

**Figure 4.** Lower panel: absorption (—) MCD (---) at 5 T and 4.2 K of Nafion films<sup>22</sup> with differing concentrations of Ir(bpy)<sub>2</sub>Cl<sub>2</sub><sup>+</sup>. Lower left of the upper panel shows the 300 K absorption spectrum of a  $\approx 10 \mu\text{m}$  thick (chloride) crystal (---) and  $\approx 300 \mu\text{m}$  thick triflate crystal. Directly above are 4.2 K (uncorrected) excitation spectra of the (triflate) crystal detected at 547 nm (—) and 640 nm (---). Also shown is the 5 K luminescence spectrum, excited at 458 nm, of the pure triflate crystal. The right-hand side shows the "pure" d-d luminescence, calculated by subtracting 10- and 200- $\mu\text{s}$  time-resolved spectra in DMF at 4 K with the least-squares fit Gaussian curve.

well with the value of  $40 \text{ cm}^{-1}$  seen in analogous MLCT transitions in [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.<sup>27,28,30</sup>

Excitation spectra are dependent upon the energy of detection. With red (640 nm) detection, a broad feature is seen in the 490–520-nm region that is absent when green (547 nm) detection is used. This low-energy feature is seen most clearly in the excitation spectrum of the single-crystal triflate salt (Figure 4). An absorption feature in this region can also be seen with a moderately thick crystal.

The MCD spectra (Figure 4), taken in dilute and very concentrated Nafion films, show a low-energy feature with electronic properties clearly different from that of the lowest MLCT transitions.

## Discussion

Our results clearly identify a weak transition below the MLCT state. Subtraction of appropriately scaled, time-resolved luminescence spectra allow us to extract the "pure" red emission (Figure 4). This spectrum is well fitted by a Gaussian curve, centered at  $14700 \text{ cm}^{-1}$  (680 nm) with a width of  $3400 \text{ cm}^{-1}$ . Comparing this to absorption and excitation spectra it seems reasonable to estimate the origin of the band to be around  $19000 \text{ cm}^{-1}$  (530 nm),  $\approx 3000 \text{ cm}^{-1}$  below the MLCT origin.

A three-level system such as scheme a (Figure 1) will, in general, give only dual-exponential behavior<sup>32</sup> irrespective of the values of  $k_{10}$ ,  $k_{20}$ ,  $k_{21}$ , and  $k_{12}$ . Our data do not fit such a model at all, and it becomes necessary to introduce an additional excited state (scheme b).

The presence of an additional level, which is strongly coupled (nonradiatively) to the ground state via the low-efficiency red emitting state is entirely consistent with our data. In particular, the reduction in lifetimes, *but with constant initial intensity*, observed in the 20–80 K range reflects a fall in quantum efficiency and not the population of a more strongly radiative electronic state. The presence of close-lying MLCT states with different electronic properties is well established in this type of complex.<sup>33</sup>

The magnitude of the deuteration shift of the MLCT band determined in this work is inconsistent with the previous analysis.<sup>9</sup>

That the d-d and MLCT processes have different relaxation shifts (Figure 2), pointed out for the first time in this work, was not taken into account. An adequate analysis of the relative intensities of the red and green emissions in viscous solutions clearly requires more detailed consideration of the extent of thermal equilibrium and the dielectric relaxation process.

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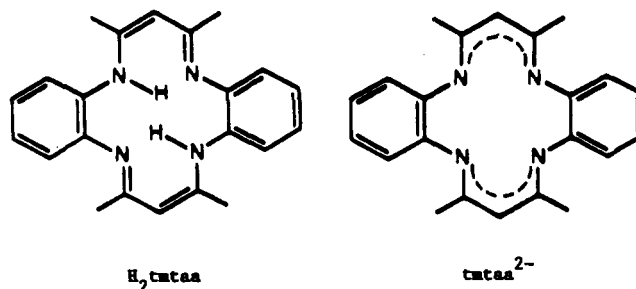
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## A New Look at the Vanadium(III) and Vanadium(IV) Complexes of the Dibenzotetramethyltetraaza[14]annulene Ligand. Synthesis and Molecular Structures of CpV(tmtaa) and (O)V(tmtaa)

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We are currently exploring the chemistry of the title macrocyclic ligand (see 1), which can form both mononuclear and binuclear complexes. In the binuclear ones, the potential steric repulsion



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of this macrocyclic ligand surprisingly does not seem to affect their stability. In our studies, we have succeeded in synthesizing many interesting mononuclear complexes such as Cr(tmtaa)Cl<sup>1</sup> and Ru(tmtaa)(PPh<sub>2</sub>Me)<sub>2</sub>,<sup>2</sup> among others, and a few fascinating unbridged metal-metal-bonded dimers of the type M<sub>2</sub>(tmtaa)<sub>2</sub>, where M = Cr,<sup>3</sup> Mo,<sup>3</sup> and Rh.<sup>4</sup> The ability of tmtaa to stabilize these and other compounds can be attributed to its two important features: (1) the ability to displace the metal out of the N<sub>4</sub> plane and (2) its flexibility to adjust the saddle shape conformation according to the size of a metal and the axial ligand.

We have decided to use this macrocyclic ligand in reactions with some vanadium starting materials because of the rather unexplored low-valent chemistry of this early transition metal. We were faced however with a 2-fold challenge, in this area of chemistry: (1) the choice and the availability of the appropriate V(II) starting materials are limited, and (2) there is a strong tendency of the low-valent vanadium materials to abstract oxygen from other molecules in the reaction solution. We report here the experimental and theoretical results on two previously communicated but never crystallographically characterized V(III) and V(IV) compounds, which were obtained by interacting the va-

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**Table I.** Crystal Data for CpV(tmtaa) and (O)V(tmtaa)-OC<sub>4</sub>H<sub>9</sub>

formula	VN <sub>4</sub> C <sub>27</sub> H <sub>27</sub>	VO <sub>2</sub> N <sub>4</sub> C <sub>26</sub> H <sub>30</sub>
fw	458.49	481.50
space group	<i>Pbca</i>	<i>P1</i>
<i>a</i> , Å	17.795 (8)	12.250 (2)
<i>b</i> , Å	28.336 (9)	12.473 (2)
<i>c</i> , Å	8.699 (2)	8.686 (9)
$\alpha$ , deg	90.00 (0)	102.25 (1)
$\beta$ , deg	90.00 (0)	102.83 (1)
$\gamma$ , deg	90.00 (0)	67.53 (1)
<i>V</i> , Å <sup>3</sup>	4386 (2)	1183.8 (4)
<i>Z</i>	8	2
<i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.388	1.351
cryst size, mm	0.75 × 0.20 × 0.45	0.70 × 0.50 × 0.15
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	4.584	4.334
data colln instrument	P3	P3
radiation monochromated in incident beam:		
$\lambda$ (Mo K $\alpha$ ), Å		
orientation retns: no.; range (2 $\theta$ ), deg	25; 20.0 < 2 $\theta$ < 30.0	25; 20.0 < 2 $\theta$ < 30.0
temp, °C	23 ± 1	23 ± 1
scan method	$\omega$	2 $\theta$ - $\omega$
data colln range of 2 $\theta$ , deg	4 ≤ 2 $\theta$ ≤ 50	4 ≤ 2 $\theta$ ≤ 50
no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$	3444; 1952	4112; 3621
no. of params refined	345	386
transm factors: max; min	1.00; 0.91	1.00; 0.92
<i>R</i> <sup>a</sup>	0.0481	0.0502
<i>R</i> <sub>w</sub> <sup>b</sup>	0.0620	0.0766
quality-of-fit indicator <sup>c</sup>	1.240	1.798
largest shift/esd, final cycle	0.07	0.47
largest peak, e/Å <sup>3</sup>	0.57	0.54

<sup>a</sup> $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = 1/\sigma^2(|F_o|)$ . <sup>c</sup>Quality-of-fit =  $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parms}})]^{1/2}$ .

niadium(II) and -(III) materials, Cp<sub>2</sub>V (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) and VCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>, with the title ligand.

### Experimental Section

**Starting Materials.** All manipulations were carried out under an argon atmosphere, using standard vacuum-line and Schlenk techniques. The solvents were freshly distilled under nitrogen from the appropriate drying agents. Bis(cyclopentadienyl)vanadium(II) and *n*-butyllithium were obtained from Aldrich. Starting materials, H<sub>2</sub>tmtaa<sup>5</sup> and VCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>,<sup>6</sup> were prepared according to the literature.

**Preparation of CpV(tmtaa).** A solution of Cp<sub>2</sub>V (0.050 g, 0.28 mmol) and H<sub>2</sub>tmtaa (0.10 g, 0.28 mmol) in 15 mL of toluene was refluxed for 24 h. The final emerald green solution was cooled to room temperature, filtered through Celite, and left at -10 °C overnight. A green solid crystallized out of the solution. The solvent was partially evaporated under reduced pressure, and the solid was recovered by filtration. Yield: 0.050 g (~40%). Purification was accomplished by dissolution in toluene, followed by careful layering with *n*-hexane. UV/vis (toluene, nm): 668 (broad), 375, 348. A solution of the compound is extremely air-sensitive.

**Preparation of (O)V(tmtaa).** VCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub> (0.06 g, 0.20 mmol) was suspended in 8 mL of THF at -10 °C. A solution of 0.20 mmol of the lithium tmtaa salt in 10 mL of THF at -10 °C was added via cannula (the salt was prepared by reacting 0.070 g of H<sub>2</sub>tmtaa (0.20 mmol) with 0.30 mL of 1.6 M *n*BuLi in 10 mL of THF). The reaction solution was stirred at room temperature for 2 h and then refluxed gently for 12 h. The final orange-brown solution was cooled to room temperature, filtered through Celite, and layered with hexanes. In 2–3 days, blocklike green crystals (~0.010 g) had formed on the walls of the Schlenk tube. IR (Nujol, cm<sup>-1</sup>): 2965 (s), 2874 (s), 1397 (s), 1378 (s), 974 (s), 751 (s), 680 (m).

**X-ray Crystallography.** Single crystals of CpV(tmtaa) and (O)V(tmtaa) were grown by layering toluene and THF solutions, respectively, with hexanes. Both compounds are air-stable in the crystalline state.

**CpV(tmtaa).** A blocklike green crystal was selected from the product and was shown to be of good quality by polarized-light microscopy. The crystal was coated with epoxy cement and mounted on the goniometer

**Table II.** Selected Bond Distances (Å) and Bond Angles (deg) for CpV(tmtaa)<sup>a</sup>

Distances			
V–N(1)	2.114 (4)	V–N(4)	2.099 (4)
V–N(2)	2.104 (4)	V–Cp(1)	2.022 (1)
V–N(3)	2.098 (4)		
Angles			
N(1)–V–N(2)	84.8 (2)	N(2)–V–N(4)	132.5 (2)
N(1)–V–N(3)	129.1 (2)	N(2)–V–Cp(1)	115.3 (1)
N(1)–V–N(4)	74.7 (2)	N(3)–V–N(4)	85.6 (2)
N(1)–V–Cp(1)	115.8 (1)	N(3)–V–Cp(1)	115.0 (1)
N(2)–V–N(3)	74.9 (2)	N(4)–V–Cp(1)	112.1 (1)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits. <sup>b</sup>Cp(1) refers to the centroid of the cyclopentadienyl ring.

**Table III.** Selected Bond Distances (Å) and Bond Angles (deg) for (O)V(tmtaa)<sup>a</sup>

Distances			
V–O(1)	1.601 (2)	V–N(3)	2.026 (3)
V–N(1)	2.017 (2)	V–N(4)	2.026 (2)
V–N(2)	2.023 (2)		
Angles			
O(1)–V–N(1)	108.7 (1)	N(1)–V–N(3)	141.26 (9)
O(1)–V–N(2)	109.78 (9)	N(1)–V–N(4)	78.65 (8)
O(1)–V–N(3)	110.0 (1)	N(2)–V–N(3)	78.7 (1)
O(1)–V–N(4)	109.81 (9)	N(2)–V–N(4)	140.41 (8)
N(1)–V–N(2)	88.14 (9)	N(3)–V–N(4)	88.65 (9)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

head of a P3 diffractometer. Indexing revealed an orthorhombic cell, and Laue class *mmm* was confirmed by an oscillation photograph. (The dimensions obtained are identical with the ones for CpTi(tmtaa) reported by Goedken.<sup>7</sup>) The data were collected to 50° in 2 $\theta$  and corrected for Lorentz and polarization effects<sup>8</sup> and for absorption.<sup>9</sup> The empirical absorption corrections made were based on  $\psi$  scans of six reflections with the Eulerian  $\chi$  angle near 90°. Inspection of the systematic absences led to the inference that the correct space group would be *Pbca* (No. 61). The entire molecule was located via the first Patterson map. The subsequent development of the structure was done by an alternating sequence of least-squares refinements and difference Fourier maps. All non-hydrogen atoms were treated anisotropically, with the exception of the cyclopentadiene ring, which was found to have all the carbon atoms disordered over two positions. The ring was modeled successfully by allowing the occupancy to refine to 0.6/0.4 for each pair of carbon atoms. All hydrogen atoms were located in difference Fourier maps and refined with an overall isotropic temperature factor. Restraints were put on two C–H interatomic distances during the last cycle of the least-squares refinement. The final cycle of full-matrix refinement gave  $R = 0.0481$  and  $R_w = 0.0620$ . Crystallographic and procedural data are presented in Table I, and the selected bond distances and angles in Table II. The atomic positional parameters are presented in Table IV.

**(O)V(tmtaa).** Indexing revealed a triclinic cell, and the axial dimensions were confirmed with oscillation photographs. All procedures for collection and reduction of data were as just described. The entire molecule was located via the first Patterson map. The subsequent development of the structure was done by an alternating sequence of least-squares refinements and difference Fourier maps. All non-hydrogen atoms, including those of the solvent molecule of THF, were treated anisotropically. All hydrogen atoms were located in difference Fourier maps and refined freely. The final cycle of full-matrix refinement gave  $R = 0.0502$  and  $R_w = 0.0766$ . Crystallographic and procedural data are presented in Table I, and the selected bond distances and angles in Table III. The atomic positional parameters are presented in Table V.

### Results and Discussion

**Syntheses.** Cp<sub>2</sub>V appeared to be an excellent starting material for reactions with the dianionic macrocyclic tmtaa, due to the

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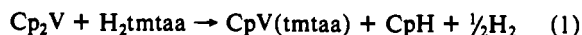
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**Table IV.** Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for CpV(tmtaa)<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>
V	0.7466 (5)	0.13997 (3)	0.0773 (1)	2.09 (2)
C(31)	0.8175 (7)	0.2100 (4)	0.112 (1)	2.6 (2)*
C(32)	0.7465 (7)	0.2233 (3)	0.044 (1)	2.5 (2)*
C(33)	0.7397 (6)	0.2020 (4)	-0.105 (1)	2.6 (2)*
C(34)	0.8547 (6)	0.1801 (4)	-0.005 (2)	2.6 (2)*
C(35)	0.8057 (8)	0.1762 (4)	-0.135 (1)	2.6 (2)*
C(41)	0.842 (1)	0.1725 (5)	-0.083 (3)	2.7 (3)*
C(42)	0.8501 (9)	0.1924 (6)	0.061 (2)	2.7 (3)*
C(43)	0.787 (1)	0.2179 (5)	0.093 (2)	2.7 (3)*
C(44)	0.7376 (9)	0.2158 (6)	-0.027 (2)	2.7 (3)*
C(45)	0.770 (1)	0.1868 (6)	-0.140 (2)	2.7 (3)*
N(1)	0.6455 (2)	0.1162 (2)	-0.0240 (5)	2.39 (9)
N(2)	0.7911 (2)	0.0754 (1)	0.0001 (5)	2.2 (1)
N(3)	0.8053 (2)	0.1124 (2)	0.2664 (5)	2.32 (9)
N(4)	0.6621 (2)	0.1566 (2)	0.2364 (5)	2.4 (1)
C(1)	0.6308 (3)	0.0768 (2)	-0.0993 (6)	2.4 (1)
C(2)	0.6859 (3)	0.0433 (2)	-0.1355 (7)	2.7 (1)
C(3)	0.7608 (3)	0.0410 (2)	-0.0861 (6)	2.3 (1)
C(4)	0.8643 (3)	0.0721 (2)	0.0614 (6)	2.3 (1)
C(5)	0.9282 (3)	0.0564 (2)	-0.0139 (8)	3.0 (1)
C(6)	0.9975 (3)	0.0581 (2)	0.0560 (8)	3.3 (1)
C(7)	1.0051 (3)	0.0768 (2)	0.2013 (7)	3.3 (1)
C(8)	0.9426 (3)	0.0955 (2)	0.2754 (8)	3.0 (1)
C(9)	0.8718 (3)	0.0920 (2)	0.2099 (6)	2.2 (1)
C(10)	0.7880 (3)	0.1128 (2)	0.4164 (7)	2.7 (1)
C(11)	0.7223 (4)	0.1342 (2)	0.4713 (7)	3.3 (1)
C(12)	0.6628 (3)	0.1529 (2)	0.3891 (7)	2.8 (1)
C(13)	0.5986 (3)	0.1728 (2)	0.1539 (7)	2.6 (1)
C(14)	0.5521 (3)	0.2101 (2)	0.1916 (8)	3.4 (1)
C(15)	0.4941 (4)	0.2230 (2)	0.0947 (9)	4.1 (2)
C(16)	0.4838 (3)	0.2005 (2)	-0.0444 (8)	3.4 (1)
C(17)	0.5320 (3)	0.1651 (2)	-0.0871 (8)	3.2 (1)
C(18)	0.5893 (3)	0.1500 (2)	0.0096 (7)	2.4 (1)
C(19)	0.5517 (3)	0.0609 (3)	-0.1400 (8)	4.2 (2)
C(20)	0.8019 (4)	-0.0032 (2)	-0.1275 (9)	3.5 (2)
C(21)	0.8346 (4)	0.0868 (3)	0.5345 (8)	3.8 (2)
C(22)	0.5969 (4)	0.1678 (2)	0.4887 (8)	4.0 (2)
H(1)	0.668 (3)	0.019 (2)	-0.197 (7)	4.0 (3)*
H(2)	0.923 (3)	0.049 (2)	-0.119 (7)	4.0 (3)*
H(3)	1.040 (3)	0.045 (2)	-0.002 (7)	4.0 (3)*
H(4)	1.059 (3)	0.077 (2)	0.246 (7)	4.0 (3)*
H(5)	0.944 (3)	0.113 (2)	0.367 (7)	4.0 (3)*
H(6)	0.716 (3)	0.136 (2)	0.569 (7)	4.0 (3)*
H(7)	0.565 (3)	0.228 (2)	0.282 (7)	4.0 (3)*
H(8)	0.464 (3)	0.248 (2)	0.118 (7)	4.0 (3)*
H(9)	0.441 (3)	0.207 (2)	-0.104 (7)	4.0 (3)*
H(10)	0.528 (3)	0.152 (2)	-0.185 (8)	4.0 (3)*
H(11)	0.516 (2)	0.070 (1)	-0.062 (4)	4.0 (3)*
H(12)	0.541 (3)	0.078 (1)	-0.234 (3)	4.0 (3)*
H(13)	0.546 (3)	0.0273 (6)	-0.161 (5)	4.0 (3)*
H(14)	0.769 (3)	-0.025 (2)	-0.157 (7)	4.0 (3)*
H(15)	0.823 (3)	-0.017 (2)	-0.041 (7)	4.0 (3)*
H(16)	0.840 (3)	0.000 (2)	-0.209 (7)	4.0 (3)*
H(17)	0.875 (3)	0.105 (2)	0.582 (7)	4.0 (3)*
H(18)	0.864 (3)	0.060 (2)	0.484 (7)	4.0 (3)*
H(19)	0.807 (3)	0.079 (2)	0.612 (7)	4.0 (3)*
H(20)	0.600 (3)	0.150 (1)	0.583 (4)	4.0 (3)*
H(21)	0.548 (2)	0.163 (1)	0.443 (5)	4.0 (3)*
H(22)	0.603 (3)	0.2011 (7)	0.511 (5)	4.0 (3)*

<sup>a</sup>Starred values indicate atoms were refined isotropically. The hydrogen atoms were refined with a common thermal parameter. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

convenient +2 oxidation state of the metal and the relatively labile Cp ligands. The reaction between Cp<sub>2</sub>V and H<sub>2</sub>tmtaa under rigorously anaerobic conditions in vigorously refluxing toluene for 24 h affords the mononuclear V(III) compound CpV(tmtaa) (see eq 1). This compound has been previously mentioned in a

**Table V.** Positional Parameters and Equivalent Isotropic Thermal Parameters and Their Estimated Standard Deviations for (O)V(tmtaa)<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>
V	0.21096 (3)	0.63801 (3)	0.07812 (5)	2.468 (9)
O(1)	0.1148 (2)	0.7138 (2)	0.1939 (2)	3.63 (4)
N(1)	0.1810 (2)	0.4878 (2)	-0.0179 (3)	2.69 (5)
N(2)	0.1524 (2)	0.6898 (2)	-0.1404 (3)	2.94 (5)
N(3)	0.3206 (2)	0.7248 (2)	-0.0760 (3)	3.05 (5)
N(4)	0.3509 (2)	0.5198 (2)	0.1967 (3)	2.68 (5)
C(1)	0.1484 (2)	0.4493 (2)	-0.1701 (3)	3.05 (6)
C(2)	0.1231 (2)	0.5169 (3)	-0.2911 (3)	3.38 (6)
C(3)	0.1253 (2)	0.6288 (3)	-0.2795 (3)	3.19 (6)
C(4)	0.1562 (2)	0.8039 (2)	-0.1209 (3)	3.33 (6)
C(5)	0.0707 (3)	0.8975 (3)	-0.1930 (4)	4.46 (8)
C(6)	0.0781 (4)	1.0088 (3)	-0.1525 (5)	5.52 (9)
C(7)	0.1681 (4)	1.0268 (3)	-0.0383 (5)	5.47 (9)
C(8)	0.2525 (3)	0.9359 (3)	0.0393 (4)	4.68 (8)
C(9)	0.2491 (2)	0.8234 (2)	-0.0015 (3)	3.44 (6)
C(10)	0.4386 (2)	0.6945 (2)	0.1279 (3)	3.42 (6)
C(11)	0.5044 (2)	0.5953 (3)	0.2012 (4)	3.43 (6)
C(12)	0.4653 (2)	0.5117 (2)	0.2317 (3)	3.03 (6)
C(13)	0.3069 (2)	0.4373 (2)	0.2262 (3)	2.88 (6)
C(14)	0.3396 (3)	0.3832 (3)	0.3617 (4)	3.64 (7)
C(15)	0.2822 (3)	0.3115 (3)	0.3804 (4)	4.22 (7)
C(16)	0.1880 (3)	0.2971 (3)	0.2670 (4)	4.21 (7)
C(17)	0.1513 (2)	0.3529 (2)	0.1328 (4)	3.66 (6)
C(18)	0.2115 (2)	0.4210 (2)	0.1090 (3)	2.79 (5)
C(19)	0.1447 (3)	0.3269 (3)	-0.2206 (4)	4.14 (7)
C(20)	0.1040 (3)	0.6745 (3)	-0.4351 (4)	4.52 (8)
C(21)	0.5101 (3)	0.7614 (3)	0.0975 (5)	4.92 (8)
C(22)	0.5620 (3)	0.4058 (3)	0.2971 (4)	3.99 (7)
O(2)	0.7643 (6)	0.9518 (4)	0.5108 (8)	15.4 (2)
C(23)	0.7857 (6)	1.0580 (5)	0.5411 (8)	10.2 (2)
C(24)	0.6894 (7)	1.1355 (6)	0.460 (1)	12.7 (3)
C(25)	0.6042 (7)	1.0866 (7)	0.392 (2)	19.4 (4)
C(26)	0.6541 (6)	0.9618 (6)	0.412 (1)	14.2 (3)
H(1)	0.100 (3)	0.483 (3)	-0.396 (4)	1.9 (7)*
H(2)	0.021 (3)	0.890 (2)	-0.248 (4)	1.4 (6)*
H(3)	0.009 (3)	1.074 (3)	-0.200 (5)	3.4 (9)*
H(4)	0.171 (3)	1.100 (3)	-0.014 (4)	2.9 (8)*
H(5)	0.305 (2)	0.944 (2)	0.109 (3)	0.9 (6)*
H(6)	0.583 (2)	0.587 (2)	0.232 (3)	1.2 (6)*
H(7)	0.404 (3)	0.391 (3)	0.435 (4)	1.8 (7)*
H(8)	0.306 (3)	0.279 (3)	0.480 (4)	2.3 (7)*
H(9)	0.139 (3)	0.253 (3)	0.284 (5)	3.4 (9)*
H(10)	0.094 (2)	0.343 (2)	0.059 (3)	0.9 (6)*
H(11)	0.158 (3)	0.301 (3)	-0.319 (4)	2.5 (8)*
H(12)	0.76 (3)	0.318 (3)	-0.202 (5)	3.5 (9)*
H(13)	0.212 (3)	0.266 (3)	-0.158 (4)	2.7 (8)*
H(14)	0.154 (3)	0.716 (3)	-0.422 (4)	3.2 (8)*
H(15)	0.035 (3)	0.720 (3)	-0.467 (5)	3.4 (9)*
H(16)	0.137 (4)	0.608 (4)	-0.505 (6)	7 (1)*
H(17)	0.466 (4)	0.816 (3)	0.033 (5)	5 (1)*
H(18)	0.604 (5)	0.696 (5)	0.059 (7)	8 (2)*
H(19)	0.518 (3)	0.811 (3)	0.188 (5)	4 (1)*
H(20)	0.569 (4)	0.416 (4)	0.418 (6)	5 (1)*
H(21)	0.536 (3)	0.333 (3)	0.245 (5)	4 (1)*
H(22)	0.631 (3)	0.403 (3)	0.268 (5)	3.2 (9)*

<sup>a</sup>Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

brief communication by Floriani,<sup>10</sup> where it was prepared by the reaction between V(tmtaa)Cl and NaCp. The compound has not been characterized by X-ray crystallography or any other means, until now. We were not too surprised to find that the bulkiness of the macrocyclic tmtaa does not favor the elimination of the cyclopentadienyl groups, but instead it favors the observed mononuclear complex. This has been seen before in this group, in the case of a bulky *N,N'*-di-*p*-tolylformamidinato ligand.<sup>11</sup>

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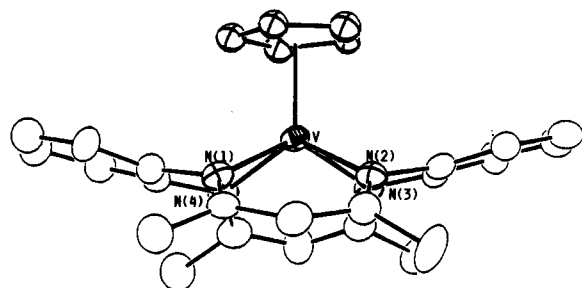
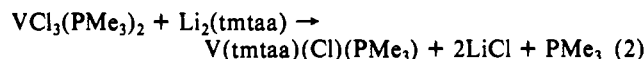


Figure 1. ORTEP diagram of the CpV(tmtaa) molecule.

Our goal in using  $\text{VCl}_3(\text{PMe}_3)_2$  as a V(III) starting material was to synthesize a mixed-ligand, 6-coordinate vanadium complex (see eq 2). However, the use of an oxygenated solvent such as



tetrahydrofuran (THF), which is the most suitable solvent for the lithiated tmtaa ligand, precluded that goal and resulted in a monomer of a different nature, the V(IV) species (O)V(tmtaa). This oxovanadium complex of tmtaa had been reported almost a decade ago,<sup>12</sup> yet its geometry has not been unequivocally established until now. A strong band at  $974 \text{ cm}^{-1}$  in the IR spectrum clearly indicates the existence of a strong  $\text{V}=\text{O}$  bond, so prevalent in the chemistry of vanadium(IV).

**Molecular Structures.** The molecular structures of CpV(tmtaa) is shown in Figure 1. It is quite similar to that previously reported<sup>10</sup> for the titanium analogue. It can be roughly regarded as a 7-coordinate 4-to-3 type of complex, with Cp occupying three positions and the tmtaa ligand four. The vanadium–nitrogen bond lengths in CpV(tmtaa) average  $2.104(4) \text{ \AA}$  and are in the same range as other V(III)–N single bonds.<sup>13</sup> The V–C(Cp) distances average  $2.36(1) \text{ \AA}$  with the V–ring (center) distance of  $2.022(1) \text{ \AA}$ . The latter can be compared with the similar distance of  $1.97(7) \text{ \AA}$  found in the CpV(CO)<sub>4</sub> complex. Even though the two compounds have the vanadium atoms in different oxidation states, the final effect on the distance of the metal to the Cp ring (center) is the same. In the case of the CpV(CO)<sub>4</sub> complex, the four CO ligands compete with the Cp ligand for the  $\pi$ -back-donation of the metal's electron density. Thus, the V–Cp(center) bond distance in the CpV(CO)<sub>4</sub> complex becomes similar to the one of the title compound. Lastly, the V(III) ion is displaced  $0.875(1) \text{ \AA}$  out of the N<sub>4</sub> plane of the saddle-shaped tmtaa.

This CpV(tmtaa) molecule containing vanadium in the +3 oxidation state has two unpaired electrons, which can be understood on the basis of some molecular orbital calculations, as shown in Figure 2.

The SCF- $X\alpha$ -SW calculations were done for CpV(tmtaa) and for the V(tmtaa) fragment having the same structure as it has in the CpV(tmtaa) molecule. The results are presented in the MO diagram. The bonding within the V(tmtaa) fragment is similar to that in other metal complexes having tmtaa as ligand.<sup>3</sup> As can be seen, the  $\pi$  orbitals of Cp interact strongly with the metal orbitals of appropriate symmetries to form Cp–V bonds. The single occupation in the 29a' and 30a' orbitals is in accord with the observation<sup>10</sup> that there are two unpaired electrons in CpV(tmtaa). Details of the calculations can be found in the supplementary material.

The true 5-coordinate (O)V(tmtaa) complex displays a square-pyramidal geometry analogous to that of a porphyrin complex, (O)V(OEP), reported in 1976.<sup>14</sup> The V(IV) atom is displaced out of the N<sub>4</sub> plane by  $0.678(1) \text{ \AA}$  toward the axially bound oxygen atom (see Figure 3). The average V–N distance of  $2.023(2) \text{ \AA}$  is very close to that of  $2.053(9) \text{ \AA}$  found in [N,N'-ethylenebis(acetylacetonate)]oxovanadium, VO-

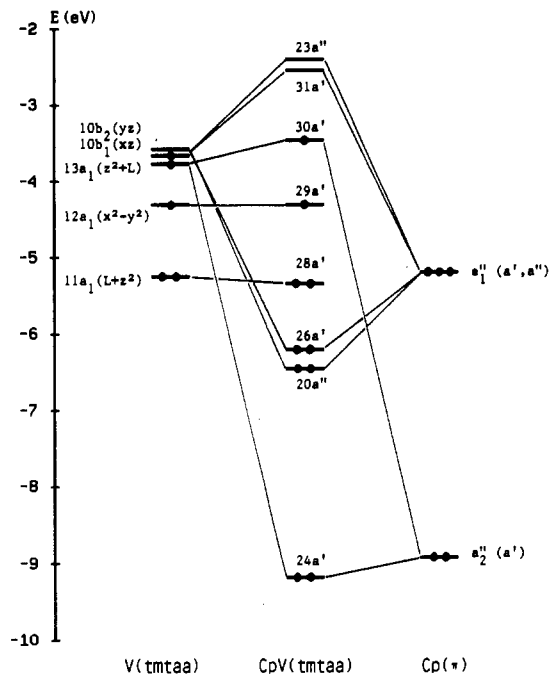


Figure 2. Molecular orbital diagram for CpV(tmtaa). For clarity, only selected MOs with their main characters are shown. The levels of V-(tmtaa) have been shifted downward by  $0.28 \text{ eV}$  to match the  $12a_1$  orbital in CpV(tmtaa), and the  $\pi$  levels of Cp have been shifted downward by  $1.5 \text{ eV}$ .

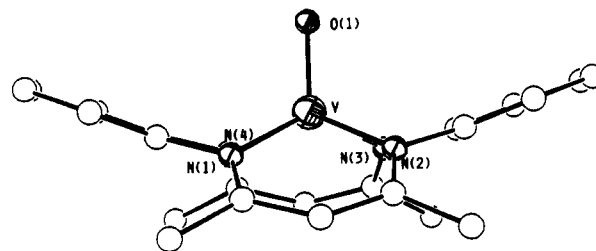


Figure 3. ORTEP diagram of the (O)V(tmtaa) molecule.

( $\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_2$ ).<sup>15</sup> The  $\text{V}=\text{O}$  bond length of  $1.601(2) \text{ \AA}$  is also typical of oxo-vanadyl complexes. The above parameters compare well with these of the porphyrinato complex, where the average V–N distance and the  $\text{V}=\text{O}$  bond length are  $2.102(6)$  and  $1.620(2) \text{ \AA}$ , respectively. The displacement of the metal out of the N<sub>4</sub> plane in this V(IV) complex is considerably smaller (ca.  $0.2 \text{ \AA}$ ) than that in the V(III) complex discussed earlier. Two factors contribute to such a difference. First, one of the features of tmtaa, as mentioned in the introduction, is its adaptability to the size of the coordinated metal ion. As we go from CpV(tmtaa) to (O)V(tmtaa), there is a contraction of the metal ionic radius because of the increased oxidation state; the ligands' saddle shape becomes less pronounced. Second, large displacement of the vanadium atom in the CpV(tmtaa) molecule prevents any steric repulsions between the macrocycle of tmtaa and the minicycle of the  $\eta^5\text{-C}_5\text{H}_5$  ring.

This report provides a new look at the two interesting vanadium–tmtaa compounds previously communicated several years ago. It establishes with certainty the coordination geometries about the vanadium centers. It also points out that the negative charges of tmtaa confer stability on the V(III) and V(IV) oxidation states. The MO treatment also throws light on the possible stabilities and electronic structures of other CpM(tmtaa) molecules. Further work to investigate these and other inferences from the present work is currently underway.

**Acknowledgment.** We thank the National Science Foundation for support.

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**Supplementary Material Available:** A textual presentation of the details of the SCF-X $\alpha$ -SW calculations, ORTEP diagrams, and tables of bond distances, bond angles, and general displacement parameters (14 pages); listings of structure factors (31 pages). Ordering information is given on any current masthead page.

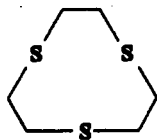
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### Benzene Trisulfide, the Strongest Field Thioether Ligand: Its Nickel(II) Complex<sup>1</sup>

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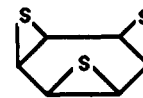
During the past few years there has been a period of intense activity in the complexation of transition-metal ions with mesocyclic (small ring) and macrocyclic thioether ligands, and several excellent review articles dealing with the coordination chemistry of these ligand systems have recently appeared.<sup>3-6</sup> Most of the work on crown thioether ligands has centered on the nine-membered-ring trithioether 1,4,7-trithiacyclononane (9S3). This important ligand has currently been complexed to over 25 transition-metal ions and p-block metal ions with the majority of this research appearing during the past 5 years.



structure of 9S3

A critical aspect relating to the unique complexation properties of 9S3 is its preferred [333] conformation in which all of the sulfur atoms are endodentate.<sup>7-9</sup> Because of this conformation, the ligand does not have to undergo any conformational changes in order to coordinate to a metal ion in a bis octahedral fashion. The importance of the preferred conformation of thioether ligands with regards to their coordination characteristics has been highlighted by other workers and by us.<sup>5,10-12</sup> We have been interested in

how structural and conformational alterations of thioether ligands affect their complexation properties, and we have recently reported a complexation study of several ten-membered trithioethers as well as the synthesis of eleven-membered and twelve-membered ring trithioether ligands.<sup>10,11</sup> In order to continue to explore the relationship between organic structure and coordination characteristics, we wish to report the preparation of the bis nickel(II) complex of the highly rigid crown trithioether benzene trisulfide, BTS (*cis*-2,5,8-trithiatetracyclo[6.1.0.0.4<sup>6</sup>.0<sup>7,9</sup>]nonane).



structure of BTS

Note that benzene trisulfide, like 9S3, can function as a tridentate ligand. The sulfur atoms in the BTS molecule are rigidly locked in a endodentate conformation. Benzene trisulfide is an example of a heterohomoaromatic system.<sup>13</sup> These interesting ligand systems (including the analogous amine and crown ether heterohomoaromatic systems) were first prepared by Prinzbach and co-workers during the 1970s.<sup>14,15</sup> Wieghardt and Chaudhuri have noted that because of difficulties in the synthesis of these ligands, the coordination behavior of these ligands has not been examined.<sup>16</sup> To our knowledge only two other transition-metal complexes containing heterohomoaromatic ligand systems have appeared in the literature.<sup>17,18</sup>

We selected nickel(II) as the first transition-metal ion to be complexed with BTS for several reasons. The d-d absorption spectra of octahedral Ni(II) complexes are readily interpretable in terms of ligand field parameters, and a plethora of electronic spectroscopic data exists for nickel(II) complexes. The syntheses and spectral data for several hexakis(thioether)nickel(II) complexes have already appeared in the literature, and structural information currently exists on five of these complexes.<sup>5,7,10,19,20</sup> Finally, Ni(II) has historically been important in examining the properties of complexes involving macrocyclic and mesocyclic thioether ligands in the pioneering works of Black and McLean with 18S6 (1,4,7,10,13,16-hexathiacyclooctadecane), Busch and Rosen with 12S3 (1,5,9-trithiacyclododecane), and Setzer and co-workers with 9S3.<sup>7,21-23</sup>

### Experimental Section

**Materials.** All materials were used as received except nitromethane, which was dried by standard methods.<sup>24</sup>

**Measurements.** Chemical analyses were performed by Galbraith Laboratories, Knoxville, TN. Solution spectra were measured by using

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