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Spectroscopy, Molecular Structure, Electrochemistry, and Reactivity of Vanadium(IV,V) Imido Complexes of 5,7,12,14-Tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine

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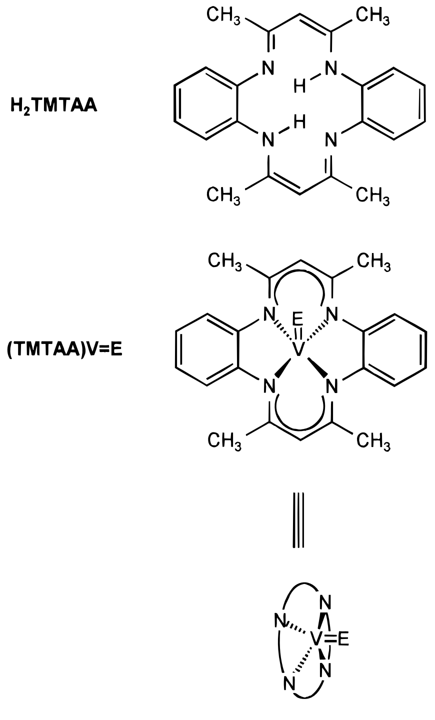
The synthesis of new imidovanadium(IV) complexes containing the tetradendate dianionic 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato moiety ($TMTAA^{2-}$) is reported. Stirring of either $[(HTMTAA)VCl_2]Cl$ or $(TMTAA)VCl_2$ in solution with NH_2R was used to prepare very moisture-sensitive, paramagnetic compounds of the type (TMTAA)V═NR (**2**, R = CH_3, *t*-C_4H_9, C_6H_5, C_6F_5 and $N(CH_3)_2$) in high yields. Complexes **2** were characterized by EPR, IR, UV/vis, and mass spectroscopic techniques. CV measurements indicate a reversible 1e-oxidation to the corresponding diamagnetic vanadium(V) cations $[(TMTAA)V{=}NR]^+$ (**4**). Complexes **4** were prepared in preparative scale by oxidation of **2** with 1 equiv of $[(C_5H_5)_2Fe]SbF_6$ (**3**) and characterized by heteronuclear NMR, IR, and UV/vis spectroscopic methods. While the V═NR group in complexes **2** does not react with $Cr(CO)_5$ or $Pt(P(C_6H_5)_3)_2$ under complexation, cycloaddition of **2a** with hexfluoracetone has been observed. This reactivity has been compared to (TMTAA)V═O (5), which is demonstrated to undergo addition and cycloaddition reactions with hexafluoracetone, hexfluorpropene oxide, sulfur trioxide and triflic anhydride (complexes **8a**−**d**). Complex **4b** (R = *t*-C_4H_9) has been crystallographically characterized and the results discussed with those of **5** and $[(TMTAA)V{=}O]SbF_6$ (**6**).

Introduction

Vanadium plays an important role in various biological processes,[2] which has invoked increased interest in the synthesis and study of vanadium +IV and +V coordination compounds over the last decade.[3] The majority of these investigations has been centered on systems containing the $VO^{2+/3+}$ moieties, while far less information is available on non-oxo vanadium centers.[4] Non-oxo vanadium centers have been identified for example in amavadin, a V^{IV} complex of unknown function isolated from mushrooms of the genus *Amanita*,[5] and for the co-factor in vanadium nitrogenase.[6] Due to the presence of additional interactions with nitrogen ligands beside the often present chelating ligands in the above mentioned biological systems, the preparation and redox chemistry of macrocyclic imidovanadium(IV,V) complexes are of interest due to the possible access to new model systems. Compounds containing a $V{=}NR^{2+/3+}$ group and a macrocyclic ligand are very rare: Buchler et al. reported the synthesis and characterization of a series of alkyl and arylimidovanadium(IV) 5,10,15,20-tetra(*p*-tolyl)porphyrinates[7] and Sundermeyer et al. described recently (*tert*-butylimido)dichloro(tris(3,5-dimethyl-1-pyrazolyl)hydridoborato) vanadium(V).[8]

Scheme 1



The synthesis, the molecular structure, and the redox chemistry of the new (Imido)vanadium(IV,V) dibenzotetraaza[14]-annulene complexes is described herein. The chemistry of the V═NR moiety is also briefly compared to those of the V═O group with respect to cycloadditions. The general structure of the macrocyclic ligand H_2TMTAA and of the complexes (TMTAA)V═E (E = O, NR) is shown in Scheme 1.

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(2) (a) Chasteen, N. D. *Struct. Bonding* **1983**, *53*, 105. (b) Rehder, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 148. (c) Rehder, D. *Biometals* **1992**, *5*, 3.

(3) Boas, L. V., Pessoa, J. C. Vanadium. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, p 453.

(4) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York 1988. (b) Mohan, M.; Holmes, S. M.; Butcher, R. J.; Jasinski, J. P.; Carrano, C. J. *Inorg. Chem.* **1992**, *31*, 2029. (c) Hughes, D. L.; Kleinkes, U.; Leigh, G. J.; Maiwald, M.; Sanders, J. R.; Sudbrake, C.; Weisner, J. *J. Chem. Soc., Dalton Trans.* **1993**, 3093. (d) Reynolds, J. G.; Jones, E. L.; Huffman, J. C.; Christou, G. *Polyhedron* **1993**, *12*, 407. (e) Vergopoulos, V.; Jantzen, S.; Julien, N.; Rose, E.; Rehder, D. Z. *Naturforsch., B* **1994**, *49*, 1127. (f) Vergopoulos, V.; Jantzen, S.; Rodewald, D.; Rehder, D. *J. Chem. Soc., Chem. Commun.* **1995**, 377.

(5) Meisch, H.-U.; Schmitt, J. A.; Reinle, W. Z. *Naturforsch., C* **1978**, *33*, 1; *Naturwissenschaften* **1979**, *66*, 620.

(6) (a) Burgess, B. K. *Chem. Rev.* **1990**, *90*, 1377. (b) Eady, R. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1994**, 2739.

(7) Buchler, J. W.; Pfeifer, S. *Z. Naturforsch., B* **1985**, *40*, 1362.

(8) Sundermeyer, J.; Putterlik, J.; Foth, M.; Field, J. S.; Ramesar, N. *Chem. Ber.* **1994**, *127*, 1201.

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Experimental Section

Materials. The ligand H_2TMTAA,[9] the complexes [(HTMTAA)-VCl_2]Cl (**1a**), (TMTAA)VCl_2 (**1b**),[10] (TMTAA)V=O (**5**),[11] and $[(C_5H_5)_2Fe]SbF_6$ (**3**)[12] were obtained as reported in the literature. The remaining required chemicals were of reagent grade (Aldrich, Merck) and dried prior to use. All syntheses were carried out in a dry/inert atmosphere of purified argon by employing standard Schlenk glassware. Due to the extreme moisture sensitivity of both educts and products, all glassware was heated under high vacuum for at least 1 h to remove last traces of moisture. The solvents were dried over CaH_2 and degassed under reflux.

Physical Measurements. Infared spectra were recorded on Perkin Elmer 580 and Bruker IFS66 spectrometers as KBr pellets, and electronic spectra were obtained with a Omega UV spectrometer. EPR spectra were obtained using a Bruker ECS 106 spectrometer with DPPH ($g = 2.0037$) as an external standard. NMR spectra were recorded on Bruker AM 400 (^1H, $^{13}C\{^1H\}$, vs internal TMS) and Bruker WM 300/AM 100 spectrometer (^{51}V; vs external 10% $VOCl_3$ in C_6D_6). Mass spectra were obtained on Finigan MAT 311 A (EI mode, 70 eV) or MAT 95 instruments (FAB mode, dimethoxybenzyl alcohol as matrix). Variable-temperature susceptibility measurements between 120 and 300 K were carried out by the Faraday method using a combination of Sartorius 4411 microbalance, Bruker B-M4 research magnet, and B-VT 1000 temperature controller. The electrochemical measurements were performed at room temperature under O_2-free conditions using a three-electrode configuration: glassy-carbon working electrode, Pt-wire counter electrode, and SCE reference electrode. The supporting electrolyte was 0.1 M $[N(C_4H_9\text{-}n)_4]ClO_4$ in CH_2Cl_2, and all solutions were ca. 1 mM in complex. A range from −2.6 to +1.0 V was measured with a scan rate of 1000 mV/s.

Synthesis of Complexes. (TMTAA)V=NCH_3 (2a) and (TMTAA)-V=N(t-C_4H_9) (2b). A stirred suspension of [(HTMTAA)VCl_2]Cl (**1a**; 1.93 g, 3.85 mmol) in 1,2-$Cl_2C_2H_4$ (30 mL) was slowly treated with either a stream of anhydrous NH_2CH_3 (excess) or by dropwise addition of $NH_2C_4H_9$-*t* (2.10 g, 28.6 mmol, excess). During the addition, the suspension dissolved and the color changed rapidly to deep green. Stirring of the mixtures was continued for 12 h, after which all volatiles were removed under vacuum. The residues were extracted with boiling toluene (3 × 25 mL). The combined extracts were concentrated to ca. 15 mL, layered with an equal volume of pentane, and kept in a freezer at −20 °C for 2 d. The obtained deep green solids were collected by filtration, washed with pentane and dried in vacuo; yields: 1.36 g, 84% (**2a**) and 1.39 g, 78% (**2b**). Anal. Calcd (found) for $C_{23}H_{25}N_5V$ (**2a**): C, 65.40 (65.67); H, 5.92 (6.17); N, 16.59 (16.39); MS {EI} calcd (found), *m/e*: 422 (422) $[M]^+$. Anal. Calcd (found) for $C_{26}H_{31}N_5V$ (**2b**): C, 67.24 (67.40); H, 6.68 (6.69); N, 15.09 (14.89); MS {EI} calcd (found), *m/e*: 464 (464) $[M]^+$.

(TMTAA)V=NR (R = C_6H_5 (2c), C_6F_5 (2d), $N(CH_3)_2$ (2e)). To a solution of in-situ prepared (TMTAA)VCl_2 (**1b**; ca. 3 mmol) in 1,2-$Cl_2C_2H_4$ (30 mL) was added NH_2R (9 mmol) as solution in CH_2Cl_2 (10 mL) over 15 min. The color changed rapidly to a deep green, and stirring was continued for 4 h. The reaction solution was then evaporated to dryness in vacuo and the residue extracted with boiling toluene. Workup as above gave deep green crystalline solids; yields: 1.23 g, 85% (**2c**), 1.15 g, 67% (**2d**), and 0.95 g, 70% (**2e**). Anal. Calcd (found) for $C_{28}H_{27}N_5V$ (**2c**): C, 69.42 (68.62); H, 5.58 (5.96); N, 14.46 (14.10); MS {EI} calcd (found), *m/e*: 484 (484) $[M]^+$. Anal. Calcd (found) for $C_{28}H_{22}F_5N_5V$ (**2d**): C, 58.54 (58.74); H, 3.83 (4.05); N, 12.20 (12.42); MS {EI} calcd (found), *m/e*: 574 (574) $[M]^+$. Anal. Calcd (found) for $C_{24}H_{28}N_6V$ (**2e**): C, 63.86 (63.64); H, 6.21 (6.15); N, 18.63 (18.50). MS {EI} calcd (found), *m/e*: 423 (423) $[M - N_2]^+$.

Alternatively, the complexes may also be prepared by reaction of [(HTMTAA)VCl_2]Cl (**1a**) with an excess of NH_2R but identical workup afforded less pure and crystalline products.

[(TMTAA)V=NR]SbF_6 (4a−e). A mixture of **2** (ca. 0.2−0.35 g, 0.54 mmol) and $[(C_5H_5)_2Fe]SbF_6$ (**3**; 0.22 g, 0.52 mmol) was stirred in CH_2Cl_2 (25 mL) for 2 h. The solution was filtered and evaporated to dryness. The formed ferrocene was removed by repeated extraction with pentane. The remaining solid was recrystallized from CH_2Cl_2/pentane at −25 °C for 12 h (**4b** from CH_3CN/ether). The deep green solids were washed with pentane and ether and dried in vacuo; yields: 0.31 g, 91% (**4a**), 0.32 g, 87% (**4b**), 0.33 g, 89% (**4c**), 0.35 g, 82% (**4d**), and 0.30 g, 85% (**4e**). Anal. Calcd (found) for $C_{23}H_{25}F_6N_5SbV$ (**4a**): C, 41.96 (41.35); H, 3.80 (3.89); N, 10.64 (10.20). Anal. Calcd (found) for $C_{26}H_{31}F_6N_5SbV \cdot CH_3CN$ (**4b**): C, 45.34 (45.88); H, 4.59 (5.07); N, 11.34 (11.24). Calcd (found) for $C_{28}H_{27}F_6N_5SbV$ (**4c**): C, 46.68 (46.08); H, 3.75 (4.11); N, 9.72 (9.40). Anal. Calcd (found) for $C_{28}H_{22}F_{11}N_5SbV$ (**4d**): C, 41.49 (41.09); H, 2.72 (2.75); N, 8.64 (8.40). Anal. Calcd (found) for $C_{24}H_{28}F_6N_6SbV$ (**4e**): C, 41.94 (41.76); H, 4.08 (3.91); N, 12.23 (11.90).

Reactions of 2a with Organometallic Agents. To a solution of **2a** (ca. 0.21 g, 0.5 mmol) in THF (10 mL) was added either (c-C_8H_{14})-$Cr(CO)_5$ (0.15 g, 0.5 mmol) or $(C_2H_4)Pt(P(C_6H_5)_3)_2$ (0.37 g, 0.5 mmol) as solid. The mixture was stirred after addition for 4 h without apparent color change. Workup consisted of solvent evaporation and repeated washings of the residue with pentane/ether 1/1. IR and EPR spectra of the deep green residue indicated only the presence of unreacted **2a**.

Reaction of 2a with Hexafluoracetone. Formation of (TMTAA)V-($C_4H_3F_6NO$) (7). A CH_2Cl_2 solution (20 mL) of **2a** (0.41 g, ca. 1 mmol) was stirred under an atmosphere of $(CF_3)_2CO$. Within minutes, the reaction solution turned dark green and stirring was continued for 4 h. Concentration to 5 mL and addition of pentane (10 mL) caused precipitation of a dark green solid. The product was filtered off, washed with ether and pentane, and dried in vacuo for 1 h at ambient temperature; yield: 0.56 g, 95%. Anal. Calcd (found) for $C_{26}H_{25}F_6N_5$-OV (**7**): C, 53.07 (53.47); H, 4.25 (4.40); N, 11.91 (12.1). MS {EI} calcd (found), *m/e*: 428 (427) $[M - C_3F_5NO]^+$, 147 $[C_3F_5O]^+$.

Reaction of 5 with Hexafluoracetone and Hexafluorpropene Oxide. Formation of (TMTAA)V($C_3F_6O_2$) (8a and 8b). A solution of **5** (1.0 g, 2.45 mmol) in CH_2Cl_2 (30 mL) was stirred under an atmosphere of either hexafluoracetone or hexafluorpropene oxide for 1 h. The solution turned from green (**5**) to dark green (**8**) within minutes, and eventually a dark solid began to separate out. Precipitation was completed by addition of ether (30 mL) and further stirring for 2 h. The dark green solids were filtered off and washed with ether; yields: 1.34 g, 95% (**8a**) and 1.28 g, 91% (**8b**). Anal. Calcd (found) for $C_{25}H_{22}F_6N_4O_2V$ (**8a/b**): C, 52.18 (**8a** 52.74, **8a** 52.45); H, 3.83 (**8a** 3.96, **8b** 4.07); N, 9.74 (**8a** 10.15, **8b** 10.21). MS {EI} calcd (found), *m/e*: 409 (409) $[M - C_3F_6O]^+$ for both **8a** and **8b**.

Reaction of 5 with SO_3 and Triflic Anhydride. Formation of (TMTAA)V(O_2SO_2) (8c) and (TMTAA)V(OSO_2CF_3)$_2$ (8d). A solution of either freshly sublimed SO_3 (0.240 g, 4.0 mmol) or $[CF_3SO_2]_2O$ (1.13 g, 4.0 mmol) in CH_2Cl_2 (20 mL) was slowly added to a solution of **5** (1.64 g, 4.0 mmol) in CH_2Cl_2 (40 mL) at 0 °C over 0.5 h. For each solution, a rapid color change from green (**5**) to brown-green (**8**) was noted and the products started to precipitate. After 2 h of stirring at ambient temperature, ether (30 mL) was added to each solution to complete the precipitation. The brown microcrystalline solids were isolated by filtration and washed repeatedly with CH_2Cl_2 and ether to remove traces of **5**; yields: 1.78 g, 91% (**8c**) and 2.71 g, 97% (**8d**). Anal. Calcd (found) for $C_{22}H_{22}N_4O_4SV$ (**8c**): C, 54.00 (54.13); H, 4.50 (4.62); N, 11.45 (11.34). Calcd (found) for $C_{24}H_{22}F_6N_4O_6S_2V$ (**8d**): C, 41.68 (40.95), H, 3.18 (3.12); N 8.11 (7.96). MS {EI} calcd (found), *m/e*: 409 (409) $[M]^+$ of **5** due to decomposition. FAB MS measurements were attempted, but no $[M]^+$ peak has been observed for either **8c** or **8d**.

X-ray Structure Determination. Single crystals of [(TMTAA)V=N-(t-C_4H_9)]SbF_6 (**4b**) were grown by layering a dilute solution of **4b** in CH_3CN with an equal amount of ether at 0 °C over 3 d. X-ray data were collected on a Siemens R3m/V diffractometer with graphite monochromated Mo Kα radiation using a $\omega-2\theta$ scan mode. Crystallographic details are given in Table 1. The unit cell dimensions were obtained by least-squares refinement of 20 automatically centered

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(9) (a) Abbreviation: TMTAA = dianion of 5,7,12,14-tetramethyldibenzo-[*b,i*][1,4,8,11]tetraazacyclotetradecine. (b) Synthesis: Goedken, V. L.; Weiss, M. C. *Inorg. Synth.* **1980**, *20*, 115.

(10) (a) Goedken, V. L.; Ladd, J. A. J. Chem. Soc., *Chem. Commun.* **1981**, 910. (b) Yang, C.-H.; Ladd, J. A.; Goedken, V. L. *J. Coord. Chem.* **1988**, *18*, 317. (c) Schumann, H. *Polyhedron*, in press.

(11) (a) Compare 10a and 10b. (b) Lee, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 145. (c) Cotton, F. A.; Czuchajowska, J.; Feng, X. *Inorg. Chem.* **1991**, *30*, 349.

(12) Schumann, H. *J. Organomet. Chem.* **1986**, *304*, 341.

Table 1. Crystallographic Data for $[(TMTAA)V{=}NC_4H_9\text{-}t]SbF_6$ (**4b**)

formula	$C_{28}H_{34}F_6N_6SbV$	V, pm	$1590.4(8) \times 10^6$
fw	741.3	Z	2
cryst size, mm	0.25 × 0.2 × 0.2	D_{calc}, g cm^{-1}	1.548
cryst syst	monoclinic	λ(MoKα), pm	71.073
space group	$P2/c$	μ, mm^{-1}	1.200
a, pm	1011.8(3)	temp, K	294
b, pm	834.4(2)	F(000)	744
c, pm	1890.7(6)	R	0.063
β, deg	94.87(2)	R_w[a]	0.062

[a] $R_w = (\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)^{1/2}$ for $F > 4.0\ \sigma(F)$.

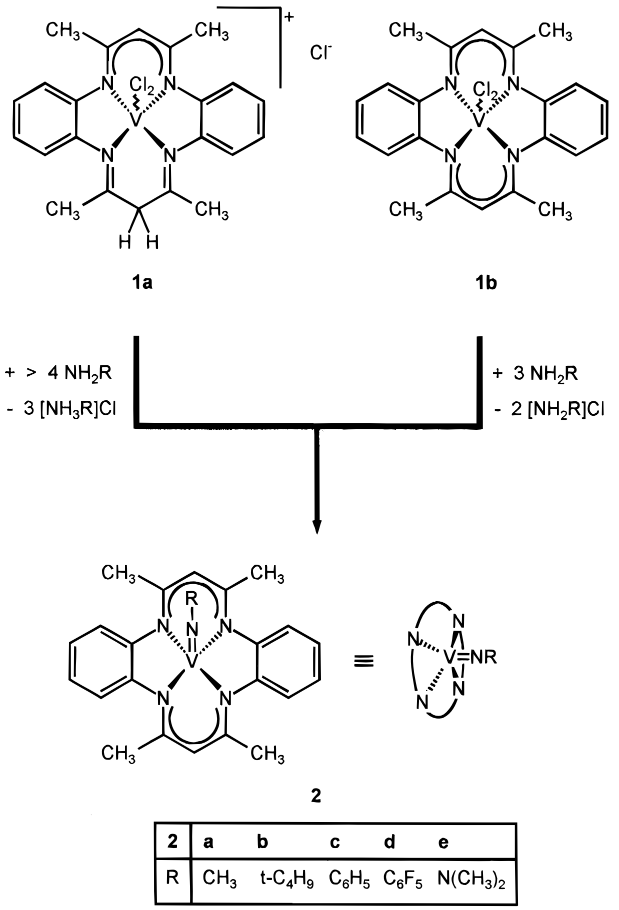
reflections. During data collection three standard reflections monitored after every 97 reflections indicated no decay, and data were corrected for absorption by empirical methods. A total of 3693 reflections were collected in the range $2\theta = 4$ to 52°, with $h = -12$ to 0, $k = 0$ to 10 and $l = \pm 23$, of which 3156 independent reflections with $F > 4\ \sigma(F)$ were used for structure determination. The structure was solved by direct methods and refined by full-matrix-least-squares techniques using the program SHELXTL PLUS (VMS).[13] Due to disorder, the atoms C(13), C(14), and C(15) have been refined with an occupancy factor of 0.5. The final least-squares refinement converged to $R = 0.063$ and $R_w = 0.062$. The numbers of parameters refined was 184, and the maximum fluctuation in the final ΔF map was in the range $+0.60 \times 10^{-6}$ to -0.69×10^{-6} e/pm^3.

Results and Discussion

Synthesis and Characterization. The macrocyclic vanadium(IV) dichloride $[(HTMTAA)VCl_2]Cl$ (**1a**)[10] reacts with an excess of NH_2R ($R = CH_3$, t-C_4H_9) or $(TMTAA)VCl_2$ (**1b**)[10c] with three equivalents NH_2R ($R = C_6H_5$, C_6F_5, $N(CH_3)_2$) under formation of the V(IV) organoimido complexes, **2** (Scheme 2). Within seconds after the addition of the amine, the violet suspension of the starting complex **1a** dissolves and the solution changes into a deep green color of the imido complex, **2**. For **1b**, a very fast color change from dark brown to deep green is observed. Independently of the vanadium educts used for the preparation, work-up of these reaction solutions affords deep green, very moisture-sensitive solids in good yields.

Characterization of the isolated complexes **2** is given in Table 2 with analytical data stated in the Experimental Section. These compounds are EPR-active ($\mu_{eff} = 1.77$ to 1.83 μ_B at 294 K) and exhibit an isotropic eight-line spectrum in CH_2Cl_2 solution with g_{iso} values around 1.978 and $A_{iso}(^{51}V) = 87-90$ G at 294 K. Measurements in the solid state between 120 and 300 K show only a single unresolved broad signal around $g = 2.0$. The EPR spectra are attributable to a single $S = {}^1/_2$ species in which the unpaired electron in a d_{xy} orbital is coupled to the nuclear spin of the vanadium nucleus ($I = {}^7/_2$).[14] CV measurements for complexes **2** (Table 3) indicate a reversible oxidation in the range 0.30−0.34 V and an irreversible reduction at ca. −1.95 V vs SCE. On the basis of the observed range for the oxidation waves, this process is attributed to the 1e-oxidation of the coordinated vanadium center from V^{IV} (**2**) to V^V (**4**). Very similar values have been found for $(TMTAA)V{=}O$ (**5**)[15] and related substituted $(TMTAA)V{=}O$ systems.[16] The irreversible reduction waves around −2 V vs SCE have been attributed to reduction processes within the ligand framework followed by polymerization upon the electrode as investigated in some details recently on substituted (TMTAA)Ni complexes.[17] While experimental verification of the reduction process was unsuccessfully attempted by addition of either $(C_5H_5)_2Co$ or Na/Hg to THF solutions of either **2a** or **2b** as describted recently for $(TMTAA)V{=}O$ (**5**),[15] the preparative oxidation of complexes **2** with $[(C_5H_5)_2Fe]SbF_6$ (**3**)[12] has been successful with the isolation of the (imido)vanadium(V) tetramethyldibenzotetraaza[14]annulene cations **4** (Scheme 3).

Scheme 2



Stirring an equal molar amount of **2** and **3** in CH_2Cl_2 for about 2 h results in the formation of orange-green solutions. Workup gives complete separation of the green, airstable but also very moisture-sensitive crystalline complexes **4** as SbF_6^- salts from the by-product ferrocene in good yield. Magnetic measurements of **4** confirm their diamagnetic nature in agreement with a V- (V^{IV} to V^V)[15] rather then a ligand-centered oxidation as observed often with Ni as coordinated metal center with tetraza[14]annulene-type ligands.[18] For the complexes **4**, the ^1H and ^{13}C NMR spectra indicate the presence of an unchanged dianionic 5,7,12,14-tetramethyldibenzo[14]annulene core together with the expected signals due to the NR group. More informative are the obtained ^{51}V NMR data (reference external $VOCl_3$): The obtained shift range is ca. 70 ppm with the extreme values observed at $\delta = -554$ ppm ($H_{1/2} = 265$ Hz; **4a**) and $\delta = -487$ ppm ($H_{1/2} = 310$ Hz; **4c**). These values are well within the known ^{51}V NMR range for V^V compounds[19a] and the upfield position of the ^{51}V NMR signal of the imido vanadium (V) complexes **4** from the position the corresponding

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(13) G. M. Sheldrick, program package SHELXTL-PLUS, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1989.

(14) Weiss, A.; Witte, H. *Magnetochemie*, Verlag Chemie: Weinheim, Germany, 1973.

(15) H. Schumann, *Z. Naturforsch., B* **1995**, *50*, 1494.

(16) Davies, D. L.; Grist, A. J. *Inorg. Chim. Acta* **1994**, *216*, 217.

(17) (a) Keita, B.; Lu, Y. W.; Nadjo, L. *J. Electroanal. Chem.* **1994**, *367*, 285. (b) Deronzier, A.; Marques, M.-J. *J. Electroanal. Chem.* **1994**, *370*, 151.

(18) (a) Dabrowiak, J. C.; Fisher, D. P.; McElroy, F. C.; Macero, D. J. *Inorg. Chem.* **1979**, *18*, 2304. (b) Wuu, Y.-M.; Peng, S.-M.; Chang, H. J. *Inorg. Nucl. Chem.* **1980**, *42*, 839. (c) Hunziker, M.; Loeliger, H.; Rihs, G.; Hilti, B. *Helv. Chim. Acta* **1981**, *64*, 2544. (d) Stach, J.; Kirmse, R.; Jäger, E.-G. *Z. Chem.* **1984**, **24**, 416.

Table 2. Spectroscopic Data for (TMTAA)V=NR (**2**) and [(TMTAA)V=NR]SbF_6 (**4**)

complex	magn suscept[a] μ_{eff}, μ_B	EPR[b] g ($A(^{51}V)$, G)	NMR[c] δ, ppm	UV[d] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	IR[e] ν, cm^{-1}
2a	1.77	1.993 (br), 1.978 (89.0)		269 (8500), 308 (8000), 377 (23000), 420 sh (8700)	751, 979, 1033, 1196, 1279, 1399, 1435, 1462, 1539, 1575
2b	1.81	1.991 (br), 1.975 (87.7)		265 (22000), 307 (12500), 376 (33500), 396 sh (21000)	747, 842, 980, 1032, 1195, 1280, 1399, 1461, 1539
2c	1.81	1.984 (br), 1.978 (89.1)		268 (15000), 308 (13000), 376 (36000), 416 (7700)	751, 840, 977, 1033, 1197, 1279, 1397, 1462, 1539, 1575
2d	1.76	1.987 (br), 1.978 (88.9)		268 (8700), 309 (8500), 374 (24500), 418 sh (5200)	752, 840, 975, 1036, 1197, 1279, 1399, 1462, 1539, 2493, 2677, 2939
2e	1.83	1.992 (br), 1.978 (88.4)		268 (13500), 307 (12500), 376 (35000), 420 (7000)	752, 975, 1033, 1197, 1280, 1397, 1462, 1539
4a			^1H: 7.33, 7.24, 7.18 (m, 8 H, C_6H_4), 6.33 (s, 2 H, CH), 3.23 (s, 3 H, NCH_3), 2.34 (s, 12 H, CH_3) ^{51}V: −554 ($H_{1/2}$ = 264 Hz)	268 (19000), 308 (14000), 379 (33000), 439 sh (5200), 690 (2000)	660, 757, 940, 992, 1198, 1277, 1311, 1398, 1433, 1462, 1537, 1565
4b			^1H: 7.78, 7.71 (m, 4 H each, C_6H_4), 6.28 (s, 2 H, CH), 3.76 (s, 9 H, t-C_4H_9), 2.75 (s, 12 H, CH_3) ^{13}C: 133.5 (CN), 129.97 (C_6H_4 C-3), 123.42 (C_6H_4 C-2), 121.00 (CH), 109.50 (C_6H_4 C-1), 44.31 ($C(CH_3)_3$), 29.2 ($C(CH_3)_3$), 23.49 (CH_3) ^{51}V: −573 ($H_{1/2}$ = 250 Hz)	265 (21800), 308 (12200), 380 (32000), 437 sh (5000), 660 (1500)	659, 766, 1029, 1224, 1311, 1347, 1398, 1433, 1461, 1533
4c			^1H: 7.35, 7.13 (m, 8 H, C_6H_4), 6.67 (br m, 5 H, C_6H_5), 6.34 (s, 2 H, CH), 1.98 (s, 12 H, CH_3) ^{51}V: −487 ($H_{1/2}$ = 310 Hz)	269 (21000), 317 (19000), 378 (40000), 440 sh (6700), 695 (4000)	659, 760, 992, 1207, 1269, 1326, 1398, 1430, 1461, 1527, 1566
4d			^1H: 7.7 to 7.5 (m, 8 H, C_6H_4), 6.20 (s, 2 H, CH), 2.48 (s, 12 H, CH_3) ^{51}V: −513 ($H_{1/2}$ = 970 Hz)	271 (13000), 322 (12000), 380 (20000), 444 (4500), 687 (2300)	558, 660, 766, 846, 991, 1036, 1171, 1259, 1327, 1375, 1398, 1432, 1525, 1567, 2492, 2678, 2941
4e			^1H: 7.26−7.20 (m, 8 H, C_6H_4), 6.34 (s, 2 H, CH), 3.47 (s, 6 H, $N(CH_3)_2$), 2.38 (s, 12 H, CH_3) ^{51}V: −536 ($H_{1/2}$ = 900 Hz)	270 (15000), 317 (13000), 378 (26500), 439 (5000), 685 (2700)	660, 763, 987, 1270, 1327, 1392, 1430, 1461, 1529, 1567

[a] Measured at 294 K for powdered solids. [b] Signals observed as powdered solid (first value) and in CH_2Cl_2 solution at 294 K (second value). [c] In CD_2Cl_2; $^1H/^{13}C$ NMR signals vs internal TMS; ^{51}V NMR signals in CD_3CN vs external 10% $VOCl_3$ in C_6D_6. [d] In CH_2Cl_2. [e] In KBr.

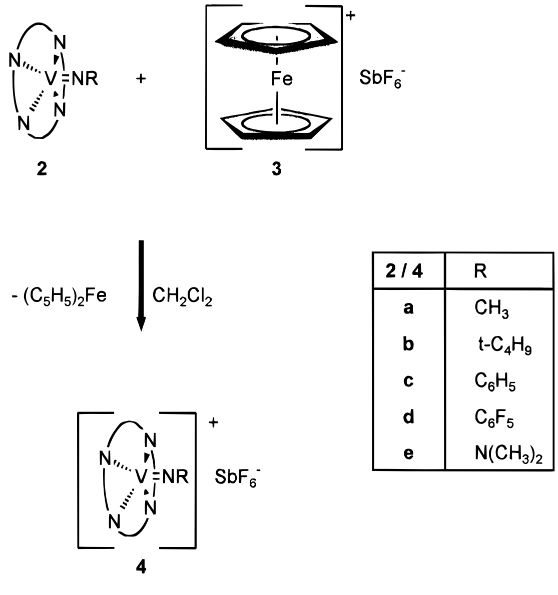
Table 3. Electrochemical Data for the Oxidation of Complexes **2** to the Cations **4**[a]

complex	E_{ox}, V	$\Delta E_{p1/2}$, mV	i_{pa}/i_{pc}
2a	0.30	108	0.98
2b	0.30	195	0.95
2c	0.34	141	0.88
2d	0.31	75	1.00
2e	0.31	97	1.00
5	0.35	90	0.96

[a] In CH_2Cl_2; irreversible reduction waves were observed for all complexes in the range −1.94 to −1.99 V.

oxo vanadium (V) complex **6** (δ = −368 ppm, $H_{1/2}$ = 90 Hz)[15] has also been noted in a recent comparison of oxo and iminoazavanadatranes.[19b] A rough correlation between the solid state ESR g values for the complexes **2** and the δ ^{51}V NMR shift of the complexes **4** has been found as to be expected for structurally similar systems differentiating only by the oxidation state of the vanadium atom.[20]

Scheme 3



2 / 4	R
a	CH_3
b	t-C_4H_9
c	C_6H_5
d	C_6F_5
e	$N(CH_3)_2$

The electronic absorption spectra of complexes **2** and **4** are characteristic of tetramethyldibenzo[14]annulene complexes with intense Soret-type bands around 270, 310 and 380 nm, which are due to $\pi \rightarrow \pi^*$ and charge transfer transitions.[21] Ligand field transitions may be assigned to absorptions at λ_{max} ca. 420 nm (**2**) or at ca. 440 nm ($^2B_2 \rightarrow {}^2A_1$) and ca. 660 to 690 ($^2B \rightarrow {}^2E$) nm (**4**). These assignments are in agreement with the reported data for (TMTAA)V=O (**5**, CH_2Cl_2; λ_{max} (ϵ) = 419

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(19) (a) Kidd, R. G.; Goodfellow, R. J. The Transition Metals. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978. (b) Plass, W.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 3762.

(20) (a) Kazanskii, L. P.; Spitsyn, V. I. *Dokl. Akad. Nauk. S.S.S.R.* **1975**, *223*, 381; *Dokl. Phys. Chem.* **1975**, *223*, 721. (b) Correlation between the ESR g values obtained for solid samples at 293 K and solution ^{51}V NMR shifts except for **2b**.

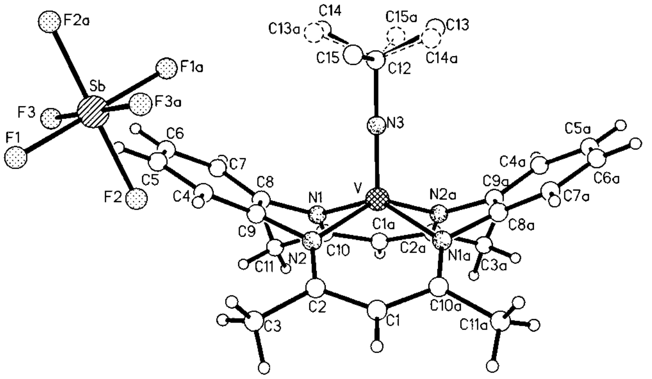

Figure 1. Molecular structure and atom-numbering scheme for [(TMTAA)V═N(*t*-C_4H_9)]SbF_6CH_3CN (**4b**). Thermal ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Distances (pm) and Angles (deg) for [(TMTAA)V═N(*t*-C_4H_9)]SbF_6 (**4b**)

V−N(1)	198.4(6)	V−N(2)	197.7(6)
V−N(3)	163.4(9)	N(1)−C(8)	141.4(10)
N(1)−C(10)	133.9(9)	N(2)−C(2)	134.8(9)
N(2)−C(9)	141.9(9)	N(3)−C(12)	142.1(14)
N(4)−C(16)	111.7(31)	C(1)−C(2)	139.7(10)
C(1)−C(l0A)	140.8(11)	C(2)−C(3)	149.4(11)
C(4)−C(5)	137.0(11)	C(4)−C(9)	139.5(11)
C(5)−C(6)	138.5(14)	C(6)−C(7)	137.3(12)
C(7)−C(8)	138.6(10)	C(8)−C(9)	140.8(10)
C(10)−C(11)	149.4(10)	Sb−F(1)	182.0(8)
Sb−F(2)	184.3(8)	Sb−F(3)	184.3(6)
N(1)−V−N(2)	81.3(2)	N(1)−V−N(3)	108.4(2)
N(2)−V−N(3)	108.3(2)	N(1)−V−N(lA)	143.2(4)
N(2)−V−N(lA)	87.3(2)	N(3)−V−N(lA)	108.4(2)
N(2)−V−N(2A)	143.3(4)	N(3)−V−N(2A)	108.3(2)
V−N(1)−C(8)	102.1(4)	V−N(1)−C(10)	131.7(5)
C(8)−N(1)−C(10)	126.2(6)	V−N(2)−C(2)	131.5(5)
V−N(2)−C(9)	102.2(4)	C(2)−N(2)−C(9)	126.3(6)
V−N(3)−C(12)	180.0(1)		

(12 200), 740 (840) nm).[15,21c,22] and [(TMTAA)V═O]SbF_6 (**6**, CH_2Cl_2; λ_{max} (ϵ) = 444 (6000), 692 (4200) nm).[15,22] The IR spectra for **2** and **4** show the expected strong bands generally observed for coordinated macrocyclic imine ligands, $\nu_{C=C,C=N}$ absorptions due to the macrocyclic skeleton in the range 1400−1470 cm^{-1} and $\nu_{C=N}$ at ca. 1530−1540 cm^{-1}. Despite the variation of the organic groups bonded to the imido nitrogen, no specific assignment for the ν_{VN} absorption is possible.[23] For all SbF_6 salts **4**, the anion shows the expected strong absorption at ca. 660 cm^{-1} [$\nu_3(F_{2u})$].[24]

Structure of 4b. Crystals of [(TMTAA)V═N(*t*-C_4H_9)]SbF_6, **4b**, suitable for single-crystal X-ray diffraction were grown by layering an acetonitrile solution of **4b** with ether. A perspective view of the (imido)vanadium(V) complex **4b** is shown in Figure 1. The bond distances and angles pertaining to the metal coordination spheres are given in Table 4. The macrocyclic framework in the [(TMTAA)V═N(*t*-C_4H_9)]$^+$ cation is saddle-shaped as observed and discussed for this type of ligand.[25] The vanadium atom is square-pyramidal coordinated with the four nitrogen atoms of the TMTAA macrocycle forming the basal plane and the t-butylimido group at the apical site. The vanadium (V) center is located 62 pm above the mean basal plane with an average V−N (macrocycle) distance of 198 pm. These data can be compared to the results obtained from the structure determinations of unsolvated (TMTAA)V═O (**5**, V^{IV}) and [(TMTAA)V═O]SbF_6 (**6**, V^{V}):[15] In these oxo vanadium (IV/V) complexes, the vanadium atoms are located 68(3)/60(2) pm above the basal N_4 plane with an average V−N (macrocycle) distance of 202.6/198.1 pm. These differences are attributed primarily to the size differences of their $V^{IV/V}$ centers. Within the experimental error, the observed values for the coordination of the TMTAA moiety to the vanadium center in both V^V complexes **4b** and **6** are identical. The V−N(5) distance within the imido group is 163.4(9) pm, which lies in the range of other (imido)vanadium(V) complexes with a coordination number of 5: V(NC_4H_9-*t*)(N(C_4H_9-*t*)Si$(CH_3)_2$N(C_4H_9-t)H)Cl_2 (V−N = 163.6(2) pm),[26a] $\{V(NCl)Cl_2\}_2(\mu\text{-}Cl)_2$ (V−N = 164.2(9) pm),[26b] and V(NP$(CH_3)_2C_6H_5$)(P$(CH_3)_2C_6H_5$)Cl_3 (V−N = 175.4(5) pm).[26c]

Chemical Reactivity of 2. All obtained complexes are extremely sensitive toward moisture hydrolyzing to [(TMTAA)V═O]$^{n+}$ (**5** or **6**) as confirmed by analytical and spectroscopic means. However, in solution or as solids under inert gas atmosphere, all complexes are stable for months.

To compare the reactivity of the imido vanadium (IV) complexes **2** with those of the related oxo vanadium (IV) compound **5**, several reactions have been performed (Scheme 4): Complexation of either the imido nitrogen atom by $(CO)_5Cr$ (starting complex (c-C_8H_{14})Cr$(CO)_5$)[27] or of the VN bond by $(C_6H_5)_3P)_2$Pt (starting complex (C_2H_4)Pt(P$(C_6H_5)_3)_2$)[28] has been attempted. As described in the Experimental Section, no reactions have been found and the starting complex **2a** could be recovered.

On the basis of recent studies on the reactivity of (TMTAA)Ti═O,[29] $[C_5H_5M(=O)_3]^-$ (M = Mo, W)[30] and (RNH)(RN═)$_2$V(OC_2H_5)$_2$ (R = *t*-Bu_3Si)[31] toward cycloaddition reactions, both complexes **2a** and **5** have been reacted with hexafluoracetone. Within a short time, dark green precipitates have been formed in both reaction solutions. On the basis of the obtained analytical and spectroscopic data (Experimental Section and Table 5), isolation affords the [2 + 2] cycloaddition products **7** and **8a** in high yield. While not unexpected for **2a** due to the higher reactivity of M═NR over most M═O bonds,[4a] the reactivity of **5** has been unexpected due to the high stability of the V═O bond.

Reaction of **5** with hexafluorpropene oxide, SO_3 and triflic anhydride also yields the related ring-opening and cycloaddition products **8b**, **8c**, and **8d** as brownish-green microcystalline solids. These compounds are stable at room temperature for months without apparent decomposition and may be handled for a short time under normal atmosphere. No reaction has been

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(21) (a) Sakata, K.; Hashimoto, M.; Tagami, N.; Murakami, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2262. (b) Snopok, B. A.; Lampeka, Y. D. *Opt. Spectrosk.* **1993**, *75*, 321; *Opt. Spectrosc. (Engl. Transl.)* **1993**, *75*, 188. (b) Sakata, K.; Yamaura, F.; Hashimoto, M. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 1043.

(22) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(23) Compare ref 4a, p 123. The in ref 19b discussed ν_{VN} range of ca. 1150−1280 cm^{-1} is dominated in both complexes **2** and **4** by IR absorption of the coordinated TMTAA ligand.

(24) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsfrequenzen I*; G. Thieme Verlag: Stuttgart, Germany, 1981.

(25) Review: Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 2553.

(26) (a) Preuss, F.; Fuchslochner, E.; Sheldrick, W. S. *Z. Naturforsch., B* **1985**, *40*, 1040. (b) Strähle, J.; Bärnighausen, H. *Z. Anorg. Allg. Chem.* **1968**, *359*, 325. (c) Hills, A.; Hughes, D. L.; Leigh, G. J.; Prieto-Alcon, R. *J. Chem. Soc., Dalton Trans.* **1993**, 3609.

(27) Grevels, F.-W.; Skibbe, V. *J. Chem. Soc., Chem. Commun.* **1984**, 681.

(28) (a) Nagel, U. *Chem. Ber.* **1982**, *115*, 1998. (b) Edelmann, F.; Spang, C.; Roesky, H. W.; Jones, P. G. *Z. Naturforsch., B* **1988**, *43*, 517.

(29) (a) Housmekerides, C. E.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 563. (b) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453.

(30) Rau, M. S.; Kretz, C. M.; Mercando, L. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1991**, *113*, 7420.

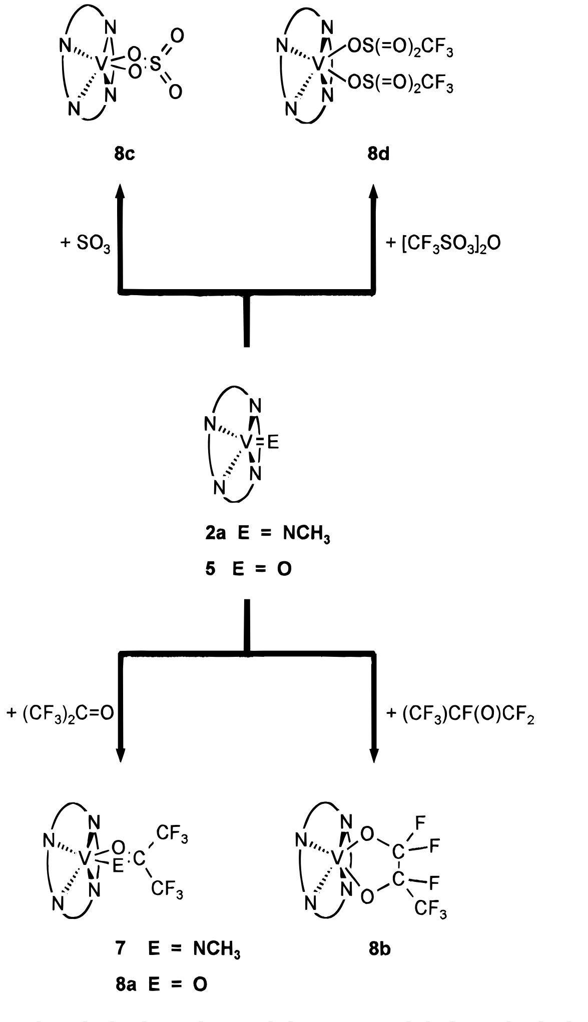
(31) de With, J.; Horton, A. D. *Organometallics* **1993**, *12*, 1493.

Table 5. Spectroscopic Characterization of the Cycloaddition Products **7** and **8**

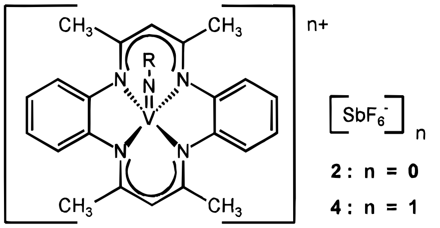
complex	magn suscept[a] μ_{eff}, μ_{B}	EPR[b] g (A(^{51}V), G)	UV[c] $\lambda_{\max}$, nm	IR[d] ν, cm^{-1}
7	1.80	1.999 (br), 1.977 (87.4)	(310, 405, 590)	720, 750, 806, 840, 942, 1033, 1077, 1123, 1161, 1241, 1279, 1312, 1398, 1435, 1462, 1541, 1577
8a	1.81	1.991 (br), 1.977 (87.2)	265, 308, 375 (320, 410, 560)	720, 750, 943, 1033, 1082, 1123, 1199, 1218, 1279, 1312, 1436, 1463, 1540, 1576, 1624
8b	1.75	2.012 (br), 1.974 (90.5)	270, 305, 377, 430 (350, 435)	482, 719, 751, 941, 1030, 1162, 1278, 1312, 1328, 1399, 1434, 1462, 1539, 1574
8c	1.78	1.995 (br)	(310, 420)	437, 579, 664, 768, 910, 924, 1031, 1154, 1179, 1276, 1338, 1429, 1456, 1530, 1575
8d	1.81	2.011 (br)	(320, 440)	517, 637, 690, 770, 1031, 1163, 1263, 1345, 1430, 1460, 1519, 1548, 1577

[a] Measured at 294 K for powdered solids. [b] Signals observed as powdered solid (first value) and in CH_2Cl_2 solution at 294 K (second value). [c] In CH_2Cl_2; data in parentheses obtained by reflection from solid samples. [d] In KBr, only strong bands stated.

Scheme 4



Scheme 5



observed with the less electrophilic agents phthalic anhydride, SO_2, and CS_2, thereby confirming the expected reduced reactivity of **5** in comparison to (TMTAA)Ti=O.[29] The imido vanadium complex **2a** also reacts with these agents but due to the extreme moisture sensitivity, workup of these reactions affords inseparable product mixtures.

Magnetic measurements and EPR spectra confirm for both **7** and **8a**−**d** the presence of a single V^{IV} center coordinated to a TMTAA unit as evident from IR and UV/vis data. Best evidence for the proposed structures of these reaction products comes from IR investigations: (a) the absence of the normally very strong $\nu_{\mathrm{V=O}}$ absorption at ca. 976 cm^{-1} for all complexes **7** and **8** together with (b) the presence of new strong absorptions in the ν_{CF} region of 1140−1210 cm^{1} for the hexafluoroacetone and hexfluoropropene oxide reaction products **7**, **8a**, and **8b**; (c) the observation of typical ν_{SO} bands at 579, 664, 713, 910, 924, 1179, and 1276 cm^{-1} for a η^2-[O_2]−SO_4 coordination in **8c** (for comparison, the ν_{SO} absorptions of (TMTAA)Ti(η^2-[O_2]−SO_4) have been assigned to 558, 671, 712, 912, 922, 1172, and 1276 cm^{-1});[29b,24] (d) absorptions assignable to the coordinated CF_3SO_3 groups of **8d** at 572, 1031 (ν_{SO}), and 1130−1230 cm^{-1} (ν_{CF}).[32] For the related (TMTAA)Ti complexes formed upon reaction of the coordinated Ti=O moiety with hexafluorpropene oxide, phthalic anhydride and SO_3, their structures have also been confirmed by single-crystal X-ray structure determination.[29] Several attempts to obtain crystals of complexes **7** and **8** suitable for single-crystal X-ray diffraction studies by different methods have been so far unsuccessful.

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Supporting Information Available: Tables of data collection and refinement details, atom positional and thermal parameters, and bond distances and angles, and a view of the unit cell content (10 pages). Ordering information is given on any current masthead page.

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(32) Nakamoto, K. *Infared and Raman Spectra of Inorganic and Coordination Compounds*, 4th. ed.; Wiley-Interscience: New York, 1986.