Synthesis and Characterization of Binuclear Oxo–Vanadium Complexes of Carbon Oxoanion Ligands. Crystal Structures of the Binuclear Vanadium(IV) Complex $(NH_4)[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$, of the Mixed-Valence Vanadium(V)/Vanadium(IV)–Squarate Species $[(n\text{-}C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ and $[(C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$, and of the Binuclear Vanadium(IV)–Oxalate Species $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]\cdot 2Ph_4Cl$

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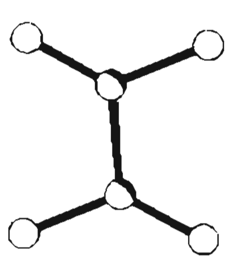
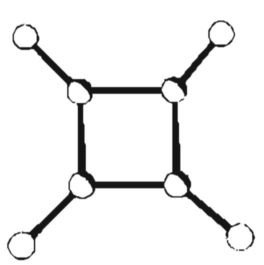
Received June 9, 1994[⊗]

Under reducing conditions, aqueous vanadium–oxo solutions react with squaric acid to give the binuclear V(IV) species $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$ (**1·H₂O**). In the absence of reducing agents and upon addition of $(C_4H_9N)_4NBr$, vanadate solutions react with squaric acid to give the binuclear mixed-valence species $[(C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (**2·3H₂O**). The structure of the anion $[V_2O_3(C_4O_4)_2(H_2O)_3]^{2-}$ consists of the $\{V_2O_3(\mu\text{-}H_2O)\}^{3+}$ core with the vanadium sites bridged additionally by two μ-1,2-squarate ligands and with an aquo ligand on each vanadium center completing the coordination. From the filtrate are isolated **2·3H₂O** and dark brown crystals of $[(C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$ (**3·6H₂O**) after 2 weeks of standing at room temperature. The tetranuclear mixed-valence V(IV)/V(V) species **3·6H₂O** exhibits a structure consisting of two binuclear $[V_2O_3(C_4O_4)(H_2O)_2]^0$ units bridged by a (μ-1,3) squarate group. The structure thus exhibits both μ-1,2- and μ-1,3-squarate ligands. While analogous oxalate derivatives were not isolated from reactions in aqueous solvent, the binuclear V(IV) species $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]\cdot 2Ph_4PCl$ (**4·2Ph₄PCl**) was prepared by the reaction of a suitable binuclear V(IV) precursor with oxalic acid in methanol. The structural core of the neutral $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]$ consists of a planar $\{V_2O_2Cl_2(C_2O_4)\}$ unit; the methanol ligands occupy positions normal to this moiety. Crystal data: **1·H₂O**, monoclinic, $P2_1/n$, $a = 11.554(2)$ Å, $b = 6.568(1)$ Å, $c = 13.436(3)$ Å, $\beta = 108.76(3)°$, $V = 965.5(5)$ Å^3, $Z = 4$, $D_{calc} = 1.638$ g cm^{-3}, 867 reflections, $R = 0.0763$; **2·3H₂O**, triclinic, $P\bar{1}$, $a = 11.628(2)$ Å, $b = 14.990(3)$ Å, $c = 10.746(2)$ Å, $\alpha = 108.49(3)°$, $\beta = 99.02(3)°$, $\gamma = 98.13(3)°$, $V = 1717.5(9)$ Å^3, $Z = 2$, $D_{calc} = 1.399$ g cm^{-3}, 2741 reflections, $R = 0.0597$; **3·6H₂O**, triclinic, $P\bar{1}$, $a = 16.670(3)$ Å, $b = 18.440(4)$ Å, $c = 20.151(4)$ Å, $\alpha = 65.96(2)°$, $\beta = 69.14(3)°$, $\gamma = 80.10(3)°$, $V = 5284(3)$ Å^3, $Z = 2$, $D_{calc} = 1.261$ g cm^{-3}, 2858 reflections, $R = 0.0832$; **4·2Ph₄PCl**, monoclinic, $P2_1/c$, $a = 10.906(2)$ Å, $b = 14.724(3)$ Å, $c = 17.574(3)$ Å, $\beta = 94.93(2)°$, $D_{calc} = 1.387$ g cm^{-3}, 1397 reflections, $R = 0.0688$.

The coordination chemistry of the oxovanadium core has received considerable attention in recent years as a consequence of its relevance to such diverse fields of interest as the role of vanadium in biological systems,[1–3] metal-mediated oxygen atom transfer reactions,[4,5] the properties of inorganic solid phases,[6–8] and the structures of polyoxoanion clusters.[9–11] While investigating the chemistry of polyoxomolybdates with various organic ligands with oxygen donor groups,[12] we noted that the structurally analogous carbon oxoanions oxalate (A) and



(A)



(B)

squarate (B) could be trapped within polyoxometalate hosts whose organization is presumably directed by the template effect of the organic guest.[13] While host/guest clusters of polyoxomolybdates with both oxalate and squarate were isolated, $[Mo_8O_{16}(OCH_3)_8(C_2O_4)]^{2-}$ [14] and $[Mo_{12}O_{36}(C_4O_4H)_4]^{4-}$,[15] re-

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[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1994.

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0020-1669/94/1333-6340$04.50/0

spectively, the oxovanadium system yielded only the analogous oxalate species $[V_8O_8(OCH_3)_{16}(C_2O_4)]^{2-}$.[16] Curiously, under the reaction conditions employed, neither smaller oligomers containing these organic ligands nor V/O/squarate species were obtained.

Although numerous oxovanadium carboxylates and dicarboxylates have been reported,[17−34] the V/O/oxalate chemistry is limited to five structurally characterized examples, the aforementioned $[V_8O_8(OCH_3)_{16}(C_2O_4)]^{2-}$, $[VO_2(C_2O_4)_2]^{3-}$,[23] $[VO(C_2O_4)(H_2O)]^-$,[24] $[VO(C_2O_4)F(H_2O)_2]^-$,[25] and $[(VO_2)_4(C_2O_4)_4(H_2O)_2]^{4-}$.[22] Furthermore, there has been a single example of structurally characterized complexes of the related V/O/squarate system.[35] As part of our continuing investigations of the aggregation of simple molecular precursors to provide polyoxometalate clusters,[12] we have isolated binuclear oxovanadium complexes with both oxalate and squarate ligands and an unusual mixed-valence V(IV)/V(V) tetranuclear complex of the $V/O/C_4O_4^{2-}$ system. The squarate complexes $(NH_4)[V_2O_2(OH)(C_4O_4)(H_2O)_3]\cdot H_2O$ (**1·H_2O**) and $[(C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (**2·3H_2O**) possess the $\{V_2O_2(\mu\text{-}OH)\}$ and $\{V_2O_3\}$ cores, respectively,[28,27] and unusual combinations of terminal and/or bridging aquo groups. Minor synthetic variations result in the formation of the unusual 1,3-squarato-bridged V(IV)/V(V) tetranuclear species $[(C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$ (**3·6H_2O**). The oxovanadium(IV)−oxalate species $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]\cdot 2Ph_4PCl$ (**4·2Ph_4PCl**) represents a relatively rare example of a structurally characterized divanadyl complex[21,27,29,36−38] with an unusual disposition of the {VOCl} moieties in the plane of the bridging oxalate ligand.

Experimental Section

Reagent grade chemicals were used throughout. $(Ph_4P)[VO_2Cl_2]$ was prepared as previously described.[39] Sodium metavanadate (Aldrich), squaric acid (Aldrich), and oxalic acid (Aldrich) were used as received from commercial sources. All reactions were carried out under strictly anaerobic conditions on a Schlenk line.

Preparation of $NH_4[V_2O_2(OH)(C_4O_4)_2(H_3O)_3]\cdot H_2O$ (1·H_2O). Solid hydrazinium sulfate (0.32 g, 2.5 mmol) was added under nitrogen to a degassed solution of $NaVO_3$ (0.92 g, 7.5 mmol) in water (55 mL) at 65 °C. After 5 min of refluxing, the resultant brown-black solution was treated with Me_3NHCl (1.91 g, 22 mmol) and squaric acid (0.86 g, 7.5 mmol), and refluxing was continued for an additional 30 min. The sky-blue solution was filtered hot and allowed to cool to room temperature. After 6 h of standing, light blue crystals of **1·H_2O** were isolated in 60% yield based on V. Anal. Calcd for $C_4H_{16}NO_{15}V_2$: C, 11.4; H, 3.81; N, 3.33. Found: C, 12.0; H, 3.96; N, 3.01. IR (KBr pellet, cm^{-1}): 1793 (m), 1624 (s), 1518 (vs, broad), 1092 (s), 985 (vs), 744 (s), 531 (w).

Preparation of $[(n\text{-}C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (2·3H_2O). A solution of $NaVO_3$ (0.61 g, 5 mmol) in water (30 mL) was added slowly to a vigorously stirred solution of squaric acid (0.57 g, 5 mmol) in water (20 mL) at 75 °C. The resulting dark brown solution was treated with 1.95 g of solid $(n\text{-}C_4H_9)_4NBr$, and the mixture was stirred for 15 min at 75 °C. After filtration of the hot solution, the dark brown filtrate was transferred to a 150 mL Schlenk tube and allow to stand at room temperature for 2 weeks, whereupon a mass of dark brown blocks of what proved to be **3·6H_2O** (*vide infra*) was isolated. After removal of the crystalline **3·6H_2O**, the mother liquor was allowed to stand at room temperature for 7−10 d. Orange brown, platelike crystals of (**2·3H_2O**) were collected in 30% yield and stored in the presence of some mother liquor. Crystals of **2·3H_2O** are insoluble in water and dichloromethane and are soluble in methanol, acetone, and CH_3CN. Solutions of **2** in acetonitrile are stable indefinitely. Anal. Calcd for $C_{24}H_{48}NO_{17}V_2$: C, 39.8; H, 6.50; N, 1.94. Found: C, 39.3; H, 6.22; N, 1.83. IR (KBr pellet, cm^{-1}): 2950−2850 (m), 1787 (s), 1665 (s), 1522 (vs, broad), 1374 (m), 1060 (vs), 970 (vs), 879 (m), 800 (v), 736 (s). UV−visible spectrum (CH_3CN solution, λ_{max} (ϵ, cm^{-1} M^{-1})): 255 (8.9×10^4).

Preparation of $[(n\text{-}C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$ (3·6H_2O). The dark brown crystals which formed initially in the preparation of **2·3H_2O** were dissolved in CH_3CN, and the mixture was allowed to stand at room temperature for a 2 week period, whereupon dark brown plates of **3·6H_2O** deposited in 55% yield, based on the original vanadium concentration. Crystals of **3** are highly soluble in CH_3CN, acetone, and methanol, somewhat less soluble with slow dissolution in ethanol, and insoluble in CH_2Cl_2 and H_2O. Anal. Calcd for $C_{84}H_{164}N_4O_{36}V_4$: C, 50.2; H, 8.17; N, 2.79. Found: C, 50.6; H, 7.82; N, 2.47. IR (KBr pellet, cm^{-1}): 1793 (m), 1639 (m), 1613 (m), 1502 (vs, broad), 1375 (sh), 1064 (w), 988 (vs), 977 (vs), 878 (w), 800 (v), 746 (s). UV−visible (CH_3CN, λ_{max} (ϵ, cm^{-1} M^{-1}): 259 (2.4×10^5), 334 (broad shoulder). EPR (CH_3CN, room temperature): 15-line spectrum, $g = 1.97$.

Preparation of $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]\cdot 2Ph_4PCl$. (4·2$Ph_4PCl$). Oxalic acid dihydrate (0.602 g, 4.9 mmol) was added to a solution of $[V_2O_2Cl_2(H_2O)_2(C_6H_5PO_3H)_2]\cdot 2Ph_4PCl$ (4.454 g, 4.8 mmol), prepared

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Table 1. Crystallographic Data for $(NH_4)[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$ (**1·H₂O**), $[(n\text{-}C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (**2·3H₂O**), $[(C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$ (**3·6H₂O**), and $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]\cdot 2Ph_4PCl$ (**4·2Ph₄PCl**)[a]

	1·H₂O	**2·3H₂O**	**3·6H₂O**	**4·2Ph₄PCl**
formula	$C_8H_{13}NO_{15}V_2$	$C_{24}H_{48}NO_{17}V_2$	$C_{84}H_{164}N_4O_{36}V_4$	$C_{54}H_{56}Cl_4O_{10}P_2V_2$
fw	476.1	723.5	2005.9	1174.6
a, Å	11.554(2)	11.628(2)	16.670(3)	10.906(2)
b, Å	6.568(1)	14.990(3)	18.440(4)	14.724(3)
c, Å	13.436(3)	10.746(2)	20.151(4)	17.574(3)
α, deg		108.49(3)	65.96(2)	
β, deg	108.76(3)	99.02(3)	69.14(3)	94.93(2)
γ, deg		98.13(3)	80.10(3)	
V, Å^3	965.5(5)	1717.5(9)	5284(3)	2812(1)
Z	4	2	2	2
space group	$P2_1/m$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
D_{calc}, g cm^{-3}	1.638	1.399	1.261	1.387
μ, cm^{-1}	10.40	6.15	4.21	6.34
R^b	0.0763	0.0597	0.0832	0.0688
$R_w{}^b$	0.0859	0.0657	0.0881	0.0717

[a] $T = -80$ °C; $\lambda = 0.710\,73$ Å (Mo Kα). [b] $R = \sum||F_0| - |F_c||/\sum|F_o|$; $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$.

Table 2. Atomic Positional Parameters ($\times 10^4$) and Isotropic Displacement Coefficients (Å^2 × 10^3) for **1·H₂O**

	x	y	z	U(eq)[a]
V(1)	2988(4)	5000	7023(3)	25(2)
V(2)	950(4)	4732(12)	8412(12)	24(2)
O(1)	3739(18)	7646(31)	6701(14)	40(4)
O(2)	3600(17)	3340(32)	6520(15)	38(4)
O(3)	1536(16)	5665(28)	5756(12)	31(4)
O(4)	−670(14)	5141(32)	3625(11)	24(4)
O(5)	−2541(16)	4754(38)	4979(13)	42(4)
O(6)	−374(14)	5395(30)	7079(12)	33(4)
O(7)	380(19)	2818(32)	8741(15)	39(4)
O(8)	234(19)	6990(32)	9076(14)	38(4)
O(9)	1946(17)	7420(27)	7894(14)	29(4)
O(10)	1958(18)	3441(27)	7655(14)	30(4)
O(11)	2371(14)	5067(32)	9739(11)	30(4)
O(12)	4516(18)	4529(36)	11857(14)	51(4)
O(13)	6531(14)	4576(31)	10549(13)	27(4)
O(14)	4359(14)	5189(31)	8431(12)	29(4)
O(15)	−1704(19)	4786(46)	8615(19)	87(5)
C(1)	398(25)	5398(41)	5553(20)	35(5)
C(2)	−562(23)	5150(44)	4580(19)	33(5)
C(3)	−1463(21)	5061(43)	5185(17)	25(5)
C(4)	−393(20)	5363(36)	6107(16)	18(5)
C(5)	3519(18)	4854(42)	9946(15)	17(4)
C(6)	4506(21)	4638(44)	10946(18)	28(5)
C(7)	5366(21)	4704(44)	10348(17)	27(5)
C(8)	4410(21)	4908(47)	9348(17)	29(5)
N(1)	−3020(27)	203(53)	6818(23)	95(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

as previously described,[40] in methanol (50 mL). After 6 h of stirring, the volume of the blue solution was reduced by evaporation to 20 mL and the solution carefully layered with 30 mL of diethyl ether. Upon 6−7 days of standing at 40 °C, blue-green crystals of **4·2Ph4PCl** were obtained in about 20% yield. Anal. Calcd for $C_{54}H_{56}O_{10}P_2Cl_4V_2$: C, 55.4; H, 4.79. Found: C, 55.2; H, 4.87. IR (KBr pellet, cm^{-1}): 2988 (m), 2756 (m), 1668 (s), 1585 (m), 1485 (m), 1440 (s), 1349 (m), 1313 (w), 1185 (w), 1107 (s), 1033 (sh), 1018 (w), 998 (w), 974 (s), 804 (m), 758 (s), 724 (s), 691 (s), 527 (s).

X-Ray Crystallographic Studies. Compounds were studied using a Rigaku AFC5S diffractometer. The crystal parameters and experimental conditions are summarized in Table 1. A complete description of the crystallographic methods is given in the supplementary material. The X-ray studies were performed at −60 °C due to crystal instability in the X-ray beam at room temperature. No significant decomposition occurred at −60 °C over the times of these data collections.

The structures were solved by direct methods and refined by full-matrix least squares. The details of the structure solutions and refinements are presented in the supplementary material. No anomalies were encountered in the refinements of the structures.

Hydrogen atoms were included in the structure factor calculations at their calculated positions but were not refined. Atomic positional parameters and isotropic temperature factors are listed in Tables 2−5 for **1·H₂O**, **2·3H₂O**, **3·6H₂O**, and **4·2Ph₄PCl**, respectively. Selected bond lengths and angles are given in Tables 6−9. Complete listings of bond lengths and angles and of temperature factors have been deposited as supplementary material.

Magnetic Susceptibility Studies. Magnetic susceptibility data for powdered samples of the compounds were obtained over the temperature range 5−300 K in an applied field of 6 G using a Quantum Design Model MPMS SQUID magnetometer. Magnetization isotherms at 298 and 77 K were recorded to correct for the presence of ferromagnetic impurities. Measurement and calibration techniques have been reported elsewhere.[41]

Results and Discussion

Syntheses and Spectroscopic Properties. a. $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$ (1·H₂O). The reduction with excess hydrazinium sulfate of a aqueous vanadate solution, followed by addition of 1 equiv of squaric acid and excess Me_3NHCl, produces a sky-blue solution, from which pale blue crystals of **1·H₂O** form over a period of 4−6 h. The infrared spectrum of **1·H₂O** exhibits characteristic squarate ligand bands at 1793 and 1518 cm^{-1}1 associated with ν(C−O) and ν(C−C), respectively, and a strong band at 985 cm^{-1} attributed to $\nu(V^{IV}{=}O)$.

The IR characteristics of squarate complexes merit comment. Complexes of the squarate anion with M(II), where M = Mn, Fe, Co, Ni, and Zn, are isostructural with the squarate acting as a tetramonodentate ligand through all four oxygen donors.[42] The IR spectra of these complexes show a single strong band at *ca.* 1500 cm^{-1}, assigned to a mixture of C−C and C−O stretching vibrations.[43] In contrast, for a series of Cu(II) complexes and for the Fe(II) complex $[Fe_2(salen)_2(CH_3OH)_2(C_4O_4)]$, in which the squarate ligand acts as either a monodentate ligand or μ-1,3 bridging ligand, a band in the 1705−1780 cm^{-1} range was ascribed to ν(C=O)[44,45] However, the ν(C=O) stretching frequency of the squarate ligand in a μ-1,3-squarato−nickel(II) chain[46] was found at 1480 cm^{-1}. When the squarate ligand adopts the μ-1,2 bridging mode, as in $[Mo_2(OMe)_2(NNPh)_4(C_4O_4)^2]^{2-}$,[47] $[Sn_2Cl_4(OCH_3)_2(C_4O_4)_2]^{2-}$,[48] and $[Cr(OH)_2(H_2O)_4$-

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Table 3. Atomic Positional Parameters ($\times 10^4$) and Isotropic Displacement Coefficients (Å^2 × 10^3) for **2·3H$_2$O**

	x	*y*	*z*	*U*(eq)^a
V(1)	8066(1)	2737(1)	897(1)	32(1)
V(2)	8406(1)	1606(1)	−2138(1)	31(1)
O(1)	9378(5)	3450(4)	2545(5)	43(3)
O(2)	6891(5)	2832(4)	1452(5)	47(3)
O(3)	8397(5)	1644(3)	1484(5)	37(2)
O(4)	8747(5)	−184(4)	2285(5)	41(3)
O(5)	8739(5)	−1402(3)	−855(5)	41(2)
O(6)	8604(5)	457(3)	−1614(5)	36(2)
O(7)	7392(5)	1055(4)	−3448(5)	47(3)
O(8)	9888(5)	1389(4)	−2892(5)	40(2)
O(9)	7530(4)	2049(3)	−836(5)	33(2)
O(10)	9866(4)	2452(3)	−132(5)	33(2)
O(11)	8746(5)	2843(3)	−2447(5)	36(2)
O(12)	9194(5)	4819(4)	−2927(5)	46(3)
O(13)	8683(5)	5939(3)	41(5)	41(2)
O(14)	8342(5)	3970(3)	592(5)	41(2)
O(15)	9776(5)	1408(4)	4631(5)	58(3)
O(16)	9070(6)	3214(4)	4717(5)	62(3)
O(17)	11751(6)	1432(4)	3608(6)	70(3)
C(1)	8492(7)	800(5)	811(7)	29(2)
C(2)	8632(7)	−40(5a)	1194(8)	31(2)
C(3)	8650(7)	−578(5)	−202(7)	30(2)
C(4)	8560(7)	289(5)	−527(7)	30(2)
C(5)	8699(7)	3692(5)	−1748(7)	29(2)
C(6)	8910(7)	4608(5)	−1991(8)	33(2)
C(7)	8672(7)	5103(6)	−647(7)	31(2)
C(8)	8508(7)	4175(5)	−430(8)	31(2)
N(1)	4138(6)	2429(5)	7774(7)	48(2)
C(9)	3805(8)	1352(6)	7459(9)	58(3)
C(10)	4782(9)	901(7)	7992(10)	64(3)
C(11)	4341(9)	−155(7)	7704(11)	78(3)
C(12)	5313(10)	−614(8)	8170(11)	93(4)
C(13)	5181(8)	2655(6)	7154(8)	50(2)
C(14)	5015(9)	2202(7)	5670(9)	70(3)
C(15)	6065(9)	2616(7)	5176(11)	77(3)
C(16)	6107(11)	3618(8)	5258(12)	105(4)
C(17)	3023(8)	2703(6)	7181(9)	58(3)
C(18)	3180(11)	3734(8)	7336(12)	100(4)
C(19)	1980(12)	3914(9)	6551(13)	105(4)
C(20)	2095(14)	4710(11)	6112(16)	79(5)
C(20A)	2308(27)	4110(19)	5422(28)	106(13)
C(21)	4525(8)	2973(6)	9259(8)	53(3)
C(22)	3661(9)	2831(7)	10129(10)	72(3)
C(23)	4104(10)	3615(8)	11569(11)	92(4)
C(24)	3357(12)	3502(10)	12493(13)	127(5)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$(C_4O_4)_2]$,[49] the C−O stretching vibrations are found in the 1730−1790 cm^{-1} range. These results suggest that little correlation exists between the number and positions of IR bands and the coordination mode of the squarate ligand.[44] While IR data have been used to infer the 1,2-bidentate and the 1,2-bisbidentate ligation mode for a number of Mn(II),[50] V(III),[51] and Fe(III)[52] species, such arguments are clearly faulty in view of the absence of structural confirmation for this coordination mode with first-row transition elements. Moreover, simple stereochemical and energetic arguments[44] lead to the conclusion that, while squarate does adopt 1,2-bidentate coordination with lanthanides,[53] this ligation mode is highly unfavorable with first-row transition metal ions.

b. $[(n\text{-}C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (2·3H$_2$O). The reaction of $NaVO_3$ with an equivalent amount of squaric acid in water, followed by the addition of excess $(n\text{-}C_4H_9)_4NBr$, yields a dark brown solution from which orange crystals of the mixed-valence species $[(n\text{-}C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)]\cdot 3H_2O$ (**2·3H$_2$O**) are isolated after a 3 week period of standing at room temperature. The infrared spectrum of **2·3H$_2$O** exhibits C−O stretching vibrations associated with the squarate ligand at 1793 cm^{-1} and features at 970 and 736 cm^{-1} attributed to ν(V=O) and ν(V−O−V), respectively.

Crystals of **2·3H$_2$O** are insoluble in water and CH_2Cl_2 and soluble in most common organic solvents such as CH_3CN, MeOH, and acetone. Solutions of **2·3H$_2$O** in acetonitrile and acetone are stable indefinitely. Conductivity measurements in acetonitrile confirm that **2** is a 1:1 electrolyte. The electronic spectrum in CH_3CN solution exhibits a single band at 255 nm.

Complex **2·3H$_2$O** is electrochemically active, displaying a quasi-reversible cathodic process at −0.72 V with respect to the ferrocene/ferrocenium couple. Controlled-potential electrolysis at −0.85 V results in the consumption of 1 faraday mol^{-1} upon complete electrolysis. The characteristic orange color of the solution of **2·3H$_2$O** slowly turns light blue during the course of the electrolysis. Chemical reduction of **2·3H$_2$O** in acetonitrile in the presence of 1 equiv of phenylhydrazine also produced a blue solution from which crystals of a material analyzing as $[(n\text{-}C_4H_9)_4N]_2[V_2O_3(C_4O_4)_2(H_2O)_3]$ may be isolated in low yield after standing for 6−8 weeks.

c. $[(C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_3]\cdot 6H_2O$ (3·6H$_2$O). Dark brown crystals of **3·6H$_2$O** are isolated as the initial product of the preparation of **2·3H$_2$O**. The synthesis of **2·3H$_2$O** would appear to proceed from the hydrolytic displacement of $C_4O_4{}^{2-}$ from **3·6H$_2$O**:

$$[V_4O_6(C_4O_4)_5(H_2O)_4]^{4-} + 2H_2O \rightarrow 2[V_2O_3(C_4O_4)_2(H_2O)_3]^- + C_4O_4{}^{2-}$$

This reaction scheme is consistent with observations on the chemistry of **2·3H$_2$O**. When crystals of **2·3H$_2$O** are dissolved in water containing excess squaric acid, **3·6H$_2$O** is formed in 50−60% yield. Furthermore, when an excess of $NaVO_3$ is used in the synthesis of **2·3H$_2$O**, **3·6H$_2$O** is not observed to form in significant yield. The infrared spectrum of **3·6H$_2$O** exhibits bands at 1793 and 1502 cm^{-1} attributed to ν(C−O) from the μ-1,2 and μ-1,3 bridging modes, respectively. There are two distinct bands at 988 and 977 cm^{-1} in the ν(V=O) region, indicating that the vanadium sites are inequivalent. The feature at 746 cm^{-1} is attributed to ν(V−O−V). The room temperature EPR spectrum of **3·6H$_2$O** exhibits a 15-line pattern centered at $g = 1.972$.

d. $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]\cdot 2PH_4PCl$ (4·2Ph$_4$PCl). Complex **4** was first isolated from the reaction of $[V_2O_2Cl_2(C_6H_5PO_3H)_2(H_2O)_2]\cdot 2Ph_4PCl$[40] with an equivalent amount of oxalic acid in methanol. Since the phenylphosphonate units of $[V_2O_2Cl_2(C_6H_5PO_3H)_2(H_2O)_2]\cdot 2Ph_4PCl$ are readily displaced by a variety of oxygen donor ligands, the complex serves as a useful source of the $\{VOCl\}^+$ core. While **4** may also be prepared directly from the reaction of $Ph_4P[VO_2Cl_2]$ with oxalic acid in methanol, only low yields of microcrystalline material were obtained. The infrared spectrum of **4** exhibits characteristic bands of the bridging oxalato group at 1668, 1349, and 804 cm^{-1} and a band at 974 cm^{-1} associated with ν(V=O) for the vanadyl group.

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Table 4. Atomic Positional Parameters (×10^4) and Isotropic Displacement Coefficients (Å^2 × 10^3) for **3·6H₂O**

	x	*y*	*z*	*U*(eq)[a]
V(1)	389(3)	8016(2)	9322(2)	41(3)
V(2)	381(3)	9700(2)	7899(2)	46(3)
V(3)	1551(3)	3429(2)	13937(2)	37(2)
V(4)	2445(3)	5151(2)	13170(2)	42(3)
O(1)	409(9)	7691(8)	10431(7)	50(5)
O(2)	366(9)	7149(9)	9369(8)	45(5)
O(3)	−857(10)	8179(9)	9797(8)	49(5)
O(4)	−2895(12)	8207(10)	10267(10)	84(6)
O(5)	−2880(11)	9941(10)	8921(9)	79(6)
O(6)	−816(10)	9897(8)	8418(8)	46(5)
O(7)	324(9)	9884(8)	7083(9)	50(5)
O(8)	508(8)	10856(7)	7782(7)	37(4)
O(9)	357(9)	8636(8)	8354(8)	46(5)
O(10)	450(9)	9342(8)	9180(8)	43(5)
O(11)	1644(10)	9706(8)	7584(8)	46(5)
O(12)	3666(12)	9724(10)	7036(10)	81(6)
O(13)	3686(11)	8023(10)	8460(9)	71(6)
O(14)	1648(10)	8046(8)	9050(9)	43(5)
O(15)	−59(9)	11179(10)	9006(9)	57(5)
O(16)	517(8)	2877(8)	14884(7)	40(4)
O(17)	1808(8)	2743(8)	13623(8)	40(4)
O(18)	630(8)	3943(9)	13475(8)	36(4)
O(19)	−638(11)	4678(9)	12502(9)	66(5)
O(20)	367(10)	6348(10)	11632(10)	70(6)
O(21)	1560(10)	5658(8)	12707(8)	50(5)
O(22)	3241(10)	5492(8)	12444(8)	50(5)
O(23)	2162(8)	6121(8)	13495(7)	39(4)
O(24)	2364(8)	4198(8)	13210(7)	32(4)
O(25)	1225(10)	4532(8)	14312(8)	37(4)
O(26)	9349(9)	3834(9)	5426(7)	37(4)
O(27)	3058(9)	4809(9)	13932(8)	44(5)
O(28)	4064(11)	4192(10)	5145(9)	76(6)
O(29)	3282(10)	2461(11)	5831(10)	76(6)
O(30)	2224(9)	3034(8)	14662(7)	38(4)
O(31)	916(10)	1478(9)	5888(9)	77(6)
O(32)	2115(10)	1315(9)	6660(9)	78(6)
O(33)	6409(14)	3297(12)	6564(12)	154(9)
O(34)	5580(11)	4118(11)	5526(10)	115(7)
O(35)	5646(26)	1699(23)	7848(24)	391(25)
O(36)	4560(26)	997(23)	9783(21)	390(26)
C(1)	−1390(18)	8655(16)	9527(14)	56(8)
C(2)	−2331(19)	8672(17)	9752(17)	67(9)
C(3)	−2338(21)	9447(18)	9143(16)	80(10)
C(4)	−1423(19)	9429(16)	8927(16)	59(8)
C(5)	2217(17)	9221(14)	7852(13)	42(7)
C(6)	3127(19)	9245(17)	7550(17)	68(9)
C(7)	3140(19)	8509(17)	8212(15)	67(9)
C(8)	2204(17)	8498(15)	8487(15)	42(7)
C(9)	187(14)	9690(15)	9621(15)	44(7)
C(10)	−27(14)	10518(17)	9549(15)	47(7)
C(11)	568(13)	4624(15)	12974(13)	31(7)
C(12)	−19(17)	4943(14)	12511(13)	48(8)
C(13)	411(15)	5704(17)	12144(15)	54(8)
C(14)	956(15)	5358(14)	12630(12)	38(7)
C(15)	3088(14)	4134(16)	14470(14)	41(7)
C(16)	3573(18)	3876(16)	15004(15)	70(9)
C(17)	3200(16)	3105(18)	5321(16)	62(9)
C(18)	2753(16)	3367(14)	14757(13)	45(8)
C(19)	560(18)	4782(13)	14690(13)	33(7)
C(20)	−274(15)	4476(16)	15196(12)	37(7)
C(21)	−219(18)	1506(15)	3516(16)	103(11)
C(22)	435(22)	1312(19)	3917(19)	147(14)
C(23)	900(34)	446(30)	4161(28)	279(29)
C(24)	1268(31)	328(29)	3664(26)	302(32)
C(25)	325(15)	2826(14)	2565(13)	78(9)
C(26)	815(18)	2534(16)	1927(16)	103(11)
C(27)	1561(21)	3064(20)	1365(19)	146(14)
C(28)	2204(23)	3059(22)	1644(21)	205(19)
C(2)	−1122(15)	2392(14)	2795(14)	70(9)
C(30)	−1475(16)	3178(15)	2414(14)	81(9)
C(31)	−2231(19)	3052(18)	2186(18)	121(12)
C(32)	−2562(24)	3693(21)	1824(21)	209(19)
C(33)	−791(15)	2732(14)	3751(13)	65(8)
C(34)	−1629(18)	2412(16)	4358(16)	104(11)
C(35)	8065(17)	2926(19)	4951(17)	119(12)
C(36)	−2141(21)	3813(19)	4470(19)	164(15)
C(37)	3956(16)	2667(14)	2958(14)	80(9)
C(38)	4628(17)	3110(15)	2218(15)	90(10)
C(39)	4628(18)	3921(16)	1715(16)	106(11)
C(40)	4900(19)	4410(17)	1070(16)	138(13)
C(41)	4431(15)	1322(14)	2890(14)	71(9)
C(42)	3749(19)	1306(17)	2574(17)	114(11)
C(43)	3935(32)	644(28)	2204(28)	250(25)
C(44)	4510(36)	755(36)	1738(33)	486(64)
C(45)	3451(16)	1486(14)	4092(14)	78(9)
C(46)	3507(19)	637(17)	4581(16)	117(12)
C(47)	2722(20)	375(18)	5258(18)	135(13)
C(48)	2617(20)	−431(18)	5749(18)	151(14)
C(49)	4994(17)	1792(16)	3582(15)	92(10)
C(50)	4921(19)	2234(19)	4065(18)	125(12)
C(51)	5694(25)	2106(23)	4345(23)	193(18)
C(52)	5769(32)	2627(28)	4633(28)	346(36)
C(53)	7846(14)	2288(13)	8530(13)	60(8)
C(54)	7722(15)	1891(14)	8061(13)	72(9)
C(55)	8568(16)	1894(15)	7416(14)	83(9)
C(56)	8467(18)	1567(16)	6901(15)	113(11)
C(57)	6321(15)	2660(14)	8988(13)	67(8)
C(58)	5512(16)	2770(15)	9602(14)	81(9)
C(59)	4863(17)	3261(16)	9229(15)	100(10)
C(60)	4025(19)	3382(18)	9793(17)	142(13)
C(61)	7301(15)	2655(12)	9683(12)	57(8)
C(62)	7369(15)	3558(13)	9290(13)	64(8)
C(63)	7576(17)	3862(14)	9794(14)	86(10)
C(64)	7652(19)	4722(16)	9486(17)	132(13)
C(65)	6826(15)	1396(13)	9796(13)	68(9)
C(66)	7520(13)	849(12)	10077(12)	43(7)
C(67)	7108(14)	110(13)	10743(13)	58(8)
C(68)	7740(14)	−478(13)	11080(13)	67(8)
C(69)	3418(25)	2718(22)	7594(22)	169(16)
C(70)	4092(37)	2382(36)	7324(36)	355(40)
C(71)	4485(39)	1714(33)	7129(32)	376(41)
C(72)	4827(62)	1433(58)	6218(51)	886(371)
C(73)	2324(22)	3719(20)	7051(19)	149(14)
C(74)	1664(17)	3194(16)	7207(15)	94(10)
C(75)	1183(19)	3532(18)	6600(16)	118(12)
C(76)	560(19)	3060(18)	6748(17)	134(13)
C(77)	2333(17)	3277(15)	8387(15)	93(10)
C(78)	1744(21)	3937(19)	8567(19)	143(14)
C(79)	1463(21)	3964(19)	9303(18)	137(13)
C(80)	820(19)	4521(18)	946(17)	136(13)
C(81)	3512(22)	4134(21)	7263(20)	160(15)
C(82)	4203(36)	4039(32)	7562(33)	375(39)
C(83)	4212(36)	5228(30)	6742(32)	345(36)
C(84)	4730(23)	5239(22)	7154(20)	193(18)
N(1)	−451(12)	2362(11)	3160(11)	76(7)
N(2)	4224(14)	1813(12)	3365(12)	75(7)
N(3)	7072(12)	2250(11)	9257(11)	60(6)
N(4)	2896(16)	3432(15)	7586(14)	99(8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor

Descriptions of the Solid State Structures. a. $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$ (1·H₂O). The structure of **1·H₂O** consists of discrete NH_4^+ cations and $[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]^-$ (**1a**) anions, with H_2O molecules of crystallization occupying the void volumes. The structure of the molecular anion may be described as two edge-sharing V(IV) octahedra. Each vanadium site is coordinated to a terminal oxo group, a bridging hydroxy group, a bridging aquo ligand, a terminal aquo ligand, and two oxygen donors from each of two 1,2-bridging squarate ligands. The structure of the anion is essentially identical to that previously reported for $Na[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot 6H_2O$.[35] The V(1)−O(1) and V(2)−O(8) bond distances of 2.05(2) and 2.04(2) Å, respectively, clearly identify these sites as aquo groups (see Tables 10 and 11 and refs 60−63). The V(1)−

Table 5. Atomic Positional Parameters ($\times 10^4$) and Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **$4\cdot 2Ph_4PCl$**

	x	*y*	*z*	*U*(eq)[a]
V(1)	3093(2)	196(2)	967(1)	43(1)
Cl(1)	1826(3)	−930(3)	1388(2)	61(2)
Cl(2)	2920(4)	301(3)	−1578(2)	63(2)
O(1)	2566(8)	1075(6)	1369(5)	53(3)
O(2)	4463(8)	930(6)	476(5)	42(2)
O(3)	3964(8)	−812(6)	253(5)	39(2)
O(4)	4431(8)	−167(6)	1772(5)	53(3)
O(5)	2000(9)	334(7)	−38(5)	59(3)
C(1)	5153(12)	501(8)	60(8)	32(4)
C(2)	4251(14)	−364(10)	2549(8)	76(5)
C(3)	1045(16)	941(13)	−132(10)	108(7)
P(1)	2262(3)	6123(2)	855(2)	36(1)
C(11)	919(11)	6246(8)	1358(7)	32(3)
C(12)	745(12)	5753(9)	2017(7)	44(4)
C(13)	−308(12)	5887(10)	2402(8)	49(4)
C(14)	−1148(17)	6392(12)	2133(10)	86(6)
C(15)	−1002(18)	7012(13)	1499(12)	104(7)
C(16)	26(15)	6845(11)	1088(10)	77(6)
C(17)	2033(11)	6538(9)	−93(7)	34(4)
C(18)	2016(12)	7482(9)	−240(8)	42(4)
C(19)	1813(13)	7796(10)	−975(9)	59(5)
C(20)	1580(13)	7181(11)	−1565(10)	67(5)
C(21)	1565(12)	6263(10)	−1436(8)	54(4)
C(22)	1826(11)	5931(10)	−695(7)	45(4)
C(23)	2651(11)	4940(8)	817(7)	29(3)
C(24)	1775(15)	4267(11)	855(8)	66(5)
C(25)	2149(15)	3364(11)	809(9)	68(5)
C(26)	3330(15)	3141(12)	712(9)	68(5)
C(27)	4187(15)	3810(11)	670(8)	70(5)
C(28)	3855(13)	4716(10)	728(8)	51(4)
C(29)	3540(12)	6696(9)	1382(7)	35(4)
C(30)	3684(13)	6605(10)	2164(8)	55(4)
C(31)	4729(13)	6992(10)	2573(9)	57(5)
C(32)	5533(14)	7469(10)	2165(8)	53(4)
C(33)	5282(13)	7578(10)	1416(8)	55(5)
C934)	4376(12)	7195(9)	991(8)	44(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **$1\cdot H_2O$**

V(1)−O(1)	2.050(21)	V(1)−O(2)	1.567(22)
V(1)−O(3)	2.016(15)	V(1)−O(10)	1.958(22)
V(1)−O(14)	2.044(14)	V(2)−O(6)	1.922(15)
V(2)−O(7)	1.549(23)	V(2)−O(8)	2.040(23)
V(2)−O(9)	2.331(21)	V(2)−O(10)	1.966(23)
V(2)−O(11)	2.012(13)	O(3)−C(1)	1.266(33)
O(4)−C(2)	1.249(30)	O(5)−C(3)	1.202(30)
O(6)−C(4)	1.300(29)	O(11)−C(5)	1.272 (26)
O(12)−C(6)	1.223(32)	O(13)−C(7)	1.287(29)
O(14)−C(8)	1.228(30)	C(1)−C(2)	1.427(31)
C(1)−C(4)	1.351(41)	C(2)−C(3)	1.514(40)
C(3)−C(4)	1.456(27)	C(5)−C(6)	1.463(26)
C(5)−C(8)	1.497(36)	C(6)−C(7)	1.466(39)
C(7)−C(8)	1.446(27)		

O(1)−V(1)−O(2)	102.6(10)	O(1)−V(1)−O(3)	86.1(7)
O(2)−V(1)−O(3)	98.9(8)	O(1)−V(1)−O(10)	153.2(9)
O(2)−V(1)−O(10)	104.2(10)	O(3)−V(1)−O(10)	91.3(8)
O(1)−V(1)−O(14)	83.6(7)	O(2)−V(1)−O(14)	96.8(8)
O(3)−V(1)−O(14)	162.8(8)	O(10)−V(1)−O(14)	91.6(7)
O(6)−V(2)−O(7)	99.3(9)	O(6)−V(2)−O(8)	86.1(8)
O(7)−V(2)−O(8)	101.2(11)	O(6)−V(2)−O(9)	83.0(7)
O(7)−V(2)−O(9)	174.8(10)	O(8)−V(2)−O(9)	83.6(9)
O(6)−V(2)−O(10)	92.4(7)	O(7)−V(2)−O(10)	100.1(11)
O(8)−V(2)−O(10)	158.6(9)	O(9)−V(2)−O(10)	75.1(8)
O(6)−V(2)−O(11)	160.9(9)	O(7)−V(2)−O(11)	97.7(9)
O(8)−V(2)−O(11)	82.0(8)	O(9)−V(2)−O(11)	80.8(7)
O(10)−V(2)−O(11)	93.2(7)	V(1)−O(10)−V(2)	122.8(9)

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **$2\cdot 3H_2O$**

V(1)−O(1)	2.025(5)	V(1)−O(2)	1.581(6)
V(1)−O(3)	1.998 (6)	V(1)−O(9)	1.777(5)
V(1)−O(10)	2.543(6)	V(1)−O(14)	1.969(6)
V(2)−O(6)	2.007(6)	V(2)−O(7)	1.587(5)
V(2)−O(8)	2.041(6)	V(2)−O(9)	1.866(6)
V(2)−O(10)	2.377(4)	V(2)−O(11)	1.983(6)
O(3)−C(1)	1.272(9)	O(4)−C(2)	1.247 (11)
O(5)−C(3)	1.240(9)	O(6)−C(4)	1.276(10)
O(11)−C(5)	1.270(9)	O(12)−C(6)	1.223(11)
O(13)−C(7)	1.233(9)	O(14)−C(8)	1.266(11)
C(1)−C(2)	1.466(13)	C(1)−C(4)	1.419(10)
C(2)−C(3)	1.466(10)	C(3)−C(4)	1.463(13)
C(5)−C(6)	1.471(13)	C(5)−C(8)	1.439(11)
C(6)−C(7)	1.489(11)	C(7)−C(8)	1.473(13)

O(1)−V(1)−O(2)	103.5(2)	O(1)−V(1)−O(3)	80.1(2)
O(2)−V(1)−O(3)	96.0(3)	O(1)−V(1)−O(9)	153.0(3)
O(2)−V(1)−O(9)	103.5(3)	O(3)−V(1)−O(9)	96.5(2)
O(1)−V(1)−O(10)	80.5(2)	O(2)−V(1)−O(10)	175.4(2)
O(3)−V(1)−O(10)	82.2(2)	O(9)−V(1)−O(10)	72.6(2)
O(1)−V(1)−O(14)	82.8(2)	O(2)−V(1)−O(14)	98.4(3)
O(3)−V(1)−O(14)	159.8(2)	O(9)−V(1)−O(14)	94.0(2)
O(10)−V(1)−O(14)	84.5(2)	O(6)−V(2)−O(7)	96.7(3)
O(6)−V(2)−O(8)	84.1(2)	O(7)−V(2)−O(8)	100.7(3)
O(6)−V(2)−O(9)	92.7(2)	O(7)−V(2)−O(9)	102.3(3)
O(8)−V(2)−O(9)	157.0(2)	O(6)−V(2)−O(10)	83.8(2)
O(7)−V(2)−O(10)	177.8(3)	O(8)−V(2)−O(10)	81.5(2)
O(9)−V(2)−O(10)	75.5(2)	O(6)−V(2)−O(11)	162.4(2)
O(7)−V(2)−O(11)	97.4(3)	O(8)−V(2)−O(11)	83.0(2)
O(9)−V(2)−O(11)	94.6(2)	O(10)−V(2)−O(11)	82.5(2)
V(1)−O(9)−V(2)	128.4(3)	V(1)−O(10)−V(2)	83.5(2)

O(9) distances of 2.49(2) and 2.33(2) Å are consistent with a bridging aquo group, with the bond distances somewhat elongated as a consequence of the *trans* influence of the oxo ligands O(2) and O(7). The V−O(10) bond lengths of 1.96(2) and 1.97(2) Å identify this oxygen donor as a bridging hydroxo group. Although some care must be exercised in identifying bridging oxo, hydroxo, or aquo groups, the trends in bond lengths and valence sums are unambiguous, as noted in Table 10. While the $\{V_2O_2(OH)_2\}$ core has been reported for binuclear V(IV) species,[64] the $\{V_2O_2(OH)(H_2O)\}$ core adopted by **$1\cdot H_2O$**, and shared by $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]$, represents a unique structural feature of the V(IV)/O/squarate system.

b. $[(n\text{-}C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ ($2\cdot 3H_2O$). The structure of **2** consists of discrete $(n\text{-}C_4H_9)_4N^+$ cations and $[V_2O_3(C_4O_4)_2(H_2O)_3]^-$ anions. As shown in Figure 2, the molecular anion is constructed from two edge-sharing vanadium octahedra and exhibits a gross geometry similar to that of **1a**

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Table 8. Selected Bond Lengths (Å) and Angles (deg) for **3·6H$_2$O**

V(1)−O(1)	2.075(16)	V(1)−O(2)	1.568(18)
V(1)−O(3)	1.979(15)	V(1)−O(9)	1.831(14)
V(1)−O(10)	2.360(17)	V(1)−O(14)	1.975(16)
V(2)−O(6)	1.945(15)	V(2)−O(7)	1.573(19)
V(2)−O(8)	2.087(15)	V(2)−O(9)	1.796(14)
V(2)−O(10)	2.432(18)	V(2)−O(11)	1.970(16)
V(3)−O(16)	2.080(11)	V(3)−O(17)	1.568(18)
V(3)−O(18)	1.980(15)	V(3)−O(24)	1.883(12)
V(3)−O(25)	2.363(17)	V(3)−O(30)	1.987(17)
V(4)−O(21)	1.928(17)	V(4)−O(22)	1.566(13)
V(4)−O(23)	2.072(16)	V(4)−O(24)	1.754(16)
V(4)−O(25)	2.461(13)	V(4)−O(27)	1.977(18)
O(3)−C(1)	1.249(32)	O(4)−C(2)	1.247(30)
O(5)−C(3)	1.234(36)	O(6)−C(4)	1.289(28)
O(10)−C(9)	1.218(36)	O(11)−C(5)	1.298(30)
O(12)−C(6)	1.235(30)	O(13)−C(7)	1.249(34)
O(14)−C(8)	1.260(25)	O(15)−C(10)	1.272(28)
O(18)−C(11)	1.266(25)	O(19)−C(12)	1.224(38)
O(20)−C(13)	1.227(29)	O(21)−C(14)	1.310(36)
O(25)−C(19)	1.236(28)	O(26)−C(20A)	1.262(33)
O(27)−C(15)	1.282(26)	O(28)−C(16A)	1.247(44)
O(29)−C(17)	1.239(30)	O(30)−C(18)	1.262(37)

O(1)−V(1)−O(2)	96.1(7)	O(1)−V(1)−O(3)	83.1(6)
O(2)−V(1)−O(2)	97.6(7)	O(1)−V(1)−O(9)	160.5(7)
O(2)−V(1)−O(9)	103.3(8)	O(3)−V(1)−O(9)	93.1(6)
O(1)−V(1)−O(10)	86.8(6)	O(2)−V(1)−O(10)	176.9(7)
O(3)−V(1)−O(10)	83.8(6)	O(9)−V(1)−O(10)	73.8(7)
O(1)−V(1)−O(14)	83.8(7)	O(2)−V(1)−O(14)	96.7(7)
O(3)−V(1)−O(14)	161.5(90	O(9)−V(1)−O(14)	95.0(6)
O(10)−V(1)−O(14)	82.6(6)	O(6)−V(2)−O(7)	99.3(8)
O(6)−V(2)−O(8)	82.8(6)	O(7)−V(2)−O(8)	98.9(7)
O(6)−V(2)−O(9)	96.0(6)	O(7)−V(2)−O(9)	104.5(8)
O(8)−V(2)−O(9)	156.4(8)	O(6)−V(1)−O(10)	80.6(6)
O(7)−V(2)−O(10)	176.9(7)	O(8)−V(2)−O(10)	84.1(6)
O(9)−V(2)−O(10)	72.5(7)	O(6)−V(2)−O(11)	159.4(9)
O(7)−V(2)−O(11)	96.2(7)	O(8)−V(2)−O(11)	81.5(6)
O(9)−V(2)−O(11)	93.1(6)	O(10)−V(2)−O(11)	84.7(6)
O(16)−V(3)−O(17)	97.0(6)	O(16)−V(3)−O(18)	82.4(5)
O(17)−V(3)−O(18)	97.8(8)	O(16)−V(3)−O(24)	161.0(7)
O(17)−V(3)−O(24)	102.0(6)	O(18)−V(3)−O(24)	94.3(6)
O(16)−V(3)−O(25)	87.3(6)	O(17)−V(3)−O(25)	175.5(5)
O(18)−V(3)−O(25)	81.2(7)	O(24)−V(3)−O(25)	73.7(6)
O(16)−V(3)−O(30)	85.7(6)	O(17)−V(3)−O(30)	97.6(7)
O(18)−V(3)−O(30)	161.5(7)	O(24)−V(3)−O(30)	92.3(6)
O(25)−V(3)−O(30)	84.1(6)	O(21)−V(4)−O(22)	98.0(7)
O(21)−V(4)−O(23)	81.2(7)	O(22)−V(4)−O(23)	97.9(7)
O(21)−V(4)−O(24)	96.7(7)	O(22)−V(4)−O(24)	103.5(8)
O(23)−V(4)−O(24)	158.6(5)	O(21)−V(4)−O(25)	83.7(5)
O(22)−V(4)−O(25)	176.5(7)	O(23)−V(4)−O(25)	85.5(5)
O(24)−V(4)−O(25)	73.2(5)	O(21)−V(4)−O(27)	157.8(7)
O(22)−V(4)−O(27)	96.6(8)	O(23)−V(4)−O(27)	80.2(7)
O(24)−V(4)−O(27)	96.0(7)	O(25)−V(4)−O(27)	82.7(6)
V(1)−O(9)−V(2)	128.0(11)	V(1)−O(10)−V(2)	85.7(7)
V(3)−O(24)−V(4)	127.9(8)	V(3)−O(25)−V(4)	85.2(5)

Table 9. Selected Bond Lengths (Å) and Angles (deg) for **4·Ph$_4$PCl**

V(1)−Cl(1)	2.320(5)	V(1)−O(1)	1.603(9)
V(1)−O(2)	2.089(9)	V(1)−O(3)	2.211(9)
V(1)−O(4)	2.014(9)	V(1)−O(5)	2.054(9)
O(2)−C(1)	1.263(16)	O(3)−C(1A)	1.236(16)
O(4)−C(2)	1.427(18)	O(5)−C(3)	1.372(20)
C(1)−O(3A)	1.236(16)	C(1)−C(1A)	1.522(23)

Ol(1)−V(1)−O(1)	101.0(4)	Cl(1)−V(1)−O(2)	165.4(3)
O(1)−V(1)−O(2)	93.5(4)	Cl(1)−V(1)−O(3)	89.9(3)
O(1)−V(1)−O(3)	168.3(4)	O(2)−V(1)−O(3)	75.8(3)
Cl(1)−V(1)−O(4)	90.1(3)	O(1)−V(1)−O(4)	99.8(4)
O(2)−V(1)−O(4)	85.8(4)	O(3)−V(1)−O(4)	84.3(3)
Cl(1)−V(1)−O(5)	91.6(3)	O(1)−V(1)−O(5)	95.5(4)
O(2)−V(1)−O(5)	88.6(4)	O(3)−V(1)−O(5)	79.8(3)
O(4)−V(1)−O(5)	164.0(4)		

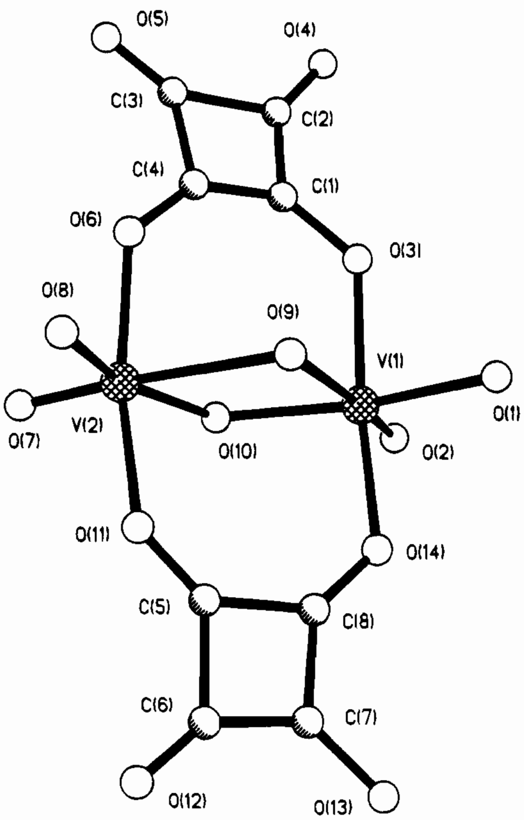

Figure 1. View of the molecular anion of **1·H$_2$O**, [V$_2$O$_2$(OH)(C$_4$O$_4$)$_2$(H$_2$O)$_3$]$^-$, showing the atom-labeling scheme.

with the exception that the bridging OH group of **1a** is replaced by an oxo group in **2a**. Thus, each vanadium site is coordinated to a terminal oxo group, the bridging oxo group, a terminal aquo ligand, the bridging aquo ligand, and two oxygen donors from each of the two 1,2-bridging squarate ligands. The V−bridging oxo distances are inequivalent and similar to those previously reported for [V$_2$O$_3$((2-pyridylethyl)iminodiacetate)$_2$].[57] The vanadium−oxygen distances to the terminal aquo group are unexceptional and may be compared to those reported for VOSO$_4$·5H$_2$O[55] and [VO(C$_2$O$_4$)$_2$(H$_2$O)]$^{2-}$ [24] of 2.006−2.019(2) and 2.033(3) Å, respectively. The vanadium−oxygen distances to the bridging aquo ligand are significantly longer as a consequence of the *trans* influence of the terminal oxo groups. It is noteworthy that these V−O(5) distances are inequivalent, as are the vanadium−bridging oxo distances, so as to produce a bridged {V$_2$(μ-O)(μ-OH$_2$)} rhombus with alternating short−long V−O distances.

The {V$_2$O$_3$} core has been reported for both V(V) binuclear species and V(V)/V(IV) mixed-valence complexes. Examples of oxidized species include [V$_2$O$_3$(OH)$_2$(1,4,7-trimethyl-1,4,7-triazacyclonananane)$_2$]$^{2+}$ [56] and the Schiff base complex [V$_2$O$_3$(OC$_6$H$_4$CHNCMeCO$_2$)$_2$],[57] while mixed-valence complexes are represented by [V$_2$O$_3$((pyridylmethyl)iminodiacetate)$_2$]$^-$,[58] [V$_2$O$_3$((2-pyridylethyl)iminodiacetate)$_2$]$^-$,[57] and [V$_9$O$_{16}$(butanediaminetetraacetate)$_4$]$^{7-}$.[58] Inequivalent vanadium−bridging oxo bonds are also present in the latter two examples of the {V$_2$O$_3$}$^{3+}$ core.

The structure of the anion of **2·3H$_2$O** reveals a number of unique features. The {O=V−O−V=O} units of the previously reported examples of the {V$_2$O$_3$}$^{3+}$ core exhibit essentially *trans* planar structures with nearly linear V−O−V bond angles. In contrast, the {V$_2$O$_3$}$^{3+}$ unit of **2·3H$_2$O** assumes a *cis* planar geometry with a V−O−V angle of 128.8(3)°. The structural feature is clearly related to the presence of the bridging aquo ligand producing a {V$_2$O$_2$(μ-O)(μ-OH$_2$)} rhombus as the bridging motif. The structural core may best be described as a unique planar {V$_2$O$_3$(H$_2$O)$_3$}$^{3+}$ unit.

Table 10. Bond Distances (Å) and Valence Sums for Vanadium Oxide Structures with Doubly Bridging Oxo, Hydroxo, and/or Aquo Ligands

complex	V–O–V	$\sum s_i$[a]	V–O(H)–V	$\sum s_i$	V–O(H$_2$)–V	$\sum s_i$	ref
$H_2V_{10}O_{28}^{4-}$	1.844(5)	1.81[f]	1.944(5)	1.34			*b*
$[V_6O_{11}(OH)_2\{(OCH_2)_3CR\}_2]$	1.823(4)	1.92	1.909(5)	1.49			*c*
$[V_3O_{10}(OH)_3\{(OCH_2)_3CR\}_2]^{2-}$	1.86(1)	1.73[f]	1.94(1)	1.36			*c*
$[V_6O_7(OH)_6\{(OCH_2)_3CR\}_2]^{2-}$			1.994(3)	1.16			*c*
$[V_4O_8(O_2CR)_4(NO_3)]^{2-}$	1.82(1)	1.94					*d*
$[V_4O_7(OH)(O_2CR)_4K]^+$	1.82(1)	1.94	1.95(1)	1.32			*e*
$[V_2O_2(OH)_2([9]aneN_3)_2]^{2+}$			1.969(5)	1.25			56
$Na[V_2O_2(OH_2)_3(OH)_2(C_4O_4)_2]$			1.97(1)	1.25	2.38(1)		35
$NH_4[V_2O_2(OH_2)_3(OH)(C_4O_4)_2]\cdot H_2O$ (**1·H$_2$O**)			1.98(2)	1.21	2.40(2)	0.35	this work
$Bu_4N[V_2O_3(OH_2)_3(C_4O_4)_2]\cdot 3H_2O$ (**2·3H$_2$O**)	1.822(7)	1.93			2.460(6)	0.30	this work
$(Bu_4N)_4[V_4O_6(OH_2)_4(C_4O_4)_5]\cdot 6H_2O$ (**3·6H$_2$O**)	1.82(1)	1.94					this work
average values	1.83	1.89	1.96	1.30	2.43	0.33	

[a] Valence sums in valence units, calculated according to ref 59. No hydrogen atom contributions. [b] Capparelli, M. V.; Goodgame, D. M. L.; Hayman, P. B.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 776. [c] Chen, Q.; Goshorn, D. P.; Scholes, C. P.; Tan, X.-L.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 4667. [d] Munrich, D. D.; Folting, K.; Streib, W. E.; Huffman, J. C.; Christou, *J. Chem. Soc., Chem. Commun.* **1989**, 1411. [e] Priebsch, W.; Rehder, D.; von Oeynhausen, M. *Chem. Ber.* **1991**, *124*, 761. [f] Strong hydrogen bonding to adjacent units.

Table 11. Comparison of Structural Parameters of Selected V(V)/V(IV) Mixed-Valence Complexes: $Na[V_2O_3(S\text{-peida})_2]\cdot NaClO_4\cdot H_2O$ (**A**), $H[V_2O_3(pmida)_2]\cdot 4H_2O$ (**B**), $K_7[V_9O_{16}(bdta)_4]\cdot 27H_2O$ (**C**), $[(n\text{-}C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (**2·3H$_2$O**), and $[(n\text{-}C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$ (**3·6H$_2$O**)[a]

	A[c]		**B**[c]	**C**[c]		**2·3H$_2$O**		**3·6H$_2$O**	
	V(1)	V(2)		V(1)	V(2)	V(1)	V(2)	V(1)	V(2)
V=O$_t$, Å	1.622(4)	1.613(4)	1.592(5)	1.57(2)	1.55(2)	1.578(7)	1.582(5)	1.57(2)	1.57(2)
V–O$_b$, Å	1.875(4)	1.763(4)	1.79(2)	1.69(2)	1.91(2)	1.733(5)	1.860(6)	1.83(1)	1.80(1)
V–L(D), Å	2.019(4)	2.13(4) (O)	2.107(8) (O)	2.25(2) (O)	2.40(2) (O)	2.021(5) (O)	2.048(6) (O)	2.08(2) (O)	2.09(2) (O)
	2.000(4) (O)	1.983(4) (O)	2.010(7) (O)	2.28(2) (O)	2.04(2) (O)	1.972(6) (O)	1.980(6) (O)	1.98(6) (O)	1.95(2) (O)
	2.100(5) (N)	2.099(5) (N)	2.282(7) (N)	1.99(2) (O)	1.96(2) (O)	1.997(6) (O)	2.010(6) (O)	1.98(2) (O)	1.97(2) (O)
	2.293(4) (N)	2.278(4) (N)	2.052(8) (N)	1.97(2) (O)	2.01(2) (O)	2.538(5) (μ-OH$_2$)	2.382(5) (μ-OH$_2$)	2.36(2) (μ-O$_1$)	2.43(2) (μ-O$_1$)
$\sum s$[b]	4.29	4.71	4.66	4.92	4.50	4.68	4.38	4.51	4.64

[a] Abbreviations: *S*-peida = (*S*)-[1-(2-pyridyl)ethyl]imino]diacetate; pmida = (pyridylmethyl)iminodiacetate; bdta = butanediaminetetraacetate; O$_t$ = terminal oxo group; O$_b$ = bridging oxo group; L = ligand; D = dnor atom; O$_1$ = ligand oxygen donor. [b] Bond numbers in valence units, calculated as indicated in ref 59. [c] References: **A**, 54; **B**, 57; **C**, 58.

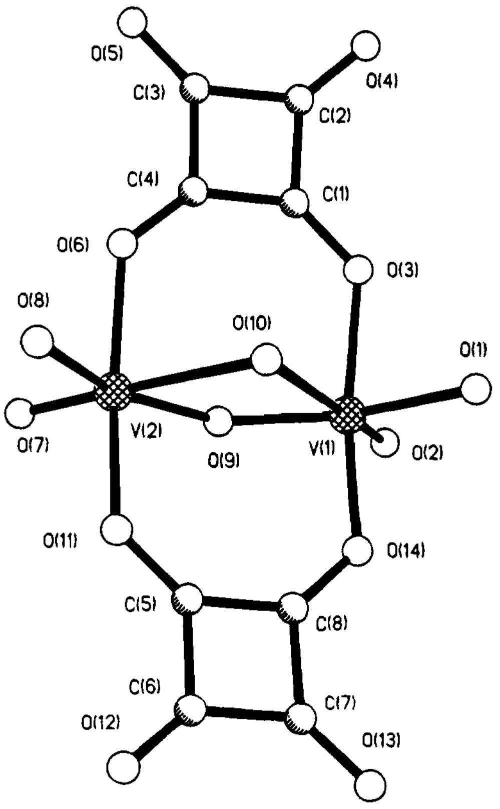

Figure 2. View of the molecular anion of **2·3H$_2$O**, $[V_2O_3(C_4O_4)_2(H_2O)_3]^-$, showing the atom-labeling scheme.

Charge balance considerations indicate that $[V_2O_3(C_4O_4)_2(H_2O)_3]^-$ is a mixed-valance V(V)/V(IV) complex. While the two vanadiums are in structurally different environments, valence bond calculations[59] do not clearly distinguish localization of valence states. As shown in Table 11, of the previously reported parameters for V(V)/V(IV) mixed-valence systems with the $\{V_2O_3\}^{3+}$ core, the bonding parameters associated with $[V_2O_3(S\text{-peida}))_2]^-$ and $[V_9O_{16}(bdta)_4]^{7-}$ suggest that the one vanadium site possesses greater V(IV) character than the other, while the structure of $[V_2O_3(pmida)]^-$ is consistent with delocalization of the site. While the valence sums for **2·3H$_2$O** suggest greater V(IV) character associated with the V(2) site, such small differences in valence sums should be viewed with caution.

The squarate ligands adopt the 1,2-bridging mode, which, while less common than the 1,3-bridging type,[44–46] has been described previously for $[Cr_2(OH)_2(H_2O)_4(C_4O_4)_2]$,[49] $[Mo_2(OMe)_2(NNPh)_4(C_4O_4)_2]^{2-}$,[47] and $[Sn_2Cl_4(OMe)_2(C_4O_4)_2]$.[48] The metrical parameters associated with the squarate ligands are unexceptional.

The three water molecules of crystallization are arranged so as to hydrogen-bond with each other and to the free carboxylate oxygens of two adjacent $[V_2O_3(C_4O_4)_2(H_2O)_3]^-$ units. This results in linear one-dimensional chains of aquo-bridged binuclear anions running parallel to the *c* axis, as shown in Figure 3.

c. $[(C_4H_9)_4N]_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$ (3·6H$_2$O). As shown in Figure 4, the structure of the molecular anion of **3·6H$_2$O**, $[V_4O_6(C_4O_4)_5(H_2O)_4]^{4-}$ (**3a**), consists of two binuclear units **2a**, the bridging oxo group of each replaced by an oxygen donor of a 1,3-bridging squarate group. The structure thus exhibits two common coordination modes for the squarate ligand, 1,2- and 1,3-bridging types. The 1,3-bridging or bismonodentate coordination mode is the most commonly observed for the squarate ligand,[41–43,64] although it has not been previously reported in conjunction with the 1,2-bridging type.

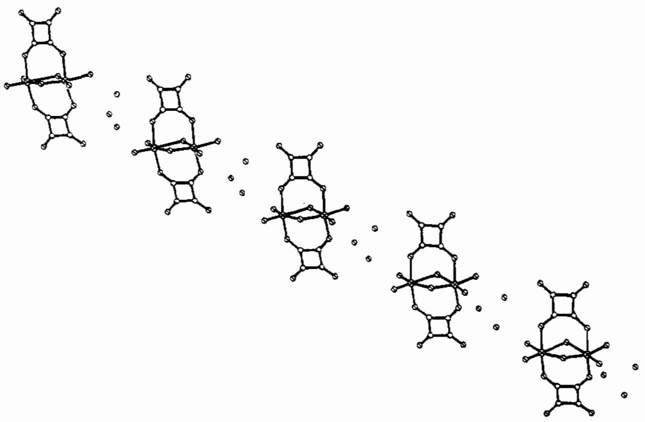

Figure 3. One-dimensional chains of aquo-bridging binuclear anions $[V_2O_3(C_4O_4)_2(H_2O)_3]^-$ in **2·3H$_2$O**.

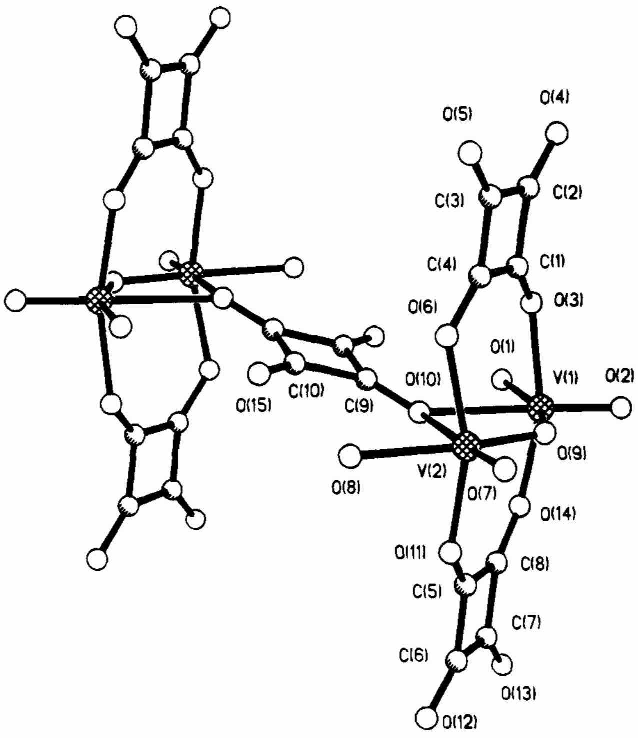

Figure 4. The molecular anion of **3·6H$_2$O**, $[V_4O_6(C_4O_4)_5(H_2O)_4]^{4-}$.

The metrical parameters associated with the binuclear units of **3a** are similar to those observed for **2a**, as shown in Tables 8 and 9. Valence bond calculations[59] and charge balance requirements confirm that **3·6H$_2$O** is a mixed-valence complex, exhibiting one V(IV)/(V) pair per binuclear moiety, and that the d^1 site is delocalized over the V centers.

d. $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]$·2Ph$_4$PCl (2·2Ph$_4$PCl). The structure of **4·2Ph$_4$Cl** consists of discrete molecules of $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]$, Ph_4P^+ cations, and Cl^- anions. As shown in Figure 5, the structure of **4** is centrosymmetric, with the crystallographic inversion center located at the midpoint of the C(1)−C(1a) bond. The vanadium sites exhibit distorted octahedral geometry with the coordination about each V(IV) center defined by a terminal oxo group, a chloro ligand, the oxygen donors of two methanol ligands, and two oxygens of the bridging bisbidentate oxalate ligand.

While previously reported examples of structurally characterized vanadium−oxalate complexes exhibit oxalate coordinated in the bidentate mode rather than the bridging bisbidentate fashion, this latter coordination geometry has been described for numerous other transition metal species, including $[Cu_2(H_2O)_2(\text{tetramethylethylenediamine})_2(C_2O_4)]^{2+}$,[65] $[Mn(C_{10}H_8N_2)(C_2O_4)]$,[66] and $[W_2(CO)_8(C_2O_4)]^{2-}$.[67] In **4** the oxalate group bridges the $\{VOCl\}^+$ groups so as to provide a planar $\{V_2O_2Cl_2(C_2O_4)\}$ core, with the methanol ligands disposed above and below the plane. This location of the V═O group in the oxalate plane is similar to the geometry of the unit in $[V_8O_8(OMe)_{16}(C_2O_4)]^{2-}$.[16] It is noteworthy that the molybdenum−oxo complex with oxalate $[(MoO_2Cl_2)_2(C_2O_4)]^{2-}$ [68] also exhibits a structure with the oxo groups copolanar with the oxalate ligand, producing a planar $\{Mo_2O_4(C_2O_4)\}^{2+}$ core. Similarly, in the chloranilate derivative $[(MoO_2Cl_2)_2(C_6O_4Cl_2)]^{2-}$,[69] the $\{MoO_2\}^{2+}$ group lies in the plane of the $(Cl_2C_6O_4)^{2-}$ ligand. While it has been assumed that in species such as $[V_2O_2)acac)_2(C_2O_4)]$ the {V═O} group is normal to the $\{V_2(C_2O_4)\}$ plane,[70] the structural data on complexes with {M═O} groups bridged by bisbidentate oxalate ligands suggests that the in-plane orientation of the oxo group is more likely.

The *trans* influence of the oxo group is reflected in the inequivalence of the bond distances from the vanadium to the oxygen donors of the oxalate ligands: 2.211(9) Å for V−O(3) and 2.089(9) Å for V−O(2). The V−O(4) and V−O(5) distances of 2.001(9) and 2.038(9) Å, respectively, establish the identity of the axial ligands as methanol groups rather than methoxy groups. These bond lengths may be compared to V−O distances of 1.824(4) and 2.036(4) Å for the V−OR and V−O(H)R bond types, respectively, in $[VO\{(HOCH_2)_2C(CH_2O)N(CH_2CH_2O)_2\}]$.[71]

Magnetic Susceptibility. Magnetic susceptibility data for powdered **1·H$_2$O**, **2·3H$_2$O**, and **3·6H$_2$O** are shown in Figures 6−8, respectively.

Compound **1** exhibits a maximum near room temperature in the temperature-dependent magnetic susceptibility data. As the temperature is lowered, the magnetic susceptibility of the sample begins to decrease from the room-temperature maximum and reaches a minimum at lower temperatures. At the lowest temperatures, the susceptibility again begins to increase because of the presence of a small amount of paramagnetic impurity. A broad maximum in the temperature-dependent magnetic susceptibility is expected for short-range antiferromagnetic exchange and is consistent with antiferromagnetic coupling in vanadium(IV) binuclear units.

The magnetic exchange that is expected in vanadium(IV) with a ^2D free ion ground term, d^1 electron structure, and spin $S = {}^1/_2$ is the isotropic Heisenberg spin Hamiltonian

$$H = -2JS_iS_j \tag{1}$$

where a negative J denotes a ground state singlet. Within the context of the crystal structure of this material, the exchange from this spin Hamiltonian may be propagated via a binuclear magnetic exchange interaction for the binuclear V(IV) core.

The behavior of the V(IV) ions can be expressed as follows:

$$\chi = \frac{2Ng^2\mu_B^{\,2}}{kT}\left(\frac{e^{2J/kT}}{1 + 3e^{2J/kT}}\right) \tag{2}$$

where all of the parameters have their usual meaning. The

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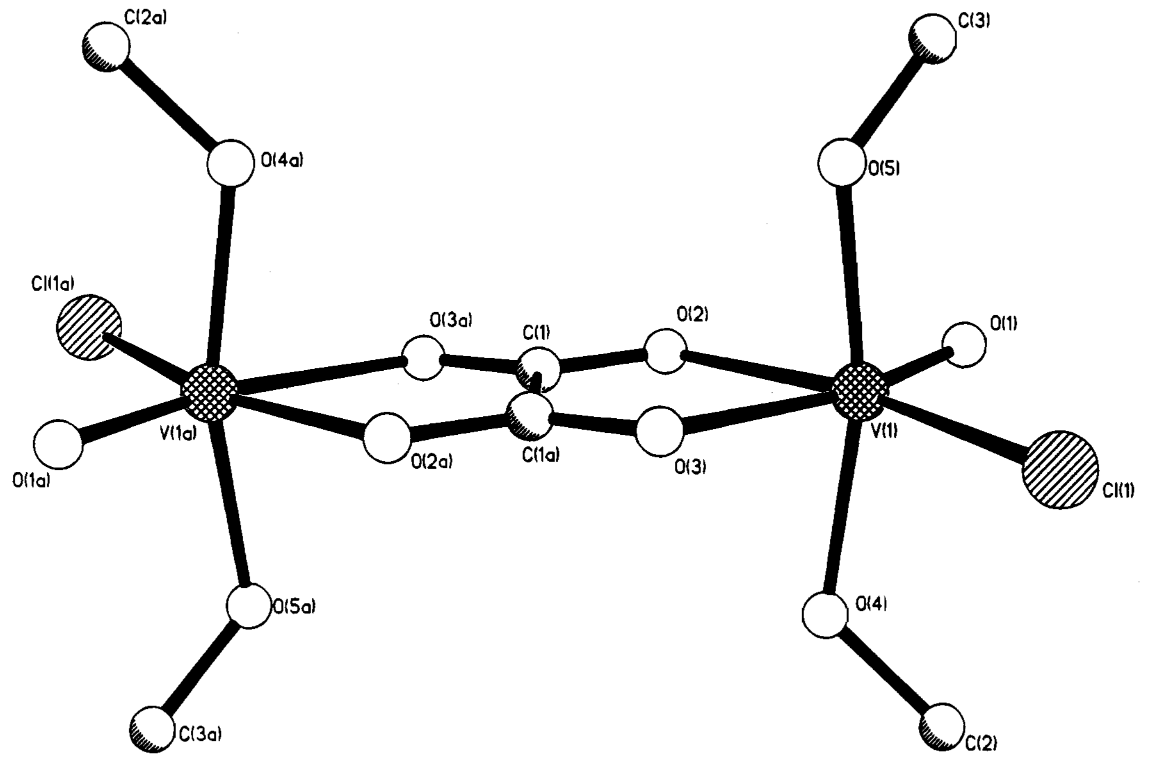

Figure 5. Structure of $[V_2O_2Cl_2(C_2O_4)(CH_3OH)_4]$.

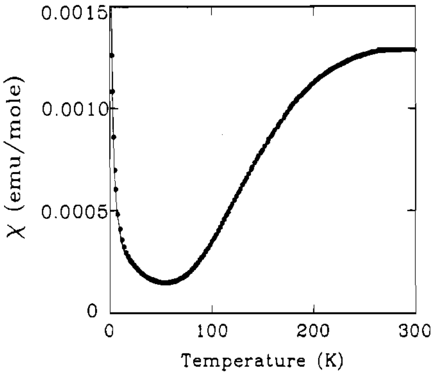

Figure 6. Magnetic susceptibility of $(NH_4)[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$ (**1·H$_2$O**) plotted as a function of temperature over the 1.7–300 K temperature region. The curve drawn through the data is the fit to the binuclear theoretical model as described in the text.

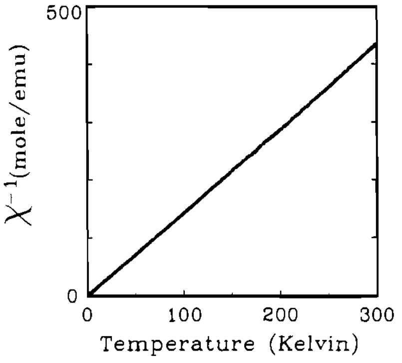

Figure 7. Magnetic susceptibility of $(n\text{-}Bu_4N)[V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (**2·3H$_2$O**) plotted as a function of temperature over the 1.7-300 K temperature region. The line drawn through the data is the fit to the Curie–Weiss model as described in the text.

results of a least-squares fit of eq 2 to the magnetic susceptibility data yield the parameters $g = 1.95$, $J/k = 240$ K, TIP = 0.000 10 emu/mol, with the data corrected for a 0.8% paramagnetic impurity. The result of this fit is illustrated in Figure 5 as magnetic susceptibility plotted as a function of temperature, and the smooth curve is the theoretical calculation.

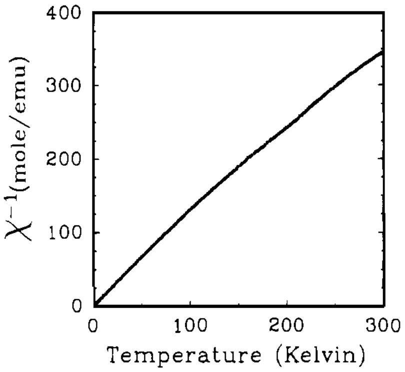

Figure 8. Magnetic susceptibility of $(n\text{-}Bu_4N)_4[V_4O_6(C_4O_5)_5(H_2O)_4]\cdot 6H_2O$ (**3·6H$_2$O**) plotted as a function of temperature over the 1.7-300 K temperature region. The line drawn through the data is the fit to the Curie–Weiss model as described in the text.

The magnitude of the antiferromagnetic interaction in **1·H$_2$O** contrasts with the weak exchange interactions observed in binuclear Cu(II) μ-1,3-bismonodentate and μ-1,2-bismonodentate squarate bridged complexes,[44,50b,72] when the J values range from 0 to 10.3 cm^{-1}. The strongest antiferromagnetic coupling for the Cu(II)–squarate system is associated with $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)]\cdot H_2O$,[72] which exhibits several unusual structural features when compared to other members of the class. The intramolecular Cu(II)···Cu(II) distance for $[Cu(SalNEt_2)_2(H_2O)(C_4O_4)]\cdot H_2O$ is 5.210 Å, compared to a range of 7.465–7.833 Å for other Cu(II) squarates. Furthermore, while all other members of the Cu(II)–squarate class of binuclear complexes exhibit significant π-delocalization within the squarato ring, as judged by small differences between the shortest and longest C–C and C–O bonds, $[Cu_2(SalNEt_2)_2(H_2O)(C_4O_4)]\cdot H_2O$ displays localized squarate ring bonds with Δ(C–C) and Δ(C–O) of 0.06 and 0.05 Å, respectively. The localized form of the squarato ligand results in an enhanced interaction of the metal orbitals with the ring HOMOs and consequently a stronger exchange interaction.[72] The vanadium species **1·H₂O** exhibits not only a short V···V distance of 3.33 Å and squarato ring parameters ($\Delta(C-C) = 0.09$ Å; $\Delta(C-O) = 0.06$ Å) consistent with multiple-bond localization but also the presence of the bridging hydroxo group providing an additional pathway for magnetic exchange.

The magnetic susceptibility data for **$2\cdot3H_2O$** and **$3\cdot6H_2O$** exhibit Curie–Weiss paramagnetism

$$\chi = \frac{C}{T - \Theta} + \mathrm{TIP} = \frac{2Ng^2\mu_B^{\ 2}S(S + 1)}{3k(T - \Theta)} + \mathrm{TIP} \qquad (3)$$

with $C = 0.345$ emu K/mol, $\Theta = +1.12$ K, and TIP = 0.000 457 emu/mol for **$2\cdot3H_2O$** and $C = 0.732$ emu K/mol, $\Theta = -12$ K, and TIP = 0.0 emu/mol for **$3\cdot6H_2O$**. For the formula units indicated, this corresponds to g values of 1.917 and 1.974 for **$2\cdot3H_2O$** and **$3\cdot6H_2O$**, respectively.

Conclusions. While molybdenum oxides form a variety of high-nuclearity clusters incorporating squarate ligands, under similar conditions vanadium oxides yield only lower nuclearity species with the central $\{VO_x\}$ polyhedral core screened by the squarate groups, acting as terminal hydrophobic ligands. However, the chemistry of the V/O/squarate system is quite rich as a consequence of the abilities of the squarate ligand to adopt a variety of bridging modes and of the vanadium centers to access multiple oxidation states. This latter observation is demonstrated by the characterization of the binuclear V(IV) species $NH_4[V_2O_2(OH)(C_4O_4)_2(H_2O)_3]\cdot H_2O$ (**$1\cdot H_2O$**) and of two mixed-valence materials, $[(C_4H_9)_4N][V_2O_3(C_4O_4)_2(H_2O)_3]\cdot 3H_2O$ (**$2\cdot3H_2O$**) and $[(C_4H_9)_4[V_4O_6(C_4O_4)_5(H_2O)_4]\cdot 6H_2O$ (**$3\cdot6H_2O$**), upon suitable modifications of reaction conditions.

Acknowledgment. This work was supported by NSF Grant CHE9318824 to J.Z. C.J.O. acknowledges support of a grant from the Louisiana Education Quality Support Fund [LEQSF-(RF/1994-94)-ENH-TR-60], administered by the Board of Regents of the State of Louisiana.

Supplementary Material Available: Tables of experimental conditions, bond lengths and angles, anisotropic temperature factors, and calculated hydrogen atom positions for the structures of **$1\cdot H_2O$**, **$2\cdot3H_2O$**, **$3\cdot6H_2O$**, and **$4\cdot2Ph_4PCl$** (30 pages).

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