis direction, and symbols with two stars indicate translation along the negative *a*-axis direction. In order to make the presentation clear, the bonds between atoms of the betaine–V(V)–2 entity are shown in light blue. (d) Arrangement of potassium polyhedra around the betaine–V(V)–2 entity. In the figure, the edges linking neighboring polyhedra are indicated. (e) Polyhedral representation of part d. (f) Polyhedral representation of the 2D network in **1**.

RESULTS

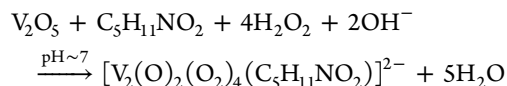
Synthesis. The synthetic exploration of the ternary V(V)–peroxido–betaine system followed carefully designed approaches. To this end, the $K_2[V_2O_2(O_2)_4\{(CH_3)_3NCH_2CO_2\}] \cdot H_2O$ (**1**) complex was synthesized in a facile fashion from simple reagents in aqueous solutions. In a typical reaction, V_2O_5 reacted with betaine in the presence of potassium hydroxide and HCl at pH 4.5. The addition of dilute hydrogen peroxide solution (vide infra) promoted efficiently the peroxidation reaction of vanadium. The overall

stoichiometric reaction leading to complex **1** is shown schematically below:

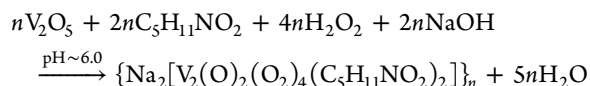


In a similar reaction, V_2O_5 reacted initially with betaine in the presence of aqueous ammonia, followed by the addition of HCl and hydrogen peroxide at pH 7. Ammonia was important for two reasons. It helped adjust the pH of the reaction medium, at

which the specific synthesis was carried out, and at the same time provided the cations necessary for balancing the negative charge on the derived anionic complex. The stoichiometric reaction leading to the formation of the compound $(\text{NH}_4)_2[\text{V}_2\text{O}_2(\text{O}_2)_4\{(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\}] \cdot 0.75\text{H}_2\text{O}$ (**2**) is shown below:



In a similar reaction, V_2O_5 reacted initially with betaine in the presence of sodium hydroxide, followed by the addition of HCl and hydrogen peroxide at pH 6. The stoichiometric reaction leading to the formation of $\{\text{Na}_2[\text{V}_2(\text{O})_2(\text{O}_2)_4\{(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\}]_n\} \cdot 4n\text{H}_2\text{O}$ (**3**) is shown below:



Ethanol, added as a precipitating solvent to the reaction mixture in all three reactions described above, afforded yellow crystalline materials, the analytical composition of which was consistent with the formulation in **1**, **2**, and **3**, respectively (*vide supra*). Positive identification of the crystalline products was achieved by spectroscopic methods and X-ray crystallographic determination for one of the isolated single crystals from **1**, **2**, and **3**. All complexes are stable, in the crystalline form, in the air, for fairly long periods of time. All three species are readily dissolved in water and insoluble in dimethyl sulfoxide (DMSO), *N,N'*-dimethylformamide (DMF), acetonitrile, alcohols (CH_3OH , *i*-PrOH), and dichloromethane at room temperature.

Description of X-ray Crystallographic Structures. The X-ray crystal structures of **1**, **2**, and **3** reveal discrete solid state lattices. Selected bond distances and angles for **1**–**3** are listed in Table 2. The molecular structures of **1**, **2**, and **3** consist of discrete anions and cations in the respective lattices. The anions are discrete dinuclear V(V) species in **1** and **2** and mononuclear V(V) entities in **3**. All compounds contain water molecules as a lattice solvent.

Labeled plots of the dinuclear V(V) anions in **1** and **2** are given in Figures 1a and 2a, respectively. The anion in both complexes is a dinuclear species consisting of two V(V) centers. Each V(V) is coordinated to two O_2^{2-} peroxide groups and one doubly bonded oxide group. Each peroxide group binds V(V) in a side-on fashion, thus occupying two coordination sites around the metal ion center. One of the four peroxide groups also acts as a monodentate bridge between the two V(V) ions. The betaine ligand is coordinated to one of the V(V) ions in the dinuclear assembly through one of its carboxylate oxygen atoms, thereby forming the betaine–V(V)–2 entity. Each V(V) ion contains an O_6 coordination chromophore (five peroxido oxygens and one oxido oxygen for one V(V) ion, and four peroxido oxygens, one oxido oxygen, and one carboxylate oxygen for the second V(V) ion). The V···V interatomic distances in the dinuclear V(V) assembly are 3.083(1) Å in **1** and 3.038(1) Å in **2** for the two crystallographically independent molecules.

The carboxylate group of the betaine ligand is deprotonated, whereas the amine group is protonated. To this end, the betaine ligand acts as a zwitterion with an overall zero charge. The overall charge of the dinuclear complex assembly is -2 . In

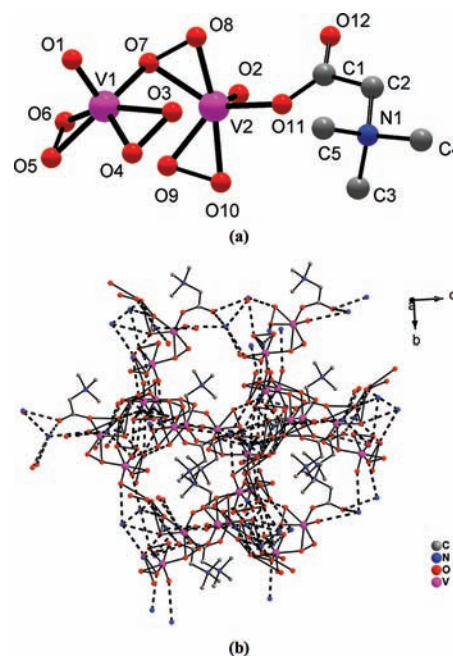


Figure 2. (a) Labeled plot of the dinuclear anions in **2** with thermal ellipsoids at the 30% probability level. Only one of the crystallographically independent dinuclear anions in **2** is shown. Hydrogen atoms were omitted for clarity. (b) Plot of the 3D network in **2** due to hydrogen bonding interactions (dashed lines).

the case of complex **1**, the counterion for balancing the negative charge is $[\text{K}]^+$, whereas in the case of complex **2**, the counterion is $[\text{NH}_4]^+$. In complex **1**, the two symmetrically independent K(1) and K(2) potassium atoms are attached to the betaine–V(V)–2 entity (Figure 1b) through (a) the O(2) and O(3) oxygen atoms (K(1) atom) and (b) the O(5)–O(6) peroxido ligand and O(11) and O(9) oxygen atoms (K(2) atom). In the same figure, also shown are the oxygen atoms bound to each potassium center, thereby revealing the nine oxygen atom coordination for each potassium counterion. Each potassium ion is coordinated through nine oxygen atoms in the range 2.586(3)–3.100(3) Å for K(1) and 2.749(3)–3.259(5) Å for K(2) (Figure 1b). Both arising potassium polyhedra have irregular shapes. The water molecule (Ow) is bound to the K(2) atom. The K(1)–[betaine–V(V)–2]–K(2) unit constitutes the contents of the asymmetric unit of the unit cell, and by translation parallel to the *a* axis, a chain is formed (Chain-0 in Figure 1c). Through application of specific symmetry operations of the space group on this chain, a two-dimensional layer emerges parallel to the *ab* crystallographic plane, based on the development of interesting bonding interactions among the different structural units. This layer is shown in Figure 1c. Looking closer at this arrangement of the structural units of compound **1**, it is clear that the betaine–V(V)–2 assembly serves as a linker of six potassium polyhedra (Figure 1d). The polyhedra forming around the potassium atoms are linked together through edges or trigonal faces as indicated by the dashed lines in Figure 1d (Figure 1e is the polyhedral representation of Figure 1d). Through edge and face sharing, the potassium polyhedra form a distorted honeycomb 2D lattice as shown in Figure 1f (in polyhedral representation). The arrangement of potassium polyhedra resembles that of Ba(II) nine-coordinate polyhedra in the structure of compound $\text{Ba}_2(\text{C}_2\text{O}_4)(\text{H}_2\text{PO}_3)_2$.³³ The shortest V···K interatomic dis-

tances within the 2D layer are in the range 3.428(1)–3.907(1) Å.

In complex **2**, the ammonium counterions and the lattice water molecules participate in hydrogen bonding interactions, with the oxygen atoms of the peroxide groups, the doubly bonded oxide groups, and the carboxylato oxygen atoms of the betaine ligand forming a 3D network and stabilizing the lattice structure (Table 1S, Figure 2b).

A labeled plot of the mononuclear anion in **3** is shown in Figure 3a. Each V(V) is coordinated to two O₂²⁻ peroxide

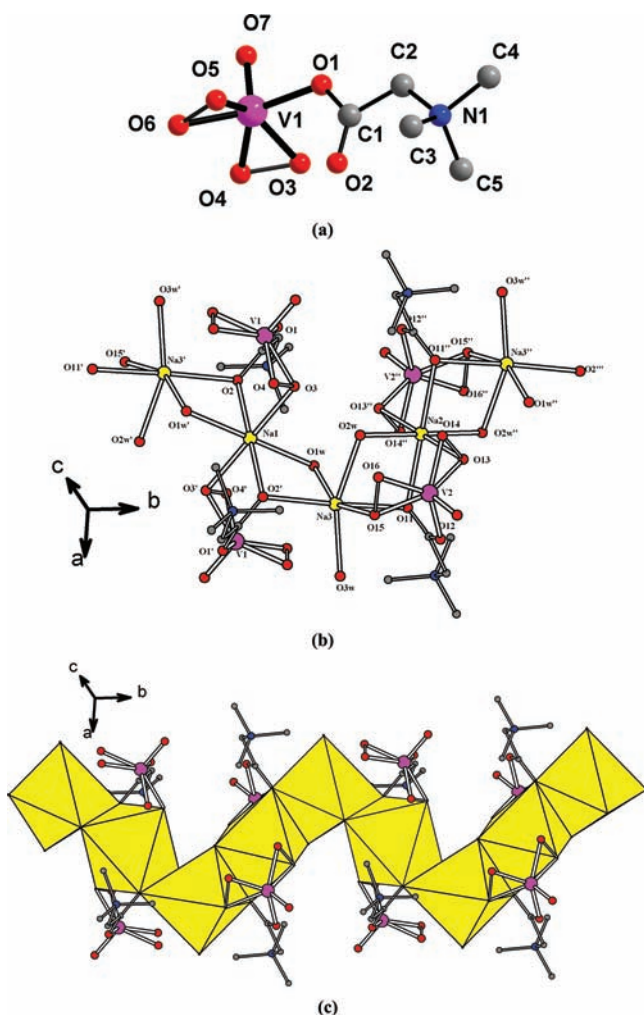


Figure 3. (a) Labeled plot of the mononuclear anion in **3** with thermal ellipsoids at the 30% probability level. Only one of the crystallographically independent molecules is shown. Hydrogen atoms were omitted for clarity. (b) Labeled plot showing the linkage of the V(V) anions and Na–O bonds. Primed atoms are generated by symmetry: (') $1 - x, 2 - y, 1 - z$; (") $1 - x, 1 - y, 1 - z$; (""') $x, 1 + y, z$. (c) Polyhedral plot of the zigzag sodium chains with a ...trans-cis-trans-cis... octahedral sequence.

groups and one doubly bonded oxide group. Each peroxide group binds V(V) in a side-on fashion, thus occupying two coordination sites around the metal ion center. The sixth place in the coordination sphere of vanadium is completed by a carboxylato oxygen atom of the betaine ligand, which exhibits its zwitterionic form as in **1** and **2**. In the crystal lattice, there are two crystallographically independent V(V) assemblies (V(1) and V(2)) and three crystallographically independent

sodium ions. Two of the sodium ions are sitting on an inversion center with half occupancy (Na(1) and Na(2)), and one is sitting on a general position with full occupancy (Na(3)). Hence, there are totally two sodium ions per two V(V) assemblies. All Na⁺ ions are coordinated to six oxygen atoms, thereby forming octahedra, with Na...O distances in the range 2.313(2)–2.586(2) Å (Figure 3b). Each of the two sodium ions Na(1) and Na(2) is coordinated to six oxygen atoms, with two of the oxygen anchors originating from water molecules, two belonging to bridging peroxide groups and two originating from the carboxylato group of the betaine ligand. Na(3) is also coordinated to six oxygen atoms, which however originate from three water molecules, two carboxylato oxygens from two different betaine ligands and one from a bridging peroxide group. The polyhedra around all sodium atoms are octahedra, with that of Na(3) showing a more distorted character as indicated by the values of the continuous symmetry measure (CSM)³⁴ parameters $S(O_h)$ and $S(itr)$ for the octahedron (O_h) and ideal trigonal prism (itr) geometries, correspondingly. These values for Na(1) are $S(O_h) = 1.14$ and $S(itp) = 17.22$, for Na(2) they are $S(O_h) = 0.91$ and $S(itp) = 16.94$, and for Na(3) they are $S(O_h) = 4.06$ and $S(itp) = 10.25$. For Na(1) and Na(2), these values are close to ideal octahedral geometry. The Na(1) and Na(3) ions are linked through a μ_2 water molecule oxygen (O(1)w) and μ_2 carboxylato oxygen atoms of the betaine ligands (O(2)"), thereby sharing the corresponding O(1)w–O(2)" octahedral edge. The Na(2) and Na(3) ions share the octahedral edge O(2)w–O(11) while concurrently being connected with the V(2) atom through the peroxido O(15) and O(13) oxygen atoms. The sodium octahedra are linked through edges and form zigzag chains with an interesting topology. As shown in Figure 3b, the polyhedra around sodium atoms with sequence Na(3)', Na(1), and Na(3) share edges and are connected in a trans fashion. This is also true for the polyhedra around the atoms with the sequence Na(3), Na(2), and Na(3)". Contrary to that, Na(1) and Na(2) are cis connected to Na(3), in the sequence Na(1), Na(3), and Na(2). An interesting observation concerns the different way that the two symmetry independent mononuclear V(V) entities are held on to the sodium polyhedra via bridging carboxylato oxygens and bridging peroxide groups. V(1) is linked through the peroxido atom O(3) and the carboxylato atom O(2) to Na(1) and Na(3)', respectively. In particular, V(1) shares an edge with the Na(1) octahedron (O(2) and O(3) atoms) and is linked to a vertex of the Na(3)' polyhedron. V(2) atoms are linked in a different way to the sodium chain atoms, and that is through the peroxido oxygen atoms O(13) and O(15) and the carboxylato atom O(11) to Na(2) and Na(3), respectively. The interesting point here is that all three oxygen atoms are vertices of the Na(2) and Na(3) octahedra. The zigzag chains run parallel to the crystallographic *b* axis (Figure 3c, polyhedral plot) in a trans-cis sequence. The shortest Na...Na interatomic distances in the zigzag chains are Na(1)⋯Na(3) = 3.568(2) Å and Na(2)⋯Na(3) = 3.591(2) Å. A zigzag chain of Al octahedra with the same topology has been previously observed in the case of compound Al₄(OH)₈[C₁₀O₈H₂].³⁵

The V–O bond distances in **1** (1.594(3)–2.057(3) Å), **2** (1.588(2)–2.030(2) Å), and **3** (1.607(2)–2.041(1) Å) are similar to the corresponding distances in other V(V)–diperoxido species, such as (H₃O)₂[V₂(O)₂(μ_2 : η^2 : η^1 -O₂)₂(η^2 -O₂)₂(C₂H₅N O₂)] (1.873(6)–2.352(2) Å), K₂[V₂(O)₂(μ_2 : η^2 : η^1 -O₂)₂(η^2 -O₂)₂(C₂H₅NO₂)] (1.864(3)–2.378(3) Å),³⁶ (Hbipy)[H{VO(O₂)₂(bipy)}₂·xH₂O₂·(6 –

x)H₂O ($x \sim 0.5$; 1.875(3)–2.480(2) Å),³⁷ (NH₄)₄[O{VO(O₂)₂}₂] (1.875(3)–2.522(3) Å),³⁸ (NH₄)₄[V₂O₁₁] (1.839(18)–2.531(18) Å),³⁹ [N(CH₃)₄]₂[V₂O₂(O₂)₄·(H₂O)]·2H₂O (1.863(4)–2.045(3) Å),⁴⁰ CymH₂[V₂O₂(O₂)₄·(H₂O)]·2H₂O (1.868(4)–2.035(4) Å),⁴¹ and V(V)–peroxido–carboxylate containing dinuclear complexes, such as (NH₄)₆[V₂O₂(O₂)₂(C₆H₄O₇)₂]·4.5H₂O (1.894(3)–2.322(3) Å),⁴² (NH₄)₂[V₂O₂(O₂)₂(C₆H₆O₇)₂]·2H₂O (1.873(2)–2.034(2) Å),⁴³ K₂[V₂O₂(O₂)₂(C₆H₆O₇)₂]·2H₂O (1.873(1)–2.039(1) Å),⁴⁴ (NH₄)₄[V₂O₂(O₂)₂(C₄H₃O₅)₂]·3H₂O (1.859(3)–2.294(3) Å),⁴⁵ K₄[V₂O₂(O₂)₂(C₄H₃O₅)₂]·4H₂O (1.868(2)–2.248(2) Å),⁴⁵ and K₂[V₂O₂(O₂)₂·(C₄H₄O₅)₂]·2H₂O (1.869(2)–2.033(2) Å).⁴⁵ The V=O bond distances (1.594(3)–1.600(2) Å (1), 1.588(2)–1.590(3) Å (2), and 1.607(2) Å (3)) are similar to those in the congener complexes (H₃O)₂[V₂(O)₂(μ₂:η²:η¹-O₂)₂(η²-O₂)₂(C₂H₅NO₂)₂] (1.609(5)–1.616(7) Å),^{3,6} K₂[V₂(O)₂(μ₂:η²:η¹-O₂)₂(η²-O₂)₂(C₂H₅NO₂)₂] (1.611(3)–1.610(4) Å),^{3,6} and (NH₄)₆[V₂O₂(O₂)₂(C₆H₄O₇)₂]·4.5H₂O (1.597(3) Å)⁴² and various V(V)–peroxido species and similar to the calculated average value of 1.609(7) Å for over 11 V(V)–peroxido structures.⁴⁶ Analogous arguments are valid for the observed angular data in 1–3, with particular emphasis on the dihedral angles in 1 and 2. Specifically, the dihedral angle O(7)–V(1)–V(2)–O(12) in 1 is 91.37(2)°, and the dihedral angle O(1)–V(1)–V(2)–O(2) in 2 is 88.35°.

In all three species 1, 2, and 3, the existence of water molecules of crystallization contribute to the stability of the respective lattice through hydrogen bond formation, thus leading to 3D network structures in all three structures (Table 1S).

UV/Visible Spectroscopy. The electronic spectra of 1 and 3 (Figure 4) were recorded in H₂O. The spectra showed a band

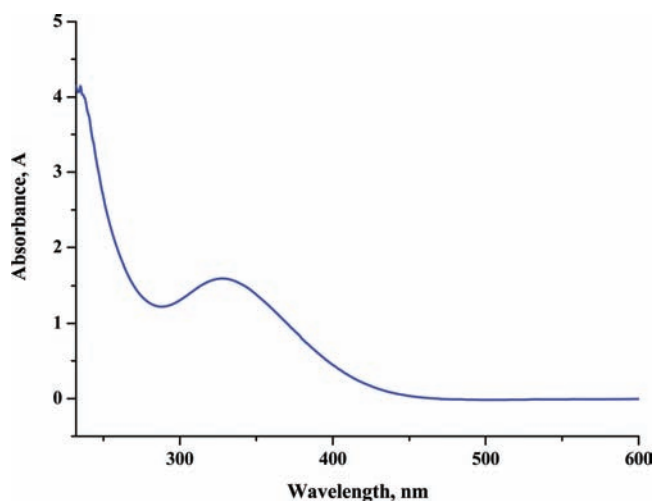


Figure 4. UV–visible spectrum of 3 in water.

at 328 nm ($\epsilon = 541 \text{ M}^{-1} \text{ cm}^{-1}$; 1) and 329 nm ($\epsilon = 183 \text{ M}^{-1} \text{ cm}^{-1}$; 3), respectively, with a rising absorbance into the ultraviolet region. An additional feature was observed at around 213.0 nm ($\epsilon = 4257 \text{ M}^{-1} \text{ cm}^{-1}$; 1) and 228 nm ($\epsilon = 612.4 \text{ M}^{-1} \text{ cm}^{-1}$; 3), respectively. The spectrum was featureless beyond 400 nm. The band at 328 nm (1) or 329 nm (3) has been attributed to the presence of a peroxide to vanadium ligand to metal charge transfer (LMCT).⁴⁷ It appears, therefore, that at the pH employed here, the peroxide group remains attached to

the vanadium ion, further supporting the idea of a stable [(V=O)(O₂)]⁺ unit in both complexes. The presence of the weak LMCT band, as suggested by Evans,⁴⁸ was also observed in other vanadium–peroxido complexes and was reasonably attributed to a $\pi^* \rightarrow d\sigma^*$ transition.⁴⁷ The intense absorption band at 213 nm in 1 and 3, in the ultraviolet region, may be associated with a $(\sigma)\pi^*\nu \rightarrow d\sigma^*$ LMCT transition. This transition had been previously proposed to occur at energies higher than that expected, due to $\pi^* \rightarrow d$ transition.⁴⁹ Further definitive assignments are difficult to make at the present time in the absence of detailed spectroscopic studies.^{47,49} Furthermore, in a time dependent experiment on 3 over a period of 90 days, it was shown that the intensity of the band at 328 nm ($\epsilon = 612.4 \text{ M}^{-1} \text{ cm}^{-1}$) decreases with time. By the end of this period, the specific band disappears. The progressive disappearance of the specific band indicates the commensurate disappearance of the peroxide to vanadium ligand to metal charge transfer (LMCT), consistent with the departure of the peroxide group from the V(V) coordination sphere. The behavior projects the (in)stability of the vanadium–peroxido assembly in solution over long periods of time. Finally, the complex becomes non-peroxido. The isolation and determination of the nature of the arisen species is currently being pursued in our lab.

FT-IR Spectroscopy. The FT-IR spectra of 1, 2, and 3 were recorded in KBr and reflected the presence of vibrationally active carboxylate groups. Antisymmetric and symmetric vibrations for the carboxylate groups of the coordinated betaine ligands were observed in all cases. Specifically, the antisymmetric stretching vibrations $\nu_{as}(\text{COO}^-)$ for the carboxylate carbonyls emerged at 1662 cm^{-1} for 1, 1634 cm^{-1} for 2, and 1632 cm^{-1} for 3. Symmetric stretching vibrations $\nu_s(\text{COO}^-)$ for the same groups appeared in the range 1467–1307 cm^{-1} for 1, 1472–1330 cm^{-1} for 2, and 1428–1338 cm^{-1} for 3. The observed carbonyl vibrations were shifted to lower frequency values in comparison to the corresponding vibrations in the free betaine ligand, suggesting changes in the vibrational status of the betaine ligand upon binding to vanadium.⁵⁰ The latter indication was attested to by the X-ray crystal structures of 1, 2, and 3. Furthermore, the $\nu(\text{O}=\text{O})$ vibration appeared at 836 cm^{-1} for both 1 and 2 and 931 cm^{-1} for 3, while the $\nu(\text{VO})$ vibration for the V=O groups was present at 975 cm^{-1} for 1, 958 cm^{-1} for 2, and 970 cm^{-1} for 3. The described tentative assignments are in agreement with those previously reported in dinuclear V(V)–peroxido complexes^{42,45,51–53} and consistent with infrared frequencies previously attributed to carboxylate-containing ligands bound to different metal ions.⁵⁴

Solid-State NMR Spectroscopy. The RampCP-MAS ¹³C NMR spectra of 1 and 3 (Figures 5A and 6A, respectively) were consistent with the binding coordination mode of the betaine ligand around the V(V) ion. Both spectra exhibit three distinct peak features. Two of those lie in the high field region, whereas the other one emerges in the low field region. The peaks in the high field region at 49.1 ppm for 1 and 54.0 ppm for 3 could be assigned to the methyl carbons bound to the nitrogen amine atom. The second resonance, in the high field region, at 61.1 ppm for 1 and 65.0 ppm for 3 could be assigned to the methylene carbon located adjacent to the coordinated carboxylate of the bound betaine ligand. In the low field region, where the carbonyl carbon resonance is expected to appear, there was a resonance at 166.0 ppm for 1 and 174.0 ppm for 3 that could be attributed to the betaine carboxylate group, bound to the V(V) ions of the central core. These

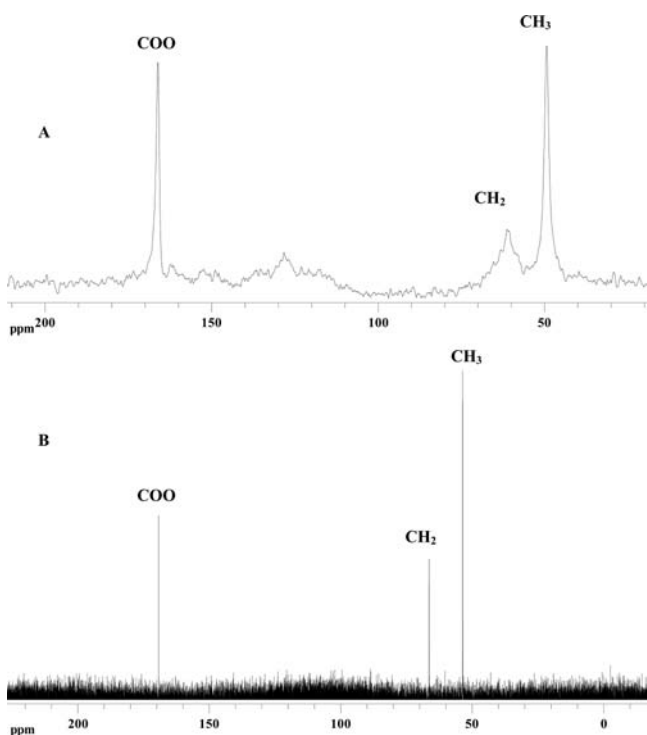


Figure 5. ^{13}C -RampCP-MAS NMR spectrum of complex **1** in the solid state (A) and ^{13}C -NMR spectrum of complex **1** in solution (B).

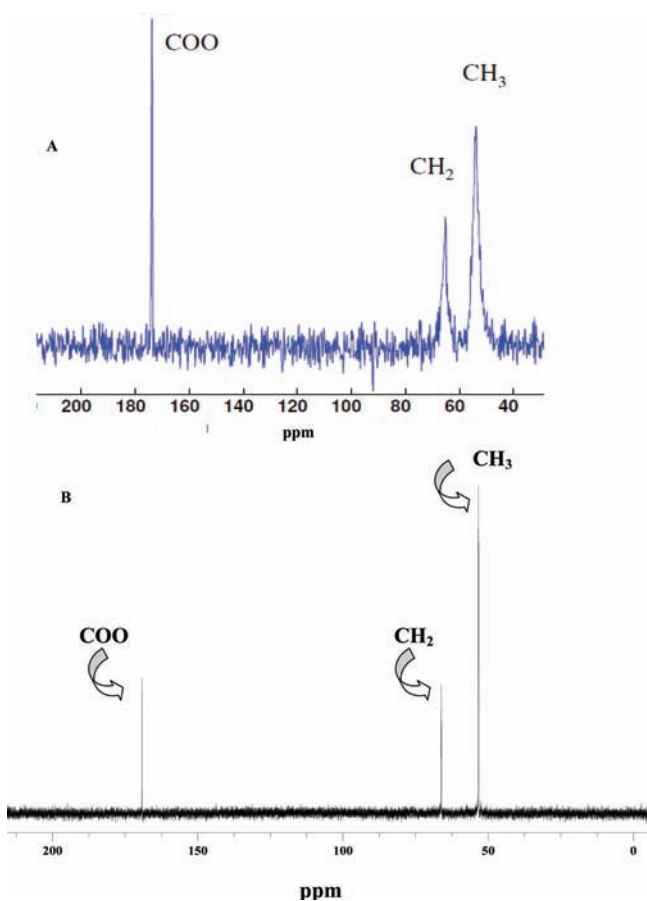


Figure 6. ^{13}C -RampCP-MAS NMR spectrum of complex **3** in the solid state (A) and ^{13}C -NMR spectrum of complex **3** in solution (B).

observations were subsequently confirmed by X-ray crystallography.

^{51}V has a spin of $7/2$, a fact that has been reportedly exploited to gain knowledge on structural features of $\text{V}(\text{V})$ compounds.⁵⁵ To this end, the ^{51}V MAS NMR spectra of **3** were obtained, with NaVO_3 as the reference (-513.0 ppm). Positive chemical shift values (δ) are taken to correspond to lower shielding in comparison to the reference. The spectrum of **3** exhibits resonances in a broad range (-300 to -600 ppm), with the main signals bearing multiple spinning sidebands because of both quadrupolar coupling and chemical shift anisotropy. The identity of the central resonances was confirmed by running experiments with different spinning frequencies. The resonance, the chemical shift of which did not change with frequency, was the one attributed to the main resonance.

The spectrum of **3** exhibits one central resonance at -586 ppm (Figure 7). It should be noted that assignments of NMR

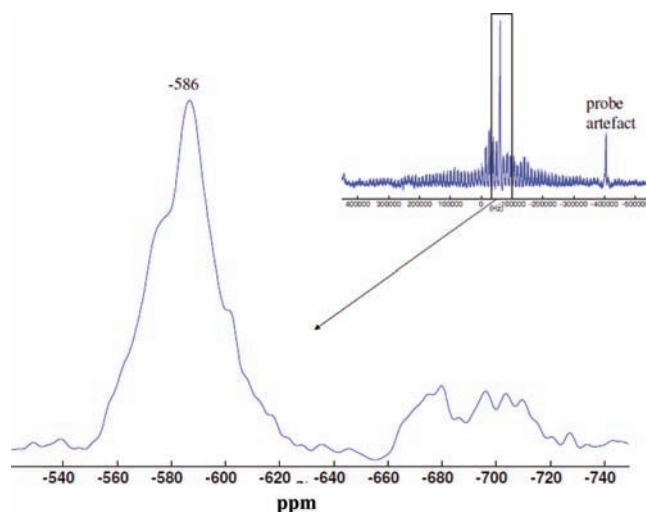


Figure 7. ^{51}V MAS NMR spectrum of complex **3** in the solid state.

shifts to different coordination numbers of $\text{V}(\text{V})$ compounds are not straightforward.⁵⁶ On the basis of past reports on several known compounds,⁵⁷ various patterns had been observed, earmarking specific regions in the ^{51}V spectrum for five, six, and seven coordinate $\text{V}(\text{V})$ ions. To this end, ^{51}V solid-state NMR is very sensitive even to small angle changes in the coordination geometry around a $\text{V}(\text{V})$ center. Consistent with the above information, six-coordinate $\text{V}(\text{V})$ compounds exhibit resonances in the range -350 and -500 ppm. The results for **3**, therefore, indicate one signal for a six-coordinate $\text{V}(\text{V})$ at -586 ppm.

Solution NMR Spectroscopy. The solution ^{13}C NMR spectra of complexes **1** and **3** were measured in D_2O (Figures 5B and 6B, respectively). The spectra revealed the presence of three resonances. The first resonance in the high field region (53.3 ppm for both **1** and **3**) was attributed to the CH_3 groups of the betaine ligand bound to the sp^3 nitrogen atom. The second resonance in the high field region (66.1 ppm for **1** and 65.1 ppm for **3**) was attributed to the CH_2 group of the betaine ligand bound to the central $\text{V}(\text{V})$ ion. The signal at 169.2 ppm for both **1** and **3** in the lower field region was assigned to the carbon of the carboxylate group coordinated to the $\text{V}(\text{V})$ ion. These signals were shifted to lower fields in comparison to the resonances in pure free betaine. The resonance shift was ~ 4.0

ppm downfield for both **1** and **3** and was comparable to that observed in the RapmCP-MAS ^{13}C NMR solid-state spectra of **1** and **3**.

The ^1H NMR spectra of **1** and **3** in D_2O showed two peaks. One of them lies at 3.1 ppm for both **1** and **3**. The resonance is consistent with the presence of the methyl protons on the betaine ligand bound to the sp^3 nitrogen atom. The second signal lies at 3.77 ppm for **1** and 3.75 ppm for **3**. The signal is consistent with the presence of the methylene protons on the betaine ligand bound to the central $\text{V}(\text{V})$ ion. A very small downfield shift of the proton resonance was also observed in this case compared to pure free betaine. Collectively, there was a consistency between the solid and solution state spectra of the two compounds, denoting the discrete nature of the $\text{V}(\text{V})$ species in **1** and **3**.

Raman Spectroscopy. $K_2[\text{V}_2\text{O}_2(\text{O}_2)_4\{(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\}] \cdot \text{H}_2\text{O}$ (**1**). Complex **1** was characterized by micro-Raman and FT-Raman spectroscopy. Vibrational spectroscopy has already been successfully utilized to characterize vanadium–peroxido complexes. $^{58-63}$ Typical bands assigned to $\text{V}-\text{O}_\text{p}$ (peroxido) and $\text{O}-\text{O}$ vibrations in $\text{V}(\text{V})$ –peroxido complexes are observed in the spectral windows 660–440 and 800–950 cm^{-1} , respectively. More precisely, the $\text{O}-\text{O}$ stretching frequencies for oxido–monoperoxido complexes $^{60-63}$ mainly appear as a strong band near 930 cm^{-1} , whereas in diperoxido complexes 36,63 this band emerges at around 880 cm^{-1} . Micro-Raman and FT-Raman spectra of complex **1** are shown together in Figure 8. In both cases,

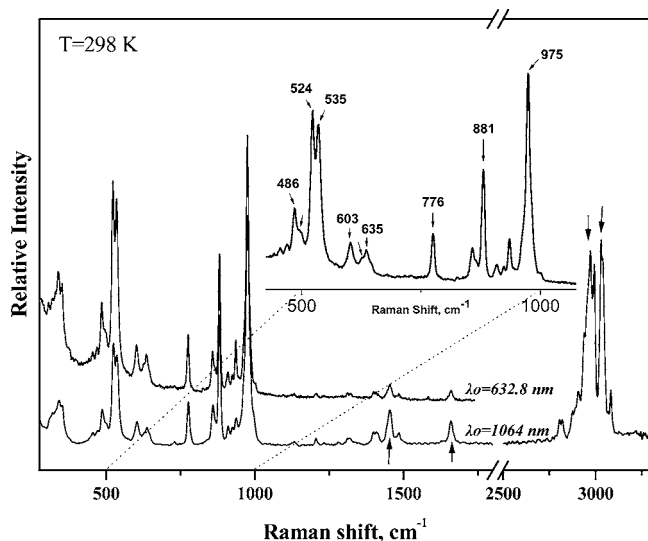


Figure 8. The micro-Raman and FT-Raman spectra of **1** in the solid state. Inset: the micro-Raman spectrum in the region where the typical vibrational bands of $\text{V}(\text{V})$ –peroxido complexes occur.

comparable spectral features along with relative scattering peak intensities were obtained, largely excluding polarization preferences of the Raman bands. However, the enhancement of the low frequency part of the excited visible spectrum is most probably accounted for by the occurrence of a fluorescent excitonic effect. The main micro-Raman scattering features of $\text{V}-\text{O}_\text{p}$ (peroxido), $\text{O}-\text{O}$, and $\text{V}=\text{O}$ stretches are separately shown as an inset. The strong Raman peak at 975 cm^{-1} is attributed to the $\text{V}=\text{O}$ stretch, while the Raman peak at ~ 881 cm^{-1} is assigned to the $\text{O}-\text{O}$ stretch of the $\text{VO}(\text{O}_2)_2$ group in typical vanadium–oxido–diperoxido complexes. 36,63 The cor-

responding $\text{V}-\text{O}_\text{p}$ stretch characteristics appear in the spectral region of 480–635 cm^{-1} . Note is made of the fact that the two vanadium centers of this dinuclear complex are chemically nonequivalent. One vanadium ion (V_1) coordinates an oxido ligand, two O_2^{2-} (η^2) ligands, and the bridging oxygen atom of the η^2, μ^1 -peroxido ligand. The other ion (V_2) coordinates the oxido ligand, two peroxido (bridging and chelating) (η^2) ligands, and the oxygen atom of the coordinated trimethylglycine molecule. In other words, these two vanadium centers exhibit different coordination environments. 64 This might be reflected onto the frequencies of the $\text{V}-\text{O}_\text{p}$ stretches that are structurally sensitive. 63 In this context, the Raman bands at 635, 603, and 486 cm^{-1} are tentatively attributed to the ν_1 , ν_2 , and ν_4 ($\text{V}-\text{O}_\text{p}$) stretches of the vanadium ion V_1 , while the intense peak at 524 cm^{-1} is tentatively assigned to the corresponding ν_3 stretching frequency. An equally intense Raman band located at 535 cm^{-1} is most probably due to the ν_3 ($\text{V}-\text{O}_\text{p}$) stretch of the vanadium ion V_2 ; this can also be correlated with the occurrence of shoulders at the low- and high-frequency side, respectively, of the ν_1 and ν_4 stretching frequencies of V_1 .

In the rest of the spectrum, the Raman peak located at 776 cm^{-1} is attributed to the symmetric stretching of the C_3N moiety. 65 The Raman bands at 1454 and 1660 cm^{-1} are assigned to the antisymmetric vibrations of the methyl (δ_{as}) and carboxylate groups, respectively. The high frequency Raman bands at ~ 2970 and 3034 cm^{-1} are correspondingly attributed to the symmetric and antisymmetric stretches of the CH_3 group.

$\{\text{Na}_2[\text{V}_2\text{O}_2(\text{O}_2)_4\{(\text{CH}_3)_3\text{NCH}_2\text{CO}_2\}]_n\} \cdot 4n\text{H}_2\text{O}$ (**3**). Complex **3** was characterized by NIR-FT-Raman and visible micro-Raman spectroscopy. $^{36,58-63}$ Typical bands assigned to $\text{V}-\text{O}_\text{p}$ (peroxido) and $\text{O}-\text{O}$ vibrations in $\text{V}(\text{V})$ –peroxido complexes are observed in the spectral windows 440–660 and 800–950 cm^{-1} , respectively. The FT-Raman spectrum of complex **3** is shown in Figure 9. The main Raman scattering features of $\text{V}-\text{O}_\text{p}$ (peroxido), $\text{O}-\text{O}$, and $\text{V}=\text{O}$ stretches are separately shown as an inset. Similar spectral features were obtained with a visible excitation (514.5 nm) in micro-Raman illumination/collection geometry (Supporting Information, Figure 1S). The strong Raman peak at 969 cm^{-1} is attributed to the $\text{V}=\text{O}$ stretch. The

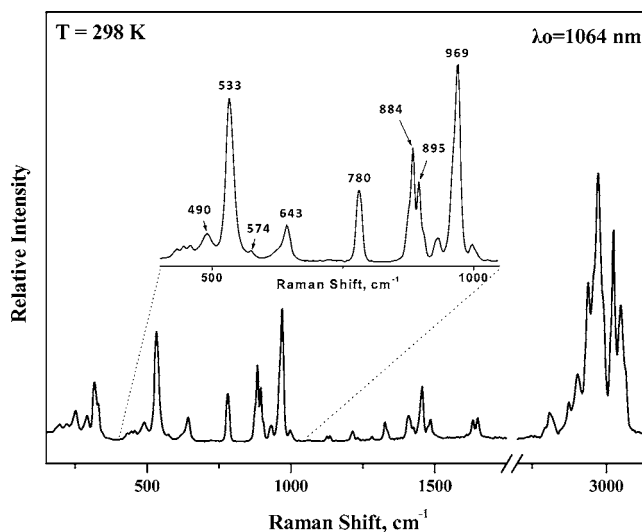


Figure 9. The FT-Raman spectrum of **3** in the solid state. Inset: the FT-Raman spectrum in the region where the typical vibrational bands of $\text{V}(\text{V})$ –peroxido complexes emerge.

related V–O_p stretch characteristics appear in the spectral region of 480–635 cm⁻¹. It is worth noting that the two vanadium centers of this dinuclear complex are almost chemically equivalent. One vanadium atom (V₁) coordinates an oxido ligand, two O₂²⁻ moieties (one of them bridging Na⁺; η² ligands), and the bridging oxygen atom of the coordinated trimethylglycine molecule. The other ion (V₂) coordinates an oxido ligand, two peroxido moieties (one of them bridging Na⁺ and chelating; η² ligands), and the oxygen atom of the coordinated trimethylglycine molecule, as well. In other words, these two vanadium ions exhibit almost a similar coordination environment.⁶⁴ This is reflected onto the frequencies of the V–O_p stretches that are structurally sensitive.⁶³ In this context, the Raman bands at 490, 574, and 643 cm⁻¹ are tentatively attributed to the ν₁, ν₂, and ν₄ (V–O_p) stretches, while the intense peak at 533 cm⁻¹ is attributed to the corresponding ν₃ stretching frequency. This limiting “high frequency” value of ν₃ (V–O_p) is accounted for by a pentagonal pyramidal arrangement around the vanadium centers with pseudotetrahedral coordination sites.⁶³ The Raman band at ~884 cm⁻¹ is well assigned to the O–O stretch of the VO(O₂)₂ group in typical vanadium–oxido–diperoxido complexes.^{36,63} The adjacent Raman band at 895 cm⁻¹ might also be attributed to the O–O stretch of an oxido–diperoxido moiety bound to the vanadium center, seemingly not strongly influenced by the presence of abutting sodium ions in the lattice. This band, which is highly polarization dependent (Supporting Information, Figure 1S), could however have arisen from the C–N stretch of the corresponding bond connecting the N(CH₃)₃ group to the acidic part of betaine.⁶⁵ In the remainder of the spectrum, the Raman peak located at 780 cm⁻¹ is attributed to the symmetric stretch of the C₃N moiety.⁶⁵ The Raman band at 1454 cm⁻¹ is assigned to the antisymmetric vibrations of the methyl (δ_{as}) group, while the high frequency Raman bands at ~2972 and 3023 cm⁻¹ are correspondingly attributed to the symmetric and antisymmetric stretch of the CH₃ group.

Cyclic Voltammetry. The cyclic voltammetry of complexes **1** and **3** (Supporting Information, Figure 2S and 3S) was studied in aqueous solutions, in the presence of KNO₃ as a supporting electrolyte. The cyclic voltammogram exhibits an ill-defined electrochemical behavior for both species, reflecting (a) a reduction wave at E_{pc} = -0.76 V for **1** and E_{pc} = -0.83 V for **3** and (b) an oxidation wave at E_{pa} = -0.57 V for **1** and E_{pa} = -0.54 V for **3** (ΔE = 200 mV, ip_a/ip_c < 1, ip_c/[(v)^{1/2}C] variable). This voltammetric behavior projects irreversible V^V/V^{IV} redox processes associated with species **1** and **3**. The observed irreversibility is not easily understood at the present time, as it might involve complex processes, encompassing concurrent oxidation state and coordination number changes associated with the presence/absence of peroxide on the V₂O₂ core. Attempts to pursue the isolation of reduced products **1**, **2**, and **3** are currently ongoing.

Thermal Studies. The thermal decomposition of complex **3** was studied by TGA-DTG under an atmosphere of oxygen (Figure 10). The complex is thermally stable up to 30 °C. From that point on, a fairly broad heat process points to the deperoxidation and dehydration of **3**, with the release of peroxides and lattice water molecules between 30 and 146 °C. The observed cumulative weight loss amounts to 22% based on the molecular formula of the title complex. Between 146 and 409 °C, there is further weight loss, in line with the departure of the oxide and peroxide groups and the decomposition of the organic structure of the molecule. No clear plateaus are reached

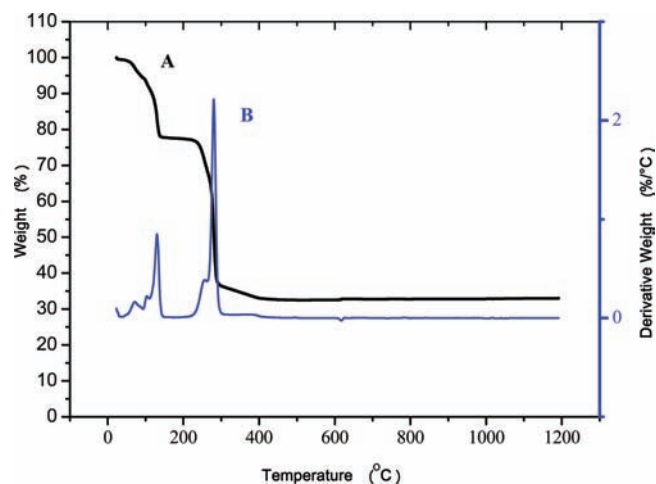


Figure 10. TGA (A) and DTG (B) analysis of **3**.

in these stages, suggesting that the derived products are unstable and decompose further. The total weight loss of 68.33% due to the decomposition of complex **3** is reached at 409 °C, with no further loss up to 800 °C, in line with the thesis that the product at that temperature and beyond (409 °C) is V₂O₅.⁶⁶ The DTG profile of the complex exhibits clear features that correspond to the aforementioned TGA processes.

DISCUSSION

The Betaine Chemistry. In view of (a) the chemical affinity of V(V) for peroxide, (b) the diverse structural chemistry of vanadium with peroxides, and (c) the ability of V(V) to form both mono- and diperoxido binary as well as ternary complexes with physiological or biomimetic ligands, employment of zwitterionic ligands capable of promoting vanadium binding could lead to new V(V)–peroxido–ligand materials. Previous work in the lab has shown that chemical reactivity in ternary V(V)–amino acid–peroxido systems can lead to ternary materials bearing zwitterionic forms of amino acids bound to V(V)–peroxido cores. To this end, the herein aqueous synthetic chemistry of V(V) with hydrogen peroxide was pursued in the presence of an electrically balanced carboxylate species—a zwitterion—trimethyl glycine. Bearing in mind the complex aqueous speciation of binary and ternary species of V(V) with peroxides and hydroxycarboxylic acid ligands, a structural speciation approach was adopted, giving emphasis to pH-dependent synthesis. Hence, the reaction of V₂O₅, betaine, and hydrogen peroxide, under carefully tuned pH conditions,⁶⁷ led to the isolation of the rare complexes **1**, **2**, and **3**. The physicochemical characterization of **1**, **2**, and **3** in the solid state and in solution through elemental analysis, multinuclear NMR in the solid state and in solution, FT-IR, Raman, TGA-DTG, and cyclic voltammetry was in line with the crystallographic structures of those species and projected well-defined species emerging from aqueous media and isolated in the solid state.

The Rare Ternary V(V)–Peroxido–Betaine Species. The explored chemical reactivity of the ternary V(V)–peroxido–betaine system led to variable nuclearity (dinuclear in **1** and **2** and mononuclear in the polymeric **3**) assemblies configured around distinctly formulated V(V)–peroxido cores. Key points in the chemical reactivity of the employed aqueous mixtures include the following:

- (a) The involvement of a base (ammonia vs potassium hydroxide and sodium hydroxide) in the reaction. When KOH was used, the K^+ ion fitted appropriately into the lattice of **1**, effectively balancing out the negative charge of the dinuclear assembly and forming a 2D topologically interesting honeycomb arrangement of nine-coordinate potassium polyhedra, with six of them held together by the dinuclear V(V) entities. When ammonia was used in **2**, ammonium was inserted right into the lattice and stabilized the arising crystal structure through weak intermolecular interactions (i.e., hydrogen bonds). When NaOH was used in **3**, on the other hand, rare zigzag chains with a trans–cis sequence of sodium octahedra emerged, held together by mononuclear V(V) entities. It appears, therefore, that the nature of the cation used in the reaction mixtures employed is important in the stabilization of uniquely derived lattices in **1**, **2**, and **3**.
- (b) The nature of the betaine ligand coordinated to V(V). Betaine, as a zwitterionic moiety, binds V(V) through the anionic carboxylate group as expected. The binding process yields an asymmetric binding of the ligand to the dinuclear assembly, with the zwitterionic ligand attached to only one vanadium center. The second vanadium center bears no ligand and retains its binary identity with oxo and peroxide moieties, thus fulfilling its coordination requirements. The deeper reasons for the selective propensity of betaine binding to a single V(V) center are currently being perused.
- (c) The mode of coordination of the betaine ligand to the dinuclear assembly. Betaine inserts itself into the coordination sphere of vanadium atoms through the carboxylate group, in a monodentate fashion. The betaine ligand, however, resembles the glycine ligand. To this end, the difference between the complexes isolated with glycine and those isolated herein with betaine is the coordination mode of the two ligands. In the former case, the glycinate ligand binds both vanadium atoms spanning the distance between the two centers, with each oxygen in the carboxylate group binding one vanadium center. In the case of the betaine ligand, the betaine is coordinated to the vanadium center in a monodentate mode, but only one of the two oxygens of the carboxylate group is coordinated to a single vanadium center. Furthermore, the selective binding of the betaine ligand to only one vanadium center differentiates the $V-O_p$ (peroxido) distances holding the dinuclear assembly together. In this regard, there is only one $V-O_p$ bond distance (2.057(3) Å) in **1** and (2.030(3) Å) **2**, reflecting the consequences of betaine binding to a single vanadium center. An analogous case is present in the coordination polymer **3**. In the case of the glycinate complexes reported previously,³⁶ the proximity of the two vanadium centers was reflected in $V-O_p$ bond distances in the range 2.328(3)–2.379(3) Å. Apart from this ostensible coordination mode variability, the peroxido-anchored divanadium core remains intact, albeit coordinatively differentiated, in the assemblies of both cases of glycinate and betaine complexes.

Consequently, the characteristic $[(V^V=O)(O_2)_2]_2$ dinuclear core assembly previously seen in the glycinate complexes is not there, because (a) in **1** and **2** the only connection between the two vanadium centers is provided by an oxygen atom from a

peroxide group, and (b) in the case of the coordination polymer **3**, Na^+ ions are interposed between the vanadium centers. Consequently, the peroxide bridge plays an important role in formulating the coordination geometry around each vanadium ion, while concurrently providing ample options for the adjustment of the spatial requirements of the two units within a single assembly. A similar case had been previously reported in complexes such as $[V_2O_2(O_2)_4(H_2O)]^{2-}$, complex units of the type $[H\{VO(O_2)_2bipy\}_2]^-$, where the bridge is a O^{2-} moiety, and the ternary V–peroxido–glycinate complexes.

The zwitterionic ligand essentially (a) dictates the $V\cdots V$ distance between the two $[V(=O)(O_2)_2]$ units in the tetraperoxido assemblies of **1** and **2**. The distance is 3.083(1) (**1**) and 3.037(1) (**2**) Å, with both $V\cdots V$ distances being similar to the ones observed in $[O(VO(O_2)_2)_2]^{4-}$ (3.044(6) Å),³⁹ $[V_2O_2(O_2)_4(H_2O)]^{2-}$ (3.120 Å),⁴⁰ and $[V_2O_2(O_2)_4(H_2O)]^{2-}$ (3.239(5) Å)⁴¹ and shorter than the ones observed in $(H_3O)_2[V_2(O)_2(\mu_2:\eta^2:\eta^1-O_2)_2(\eta^2-O_2)_2(C_2H_5NO_2)]\cdot 5/4H_2O$ (3.373(7) Å)³⁶ and $K_2[V_2(O)_2(\mu_2:\eta^2:\eta^1-O_2)_2(\eta^2-O_2)_2(C_2H_5NO_2)]\cdot H_2O$ (3.380(4) Å).³⁶ In the case of complex **3**, the distance between the two V(V) ions is extremely long because there is no direct proximity between the two V(V) centers.

Potential Linkage to Influence (Bio)chemical Processes. V(V)–peroxido complexes of the general formula $M_x[V(=O)(O_2)L]$ and $M_x[V(=O)(O_2)_2L]$ (where L is an appropriate organic vanadium binder and x is a function of the charge of L) have been shown to exert insulin mimetic activity in *in vitro* experiments.⁶⁸ Peroxido vanadates have also been shown to participate in homogeneous catalysis,⁶⁹ as possible models in the mechanism of vanadium haloperoxidase.⁷⁰ In the present work, **1** and **2** bear the fundamental features of species potentially involved in such activity, i.e., diperoxido vanadium units, in tetraperoxido assemblies. There is a striking difference, however, between the herein described species and the previously reported divanadium (tetra)peroxido complexes bearing the amino acid glycinate.³⁶ In the latter complexes, both vanadium centers are seven coordinate, exhibiting pentagonal bipyramidal geometry. Moreover, the nature of glycine vs betaine appears to be important in guiding the aqueous assembly chemistry, ultimately leading to the isolation of distinctly differentiated compounds in the solid state. It is either the chemical nature, reactivity, or both and the resulting chemistry involved that directs the modulation of the coordination process around the vanadium–peroxido unit. In view of the variable chemical reactivity of vanadium–peroxido systems, the fundamental $[(V^V=O)(O_2)_2]$ units emerging from glycine and its derivative betaine (a) are generated in aqueous media, albeit differentiated, (b) bear bound physiological heteroligands in a zwitterionic form, and (c) may reflect a chemical propensity of variable nature toward cellular targets and processes affecting cell physiology/pathology. It remains to be seen whether the herein unusual dinuclear V(V)–tetraperoxido species could influence cellular events *in vitro* and exhibit a different bioreactivity vs the glycinate derivatives.

CONCLUSIONS

Three new ternary vanadium–peroxido–betaine species were synthesized, isolated, and characterized in the solid state and in solution. The structural features in **1**–**3** are distinct from those of simple vanadium–peroxido species, which themselves are very few. The nature and nuclearity of vanadium–peroxido moieties deviate significantly from that of the thus far known

dinuclear species. Ostensibly, the presence of betaine provides solubility and stability characteristics to the existing species. Given that betaine-like molecules are present in biological fluids, it would be important to discover if betaine-bearing vanadium–peroxido species exhibit biological activity of modulated strength under varying conditions. In view of this new discovery in vanadium–peroxido chemistry, it would also be worth investigating the possibility that other betaine-like substrates, apart from this simple betaine, can promote the same or similar chemistry to the one shown here with vanadium and hydrogen peroxide. In this regard, the physicochemical properties of variable nature and structure binary vanadium–tetraperoxido species interacting with betaine ligands could be modulated, providing finely tuned soluble and potentially bioavailable forms of vanadium capable of promoting further complex interactions with higher molecular mass biomolecules. Such ternary interactions reflect adequately the complexity of vanadium reactivity patterns that might be responsible for initiating or promoting diverse yet distinct events in signal transduction pathways linked to insulin mimesis or antitumorigenesis. Such chemistries are currently being investigated in our lab.

■ ASSOCIATED CONTENT

■ Supporting Information

X-ray crystallographic files, in CIF format (CCDC 873654 (1), 873655 (2), and 873656 (3)), and listings of positional and thermal parameters and H-bond distances and angles for **1**, **2**, and **3**. Micro-Raman spectra in the solid state of **3** and cyclic voltammetry of **1** and **3**. This material is available free of charge via Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

■ Corresponding Author

*Tel.: +30-2310-996-179. Fax: +30-2310-996-196. E-mail: salif@auth.gr.

■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Greek State Scholarships Foundation “IKY”, and cofinanced by the EU–ESF and Greek national funds through the NSRF–Heracleitus II program. The authors would like to thank the DFG (Deutsche Forschungsgemeinschaft) and the Experimental Physics Institutes of Leipzig University for support (Dr. Bertmer) with the Avance NMR spectrometer.

■ REFERENCES

- (1) (a) Baran, E. J. *J. Inorg. Biochem.* **2000**, *80*, 1–10. (b) Rehder, D. *Biometals* **1992**, *5*, 3–12. (c) Zubieta, J. *Comments Inorg. Chem.* **1994**, *3*, 153–183. (d) Chen, Q.; Salta, J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 4485–4486. (e) Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 148–167. (f) Wever, R.; Kustin, K. *Advances in Inorganic Chemistry: Vanadium, a Biologically Relevant Element*; Sykes, A. G., Ed.; Academic Press, Inc.: New York, 1990; Vol. 35, pp 103–137.
- (2) (a) Bayer, E. *Metal Ions in Biological Systems: Amavadin, the Vanadium Compound of Amanitae*; Sigel, H., Sigel, A., Eds.; Marcel Dekker, Inc.: New York, 1995; Vol. 31, Chapter 12, pp 407–421. (b) Smith, M. J.; Ryan, D. E.; Nakanishi, K.; Frank, P.; Hodgson, K. O. *Metal Ions in Biological Systems: Vanadium in Ascidiarians and the Chemistry in Tunichromes*; Sigel, H., Sigel, A., Eds.; Marcel Dekker,

Inc.: New York, 1995; Vol. 31, Chapter 13, pp 423–490. (c) Fraústo da Silva, J. J. R. *Chem. Speciation Bioavailability* **1989**, *1*, 139–150.

(3) Liang, J.; Madden, M.; Shah, V. K.; Burris, R. H. *Biochemistry* **1990**, *29*, 8577–8581.

(4) (a) Weyand, M.; Hecht, H.; Kiess, M.; Liaud, M.; Vilter, H.; Schomburg, D. *J. Mol. Biol.* **1999**, *293*, 595–611. (b) Vilter, H. *Metal Ions in Biological Systems: Vanadium and its Role in Life*; Sigel, H., Sigel, A., Eds.; Marcel Dekker, Inc.: New York, 1995; Vol. 31, Chapter 10, pp 325–362. (c) Butler, A. *Curr. Opin. Chem. Biol.* **1998**, *2*, 279–285.

(5) Butler, A. *Coord. Chem. Rev.* **1999**, *187*, 17 and references cited therein.

(6) Pecoraro, V.; Sleboznick, C.; Hamstra, B. *Vanadium Compounds: Chemistry, Biochemistry, and Therapeutic Applications*; Crans, D. C., Tracey, A., Eds.; American Chemical Society: Washington, DC, 1998; ACS Symposium Series 711, chapter 12.

(7) Ligtenbarg, A. G. J.; Hage, R.; Feringa, B. L. *Coord. Chem. Rev.* **2003**, *237*, 89.

(8) Van Schijndel, J. W. P. M.; Vollenbroek, E. G. M.; Wever, R. *Biochim. Biophys. Acta* **1993**, *1161*, 249.

(9) (a) Djordjevic, C. *Metal Ions in Biological Systems: Antitumorigenic Activity of Vanadium Compounds*; Sigel, H., Sigel, A., Eds.; Marcel Dekker, Inc.: New York, 1995; Vol. 31, Chapter 18, pp 595–616. (b) Köpf-Maier, P.; Köpf, H. *Metal Compounds in Cancer Therapy*; Fricker, S. P., Ed.; Chapman and Hall: London, 1994; pp 109–146. (c) Djordjevic, C.; Wampler, G. L. *J. Inorg. Biochem.* **1985**, *25*, 51–55.

(10) (a) Klarlund, J. K. *Cell* **1985**, *41*, 707–717. (b) Smith, J. B. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 6162–6167.

(11) (a) Walton, K. M.; Dixon, J. E. *Annu. Rev. Biochem.* **1993**, *62*, 101–120. (b) Lau, K.-H. W.; Farley, J. R.; Baylink, D. J. *Biochem. J.* **1989**, *257*, 23–36.

(12) (a) Brand, R. M.; Hamel, F. G. *Int. J. Pharm.* **1999**, *183*, 117–123. (b) Drake, P. G.; Posner, B. I. *Mol. Cell. Biochem.* **1998**, *182*, 79–89. (c) Drake, P. G.; Bevan, A. P.; Burgess, J. W.; Bergeron, J. J.; Posner, B. I. *Endocrinology* **1996**, *137*, 4960–4968. (d) Eriksson, J. W.; Lönnroth, P.; Posner, B. I.; Shaver, A.; Wesslau, C.; Smith, U. P. *Diabetologia* **1996**, *39*, 235–242. (e) Tatierysk, J.; Pacigová, S.; Sivák, M.; Schwendt, P. *J. Arg. Chem. Soc.* **2009**, *97*, 181–198.

(13) (a) Sakurai, H.; Kojima, Y.; Yoshikawa, Y.; Kawabe, K.; Yasui, H. *Coord. Chem. Rev.* **2002**, *226*, 187–198. (b) Sasagawa, T.; Yoshikawa, Y.; Kawabe, K.; Sakurai, H.; Kojima, Y. *J. Inorg. Biochem.* **2002**, *88*, 108–112. (c) Kanamori, K.; Nishida, K.; Miyata, N.; Okamoto, K.; Miyoshi, Y.; Tamura, A.; Sakurai, H. *J. Inorg. Biochem.* **2001**, *86*, 649–656. (d) Takino, T.; Yasui, H.; Yoshitake, A.; Hamajima, Y.; Matsushita, R.; Takada, J.; Sakurai, H. *J. Biol. Inorg. Chem.* **2001**, *6*, 133–142. (e) Melchior, M.; Rettig, S. J.; Liboiron, B. D.; Thompson, K. H.; Yuen, V. G.; McNeill, J. H.; Orvig, C. *Inorg. Chem.* **2001**, *40*, 4686–4690. (f) Sun, Q.; Sekar, N.; Goldwasser, I.; Gershonov, E.; Fridkin, M.; Shechter, Y. *Am. J. Physiol. Endocrinol. Metab.* **2000**, *279*, E403–E410. (g) Goldwasser, I.; Gefel, D.; Gershonov, E.; Fridkin, M.; Shechter, Y. *J. Inorg. Biochem.* **2000**, *80*, 21–25. (h) Woo, L. C.; Yuen, V. G.; Thompson, K. H.; McNeill, J. H.; Orvig, C. *J. Inorg. Biochem.* **1999**, *76*, 251–257.

(14) Crans, D. C.; Smees, J. J.; Gaidamauskas, E.; Yang, L. *Chem. Rev.* **2004**, *104*, 849.

(15) Thompson, K. H.; McNeill, J. H.; Orvig, C. *Chem. Rev.* **1999**, *99*, 2561.

(16) Leifer, A.; Lippincott, E. R. *J. Am. Chem. Soc.* **1957**, *79*, 5098.

(17) Blunden, G.; Gordon, S. M. *Prog. Phycol. Res.* **1986**, *4*, 39.

(18) Ciszewska, R. *Postepy Nauk Rohn.* **1981**, *28*, 55.

(19) Yukawa, Y.; Inomata, Y.; Takeuchi, T. *Bull. Chem. Soc. Jpn.* **1982**, *56*, 2125.

(20) Yukawa, Y.; Inomata, Y.; Takeuchi, T.; Shimoi, M.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1982**, *553*, 135.

(21) Brill, W.; Schildkamp, W.; Spilker, J. Z. *Kristallogr.* **1985**, *172*, 281.

(22) (a) Chen, X.-M.; Mak, T. C. W. *Inorg. Chim. Acta* **1991**, *182*, 139. (b) Chen, X.-M.; Mak, T. C. W. *Polyhedron* **1991**, *10*, 273. (c) Chen, X.-M.; Mak, T. C. W. *J. Cryst. Spectrosc. Res.* **1991**, *21*, 21.

- (d) Chen, X.-M.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1991**, 3253. (e) Chen, X.-M.; Mak, T. C. W. *Aust. J. Chem.* **1991**, *44*, 1783.
- (23) Agrell, J. *Acta Chem. Scand.* **1970**, *24*, 3575.
- (24) Goher, M. A. S.; Mak, T. C. W. *Inorg. Chim. Acta* **1985**, *99*, 223.
- (25) Real, J. A.; Munno, G. D.; Carmen, M. M.; Julve, M. *Inorg. Chem.* **1991**, *30*, 2701.
- (26) Beauchamp, A. L.; Pazdernok, L.; Rivest, R. *Acta Crystallogr., Sect. B* **1976**, *32*, 650.
- (27) Peterson, E. J.; Von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1976**, *15*, 309.
- (28) (a) Cannas, M.; Carta, G.; Cvistini, A.; Marougiu, G. *J. Chem. Soc., Dalton Trans.* **1976**, 210. (b) Cannas, M.; Carta, G.; Cvistini, A.; Marougiu, G. *Inorg. Chem.* **1977**, *16*, 228.
- (29) (a) Drew, M. G. B.; Hamid bin Othman, A.; McFall, S. G.; McLroy, P. D. A.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1173. (b) Drew, M. G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 48, 1.
- (30) Metz, G.; Wu, X. L.; Smith, S. O. *J. Magn. Reson., Ser. A* **1994**, *110*, 219–227.
- (31) *CrystalClear*; Rigaku/MSI Inc.: The Woodlands, TX, 2005.
- (32) *SHELXTL-NT*, version 5.1; Bruker AXS: Madison, WI, 1998.
- (33) Iveson, S. J.; Johnston, C. B.; Harrison, W. T. A. *Crystals* **2011**, *1*, 59.
- (34) Alvarez, S.; Anvir, D.; Lulunell, M.; Pinsky, M. *New J. Chem.* **2002**, *26*, 996.
- (35) Volklinger, C.; Loiseau, T.; Haouas, M.; Taulelle, F.; Popov, D.; Burghammer, M.; Riekel, C.; Zlotea, C.; Cuevas, F.; Latroche, M.; Phanon, D.; Knöfel, C.; Llewellyn, P. L.; Ferey, G. *Chem. Mater.* **2009**, *21*, 5783–5791.
- (36) Gabriel, C.; Kaliva, M.; Venetis, J.; Baran, P.; Rodriguez-Escudero, I.; Voyiatzis, G.; Zervou, M.; Salifoglou, A. *Inorg. Chem.* **2009**, *48* (2), 476–487.
- (37) Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand. A* **1984**, *38*, 101–107.
- (38) Stomberg, R.; Olson, S.; Svensson, I.-B. *Acta Chem. Scand. A* **1984**, *38*, 653–656.
- (39) Stomberg, R.; Svensson, I.-B. *Acta Chem. Scand.* **1971**, *25*, 898–910.
- (40) Lapshin, A. E.; Smolin, Y. I.; Shepelev, Y. F.; Gyepesova, D.; Schwendt, P. *Acta Crystallogr.* **1989**, *C45*, 1477–1479.
- (41) Suchá, V.; Sivák, M.; Tyršlová, J.; Marek, J. *Polyhedron* **1997**, *16*, 2837–2842.
- (42) Kaliva, M.; Raptopoulou, C. P.; Terzis, A.; Salifoglou, A. *Inorg. Chem.* **2004**, *43*, 2895–2905.
- (43) Tsaramyrsi, M.; Kavousanaki, D.; Raptopoulou, C. P.; Terzis, A.; Salifoglou, A. *Inorg. Chim. Acta* **2001**, *320*, 47–59.
- (44) Djordjevic, C.; Lee, M.; Sinn, E. *Inorg. Chem.* **1989**, *28*, 719–723.
- (45) Kaliva, M.; Giannadaki, T.; Raptopoulou, C. P.; Tangoulis, V.; Terzis, A.; Salifoglou, A. *Inorg. Chem.* **2001**, *40*, 3711–3718.
- (46) Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand. A* **1983**, *37*, 709.
- (47) (a) Lever, A. B. P.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 1823–1824. (b) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348–355.
- (48) Evans, D. F. *J. Chem. Soc.* **1957**, 4013–4018.
- (49) Bhattacharjee, M.; Chaudhuri, M. K.; Islam, N. S.; Paul, P. C. *Inorg. Chim. Acta* **1990**, *169*, 97–100.
- (50) Deacon, G. B.; Philips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227–250.
- (51) (a) Wright, D. W.; Humiston, P. A.; Orme-Johnson, W. H.; Davis, W. M. *Inorg. Chem.* **1995**, *34*, 4194–4197. (b) Zhou, Z.-H.; Wan, H.-L.; Tsai, K.-R. *Chin. Sci. Bull.* **1995**, *40*, 749. (c) Velayutham, M.; Varghese, B.; Subramanian, S. *Inorg. Chem.* **1998**, *37*, 1336–1340.
- (52) Griffith, W. P.; Wickins, T. D. *J. Chem. Soc. A* **1968**, 397–400.
- (53) Vuletic, N.; Djordjevic, C. *J. Chem. Soc., Dalton Trans.* **1973**, 1137–1141.
- (54) (a) Matzapetakis, M.; Raptopoulou, C. P.; Terzis, A.; Lakatos, A.; Kiss, T.; Salifoglou, A. *Inorg. Chem.* **1999**, *38*, 618–619.
- (b) Matzapetakis, M.; Raptopoulou, C. P.; Tsohos, A.; Papefthymiou, B.; Moon, N.; Salifoglou, A. *J. Am. Chem. Soc.* **1998**, *120*, 13266–13267. (c) Matzapetakis, M.; Dakanali, M.; Raptopoulou, C. P.; Tangoulis, V.; Terzis, A.; Moon, N.; Giapintzakis, J.; Salifoglou, A. *J. Biol. Inorg. Chem.* **2000**, *5*, 469–474. (d) Matzapetakis, M.; Karligiano, N.; Bino, A.; Dakanali, M.; Raptopoulou, C. P.; Tangoulis, V.; Terzis, A.; Giapintzakis, J.; Salifoglou, A. *Inorg. Chem.* **2000**, *39*, 4044–4051. (e) Matzapetakis, M.; Kourgiantakis, M.; Dakanali, M.; Raptopoulou, C. P.; Terzis, A.; Lakatos, A.; Kiss, T.; Banyai, I.; Iordanidis, L.; Mavromoustakos, T.; Salifoglou, A. *Inorg. Chem.* **2001**, *40*, 1734–1744.
- (55) (a) Lapina, O. B.; Khabibulin, D. F.; Shubin, A. A.; Terskikh, V. V. *Prog. Nucl. Magn. Reson. Spectrosc.* **2008**, *53*, 128–191. (b) Nielsen, U. A.; Jakobsen, H. J.; Skibsted, J. *Inorg. Chem.* **2000**, *39*, 2135–2145. (c) Rehder, D.; Polenova, T.; Bühl, M. *Annu. Rep. NMR Spectrosc.* **2007**, *62*, 49–114.
- (56) (a) Hagen, H.; Bezemer, C.; Boersma, J.; Kooijman, H.; Lutz, M.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **2000**, *39*, 3970–3977. (b) Rehder, D. In *Studies in Inorganic Chemistry 13: Transition Metal NMR*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, The Netherlands, 1991.
- (57) Ooms, K. J.; Bolte, S. E.; Baruah, B.; Choudhary, M. A.; Crans, D. C.; Polenova, T. *Dalton Trans.* **2009**, 3262–3269.
- (58) Campbell, N. J.; Dengel, A. C.; Griffith, W. P. *Polyhedron* **1989**, *8*, 1379–1386.
- (59) Bhattacharjee, M.; Chaudhuri, M. K.; Paul, P. C. *Can. J. Chem.* **1992**, *70*, 2245–2248.
- (60) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101–3110.
- (61) Ahmed, M.; Schwendt, P.; Sivak, M. *Transition Met. Chem. (Dordrecht, Neth.)* **2004**, *29*, 675–680.
- (62) Tatiersky, J.; Schwendt, P.; Sivak, M.; Marek, J. *Dalton Trans.* **2005**, 2305–2311.
- (63) (a) Schwendt, P.; Ahmed, M.; Marek, J. *Inorg. Chem. Commun.* **2004**, *7*, 631–633. (b) Schwendt, P.; Volka, K.; Suchánek, M. *Spectrochim. Acta* **1988**, *44A*, 839–844. (c) Schwendt, P.; Pisarcik, M. *Spectrochim. Acta* **1990**, *46A*, 397–399. (d) Schwendt, P.; Tyršlová, J.; Pavelcik, F. *Inorg. Chem.* **1995**, *34*, 1964–1966.
- (64) Sergienko, V. S. *Crystallogr. Rep.* **2004**, *49*, 401–426.
- (65) Ilczyszyn, M. M.; Ratajczak, H. *Vib. Spectrosc.* **1996**, *10*, 177–189.
- (66) Duval, C. *Inorganic Thermogravimetric Analysis*, second and revised ed.; Elsevier Publishing Co.: Amsterdam, 1963; pp 294–300.
- (67) (a) Kaliva, M.; Gabriel, C.; Raptopoulou, C. P.; Terzis, A.; Salifoglou, A. *Inorg. Chim. Acta* **2008**, *361*, 2631–2640. (b) Kaliva, M.; Kyriakakis, E.; Gabriel, C.; Raptopoulou, C. P.; Terzis, A.; Tuchagues, J.-P.; Salifoglou, A. *Inorg. Chim. Acta* **2006**, *359*, 4535–4548.
- (68) (a) Shaver, A.; Ng, J. B.; Hall, D. A.; Loon, B. S.; Posner, B. I. *Inorg. Chem.* **1993**, *32*, 3109. (b) Yraola, F.; García-Vicente, S.; Marti, L.; Albericio, F.; Zorzano, A.; Royo, M. *Chem. Biol. Drug Des.* **2007**, *69*, 423–428.
- (69) (a) Di Furia, F.; Modena, G. *Rev. Chem. Intermed.* **1985**, *6*, 51. (b) Köpf-Maier, P.; Wagner, W.; Hesse, B.; Köpf, H. *Eur. J. Cancer* **1981**, *17*, 665.
- (70) (a) Djordjevic, C.; Lee, M.; Jacobs, B. A.; Puryear, B. C. *J. Inorg. Biochem.* **1989**, *36*, 239. (b) Wever, R.; Kustin, K. *Advances in Inorganic Chemistry: Vanadium, a Biologically Relevant Element*; Sykes, A. G., Ed.; Academic Press, Inc.: New York, 1990; Vol. 35, p 81.