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Synthesis and NMR Contact Shift of Paramagnetic Tris(tropolonato)vanadium(III)

by

Katsuma HIRAKI*, Masayoshi ONISHI*, and Khozo SONODA*

A paramagnetic complex of tris(tropolonato)vanadium(III) was prepared and a 'H–NMR spectrum of the complex was studied. From a consideration of the signs and magnitudes of paramagnetic shifts, it was concluded that the shifts were primarily due to unpaired electron delocalization via metal to ligand parallel spin transfer.

Interactions between unpaired electrons on transition metal ions and nuclei with magnetic moments on ligands coordinated to the metal ions have been the subject of recent NMR studies, and afforded useful informations on the electronic and structural properties of transition metal complexes.1,2,3) In our previous paper,4) we studied NMR spectra of some tris(β-diketonato)vanadium(III) complexes, and explained paramagnetic shifts on the basis of IT-contact mechanism. There was a relationship between the paramagnetic shifts of α-CH₃ protons and σₓ values of γ-substituents in the β-diketonate chelate. The σₓ values represent a term of the resonance effect of each meta-substituent composing Hammett value σₓ, and this relationship indicated quasi-aromatic character of the β-diketonate system. The present work deals with the paramagnetic shifts of tris(tropolonato)vanadium(III), which has an α-ketoenolate chelate.

Vanadium(III) chloride was reacted with three-fold moles of tropolone in the presence of sodium carbonate to give dark green microcrystals of tris(tropolonato)vanadium(III). Upon complexation, a ν(C=O) band shifted to 1585 cm⁻¹, from 1615 cm⁻¹ of free tropolone. The microcrystals were fairly air-sensitive, and color of the solid was bleached after exposure to the air for 1 day. Appearance of a new ν(V=O) band at 990 cm⁻¹ and elemental analysis indicated that the original vanadium(III) complex was changed to bis(tropolonato)oxovanadium(IV).

In the 'H–NMR (100 MHz) spectrum of tris(tropolonato)vanadium(III) in CDCl₃, there were three signals at δ 14.25(2H), 8.45 (1H), and 1.35 (2H), as listed in Table 1. The signal at δ 8.45 was assignable to 5–H by the intensity ratio. Paramagnetic shifts were determined relative to the diamagnetic tris(tropolonato)aluminum(III).

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Concerning paramagnetic shifts it is usual to recognize the contributions of both contact and pseudo-contact (or dipolar) shifts.\textsuperscript{1,2,5) Although the pseudo-contact shift is important in complexes of rare-earth metals and transition metals in the second row, it is believed that the contact shift is dominant in complexes of transition metals in the first row.\textsuperscript{1,2,5) In the latter case, there is spin transfer from metal to ligands or vice versa through $\sigma$- or $\pi$-type molecular orbitals.\textsuperscript{1,2,5)\textsuperscript{5} Tropolonate group.\textsuperscript{5} Tropolonate group.

Table 1. $^1$H-NMR data for tropolonate complexes \textsuperscript{a)}

<table>
<thead>
<tr>
<th></th>
<th>Aluminum Complex</th>
<th>Vanadium(III) Complex</th>
<th>paramagnetic shift ($\nu(\text{V})-\nu(\text{Al})$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$-H</td>
<td>$\nu(\text{Al})$</td>
<td>$\nu(\text{V})$</td>
<td>$\nu(\text{V})-\nu(\text{Al})$</td>
</tr>
<tr>
<td>$^7$-H</td>
<td>-749</td>
<td>-1425</td>
<td>-676</td>
</tr>
<tr>
<td>$^4$-H</td>
<td>-757</td>
<td>-135</td>
<td>+622</td>
</tr>
<tr>
<td>$^6$-H</td>
<td>-711</td>
<td>-845</td>
<td>-134</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} 100 MHz NMR spectrometer; Chemical shifts in cps from TMS; In CDCl$_3$.

Table 2 shows that energy level of the highest occupied molecular orbital (HOMO) in a $\pi\tau$-system of the tropolonate anion\textsuperscript{6) locates between those of acetylacetone\textsuperscript{5) and aminotropolonate\textsuperscript{5) anions. Moreover, energy level of the lowest unoccupied molecular orbitals (LUMO)\textsuperscript{7)} was reported to be lower than those of acetylacetone and aminotropolonate anions, suggesting easier spin transfer from vanadium to LUMO of the tropolonate chelate. As for tris(acetylacetono)vanadium(III)\textsuperscript{8,5) and some other related complexes,\textsuperscript{8) paramagnetic shifts have been ascribed to dominant $\pi$-delocalization of parallel spin from vanadium to LUMO of ligands. In addition, D. R. Eaton and his coworker\textsuperscript{9) mentioned donation from the metal to LUMO in tris(aminotropolonate)vanadium(III), in contrast to that from HOMO to the metal in nickel(II) analogues.\textsuperscript{1,9)}}
Accordingly, similar spin-delocalization occurred probably from vanadium to LUMO in tris(tropolonato)vanadium (III). Spin-density distributions of the \( \pi \)-electron system were obtained for the tropolonate anion from Hückel molecular orbitals, which were calculated by Y. Kurita and M. Kubo\(^6,7\) with a semi-empirical Wheland-type S. C. F. treatment. Parallel-spin transfer to LUMO was expected to give large high-field shifts for 4-H and 6-H.\(^1,2\) Moreover, the calculated spin-distributions suggested also small high-field shifts or possible low-field shifts for 3-H, 5-H, and 7-H.\(^1,2\) Therefore, the observed resonance at \( \delta \) 1.35 was assigned to 4-H and 6-H, and that at \( \delta \) 14.25 was to 3-H and 7-H. Each proton on a cycloheptatrienyl ring shifted in opposite directions to those of adjacent protons, similarly to the cases of tris(salicylaldehydato)- and tris(salicylaldiminato)vanadium (III).\(^8\) This behavior was consistent with the \( \pi \)-contact shift mechanism.

An alternative possibility might be parallel-spin transfer from HOMO to metal orbitals,\(^9\) leaving anti-parallel spin in HOMO. In this case, large low-field shifts were expected for 3-H, 5-H, and 7-H, and small shifts were for 4-H and 6-H.\(^1,2\) However, this characterization was not compatible with the high-field resonance at \( \delta \) 1.35 and a small low-field shift of 5-H.

In case of tris(\( \beta \)-diketonato)vanadium(III) dominant \( \pi \)-delocalization brought about very large paramagnetic shifts, and contributions by \( \sigma \)-contact and pseudo-contact shifts were negligible.\(^5\) On the contrary, the observed paramagnetic shifts were not so large as those of tris(\( \beta \)-diketonato)vanadium(III), probably owing to the fact that the cycloheptatrienyl ring does not include vanadium, but is only fused with the \( \alpha \)-ketoeno1ate chelate coordinated to the metal. It is noteworthy that 3-H and 7-H with calculated spin-densities of the small positive value showed a moderate low-field shift. This may be related to a possible negative shift through \( \sigma \)-contact and pseudo-contact interactions,\(^1,2\) and to the Hückel method of calculation which does not take account of spin correlations.\(^1,2\) The correlations are well-known to give rise to negative spin densities in a nonalternant system such as the tropolonate group.\(^1\)

### Experimental

**General Procedures.**

Tropolone was prepared according to the methods reported by H. C. Stevens et al.\(^10\) Preparations and recrystallization of air-sensitive vanadium(III) complexes were carried out under a dinitrogen atmosphere. \(^1\)H-NMR spectra were run on a JEOL Model PS-100 spectrometer, and NMR tubes of the vanadium(III) complexes in CDCl\(_3\) were sealed in vacuo. Chemical shifts were referenced to chloroform whose resonance was \( \delta \) 7.26 ppm downfield from tetramethylsilane. IR spectra were obtained using a Hitachi Model 285 spectrometer.

**Preparation of tris(tropolonato)vanadium(III).** An aqueous solution (15ml) of tropolone (3.0g) and sodium carbonate (2.0g) was added dropwise to a solution (15ml) of vanadium (III) chloride (1.3g), and the mixture was refluxed for 1 h. Resulting precipitates were collected and recrystallized from benzene and petroleum ether to give dark-green microcrystals of tris(tropolonato)vanadium(III) in a 88\% yield.

**Preparation of tris(tropolonato)aluminum(III)**
Pale yellow aluminum(III) complex was obtained in a similar way except that aluminum sulfate was used in place of vanadium(III) chloride. Yield: 65%

Acknowledgment

We wish to express our thanks to Professor Y. Kurita in Yokohama National University for his presentation of LUMO in the tropolonate anion.

References and Notes

7) According to the calculation by Y. Kurita, LUMO is expressed as follows.
   \[ \Psi (-0.5081) = 0.3340 (\phi_2 - \phi_1) + 0.2999 (\phi_3 - \phi_4) 
   - 0.5014 (\phi_5 - \phi_6) - 0.2171 (\phi_7 - \phi_8) \]