Synthesis, Structure, and Molecular Orbital Calculations of (Pyrazolato)vanadium(III) Complexes − Understanding η^2-Pyrazolato Ligand Coordination on d^2 Metal Centers

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Keywords: Vanadium / Pyrazolato ligands / Ab initio calculations / N ligands / Coordination modes

Treatment of trichlorotris(tetrahydrofuran)vanadium(III) with (3,5-di-*tert*-butylpyrazolato)potassium (1, 2, or 3 equiv.) in tetrahydrofuran afforded $V(tBu_2Pz)Cl_2(THF)_2$ (48%), $V(tBu_2Pz)_2Cl(THF)_2$ (67%), and $V(tBu_2Pz)_3(THF)$ (77%), respectively, as purple crystalline solids. The X-ray crystal structures of $V(tBu_2Pz)Cl_2(THF)_2$, $V(tBu_2Pz)_2Cl(THF)_2$, and $V(tBu_2Pz)_3(THF)$ reveal six- and seven-coordinate vanadium centers with η^2-pyrazolato ligands. Molecular orbital calculations were carried out to understand the electronic nature of pyrazolato coordination to transition metal centers containing d electrons. It is demonstrated that η^2-pyrazolato ligand coordination occurs through interaction of filled symmetric and antisymmetric combinations of the nitrogen lone pairs with empty d_{z^2} and d_{yz} orbitals. The complexes described herein are the first examples of η^2-pyrazolato ligand coordination to a d^2 metal center.

Introduction

Pyrazolato ligand coordination has been extensively investigated among complexes of the main-group, d-block, and lanthanide metals.[1−6] Structurally documented coordination modes in mid to late d-block metals have been restricted to η^1-bonding to a single metal ion,[1] μ-η^1:η^1-bonding between two metal centers,[1] and our recent report of η^5-bonding in a ruthenium complex.[7] Prior to 1997, only one example of η^2-pyrazolato coordination to a d-block metal had been reported.[3] Since 1997, we have reported many examples of η^2-pyrazolato ligand coordination among d^0 group-4 and -5 complexes.[4,5]

Until recently, η^2-pyrazolato ligand coordination in d-block metals was limited to systems with empty d shells.[1,3−5] In our original report of titanium complexes containing η^2-pyrazolato ligands,[4] molecular orbital calculations demonstrated that the η^2-coordination occurs through interaction of symmetric and antisymmetric combinations of the nitrogen lone pairs with empty d orbitals on titanium. A significant open question relates to the occurrence of η^2-pyrazolato ligands among d-block metal complexes with partially filled d shells, where repulsions between the filled d orbitals and pyrazolato nitrogen atoms might destabilize η^2-pyrazolato coordination in favor of other coordination modes. In this vein, Mösch-Zanetti has reported the synthesis and structure of tris(3,5-di-*tert*-butylpyrazolato)titanium(III) and several other (pyrazolato)titanium(III) complexes, and found η^2-coordination of the pyrazolato ligands in these d^1 systems.[8] In addition, we have recently described the synthesis, structure, and bonding of tris(3,5-di-*tert*-butylpyrazolato)chromium(III) and -iron(III).[9] These d^3 and d^5 complexes contain η^2-pyrazolato ligands, and suggest that many transition metal complexes with partially filled d shells may be able to support η^2-pyrazolato ligands. As part of our general studies, we sought to explore pyrazolato ligand coordination to d^2 metal centers.

Herein, we report the synthesis, structure, and characterization of a series of vanadium(III) complexes that exhibit η^2-pyrazolato ligand coordination. Molecular orbital calculations performed on a model vanadium(III) complex demonstrate that η^2-pyrazolato ligand coordination is preferred over η^1-coordination by 4.1 kcal/mol. The η^2-coordination occurs through overlap of symmetric and antisymmetric combinations of the nitrogen lone pairs with empty d orbitals on the vanadium(III) centers. These complexes are the first examples of η^2-pyrazolato ligand coordination to a d^2 metal center.

Results and Discussion

Synthesis of New Complexes

Treatment of trichlorotris(tetrahydrofuran)vanadium(III) with 1, 2, or 3 equiv. of (3,5-di-*tert*-butylpyrazolato)potas-

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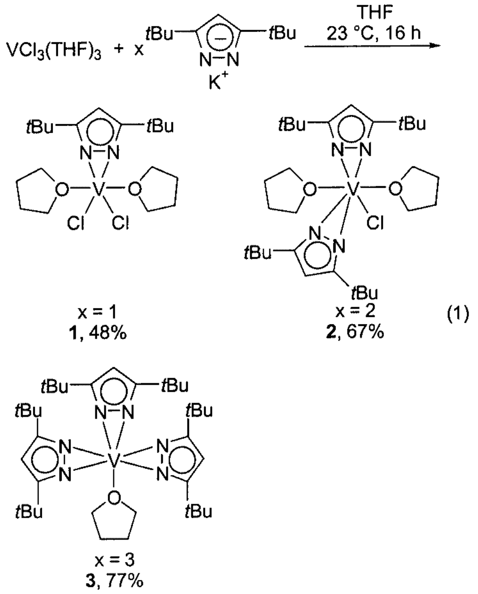
sium afforded dichloro(3,5-di-*tert*-butylpyrazolato)bis(tetrahydrofuran)vanadium(III) (**1**), chlorobis(3,5-di-*tert*-butylpyrazolato)bis(tetrahydrofuran)vanadium(III) (**2**), and tris(3,5-di-*tert*-butylpyrazolato)tetrahydrofuranvanadium(III) (**3**), respectively, as purple crystalline solids (Scheme 1). Compounds **1−3** are air-sensitive in solution and in the solid state, but are thermally stable indefinitely at ambient temperature under argon. The structures of **1−3** were assigned by ^{1}H NMR spectroscopy, IR spectroscopy, microanalysis, and by X-ray structure determinations (vide infra). Complexes **1−3** are paramagnetic, and exhibited broad resonances in the ^{1}H NMR spectra. Magnetic moments (μ_{eff}) of **1−3** were also determined and ranged between 2.60 and 2.82 BM. These values are close to the spin-only magnetic moment expected for the two unpaired electrons of a vanadium(III) center (μ_s = 2.83 BM).[10] EPR spectra were not recorded, since even-electron systems generally do not give useful spectra.[11]



Scheme 1

X-ray Crystal Structures of 1−3

The X-ray crystal structures of **1−3** were determined to establish the geometry about the metal center and the bonding modes of the pyrazolato ligands. Experimental crystallographic data are summarized in Table 4, selected bond lengths and angles are given and perspective views are presented for **1** (Figure 1, Table 1), **2** (Figure 2, Table 2), and **3** (Figure 3, Table 3).

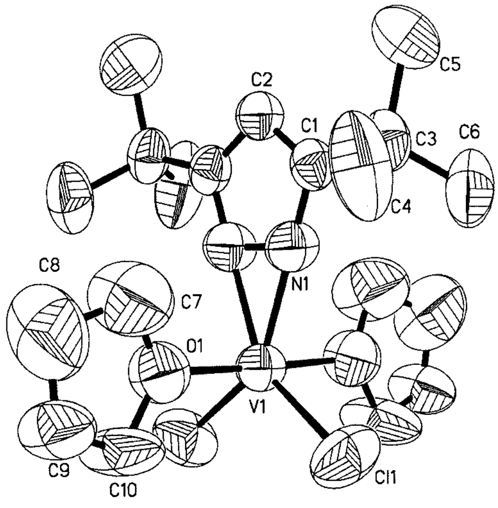


Figure 1. Perspective view of V(tBu$_2$Pz)Cl$_2$(THF)$_2$ (**1**) with thermal ellipsoids at the 50% probability level

Table 1. Selected bond lengths [Å] and angles [°] for **1**

V−N(1)	2.021(3)	V−Cl(1)	2.2655(9)
V−O(1)	2.097(2)	N(1)−N	1.356(5)
V−centroid[N(1),N(1)′]	1.904(3)		
N(1)−V−N	39.19(12)	N(1)−V−O(1)	90.27(11)
N−V−O(1)	87.73(10)	N−V−O	90.27(11)
N(1)−V−O	87.73(10)	O(1)−V−O	177.88(13)
N−V−Cl(1)	142.84(7)	N(1)−V−Cl(1)	103.78(7)
N(1)−V−Cl	142.84(7)	N−V−Cl	103.78(7)
O(1)−V−Cl(1)	90.03(8)	O−V−Cl(1)	91.14(8)
O−V−Cl	90.03(8)	O(1)−V−Cl	91.14(8)
Cl(1)−V−Cl	113.36(6)	N−N(1)−V	70.41(7)
Cl(1)−V−centroid[N(1),N(1)′]	123.3(1)		
Cl(1)−V−centroid[N(1),N(1)′]	88.9(1)		

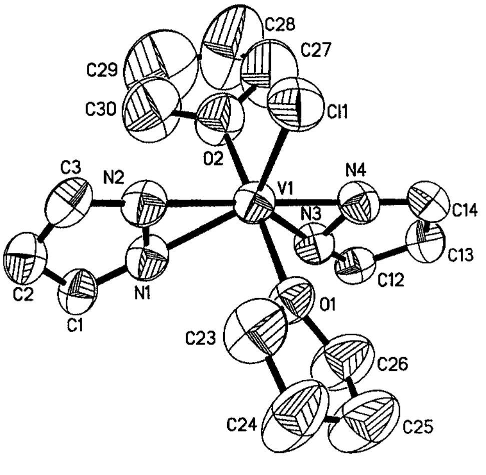


Figure 2. Perspective view of V(tBu$_2$Pz)$_2$Cl(THF)$_2$ (**2**) with *tert*-butyl groups removed for clarity; thermal ellipsoids are at the 50% probability level

Complex **1** contains one η^2-pyrazolato, two chloride, and two tetrahydrofuran ligands. The coordination sphere about the vanadium atom possesses approximate trigonal-bipyramidal geometry, if the center of the nitrogen−nitrogen bond in the 3,5-di-*tert*-butylpyrazolato ligand is considered as a monodentate donor. The tetrahydrofuran ligands comprise the axial substituents, with an oxygen−vanadium−oxygen angle of 177.88(13)°. The vanadium−oxygen bond length is 2.097(2) Å. The pyrazolato ligand lies in the equatorial plane, with nitrogen−vanadium−oxygen angles ranging from 87.73(10) to 90.27(11)°. The two chlorine atoms also lie in the equatorial plane, with oxygen−vanadium−chlorine angles ran-

Table 2. Selected bond lengths [Å] and angles [°] for **2**

V−N(1)	2.094(4)	V−N(2)	2.040(4)
V−N(3)	2.106(4)	V−N(4)	2.014(4)
V−O(1)	2.112(3)	V−O(2)	2.118(3)
V−Cl	2.3338(14)	N(1)−N(2)	1.354(4)
N(3)−N(4)	1.367(4)		
V−centroid[N(1),N(2)]	1.953(4)		
V−centroid[N(3),N(4)]	1.944(4)		
N(1)−V−N(2)	38.20(12)	N(3)−V−N(4)	38.68(12)
O(1)−V−O(2)	174.49(13)		
N(1)−V−O(1)	86.70(13)	N(1)−V−O(2)	91.17(15)
N(2)−V−O(1)	91.29(13)	N(2)−V−O(2)	90.18(14)
N(3)−V−O(1)	90.35(13)	N(3)−V−O(2)	85.28(13)
N(4)−V−O(1)	86.62(13)	N(4)−V−O(2)	92.03(14)
N(1)−V−Cl	127.33(11)	N(2)−V−Cl	89.22(11)
N(3)−V−Cl	127.77(11)	N(4)−V−Cl	89.56(11)
O(1)−V−Cl	93.40(9)	O(2)−V−Cl	91.94(11)
N(1)−N(2)−V	73.1(3)	N(2)−N(1)−V	68.7(2)
N(3)−N(4)−V	74.3(2)	N(4)−N(3)−V	67.0(2)
Cl(1)−V−centroid[N(1),N(2)]	108.5(1)		
Cl(1)−V−centroid[N(3),N(4)]	109.1(1)		
O(1)−V−centroid[N(1),N(2)]	88.9(1)		
O(1)−V−centroid[N(3),N(4)]	88.4(1)		
O(2)−V−centroid[N(1),N(2)]	90.7(1)		
O(2)−V−centroid[N(3),N(4)]	88.5(1)		
centroid[N(1),N(2)]−V−centroid[N(3),N(4)]	142.3(1)		

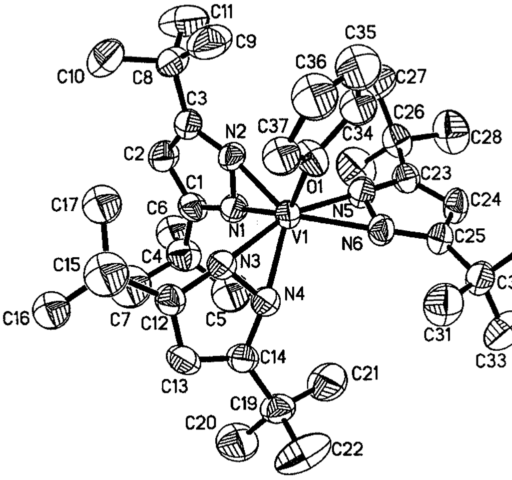


Figure 3. Perspective view of V(tBu$_2$Pz)$_3$(THF) (**3**) with thermal ellipsoids at the 50% probability level

ging from 90.03(8) to 91.14(8)°. The vanadium−chlorine bond length is 2.2655(9) Å. The pyrazolato ligand displays symmetric η^2-coordination with a vanadium−nitrogen bond length of 2.021(3) Å. The nitrogen−nitrogen distance [1.356(5) Å] and the bite angle [39.19(13)°] of the pyrazolato ligand in **1** are similar to the corresponding values found in η^2-pyrazolato complexes of the early transition metals.[5]

Complex **2** contains two η^2-pyrazolato, one chloride, and two tetrahydrofuran ligands. The coordination sphere about the vanadium atom possesses approximate trigonal bipyramidal geometry, if the centers of the nitrogen−nitrogen bonds in both 3,5-di-*tert*-butylpyrazolato ligands are considered to be monodentate donors. The tetrahydrofuran ligands comprise the axial ligands, with an oxygen−vanadium−oxygen angle of 174.49(13)°. The vanadium−oxygen distances are 2.112(3) and 2.118(3) Å. The chlorine atom lies in the equatorial plane, with chlorine−vanadium−oxygen angles of 93.40(9) and 91.94(11)°. The vanadium−chlorine bond length of 2.3338(14) Å is longer than the vanadium−chlorine bond length in **1**, due to the coordination number of seven in **2** compared to six in **1**. The two pyrazolato ligands are approximately coplanar and lie in the equatorial plane. The nitrogen−vanadium−oxygen angles range from 85.28(13) to 92.03(14)°. The pyrazolato ligands exhibit η^2-coordination to the vanadium atom, with vanadium−nitrogen bond lengths ranging from 2.014(4) to 2.106(4) Å. The longer vanadium−nitrogen bond lengths [to N(1) and N(3)] are farthest from the chlorine atom, and are the result of steric crowding between the *tert*-butyl groups containing C(4) and C(15). The nitrogen−nitrogen bond lengths [1.354(4) and 1.367(4) Å] and bite angles [38.20(12) and 38.68(12)°] of the pyrazolato ligands in **2** are similar to the corresponding values found in η^2-pyrazolato complexes of the early transition metals.[5]

Complex **3** contains three η^2-pyrazolato and one tetrahydrofuran ligands. The coordination sphere about the vanadium atom possesses a pseudo-tetrahedral geometry, if the centers of the nitrogen−nitrogen bonds in the 3,5-di-*tert*-butylpyrazolato ligands are considered as monodentate donors. The vanadium−nitrogen bond lengths range from 2.035(2) to 2.102(2) Å. The pyrazolato ligand containing N(1) and N(2) exhibits symmetric η^2-bonding to the vanadium atom within 5σ. However, the pyrazolato ligands containing N(3)−N(6) show a slight (0.062−0.066 Å) asymmetry in the vanadium−nitrogen bond lengths. In the pyra-

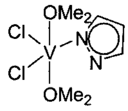
Table 3. Selected bond lengths [Å] and angles [°] for **3**

V−N(1)	2.053(2)	V−N(2)	2.043(2)
V−N(3)	2.097(2)	V−N(4)	2.035(2)
V−N(5)	2.036(2)	V−N(6)	2.102(2)
V−O	2.1289(17)	N(1)−N(2)	1.382(2)
N(3)−N(4)	1.374(3)	N(5)−N(6)	1.368(3)
V−centroid[N(1),N(2)]	1.928(2)		
V−centroid[N(3),N(4)]	1.948(2)		
V−centroid[N(5),N(6)]	1.953(2)		
N(1)−V−N(2)	39.44(7)	N(3)−V−N(4)	38.82(7)
N(5)−V−N(6)	38.56(8)		
N(1)−V−N(3)	91.71(9)	N(1)−V−N(4)	96.91(9)
N(1)−V−N(5)	94.96(9)	N(1)−V−N(6)	126.81(9)
N(2)−V−N(3)	97.56(9)	N(2)−V−N(4)	124.39(9)
N(2)−V−N(5)	97.95(9)	N(2)−V−N(6)	135.96(9)
N(3)−V−N(5)	162.37(9)	N(3)−V−N(6)	126.48(9)
N(1)−V−O	136.86(8)	N(2)−V−O	97.51(8)
N(3)−V−O	92.11(8)	N(4)−V−O	112.31(8)
N(5)−V−O	94.12(8)	N(6)−V−O	82.99(7)
N(1)−N(2)−V	70.68(13)	N(2)−N(1)−V	69.89(13)
N(3)−N(4)−V	73.02(13)	N(4)−N(3)−V	68.16(13)
N(5)−N(6)−V	68.12(13)	N(6)−N(5)−V	73.32(13)
O(1)−V−centroid[N(1),N(2)]	117.2(1)		
O(1)−V−centroid[N(3),N(4)]	102.6(1)		
O(1)−V−centroid[N(5),N(6)]	88.4(1)		
centroid[N(1),N(2)]−V−centroid[N(3),N(4)]	103.6(1)		
centroid[N(1),N(2)]−V−centroid[N(5),N(6)]	116.0(1)		
centroid[N(3),N(4)]−V−centroid[N(5),N(6)]	127.9(1)		

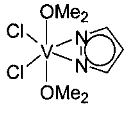
zolato ligand containing N(3) and N(4), the slightly longer bond to N(3) can be rationalized as arising through steric repulsion between the *tert*-butyl group containing C(15) and the tetrahydrofuran ligand. Similarly, the pyrazolato ligand containing N(5) and N(6) shows a slightly longer bond from the vanadium atom to N(6) due to steric crowding between the *tert*-butyl groups containing C(19) and C(30). This steric crowding causes these two pyrazolato ligands to be canted with respect to each other, as opposed to the coplanar pyrazolato ligands observed in **2**. The vanadium−oxygen bond length is 2.1289(17) Å. This value is similar to the related bond lengths in seven-coordinate **2**. The nitrogen−nitrogen bond lengths range from 1.368(3) to 1.382(2) Å. The pyrazolato bite angles range from 38.56(8) to 39.44(7)°. These values are similar to those found in **1**, **2**, and other complexes containing η^2-pyrazolato ligands.[5]

Molecular Orbital Calculations

To understand the nature of the pyrazolato ligand bonding to vanadium(III), ab initio calculations were performed using the Gaussian suite of programs.[12] The simplified models used in this study are the η^1- and η^2-pyrazolato complexes **4** and **5**. A previous study of ours has shown that a simplified model (pyrazolato)titanium(IV) complex does not significantly change the electronic distribution relative to homoleptic pyrazolato complexes.[4] Model complexes **4** and **5** optimized using the B3LYP/6−311G* level of theory.[13] The bond lengths and angles associated with the pyrazolato ligand in the optimized structure of **5** are in good agreement with the X-ray crystal structures of **1**−**3** [V−N(calcd) = 2.040, 2.042 Å versus V−N (X-ray) = 2.014−2.106 Å; N−N(calcd) = 1.350 Å versus N−N(X-ray) = 1.354−1.382 Å; N−N−V(calcd) = 70.86° versus N−N−V(X-ray) 67.0−74.3°]. Complex **5** is calculated to be 4.09 kcal/mol more stable than the η^1 complex **4**.



4



5

Natural population analysis[14] shows that the charges on the pyrazolato ligands are −0.556 in **4** and −0.561 in **5**. These values can be compared to charges of −0.32 for (η^2-Me_2pz)$TiCl_3$[4] and −0.75 in (η^2-pz)$YCl_2(NH_3)_2$[15a] that have been previously reported by our group. Natural bond order analysis[14] indicates that there is very little interaction between the occupied vanadium d orbitals and the unoccupied pyrazolato ligand orbitals. A more significant stabilization occurred by the symmetric and antisymmetric occupied nitrogen lone pair orbitals interacting with empty vanadium d orbitals. The fragment orbitals involved are shown in Figure 4. The symmetric combination of the nitrogen lone pair combines with the empty d_{z^2} vanadium orbital and appropriate in-plane orbitals based on the carbon and chlorine atoms. The antisymmetric combination of the nitrogen lone pairs interacts with an antisymmetric combination of vanadium−chlorine σ^* orbitals. These vanadium−chlorine orbitals consist primarily of the metal d_{yz} orbital and a smaller, antibonding contribution from a chlorine p orbital.

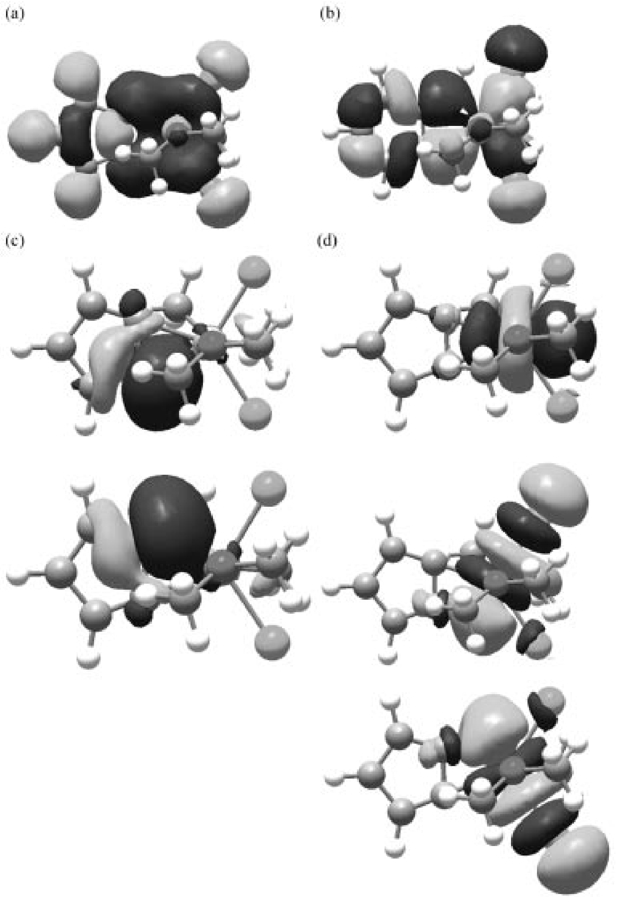


Figure 4. Calculated molecular orbitals of **5**: (a) symmetric combination of the nitrogen lone pairs that interact with the empty d_{z^2} fragment; (b) antisymmetric combination of the nitrogen lone pairs that interact with the empty d_{yz} fragment; (c) pyrazolato nitrogen atom lone pair fragments that add together to form symmetric and antisymmetric combinations; (d) empty d_{z^2} and d_{yz} fragments that interact with the symmetric and antisymmetric combinations of the pyrazolato nitrogen atom lone pair fragments

Additionally, there is some mixing between the HOMO π orbital on the pyrazolato fragment and an occupied d_{xz} orbital, but the NBO analysis indicates that this does not stabilize the complex significantly. Thus, the most important orbital contributions to the bonding between the pyrazolato ligand and the vanadium center are the symmetric and antisymmetric combinations of the nitrogen lone pairs interacting with the unoccupied vanadium d_{z^2} and d_{yz} orbitals.

Discussion

The central discovery highlighted herein is the η^2-pyrazolato ligands bonded to the d^2 vanadium(III) centers in **1−3**. These are the first examples of η^2-pyrazolato ligand coordination to a metal center with a d^2 electronic configuration. In addition, **1−3** constitute rare examples of η^2-pyrazolato ligand coordination to d-block metal centers with partially filled d shells.[8,9] There has been one previous report of a (pyrazolato)vanadium complex, [(Tp*i*Pr^{2}V(O)(μ-OH)(μ-Pz*i*Pr^2)V(O)(μ-OH)(μ-Pz*i*Pr^2)V(O)Tp*i*Pr^2)], which was obtained by partial hydrolysis of a vanadium(IV) hydrotris(3,5-diisopropyl-1-pyrazolyl)borate complex.[16] The 3,5-diisopropylpyrazolato ligands in this complex bridge between two vanadium(IV) ions with the well-documented μ-η^1:η^1-coordination mode. There have been 70 tris(pyrazolyl)borate complexes of vanadium whose structures are listed in the Cambridge Crystallographic Database (version 5.22; October 2001).[17] These complexes contain μ-η^1:η^1-pyrazolato ligands bridged between boron(III) and vanadium ions in various oxidation states. Traditional wisdom[1] holds that the lone pairs of electrons on each nitrogen atom within a pyrazolato ligand are pointed in geometrically inappropriate directions to allow η^2-coordination to a small metal ion such as vanadium(III), and the μ-η^1:η^1 coordination mode is therefore favored. Instead, our theoretical studies[4,14] demonstrate that η^2-pyrazolato ligand coordination occurs through overlap of symmetric and antisymmetric combinations of the nitrogen-based lone pairs with empty d orbitals on the metal center. Recent reports of η^2-pyrazolato ligands among main-group metal and d^0, d^1, d^3, and d^5 transition metal complexes,[2−5,8,9] together with the present work, suggest that this previously rare coordination mode may be generally accessible among the transition metals. In particular, most of the known η^2-pyrazolato complexes contain the bulky 3,5-di-*tert*-butylpyrazolato ligand. Molecular orbital calculations described above demonstrate that η^2-pyrazolato ligand coordination is thermodynamically preferred over η^1 coordination, even in the absence of steric effects. However, very bulky pyrazolato ligands or extremely bulky ancillary ligands may be required to destabilize the μ-η^1:η^1 coordination mode and make η^2-pyrazolato ligands feasible.

There is an analogy between **1−3** and related vanadium(III) complexes containing other bidentate, monoanionic donor ligands.[18−21] In particular, vanadium(III) complexes containing amidinate or formamidinate ligands are highly relevant, since these ligands are bidentate nitrogen donors that are similar to η^2-pyrazolato ligands. The complexes V(RNCR′NR)$_3$ (R = *p*-tol, R′ = H;[18] R = C_6H_{11}, R′ = CH_3[19]) contain six-coordinate metal centers with distorted D_3 geometries. Unlike seven-coordinate **3**, which contains a coordinated tetrahydrofuran molecule in addition to the η^2-pyrazolato ligands, V(RNCR′NR)$_3$ did not crystallize with coordinated tetrahydrofuran. The smaller bite angle of the η^2-pyrazolato ligands (38−40°), compared to the related values for V(RNCR′NR)$_3$ (63−64°), make the vanadium(III) center in **3** more accessible sterically and allows tetrahydrofuran coordination. The benzamidinate complex VCl[N(SiMe$_3$)CPhN(SiMe$_3$)]$_2$ is related structurally to **2**.[20] However, **2** contains two tetrahydrofuran ligands, while VCl[N(SiMe$_3$)CPhN(SiMe$_3$)]$_2$ does not contain any neutral donor ligands. Again, tetrahydrofuran coordination in **2** occurs due to the more open coordination sphere, compared to VCl[N(SiMe$_3$)CPhN(SiMe$_3$)]$_2$.

Experimental Section

General Considerations: All reactions were performed under argon using either glovebox or Schlenk line techniques. Toluene was distilled from sodium, tetrahydrofuran was distilled from sodium benzophenone ketyl, and hexane was distilled from P_2O_5. Trichlorotris(tetrahydrofuran)vanadium(III) was purchased from Aldrich Chemicals, Inc. (3,5-Di-*tert*-butylpyrazolato)potassium was prepared by a literature procedure.[22] ^{1}H and ^{13}C{^{1}H} NMR were obtained at 300 or 75 MHz in [D$_6$]benzene. IR spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained with a Haake−Buchler HBI digital melting point apparatus and are uncorrected. Magnetic susceptibility measurements were determined using a Johnson−Matthey magnetic susceptibility balance.

Preparation of Dichloro(3,5-di-*tert*-butylpyrazolato)bis(tetrahydrofuran)vanadium(III) (1): A 100-mL Schlenk flask was charged with trichlorotris(tetrahydrofuran)vanadium(III) (0.856 g, 2.29 mmol), (3,5-di-*tert*-butylpyrazolato)potassium (0.502 g, 2.29 mmol), and tetrahydrofuran (50 mL). The resultant purple solution was stirred for 16 h. The solvent was then removed under reduced pressure to yield a purple solid. This solid was extracted with hexane (50 mL), and the resultant solution was filtered through a 2-cm pad of Celite on a coarse glass frit. The filtrate was concentrated to a volume of about 20 mL, and was then placed in a −20 °C freezer for 36 h. Decanting of the solvent, followed by vacuum drying for 1 h, afforded **1** as purple crystals (0.49 g, 48%), m.p. 115 °C (dec). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1589 (w), 1563 (w), 1250 (s), 1030 (s), 862 (w), 795 (m). ^{1}H NMR (C_6D_6, 22 °C, ppm): δ = 2.86 (broad, C_4H_8O), 1.49 [broad, $C(CH_3)_3$]. μ_{eff} = 2.82 BM. $C_{19}H_{35}Cl_2N_2O_2V$ (445.3): calcd. C 51.24, H 7.92, N 6.29; found C 51.27, H 8.12, N 6.26.

Preparation of Chlorobis(3,5-di-*tert*-butylpyrazolato)bis(tetrahydrofuran)vanadium(III) (2): In a fashion similar to the preparation of **1**, trichlorotris(tetrahydrofuran)vanadium(III) (1.189 g, 3.18 mmol) was treated with (3,5-di-*tert*-butylpyrazolato)potassium (1.388 g, 6.36 mmol) to afford **2** as purple crystals (1.26 g, 67%), m.p. 117 °C. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1515 (m), 1498 (m), 1415 (m), 1361 (s), 1312 (w), 1251 (s), 1234 (s), 1208 (w), 1171 (w), 1030 (s), 919 (w), 874 (s), 792 (s), 725 (m), 712 (m). ^{1}H NMR (C_6D_6, 22 °C, ppm): δ = 1.63 [broad, C_4H_8O and $C(CH_3)_3$]. μ_{eff} = 2.60 BM. $C_{30}H_{65}N_6OV$ (1589.2): calcd. C 61.16, H 9.24, N 9.51; found C 61.42, H 9.27, N 9.36.

Preparation of Tris(3,5-di-*tert*-butylpyrazolato)tetrahydrofuranvanadium(III) (3): In a fashion similar to the preparation of **1**, trichlorotris(tetrahydrofuran)vanadium(III) (0.804 g, 2.15 mmol) was treated with (3,5-di-*tert*-butylpyrazolato)potassium (1.500 g, 6.87 mmol) to afford **3** as purple crystals (1.11 g, 77%), m.p. 149 °C dec. IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1567 (w), 1515 (m), 1310 (w), 1251 (s), 1278 (m), 1202 (w), 1017 (m), 874 (w), 783 (m), 715 (m). ^{1}H NMR (C_6D_6, 22 °C, ppm): δ = 4.80 (broad, C_4H_8O), 2.26 [broad, $C(CH_3)_3$]. μ_{eff} = 2.71 BM. $C_{37}H_{65}N_6OV$ (660.9): calcd. C 67.24, H 9.91, N 12.72; found C 67.36, H 10.01, N 12.73.

X-ray Crystallography for 1−3: The crystalline samples were mounted in thin-walled glass capillaries under nitrogen. All crystallographic data were collected at room temperature with a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. 1650 frames were collected at 10 s/frame and integrated with the manufacturer's SMART and SAINT software. Absorption corrections were applied with Sheldrick's SADABS program and the structure was solved and refined using the programs of SHELX-97. The molecules crystallize as neutral complexes. Hydrogen atoms were calculated and assigned to ride on the carbon atoms to which they are bound. CCDC-178824 (**1**), -178825 (**2**), and -178826 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Complex **1** crystallized as purple rods in *C*2/*c* with *Z* = 4. The vanadium atoms occupy a crystallographic twofold axis. Atoms C9 and C10 in the coordinated THF were assigned alternate partial positions to model the disorder. Complex **2** crystallized as purple rods in *P*4(2)/*n* with *Z* = 8. All atoms in the vanadium complex occupied general positions, but there is an indeterminate solvent region near the twofold axis. Any placement and refinement of atoms in this solvent region becomes unreasonable. There was no evidence for any solvate inclusion in the C,H,N microanalysis. The coordinated THF exhibits typically large thermal parameters. Complex **3** crystallized as purple rectangles in $P2_1/c$ with *Z* = 4. All atoms occupy general positions. Partially occu-

Table 4. Experimental crystallographic data for **1−3**

	1	**2**	**3**
Empirical formula	$C_{19}H_{35}Cl_2N_2O_2V$	$C_{30}H_{54}ClN_4O_2V$	$C_{37}H_{65}N_6OV$
Formula mass	445.33	589.16	660.89
Space group	*C*2/*c*	*P*4(2)/*n*	$P2_1/c$
a [Å]	16.2481(17)	25.754(3)	9.8014(11)
b [Å]	15.1194(16)	25.754(3)	22.247(3)
c [Å]	9.9232(9)	10.8091(15)	18.857(2)
β [°]	96.968(2)	90	101.448(2)
V [Å^3]	2419.7(4)	7169.4(15)	4030.0(8)
Z	4	8	4
T [K]	295(2)	295(2)	295(2)
λ [Å]	0.71073	0.71073	0.71073
ρ(calcd.) [g·cm^3]	1.222	1.092	1.089
μ [mm^{-1}]	0.645	0.379	0.280
$R(F) = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ (%)	5.69	5.74	4.80
$Rw(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (%)	17.43	16.60	10.87

pied positions (60:40) and isotropic parameters were assigned to C5−7, C16−18, and C34−37 to describe their positional disorder; all other non-hydrogen atoms were defined anisotropically.

Acknowledgments

We are grateful to the National Science Foundation (grant no. CHE-9807269) for support of this research.

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[1] For reviews, see: [1a] A. P. Sadimenko, *Adv. Heterocycl. Chem.* **2001**, *80*, 157−240. [1b] J. E. Cosgriff, G. B. Deacon, *Angew. Chem. Int. Ed.* **1998**, *37*, 286−287; *Angew. Chem.* **1998**, *110*, 298−299. [1c] G. La Monica, G. A. Ardizzoia, *Progr. Inorg. Chem.* **1997**, *46*, 151−238. [1d] A. P. Sadimenko, S. S. Basson, *Coord. Chem. Rev.* **1996**, *147*, 247−297. [1e] S. Trofimenko, *Progr. Inorg. Chem.* **1986**, *34*, 115−210. [1f] S. Trofimenko, *Chem. Rev.* **1972**, *72*, 497−508.

[2] [2a] G. B. Deacon, A. Gitlits, P. W. Roesky, M. R. Burgstein, K. C. Lim, B. W. Skelton, A. H. White, *Chem. Eur. J.* **2001**, *7*, 127−138. [2b] A. Steiner, G. T. Lawson, B. Walfort, D. Leussser, D. Stalke, *J. Chem. Soc., Dalton Trans.* **2001**, 219−221. [2c] W. J. Zheng, H. W. Roesky, M. Noltemeyer, *Organometallics* **2001**, *20*, 1033−1035. [2d] W. J. Zheng, N. C. Mösch-Zanetti, T. Blunck, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, *Organometallics* **2001**, *20*, 3299−3303. [2e] W. Zheng, H. Hohmeister, N. C. Mösch-Zanetti, T. Blunck, H. W. Roesky, M. Noltemeyer, H-G. Schmidt, *Inorg. Chem.* **2001**, *40*, 2363−2367. [2f] G. B. Deacon, E. E. Dellbridge, C. M. Forsyth, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **2000**, 745−751. [2g] D. Pfeiffer, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **2000**, *39*, 2377−2384. [2h] G. B. Deacon, E. E. Delbridge, C. M. Forsyth, B. W Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **2000**, 745−751. [2i] W. Zheng, N. C. Mösch-Zanetti, H. W. Roesky, M. Hewitt, F. Cimpoesu, T. R. Schneider, A. Stasch, J. Prust, *Angew. Chem. Int. Ed.* **2000**, *39*, 3099−3101; *Angew. Chem.* **2000**, *112*, 3229−3231. [2j] E. E. Pullen, D. Rabinovich, C. D. Incarvito, T. E. Concolino, A. L. Rheingold, *Inorg. Chem.* **2000**, *39*, 1561−1567. [2k] G. B. Deacon, E. E. Delbridge, C. M. Forsyth, P. C. Junk, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1999**, *52*, 733−739. [2l] E. E. Pullen, A. L. Rheingold, D. Rabinovich, *Inorg. Chem. Commun.* **1999**, *2*, 194−196. [2m] H. Witte-Abel, C. Drost, U. Klingebiel, M. Noltemeyer, *J. Organomet. Chem.* **1999**, *585*, 341−347. [2n] J. Lewinksi, J. Zachara, T. Kopec, I. Madura, I. Prowotorow, *Inorg. Chem. Commun.* **1999**, *2*, 131−134. [2o] D. Pfeiffer, M. J. Heeg, C. H. Winter, *Angew. Chem. Int. Ed.* **1998**, *37*, 2517−2519; *Angew. Chem.* **1998**, *110*, 2674−2676. [2p] M. V. Capparelli, P. Hodge, B. Piggot, *Chem. Commun.* **1997**, 937−938.

[3] D. Röttger, G. Erker, M. Grehl, R. Frölich, *Organometallics* **1994**, *13*, 3897−3902.

[4] I. A. Guzei, A. G. Baboul, G. P. A. Yap, A. L. Rheingold, H. B. Schlegel, C. H. Winter, *J. Am. Chem. Soc.* **1997**, *119*, 3387−3388.

[5] [5a] C. Yélamos, K. R. Gust, A. G. Baboul, M. J. Heeg, H. B. Schlegel, C. H. Winter, *Inorg. Chem.* **2001**, *40*, 6451−6462. [5b] K. R. Gust, M. J. Heeg, C. H. Winter, *Polyhedron* **2001**, *20*, 805−813. [5c] C. Yélamos, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1999**, *38*, 1871−1878. [5d] C. Yélamos, M. J. Heeg, C. H. Winter, *Organometallics* **1999**, *18*, 1168−1176. [5e] I. A. Guzei, G. P. A Yap, C. H. Winter, *Inorg. Chem.* **1997**, *36*, 1738−1739.

[6] [6a] G. B. Deacon, A. Gitlits, P. W. Roesky, M. R. Burgstein, K. C. Lim, B. W. Skelton, A. H. White, *Chem. Eur. J.* **2001**, *7*, 127−138. [6b] G. B. Deacon, A. Gitlits, B. W. Skelton, A. H. White, *Chem. Commun.* **1999**, 1213−1214. [6c] G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, *Eur. J. Inorg. Chem.* **1999**, 751−761. [6d] J. G. Cederberg, T. D. Culp, B. Bieg, D. Pfeiffer, C. H. Winter, K. L. Bray, T. F. Kuech, *J. Appl. Phy.* **1999**, *85*, 1825−1831. [6e] J. G. Cederberg, T. D. Culp, B. Bieg, D. Pfeiffer, C. H. Winter, K. L. Bray, T. F. Kuech, *J. Cryst. Growth* **1998**, *195*, 105−111. [6f] T. D. Culp, J. G. Cederberg, B. Bieg, T. F. Kuech, K. L. Bray, D. Pfeiffer, C. H. Winter, *J. Appl. Phys.* **1998**, *83*, 4918−4927. [6g] G. B. Deacon, E. E. Delbridge, B. W. Skelton, A. H. White, *Angew. Chem. Int. Ed.* **1998**, *37*, 2251−2252; *Angew. Chem.* **1998**, *110*, 2372−2373. [6h] J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, *Aust. J. Chem.* **1993**, *46*, 1881−1896. [6i] D. S. Black, G. B. Deacon, G. L. Edwards, B. M. Gatehouse, *Aust. J. Chem.* **1993**, *43*, 1323−1336. [6j] J. E. Cosgriff, G. B. Deacon, B. M. Gatehouse, H. Hemling, H. Schumann, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 874−875; *Angew. Chem.* **1993**, *105*, 906−907.

[7] J. R. Perera, M. J. Heeg, H. B. Schlegel, C. H. Winter, *J. Am. Chem. Soc.* **1999**, *121*, 4536−4537.

[8] N. C. Mösch-Zanetti, R. Kratzner, C. Lehmann, T. R. Schneider, I. Uson, *Eur. J. Inorg. Chem.* **2000**, 13−16.

[9] K. R. Gust, J. E. Knox, M. J. Heeg, H. B. Schlegel, C. H. Winter, *Angew. Chem. Int. Ed.*, **2002**, *41*, 1591−1594. *Angew. Chem.*, **2002**, *114*, 1661−1664.

[10] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 3rd ed., Wiley, New York, **2001**, pp. 454−461.

[11] For leading references, see: [11a] P. L. W. Tregenna-Piggott, H. Weihe, J. Bendix, A.-L. Barra, H.-U. Güdel, *Inorg. Chem.* **1999**, *38*, 5928−5929. [11b] T. Weyermuller, K. Weighardt, P. Chaudhari, *J. Chem. Soc., Dalton Trans.* **1998**, 3805−3813. [11c] R. S. Drago, *Physical Methods for Chemists*, 2nd ed., Surfside Scientific Publishers, Gainesville, Florida, **1992**, pp. 559−603.

[12] M. J Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, B. Mennuci, M. Cossi, C. Adamo, J. Jaramillo, R. Cammi, C. Pomelli, J. Ochterski, G. A. Peterson. P. Y. Ayala, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 99, Development Version (Revision B.08+)*, Gaussian, Inc., Pittsburgh, PA, **2000**.

[13] [13a] D. A. Becke, *Phys. Rev. A* **1988**, *38*, 3098−3100. [13b] C. Lee, R. D. Parr, *Phys. Rev. B* **1988**, *37*, 785−789. [13c] D. A. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652. [13d] A. J. H. Wachters, *J. Chem. Phys.* **1970**, *52*, 1033−1036. [13e] P. J. Hay, *J. Chem. Phys.* **1977**, *66*, 4377−4384.

[14] [14a] J. E. Carpenter, F. Weinhold, *J. Mol. Struct. (Theochem)* **1988**, *46*, 41−62. [14b] J. E. Carpenter, Ph. D. Thesis, University of Wisconsin, **1987**. [14c] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211−7218. [14d] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066−4073. [14e] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736−1740. [14f] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735−746. [14g] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899−926. [14h] F. Weinhold, J. E. Carpenter, *The Structure of Small Molecules and Ions*, Plenum, Amsterdam, **1988**, p. 227.

[15] [15a] D. Pfeiffer, B. J. Ximba, L. M. Liable-Sands, A. L. Rheingold, M. J. Heeg, D. M. Coleman, H. B. Schlegel, T. F Kuech, C. H. Winter, *Inorg. Chem.* **1999**, *38*, 4539−4548. [15b] C. Yélamos, K. R. Gust, A. G. Baboul, M. J. Heeg, H. B. Schlegel, C. H. Winter, *Inorg. Chem.* **2001**, *40*, 6451−6462.

[16] M. Kosugi, S. Hikichi, M. Akita, Y. Moro-oka, *Inorg. Chem.* **1999**, *38*, 2567−2578.

[17] For leading recent references, see: [17a] M. Kosugi, S. Hikichi, M. Akita, Y. Moro-Oka, *J. Chem. Soc., Dalton Trans.* **1999**, 1369−1371. [17b] P. J. Bonitatebus Jr., W. H. Armstrong, *Chem. Commun.* **1999**, 55−56. [17c] T. Oshiki, K. Mashima, S. Kawa-

mura, K. Tani, K. Kitaura, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1735−1748.

[18] F. A. Cotton, L. M. Daniels, C. A. Murillo, *Inorg. Chem.* **1993**, *32*, 2881−2885.

[19] S. Hao, P. Berno, R. K. Minhas, S. Gambarotta, *Inorg. Chim. Acta* **1996**, *244*, 37−49.

[20] E. A. C. Brussee, A. Meetsma, B. Hessen, J. H. Teuben, *Organometallics* **1998**, *17*, 4090−4095.

[21] See also: [21a] A. Spannenberg, A. Tillack, P. Arndt, R. Kirmse, R. Kempe, *Polyhedron* **1998**, *17*, 845−850. [21b] B. Morosin, H. Montgomery, *Acta Crystallogr., Sect. B* **1969**, *25*, 1354−1359.

[22] C. Yélamos, M. J. Heeg, C. H. Winter, *Inorg. Chem.* **1998**, *37*, 3892−3894.

Received February 7, 2002
[I02064]