were obtained cryoscopically in benzene. A No. 8163B platinum resistance thermometer and a Mueller temperature bridge, Leeds and Northrup Model No. 8069, were used to measure the temperature differences. The results are listed in Table III.

Spectra.—Temperature-dependent nuclear magnetic resonance spectra were obtained on a Varian A-60R high-resolution spectrometer. The spectra were run in deuteriochloroform down to −60° and in toluene down to −80°. Proton nuclear magnetic spectra were obtained on a Varian A-60 spectrometer. Tetramethylsilane was used as a standard. Results are listed in Table I.

A Perkin-Elmer Model 21 spectrophotometer was used to obtain the infrared spectra. Mulls of Nujol and Fluorolube were employed for the solids. Solution spectra were obtained in benzene and methylene chloride. The results are listed in Table II.

Melting Points.—Melting points (Table III) were obtained on a Perkin-Elmer Model DSC-1 differential scanning calorimeter under an argon atmosphere.

Acknowledgment.—We wish to thank the microanalytical group at Olin Mathieson Chemical Corp., headed by Dr. R. C. Rittner, for their expert handling of these samples and Mr. D. Vickers for his assistance in obtaining and interpreting the nuclear magnetic resonance data. Also, we wish to acknowledge the interesting and helpful discussions with Dr. T. L. Heying and Mr. J. J. Pitts. This work was supported in part by the Office of Naval Research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

Nuclear Resonance Studies of Vanadium(III) Complexes. I. Stereochemistry and Electron Delocalization of Tris β-Diketonates

BY F. RÖHRSCHEID, R. E. ERNST,[1] AND R. H. HOLM[2]

Received February 17, 1967

The isotropic proton hyperfine contact shifts of a series of five tris(β-diketonate)vanadium(III) complexes, $V(R_\alpha COCR_\beta COR_\gamma)_3$, have been measured in order to determine structures in solution and to define qualitatively the mode of unpaired spin delocalization predominantly responsible for these shifts. In addition to the known complexes $V(acac)_3$ ($R_\alpha = R_\gamma = CH_3$, $R_\beta = H$) and $V(mmm)_3$ ($R_\alpha = R_\beta = R_\gamma = CH_3$), three complexes having unsymmetrical chelate rings, $V(mhh)_3$ ($R_\alpha = R_\beta = H$, $R_\gamma = CH_3$), $V(mmh)_3$ ($R_\alpha = H$, $R_\beta = R_\gamma = CH_3$), and $V(tfac)_3$ ($R_\alpha = CH_3$, $R_\beta = H$, $R_\gamma = CF_3$), all prepared for the first time, were examined. The *cis* and *trans* isomers of the latter three complexes are readily detected by virtue of their considerably different contact interactions. The isomers of $V(tfac)_3$ are not formed in statistical amounts. From consideration of the signs of the contact shifts of protons and methyl groups of the chelate rings and by comparison of these shifts with calculated spin density distributions for the ligands treated as π radicals, it is concluded that metal-to-ligand parallel spin transfer is the principal mode of spin delocalization. The contact shifts of solutions of $V(H_2O)_6^{3+}$ have been measured and the results interpreted in terms of ligand-to-metal parallel spin transfer by π bonding.

Introduction

A recent investigation of the proton magnetic resonance spectra of paramagnetic tris acetylacetonates by Eaton[3] has revealed that of all trivalent ions of the first transition series, vanadium(III) produced the narrowest line width of the chelate ring methyl signal (~25 cps at 60 Mc). The observation of nuclear resonances in complexes such as these indicates that $1/T_1 >> A_i$, the usual criterion for such observation in paramagnetic compounds,[4] where T_1 is the electronic relaxation time of the coordinated metal ion and A_i is the electron–nuclear coupling constant for the ith nucleus. While T_1 for a given metal ion is certainly dependent upon the details of its structural and electronic environment, Eaton's observation implies that reasonably well-resolved nuclear resonance spectra might be obtainable for vanadium(III) complexes similar to acetylacetonates, and possibly for vanadium(III) complexes in general.

Compared to the paramagnetic complexes of other metals,[5] especially those of Co(II) and Ni(II), there have been only a few reports of the nuclear resonance spectra and attendant isotropic contact shifts of vanadium(III) complexes, or of paramagnetic vanadium complexes in any other formal oxidation state. Contact shifts have been observed for polycrystalline vanadocene[6] and for vanadocene[7] and 1,1′-dimethylvanadocene[8] in solution, and the proposed interpretation[9] of the contact shifts in vanadocene has recently been questioned.[8] In one of the earliest demonstrations by nuclear resonance of spin delocalization in metal complexes, Forman, Murrell, and Orgel[10]

---

[1] National Institutes of Health Predoctoral Fellow.

[2] Alfred P. Sloan Foundation Fellow; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

[3] D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

[4] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

[5] For a general review of the nuclear magnetic resonance properties of paramagnetic compounds, see D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965).

[6] H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **28**, 749 (1958).

[7] H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *Z. Naturforsch.*, **21b**, 809 (1966); *J. Organometal. Chem.* (Amsterdam), **7**, 105 (1967).

[8] M. F. Rettig and R. S. Drago, *Chem. Commun.*, 891 (1966).

[9] D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

[10] A. Forman, J. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, **31**, 1129 (1959).

found that in the spectra of tris(acetylacetonato)vanadium(III) and tris(3-methylacetylacetonato)vanadium(III) the contact shifts of 3-H and 3-CH_3 are of opposite sign, in agreement with predominant π-spin delocalization in the chelate rings. No contact shifts were observed for dimeric, weakly paramagnetic vanadium(III) acetate.[11] The probable mode of spin delocalization in tris(aminotroponeiminato)vanadium(III) complexes inferred from proton resonance measurements has been briefly mentioned.[12] Finally, no signals were observed at room temperature for vanadyl acetylacetonate in solution,[3] a result which is not surprising inasmuch as the paramagnetic resonance of this complex is readily detected under the same conditions.[13]

By way of assessing the utility of contact shifts in vanadium(III) complexes for the purpose of investigating stereochemistry and, possibly, pathways of spin delocalization, we have carried out a rather broad investigation of the proton resonance spectra of chelated complexes containing conjugated ligand systems. In all cases spectra of useful resolution have been obtained from which conclusions may be drawn concerning stereochemistry and the qualitative nature of unpaired spin delocalization. Herein we report the results of our investigation of β-diketone complexes. Future articles will deal with complexes of β-ketoamines, salicylaldehydes, and salicylaldimines.[14]

Experimental Section

Preparation of Complexes.—Because of the considerable sensitivity of vanadium(III) β-diketonates to oxidation, particularly in the presence of water, all operations were carried out under rigorously dry and oxygen-free nitrogen in closed systems. Sublimations were performed in an evacuated glass tube without a cold finger. All complexes were stored under dry nitrogen.

Tris(3-oxobutanalato)vanadium(III), V(mhh)$_3$.—3-Oxobutanalatosodium[15] (6.2 g, 57 mmoles) was dissolved in 50 ml of water. A solution of 3.0 g (19 mmoles) of vanadium trichloride in 50 ml of water was added with stirring. After 1 hr of stirring the brown precipitate was collected by filtration, washed with water, and dried *in vacuo*. The product was purified by two sublimations at 145° (10^{-2} mm); dark brown crystals were obtained. *Anal.* Calcd for $C_{12}H_{15}O_6V$: C, 47.07; H, 4.94. Found: C, 46.97; H, 4.94.

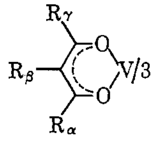
Tris(2-methyl-3-oxobutanalato)vanadium(III), V(mmh)$_3$.—An aqueous solution of 8.5 g (70 mmoles) of 2-methyl-3-oxobutanalatosodium[16] was treated with a solution of 3.0 g (19 mmoles) of vanadium trichloride in 40 ml of water. A tarry brown precipitate formed immediatedly. Sodium carbonate (1 g) was added and the solution was then heated to 90° to complete the reaction. After cooling to room temperature the crude product was collected by filtration, dried, and recrystallized from a small volume of heptane. The slightly oily product which resulted was sublimed three times at 160° (10^{-3} mm). The final product was obtained as brown crystals. *Anal.* Calcd for $C_{15}H_{21}O_6V$: C, 51.73; H, 6.08. Found: C, 51.72; H, 5.95.

Tris(1,1,1-trifluoropentane-2,4-dionato)vanadium(III), V(tfac)$_3$.—This complex was prepared using trifluoroacetylacetone and a procedure analogous to that for the preparation of vanadium(III) acetylacetonate.[17] The pure product was obtained as brown crystals after two sublimations at 160° (10^{-3} mm). *Anal.* Calcd for $C_{15}H_{12}F_9O_6V$: C, 35.31; H, 2.37. Found: C, 35.26; H, 2.44.

Nuclear Resonance Measurements.—Proton resonance spectra were measured with a Varian HR-100 spectrometer using $CDCl_3$ solutions with tetramethylsilane as an internal reference. Fluorine resonance spectra were obtained on a Varian HR-60 spectrometer operating at 56.4 Mc/sec using $CHCl_3$ solutions with $CFCl_3$ as an internal reference. Oxygen-free aqueous solutions of vanadium trichloride in 0.3 *M* $HClO_4$ were examined at 60 Mc/sec using dioxane as an internal reference. Contact shifts were calculated from the relation $\Delta\nu_i = \nu_i(\text{complex}) - \nu_i(\text{dia})$, where ν_i(dia) values for the following complexes were taken from the indicated reference compounds: V(mhh)$_3$, γ-CH_3 and β-H from Co(acac)$_3$, α-H from crotonaldehyde; V(mmh)$_3$, γ-CH_3 and β-CH_3 from tris(3-methylacetylacetonato)cobalt(III), α-H from crotonaldehyde; V(tfac)$_3$, from Co(tfac)$_3$.[18] The ^{19}F resonance of Htfac occurs 4368 cps upfield from $CFCl_3$. The separation between the protons of dioxane and water is 62 cps at 34°.

Results and Discussion

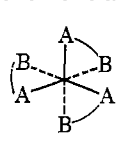
The complexes investigated are of general type I and are designated according to chelate ring substituents as indicated below. The complexes are of course all paramagnetic with triplet ground states. For example, the magnetic moment of crystalline V(tfac)$_3$ is 2.78 BM at 25°, essentially identical with the moment of V(acac)$_3$ at the same temperature.[19]



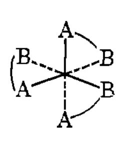
I

$R_\alpha = R_\gamma = CH_3, R_\beta = H$: V(acac)$_3$
$R_\alpha = R_\beta = R_\gamma = CH_3$: V(mmm)$_3$
$R_\alpha = R_\beta = H; R_\gamma = CH_3$: V(mhh)$_3$
$R_\alpha = H; R_\beta = R_\gamma = CH_3$: V(mmh)$_3$
$R_\alpha = CH_3, R_\beta = H, R_\gamma = CF_3$: V(tfac)$_3$

Geometrical Isomerism.—Tris-chelate complexes containing symmetrical chelate rings possess idealized D_3 symmetry, in which case those ring substituents of the same type and having the same location in each chelate ring are equivalent, as for V(acac)$_3$ and V(mmm)$_3$. However, if the chelate rings are unsymmetrical ($R_\alpha \neq R_\gamma$), as in V(mmh)$_3$, V(mhh)$_3$, and V(tfac)$_3$, *cis* (II) and *trans* (III) isomers are possible in which A and B convey the ring asymmetry. The *cis* isomer has a C_3 axis whereas the *trans* isomer possesses no symmetry at all. Thus, in principle, a given substituent on each chelate ring in III will produce a separate resonance, but only a single resonance for corresponding



II



III

---

(11) N. N. Greenwood, R. V. Parish, and P. Thornton, *J. Chem. Soc., Sect. A*, 320 (1966).

(12) D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, **43**, 392 (1965).

(13) I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963); D. Kivelson and S.-K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).

(14) F. Röhrscheid, R. E. Ernst, and R. H. Holm, to be published.

(15) J. P. Collman, E. T. Kittleman, W. S. Hurt, and N. A. Moore, *Inorg. Syn.*, **8**, 144 (1966).

(16) O. Diels and K. Ilberg, *Ber.*, **49**, 158 (1916).

(17) A. Rosenheim, E. Hilzheimer, and J. Wolf, *Z. Anorg. Allgem. Chem.*, **201**, 168 (1931).

(18) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 500 (1963).

(19) B. N. Figgis, J Lewis, and F. Mabbs, *J. Chem. Soc.*, 2480 (1960).

substituents will occur in II. In a number of diamagnetic β-diketones[18,20,21] and Schiff base complexes,[22,23] principally those of Co(III), resolvable chemical shift differences have been found in the *trans* form, thereby permitting its unambiguous detection alone or in the presence of the *cis* isomer.

The proton resonance spectra of the three complexes capable of *cis–trans* isomerism are shown in Figures 1–3. Contact shift data are set out in Table I. Statistical formation of the geometrical isomers will result in a *cis–trans* ratio of 1:3 and, for a given ring substituent, four signals of equal intensity. In two of the complexes, $V(mhh)_3$ and $V(mmh)_3$, essentially statistical mixtures of isomers exist in the purified products. Integration of signals by planimetry shows that in these cases the γ-CH_3, β-H, and β-CH_3 signals occur as four distinct features of equal intensity. (Because of their excessive widths the α-H signals of $V(mhh)_3$ and $V(mmh)_3$ cannot be completely resolved.) The ^{19}F spectrum of $V(tfac)_3$ reveals four signals (*cf.* Figure 1) of relative intensity 1:1:1:0.5, with that at +2011 cps being due to the *cis* form. The *cis*:*trans* ratio obtained from the relative intensities is 1:6. With this information it is possible to assign all signals in the pmr spectrum as shown in Figure 1. Because of the essentially statistical *cis*:*trans* ratio found with $V(mhh)_3$ and $V(mmh)_3$, it is not possible to assign signals to a particular isomer in these cases.

In seeking to ascertain structural differences and to make stereochemical assignments based on chemical shift effects, a conspicuous advantage of dealing with paramagnetic complexes with sufficiently narrow line widths is the considerable amplification of chemical shifts produced by contact interactions This situation is dramatically exemplified by a comparison of the spectra of $V(tfac)_3$ and $Co(tfac)_3$, whose signals have been completely identified by means of chromatographic separation of the *cis* and *trans* isomers.[18] At 100 Mc in $CDCl_3$ solution at ambient temperature the total spread of the pmr spectrum of $Co(tfac)_3$ is 368 cps, whereas for $V(tfac)_3$ it is 4552 cps. Further, the spread in signals of a given ring substituent for $Co(tfac)_3$ and $V(tfac)_3$, respectively, in their *trans* forms is as follows: α-CH_3, 5, 1673 cps; β-H, 5, 3229 cps; γ-CF_3 (56.4 Mc), 10, 868 cps. Because of the contact effect it is possible to resolve all signals of a given substituent in the *cis* and *trans* forms of a wide variety of tris-chelate vanadium(III) complexes[14]. Certain chemical shift differences in the *trans* forms of some diamagnetic tris-benzoylacetonato complexes have been found (at 60 Mc) to be beyond the limit of resolution.[20]

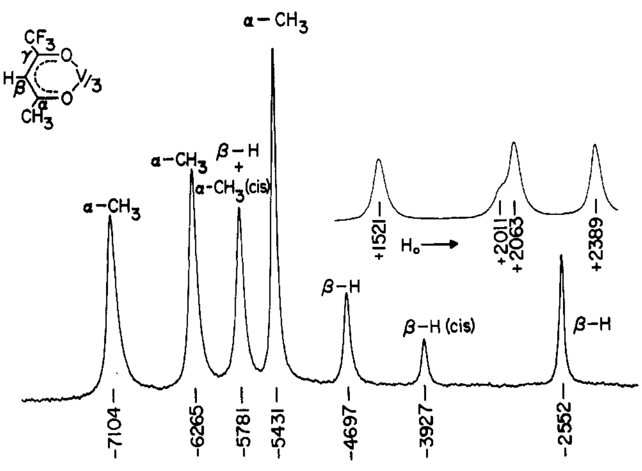


Figure 1.—Nuclear resonance spectra of $V(tfac)_3$ in $CDCl_3$ solution at room temperature: bottom, pmr spectrum; insert, ^{19}F spectrum. Frequencies (cps) are the chemical shifts.

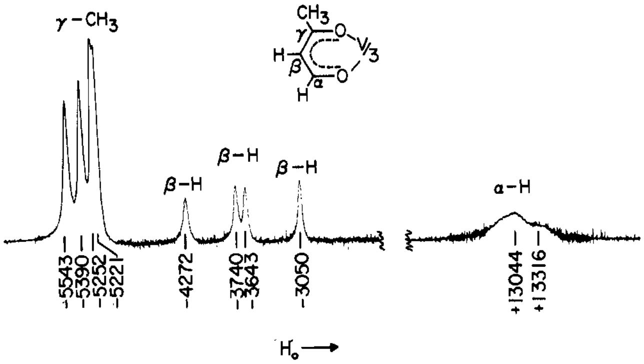


Figure 2.—Proton resonance spectrum of $V(mhh)_3$ in $CDCl_3$ solution at room temperature. Frequencies (cps) are the chemical shifts.

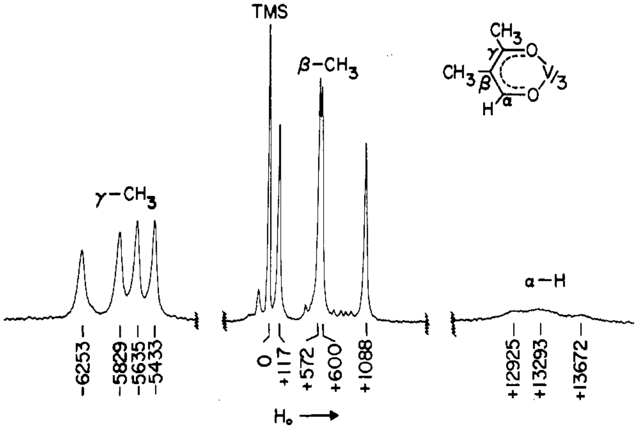


Figure 3.—Proton resonance spectrum of $V(mmh)_3$ in $CDCl_3$ solution at room temperature. Frequencies (cps) are the chemical shifts.

Spin Delocalization in $V(H_2O)_6^{3+}$.—Among the more conventional complexes whose proton contact shifts have been analyzed, the octahedral and pseudo-octahedral complexes of V(III) are distinguished by possessing a less than half-filled set of dπ orbitals. In the event that ligand-to-metal π-spin transfer is the dominant spin-delocalization mechanism, the net spin transferred is expected to be parallel to the spin of the metal electrons because of exchange effects. A case in point is $V(H_2O)_6^{3+}$, whose contact shifts have been determined in 0.3 *M* $HClO_4$ and are given in Table II. The compositions of the solutions measured were checked by a comparison of their electronic spectra with those obtained by Furman and Garner on elec-

---

(20) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).

(21) R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

(22) A. Chakravorty and R. H. Holm, *ibid.*, **3**, 1521 (1964).

(23) A. Chakravorty and K. C. Kalia, *ibid.*, **6**, 690 (1967).

TABLE I

CONTACT SHIFTS OF TRIS(β-DIKETONE)VANADIUM(III) COMPLEXES IN $CDCl_3$ SOLUTION AT 100 MC/SEC

Complex	$\Delta\nu_i$, cps[a]		
	R_α	R_β	R_γ
$V(acac)_3$[b]	−4,351	−3455	−4351
$V(mmm)_3$[c]	−4,367	+506	−4367
cis,trans-$V(mhh)_3$	+14,266[d]	−3720	−5321
	...	−3188	−5168
	...	−3091	−5030
	+13,994[d]	−2498	−4999
cis,trans-$V(mmh)_3$	+14,622[d]	+1278	−6034
	...	+790	−5610
	...	+762	−5416
	+13,875[d]	+307	−5214
cis-$V(tfac)_3$	−5,539	−3322	−2357[e]
trans-$V(tfac)_3$	−6,862	−5176	−2847[e]
	−6,023	−4092	−2305[e]
	−5,189	−1947	−1979[e]

[a] All data refer to ~30°. [b] Data from ref 3 converted to 100 Mc. [c] Data from ref 10 converted to 100 Mc. [d] Limits of broad, poorly resolved signal. [e] ^{19}F data at 56.4 Mc/sec.

TABLE II

PROTON CONTACT SHIFT DATA FOR HEXAAQUOVANADIUM(III) CHLORIDE

g of VCl_3	g of H_2O added	$10^2 \cdot f_{com}$[a]	$-\Delta\nu_{obsd}$, cps	$10^{-3}(-\Delta\nu_{com})$, cps
0.2369	5.5562	2.930	392	13.38
0.2079	7.4895	1.907	258	13.53
0.2591	11.4548	1.554	206	13.26
0.1859	10.4329	1.224	165	13.48
0.1702	21.7942	0.536	73	13.62

[a] f_{com} is the fraction of water complexed and is calculated using the assumption that V(III) is six-coordinate. [b] $\Delta\nu_{com}$ is the proton shift calculated for the complexed water relative to uncomplexed water assuming rapid exchange.

trolytically prepared acidic solutions of vanadium(III) perchlorate free of hydrolysis products.[24] Maxima were observed at 17,000 (ϵ 6.3) and 25,000 cm^{-1} (ϵ 9.4). These frequencies together with the ratio of extinction coefficients (0.67) are in nearly exact agreement with the data previously reported.[24] Further, the intensities in the 20,000–25,000-cm^{-1} region give no indication of the presence of chloroaquo species, whose band positions in this range have been measured or calculated.[25] The proton resonance results and the following discussion complement two recent reports of the contact shifts of hexaaquometal ions.[26,27]

For consistency the data were treated in the manner of Wayland and Rice.[27] Coupling constants were obtained from the reaction

$$\frac{\Delta\nu_{com}}{\nu} = -A\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g|\beta|S(S+1)}{3kT} \qquad (1)$$

in which $\Delta\nu_{com}$ is the contact shift of the coordinated water protons assuming a coordination number of six and A is the electron–nuclear hyperfine coupling constant. The remaining symbols have their usual meanings.[27] The g value was obtained from the susceptibility of vanadium alum in dilute acid solution[19] using the relation $g = \mu_{eff}[S(S+1)]^{-1/2}$. The contact shifts are linear with concentration of V^{3+} and are negative, leading to a positive coupling constant $A/h = 32.1 \times 10^5$ cps. The predominant mode of spin delocalization has been inferred previously from the signs of coupling constants or contact shifts using a simple molecular orbital model.[26,27] The model may be simplified to the interaction of a single water molecule and the metal ion[26] as is done here. Taking the metal at the origin, the water molecule in the yz plane, and the oxygen lone pair along the z axis, the following ligand orbitals can mix with the $d\pi$ metal orbitals: (i) an orbital of b_1 symmetry consisting mainly of the oxygen p_x orbital and (ii) an orbital of b_2 symmetry consisting of a linear combination of the oxygen p_y and hydrogen 1s functions. In the latter case any spin imbalance would result in a direct contact interaction, whereas in the former case the contact interaction would be of the indirect π–σ type[4] and would lead to a shift of the opposite sign owing to the negative sign of the hyperfine splitting constant for an O–H fragment ($Q_{OH} = -27$ gauss in the hydroxyl radical[28]). In all aquo ions previously studied having incomplete t_{2g} subshells the $d\pi$ orbitals are at least half-filled, resulting in net antiparallel (β) ligand-to-metal spin transfer to these orbitals *via* π bonding and a partial α spin on the ligand. Because in all of these cases the resulting contact shifts were found to be negative, the predominant spin-delocalization path involves the b_2 orbital of water. However, in octahedral V(III) it is reasonable to assume *net* α-spin transfer to maintain maximum spin multiplicity on the metal, thereby leaving *net* β spin on the ligands. If the same delocalization path predominates in $V(H_2O)_6{}^{3+}$, a negative coupling constant (positive contact shift) is expected. Because a negative contact shift is observed, it is inferred that the main path of π-spin delocalization proceeds *via* the b_1 orbital of water and the attendant indirect contact interaction.

Spin Delocalization in Tris β-Diketonates.—Previous analyses of the contact shifts of chelate complexes having unsaturated ligand systems have frequently led to a determination of the π-spin densities ρ_{C_i} of the ring carbon atoms by the use of coupling constants from eq 1, or its equivalent, in the familiar relation $a_i = Q\rho_{C_i}$[4]. Q is the hyperfine splitting constant for an aromatic fragment such as $\dot{C}$–H, $\dot{C}$–CH_3, or $\dot{C}$–CF_3. This procedure is strictly correct if, and only if, the hyperfine interactions derive solely from π (as opposed to σ) spin densities and pseudo-contact effects are negligible, assumptions which have been pragmatically useful in analyses of contact shifts and spin-density distributions in pseudo-tetrahedral bis-chelate nickel(II) complexes[12,29] despite the lack of strict separation of σ and π bonding by symmetry. In tris chelates separation of metal–ligand bonding into σ and π components is also

---

[24] S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

[25] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **3**, 1173 (1964).

[26] Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

[27] B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **5**, 54 (1966).

[28] H. E. Radford, *Phys. Rev.*, **126**, 1035 (1963).

[29] (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); (b) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964); (c) G. W. Everett, Jr., and R. H. Holm, *ibid.*, **87**, 2117 (1965).

symmetry disallowed, with the result that detailed, quantitative analysis of spin density distributions from measured contact shifts is not possible, a conclusion which follows readily from consideration of a simple molecular orbital bonding model of tris acetylacetonates.[30]

Despite the fact that strictly correct π-spin densities cannot be obtained from experimental data, we have attempted to assess more fully than has been done previously the possible predominance of one mode of spin delocalization over another, *i.e.*, π over σ delocalization or *vice versa.* The approach follows from the work of Eaton[3] and the single observation of Forman, Murrell, and Orgel,[10] mentioned above, that the signs of the contact shifts of $R_\beta = H$ and CH_3 in V(acac)$_3$ and V-(mmm)$_3$, respectively, are of opposite sign (*cf.* Table I). Because Q_{CH} is negative and Q_{CCH_3} is positive (although its apparent value is variable[29b,31]), the behavior of the contact shifts reflects predominant π delocalization. Reference to Table I reveals that this same behavior is observed for the R_β substituent in the pairs V(acac)$_3$–V(mmh)$_3$ and V(mmh)$_3$–V(mhh)$_3$. A similar reversal of sign occurs for the contact shift of the R_α substituent in the pairs V(acac)$_3$–V(mhh)$_3$ and V-(mmm)$_3$–V(mmh)$_3$. Available evidence from contact shift studies suggests that spin is transferred from an aromatic carbon atom to the fluorine atoms of a directly bonded CF_3 group by a hyperconjugative mechanism.[32] Q_{CCF_3}, like Q_{CCH_3}, is positive on the basis of presently available values.[32] It is observed that the CH_3 and CF_3 groups in V(acac)$_3$ and V(tfac)$_3$, respectively, have contact shifts of the same sign. These observations taken collectively strongly infer that the predominant mode of spin delocalization involves the local π orbitals of the chelate rings in these complexes. An additional although less strongly supported inference is that pseudo-contact shifts are small compared to the total isotropic shifts. Eaton's previous considerations[3] have shown that replacement of H by CH_3 at a given chelate ring position will not reverse the sign of the pseudo-contact interaction and he has concluded that direct contact interactions are chiefly responsible for the observed shifts. Because the magnitude and sign of the g-tensor anisotropy of V(acac)$_3$ or any other axially symmetric tris-chelate V(III) complex are unknown,[33] no meaningful determination of pseudo-contact shifts is possible at present.

Accepting π delocalization as predominant, it is relevant to inquire which ligand orbitals are involved and therewith the direction and sense of the spin transferred using a model in which the complexes are derived from V^{3+} and three β-diketonate anions. On the basis of magnetic[19] and spectral results,[34] V(acac)$_3$ and the other complexes studied have a ${}^3A$ (e^2) ground state in true (*cis* isomers) or effective (*trans* isomers) C_3 symmetry. Symmetry arguments[3,35] show that in this point group the ligand π orbitals which are likely to be most involved in delocalization of odd spin, *viz.*, the highest filled and lowest unoccupied molecular orbitals (HFMO and LUMO), may mix with the spin-containing metal e orbitals. The possible paths of spin transfer involving the metal e and a orbitals and the HFMO and LUMO in tris acetylacetonates have been set out elsewhere and the conclusion was reached that the metal-to-ligand spin-transfer component of the total delocalization process decreases from Ti(acac)$_3$ to Fe(acac)$_3$.[3] We have reinvestigated the mode of spin delocalization in V(acac)$_3$ and related complexes by a comparison of theoretical spin densities calculated by the Hückel and McLachlan[36] methods (the latter being the simplest method by which to estimate negative spin densities) with measured contact shifts. In the limit of pure π delocalization these quantities are directly proportional according to eq 1.[37] Spin densities of the HFMO and LUMO of acac$^-$ calculated by these procedures and by an SCF treatment[38] are shown in Table III. The parameters used in the Hückel and McLachlan calculations differ from those employed previously.[3,39] The most important difference occurs in the choice of the oxygen Coulomb integral $\alpha_O = \alpha + h\beta$. In an attempt to simulate the effect of the coordinated metal,[30,40] spin densities have been obtained in the interval $1 \leqslant h \leqslant 2$. The other parameters used, which are essentially those suggested by Streitwieser,[40] and the results for $h = 1.5$ are given in Table III. In the McLachlan and Hückel calculations the ratio of spin densities $\rho_{C_\beta}/\rho_{C_{\alpha,\gamma}}$ in HFMO does not vary significantly with h. This ratio in LUMO does change with h, but the variation is of little significance because of the small or zero value of ρ_{C_β}. The most important conclusions are that, independent of h, $\rho_{C_\beta} > \rho_{C_{\alpha,\gamma}}$ in HFMO and $\rho_{C_{\alpha,\gamma}} > \rho_{C_\beta}$ in LUMO.

TABLE III

SPIN DENSITY CALCULATIONS FOR ACETYLACETONATE

	HFMO ($\psi_1^2\psi_2^2\psi_3^1$)		LUMO ($\psi_1^2\psi_2^2\psi_3^2\psi_4^1$)	
Method	α,γ	β	α,γ	β
HMO[a]	+0.0879	+0.4566	+0.4161	0
SCF[b]	+0.019	+0.413	+0.377	0
McLachlan[a,c]	+0.0705	+0.5680	+0.5598	−0.1659

[a] $\alpha_O = \alpha + 1.5\beta$; $\alpha_{C_{\alpha,\gamma}} = \alpha - 0.1\beta$; $\beta_{CO} = 0.9\beta$; $E(\text{HFMO}) = +0.8776\beta$; $E(\text{LUMO}) = -0.5042\beta$. [b] Results from ref 38. [c] $\lambda = +1.2$.

In all cases it is observed that the contact shifts of α,γ-CH_3, γ-CF_3, and β-H are *negative* whereas those of

---

[30] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); **22**, 183 (1961). Examination of the molecular orbital diagrams in these references and in ref 3 may be useful in following the argument concerning spin delocalization given here.

[31] D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).

[32] D. R. Eaton, A. D. Josey, and W. A. Sheppard, *ibid.*, **85**, 2689 (1963).

[33] Paramagnetic resonance of crystalline V(acac)$_3$ could not be observed at liquid nitrogen temperature or above [H. S. Jarrett, *J. Chem. Phys.*, **27**, 1298 (1957)], a result consistent with a short electron spin relaxation time and ready observation of nuclear resonance at room temperature.

[34] T. S. Piper and R. L. Carlin, *Inorg. Chem.*, **2**, 260 (1963).

[35] L. E. Orgel, *J. Chem. Soc.*, 3683 (1961).

[36] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[37] The contact shifts of a typical complex, V(tfac)$_3$, show Curie behavior in the range 218–317°K.

[38] K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963).

[39] The parameters used by Eaton[3] were not explicitly stated but are $\alpha_O = \alpha + 2.6\beta$ and $\beta_{CO} = 1.4\beta$ [from L. E. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951)].

[40] L. S. Forster, *J. Am. Chem. Soc.*, **86**, 3001 (1964).

β-CH_3 and α-H are *positive*. Because $Q_{\mathrm{CH}} \cong 23$ gauss and $Q_{\mathrm{CCH_3}}$ ranges from +5 to +30 gauss,[31] it is quite likely that in general $|Q_{\mathrm{CCH_3}}| \leqslant |Q_{\mathrm{CH}}|$.[41] Experimentally, $|A_{\alpha,\gamma}| > |A_\beta|$ so that it follows that $|\rho_{\mathrm{C}\alpha,\gamma}| > |\rho_{\mathrm{C}\beta}|$. These results are consistent only with the *predominant* mode of delocalization being metal-to-ligand parallel spin transfer, *i.e.*, partial α-spin transfer from the metal e orbitals to appropriate linear combinations of the LUMO's.[42] This conclusion conforms to Eaton's model of spin delocalization in tris acetylacetonates.[3]

Finally, one other observation is worth noting. From the signals of a *trans* isomer it is not generally possible to find constant ratios of $\Delta\nu_\alpha/\Delta\nu_\beta$ and/or $\Delta\nu_\gamma/\Delta\nu_\beta$. This indicates that the spin density distribution conforms to the full molecular asymmetry and not to the simpler situation in which a different total amount of spin is delocalized in each ring but the relative spin densities within each ring are the same.

Acknowledgment.—This research was supported by the Public Health Service through National Institutes of Health Grant GM 12920.

[41] For a complex with structurally related ligands, bis(4-isopropylamino-3-penten-2-onato)nickel(II), $Q_{\mathrm{CCH_3}}$ values at the α and γ positions have been estimated as +15 to +20 gauss.[29c]

[42] It is evident that in some cases the data indicate contributions to the total isotropic shifts from other mechanisms as well. In $V(mhh)_3$ and $V(mmh)_3$ the contact shifts of α-H are too large to be accommodated only by π delocalization in the ring LUMO's. For these complexes it is expected that $\rho_{\mathrm{C}\alpha} \sim \rho_{\mathrm{C}\gamma}$ and, therefore, that $|\Delta\nu_{\alpha\text{-H}}| \sim |\Delta\nu_{\gamma\text{-CH}_3}|$ for π delocalization.[41] The observed $|\Delta\nu_{\alpha\text{-H}}| \sim 3|\Delta\nu_{\gamma\text{-CH}_3}|$ is not consistent with this expectation. Furthermore, the apparent $Q_{\mathrm{CCH_3}}$ value calculated for the β position in $V(mmm)_3$ is only +3.3 gauss, taking $\rho_{\mathrm{C}\beta}$ as that calculated from the β-H shift in $V(acac)_3$, an unusually low value to be obtained by substituting CH_3 for H in a π radical. Possibly spin imbalance in the chelate ring systems, produced by actual delocalization and/or spin polarization, and pseudo-contact interactions also make contributions of as yet undetermined magnitudes.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

An Electrochemical Study of π-Cyclopentadienyl-π-cycloheptatrienylvanadium(0)

BY WILSON M. GULICK, JR.,[1a] AND DAVID H. GESKE[1b]

Received December 14, 1966

Electrochemical and spectrophotometric properties of π-cyclopentadienyl-π-cycloheptatrienylvanadium(0) (CpVTr) have been studied. CpVTr was found to undergo electrooxidation in acetonitrile solution on mercury and platinum electrodes at about 0.19 v *vs.* aqueous saturated calomel electrode. The electron-transfer step of the electrooxidation is reversible, but the cation, $CpVTr^+$, decomposes slowly, even in the temperature range −25 to −40°. The decomposition reaction appears to involve 2 moles of cation which react to regenerate 1 mole of CpVTr. Other decomposition products remain unidentified. Macroscopic electrolyses were employed to generate solutions of the cation, and ultraviolet and visible spectra of this species were secured. Observation of the time dependence of these spectra permitted differentiation of absorbance due to $CpVTr^+$ from that due to decomposition products.

Introduction

The mixed sandwich complex, π-cyclopentadienyl-π-cycloheptatrienylvanadium(0), $C_5H_5VC_7H_7$ (hereafter abbreviated CpVTr), reported by King and Stone[2] is one of the relatively few organometallic complexes which contain a π-C_7H_7 group.[3] Although an infrared study[4] of CpVTr prompted reexamination of the structure of the complex, X-ray crystallography[5] confirmed unequivocally a structure in which both rings are planar, parallel, and symmetrically bound to vanadium as depicted approximately in Figure 1.

We report here an examination of the electrooxidation of CpVTr to $CpVTr^+$ in acetonitrile solution. Since the course of the electrochemical experiments was followed spectrophotometrically, electronic spectra of both CpVTr and $CpVTr^+$ were secured. The relative instability of $CpVTr^+$ required low-temperature electrochemical and spectrophotometric techniques. We regard the acquisition of accurate spectral data for these molecules as of potential use in testing the molecular orbital theory of transition metal π complexes.

Experimental Section

Reagents.—Acetonitrile for use in ultraviolet spectrophotometry (Eastman Spectro Grade) was dried by stirring at ambient temperature with calcium hydride for 12 hr followed by filtration through sintered glass. Such solvent had useful transmission characteristics in the far-ultraviolet region, showing an absorbance of 0.85 at 210 mμ and 1.29 at 200 mμ when observed in a 1-cm cell *vs.* an empty cell. This solvent was considered satisfactory for use to 200 mμ in 0.1-cm cells. For experiments in which ultraviolet transparency was not a critical criterion, acetonitrile (Union Carbide Co.) purified by method E of Coetzee, *et al.*,[6] was employed. 2,2,4-Trimethylpentane (Eastman

---

[1] (a) Abstracted in part from the Ph.D. thesis of W. M. G., Cornell University, 1965; (b) Alfred P. Sloan Foundation Fellow.

[2] R. King and F. Stone, *J. Am. Chem. Soc*, **81**, 5263 (1959). Despite the name chosen by these authors, we regard CpVTr as a more euphonious abbreviation than CpVCh.

[3] The analogous chromium complex, CpCrTr, has been reported by: (a) E. Fischer and S. Breitshaft, *Angew. Chem.*, **75**, 94 (1963); *Chem. Ber.*, **99**, 2905 (1966); (b) R. King and M. Bisnette, *Tetrahedron Letters*, 1137 (1963); (c) R. King and M. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

[4] H. Fritz and R. Schneider, *Chem. Ber.*, **93**, 1171 (1960).

[5] R. Rundle and G. Engebretson, *J. Am. Chem. Soc.*, **85**, 487 (1963).

[6] J. F. Coetzee, G. Cunningham, D. McGuire, and G. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).