Table III. Molecular Geometry of Hexakis(*tert*-butyl isocyanide)vanadium(II) Hexacarbonylvanadate(−I)[a]

Cation

Bond Length (Å)			Angle	Deg	
	Mo/Cu	Mean		Mo/Cu	Mean
V(1)-C(1)	2.086(18) 2.097(21)	2.091(14)	C(1)-V(1)-C(2)	89.6(6) 89.1(7)	89.4(5)
V(1)-C(2)	2.128(19) 2.118(22)	2.124(14)	C(1)-V(1)-C(3)	93.3(6) 92.6(7)	93.0(5)
V(1)-C(3)	2.090(19) 2.089(17)	2.090(13)	C(2)-V(1)-C(3)	91.0(6) 90.9(7)	91.0(5)
C(1)-N(1)	1.148(16) 1.152(19)	1.150(12)	V(1)-C(1)-N(1)	176.7(14) 175.4(18)	176.2(11)
C(2)-N(2)	1.117(16) 1.121(20)	1.119(12)	V(1)-C(2)-N(2)	175.2(15) 174.7(19)	175.0(12)
C(3)-N(3)	1.174(17) 1.130(18)	1.153(12)	V(1)-C(3)-N(3)	174.4(15) 175.4(16)	174.9(11)
N(1)-C(11)	1.43 (2) 1.44 (3)	1.43 (2)	C(1)-N(1)-C(11)	178 (2) 178 (2)	178 (1)
N(2)-C(21)	1.42 (2) 1.43 (3)	1.42 (2)	C(2)-N(2)-C(21)	179 (2) 177 (2)	178 (1)
N(3)-C(31)	1.45 (2) 1.43 (3)	1.44 (2)	C(3)-N(3)-C(31)	177 (2) 177 (2)	177 (2)
C(11)-C(12)	1.41 (3) 1.37 (4)	1.39 (3)	N(1)-C(11)-C(12)	111 (2) 110 (3)	110 (2)
C(11)-C(13)	1.42 (3) 1.44 (4)	1.42 (3)	N(1)-C(11)-C(13)	110 (2) 110 (2)	110 (2)
C(11)-C(14)	1.49 (3) 1.49 (4)	1.49 (2)	N(1)-C(11)-C(14)	110 (2) 109 (2)	110 (2)
			C(12)-C(11)-C(13)	106 (3) 108(3)	107 (2)
			C(12)-C(11)-C(14)	108 (3) 111 (4)	109 (2)
			C(13)-C(11)-C(14)	112 (3) 110 (3)	111 (2)
C(21)-C(22)	1.31 (4) 1.34 (5)	1.32 (3)	N(2)-C(21)-C(22)	113 (2) 113 (3)	113 (2)
C(21)-C(23)	1.52 (3) 1.43 (4)	1.48 (3)	N(2)-C(21)-C(23)	108 (2) 110 (3)	109 (2)
C(21)-C(24)	1.53 (4) 1.56 (4)	1.54 (3)	N(2)-C(21)-C(24)	107 (2) 106 (2)	107 (2)
			C(22)-C(21)-C(23)	105 (3) 107 (4)	106 (3)
			C(22)-C(21)-C(24)	117 (4) 114 (4)	116 (3)
			C(23)-C(21)-C(24)	106 (2) 106 (3)	106 (2)
C(31)-C(32)	1.37 (3) 1.36 (3)	1.37 (2)	N(3)-C(31)-C(32)	111 (2) 113 (2)	112 (2)
C(31)-C(33)	1.38 (3) 1.41 (3)	1.39 (2)	N(3)-C(31)-C(33)	114 (2) 114 (2)	114 (1)
C(31)-C(34)	1.68 (4) 1.69 (5)	1.68 (3)	N(3)-C(31)-C(34)	102 (2) 104 (3)	102 (2)
			C(32)-C(31)-C(33)	127 (2) 124 (3)	126 (2)
			C(32)-C(31)-C(34)	95 (2) 96 (3)	95 (2)
			C(33)-C(31)-C(34)	103 (3) 101 (3)	102 (2)
Anion					
V(2)-C(4)	1.894(25) 1.954(27)	1.922(18)	C(4)-V(2)-C(5)	89.0(10) 88.2(13)	88.7(8)
V(2)-C(5)	1.883(29) 1.872(38)	1.879(23)	C(4)-V(2)-C(6)	94.0(10) 93.2(12)	93.7(8)
V(2)-C(6)	1.874(27) 1.952(30)	1.909(20)	C(4)-V(2)-C(7)	88.4(9) 89.2(12)	88.7(7)
V(2)-C(7)	1.865(21) 1.874(27)	1.868(17)	C(4)-V(2)-C(8)	89.6(9) 88.9(10)	89.3(7)
V(2)-C(8)	1.871(24) 1.930(26)	1.898(18)	C(4)-V(2)-C(9)	174.8(9) 174.8(12)	174.8(7)
V(2)-C(9)	1.852(23) 1.906(27)	1.875(18)	C(5)-V(2)-C(6)	88.6(10) 88.5(12)	88.6(8)
			C(5)-V(2)-C(7)	176.7(9) 176.6(13)	176.7(7)
			C(5)-V(2)-C(8)	93.9(9) 93.2(11)	93.6(7)
			C(5)-V(2)-C(9)	87.3(9) 88.3(13)	87.6(7)
			C(6)-V(2)-C(7)	89.6(9) 89.5(11)	89.6(7)
			C(6)-V(2)-C(8)	175.6(9) 177.4(10)	176.4(7)
			C(6)-V(2)-C(9)	89.7(11) 90.6(13)	90.1(8)
			C(7)-V(2)-C(8)	88.1(8) 89.0(10)	88.5(6)
			C(7)-V(2)-C(9)	95.4(9) 94.4(11)	95.0(7)
			C(8)-V(2)-C(9)	86.9(9) 87.4(11)	87.1(7)
C(4)-O(4)	1.14 (2) 1.13 (2)	1.14 (2)	V(2)-C(4)-O(4)	178 (3) 177 (3)	178 (2)
C(5)-O(5)	1.22 (2) 1.24 (3)	1.22 (2)	V(2)-C(5)-O(5)	175 (2) 173 (3)	175 (2)
C(6)-O(6)	1.23 (2) 1.19 (3)	1.22 (2)	V(2)-C(6)-O(6)	170 (2) 170 (3)	170 (2)
C(7)-O(7)	1.17 (2) 1.17 (2)	1.17 (1)	V(2)-C(7)-O(7)	176 (2) 175 (2)	175 (2)
C(8)-O(8)	1.19 (2) 1.17 (2)	1.18 (2)	V(2)-C(8)-O(8)	175 (2) 178 (3)	176 (2)
C(9)-O(9)	1.18 (2) 1.14 (2)	1.16 (2)	V(2)-C(9)-O(9)	180 (2) 179 (3)	179 (2)

[a] The mean bond lengths and angles quoted are the weighted averages of the Cu and Mo data set refinements. See footnote *a* in Table II.

Prior to the crystallographic study, the structure of [V-(CN-*t*-Bu)$_6$][V(CO)$_6$]$_2$ was adumbrated by its infrared spectrum, which is a composite of the absorptions previously observed for the [V(CN-*t*-Bu)$_6$]$^{2+}$ cation[1] and the characteristic absorptions of the [V(CO)$_6$]$^-$ anion.[14] The proton NMR spectrum of the paramagnetic complex, takin in CD_2Cl_2 at 30 °C, consists of a single broad peak centered at 5 ppm with a half-width of 250 Hz. Because of the octahedral symmetry of the cation, there can be no anisotropic contribution to the paramagnetic NMR shift. Therefore the downfield shift of ~3 ppm of the *tert*-butyl isocyanide absorption from its typical absorption position in diamagnetic complexes arises from the Fermi contact term.

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Registry No. [V(CH-*t*-Bu)$_6$][V(CO)$_6$]$_2$, 77966-15-5; tetraethylammonium hexacarbonylvanadate(−I), 13985-78-9; trichlorotris(*tert*-butyl isocyanide)vanadium(III), 74562-45-1.

Supplementary Material Available: Tables S1 and S2 listing final atomic parameters and fixed hydrogen atom positions for the Mo data set. Tables S3 and S4 listing similar information for the Cu data, and Tables S5 and S6 giving the observed and calculated structure factors for the Mo and Cu data sets, respectively (16 pages). Ordering information is given on any current masthead page.

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Effective Spin Hamiltonian for D_{3h} Symmetry: Trigonal-Prismatic and Trigonal-Bipyramidal Geometries

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Received August 12, 1980

Although spectroscopic properties of transition-metal centers can often be interpreted with assumption of octahedral or tetrahedral limiting behavior, those of trigonal-prismatic and trigonal-bipyramidal centers cannot. These trigonal geometries are characterized by D_{3h} point group symmetry, and D_{3h} is not a subgroup of O_h or T_d. The creation of a trigonal-prismatic molecule from an octahedral molecule requires the creation of a symmetry element not originally present in O_h.[1] Similarly, the creation of a trigonal-bipyramidal molecule from a square-pyramidal molecule requires symmetry elements not originally present in C_{4v}.[2] Effects of D_{3h} symmetry on the crystal field spectra of d^n systems have been investigated by numerous authors.[1-3] We extend consideration to the fine structure of the ground state and specifically to $^6A_1$ ground states of d^5 systems. Fine structure is due primarily to spin-orbit interaction and the external ligand field. It can be described with an effective spin Hamiltonian and an effective spin basis whose dimension corresponds to the degeneracy of the ground state.[4]

An effective spin Hamiltonian is invariant under a point group G and is usually formulated with operator equivalents defined in terms of effective spin operators. Although this Hamiltonian is not normally[4] expanded in terms of linear combinations of tensor operators symmetry adapted to G, as is the crystal field Hamiltonian,[5,6] such a procedure is ap-

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0020-1669/81/1320-3109$01.25/0

propriate and has been forumlated.[6] Examples for which an expansion using symmetry adapted tensor operators will result in an effective spin Hamiltonian indistinguishable in form from that generated with the traditional approach include G = D_{3h}, D_{5h}, and D_{6h} as well as O_h and T_d.

Considering only the fine structure component of an effective spin Hamiltonian for d^n systems, we project[5,6]

$$H_{\mathrm{FS}} = \sum_K A^{K,\tau}|\tau \mathrm{A}_1\mathrm{a}_1|^K_{\mathrm{G}} \qquad (1)$$

where the $|\tau \mathrm{A}_1\mathrm{a}_1|^K_{\mathrm{G}}$ are orthonormal linear combinations of tensor operators of rank K which transform as the A_1 (or A_{1g}) irreducible representation of the point group G. The requirement that H_{FS} be Hermitian and invariant under the time reversal operator restricts K to even values.[6] The coefficients $A^{K,\tau}$ serve as empirical symmetry parameters. The index τ distinguishes $|\tau \mathrm{A}_1\mathrm{a}_1|^K_{\mathrm{G}}$ projected from tensor operators of the same rank. The effective spin of the ground state determines the maximum K value and hence the number of symmetry parameters which can arise. For a $^6\mathrm{A}_1$ ground state the effective spin $S = {}^5/_2$ and for D_{3h} symmetry (and D_{nh}, $n \geq 5$)

$$H_{\mathrm{FS}} = 3D|\mathrm{A}_1|^2_{D_{3h}} + F/180|\mathrm{A}_1|^4_{D_{3h}} \qquad (2)$$

where

$$\begin{aligned} |\mathrm{A}_1|^2_{D_{3h}} &= \mathcal{O}^0_2(S) \\ &= 3S_z^2 - S(S+1) \qquad (3) \end{aligned}$$

$$\begin{aligned} |\mathrm{A}_1|^4_{D_{3h}} &= \mathcal{O}^0_4(S) \\ &= 35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6(S+1) + 3S^2(S+1)^2 \qquad (4) \end{aligned}$$

and the $\mathcal{O}^0_K(S)$ are operator equivalents which transform in the same way as the corresponding tesseral harmonics.[4,5,7] Empirical symmetry parameters are named $3D$ and $F/180$ in agreement with previous definitions.[4] Zero-field doublets for $S = {}^5/_2$ lie at

$$\mathrm{Eng}(\Gamma_7) = -{}^8\!/_3D + {}^2\!/_3F \qquad \mathrm{Eng}(\Gamma_8) = {}^{10}\!/_3D + {}^1\!/_3F \qquad \mathrm{Eng}(\Gamma_9) = -{}^2\!/_3D - F \qquad (5)$$

and are identified by irreducible representations of the double group of D_{3h}. We note that no fine structure is predicted for $S = {}^1/_2$ systems and that fine structure is described with the parameter D alone for $S = 1, {}^3/_2$. Similarly we find that H_{FS} for O_h or T_d symmetry has one term projected from tensor operators of rank 4 which gives rise to the previously defined[4] fine structure parameter a. Hence fine structure arises for octahedral or tetrahedral $^6\mathrm{A}_1$ ground states but not for $S = {}^1/_2$, 1, or $^3/_2$ systems.

While the relative magnitudes of D and F remain to be established by experiment for D_{3h} systems, we note that F has been neglected in the fitting of ESR parameters for the tris(acetylacetonato)manganese(II) anion, an essentially trigonal-prismatic d^5 system with a $^6\mathrm{A}_1$ ground state.[8] This experimental result illustrates that F, which appears only along the diagonal of the representation of H_{FS}, will be most obvious when it is substantially larger than the uncertainty in the $H\|z$ bands. Empirical ligand field calculations which include spin-orbit interaction and the effects of an external magnetic field and which are complete within the d^5 basis indicate that F will often be smaller than D.[9] The calculations predict that D is normally negative for both trigonal-prismatic and trigonal-bipyramidal $^6\mathrm{A}_1$ ground state d^5 systems, in agreement with experimental results for the tris(acetylacetonato)manganese(II) anion. The effect of F on ESR resonance positions is emphasized in Figures 1 and 2 where resonance positions for allowed transitions (ΔM_S =]) are plotted as solid lines for $F/D = 2$ and the external magnetic field parallel or perpendicular to the threefold rotation axis. Dotted lines illustrate how resonance positions shift when F is set equal to zero, and further calculations demonstrate that, as F ranges, resonance positions shift smoothly as indicated in Figures 1 and 2. The figures, which correspond to $g = 2.00$ and $h\nu = 0.310$ cm^{-1},

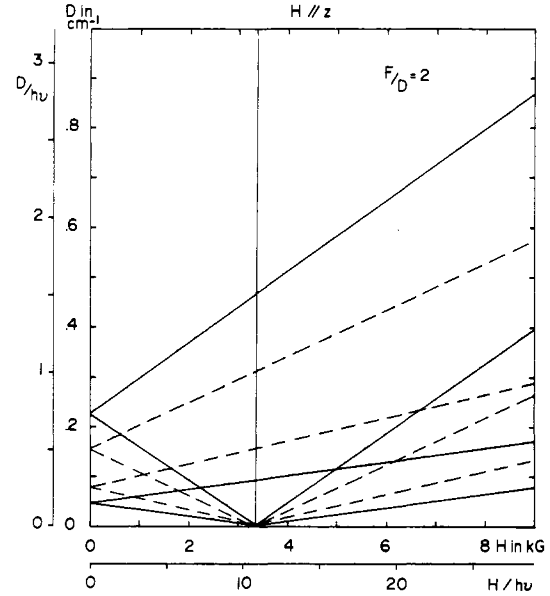

Figure 1. Allowed ESR resonance positions for D_{3h} symmetry and $S = {}^5/_2$ with the external magnetic field parallel to the threefold molecular symmetry axis ($\Delta M = 1$). Solid lines correspond to $F/D = 2$, and dashed lines correspond to $F = 0$.

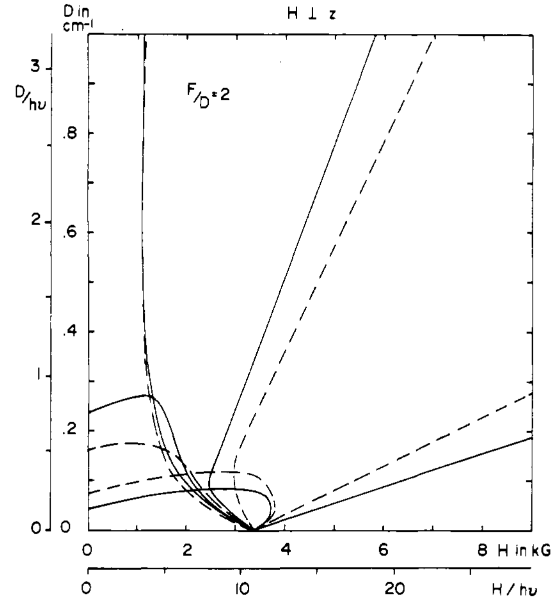

Figure 2. Allowed ESR resonance positions for D_{3h} symmetry and $S = {}^5/_2$ with the external magnetic field perpendicular to the threefold molecular symmetry axis. Solid lines correspond to $F/D = 2$, and dashed lines correspond to $F = 0$.

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are compatible with those of previous workers for other symmetries.[10] The authors will be pleased to furnish larger versions of the figures upon request.

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Reaction of Electrophiles with Metal(II) Complexes of Formamides

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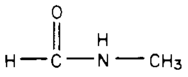
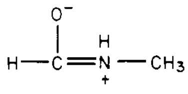
A number of years ago, we reported the preparation of metal(II) complexes of *N*-methylformamide (NMF).[1] These were perchlorate and/or nitrate complexes of Mg, Mn, Co, Ni, Cu, and Zn. All are octahedral except Cu which is approximately square planar, and none contain coordinated anion. The ligand is coordinated to the metal via the oxygen, which will increase the importance of resonance from II relative to I.



$\mathrm{H-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-CH_3}$

I



$\mathrm{H-\overset{\overset{O^-}{|}}{C}=\underset{+}{\overset{H}{N}}-CH_3}$

II

Since NMF can be dehydrated by various electrophiles to produce isocyanides,[2] it was anticipated that metal complexes of NMF should be more reactive than the free ligand. This was not the case, however. None of the complexes reacted with tosyl chloride, which does react with NMF itself. Although the lack of reactivity of the octahedral complexes could be explained on the basis that attack at oxygen is sterically hindered, such is not the case for the Cu complex. therefore, work was continued in order to determine more precisely the effect of metal ions on the reactivity of formamides, and we report here the results of those studies.

Experimental Section

Preparation of Formamide Complexes. The synthesis of all of the metal chloride complexes of NMF as well as the ZnI$_2$ complex has been previously reported.[3] The preparation of the nitrate and perchlorate complexes is described in ref 1. The NMF complex of ZnBr$_2$ was prepared by dissolving 0.01 mol of the hydrated metal salt in 5 mL of NMF, then adding 5 mL of ethylorthoformate (EOF), and stirring about 1 h. Addition of 50 mL of ether produced an oil. The ether was decanted off, and the oil was triturated with another 50 mL of ether and then 25 mL of petroleum ether (30–60 °C), resulting in the formation of a white paste. After decantation the paste was dissolved in 2 mL of 1-butanol, followed by addition of 50 mL of ether. Upon stirring, the white, cloudy oil phase became a sticky solid and finally a fine white powder. The solid was filtered, washed with ether, and dried in a vacuum desiccator over P$_2$O$_5$. Anal. Calcd for ZnBr$_2$(NMF)$_{2.3}$: C, 15.4; H, 3.2; N, 8.9; Br, 44.2; Zn, 18.1. Found: C, 14.8; H, 3.2; N, 9.1; Br, 43.0; Zn, 17.1.

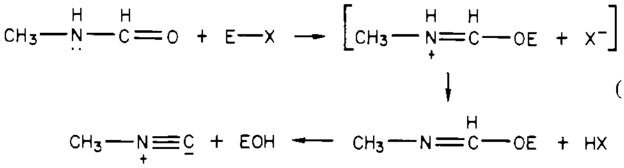
Preparation of Thioformamide ZnCl$_2$ Complexes. The *tert*-butylthioformamide (TBTF) was prepared by dissolving 5.0 mL of *tert*-butylformamide in 50 mL of benzene, adding 20 g of P$_2$S$_5$, and refluxing for 1 h with vigorous stirring. The benzene was stripped off, the remaining yellow solid treated with 50 mL of cold 5% NaOH, and the suspension stirred for 1 h in an ice bath. An additional 1 mL of cold 10% NaOH was added, and the solid was filtered off, washed with water, and dried in a vacuum desiccator. The product was recrystallized from 200 mL of hexane–benzene and separated as 2.5 g of fine white needles, mp 121–122 °C (reported value, 124–125 °C).[4] Anal. Calcd for C$_5$H$_{11}$NS: C, 50.9; H, 9.4; S, 27.2. Found: C, 51.1; H, 9.4; S, 27.1. The *N*-methylthioformamide (NMTF) was prepared according to the procedure of Willstatter and Wirth.[5] Hydrated ZnCl$_2$ (3 mmol) was dissolved in 5 mL of ethanol and 1 mL of EOF. After stirring for 1 h, thioformamide (10 mmol) was added, the solution stirred for a few hours and filtered, and 25 mL of ether added to the filtrate. After stirring for 1 h, the white solid was filtered off, washed with ether, and dried as above. Anal. Calcd for ZnCl$_2$(NMTF)$_2$: C, 16.8; H, 3.5; N, 9.8; Cl, 24.8; Zn, 22.8; S, 22.3. Found: C, 17.2; H, 3.6; N, 9.5; Cl, 24.5; Zn, 22.5; S, 22.1. Anal. Calcd for ZnCl$_2$(TBTF)$_2$: C, 32.4; H, 5.9; N, 7.6; Cl, 19.1; Zn, 17.7; S, 17.3. Found: C, 30.1; H, 5.7; N, 7.0; Cl, 21.8; Zn, 19.4; S, 14.9.

Reaction Studies. Semiquantitative studies of the reaction of the metal complexes with the various electrophiles were performed in the apparatus employed by Crabtree, Poziomek, and Hoy[6] for the colorimetric detection of alkyl isocyanides. The reagents were mixed and allowed to react at room temperature, and the presence of isocyanide was determined by a white to blue color change in the detector tube. The yield of isocyanide can be semiquantitatively estimated from the intensity of the color. The lowest detectable amount of methyl isocyanide is approximately 0.1 μg.

Analyses. All elemental analyses were performed by the Analytical Branch, Chemical Systems Laboratory, Aberdeen Proving Ground, MD.

Results and Discussion

The mechanism in the dehydration of the formamide by an electrophile (EX) is undoubtedly a nucleophilic attack by the formyl oxygen followed by an elimination (eq 1). Coordination of the formamide oxygen by metal, as mentioned above, should increase the importance of resonance form II relative to I. This should weaken the C–O bond and also cause the oxygen to become more negative, causing an enhancement in reactivity. However, the reverse was observed.[1] The octahedral nitrate and perchlorate salts of M(NMF)$_6^{2+}$ did not react with tosyl chloride, which itself does react directly with NMF. The lack of reactivity of the octahedral complexes can be attributed to steric hindrance of the approach of the sulfur atom of the tosyl chloride to the formamide oxygen. However, in the (approximately) square-planar copper complex,[1] no such hindrance exists.



(1)

Following the preparation of the nitrate and perchlorate complexes of NMF, a number of chloride complexes were

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