same as those of $Al(acac)_3$ (average 1.380 (14) Å). C(3)–O(2), the hydroxyl bond length (1.281 (5) Å), is exactly the average for C–O in $Al(acac)_3$ while the ketonic bond is actually shorter (1.261 (5) Å). Overall, the ligand is significantly delocalized on bonding to aluminum, almost as much as is the acac anion.

Solution potentiometry demonstrates that isomaltol is a weak acid and that the isomaltolato anion is not an outstanding binding group for the group IIIA (13) metal ions (Table V). Isomaltol should have potential as the metal-binding component of higher dentate chelating agents, however. Table V lists both the stepwise formation constants K_n and the overall formation constants β_n defined by

$$K_n = \frac{[ML_n^{(3-n)+}]}{[ML_{n-1}^{(4-n)+}][L^-]} \qquad \beta_n = \frac{[ML_n^{(3-n)+}]}{[M^{3+}][L^-]^n}$$

and determined from the potentiometric titration data by the methods outlined in the Experimental Section. The number in parentheses represents the standard deviation between successive runs. The formation constants are less than those for the group IIIA (13) M^{3+} complexes of the 2,4-pentanedionato (acac) anion, where $\log \beta_1$ is ~8.7, $\log \beta_2$ ~16.5, and $\log \beta_3$ ~23.[29] Clearly, the similarity noted above between the ^{27}Al NMR spectral properties of $Al(ima)_3$ and $Al(acac)_3$ does not extend to the thermodynamic binding parameters of the respective complexes.

Speciation diagrams for the $M(ima)_3$ complexes as a function of $-\log [H^+]$ are presented in Figure 2, and from these the hydrolysis of the complexes can be easily discerned. The higher second formation constant of ima^- for Ga compared with those for Al and In is demonstrated by the maximum for GaL_2^+ at pH 3.5 rather than 4 or greater. Comparison of the high-pH regions (>6) of the diagrams shows that isomaltol is incapable of preventing the hydrolysis of its simple tris(ligand)metal complexes, at least at the millimolar concentrations studied. As the pH rises, the isomaltolato anion cannot compete with hydroxide for the M^{3+}. With In^{3+} the situation is more complicated by the formation of various chloride species in addition to hydrolysis.[8] Mixed-ligand chloro- or hydroxo–In–ima complexes were not sought. From the high-yield syntheses of the complexes in water, it is obvious that this hydrolysis is minimized by increased concentrations of M^{3+} and isomaltol.

In conclusion, we have shown that the isomaltol moiety is a useful chelating group for some trivalent nontransition-metal ions. Our concern was to find a low molecular weight binding group with a functionalizable site near the metal, and Hima is a successful candidate. We have attempted the synthesis of its methylimine analogue; however, the reaction of isomaltol and methylamine results, through a rearrangement,[30] in a 3-hydroxy-4-pyridinone rather than producing the desired Schiff base condensation at the ketone. Our goal is to prepare tris(2-acyl-3-hydroxyfuran)-based hexadentate chelating agents, and the work reported here suggests that this area will prove fruitful.

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Supplementary Material Available: Tables of anisotropic thermal parameters (Table SI), calculated hydrogen coordinates (Table SII), torsion angles (Table SIII), and intraannular torsion angles (Table SIV) (5 pages); a table of measured and calculated structure factor amplitudes (Table SV) (18 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, The College of William and Mary, Williamsburg, Virginia 23185, and University of Virginia, Charlottesville, Virginia 22901

Oxoperoxo(citrato)- and Dioxo(citrato)vanadates(V): Synthesis, Spectra, and Structure of a Hydroxyl Oxygen Bridged Dimer, $K_2[VO(O_2)(C_6H_6O_7)]_2 \cdot 2H_2O$

Cirila Djordjevic,*[1] Myunghi Lee,[1] and Ekk Sinn[2]

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The first citrato complexes of vanadium have been prepared: $M^I[VO(O_2)(C_6H_6O_7)] \cdot H_2O$ (M^I = K, NH_4, Cs) and $K[VO_2(C_6H_6O_7)]$. They crystallized from aqueous solution and were characterized by elemental analysis, IR and UV–visible spectroscopy, and X-ray structure analysis. Assignment of the characteristic peroxo IR bands in oxomonoperoxo(citrato)vanadates(V) was done by comparison with the spectrum of potassium dioxo(citrato)vanadate(V). X-ray structure analysis of $K_2[VO(O_2)(C_6H_6O_7)]_2 \cdot 2H_2O$ revealed the presence of a novel stereochemical ligation of the tridentate citrate, involving bridging hydroxyl oxygens to form a dimer and enclosing vanadium in slightly distorted pentagonal bipyramids. A relatively short O–O bond of 1.427 (1) Å was found in symmetrically coordinated peroxo ligands, corresponding well with the observed high ν(O–O) stretching frequency of 933 cm^{-1}. The relationship of these compounds to the biochemistry of vanadium is discussed.

Introduction

Citric acid, the hydroxyl tricarboxylic acid of the formula $HOOCCH_2C(OH)(COOH)CH_2COOH$, and citrate ions are the omnipresent small molecular weight species in most plant and animal tissues. Citrates appear at about 0.1 mM in blood plasma[3] and occur 0.3% by weight in teeth and bone.[4,5] They regulate some fundamental physiological processes and are intermediates in carbohydrate metabolism, e.g. in the "Krebs cycle." The combination of citrato and peroxo ligands on vanadium, a bioessential metal ion of an as yet unknown biological function,[6]

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is of interest to biochemistry for several reasons. For example, the recently discovered vanadium enzymes, the bromoperoxidases, contain V(V).[7,8] In the process of purification and characterization of these enzymes, two operations are directly related to the properties of the peroxo(citrato)vanadates(V), the first of which is the formation of a product with a λ_{max} of 420 nm, which gradually converts in slightly acidic solutions into a different substance by increasing the absorption at 460 nm.[9] In monoperoxovanadates(V) the LMCT bands occur typically between 415 and 430 nm, and in more acid solution they gradually develop the absorption at 450–460 nm, due to the formation of the $VO(O_2)^+$ cation.[10,11] Second, a citrate/phosphate buffer is used, and bonding of some vanadium to the citrate is very likely. The numerous studies of vanadium inhibition of the activity of specific enzymes,[6,12] of the glucose metabolism,[13] and of the binding to proteins[14,15] all demonstrate the importance of the oxidation state of vanadium for a specific function in the living cell, still under investigation even in the long known vanadocytes.[16] Vanadium(V) toxicity and moderate antitumor activity in mice has also been found to depend upon peroxo group presence and the type of peroxo complex, including the oxoperoxo(citrato)vanadates(V).[17]

Coordination of citrate to vanadium has interesting stereochemical alternatives. Citrates have been found to act as monodentate or polydentate (di- and tridentate) ligands, involving generally the central hydroxyl and carboxyl groups.[4] Of the four ionizable protons, three or four dissociate usually upon coordination,[4,18–22] and a citrate with the charge −2 is less common.[23] Brief reports of some of the work reported here have already appeared.[24]

Experimental Section

Materials. Reagent grade V_2O_5, NH_4VO_3, KOH, NaOH, CsCl, citric acid, and H_2O_2 (30% Mallinckrodt, analytical grade) were used. All solvents were of reagent grade.

Preparative work has to be done in the hood with a protective shield, as sometimes unexpectedly violent reactions occur.

Preparation of $K[VO(O_2)(C_6H_6O_7)]\cdot H_2O$ (1). A colorless solution of potassium vanadate(V) was made by dissolving V_2O_5 (0.5 g, 5 mM) in an aqueous solution (10 mL) of KOH (0.3 g, 5 mM) at 40 °C. The clear solution was cooled in ice, and hydrogen peroxide (30%, 2 mL, 18 mM) was added dropwise with stirring. Citric acid (1.16 g, 6 mM) dissolved in water (5 mL) was then added dropwise with constant stirring to the ice-cooled solution, which turned red-orange; pH ~4. Cold ethanol (95%) was then added dropwise, until turbidity persisted, and the reaction mixture was stored overnight in a refrigerator. Orange crystals obtained were filtered and washed in turn with 50%, 95%, and absolute ethanol and dried over Drierite. Yield: ~45%. Anal. Calcd for $KVC_6H_8O_{11}$: K, 11.3; V, 14.7; C, 20.8; H, 2.3; O_2^{2-}, 9.2. Found: K, 11.5; V, 14.2; C, 20.7; H, 2.4; O_2^{2-}, 8.8.

Preparation of $NH_4[VO(O_2)(C_6H_6O_7)]\cdot H_2O$ (2). NH_4VO_3 (0.59 g, 5 mM) was dissolved in water (10 mL), and hydrogen peroxide (30%, 2 mL, 18 mM) was added with a few drops of NH_4OH (30%). The clear yellow solution was cooled in ice, and citric acid (1.05 g, 5 mM) dissolved in water (5 mL) was added dropwise with stirring. Cold 95% ethanol was then added to initiate the precipitation, and the procedure described for **1** was followed. Yield: ~65%. Anal. Calcd for $VC_6H_{12}NO_{11}$: V, 15.7; C, 22.2; H, 3.7; N, 4.3; O_2^{2-}, 9.8. Found: V, 14.9; C, 23.5; H, 3.6; N, 4.5; O_2^{2-}, 9.6.

Preparation of $Cs[VO(O_2)(C_6H_6O_7)]\cdot H_2O$ (3). The procedure described for **1** was followed, preferably using NaOH instead of KOH, but before the addition of ethanol to induce the precipiration, CsCl (0.99 g, 5 mM) dissolved in water (3 mL) was added to the solution. A red-orange crystalline precipitation was usually obtained overnight. Yield: ~35%. The compound is much less soluble in water or acids than the analogous potassium and ammonium salts. Anal. Calcd for $CsVC_6H_8O_{11}$: V, 11.6; C, 16.4; H, 1.8; O_2^{2-}, 7.3. Found: V, 12.7; C, 19.6; H, 2.3; O_2^{2-}, 8.0.

Compounds **1**–**3** are stable over a year if originally pure and stored in a dark, dry atmosphere.

Preparation of $K[VO_2(C_6H_6O_7)]\cdot H_2O$ (4). V_2O_5 (0.5 g, 5 mM) was dissolved as described for **1**. The colorless, clear solution was cooled on ice, and citric acid (1.16 g, 6 mM) dissolved in water (5 mL) was added dropwise. The reaction mixture was left in the ice bath until the pale green precipitate settled. It was filtered, washed with ethanol as described above, and dried over drierite. Yield: ~50%. Anal. Calcd for $KVC_6H_6O_{10}$: K, 12.5; V, 16.3; C, 23.1; H, 1.9. Found: K. 11.6; V, 16.1; C, 23.4; H, 2.0.

Physical Measurements and Analyses. Infrared spectra were recorded as Nujol or hexachlorobutdiene mulls with a Perkin-Elmer Model 983 spectrophotometer. Electronic absorption spectra were recorded on a Beckman Acta VI spectrophotometer.

C, H, N, K, and V analyses were performed by Atlantic Microlab, Inc., and Galbraith Laboratories, Inc. K and V were also determined by atomic absorption spectroscopy. In addition, vanadium was obtained by difference from the thiosulfate titration determining the sum of peroxide and vanadium.[25] Peroxides were determined by Ce(IV) titration on a Brinkmann E536 potentiograph or by difference from the thiosulfate titration.

X-ray Structure Determination. Cell dimensions and space group data were obtained by standard methods; crystallographic data are given in Table II. The intensities of three standard reflections showed no greater

Table I. Relevant Infrared Data (cm^{-1})[a] for Compounds **1**–**4**[b] and Citric Acid

citric acid	1	2	3	4	assignt
3495 vs 3448 w 3298 s, br	3590 s, vs 3500 s, br	3576 s 3474 s, br	3592 s, vs 3480 s, br		ν(OH)
		3278 vs, br 3040 vs, br			ν(NH)
1750 vs 1704 vs, br	1720 vs 1673 vs 1612 vs	1727 vs 1678 vs 1612 vs	1720 vs 1678 vs 1612 vs	1690 s, br	ν_{as}(COO)
1430 s 1390 s 1359 s	1417 vs 1395 m 1317 m	1416 vs, br 1314 m	1416 vs 1394 sh 1317 m	1395 m 1330 m	ν_s(COO)
	988 vs	988 vs	988 vs		ν(V=O)
				955 s	$\nu_s(VO_2)$
				890 m	$\nu_{as}(VO_2)$
	933 vs	929 s, vs	933 s, vs		ν(O–O)

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder. [b] $M^I[VO(O_2)(C_6H_6O_7)](H_2O)$ (M^I = K (**1**), NH_4 (**2**), Cs (**3**)); $K[VO_2(C_6H_6O_7)]$ (**4**).

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fluctuations during this data collection than those expected from Poisson statistics. The raw intensity data were corrected from the Lorentz–Polarization effect and absorption. A three-dimensional Patterson synthesis was used to determine the heavy-atom position, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier synthesis. Full-matrix least-squares refinement was carried out as previously described.[11a] Anisotropic temperature factors were introduced for the non-hydrogen atoms. A listing of the observed and calculated structure factors is available as supplementary material. The principal programs used are as previously described.[11a]

Results

Oxo monoperoxo citrato complexes of the formula $M^I[VO(O_2)(C_6H_6O_7)]\cdot H_2O$ (M^I = K, NH_4, Cs) have been prepared from aqueous solutions. They demonstrate that V(V) is stabilized by peroxides in a citrato ligand sphere. The orange crystalline compounds are insoluble in organic solvents, slightly soluble in water, and remarkably stable toward decomposition. In acid aqueous solutions below pH 2 they decompose, and these solutions show the typical absorption at λ_{max} = 450 cm^{-1}, characteristic of the $VO(O_2)^+$ ion.[10] The potassium and ammonium salts were tested among 14 other vanadium(V) complexes for toxicity and antitumor activity against L1210 murine leukemia, showing a marginal activity and toxicity at a relatively high dose.[17]

IR spectra of the complexes display characteristic features of the coordinated citrato ligand and of the oxo and peroxo groups. In order to assign the ν(O–O) stretchings in the spectrum crowded by citrato bands, the dioxo citrato complex, a pale white-green anhydrous microcrystalline powder of the formula $K[VO_2(C_6H_6O_7)]$ was prepared. In Table I the relevant bands in IR spectra of oxoperoxo(citrato)vanadates(V) are compared to spectra of citric acid and dioxo(citrato)vanadate(V), and the empirical assignment of characteristic bands is given. Additional medium strong bands appear in the region between 2850 and 2510 cm^{-1}, originating in the hydrogen-bonded protonated carboxylato groups. Typical for the spectra of the oxoperoxo(citrato)vanadates(V) are the three well-resolved strong bands between 1727 and 1612 cm^{-1}, assigned to ν_{as}(COO); ν_s(COO) bands follow between 1417 and 1317 cm^{-1}. They are all shifted to lower frequencies with regard to citric acid and are not as well resolved in **4**. The differences between the asymmetric and symmetric COO stretchings, $\Delta(\nu_{as}-\nu_s)$, is of the order of 300 cm^{-1}, implying the presence of free or unidentately coordinated carboxylato groups, which have been found by X-ray structural analysis. This observation demonstrates that the $\Delta(\nu_{as}-\nu_s)$ relationship with the carboxylato group coordination, thoroughly studied in acetato complexes,[26] holds also for a polycarboxylate such as citrate. The V=O stretchings occur as very strong sharp bands at 988 cm^{-1} in the oxo peroxo citrates and appear at a lower frequency in the dioxo citrato compound.[27] The ν_1(O–O) stretchings were easily detected as a strong additional band[11,28] near 933 cm^{-1} by comparing the spectra of the three oxoperoxo(citrato)vanadates(V) to the spectra of the dioxo citrato complex and citric acid. They occur at a higher frequency than in the spectra of oxodiperoxo(heteroligand)vanadates(V).[11,25,28] Additional bands occur in the 616–555 cm^{-1} region in the spectra of peroxo citrato complexes; however, an arbitrary choice in assigning one of the present bands to a particular peroxo vibrational mode is meaningless without an isotopic substitution study. The citric acid spectrum has a few bands in the region between 420 and 300 cm^{-1}, and additional bands occur in the spectra of peroxo complexes. Some of these must belong to V–O stretchings, but an arbitrary selection of a particular frequency without the isotopic substitution is again pointless.

UV/vis spectra of peroxo citrato complexes in aqueous solutions (0.1 M KCl) show a weak broad peroxo LMCT band around 415 nm. Below pH 2 a red shift of this band to about 450 nm is observed, as expected due to $VO(O_2)^+$ present in acid solutions.[10,11] In the solid state (Nujol mull) the peroxo LMCT bands occur as a broad absorption with λ_{max} at about 425 nm.

Table II. Crystal Data for $K_2[VO(O_2)(C_6H_6O_7)]_2\cdot 2H_2O$

formula	$K_2V_2C_{12}H_{16}O_{22}$
fw	692.34
space group	$P2_1/n$
a, Å	9.341 (2)
b, Å	12.214 (4)
c, Å	10.675 (3)
β, deg	110.53 (2)
V, Å^3	1141
Z	2
d_{calcd}, g/cm^3	2.02
crystal size, mm	0.02 × 0.32 × 0.29
μ(Mo Kα), cm^{-1}	6.7
data col instrument	Enraf-Nonius four-cycle CAD-4
radiation, monochromated in incident beam (λ, Å)	Mo Kα (0.71073)
temp, °C	23
scan method	θ–2θ
data col range (2θ), deg	$1 < 2\theta < 60$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	3034, 2595
trans factors: max, min	0.917, 0.850
R^a	0.034
R_w^b	0.037
quality of fit indicator^c	1.5
largest shift/esd, final cycle	0.00

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$. ^{c} Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table III. Positional Parameters and Their Estimated Standard Deviations for $K_2[VO(O_2)(C_6H_6O_7)]_2\cdot 2H_2O$

atom	x	y	z
V	0.13786 (4)	0.06459 (3)	0.11383 (4)
K	0.04296 (8)	0.36302 (6)	0.14965 (8)
O(1)	0.3354 (2)	0.0123 (2)	0.1428 (2)
O(2)	0.3273 (2)	0.0700 (2)	0.2564 (2)
O(3)	0.1376 (2)	0.1818 (1)	0.0467 (2)
O(1A)	0.1229 (2)	−0.1170 (2)	0.2285 (2)
O(1B)	−0.0095 (3)	−0.2660 (2)	0.2499 (2)
O(3A)	−0.0824 (2)	0.0248 (1)	0.0580 (2)
O(5A)	−0.4684 (2)	0.1912 (2)	−0.0323 (2)
O(5B)	−0.2301 (2)	0.2449 (2)	0.0884 (2)
O(6A)	0.0812 (2)	0.1241 (2)	0.2661 (2)
O(6B)	−0.0826 (2)	0.1124 (2)	0.3734 (2)
O(W)	−0.3131 (3)	0.0175 (2)	0.4755 (2)
C(1)	0.0050 (3)	−0.1601 (2)	0.2311 (2)
C(2)	−0.1427 (3)	−0.0998 (2)	0.2124 (2)
C(3)	−0.1461 (2)	0.0188 (2)	0.1621 (2)
C(4)	−0.3103 (3)	0.0607 (2)	0.1144 (2)
C(5)	−0.3286 (3)	0.1751 (2)	0.0562 (2)
C(6)	−0.0442 (3)	0.0912 (2)	0.2767 (2)
H(21)	−0.160 (4)	−0.101 (3)	0.291 (3)
H(22)	−0.224 (4)	−0.142 (3)	0.155 (3)
H(41)	−0.376 (4)	0.013 (3)	0.048 (3)
H(42)	−0.347 (4)	0.065 (3)	0.189 (3)
H(W1)	−0.254 (5)	0.057 (3)	0.446 (4)
H(W2)	−0.257 (5)	−0.021 (4)	0.543 (4)

Crystals large enough for an X-ray structure analysis were obtained for the potassium oxoperoxo(citrato)vanadate(V) only. Crystallographic parameters are summarized in Table II, and the final positional parameters are given in Table III. The most important bond lengths and the nearest intermolecular contacts with the bond angles are listed in Table IV. The digits in parentheses in the tables are the estimated standard deviations in the last significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 shows the structure and labeling scheme of the dimeric complex anion. The structure consists of these dimers, potassium cations, and water molecules. The complex dimer can be described as two distorted pentagonal bipyaramids, doubly bridged by the hydroxyl oxygens occupying two sites of the equatorial pentagonal plane. This plane also contains the two oxygens of the coordinated peroxo group and an oxygen from the central C(6) carboxylato group. The axial sites are occupied by the oxo group and an

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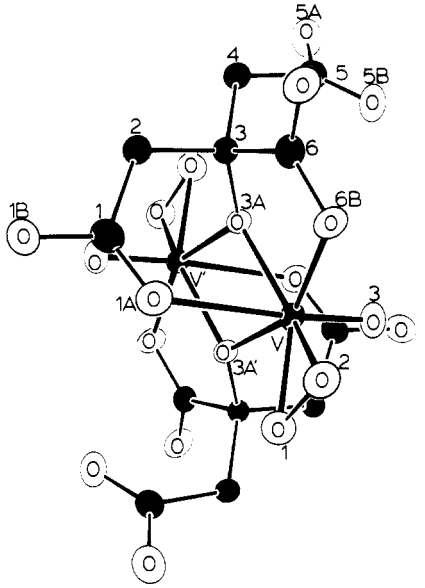

Figure 1. Structure and labeling scheme for the dimeric anion $[VO(O_2)(C_6H_6O_7)]_2^{2-}$.

oxygen from the terminal C(1) carboxylato group. The three-coordinated citrate is therefore wrapped around the metal ion, leaving a dangline $C(4)H_2C(5)OOH$ group. The backbone of the citrate ion, the C(1)–C(5) chain, is fully extended in a planar zigzag pattern with a span of 4.17 Å. C(1) lies farthest above (0.11 Å) and C(3) farthest below (0.14 Å) the C(1)C(2)C(3)C(4)C(5) least-squares plane. Bridging atoms V–O(3A)–V′–O(3A′) form a perfect rhomboidal plane, oriented about 80° toward the plane containing the C(1)–C(5) zigzag chain and the plane of axial ligands O(1A)–V–O(1A′)–V′–O(3′). The plane of axial ligands is perpendicular to the equatorial plane containing the peroxo O(1)–O(2), hydroxyl O(3A), and carboxyl O(6A) oxygens. The fifth oxygen of the distorted pentagonal equatorial plane, O(3A′), is about 0.41 Å below the O(1)O(2)O(3A)O(6A) least-squares plane, and the vanadium is drawn about 0.24 Å out of this plane toward the oxo group. The equatorial V–O (peroxo) bonds are fairly symmetrical: 1.873 (1) and 1.883 (1) Å, with a short O–O bond distance of 1.427 (2) Å.

Two protons of this dibasic coordinated citrate are most likely located on the two terminal carboxylato groups, one of which, C(5), is free. An oxygen of the other, C(1), is coordinated to vanadium trans to the oxo group via a V–O bond of 2.561 (1) Å. This bond is much longer than the equatorial V–O(6A) distance of 2.013 (1) Å, involving the deprotonated central carboxylato group. Fairly short and not much different V–O bonds in the O(3A)–V–O(3A′)–V′ bridge, 1.991 (1) and 2.039 (1) Å, indicate that the bridging hydroxyl oxygens are deprotonated, as previously observed in some transition-metal citrato complexes.[4,20] Proton dissociation of a coordinated citrate ion does not necessarily follow the pK_1–pK_4 sequence established for citric acid in aqueous solutions.[4] The remaining protons on the terminal carboxylato groups are most likely delocalized and hydrogen-bonded to the adjacent oxygens.

Discussion

Current interest in peroxo(heteroligand)vanadates(V) is due mainly to two recent events in vanadium chemistry. First, vanadium enzymes were discovered recently, the bromoperoxidases[7-9] and nitrogenases,[29-31] and somewhat earlier it had been found that peroxovanadates(V) act as selective oxidation catalysts,[28,32] much like the previously known peroxo(heteroligand)molybdates(VI).[33,34]

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $K_2[VO(O_2)(C_6H_6O_7)]_2 \cdot 2H_2O$[a]

		Distances	
V–O(1)	1.873 (1)	C(4)–C(5)	1.515 (2)
V–O(2)	1.888 (1)	⟨C–H⟩	0.95
V–O(3)	1.601 (1)	⟨O–H⟩	0.87
V–O(1A)	2.561 (1)		
V–O(3A)	1.991 (1)	V–V′	3.262 (1)
V–O(3A)′	2.039 (1)	K–O(1)	2.786 (1) (A)
V–O(6A)	2.013 (1)	K–O(2)	2.831 (1) (A)
O(1)–O(2)	1.427 (2)	K–O(1A)	2.940 (1) (A)
O(1A)–C(1)	1.229 (2)	K–O(W)	3.024 (1) (B)
O(1B)–C(1)	1.324 (2)	K–O(W)	2.818 (1) (C)
O(3A)–C(3)	1.435 (2)	O(1)–O(1B)	3.159 (1) (A)
O(5A)–C(5)	1.331 (2)	O(2)–O(1B)	2.645 (1) (A)
O(5B)–C(5)	1.212 (2)	O(2)–O(W)	3.100 (2) (D)
O(6A)–C(6)	1.280 (2)	O(1A)–O(W)	3.268 (2) (D)
O(6B)–C(6)	1.233 (2)	O(1B)–O(5A)	3.136 (2) (E)
C(1)–C(2)	1.515 (3)	O(1B)–C(5)	3.046 (2) (E)
C(2)–C(3)	1.541 (2)	O(5A)–O(6A)	3.262 (1) (F)
C(3)–C(4)	1.525 (2)	O(5A)–O(6B)	2.675 (1) (F)
C(3)–C(6)	1.539 (2)		
		Angles	
O(1)–V–O(2)	44.61 (6)	V–O(1A)–C(1)	125.54 (12)
O(1)–V–O(3)	103.02 (7)	V–O(3A)–V′	108.04 (5)
O(1)–V–O(1A)	80.89 (5)	V–O(3A)–C(3)	116.49 (9)
O(1)–V–O(3A)	145.20 (5)	V′–O(3A)–C(3)	128.75 (9)
O(1)–V–O(3A)′	83.73 (5)	V–O(6A)–C(6)	117.81 (11)
O(1)–V–O(6A)	120.83 (6)	O(1A)–C(1)–O(1B)	124.3 (2)
O(2)–V–O(3)	100.57 (7)	O(1A)–C(1)–C(2)	124.79 (16)
O(2)–V–O(1A)	80.65 (5)	O(1B)–C(1)–C(2)	110.95 (16)
O(2)–V–O(3A)	145.89 (6)	C(1)–C(2)–C(3)	114.15 (15)
O(2)–V–O(3A)′	127.92 (6)	O(3A)–C(3)–C(2)	110.77 (13)
O(2)–V–O(6A)	76.93 (6)	O(3A)–C(3)–C(4)	111.41 (13)
O(3)–V–O(1A)	175.54 (6)	O(3A)–C(3)–C(6)	106.11 (13)
O(3)–V–O(3A)	104.19 (6)	C(2)–C(3)–C(4)	109.10 (13)
O(3)–V–O(3A)′	96.68 (6)	C(2)–C(3)–C(6)	109.41 (14)
O(3)–V–O(6A)	94.55 (7)	C(4)–C(3)–C(6)	109.99 (14)
O(1A)–V–O(3A)	73.02 (5)	C(3)–C(4)–C(5)	113.73 (14)
O(1A)–V–O(3A)′	85.82 (5)	O(5A)–C(5)–O(5B)	123.8 (2)
O(1A)–V–O(6A)	81.52 (5)	O(5A–C(5)–C(4)	111.61 (16)
O(3A)–V–O(3A)′	71.96 (5)	O(5B)–C(5)–C(4)	124.6 (2)
O(3A)–V–O(6A)	78.05 (5)	O(6A)–C(6)–O(6B)	123.5 (2)
O(3A)′–V–O(6A)	149.72 (5)	O(6A)–C(6)–C(3)	116.08 (15)
V–O(1)–O(2)	68.24 (8)	O(6B)–C(6)–C(3)	120.35 (16)
V–O(2)–O(1)	67.15 (8)		

[a] Symmetry transformations: (A) $^1/_2 - x, ^1/_2 - y, ^1/_2 - z$; (B) $^1/_2 - x, ^1/_2 + y, -^1/_2 - z$; (C) $x - ^1/_2, ^1/_2 - y, ^1/_2 + z$; (D) $-x, -y, ^1/_2$; (E) $-^1/_2 - x, y - ^1/_2, ^1/_2 - z$; (F) $x - ^1/_2, ^1/_2 - y, z - ^1/_2$.

It has been confirmed that bromoperoxidases involve vanadium in oxidation state V,[7-9] and peroxovanadates known so far contain vanadium only in this highest possible, d^0, V(V) oxidation state. The biological activity of vanadium is obviously dependent upon the oxidation state,[6,14] and for V(V) to exist in the enzymes, a ligand environment must be present that stabilizes the d^0 electron configuration of vanadium ion. Peroxides, which can enter a variety of ligand spheres, always acquire V(V). Peroxo(heteroligand)vanadates(V) therefore represent an appropriate and useful model system to study properties and stereochemistry of vanadium for surroundings likely to exist in biochemical interactions involving V(V).

Peroxides possess a strong affinity for binding to vanadium and have been used for a spectrophotometric vanadium analysis.[35] The V(V)/V(IV), d^0/d^1, interplay is an essential feature of vanadium chemistry in most solvents and aqueous solution where V(V) acts as a mild oxidant, strongly dependent upon the environment. In biochemistry or catalysis, this property of vanadium probably plays the central role in the mechanism of a specific reactivity. The electron transfer is tuned by the composition and the stereo-

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chemistry of ligand spheres. We have observed that in aqueous solutions reduction of V(V) occurs at different rates in the presence of a number of bioligands, including citrates or α-amino acids. An excess of peroxides stabilizes V(V) in these solutions, and the redox process, which is sometimes reversible, can often be followed by the color change. In the biochemistry of vanadium, the V(V) peroxo heteroligand spheres are very likely involved as intermediates in chain reactions, undergoing ligand rearrangements with or without an electron transfer, governed by complex equilibria, and possibly radical interactions of short-lived intermediates, proposed to proceed in the catalytic processes involving V(V) peroxo complexes.[32,34,37]

In the environment of a living cell mono- rather than diperoxo(heteroligand)vanadates(V) are expected to exist because they form easily at a low or moderate hydrogen peroxide concentration. The monoperoxo complexes also proved to be more efficient catalysts.[28,32-34] Unusual and interesting rearrangement of bipyridyl[36] and substitution of nicotinic acid[37] have also been observed in monoperoxovanadates(V). Triperoxovanadates are very rare, are unstable, and exist only in alkaline media with a large excess of peroxides.[38]

Vanadium citrato complexes are of interest from yet another point of view, regarding the interaction of vanadium with transferrin. Citrato ligands are supposed to compete in the cell with transferrin for the iron and aluminum ions,[3] which form stable complexes with citrates. Experiments have shown that vanadium binds to transferrin,[14,15a,39,40] an iron-transfer protein, which may also transport vanadium.[41] Analogous ligand competition between citrates and transferrin proposed for iron may well operate for vanadium, and the character of the vanadium–citrato bond is of great interest in this respect.

Only a few stable and well-characterized monoperoxovanadates(V) are known,[11,28,36,37,42] and the oxo peroxo citrato complexes described here are an intriguing addition to the existing set of these compounds.

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Supplementary Material Available: A listing of thermal parameters (1 page); a table of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12222

Synthesis and Chemical Characterization of Complexes Containing Semiquinone Units Bridged by Pentaoxodimolybdate Groups. Structural and Electrochemical Studies of $[(n\text{-}C_4H_9)_4N]_2[Mo_4O_{10}(C_6H_2O_4)_2]$ and $[(n\text{-}C_4H_9)_4N]_3[Mo_6O_{15}(C_6O_6)_2]$ and of an Analogous Tetraoxydibenzofuran Complex, $[(n\text{-}C_4H_9)_4N]_2[Mo_4O_{10}(C_{12}H_4O_5)_2]$, Prepared from Metal-Mediated Radical Coupling of 1,2,4-Trihydroxybenzene Precursors

Shuncheng Liu, Shahid N. Shaikh, and Jon Zubieta*

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Reaction of $(Bu_4N)_2[Mo_2O_7]$ with 2,5-dihydroxybenzoquinone in acetonitrile yields $(Bu_4N)_2[Mo_4O_{10}(C_6H_2O_4)_2]$ (I), a tetranuclear complex with two $[Mo_2O_5]^{2+}$ units bridging two planar $(C_6H_2O_4)^{n-}$ groups, stacked in a parallel staggered orientation. The most significant feature is the short interplanar distance between ligands of 2.67 Å, allowing magnetic coupling of the radical anion semiquinoid-type ligands. Reactions of organic solvent soluble polyoxomolybdates with tetrahydroxybenzoquinone and 1,2,4-trihydroxybenzene yield the structurally analogous complexes $(Bu_4N)_3[Mo_6O_{15}(C_6O_6)_2]$ (III) and $(Bu_4N)_2[Mo_4O_{10}(C_{12}H_4O_5)_2]$ (IV). In contrast to I and IV, III is paramagnetic with an EPR spectrum consistent with electron localization in a ligand-centered orbital. The steric constraints introduced with the chlorine substituents of chloranilic acid, $C_6Cl_2O_4H_2$, prevent parallel stacking of the ligands, and the mononuclear complex $(Bu_4N)[MoO_2(C_6Cl_2O_4)(C_6Cl_2O_4H)]$ (II) is isolated from the reaction of chloranilic acid with $(Bu_4N)_2[Mo_2O_7]$. Crystal data for I: orthorhombic space group *Pbca*, a = 15.527 (3) Å, b = 17.192 (3) Å, c = 21.094 (4) Å, Z = 4, D_{calc} = 1.54 g cm^{-3}; structure solution and refinement based on 1022 reflections ($F_o \geq 6\sigma(F_o)$; Mo Kα radiation λ = 0.710 73 Å in all cases), R = 0.060. Crystal data for II: triclinic $P\bar{1}$, a = 10.383 (2) Å, b = 13.197 (3) Å, c = 14.191 (3) Å, α = 88.11 (1)°, β = 87.57 (1)°, γ = 78.11 (2)°, Z = 2, D_{calc} = 1.37 g cm^{-3}; 4239 reflections, R = 0.055. Crystal data for III: monoclinic $P2_1/a$, a = 27.384 (5) Å, b = 10.290 (2) Å, c = 29.338 (6) Å, β = 110.98 (1)°, Z = 4, D_{calc} = 1.62 g cm^{-3}; 6125 reflections, R = 0.053. Crystal data for IV: monoclinic $P2_1/n$, a = 16.789 (3) Å, b = 9.395 (2) Å, c = 20.832 (3) Å, β = 112.72 (1)°, Z = 2, D_{calc} = 1.63 g cm^{-3}; 3030 reflections, R = 0.052.

Catechol and benzoquinone complexes of transition metals are of general interest in the investigation of ligand-centered redox processes,[1-7] in the preparation of metal semiquinone species,[8-12] and as models for metallo–biochemical processes as diverse as microbial ion transport,[13] dioxygenase activity,[14] and electron

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