Inorg. Chem. **1990**, *29*, 434-438

Contribution from the Department of Chemistry, University of Queensland, Brisbane, Australia 4067,
Department of Physical & Inorganic Chemistry, Adelaide University, Adelaide, Australia 5001,
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

An Oxo-Bridged Binuclear Vanadium(III) 2,2′-Bipyridine Complex and Its Vanadium(IV) and Vanadium(V) Oxidation Products

Stephen G. Brand,[1a] Norman Edelstein,[1b] Clifford J. Hawkins,*[,1a] George Shalimoff,[1b]
Michael R. Snow,[1c] and Edward R. T. Tiekink[1c]

Received December 15, 1988

Vanadium(III) in water reacts with 2,2′-bipyridine to form an oxo-bridged binuclear complex that crystallizes as $[\{VCl(bpy)_2\}_2O]_{0.5}Cl\cdot 3H_2O$ in the orthorhombic space group $Pbcn$ with unit cell dimensions a = 18.820 (8) Å, b = 9.507 (2) Å, c = 25.792 (6) Å, V = 4614.8 Å^3, and Z = 8. The complex in its crystalline form has a magnetic moment per vanadium of 3.176 ± 0.002 μ_B, an unusually high value, considering all available evidence supports the III oxidation state. Aerial oxidation yields an oxovanadium(IV) complex that crystallizes from an aqueous acetone perchlorate solution as $[VOCl(bpy)_2]ClO_4$ in the monoclinic space group $P2_1/c$ with a = 12.960 (3) Å, b = 12.310 (4) Å, c = 13.642 (3) Å, β = 105.78 (2)°, V = 2094.4 Å^3, and Z = 4. Further oxidation in aqueous tetrahydrofuran produces crystals of $[VO_2(bpy)_2]Cl\cdot 4H_2O$ with the triclinic space group $P\bar{1}$ with a = 11.527 (5) Å, b = 15.102 (5) Å, c = 6.738 (3) Å, α = 97.33 (4)°, β = 97.26 (4)°, γ = 101.31 (3)°, V = 1126.9 Å^3, and Z = 2. The structures of the first and third complexes were refined by a full-matrix least-squares procedure, and a blocked-matrix procedure was employed for the refinement of the vanadyl complex. Refinement on 2364 statistically significant reflections yielded final R = 0.063 and R_w = 0.071 for the oxo-bridged complex; on 2402 reflections, R = 0.065 and R_w = 0.071 for the vanadyl complex; and on 2212 reflections, R = 0.076 and R_w = 0.084 for the dioxovanadium(V) complex. The coordination geometries show similar distortions from a regular octahedral structure dictated by repulsions between the two anionic ligands, the small bite angle of the chelates, and the effects of trans ligands on the coordinate bond lengths. The binuclear complex has a C_2 axis relating the two units, which are twisted 61.6° relative to each other. The V–O–V group is close to linear with a bond angle of 173.5 (4)°.

Introduction

In an attempt to learn more about the coordination chemistry of vanadium in the blood of ascidians, various living specimen, and, in some instances, the whole blood, were exposed to saline solutions of a number of ligands including 2,2′-bipyridine. In some aplousobranch and phlebobranch species that are known to concentrate vanadium within their blood cells,[2] it was noted that in the presence of 2,2′-bipyridine an intense purple coloration formed within the compartment cells and, in some species, unpigmented morula cells.[3] Extraction with ethanol gave a solution that showed characteristics in the visible absorption spectrum very similar to those of the dark purple vanadium binuclear complex of 2,2′-bipyridine reported first by Brandt and co-workers[4] and later by Murray and Sheahan[5] as being either a vanadium(III) dihydroxo-bridged complex or a mixed-valence vanadium(II,III) dihydroxo- or dioxo-bridged complex, respectively. Recently, Shah and Maverick[6] and Toma and co-workers[7] have presented evidence favoring the former structure.

This paper reports the syntheses, crystal structures, and spectral properties of the binuclear compound and its vanadium(IV) and vanadium(V) oxidation products.[8]

Experimental Section

Materials. All reagents and solvents were AnalaR grade except for nitric and perchloric acids that were Aristar grade. Methanol was dried by distillation from magnesium turnings and iodine, and acetonitrile was dried by distillation from calcium hydride. Analyses for C, H, and N were carried out by the University of Queensland's microanalytical service. Chloride analyses were carried out by potentiometric titration, and vanadium analyses following nitric/perchloric acid digestion by graphite furnace atomic absorption.

For the synthesis of the complexes some operations were carried out under dry, oxygen-free dinitrogen in a VAC Dri-lab Model M040-1.

(μ-Oxo)bis[bis(2,2′-bipyridine)chlorovanadium(III)] Chloride Hexahydrate. In the Dri-lab 4.57 g (0.01 mol) of vanadium trichloride (Fluka) was dissolved in a minimum volume of deoxygenated water (40 mL), and 4.69 g (0.03 mol) of solid 2,2′-bipyridine was added with stirring. The color of the solution changed from greenish brown to a deep chocolate brown and then to purple-black within 30 s. Four volumes of acetone were added, and the solution was left standing for 24 h to yield a purple crystalline product, yield 4.2 g (80%). Anal. Calcd for $C_{40}H_{44}Cl_4N_8O_7V_2$: C, 48.4; H, 4.5; N, 11.3; V, 10.3. Found: C, 49.0; H, 4.3; N, 11.5; V, 10.1.

Bis(2,2′-bipyridine)chlorooxovanadium(IV) Chloride Dihydrate. The above preparation was repeated to form the purple-black solution. This was removed from the Dri-lab, and air was bubbled through the solution for 24 h to form an emerald green solution. Acetone was added until the first sign of localized precipitation was observed. The solution was placed in a refrigerator for a few hours to yield emerald green crystals, which were filtered out, washed with acetone and then ether, and dried in vacuo, yield 2.6 g (54%). Anal. Calcd for $C_{20}H_{20}Cl_2N_4O_3V$: C, 49.4; H, 4.2; Cl, 14.6; N, 11.5; V, 10.5. Found: C, 49.1; H, 4.0; Cl, 15.0; N, 11.2; V, 10.4. IR ν(VO): 964.0 (s), 892.9 (m) cm^{-1}.

Bis(2,2′-bipyridine)chlorooxovanadium(IV) Perchlorate. The purple-black binuclear complex solution, prepared as described above, was removed from the Dri-lab, and a concentrated aqueous solution of sodium perchlorate was added with stirring to yield a purple powder, which was filtered out and sucked dry. The solid was dissolved in hot acetonitrile to produce an intense purple solution that quickly turned green, precipitating an emerald green solid, which was recrystallized from hot acetonitrile to give green crystals. These crystals were filtered out and dried in vacuo; yield 3.6 g (70%). Anal. Calcd for $C_{20}H_{16}Cl_2N_4O_5V$: C, 46.7; H, 3.1; Cl, 13.8; N, 10.9; V, 9.9. Found: C, 47.6; H, 3.3; Cl, 13.9; N, 11.0; V, 10.1.

Bis(2,2′-bipyridine)dioxovanadium(V) Chloride Hydrate. The reaction to form the emerald green solution of the chloro oxo complex was repeated. Four volumes of tetrahydrofuran were added, the mixture was allowed to stand at room temperature for 12 h, during which the solution turned orange, and red-brown needles precipitated. These were filtered out and recrystallized from acetonitrile to give red-brown plates that were dried in vacuo; yield 1.4 g (30%). Anal. Calcd for $C_{20}H_{18}ClN_4O_3V$: C, 53.5; H, 4.0; N, 12.5; V, 11.4. Found: C, 53.2; H, 4.4; N, 12.2; V, 11.2. IR ν(VO): 962.9 (m), 943.2 (s), 921.0 (m), 904.3 (m), 889.5 (m) cm^{-1}. Crystals for X-ray diffraction study were not dried in vacuo and analyzed as the tetrahydrate.

Physical Measurements. Infrared spectra were obtained with the compounds dispersed in KBr pellets using a Mattson Sirius 100 FT-IR spectrophotometer. UV–visible spectra were measured with a Hewlett Packard 8450A spectrophotometer. Electron paramagnetic resonance spectra were measured with a Bruker ER200D X-band spectrometer at 9.25 GHz and at 77 or 110 K. The magnetic field and microwave frequency were calibrated with a Bruker 035M gaussmeter and an EIP

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(1) (a) University of Queensland. (b) University of California. (c) University of Adelaide.

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Table I. Crystallographic Data

compd	$[\{V(bpy)_2Cl\}_2O]_{0.5}Cl\cdot 3H_2O$	$[VOCl(bpy)_2]ClO_4$	$[VO_2(bpy)_2]Cl\cdot 4H_2O$
formula	$C_{20}H_{22}Cl_2N_4O_{3.5}V$	$C_{20}H_{16}Cl_2N_4O_5V$	$C_{20}H_{24}ClN_4O_6V$
fw	496.3	514.2	502.8
space group	*Pbcn* (D_{2h}^{14}, No. 60)	$P2_1/c$ (C_{2h}^{5}, No. 14)	$P\bar{1}$ (C_i^1, No. 2)
a, Å	18.820 (8)	12.960 (3)	11.527 (5)
b, Å	9.507 (2)	12.310 (4)	15.102 (5)
c, Å	25.792 (6)	13.642 (3)	6.738 (3)
α, deg	90	90	97.33 (4)
β, deg	90	105.78 (2)	97.26 (4)
γ, deg	90	90	101.31 (3)
V, Å^3	4614.8	2094.4	1126.9
Z	8	4	2
λ(Mo Kα), Å	0.71073	0.71073	0.71073
ρ_{obs}, g cm^{-3}	1.44	1.62	1.46
ρ_{calc}, g cm^{-3}	1.429	1.631	1.482
T, K	298	298	298
μ, cm^{-1}	6.36	7.07	5.49
transm coeff	0.8112–0.7794	n/a	0.9587–0.8428
$R(F_o)$	0.063	0.065	0.076
$R_w(F_o)$	0.071	0.071	0.084

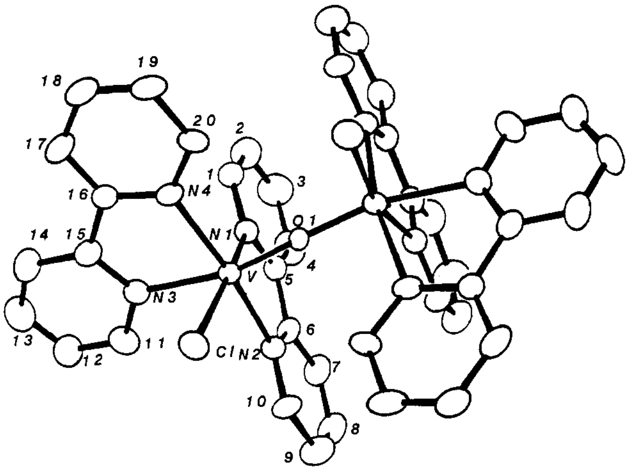

Figure 1. ORTEP view of the $[\{VCl(bpy)_2\}_2O]^{2+}$ cation drawn with 30% probability ellipsoids, giving the atom numbering.

841A microwave frequency counter. Parameters were calculated by spectrum simulations. Magnetic susceptibility measurements of crystalline material were carried out on a SHE 905 SQUID magnetometer. Powdered samples were weighed and sealed into calibrated containers in an inert-atmosphere box. All data were obtained with applied fields between 5 and 40 kG and temperatures from 1.7 to 302 K.

X-ray Diffraction Data Collection, Structure Solution, and Refinement. Intensity data were measured at room temperature, 295 (2) K, with the use of Mo Kα (graphite monochromator) radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4F diffractometer employing the ω 2θ scan technique. Corrections were routinely applied for Lorentz and polarization effects, and an absorption correction was applied for the vanadium(III) and vanadium(V) complexes with the use of an analytical procedure.[9] For the vanadium(III) binuclear complex the data were also corrected for the observed decrease in the net intensity values (−7%) of three standard reflections monitored after every 1-h X-ray exposure time. All relevant data collection parameters and crystal data are listed in Table I.

The structures were solved from the interpretation of the Patterson synthesis in each case and refined by a full-matrix least-squares procedure (block matrix for the vanadium(IV) complex) in which the function $\sum w\Delta^2$ was minimized, where *w* was the weight applied to each reflection and $\Delta = ||F_o| - |F_c||$.[9] Non-hydrogen atoms on the bipyridine ligands were located from a difference map for the vanadium(III) complex and included in their calculated positions in the model for the vanadium(V) complex. A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was introduced in each calculation, and the refinements were continued until convergence. Refinement details are given in Table I.

Fractional atomic coordinates are given in Tables II–IV, and the numbering schemes employed are shown in Figures 1–3. The scattering factors for C, H, Cl, N, and O were those incorporated in the SHELX program,[9] and those for neutral V were (corrected for f' and f'') from ref 10.

Table II. Positional Parameters ($\times 10^4$) for $[\{V(bpy)_2Cl\}_2O]_{0.5}Cl\cdot 3H_2O$

atom	*x*	*y*	*z*
V	834 (1)	1926 (1)	2171 (1)
Cl(1)	1388 (1)	−162 (2)	2483 (1)
Cl(2)	8072 (2)	1028 (5)	403 (2)
O(1)	0	1820 (6)	2500
N(1)	611 (3)	3980 (5)	1888 (2)
N(2)	1316 (3)	3266 (6)	2738 (2)
N(3)	1717 (3)	2052 (6)	1627 (2)
N(4)	476 (3)	897 (5)	1497 (2)
C(1)	263 (5)	4246 (8)	1449 (3)
C(2)	100 (6)	5602 (11)	1298 (4)
C(3)	317 (7)	6692 (10)	1615 (5)
C(4)	692 (6)	6425 (9)	2068 (4)
C(5)	836 (4)	5065 (7)	2190 (3)
C(6)	1233 (4)	4670 (7)	2651 (3)
C(7)	1507 (5)	5666 (8)	3003 (3)
C(8)	1856 (5)	5206 (12)	3439 (3)
C(9)	1940 (6)	3760 (11)	3528 (3)
C(10)	1664 (5)	2839 (9)	3165 (3)
C(11)	2348 (4)	2697 (8)	1715 (3)
C(12)	2882 (5)	2684 (11)	1376 (4)
C(13)	2817 (5)	1983 (12)	921 (5)
C(14)	2206 (5)	1251 (12)	829 (3)
C(15)	1636 (4)	1354 (8)	1180 (3)
C(16)	934 (4)	697 (7)	1101 (3)
C(17)	742 (5)	−86 (9)	670 (3)
C(18)	59 (5)	−630 (8)	631 (3)
C(19)	−404 (5)	−382 (8)	1014 (3)
C(20)	−195 (4)	378 (7)	1452 (3)
O(2)	721 (3)	−3810 (6)	−284 (3)
O(3)	6815 (3)	2853 (6)	477 (2)
O(4)	9204 (5)	3654 (11)	4870 (4)

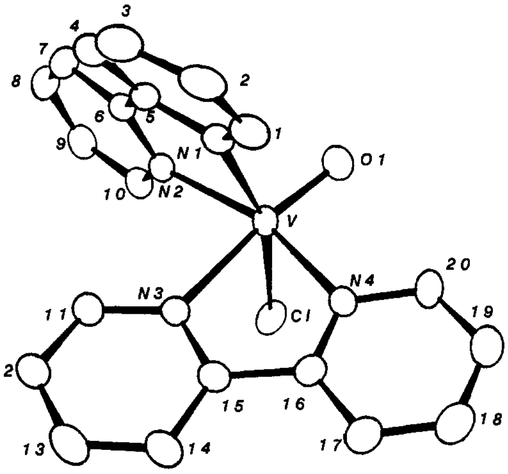

Figure 2. ORTEP view of the $[VOCl(bpy)_2]^+$ cation drawn with 30% probability ellipsoids, giving the atom numbering.

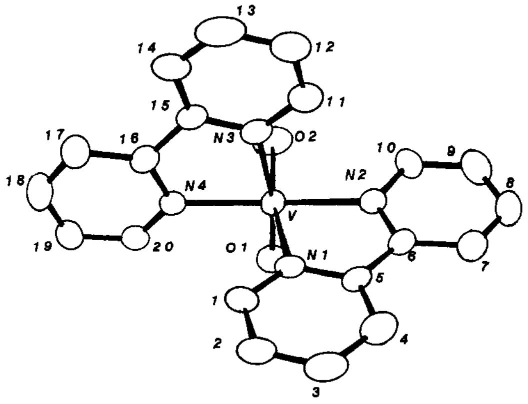

Figure 3. ORTEP view of the $[VO_2(bpy)_2]^+$ cation drawn with 30% probability ellipsoids, giving the atom numbering.

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[9] Sheldrick, G. M. "SHELX76, Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1976.

Table III. Positional Parameters (×10^4) for $[VO(bpy)_2Cl]ClO_4$

atom	*x*	*y*	*z*
V	2395 (1)	1307 (1)	2105 (1)
O(1)	1557 (3)	2303 (4)	1770 (3)
Cl(1)	3302 (1)	1353 (1)	849 (1)
N(1)	3707 (4)	139 (4)	2958 (4)
N(2)	3638 (4)	2268 (4)	3079 (4)
C(1)	3664 (5)	955 (5)	2913 (5)
C(2)	4520 (5)	1613 (5)	3382 (5)
C(3)	5487 (6)	1121 (6)	3890 (6)
C(4)	5554 (5)	13 (6)	3933 (6)
C(5)	4631 (5)	627 (5)	3459 (4)
C(6)	4586 (5)	1815 (5)	3536 (5)
C(7)	5446 (5)	2434 (6)	4084 (5)
C(8)	5342 (6)	3550 (6)	4152 (5)
C(9)	4338 (6)	4016 (5)	3685 (5)
C(10)	3510 (5)	3357 (5)	3151 (5)
N(3)	1484 (4)	72 (4)	1426 (4)
N(4)	1736 (4)	737 (4)	3278 (4)
C(11)	1395 (5)	443 (5)	485 (5)
C(12)	687 (5)	1266 (5)	46 (5)
C(13)	52 (6)	1710 (5)	608 (5)
C(14)	136 (5)	1346 (5)	1586 (5)
C(15)	890 (4)	−541 (5)	1996 (4)
C(16)	1127 (4)	−173 (5)	3055 (5)
C(17)	820 (5)	755 (6)	3820 (5)
C(18)	1114 (6)	355 (6)	4803 (5)
C(19)	1675 (5)	633 (7)	5018 (5)
C(20)	1970 (5)	1148 (5)	4236 (5)
Cl(0)	1982 (2)	1232 (2)	2274 (2)
O(01)	935 (8)	6528 (10)	2546 (10)
O(02)	2499 (8)	6535 (10)	2041 (6)
O(03)	2454 (12)	6580 (18)	3598 (8)
O(04)	1847 (12)	5225 (11)	2808 (19)

Table IV. Positional Parameters (×10^4) for $[VO_2(bpy)_2]Cl{\cdot}4H_2O$

atom	*x*	*y*	*z*
V	2455 (1)	917 (1)	2048 (2)
O(1)	3464 (5)	687 (4)	3730 (8)
O(2)	1167 (4)	424 (3)	2523 (8)
N(1)	2527 (5)	2245 (3)	3527 (9)
N(2)	1507 (4)	1618 (4)	−246 (8)
N(3)	2525 (4)	−112 (3)	−385 (8)
N(4)	3959 (4)	1514 (4)	382 (9)
C(1)	3116 (6)	2540 (5)	5407 (11)
C(2)	3065 (8)	3382 (6)	6489 (14)
C(3)	2429 (8)	3930 (6)	5610 (14)
C(4)	1842 (8)	3651 (5)	3638 (14)
C(5)	1890 (6)	2793 (5)	2613 (11)
C(6)	1308 (6)	2437 (5)	536 (11)
C(7)	593 (7)	2894 (6)	−590 (14)
C(8)	79 (7)	2476 (7)	−2580 (13)
C(9)	299 (6)	1658 (6)	−3361 (12)
C(10)	1016 (6)	1243 (5)	−2154 (11)
C(11)	1751 (6)	−918 (5)	−702 (11)
C(12)	1835 (7)	−1655 (5)	−2080 (12)
C(13)	2779 (8)	−1532 (6)	−3127 (11)
C(14)	3585 (7)	−715 (5)	−2833 (10)
C(15)	3429 (6)	−3 (5)	−1434 (9)
C(16)	4257 (5)	913 (5)	−995 (9)
C(17)	5248 (6)	1147 (6)	−1952 (11)
C(18)	5904 (7)	1995 (8)	−1513 (14)
C(19)	5611 (7)	2637 (6)	−96 (15)
C(20)	4630 (6)	2365 (5)	816 (13)
Cl	5797 (9)	5276 (5)	8581 (12)
O(3)	8907 (12)	4079 (8)	3845 (28)
O(4)	8427 (18)	4553 (9)	−166 (24)
O(5)	5618 (16)	4105 (12)	4804 (23)
O(6)	2452 (21)	6328 (9)	4158 (31)

Results and Discussion

Crystal Structures. The three complexes have a cis configuration of ligands about the metal. The coordinate bond lengths and angles are given in Table V. The major distortions from the octahedral coordination are illustrated in Figure 4. Of particular interest are the angles formed between trans bonds, which are markedly distorted from 180° with the average value for oxidation state III being 167.0°, for IV, 162.5°, and for *V*, 160.5°.

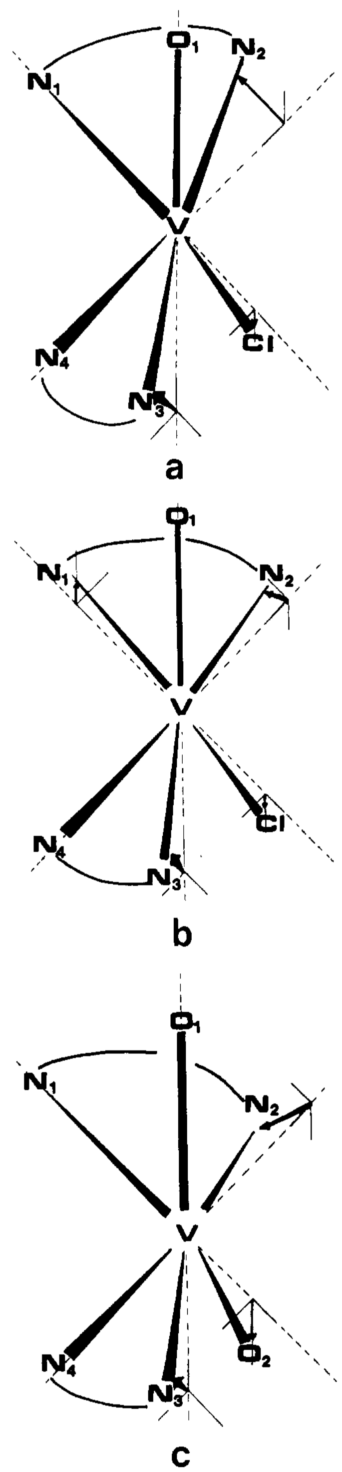

Figure 4. Distortions from octahedral structure of the cations (a) $[\{VCl(bpy)_2\}_2O]^{2+}$, (b) $[VOCl(bpy)_2]^+$, and (c) $[VO_2(bpy)_2]^+$.

The V–N bond lengths are determined by the ligands trans to them and are independent of the oxidation state: V–N trans to N, 2.126 ± 0.017 Å; V–N trans to O^{2-}, 2.281 ± 0.111 Å (cf. 2.290 Å for the V state in $[H\{VO(O_2)(bpy)\}_2]^-$);[11,12] V–N trans to Cl^-, 2.126 ± 0.001 Å (cf. 2.130 Å for the V state in $[VCl_3(bpy)(NCl)]$);[13] V–N trans to O–V in the III state, 2.178 Å (cf. 2.192

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(10) Hamilton, W. C.; Ibers, J. A. *International Tables of X-Ray Crystallography*"; Kynoch: Birmingham, England, 1974; Vol. IV.

(11) Abbreviations: bpy, 2,2′-bipyridine; py, pyridine; thf, tetrahydrofuran; ttha, triethylenetetraminehexaacetate.

(12) Szentivanyi, H.; Stomberg, R. *Acta Chem. Scand., Ser. A* **1984**, *38*, 101.

Table V. Interatomic Distances (Å) and Angles (deg) Relevant to the Vanadium Coordination Sphere

	$[\{VCl(bpy)_2\}_2O]Cl_2\cdot 6H_2O$ ($X = Cl^-$)	$[VOCl(bpy)_2]ClO_4$ ($X = Cl^-$)	$[VO_2(bpy)_2]Cl\cdot 4H_2O$ ($X = O^{2-}$)
V–O(1)	1.787 (1)	1.619 (4)	1.614 (5)
V–X	2.381 (2)	2.328 (2)	1.638 (5)
V–N(1)	2.126 (5)	2.127 (6)	2.270 (5)
V–N(2)	2.140 (5)	2.131 (5)	2.104 (5)
V–N(3)	2.178 (6)	2.289 (5)	2.284 (5)
V–N(4)	2.106 (5)	2.143 (4)	2.131 (5)
O(1)–V–X	100.2 (2)	102.0 (2)	106.5 (2)
O(1)–V–N(1)	92.4 (2)	94.9 (2)	89.2 (2)
O(1)–V–N(2)	94.7 (2)	103.3 (2)	98.5 (2)
O(1)–V–N(4)	94.8 (2)	95.2 (2)	95.5 (2)
N(1)–V–N(2)	76.8 (2)	77.0 (2)	73.9 (2)
N(3)–V–N(4)	74.8 (2)	72.7 (2)	72.9 (2)
N(1)–V–N(4)	94.6 (2)	96.0 (2)	88.2 (2)
N(2)–V–X	94.6 (2)	91.7 (2)	95.5 (3)
N(4)–V–X	91.8 (2)	89.9 (2)	97.9 (3)
N(3)–V–X	86.0 (2)	86.3 (2)	88.8 (2)
N(3)–V–N(1)	83.0 (2)	78.8 (2)	77.3 (2)
N(3)–V–N(2)	94.8 (2)	88.2 (2)	88.2 (2)
O(1)–V–N(3)	168.2 (2)	165.5 (2)	162.2 (2)
N(1)–V–X	165.4 (2)	161.5 (1)	162.4 (3)
N(2)–V–N(4)	167.4 (2)	160.6 (2)	157.0 (2)

Å for the V state in $[\{VOF(bpy)\}_2(O)_2]$).[14] The V=O bonds also do not show a major change with oxidation state where they are trans to N: IV state, 1.619 Å; V state, 1.614 and 1.638 Å. Other dioxovanadium(V) complexes are in the literature where V=O is trans to a range of ligands, and the bond lengths range from 1.613 to 1.670 Å.[15-19] Contrary to the above, V–Cl seems to decrease as the oxidation state of vanadium increases. For those trans to N, the III complex has V–Cl = 2.381 Å, and the IV complex, 2.328 Å, and in $[VCl_3(bpy)(NCl)]$ it is 2.284 Å.[13] A similar sensitivity is found in the literature for V–Cl trans to Cl: $[VCl_2(py)_4]$ (II state), 2.462 Å;[20] $[\{V(thf)_3Cl_2\}_2O]$ (III state), 2.390 and 2.384 Å;[21] $[VCl_3(bpy)(NCl)]$ (V state), 2.317 and 2.327 Å.[13]

The factors that appear to have the largest influences on the structures are the repulsions between the two anionic ligands and the N–V–N angle spanned by the chelate rings, the so-called bite angle. The chloride and the second oxide ligands (X) are distorted away from O(1) causing N(3) in turn to be pushed away from its octahedral position. The O(1)–V–X angle ranges from 100.2° in the III complex to 106.5° in the dioxovanadium(V) complex. For other dioxovanadium(V) complexes this angle ranges from 103.8 to 107.5°.[15-19]

The relatively inflexible 2,2′-bipyridine chelate ring enforces a N–V–N angle less than 80° for the three complexes. For those chelate rings in which V–N is lengthened by the effect of a trans O^{2-}, the value for N–V–N is reduced to about 73°.

The distortions to the octahedral structure generated by the above two factors result in the reduction in the angle formed by the trans coordinate bonds from 180° to between 168.2 and 157.0°.

V–O–V Unit. There are a number of oxo-bridged binuclear vanadium complexes whose structures are described in the literature, all but one of which have a single oxo bridge,[21-28] with the exception, $[\{VOF(bpy)\}_2(O)_2]$, possessing a dioxo bridge.[14] Most of the mono-oxo-bridged complexes have a V–O–V unit close to 180° and a V···V distance of about 3.6 Å, but in $[(VL)_2O(\mu\text{-}CH_3CO_2)_2]I_2\cdot 2H_2O$, where L is 1,4,7-triazacyclononane, V–O–V is 130.2° and V···V is 3.250 Å.[28] Three of these complexes have both vanadiums in the III oxidation state, $[\{V(thf)_3Cl_2\}_2O]$,[14] $[\{V(SCH_2CH_2NMe_2)_2\}_2O]$,[27] and the 1,4,7-triazacyclononane complex.[28] The first of these has a V–O bond length of 1.769 Å, a V···V distance of 3.538 Å, and a V–O–V angle of 180°. The second complex's values are V–O = 1.803 and 1.822 Å and V–O–V = 177.84°. The present vanadium(III) dimer has V–O = 1.787 Å, V···V = 3.568 Å, and V–O–V = 173.5°. In $[\{VCl(bpy)_2\}_2O]Cl_2$ the two coordination spheres are twisted 61.6° relative to one another.

Table VI. UV–Visible Spectral Data

	H_2O		MeOH		MeCN	
	λ[a]	ε[b]	λ[a]	ε[b]	λ[a]	ε[b]
$[\{VCl(bpy)_2\}_2O]Cl$	646	4130	660	6520	656	5500
	528	4500	546	5900	546	4970
	303[c]	25200	296[c]	37500	304	39000
	283	37500	287	38800	241	38600
	234	38300	236	39600		
$[VOCl(bpy)_2]Cl$	748	24	722	30	718	40
	358[c]	350	376	580	576[c]	31
	313[c]	4090	305[c]	6290	372	409
	280	26400	282	15400	305	14600
	232	23400	234	15100	285[c]	11500
$[VO_2(bpy)_2]Cl$	430	275	454	191	474	340
	314	19620	308	10700	303[c]	14000
	280[c]	12600	282	17800	282	20200
	241	19200	230	20500	238	17700

[a] nm. [b] M^{-1} cm^{-1}. [c] Shoulder.

The formation of $[\{VCl(bpy)_2\}_2O]^{2+}$ follows the generation of the $[VOV]^{4+}$ unit, a hydrolysis product of vanadium(III),[29-31] which is also formed as an intermediate in the reaction between vanadium(II) and vanadium(IV).[6,29,30] The purple complex is not formed in acid solutions (pH < 1), in which the hexaaquavanadium(III) complex is stable to hydrolysis, nor is it formed in dry nonaqueous solutions.[7,32]

The crystal structure of $[\{VCl(bpy)_2\}_2O]Cl_2$ has a C_2 axis that passes through the bridging oxygen and relates the two vanadium "octahedra". This is consistent with the conclusion of Shah and Maverick[6] that the complex has two vanadium(III) centers. Earlier work had proposed vanadium(II)–vanadium(III) mixed oxidation states for the complex.[5]

Visible Absorption Spectra. The data for the three complexes are given in Table VI. The reaction mixture in the preparation of the purple binuclear complex has its charge-transfer bands at 624 and 518 nm, almost identical with the spectrum of the ethanol extract of *Leptoclinides lissus* that had been treated with 2,2′-bipyridine (626 and 522 nm).[3] This confirms the presence of vanadium(III) in the compartment cells that stained purple with 2,2′-bipyridine.[3] The absorption bands for the isolated complex in water, methanol, and acetonitrile are at higher wavelength.

The $[VOV]^{4+}$ unit in the aqua complex has an intense absorption at 425 nm. A similar intense bands occurs at 487 nm in tetrahydrofuran and acetonitrile solutions of $[\{VCl_2(thf)_3\}_2O]$ and at 482 nm in dimethylformamide.[21] [{V-

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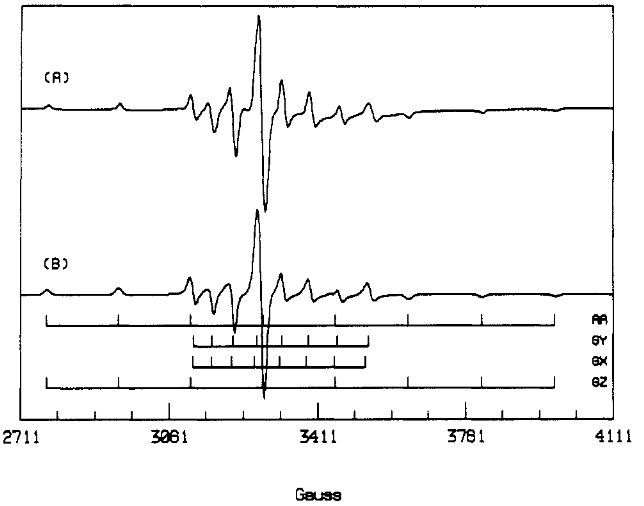

Figure 5. EPR spectra of $[VOCl(bpy)_2]^+$ in methanol at 120 K with ν = 9.2524 GHz: (A) experimental; (B) simulated.

$(SCH_2CH_2NMe_2)_2\}_2O]$ absorbs at 463 nm in acetonitrile and at 458 nm in dimethylformamide.[27] A similar band has been observed in $[V_2O(ttha)]^{2-}$ at 450 nm.[33] The 1,4,7-triazacyclononane complex, $[(VL)_2O(\mu\text{-}CH_3CO_2)_2]^{2+}$, has two visible bands at 709 and 449 nm.[28] The two bands observed in the visible region for $[\{VCl(bpy)_2\}_2O]^{2+}$ have been assigned by Toma and co-workers to transitions of π-symmetry electrons to nonbonding and π-symmetry orbitals within the $[VOV]^{4+}$ unit with some mixing of the vanadium(III) dπ and bipyridine pπ orbitals.[7]

The oxovanadium(IV) complex has a d–d band at about 720 nm in methanol and acetonitrile. In water it is at 748 nm. The shift would be associated with some dissociation of the complex in the aqueous solution.

Electron Paramagnetic Resonance. A dry methanolic solution of $[\{VCl(bpy)_2\}_2O]Cl_2$ gave no spectrum at room temperature or at 110 K. A similar solution of $[VOCl(bpy)_2]Cl$ at 110 K has the spectrum in Figure 5 together with the simulated spectrum for $g_x = 1.9850$, $g_y = 1.9820$, $g_z = 1.9581$ and $A_x = 53.80$, $A_y = 54.48$, $A_z = 156.58 \times 10^{-4}$ cm^{-1} (LSE = 0.00227).[34] These parameters differ significantly from those for $[VO(bpy)_2]^{2+}$, prepared by adding excess bipyridine to an aqueous solution of vanadyl perchlorate: $g_\parallel = 1.948$, $g_\perp = 1.981$; $A_\parallel = 161.19$, $A_\perp = 56.42 \times 10^{-4}$ cm^{-1}.[35]

Magnetic Susceptibility. The data for the inverse susceptibility against temperature for $[\{VCl(bpy)_2\}_2O]Cl_2$ in powder form, given in Figure 6, fits the Curie–Weiss equation, $\chi = c/(T - \Theta)$, with $c = 1.261$ and $\Theta = -0.64$ K. A plot of magnetic moment against temperature is also given in Figure 6. The average value of the magnetic moment per vanadium is 3.176 ± 0.002 μ_B/V. This is high relative to the spin-only value for a d^2 system of 2.83 μ_B but is approximately the same value found earlier by Sheahan and Murray[5] and was reproducible with different crystalline samples. Toma and co-workers quote a moment of 2.82 μ_B/V for the complex in acetone at room temperature.[7] This difference in magnetic moment must arise from a solid-state effect. $[\{V(SCH_2CH_2NMe_2)_2\}_2O]$ has a moment of 2.93 μ_B/V at 296 K in C_6D_6 and in the solid state. On the other hand, Wieghardt and co-workers' 1,4,7-triazacyclononane complex, $[(VL)_2O(\mu\text{-}CH_3CO_2)_2]I_2\cdot 2H_2O$, showed ferromagnetic coupling with the magnetic moment increasing from 3.25 μ_B/V at 293 K to 3.44 μ_B/V at 98 K.[28]

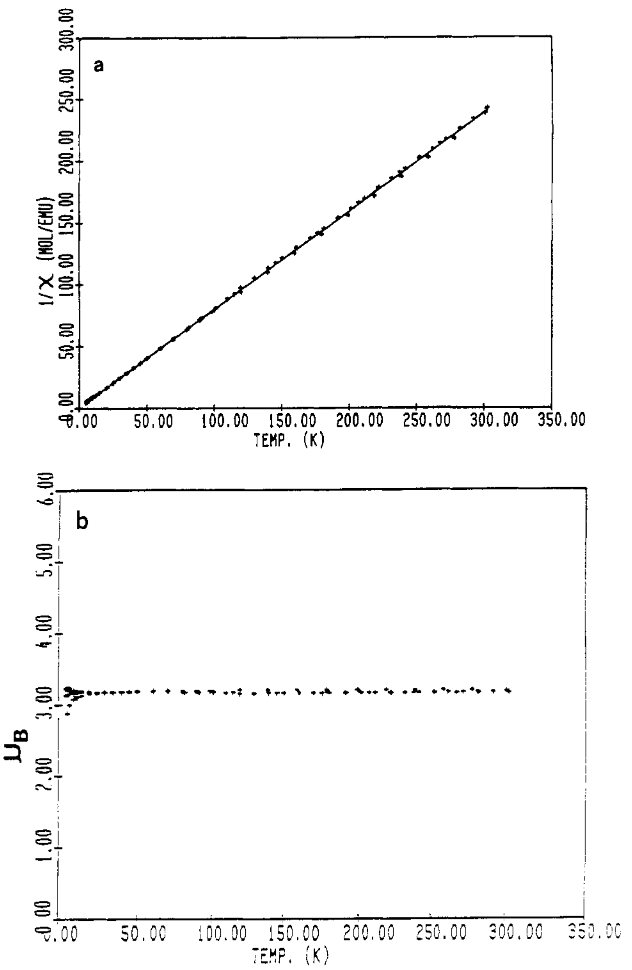

Figure 6. Plot of (a) the inverse magnetic susceptibility and (b) the effective magnetic moment against temperature for $[\{VCl(bpy)_2\}_2O]Cl_2$.

The insensitivity of the moment for $[\{VCl(bpy)_2\}_2O]Cl_2$ in powder form to temperature is also of interest. The small Curie–Weiss parameters are consistent with the low symmetry of the vanadium coordination and the lack of significant antiferromagnetic coupling in this linear $[VOV]^{4+}$ complex in which the axes of the two octahedra are rotated by about 62°.

Oxidation of the Vanadium(III) Complex. Oxidation in water yields a solution that contains two vanadium(IV) species according to the EPR spectrum, a mono- and a bis(2,2′-bipyridine) species.[35] When acetone is added, $[VOCl(bpy)_2]Cl$ precipitates. Oxygen does not oxidize the oxovanadium(IV) complex dissolved in water, alcohol, or acetonitrile. However, if tetrahydrofuran is added to an aqueous solution of $[VOCl(bpy)_2]Cl$ when oxygen is present, $[VO_2(bpy)_2]^+$ is formed.

Acknowledgment. Financial assistance from the Australian Research Grants Scheme (C.J.H., M.R.S.) is gratefully acknowledged. We thank Dr. Graeme R. Hanson for the simulation program for the EPR spectra and for advice regarding the simulations.

Supplementary Material Available: Tables SI–SXII, listing crystallographic data, thermal parameters, hydrogen atom positional and thermal parameters, and angles and distances associated with the ligands (11 pages); Tables SXIII–SXV, giving calculated and observed structure factors for the three compounds (41 pages). Ordering information is given on any current masthead page.

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