tion" to the antibonding CO orbitals. Haas and Sheline[4] have observed, in the gas-phase infrared spectrum, a broadening in the CO stretching region which could be ascribed to such an effect on the CO bonds. This explanation of our results, though probably oversimplified, supports the concept of "back-donation" in metal carbonyls. In our experiments, the existence of intermolecular effects cannot, of course, be entirely ruled out and further experiments to test these ideas are in progress.

No resolvable hyperfine structure was observed in any of the spectra recorded in these experiments. Since the nuclear spin of $^{51}V$ is $^7/_2$, an upper limit for the isotropic coupling constant would be about one-seventh of the line width, or 30 gauss or less for the widest lines observed. This is considerably smaller than normally observed for paramagnetic vanadium compounds and suggests the presence of an exchange interaction in our samples. Further evidence for exchange is provided by a closer inspection of the line shapes.[6] The existence of such an interaction in the *n*-pentane glass samples could be the result of precipitation of $V(CO)_6$ which may occur during the freezing process; however, experiments with benzene as a solvent also yielded no hyperfine structure. The benzene spectra were asymmetric even at low power levels; the *g* values measured from the benzene spectrum ($g_{\|} = 2.023$ and $g_{\perp} = 2.126$) do not agree with those calculated on the basis of either tetragonal or trigonal models. It is possible that this is due to the formation of an associated $V(CO)_6$–benzene species.

The presence of rather strong exchange forces can, in some cases, produce unusual variations in esr line shapes when the spectrum is power saturated. For example, Goldsborough, *et al.*,[13] have observed that in pure crystalline free-radical systems such as DPPH, a pronounced narrowing of the resonance line occurs when it is power saturated. In such systems, spin-lattice relaxation occurs *via* an exchange reservoir and the narrowing occurs when the exchange "temperature" exceeds the lattice temperature. It is possible that such a mechanism accounts for some, if not all, of the observed variations in the shape of the $V(CO)_6$ spectra.

**Acknowledgments.** The authors are grateful to Professor L. V. Interrante and Mr. G. V. Nelson for assistance in the preparation of $V(CO)_6$. This work was performed under the auspices of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

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# Nuclear Resonance Studies of Vanadium(III) Complexes. III.[1] Synthesis, Stereochemistry, and Electron Delocalization Properties of Tris(salicylaldehydes) and Tris(salicylaldimines)

**F. Röhrscheid, R. E. Ernst,[2] and R. H. Holm[3]**

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**Abstract:** The first synthesis of a series of tris(salicylaldehydo)- (**1**) and tris(salicylaldimino)vanadium(III) complexes (**2**) is reported. The complexes prepared are $V(X\text{-sal})_3$ (**1**) (X = 3-, 5-Me) and $V(X\text{-}R\text{-sal})_3$ (**2**) (R = Me, X = H; R = *n*-Pr, X = H, 3-, 4-, 5-Me). These complexes exhibit large isotropic proton contact shifts which unequivocally demonstrate the *trans* stereochemistry for all. No amount of *cis* isomer was detected in any case. A necessarily qualitative analysis of the contact shifts has led to the conclusion that they are effected principally by delocalization of parallel spin from the metal to the lowest unoccupied $\pi$-molecular orbital of the ligands. The mechanisms of spin delocation in V(III) and Ni(II) salicylaldimine complexes are compared.

Previous work in this series[1,4] together with the results of Eaton[5] has demonstrated that the line widths of most signals in the proton magnetic resonance spectra of pseudo-octahedral vanadium(III) complexes containing conjugated ligand systems are sufficiently narrow that useful information concerning stereochemistry and unpaired electron delocalization can be obtained. Tris-β-diketone[4,5] and -β-ketoamine[1] V(III) complexes exhibit extremely large chemical shifts which at room temperature occur in the range *ca.* +150 to −60 ppm relative to tetramethylsilane. The overwhelming contribution to these shifts is the isotropic electron–nuclear contact interaction, which is highly sensitive to the fine details of molecular structure.[6] This situation has facilitated the unambiguous identification of the geometrical isomers (*cis*, *trans*) of the tris-chelate V(III) complexes in solution.[1,4]

In order to further our investigation of the stereochemistry of tris-chelate complexes, we have prepared a

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(1) Part II: F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1607 (1967).

(2) National Institutes of Health Predoctoral Fellow.

(3) Alfred P. Sloan Foundation Fellow; Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

(4) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).

(5) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(6) For examples, *cf.* (a) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 397 (1964); (b) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964); (c) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967).

series of tris-salicylaldehyde and tris-salicylaldimine complexes of V(III). Like the β-diketonates and β-ketoamines, these complexes possess large isotropic proton contact shifts, the multiplicity of which permit a definite structural assignment. As will become evident, the present investigation complements previous pmr structural assignments of tris(salicylaldimino)-[7] and tris(*o*-hydroxyacetophenoneimino)cobalt(III)[8] complexes.

Inasmuch as tris(salicylaldimino)vanadium(III) complexes have not been previously reported, this work represents a contribution to the systematics of the chemistry of tris-chelate complexes derived from N-substituted salicylaldimines. Heretofore complexes of Co(III),[7-9] Fe(III),[10,11] Mn(III),[10] and Cr(III)[10] have been prepared, leaving those of Sc(III) and Ti(III) as remaining synthetic objectives, the accomplishment of which would complete the series of neutral tris complexes of the $d^0$–$d^6$ metal ions of the first transition series. Prior work on the salicylaldimine complexes of vanadium has involved almost exclusively vanadyl species.[12]

Proton resonance studies of paramagnetic vanadium complexes other than those in this series of investigations[1,4] are summarized elsewhere.[4]

## Experimental Section

**Preparation of Compounds.** In the following preparations all reactions and manipulations were carried out in a nitrogen atmosphere using degassed solvents. Characterization data for all complexes prepared in this work are set out in Table I.

**Table I.** Characterization of Tris(salicylaldimino)- and Tris(salicylaldehydo)vanadium(III) Complexes

| Complex | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|
| V(Me-sal)$_3$[a] | 63.76 | 5.31 | 9.22 | 63.97 | 5.42 | 8.96 |
| V(*n*Pr-sal)$_3$[b] | 67.03 | 6.75 | 7.82 | 66.65 | 6.67 | 7.76 |
| V(3Me-*n*Pr-sal)$_3$[c] | 68.38 | 7.30 | 7.25 | 68.02 | 7.40 | 7.19 |
| V(4Me-*n*Pr-sal)$_3$ | 68.38 | 7.30 | 7.25 | 68.04 | 7.30 | 7.36 |
| V(5Me-*n*Pr-sal)$_3$ | 68.38 | 7.30 | 7.25 | 68.08 | 7.35 | 7.24 |
| V(3-Me-sal)$_3$ | 63.13 | 4.64 | ... | 63.47 | 4.93 | ... |
| V(5Me-sal)$_3$[d] | 63.13 | 4.64 | ... | 62.83 | 4.92 | ... |

[a] Mp 240–242°. [b] Mp 201–202°. [c] Mp 131–132°. [d] Mp 238–240° (all melting points are uncorrected).

**Tris(methylsalicylaldehydo)vanadium(III).** The methylsalicylaldehyde (5.0 g, 37 mmoles) was dissolved in 20 ml of ethanol and treated with a solution of 2.1 g (37 mmoles) of potassium hydroxide in 25 ml of water. The resultant yellow solution was degassed and then slowly added to a vigorously stirred solution of 2.4 g (15 mmoles) of vanadium trichloride in 50 ml of water. Stirring was continued for 2 hr, leading to a finely divided brown powder. The powder was collected on a frit, dried under vacuum, and dissolved in 150 ml of dry dichloromethane. The dark brown solution was filtered and the volume reduced to ~10 ml. Dry benzene (20 ml) was added and the resultant mixture heated to boiling for 5 min while stirring. The finely divided brown powder obtained upon allowing the solution to cool to room temperature was collected on a frit and washed with dry heptane. Drying at 25° ($10^{-3}$ mm) for 4 hr yielded the product as a brown powder in 50% yield.

**Tris(salicylaldimino)vanadium(III).** All complexes were prepared by the same general method, which is illustrated by the preparation of tris(N-methylsalicylaldimino)vanadium(III).

To 3.7 g (30 mmoles) of salicylaldehyde in 40 ml of ethanol was added 7 ml of a 40% aqueous methylamine solution. Vanadium trichloride (1.7 g, 11 mmoles) dissolved in 100 ml of water was added slowly, producing an orange-brown precipitate which was stirred with the reaction solution for 2 hr. The precipitate was collected on a frit, washed twice with 30 ml of water, and dried under vacuum. The product was dissolved in 70 ml of dichloromethane; the resultant solution was filtered and brought to dryness under vacuum. The residue was recrystallized twice from dry benzene, yielding orange-red crystals which were washed with petroleum ether and dried at 25° ($10^{-2}$ mm).

The other salicylaldimine complexes (*cf.* Table I) were prepared on the same scale. They were not recrystallized from benzene but were purified by two Soxhlet extractions, using 50 ml of *n*-heptane, and isolated as red-brown to dark brown crystals.

**Proton Resonance Measurements.** Pmr spectra were obtained on a Varian HR-100 spectrometer using $CDCl_3$ solutions containing tetramethylsilane as an internal standard. Chemical shifts were measured using the conventional side-band technique. The data are presented in Table II in terms of contact shifts which for the *i*th nucleus are obtained from the relation $\Delta f_i$ (cps) = $f_i$(complex) − $f_i$(dia), in which $f_i$(dia), the chemical shift in the absence of the contact interaction, is obtained from the spectra of the appropriate free salicylaldehyde or salicylaldimine.

**Table II.** Proton Contact Shifts of Tris(salicylaldehydo)- and Tris(salicylaldimino)vanadium(III) Complexes[a]

| Complex | $\Delta f_i$, cps, at position 3 | 4 | 5 | 6 |
|---|---|---|---|---|
| V(Me-sal)$_3$ | −970 | +1574 | −794 | +1019(2)[b] |
| | (~−100)[c] | +2096 | −528 | +1130 |
| | ...[d] | +2280 | (~−100)[c] | |
| V(*n*Pr-sal)$_3$[f] | −910 | +2168 | −738 | +814 |
| | (~−100)[c] | +1962 | −380 | +1006 |
| | ...[d] | +1628 | (~−100)[c] | +1056 |
| V(3Me-*n*Pr-sal)$_3$ | +334 | +1932 | −686 | |
| | +557 | +2042 | −437 | ...[e] |
| | ...[d] | +2318 | (~−100)[c] | |
| V(4Me-*n*Pr-sal)$_3$[g] | (~−100)[c] | −1825 | −671 | +803 |
| | ...[d] | −1595 | −421 | +1011 |
| | | −1493 | (~−130)[c] | +1066 |
| V(5Me-*n*Pr-sal)$_3$ | −255[c] | +1615 | −391 | +810 |
| | −755[c] | +2035 | +494 | +1126 |
| | −985[c] | +2215 | +868 | ...[d] |
| V(3Me-sal)$_3$ | +351 | +1951 | −1059 | +885 |
| | +581 | +2081 | −645 | +1556 |
| | +780 | +2947 | +475 | ...[d] |
| V(5Me-sal)$_3$ | −1333 | +1742 | −499 | +857 |
| | −901 | +2037 | +657 | ...[d] |
| | −263 | +2855 | +1151 | |

[a] Data obtained at 100 Mcps and ~30°. [b] Signals occur with 2:1 intensity ratio. [c] Approximate center of broad, poorly resolved signal. [d] All three signals could not be located with certainty due, in some cases, to overlap of signals. [e] No 6-H signals could be located with certainty and may be obscured by very broad 3Me absorptions. [f] Azomethine proton, +11,660 cps. [g] Azomethine proton, +11,440 cps.

## Results and Discussion

The new complexes which have been prepared in this work are listed in Table I. The salicylaldehyde and salicylaldimine complexes have the general structures **1** and **2**, respectively. Throughout the text they are referred to as V(X-sal)$_3$ (**1**) and V(X-R-sal)$_3$ (**2**). (When X = H, it is not included in the abbreviated formulas.) All are brown, orange-red, or reddish brown crystalline

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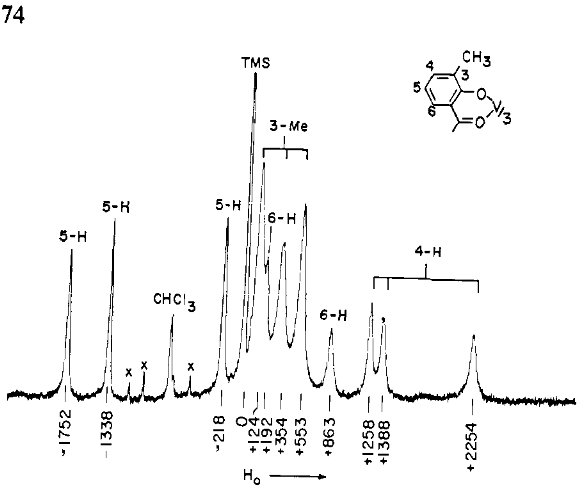


Figure 1. 100-Mc proton resonance spectrum of tris(3-methylsalicylaldehydo)vanadium(III), V(3Me-sal)$_3$, in CDCl$_3$ solution. Frequencies (cps) are the chemical shifts.

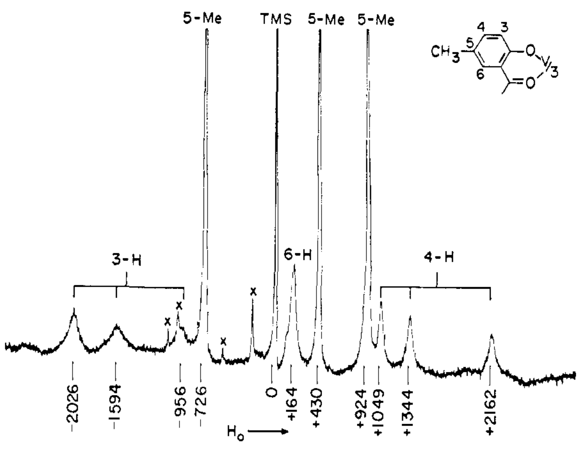
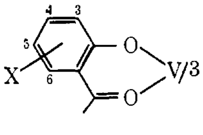


Figure 2. 100-Mc proton resonance spectrum of tris(5-methylsalicylaldehydo)vanadium(III), V(5Me-sal)$_3$, in CDCl$_3$ solution. Frequencies (cps) are the chemical shifts.

solids which in the presence of air and moisture are decomposed, especially readily in solution. The decomposition products have not been characterized but



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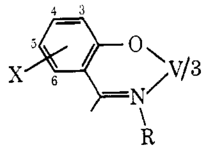

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it is likely that they are composed, at least in part, of the corresponding bis-chelate vanadyl species similar to those obtained directly from vanadyl salts.[12] In the absence of air the complexes are readily prepared in aqueous ethanol by a procedure which is unsuccessful for the tris-β-ketoamine complexes. This result, together with previous observations,[1,6a,c,13] emphasizes the general hydrolytic stability of salicylaldimine compared to β-ketoamine complexes.

**Stereochemical Determination.** Complexes **1** and **2** contain three identical, unsymmetrical chelate rings and can, therefore, exist as *cis* and/or *trans* isomers in which like donor atoms are arranged facially (**3**) or

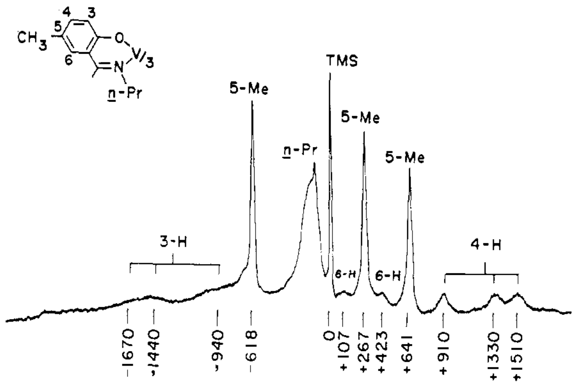
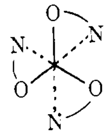


Figure 3. 100-Mc proton resonance spectrum of tris(5-methyl-N-*n*-propylsalicylaldimino)vanadium(III), V(5Me-*n*Pr-sal)$_3$, in CDCl$_3$ solution. Frequencies (cps) are the chemical shifts.

meridianally (**4**), respectively. Unambiguous isomer identification by proton resonance is straightforward,



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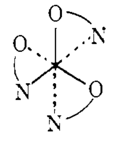

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for the idealized C$_3$ symmetry of the *cis* form renders the three chelate rings in **3** magnetically equivalent, whereas the three chelate rings in **4** are all nonequivalent. Hence, the *cis* isomer will produce one signal for each ring substituent (H, CH$_3$) while three signals should in principle occur for each substituent of the *trans* isomer.

Pmr spectra of representative complexes of types **1** and **2** are set out in Figures 1–3. Both groups of complexes exhibit substantial isotropic contact shifts which for most chelate ring substituents constitute the major fraction of their total chemical shifts (*e.g.*, compare the chemical shifts in Figure 3 with those of diamagnetic Co(R-sal)$_3$[7] and tris(*o*-hydroxyacetophenoneimine)-cobalt(III) complexes[8]). The signal assignments indicated in the figures and given in the list of contact shifts found in Table II are discussed in the following section. Considering first the salicylaldehyde complexes, it is observed that three well-resolved equally intense signals of 3-Me, 4-H, and 5-H in V(3Me-sal)$_3$ and of 3-H, 4-H, and 5-Me in V(5Me-sal)$_3$ appear. The 6-H signals are less easily observed but at least two of these are assignable in the spectrum of V(3Me-sal)$_3$. The line widths in the spectra of the salicylaldimines are generally broader than those of the salicylaldehydes as a comparison of Figures 1 and 2 with Figure 3 indicates. However, the spectra of all of the complexes **2** reveal more than one signal for most ring substituents, as is evident from that of a typical member, V(5Me-*n*Pr-sal)$_3$ (Figure 3). In each case the chelate ring inequivalences are especially well demonstrated by the 4-H signals, which occur as a chemically shifted triplet of equally intense features. Because of their considerable breadth, the 3-H and 5-H resonances of **2** are much less clearly resolved and the three signals expected for each cannot all be definitely located (*cf.* Table II).

The pmr spectra demonstrate unequivocally the *trans* stereochemistry **4** for all of the complexes of types **1** and **2**. In no case was any amount of the *cis* isomer detectable. This finding for the salicylaldimine com-

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plexes is entirely consistent with earlier pmr-based stereochemical assignments of the *trans* isomer to Co(R-sal)$_3$[7], tris(N-alkyl-*o*-hydroxyacetophenoneimino)-cobalt(III)[8], and tris(N-alkylpyrrole-2-aldimino)cobalt-(III)[7] and -vanadium(III)[1] complexes. In particular, it is noted that the *trans* structures of the pairs Co(Me-sal)$_3$–V(Me-sal)$_3$ and tris(N-methylpyrrole-2-aldimino)cobalt(III) and -vanadium(III) have been definitely established. There can be little doubt that the apparent exclusive population of the *trans* form is *ligand-directed*, being a consequence of steric interactions among the nitrogen substituents which are considerably alleviated when these groups project from an octahedral edge rather than from the vertices of a common face.[7] Inspection of space-filling models clearly reveals the accentuated steric interplay in the *cis* isomers. Because the effective radius of the coordinated metal in the series M(R-sal)$_3$, M = Sc(III)–Co(III), will almost certainly not vary by more than 0.20 A, it is concluded that all such complexes with R = CH$_3$ or larger will exist as the *trans* isomer under normal conditions. The only six-coordinate salicylaldimino complexes of the M–O$_3$N$_3$ type having a *cis* structure are the Co(III) and Fe(III) species derived from the condensates of salicylaldehyde with 2-aminomethyl-1,3-diaminopropane and axial 1,3,5-triaminocyclohexane.[14] In these cases the ligands impose a necessarily *cis* arrangement of donor atoms.

The apparently complete preference of V(X-sal)$_3$ for the *trans* isomer was not expected. We have recently pointed out[1] that both *cis* and *trans* isomers of a given tris-chelate complex have been isolated or detected in solution when the donor atoms or groups do not differ significantly in their relative steric properties. Examples include tris($\beta$-diketone)chromium(III), -cobalt(III), -rhodium(III),[15] and -vanadium(III)[4] complexes, tris-(hydroxymethylenecamphorato)cobalt(III),[16] and tris-(amino acid)cobalt(III) complexes.[17] The tris-salicylaldehyde complexes would appear to resemble these complexes inasmuch as there is no obvious steric destabilization of either *cis* or *trans* isomers, as revealed by space-filling Stuart–Briegleb metal chelate scale models. In V(3Me-sal)$_3$ nonbonded repulsions among the 3-Me groups might be important in destabilizing the *cis* isomer, but this effect is absent in V(5Me-sal)$_3$. The steric situation in these complexes is extremely similar to that found with tris(2-methyl-3-oxobutanalato)-vanadium(III), V(CH$_3$COC(CH$_3$)CHO)$_3$, and tris(3-oxobutanalato)vanadium(III), V(CH$_3$COCHCHO)$_3$, both of which exist as a *cis–trans* mixture in chloroform solution.[4] We are unable to offer any convincing rationale, based on either steric or electronic grounds, for the preferential formation of the *trans* isomer of **1**. In this connection it is noted that neither isomer of tris(4-mercapto-pent-3-en-2-onato)cobalt(III) is sterically destabilized, yet, on the basis of published pmr spectra of this complex and its 3-bromo derivative,[18] both of these complexes exist exclusively as the *cis* isomer in solution. Electronic factors presumably contribute significantly to the stabilization of the preferential isomers of V(X-sal)$_3$ and the $\beta$-thioxoketone Co(III) complexes, and this question is being further investigated.

**Signal Assignments.** An internally consistent assignment of signals of the salicylaldimine and salicylaldehyde complexes was obtained by a series of methyl substitutions on the benzene rings. The simplest complex of type **1** is obviously V(sal)$_3$. A sample of this compound was prepared but not completely characterized; its solubility is considerably less than that of either ring methylated derivative and it was not investigated. The simplest type **2** complex prepared was V(Me-sal)$_3$. Its spectrum revealed that all ring proton signals occurred at least +320 cps or more upfield and −800 cps or more downfield relative to TMS. Further investigations were carried out with the far more soluble R = *n*-Pr complexes. The pmr data, expressed as contact shifts, are given in Table II together with the signal assignments. The 3-H signals and one of the 5-H signals of **2** were generally extremely broad and could not always be located or assigned with certainty. The 6-H signals in **1** and **2** were in some instances partially obscured by overlap with other features. Signals of the formyl or azomethine protons occur at very high field as extremely broad features and were measured accurately in only several cases.

As is the case with previously investigated *trans* tris-chelate V(III) complexes,[1,4] it has not proven possible to obtain an unequivocal assignment of ring substituent signals to individual chelate rings. Because the magnetic nonequivalence of the chelate rings is manifested principally because of differences in contact interactions, it must be concluded that the total isotropic contact interactions, including the direct contact shifts and contributions from whatever pseudo-contact interactions are significant, conform to the full molecular asymmetry of the *trans* form. From this observation it follows that observed contact shifts do not represent the simple situation in which a different total amount of spin is delocalized in each chelate ring with the relative spin densities at the various positions in each ring being essentially the same.

**Spin Delocalization.** As already pointed out,[1,4] the contact shifts of trigonal chelate complexes cannot be rigorously analyzed in terms of $\pi$ spin densities in the chelate rings because of the lack of strict $\sigma$–$\pi$ separation and the unknown contribution of pseudo-contact interactions. Indeed, in the *trans* isomer the ligand field has only rhombic symmetry, and the location of the molecular principal magnetic axis system and the full anisotropy of the *g* tensor, information necessary for calculation of pseudo-contact shifts in such cases,[19] cannot be estimated with confidence. However, previous considerations[1] do suggest that pseudo-contact contributions do not dominate the total isotropic shifts of complexes such as **1** and **2**.

For paramagnetic molecules there are in general four distinct mechanisms which can lead to finite scalar or dipolar coupling between electron and nuclear spins[20]

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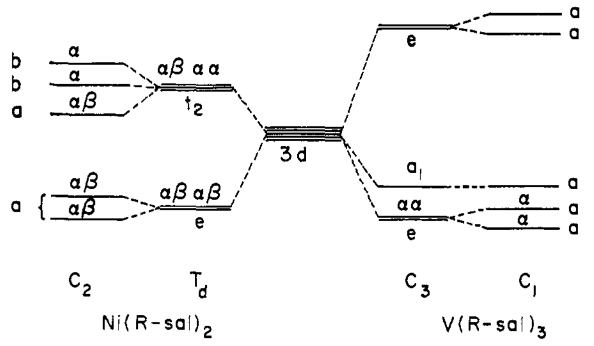


Figure 4. Qualitative one-electron energy level diagram of the d orbitals of the metal in tetrahedral and digonal Ni(II) and trigonal and rhombic V(III) complexes.

and, hence, to isotropic contact shifts in solution. Analysis of the contact shifts in terms of unpaired $\pi$-electron distribution is meaningful only when delocalization into the ligand $\pi$ system, usually by metal–ligand $d\pi$–$p\pi$ mixing, is the predominant mechanism. Although other mechanisms cannot be excluded in **1** and **2**, the observed contact shifts do strongly suggest that $\pi$-electron delocalization is principally responsible for these shifts. First, it is observed that the contact shifts of 3-H, 4-H, 5-H, and 6-H generally alternate in sign, a characteristic behavior of nonalternant systems such as aminotroponeimine,[21] $\beta$-ketoamine,[6c,13] and salicylaldimine[6] groups. An exception is V(3Me-sal)$_3$ in which one 5-H signal has a positive shift. Second, replacement of a proton by a methyl group usually results in a change in sign of the contact shifts, with possible exceptions to this behavior being the 5-Me signals of V(5Me-sal)$_3$ and V(5Me-*n*Pr-sal)$_3$. Contact shifts, electron-nuclear coupling constants $a_i$, and carbon $p\pi$ spin densities $\rho_{C_i}$ are interrelated by the familiar expressions

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g|\beta|S(S+1)}{6SkT}$$

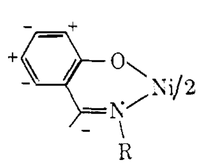
and

$$a_i = Q_X\rho_{C_i}$$

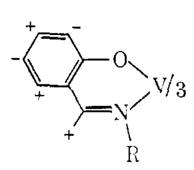
in which the symbols have their usual meanings.[5,21] The V(III) complexes have spin-triplet ($S = 1$) ground states. Because $Q_{CH}$ and $Q_{CCH_3}$ are of opposite sign (− and +, respectively), the observed change in sign upon substituting CH$_3$ for H is indicative of predominant $\pi$ spin delocalization producing contact shifts at positions 3 and 4. The situation at the 5 position in at least one of the chelate rings is less clear, and pseudocontact effects and/or a delocalization process involving spin of an opposite sense (*vide infra*) may contribute here.

If $\pi$-delocalization of spin is accepted as the predominant mechanism for effecting contact shifts, an interesting comparison between the contact shifts of pseudo-octahedral V(R-sal)$_3$ and pseudo-tetrahedral Ni(R-sal)$_2$ can be made. There are three limiting paths, symmetry permitting, by which unpaired $\pi$ spin can be placed on the ligand system: (i) parallel or $\alpha$-spin transfer from the highest filled MO (HFMO) of the ligand anion to the spin-containing metal orbitals; (ii) antiparallel or $\beta$-spin transfer involving the same orbitals as in path i; (iii) parallel spin transfer from the metal to the lowest unoccupied MO (LUMO) of the ligand anion. (The term "parallel" refers to a spin direction in the magnetic field which is parallel to the spin polarization of the metal.) Path i results in a net $\beta$ spin on the ligand while paths ii and iii leave a net $\alpha$ spin on the ligand. Reference to the simplified one-electron orbital energy diagram in Figure 4,[22] which is of qualitative significance only, indicates that path i is excluded for tetrahedral and digonal Ni(II) complexes and that path ii is unlikely for trigonal and rhombic V(III) inasmuch as such complexes are high spin and exchange effects would probably tend to favor $\alpha$- rather than $\beta$-spin transfer to the metal. The importance of ii *vs.* iii for Ni(II) and i *vs.* iii for V(III) will depend upon the energies of HFMO and LUMO relative to the d-orbital energies of the metal.

A detailed consideration of the contact shifts of a series of Ni(X-R-sal)$_2$ complexes (X = H, CH$_3$) has shown that path ii predominates,[6a] as reflected by the pattern of contact shifts shown in **5** (X = H). The order of shifts, $|\Delta f_{3H,5H}| > |\Delta f_{4H,6H}|$, is in good agreement with spin densities calculated for the neutral salicylaldimine radical by VB[6a] and HMO procedures, including an estimate of negative spin densities by McLachlan's method.[23] This pattern is to be contrasted with that observed for V(X-R-sal)$_3$ complexes (note the several exceptions mentioned above) and indicated in **6** (X = H). The signs of the observed shifts completely rule out path ii but are in qualitative agreement with paths i and iii. However, the consistent observation that the 4-H contact shifts are the largest is in sharp disagreement with the valence-bond calculations of spin densities in the salicylaldimino neutral radical. This leaves path iii as the most probable. HMO calculations are consistent with this conclusion, indicating that 4-C and 6-C are positions of large spin density compared to 3-C and 5-C,[24] whose spin densities are presumably rendered negative by the effects of spin correlation. The net $\alpha$ spin produced by iii at 4-C, 6-C, and the azomethine carbon[25] will, by virtue of the signs of $Q_{CH}$ and $Q_{CCH_3}$, effect negative and positive spin densities at the aromatic and methyl proton nuclei, respectively, leading to the corresponding positive and negative contact shifts. The reverse situation obtains at 3-C and 5-C. Therefore, a comparison of V(III) and Ni(II)



**5**



**6**

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[22] For discussion of the symmetry of the spin-containing orbitals of the metal in pseudo-tetrahedral nickel complexes, *cf.* ref 6b and D. R. Eaton and W. D. Phillips, *J. Chem. Phys.*, 43, 392 (1965). The electronic structures of trigonal V(III) complexes are considered in references cited in ref 4.

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[24] Typical HMO spin densities for a single electron in the LUMO are the following: 3-C, +0.0771; 4-C, +0.1442; 5-C, +0.0024; 6-C, +0.1674; azomethine C, +0.2521.

[25] The extremely large, positive contact shifts observed for azomethine protons (*cf.* Table II) cannot result only from $\pi$-spin delocalization. Protons in similar positions also exhibit positive shifts of comparable magnitude which are believed to be effected, at least in part, by $\sigma$-spin delocalization.[1,4]

complexes with identical ligands, whose contact shifts are primarily the result of direct contact interactions produced by unpaired $\pi$-electron density, reveals that the d orbitals of the lighter metal interact preferentially with the ligand antibonding orbitals. This observation is in full agreement with Eaton's argument, based on the contact shifts for metal acetylacetonates,[5] that with increasing nuclear charge the d orbitals contract and become relatively more stable.

Although the foregoing interpretation of the contact shifts of **1** and **2** is necessarily qualitative, it is believed to be essentially correct. By way of supporting evidence, it is noted that delocalization *via* path iii has also been concluded to be primarily responsible for the contact shifts of $\beta$-diketone[4,5] and $\beta$-ketoamine[1] V(III) complexes, which are structurally and electronically similar to **1** and **2**, respectively, and for which the neglect of pseudo-contact interactions, particularly in the *cis* isomers, is on firmer ground. Further analysis of the contact shifts of any of these complexes is not feasible until or unless the magnitude and directions of *g* tensors are determined and the effects of $\sigma$-spin delocalization[25,26] can be semiquantitatively assessed.

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# A Mass Spectrometric Investigation of the Low-Pressure Pyrolysis of Diphosphine-4

**T. P. Fehlner**

*Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.* *Received June 9, 1967*

**Abstract:** Diphosphine-4, $P_2H_4$, thermally decomposes in a Pyrex reactor over the pressure range of 0.5–50 mtorr into phosphine and diphosphine-2 by a reaction which is zero order in diphosphine-4. Over the temperature range 570–650°K, the rate of the reaction is expressed by $\log h(T) = 20.8 - 4800/T$ molecules cm$^{-2}$ sec$^{-1}$. In addition, the intermediate product diphosphine-2 decomposes to give tetraatomic phosphorus as one product in a reaction which is inhibited by phosphorus hydrides. The relevance of these results to the thermal stability of diphosphine-4 is discussed.

The nature of the reactions of diphosphine-4, $P_2H_4$, is of considerable interest and importance as this is one of the simplest molecules containing a phosphorus–phosphorus bond. Pyrolysis is perhaps the simplest reaction that this compound can undergo, at least from the point of view of number of reactants. In possibly the most complete study to date, Evers and Street have examined the final products of the thermal decomposition of diphosphine-4 in the liquid and/or gaseous phases under anhydrous conditions.[1] They found phosphine and a hydride having a composition $P_9H_4$ as final products. However, it has been noted in several instances that the decomposition of diphosphine-4 is also sensitized by light and various impurities[1-3] and, as yet, no study of the gas-phase pyrolysis in the absence of light and other impurities has been published.

Some preliminary results of this study in which intermediate products of the pyrolysis were identified have been reported.[4,5] Diphosphine-2 was definitely identified in the low-pressure pyrolysis of diphosphine-4 in a quartz tubular flow reactor. Later, this molecule was found to be produced in the ion source of a mass spectrometer probably by pyrolysis on the filament or source walls.[6] Triphosphine-5 was tentatively identified in these studies and was also prepared in substantial quantities outside of the mass spectrometer.[5] Evidence for the existence of this compound has been presented by others also.[7-9] Here we present a more comprehensive report of the low-pressure pyrolysis of diphosphine-4 which includes a detailed study of the products, reaction order, stoichiometry, and reaction rate.

## Experimental Section

The pyrolytic reactor for these studies was patterned after a reactor pictured and theoretically described by LeGoff in a series of papers.[10-12] This short, cylindrical reactor, which is illustrated on the left side of Figure 1, was fabricated completely out of Pyrex glass (80% $SiO_2$, 14% $B_2O_3$, 4% $Na_2O$, 2% $Al_2O_3$) and had a volume of 3.2 cc. The reactant gas entered through a 0.35-mm diameter capillary leak and exited through a 0.40-mm diameter thin-walled orifice. The capillary leak was cooled with water both to prevent a change in conductance and to prevent decomposition in the capillary. The cylindrical sides of the furnace were heated with noninductively wound nichrome wire imbedded in Sauereisen

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