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Nuclear Resonance Studies of Vanadium(III) Complexes. II. Synthesis, Stereochemistry, and Electron Delocalization Properties of Tris β-Ketoamines

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The first synthesis of a series of pseudo-octahedral β-ketoamino vanadium(III) complexes is reported. The complexes were prepared by a nonaqueous chelation procedure and are of two structural types. Tris-chelate complexes of general formulation $V[R_\alpha C(NR)CHCOR_\gamma]_3$ (R_α = CH_3, R = CH_3, C_6H_5, R_γ = CH_3, CF_3, C_6H_5) exhibit large proton and fluorine hyperfine contact shifts in their nmr spectra which unambiguously demonstrate exclusive *trans* stereochemistry. The complex formed from the condensate of axial 1,3,5-triaminocyclohexane and acetylacetone also shows large contact shifts and a spectrum consistent with the expected *cis* structure. The *trans* stereochemistry of the tris complexes is sterically forced and is consistent with previous nmr structural determinations of tris(R-N-salicylaldimino)cobalt(III) complexes. Tris(N-methylpyrrole-2-aldimino)vanadium(III), also prepared for the first time, is shown to have the *trans* structure of its Co(III) analog. From a consideration of the signs and magnitudes of chelate ring methyl and proton contact shifts in the *cis*- and *trans*-β-ketoamine complexes, it is concluded that unpaired electron delocalization *via* metal-to-ligand parallel spin transfer is primarily responsible for the shifts. The same delocalization mechanism has been concluded to predominate in tris(β-diketone)vanadium(III) complexes.

Introduction

In this laboratory we are currently engaged in an investigation of the proton magnetic resonance spectra of pseudo-octahedral complexes of vanadium(III) containing conjugated ligand systems. Prompted by the results of Eaton,[3] which show that of all of the paramagnetic tris acetylacetonates of the first transition series tris(acetylacetonato)vanadium(III) possesses the narrowest line width of the ring methyl signal, we have recently found that the pmr spectra of other tris(β-diketonato)vanadium(III) complexes also reveal reasonably well-resolved signals.[4] The extremely large isotropic contact interactions in these complexes produce chemical shifts of *ca.* +150 to −60 ppm relative to tetramethylsilane, thereby allowing unambiguous detection, and occasionally identification, of geometrical isomers and a qualitative definition of the mode of unpaired electron delocalization which is primarily responsible for the contact interactions.[4]

By way of extending these studies to ligand systems of related structure and current interest, we report herein the initial synthesis and the pmr spectra of a series of tris(β-ketoamino)vanadium(III) complexes. As is the case with the β-diketonates, most of the chelate ring substituents in these complexes produce signals having usefully narrow line widths and large isotropic contact shift components of the total chemical shifts. The geometrical isomer present in solution has been definitely identified and the predominant path of unpaired spin delocalization elucidated. This study complements our previous one of the β-diketonates,[4] as well as recent investigations of the stereochemistry of bis(β-ketoamino)nickel(II)[5,6] and -cobalt(II)[6] complexes and electron delocalization in the Ni(II) complexes.[5] A forthcoming report will deal with the synthesis and pmr spectra of tris(salicylaldehyde)- and tris(salicylaldimino)vanadium(III) complexes.[7] Proton resonance studies of other paramagnetic vanadium complexes have been summarized previously.[4]

Experimental Section

Preparation of Complexes.—The marked sensitivity of β-ketoamine complexes to oxidation and hydrolysis necessitated the following precautions. All reaction and purification steps were carried out under rigorously dry and oxygen-free nitrogen in

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(3) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).
(4) Part I: F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).
(5) G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964); *J. Am. Chem. Soc.*, **87**, 2117 (1965).
(6) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966).
(7) F. Röhrscheid, R. E. Ernst, and R. H. Holm, to be published.

TABLE I
CHARACTERIZATION OF TRIS(β-KETOAMINO)VANADIUM(III) COMPLEXES

Complex		Mp, °C	% C		% H		% N	
			Calcd	Found	Calcd	Found	Calcd	Found
$V(Me\text{-}acac)_3$	$C_{18}H_{30}N_3O_3V$	163–164	55.83	56.17	7.75	8.00	10.85	10.74
$V(Ph\text{-}acac)_3$	$C_{33}H_{36}N_3O_3V$	178	69.10	68.94	6.33	6.40	7.32	7.39
$V(Me\text{-}bzac)_3$	$C_{33}H_{36}N_3O_3V$	225–227	69.10	68.83	6.33	6.29	7.32	7.55
$V(Me\text{-}mhh)_3$	$C_{15}H_{24}N_3O_3V$	*a*	52.17	52.78	7.00	7.20	12.17	11.57
$V(Me\text{-}tfac)_3$	$C_{18}H_{21}F_9N_3O_3V$	177–178	39.36	39.44	3.85	3.68	7.65	7.82
$V(Ph\text{-}tfac)_3$	$C_{11}H_{27}F_9N_3O_3V$	207–208	53.89	54.42	3.70	3.85	5.71	6.03
$V(chxn\text{-}acac_3)$	$C_{21}H_{30}N_3O_3V$	180–188[b]	59.57	60.74	7.14	7.46	9.92	10.02

[a] No definite melting point observed. [b] Slightly impure product.

closed systems. Solvents were treated as follows. *t*-Butyl alcohol was dried over anhydrous sodium sulfate, refluxed with 30 g of sodium/l., and distilled. *n*-Heptane was dried over molecular sieves. Benzene was refluxed over sodium wire for 2 days and distilled. Solvents were deoxygenated by refluxing in a dry nitrogen atmosphere. In those cases in which purification of the β-ketoamine complexes was achieved by Soxhlet extraction, the thimbles were first extracted with dry solvent to remove water from them. Sublimations were carried out in an evacuated glass tube without a cold finger. All complexes were stored under dry nitrogen. Melting points were obtained on samples sealed under nitrogen and are uncorrected. Characterization data for the complexes are given in Table I.

Tris(4-methylaminopent-3-en-2-ono)vanadium(III), V(Me-acac)$_3$.—Potassium (2.7 g, 69 mg-atoms) was dissolved in 150 ml of *t*-butyl alcohol. To the solution 7.0 g (62 mmoles) of 4-methylaminopent-3-en-2-one[8] was added and the mixture kept at 60° for 15 min. After cooling to room temperature 6.8 g (21 mmoles) of tetraethylammonium tetrachlorovanadate(III)[9] was added and stirred vigorously for 20 hr at room temperature. The solvent was then removed *in vacuo*. To the remaining pink powder was added 200 ml of benzene. After stirring for 5 min at 40° the solution was filtered and the filtrate evaporated to dryness *in vacuo*. The red-brown residue was sublimed twice at 170° (10^{-3} mm), yielding the product as red-brown crystals (6.0 g, 75% yield based on the ligand).

Tris(4-phenylaminopent-3-en-2-ono)vanadium(III), V(Ph-acac)$_3$.—Potassium (3.13 g, 80 mg-atoms), 4-phenylaminopent-3-en-2-one[10] (11.4 g, 65 mmoles), and vanadium trichloride (3.5 g, 22 mmoles) were allowed to react in 300 ml of *t*-butyl alcohol in a manner analogous to the preceding preparation. The butanol was removed *in vacuo*, the residue extracted with 150 ml of benzene, and the benzene solution filtered. After evaporation of the filtrate to dryness *in vacuo*, the extraction, filtration, and evaporation steps were repeated. The residue was then Soxhlet-extracted using 70 ml of heptane. Brown-black crystals (5.3 g, 43%) were obtained.

Tris(3-methylamino-1-phenylbut-2-en-1-ono)vanadium(III), V(Me-bzac)$_3$.—Potassium (2.93 g, 75 mg-atoms), 3-methylamino-1-phenylbut-2-en-1-one[11] (10.7 g, 61 mmoles), and vanadium trichloride (3.3 g, 21 mmoles) were allowed to react in *t*-butyl alcohol for 2 days with continuous stirring. The compound was isolated and purified using the method given in the preceding preparation. Brown-black crystals (3.1 g, 25%) were obtained.

Tris(4-methylaminobut-3-en-2-ono)vanadium(III), V(Me-mhh)$_3$.—Potassium (3.13 g, 30 mg-atoms), 4-methylaminobut-3-en-2-one[12] (6.45 g, 64.5 mmoles) and vanadium trichloride (3.46 g, 22 mmoles) were allowed to react as usual in 80 ml of *t*-butyl alcohol for 1 day with continuous stirring. The tarry residue left after the removal of *t*-butyl alcohol was extracted with 100 ml of dry, oxygen-free dichloromethane. This solution was filtered and evaporated to dryness under reduced pressure. Extraction of the residue with 150 ml of *n*-heptane, followed by filtration and removal of the solvent *in vacuo*, yielded again a brown, tarry material, which when cooled with liquid nitrogen became glassy and could be transferred to a sublimation tube. Three sublimations at 140° (10^{-3} mm) gave in low yield a dark red crystalline material.

Tris(4-methylamino-1,1,1-trifluoropent-3-en-2-ono)vanadium(III), V(Me-tfac)$_3$.—The free ligand was prepared in a manner analogous to that for the preparation of 4-methylaminopent-3-en-2-one[8] and was used without further purification. Potassium (3.32 g, 85 mg-atoms), 11.8 g (71 mmoles) of crude 4-methylamino-1,1,1-trifluoropent-3-en-2-one, and 8.1 g (25 mmoles) of tetraethylammonium tetrachlorovanadate(III) were allowed to react for 2 days with continuous stirring, and the reaction mixture was worked up following the procedure given for $V(Me\text{-}bzac)_3$. The complex was sublimed twice at 150° (10^{-3} mm) to yield red-brown crystals (4.2 g, 33%).

Tris(4-phenylamino-1,1,1-trifluoropent-3-en-2-ono)vanadium(III), V(Ph-tfac)$_3$.—Preparation of the free ligand follows that for 4-phenylaminopent-3-en-2-one;[10] the product was not purified. Potassium (1.87 g, 48 mg-atoms), 10 g (44 mmoles) of crude 4-phenylamino-1,1,1-trifluoropent-3-en-2-one, and 4.73 g (14 mmoles) of tetraethylammonium tetrachlorovanadate(III) were allowed to react in 150 ml of *t*-butyl alcohol for 2 days with continuous stirring. The residue after removal of the solvent was extracted with 150 ml of hot benzene. The benzene was stripped off *in vacuo* and the residue subjected to Soxhlet extraction with 60 ml of *n*-heptane. The pure product was obtained as brown crystals.

1ε,3ε,5ε-Tris(pent-3-en-2-on-4-amino)cyclohexanevanadium(III), V(chxn-acac$_3$).—The free ligand has not been previously reported and was synthesized as follows from 1ε,3ε,5ε-triaminocyclohexane, which was obtained by reduction of 1,3,5-cyclohexanetrione trioxime.[13]

To 1.8 g of the triamine in 3 ml of absolute ethanol was added 9 g of 2,4-pentanedione. A white precipitate formed and disappeared as the yellow solution was heated to 130°. The addition of 7 ml of heptane to the hot solution followed by slow cooling yielded small white plates, which were filtered off and washed with 1:1 v/v *n*-heptane–benzene (2 5-ml portions). A yield of 4.4 g (84%) was obtained, mp 161°. (Some crystals are present in the melt up to 200°. A further recrystallization from benzene gave a product with the same melting characteristics.)

Anal. Calcd for $C_{21}H_{33}N_3O_3$: C, 67.18; H, 8.86; N, 11.19. Found: C, 67.30; H, 8.70; N, 10.73.

The complex was prepared by the reaction of 1.29 g (33 mg-atoms) of potassium, 3.60 g (9.6 mmoles) of 1ε,3ε,5ε-tris(pent-3-en-2-on-4-amino)cyclohexane, and 3.10 g (9.6 mmoles) of tetraethylammonium tetrachlorovanadate(III) in 100 ml of *t*-butyl alcohol. The reaction mixture was stirred continuously for 48 hr. Removal of the solvent *in vacuo* left a tarry residue, which was extracted with benzene. Filtration of this solution followed by evaporation of the solvent *in vacuo* produced a sticky brown residue which could be partially sublimed at 210° (10^{-3} mm). Two subsequent slow sublimations at 180° (10^{-3} mm) gave brown

(8) E. Knoevenagel and W. Ruschhaupt, *Ber.*, **31**, 1030 (1898).
(9) R. J. H. Clark, R. S. Nyholm, and D. E. Scaife, *J. Chem. Soc., Sect. A*, 1296 (1966).
(10) W. Königs and A. Mengel, *Ber.*, **37**, 1325 (1904).
(11) A. V. Baeyer, *ibid.*, **24**, 1669 (1891).
(12) E. Benary, *ibid.*, **63**, 1573 (1930).
(13) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 1572 (1957).

crystals (1.2 g, 34%). The analytical results and the pmr spectrum (Figure 4) indicate a slight contamination with free ligand. Exhaustive attempts to effect further purification by sublimation or recrystallization were not successful.

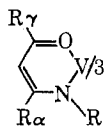
Tris(N-methylpyrrole-2-aldimino)vanadium(III).—Potassium (2.46 g, 63 mg-atoms) was dissolved in 120 ml of dry, air-free *t*-butyl alcohol; 6.2 g (57 mmoles) of N-methylpyrrole-2-aldimine was added and the mixture heated to 60°. After cooling to room temperature, 6.3 g (19 mmoles) of tetraethylammonium tetrachlorovanadate(III) was added and the mixture was stirred at room temperature for 2 days. The red-brown reaction product was isolated by filtration, dried, and sublimed at 170–180° (10^{-3} mm). The red sublimate was resublimed at 180° (10^{-3} mm) in a glass tube within an iron tube whose effect was to produce a smoother temperature gradient. The most volatile third of the sublimate was discarded. The remainder consisted of brilliant red crystals, mp 214–216°.

Anal. Calcd for $C_{18}H_{21}N_6V$: C, 58.06; H, 5.68; N, 22.57. Found: C, 57.91; H, 5.81; N, 22.48.

Physical Measurements.—Magnetic susceptibilities of solids and solutions were determined by the Gouy method using aqueous nickel chloride solutions and freshly boiled distilled water as the calibrants, respectively. Proton resonance spectra were obtained on 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 using $CHCl_3$ solutions with $CFCl_3$ as an internal reference. Resonance frequencies were measured using the conventional side-band technique.

Results and Discussion

The β-ketoamine complexes characterized in this work are set out in Table I. The first six of these possess the general structure **1** and are designated by prefixing the conventional abbreviation of the parent β-diketone of the ligand with the nitrogen substituent, as indicated below.



1

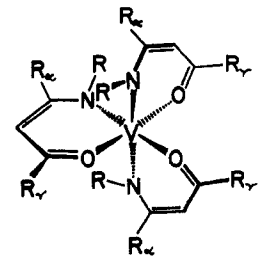
V(Me-acac)$_3$: $R_\alpha = R_\gamma = R = CH_3$
V(Ph-acac)$_3$: $R_\alpha = R_\gamma = CH_3$, $R = C_6H_5$
V(Me-bzac)$_3$: $R_\alpha = R = CH_3$, $R_\gamma = C_6H_5$
V(Me-mhh)$_3$: $R_\alpha = H$, $R_\gamma = R = CH_3$
V(Me-tfac)$_3$: $R_\alpha = R = CH_3$, $R_\gamma = CF_3$
V(Ph-tfac)$_3$: $R_\alpha = CH_3$, $R_\gamma = CF_3$, $R = C_6H_5$

The remaining complex, V(chxn-acac$_3$), is derived from the condensate of acetylacetone and 1,3,5-triaminocyclohexane, in which all three amino groups are axial. Like the analogous 1,3,5-tris(salicylidenamino)-cyclohexane,[13] this ligand can form only complexes with a *cis* arrangement of donor atoms. The configurations of this sexadentate complex and the *trans* isomer of the tris-chelate species are given in Figure 1.

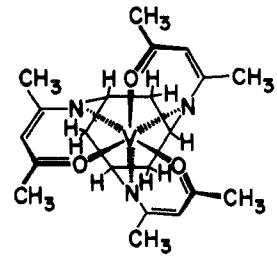
Synthesis and Properties of Complexes.—Synthesis of this series of new β-ketoamine complexes was effected by a nonaqueous chelation reaction in *t*-butyl alcohol employing *t*-butoxide as the base for deprotonating the weakly acidic ligand. This reaction is of considerable scope with regard to both ligand structure and metal ion and has been successful in preparing β-ketoamine complexes of Ni(II),[5,6,14] Co(II),[6,14] Fe(II),[15] and

(14) R. H. Holm, F. Röhrscheid, and G. W. Everett, Jr., *Inorg. Syn.*, in press.

(15) D. H. Gerlach and R. H. Holm, unpublished work.



(a) trans-V(R_γCOCHC(NR)R_α)$_3$



(b) V(chxn-acac$_3$)

Figure 1.—Configurations of one enantiomer of (a) *trans*-tris-(R-N-β-ketoamino)vanadium(III) and (b) 1ε,3ε,5ε-tris(pent-3-en-2-on-4-amino)cyclohexanevanadium(III), V(chxn-acac$_3$), viewed down the pseudo-threefold axis (a) and the true threefold axis (b).

Cu(II),[15] as well as bis-[16] and tris-chelate[17] complexes derived from pyrrole-2-aldimines. In this work tris-(N-methylpyrrole-2-aldimino)vanadium(III) was prepared by this route. Either VCl_3 or $[(C_2H_5)_4N)]VCl_4$[9] can be employed as the anhydrous vanadium(III) starting material. In the few cases for which competitive yields were measured, the complex salt gave improved yields in comparable reaction times. This behavior is probably due to the somewhat greater solubility and lability of $[(C_2H_5)_4N]VCl_4$. Tris(β-ketoamine)vanadium(III) complexes are brown or red-brown in the solid state and red-brown in solution. Both solids and solutions must be protected from air and moisture; solutions are easily oxidized and hydrolyzed in the presence of moist air. The complexes all have triplet ground states; magnetic moments are in the usual range for pseudo-octahedral vanadium-(III)[18] and are given in Table II. The only other tris-β-ketoamine complexes reported are those of chromium(III) with R = benzyl or aryl[19] and were prepared by a similar method.

Geometrical Isomerism.—Tris-chelate complexes containing three identical, unsymmetrical chelate rings can exist as *cis* and *trans* isomers in which like donor atoms are arranged facially or meridianally, respectively. Three separate signals for each of the ring substituents R_α, R_β, R_γ, and R in the *trans* form are possible owing to lack of symmetry, whereas the ideal-

(16) (a) R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966); (b) J. H. Weber, *ibid.*, **6**, 258 (1967).

(17) (a) A. Chakravorty and R. H. Holm, *ibid.*, **3**, 1521 (1964); (b) A. Chakavorty, K. C. Kalia, and T. S. Kannan, *ibid.*, **5**, 1623 (1966).

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

(19) (a) J. P. Collman and E. T. Kittleman, *Inorg. Chem.*, **1**, 499 (1962); (b) J. P. Collman and E. T. Kittleman, *Inorg. Syn.*, **8**, 149 (1966).

TABLE II

MAGNETIC MOMENTS IN SOLID AND SOLUTION PHASES

Complex	μ_{eff}, BM[a] Solid	$CHCl_3$ soln
$V(Me\text{-}acac)_3$	2.83	2.75
$V(Ph\text{-}acac)_3$	2.74	2.74
$V(Me\text{-}tfac)_3$	2.80	2.78
$V(Ph\text{-}tfac)_3$	2.77	2.74

[a] All values were obtained at ambient room temperature (25–28°) and are corrected for diamagnetism.

ized C_3 symmetry of the *cis* form requires only one signal from each such substituent. Representative spectra of these complexes are shown in Figures 2 and 3 and the complete set of contact shifts of the β-ketoamine

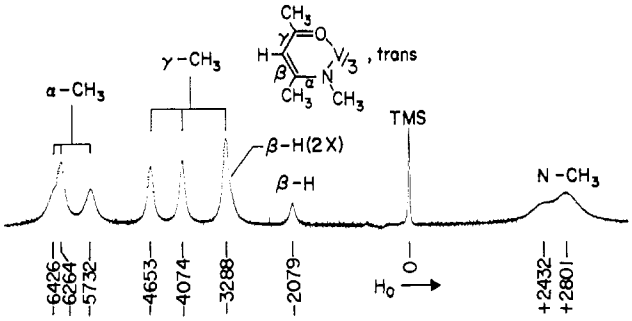


Figure 2.—Proton resonance spectrum (100 Mc) of $V(Me\text{-}acac)_3$ in $CDCl_3$ solution at room temperature. Frequencies (cps) are the chemical shifts.

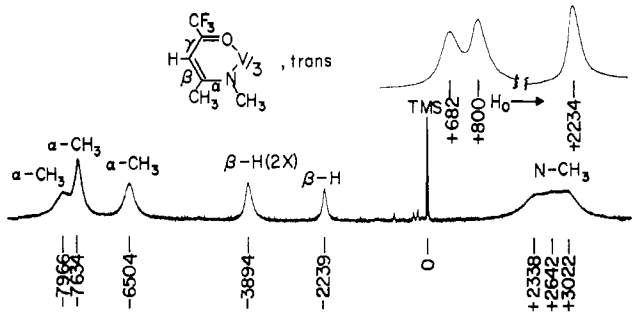


Figure 3.—Nuclear resonance spectra of $V(Me\text{-}tfac)_3$ in chloroform solution at room temperature: bottom, 100-Mc pmr spectrum; insert, ^{19}F spectrum. Frequencies (cps) are the chemical shifts.

complexes is given in Table III. Assignment of signals is discussed in the next section. Inspection of the results reveals that, except for occasional degeneracies in shifts and instances where excessive signal broadening prohibits complete resolution, three signals of equal intensity for each substituent are observed. The situation is especially clear-cut in the case of $V(Me\text{-}tfac)_3$ (Figure 3), which exhibits three well-resolved α-CH_3 and γ-CF_3 signals and three evident though incompletely resolved NCH_3 resonances; two of the three β-H resonances are coincident. For $V(Ph\text{-}acac)_3$ the three signals each of R_α, R_β, and R_γ are resolvable. Further, the ^{19}F spectra of $V(Me\text{-}tfac)_3$ and $V(Ph\text{-}tfac)_3$ show three signals of equal intensity and two signals of 2:1 intensity ratio, respectively. These results demonstrate conclusively that in solution all of the complexes have the *trans* structure shown in Figure 1. In no case was any amount of *cis* form detectable. The spectra of the tris-chelate species are to be contrasted with that of necessarily *cis*-$V(chxn\text{-}acac_3)$ (*cf.* Figures 1 and 4) in which there appears only one signal for each ring substituent.

TABLE III

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

Complex	Δf_i, cps[a] R_α	R_β	R_γ[b]	R[b]
	−6,234	−2791	−4461	+3099[c]
$V(Me\text{-}acac)_3$	−6,072	−2791	−3882	...
	−5,540	−1582	−3096	+2720[c]
	−7,147	−3258	−4457	...
$V(Ph\text{-}acac)_3$	−6,155	−1754	−3777	...
	−5,198	−1406	−1414	...
	−7,069	−3547	...	+3830[c]
$V(Me\text{-}bzac)_3$	−7,069	−2954	...	...
	−5,478	−2333	...	+2890[c]
	+12,320[c]	−3785	−5469	+3975
$V(Me\text{-}mhh)_3$	...	−3478	−4302	+3326
	+11,830[c]	−1096	−4302	+2982
	−7,758	−3359	−3648[d]	+3329
$V(Me\text{-}tfac)_3$	−7,426	−3359	−3530[d]	+2949
	−6,926	−1704	−2096[d]	+2645
	−8,105	−3523	−3294[d]	...
$V(Ph\text{-}tfac)_3$	−7,408	−2944	−1650[d]	...
	−5,427	− 937	−1650[d]	...
$V(chxn\text{-}acac_3)$	−2,453[e]	−2761	−4415[e]	+1156 (CH); +20, −570 (CH_2)

[a] $\Delta f_i = f_i$(complex) − f_i(dia); all data refer to ~30°; ±10 cps unless otherwise noted. [b] Signals due to phenyl groups are complex and their shifts were not measured accurately. [c] Limits of broad, poorly resolved signals; accurate to ±100 cps. [d] ^{19}F shifts at 56.4 Mc/sec. [e] Assignment uncertain; see text.

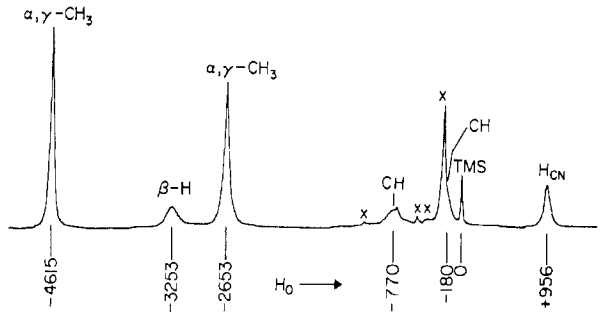


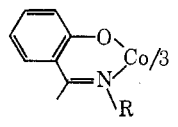
Figure 4.—Proton resonance spectrum (100 Mc) of $V(chxn\text{-}acac_3)$ in $CDCl_3$ solution at room temperature. Frequencies (cps) are the chemical shifts. The signals marked with an x are due to impurities; those labeled CH refer to one of the two cyclohexyl methylene protons.

The apparent exclusive population of the *trans* stereoisomer is consistent with earlier results on the solution structures of tris-chelate complexes having similar ligand systems. Tris complexes of Co(III) derived from N-substituted salicylaldimines (**2**),[17a,20,21]

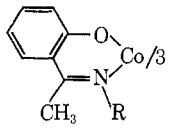
(20) B. O. West, *J. Chem. Soc.*, 4944 (1960).

(21) M. Ciampolini, F. Maggio, and F. P. Cavasino, *Inorg. Chem.*, **3**, 1188 (1964).

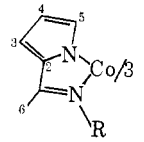
o-hydroxyacetophenone imines (**3**),[22] and pyrrole-2-aldimines (**4**),[17a] in which the N-substituent is methyl or a larger group, all have the *trans* structure. Space-filling Stuart–Briegleb metal chelate scale models indicate that the *trans* configuration is sterically forced. Stable models of *cis* isomers having R = CH_3, C_6H_5, or any group larger than H could not be assembled.



2

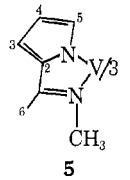


3



4

Collman and Kittleman[19a] have also concluded from their consideration of the geometries of tris(R-N-β-ketoamino)chromium(III) complexes (R = benzyl, aryl) that the *cis* isomer is sterically destabilized relative to the *trans*.[23] This same situation exists for tris-(N-substituted salicylaldimine) complexes,[17a,20] and the arguments given previously[17a] to explain the apparently complete preference for the *trans* isomer in those systems also apply to the tris-β-ketoamine complexes, in which the ligand geometry is similar. The interaction among R groups which project from octahedral edges is considerably less than that produced by the projection of three groups from a common face. Because geometrical considerations show that the *cis* isomer of **4** is more stable than that of **2** or **3** with the same R group,[17a] we have examined the pmr spectrum of **5** to determine if any of the *cis* form is present. The three equally intense 5-H signals together with two 6-H and N-CH_3 signals, each of 2:1 intensity ratio (*cf.* Table IV), prove the *trans* structure of this complex. No amount of *cis* isomer was detectable.



5

Both *cis* and *trans* isomers of tris-chelate complexes have been isolated or detected only in those instances in which donor atoms or donor groups of the same ligand have small differences in relative steric requirements[24] or effectively no difference at all.[4,25] In such cases the donor atoms or groups can be disposed facially or meridianally without the free energy differences between the isomers being so large that, as a consequence in a thermodynamically controlled system, only one stereochemical form is detectably populated. The relative stabilities of *cis* and *trans* forms will then depend upon the specifics of intramolecular interactions.

TABLE IV

PROTON CHEMICAL SHIFTS OF TRIS(N-METHYLPYRROLE-2-ALDIMINO)VANADIUM(III)

Position[a]	Δf_i, cps[b]
3,4[c]	−1346 (1), −1280 (1), −480 (2), +1824 (1), +5560 (1)
5	+3548 (1), +3970 (1), +6453 (1)
6	+12844 (2), +14296 (1)
CH_3	+4460 (1), +5162 (2)

[a] *Cf.* **5** in text. [b] $CDCl_3$ solution, ~30°, 100 Mc/sec, relative intensities in parentheses. [c] Assignments for each position not possible.

In connection with the determination of structural isomers by nuclear resonance it is worth emphasizing, as has been done previously,[4] that contact interactions in paramagnetic complexes frequently accentuate chemical shift differences present in diamagnetic complexes of the same structure. In **4** (R = CH_3)[17a] the 5-H resonance occurs in the complicated multiplet from 5.9 to 6.8 ppm, whereas in **5** three distinct 5-H signals occur at 35.5, 39.7, and 64.5 ppm. Similarly, the two 6-H signals of **5** are separated by 14.5 ppm, while this separation in **4** is 0.15 ppm. Although three NCH_3 signals cannot be resolved in the spectrum of **5**, the separation (7.0 ppm) between the two observed signals is much greater than the larger chemical shift difference (0.39 ppm) between two of the three observable NCH_3 signals of **4**. The spread of the R_α = CH_3 shifts in **1** is 6.9–27 ppm, whereas for the azomethine methyl group in **3** the spread is 0.64–0.75 ppm for a number of alkyl nitrogen substituents. Further, the shift difference between any two such methyl signals in **3** never exceeds 0.52 ppm, while in **1** this difference is never less than ~1.6 ppm, except for V(Me-bzac)$_3$, in which case two of the R_α signals must be considered accidentally degenerate. The usually large chemical shift differences among ring substituent signals, effected predominantly by contact interactions, coupled with line widths which are small compared to these differences, result in spectra which for **1** and **5** unambiguously demonstrate the *trans* stereochemistry.

Signal Assignments.—An internally consistent set of signal assignments can be obtained for the *trans*-β-ketoamine complexes from consideration of the spectra of the six compounds listed in Table III. The N-CH_3 signals are identifiable as the broad, poorly resolved features with contact shifts of *ca.* +2600 to +4000 cps from the spectra of V(Ph-acac)$_3$ and V(Ph-tfac)$_3$ in which these features are absent. Broadening of the N-CH_3 signals is expected because of the relatively close proximity of these groups to the paramagnetic metal. β-H signals are generally assignable on intensity grounds. In several cases (*e.g.*, V(Me-acac)$_3$ and V(Me-mhh)$_3$) these signals are coincident with or partially overlap methyl signals. In such cases integration of all spectral features by planimetry yields a relative intensity pattern which is accommodated by a unique assignment. For V(Me-tfac)$_3$, V(Ph-tfac)$_3$, and V(Me-

(22) A. Chakravorty and K. C. Kalia, *Inorg. Chem.*, **6**, 690 (1967).

(23) The statement that two diastereoisomeric racemates are possible for tris-β-ketoamine complexes[19a] is incorrect. These complexes can in principle exist as two geometrically isomeric racemates, in which the only center of asymmetry is at the metal, provided no ligands with asymmetric centers are involved.

(24) Tris(amino acid)cobalt(III) complexes; *cf.* R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966), and references therein.

(25) (a) Tris(hydroxymethylenecamphorato)cobalt(III): J. H. Dunlop and R. D. Gillard, *J. Chem. Soc., Sect. A*, 1540 (1966); (b) tris(β-diketone)-chromium(III), -cobalt(III), and -rhodium (III) complexes (Rα = Rγ): R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962); **85**, 500 (1963).

TABLE V

SPIN DENSITY CALCULATIONS FOR A β-KETOAMINE

	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	β	γ	α	β	γ
HMO[a,c]	+0.032	+0.508	+0.055	+0.381	+0.003	+0.326
McLachlan[a,b,d]	−0.046	+0.615	+0.032	+0.500	−0.137	+0.403
VB[e]	−0.282	+0.697	−0.249	...	...	...

[a] $\alpha_O = \alpha + 1.5\beta$; $\beta_{CO} = 1.5\beta$; $\beta_{CN} = 1.2\beta$; $\alpha_N = \alpha + 1.0\beta$. [b] $\lambda = +1.2$; *cf.* A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960). [c] $\rho_O = +0.132$, $\rho_N = +0.158$ (LUMO). [d] $\rho_O = +0.098$, $\rho_N = +0.135$ (LUMO). [e] Reference 5.

bzac)$_3$ α-CH_3 assignments are unambiguous, with contact shifts falling in the range −5400 to −8100 cps. The α-CH_3 signals of V(Me-acac)$_3$ and V(Ph-acac)$_3$ are assigned as those within this range. The remaining three features in the spectra of these complexes (excluding C_6H_5 signals) are due to the γ-CH_3 groups. Assignment of γ-CH_3 resonances in V(Me-mhh)$_3$ is readily made from relative intensities; the very broad absorption in the +11,800 to +12,300 cps region contains unresolved α-H signals.

Far more difficult is the problem of assigning particular sets of R_α–R_β–R_γ signals to the *individual* chelate rings of the *trans* isomers. Despite considerable effort we have not been able to devise a procedure leading to unambiguous assignments of this kind.[26] In particular, it has not been possible to find from the data in Table III convincingly constant ratios of $\Delta f_\alpha/\Delta f_\beta$ and/or $\Delta f_\gamma/\Delta f_\beta$ for the various complexes. This situation indicates that the isotropic contact interactions conform to the full molecular asymmetry, and not to the idealized case in which pseudo-contact shifts are negligible and the contact shifts are solely a consequence of a different total amount of spin delocalized in each ring, the relative spin densities within each ring being the same.

Spin Delocalization in *trans* Complexes.—For reasons pointed out previously,[4] no rigorous analysis of contact shifts in terms of π-spin densities is possible for trigonal chelate complexes even if pseudo-contact shifts are known. Unfortunately, the situation is complicated further in the *trans* form by the inability to assign sets of contact shifts to individual chelate rings, the rhombic symmetry of the ligand field, and the uncertainty in the location of the molecular magnetic principal axis system. The difficulties prevent estimates of pseudo-contact shifts even if a set of *g*-value anisotropies were to be assumed. However, it is unlikely that pseudo-contact contributions would dominate the total isotropic contact shifts of these complexes, which have orbitally nondegenerate ground states and magnetic moments near the spin-only value. The shifts do strongly suggest that unpaired spin delocalization is mainly responsible for the contact interactions. Their signs and, to a lesser extent, their relative magnitudes parallel those of the analogous β-diketonates[4] (compare V(acac)$_3$–V(Me-acac)$_3$, V(tfac)$_3$–V(Me-tfac)$_3$, and V(mhh)$_3$–V(Me-mhh)$_3$), implying that partial transfer of a metal α spin to the lowest unoccupied π-molecular orbital (LUMO) of the chelate rings is the predominant delocalization process. This conclusion is strengthened by reference to the calculated spin densities in Table V, which are estimates of those expected if one full spin were present in the LUMO or HFMO (highest filled π-molecular orbital) of a β-ketoamine. These spin densities are most applicable to complexes having methyl and hydrogen ring substituents.

Contact shifts and electron–nuclear coupling constants a_i are related by the familiar equation

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g|\beta|S(S+1)}{3kT}$$

in which the symbols have their usual meanings.[3,27] Coupling constants are related to aromatic carbon pπ spin densities by $a_i = Q\rho_{C_i}$. Because Q_{CH} is negative and Q_{CCH_3} positive and in general $|Q_{CCH_3}| \leqslant |Q_{CH}|$,[4] it follows from the observed $|a_{\alpha,\gamma}| > |a_\beta|$ (neglecting pseudo-contact effects) that $|\rho_{C\alpha,\gamma}| > |\rho_{C\beta}|$. These results were also obtained with the β-diketonates and are consistent with α-spin transfer from the metal orbital to appropriate linear combinations of the LUMO'S (metal-to-ligand parallel spin transfer) as the predominant pathway of spin delocalization.[3,4]

V(chxn-acac$_3$): Signal Assignments and Spin Delocalization.—The chief interest in this compound is due to its axial symmetry (demonstrated by its spectrum in Figure 4), which permits an estimate of pseudo-contact shifts if a *g*-value anisotropy is assumed. Chelate ring signals are assigned as those with large negative contact shifts (*cf.* Table III). Because of the rigid nature of the cyclohexyl ring, three signals are observed owing to the tertiary proton (H_{CN}) and the axial and equatorial methylene protons. The large positive contact shift is assigned with some certainty to H_{CN}. Negative (β) spin density is believed induced in the nitrogen σ orbitals by partial transfer of α spin from the σ-donor orbital. Delocalization of β spin in the σ system will result in a direct contact interaction and positive contact shifts.[28] The two remaining contact shifts of +20 and −570 cps are then due to the

(26) It might be anticipated that a partial assignment could be made on the basis of the near equivalence of two chelate rings compared to the third due to a pseudo-threefold rotation axis (*cf.* Figure 1). Although the data in Table III do show that for certain complexes two of the three R_α, R_β, R_γ signals are relatively close in shift, signals of the other ring substituents are generally not as clearly grouped and are thus not easily related to the grouped signals. Furthermore, any assignments of signals to separate rings based on near equivalence of contact shifts neglects possible pseudo-contact effects.

(27) The strict Curie dependence of the contact shifts observed from −50 to 60° for a representative complex, V(Ph-tfac)$_3$, ensures that this expression holds for the tris(β-ketoamino)vanadium(III) complexes.

(28) Evidence has been given previously that with Ni(II) β-ketoamines contact shifts of protons near the chelate ring C–N bond are affected by transmission of σ-spin density.[5] In these cases the σ-spin density produced by ligand-to-metal spin transfer must necessarily be of sense α, leading to negative contact shifts.

methylene protons, but there appears no way to make a specific assignment for each proton. The spectrum in this region is complicated by the presence of free ligand as an impurity. In $CDCl_3$ there is some overlapping of ligand and complex signals, but in CCl_4 solution the methylene signals of the complex are clearly observable and were further differentiated from ligand resonances by their reduced tendency to saturate at high radiofrequency power.

For complexes following the Curie law and possessing well-resolved nuclear resonance spectra, the pseudo-contact shifts are expressed by[29]

$$\frac{\Delta f_i}{f} = -\frac{\beta^2 S(S+1)}{45kT}\left(\frac{3\cos^2\chi_i - 1}{r_i^3}\right) \times (g_{\parallel} - g_{\perp})(3g_{\parallel} + 4g_{\perp})$$

in which r_i is the distance between the metal and the ith nucleus and χ_i is the angle between the principal magnetic axis system and the line connecting these points. By making reasonable estimates of the geometrical factors[30,31] and taking $\langle g \rangle = 1.97$ ($\mu_{eff} = 2.78$ BM) and $|g_{\parallel} - g_{\perp}| = 1$, it is found that without regard to sign a pseudo-contact contribution could amount to ~60% of the observed β-H shift. Similarly, the larger ring methyl shift can be no more than about 37 or 33% pseudo-contact depending upon its assignment as γ-CH_3 or α-CH_3, respectively. If the signs of the contact and pseudo-contact shifts are opposite, the pseudo-contact contribution to the total isotropic shift would be even less. Because $|\Delta g| = 1$ is almost certainly a large overestimate of the anisotropy,[32-34] it follows that pseudo-contact interactions have only a minor effect on the contact shifts, which then arise principally from spin delocalization.

From the argument given for the *trans* complexes the observation of one methyl shift larger than that for β-H strongly indicates that the predominant spin delocalization path is metal-to-ligand (LUMO) α-spin transfer. It is tempting to postulate that the methyl group with the smaller contact shift is α-CH_3 and that its shift is less negative than the delocalization model requires (*cf.* Table V) because of the combined effects of σ-spin delocalization and possibly pseudo-contact interaction,[30,32] which could produce positive contact shift contributions. Finally, the present conclusion that metal-to-ligand spin transfer is dominant in *cis*- and *trans*-β-ketoamine V(III) complexes, coupled with the previous finding that ligand-to-metal spin transfer is the major delocalization path in tetrahedral β-ketoamine Ni(II) complexes,[5] conforms to Eaton's contention[3] that with increasing nuclear charge d orbitals contract and interact less effectively with antibonding ligand π MO's.

Acknowledgment.—This research was supported by the U. S. Public Health Service through NIH Grant GM 12920.

(29) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958); G. N. LaMar, *ibid.*, **43**, 235 (1965).

(30) The complex was assumed to have C_3 symmetry with an octahedral $V-O_3N_3$ coordination sphere and the cyclohexyl ring in the chair form with normal angles and distances. The V–N and V–O distances were taken as 2.00 A. Chelate rings were assumed to be planar and to make a 45° dihedral angle with the NCH plane of the cyclohexylamino grouping. Chelate ring angles and distances consistent with these molecular parameters were inferred from the structure of dimeric 4-*o*-oxyphenylaminopent-3-en-2-onocopper(II),[31] the only β-ketoamine complex whose detailed structure has been accurately determined. The following values of $(3\cos^2\chi - 1)/r^3$ (A^{-3}) were obtained: γ-CH_3, −0.0125; β-H, −0.0131; α-CH_3, −0.0109; H_{CN}, +0.0131; H_{eq}, +0.0125; H_{ax}, +0.0190. Note that because all three cyclohexyl proton contact shifts are not of the same sign and are of widely different magnitudes, they cannot be assumed to arise only from pseudo-contact effects and, hence, cannot be used with confidence to gauge pseudo-contact shifts at the chelate ring positions.

(31) G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

(32) g-Value anisotropies in trigonally distorted $V(H_2O)_6^{3+}$ are much smaller. For the $^3A_2$ ground state of V^{3+} in Al_2O_3,[33] $(g_{\parallel} - g_{\perp}) = +0.190$. From the susceptibility of vanadium ammonium alum,[34] $(g_{\parallel} - g_{\perp}) = +0.16$. If $(g_{\parallel} - g_{\perp})$ is also positive in V(chxn-acac)$_3$, any pseudo-contact shift of α-CH_3, β-H, or γ-CH_3 will be positive and must be small compared to the negative contact shifts arising from electron delocalization.

(33) R. M. McFarlane, *J. Chem. Phys.*, **40**, 373 (1964).

(34) J. Van der Handel and A. Siegert, *Physica*, **4**, 871 (1937).