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# A Study of Metal-Ligand Vibrations in Nickelocene and Ferrocene

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Raman and infrared spectra of nickelocene and ferrocene were studied as regards metal-ligand vibrations. It was found that the $C_5H_5$-ring tilt vibration, $\nu_{16}(e_{1g})$, of nickelocene has considerably low frequency. This was discussed in view of metal-ligand binding between both metallocenes.

Nickelocene is a member of the ferrocene homologues but is thermally more unstable than ferrocene.[1] The Ni–cyclopentadienyl (Cp for short) distance is known to be greater than the Fe–Cp beyond the difference in covalent metallic radii of Ni and Fe.[2] This was accounted for by the difference in outer shell electron configurations, since $Ni(Cp)_2$ has two anti-bonding electrons in addition to the closed shell of $Fe(Cp)_2$ in MO representations.[3] In accordance with this, the infrared and Raman spectra[4,5] show that the metal–ligand vibrations of $Ni(Cp)_2$ have in general considerably lower frequencies than those of $Fe(Cp)_2$. Most striking is the difference observed for the Cp-ring tilt vibration $\nu_{16}(e_{1g})$[a], whose frequency is reduced as much as to half from $Fe(Cp)_2$ to $Ni(Cp)_2$, resulting in a reversed frequency order of $\nu_{16}$ and $\nu_4$ ($a_{1g}$ metal–Cp stretching) between both compounds. Since such behavior is evidently anomalous among other metal–ligand vibrations, a special mechanical condition associated with the $\nu_{16}$ mode of $Ni(Cp)_2$ may be found. As was suggested by Gächter *et al.*,[5] the antibonding electrons of $Ni(Cp)_2$ can be considered to be responsible for the anomaly. Since the problem is closely related to the nature of metal–Cp bindings, we have carried out a comparative study of the metal–ligand vibrations of $Fe(Cp)_2$ and $Ni(Cp)_2$ with particular attention to the behavior of $\nu_{16}$.

The difference in metal–Cp bindings as above is expected to appear in the infrared and Raman intensities. The effect may be remarkable not only in the metal–Cp vibrations but also for such internal modes of Cp as appreciably perturb the electronic interaction between the metal and Cp-ring. These intensity features are also presented and discussed.

## Experimental

Raman spectra were obtained for cyclohexane solutions of metallocenes, with 632.8 nm (He-Ne) exciting radiation for $Fe(Cp)_2$ and 514.5 nm ($Ar^+$) for $Ni(Cp)_2$. Since $Ni(Cp)_2$ slightly absorbs the latter radiation ($\varepsilon \approx 10$), the solution was prepared with a completely degassed solvent and irradiated in a vacuum sealed cell with a somewhat defocussed laser beam. Relative Raman intensity was determined by comparing the recorded band area with a solvent band at 426 $cm^{-1}$. Infrared intensities were determined in carbon tetrachloride, cyclohexane, and tetrahydrofuran solutions by means of Beer's law plots for integrated band area.

## Results and Discussion

The observed Raman and infrared frequencies are given in Table 1 together with the frequencies and assignments previously given. Although Gächter *et al.*[5] tentatively assigned considerably higher frequencies than those of Lippincott and Nelson[4] to $\nu_{11}$ and $\nu_{21}$ of $Ni(Cp)_2$, it remains unexplained why they preferred these extremely weak Raman lines to the intense 355 $cm^{-1}$ infrared band. On the other hand, the broad and asymmetric profile of 355 $cm^{-1}$ absorption suggests a possibility of overlapping $\nu_{11}$ and $\nu_{21}$ which lie very close to each other in $Fe(Cp)_2$. Thus the assignment by Lippincott and Nelson[4] seems to be more reasonable, and can be adopted in the following discussion. The parenthesized frequencies of $Ni(Cp)_2$ in Table 1 are their estimated values based on the infrared frequencies and simple valence force field.

It is notable that the observed $\nu_{16}$ frquency of $Ni(Cp)_2$ is remarkably deviated from the above estimation, suggesting the presence of a special mechanical condition associated with the vibration of $Ni(Cp)_2$. Table 2 shows the ratios of force constants between $Ni(Cp)_2$ and $Fe(Cp)_2$ for some metal–ligand modes. Each vibration was assumed to be of an entirely metal–Cp character with no contribution of Cp-internal motions. Such an approximation may be sufficient for the present semi-quantitative discussion, since the changes of these metal–Cp frequencies from $Fe(Cp)_2$ to $Fe(C_5D_5)_2$ are generally as small as expected from the change of mass.

A number of theoretical studies have been devoted to the electronic structure of metallocenes.[6] They generally give the outer shell MO configurations:

$$\cdots\cdots(e_{1g})^4(e_{2g})^4(a_{1g})^2, \qquad {}^1A_{1g} \text{ for } Fe(Cp)_2$$
$$\cdots\cdots(e_{1g})^4(e_{2g})^4(a_{1g})^2(e_{1g}^*)^2, \qquad {}^3A_{2g} \text{ for } Ni(Cp)_2$$

where ($e_{1g}$) and ($e_{1g}^*$) are the metal–Cp bonding and anti-bonding orbitals, respectively, both of which are composed of the metal 3d(xz,yz) AO's and Cp-ring $\pi(e_1'')$ MO's. On the other hand, the ($e_{2g}$) and the ($a_{1g}$) orbitals are essentially non-bonding and represented by the metal $3d(x^2-y^2,xy)$ and $3d(z^2)$, respectively. A recent study by electron spectroscopy showed that the order of orbital energies in $Fe(Cp)_2$ is $(a_{1g})<(e_{2g})$.[7]

The perturbation theory gives the following expression for vibrational force constant[8]

$$k = k_1 - k_2$$
$$k_1 = \int \psi_o^{o*}(\partial^2 H/\partial Q^2)_o \psi_o^o \mathrm{d}\tau$$
$$k_2 = 2\sum_{i\neq 0} \left| \int \psi_o^{o*}(\partial H/\partial Q)_o \psi_i^o \mathrm{d}\tau \right|^2 / (E_i^o - E_o^o).$$

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[a] $D_{5d}$ symmetry is assumed on the basis of crystalline data (J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Crystallogr.*, **9**, 373 (1956)). No essential change is necessary in the following considerations for $D_{5h}$ or $D_5$ symmetries.

Table 1. Vibrational frequencies of $Fe(Cp)_2$ and $Ni(Cp)_2$

| Species | | $Fe(Cp)_2$ | | | $Ni(Cp)_2$ | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\nu$ ($cm^{-1}$)[a)] | $\nu$ ($cm^{-1}$) | $\rho$ | $\nu$ ($cm^{-1}$)[a)] | $\nu$ ($cm^{-1}$)[b)] | $\nu$ ($cm^{-1}$) | $\rho$ |
| $A_{1g}$ | 1 | 3099 | 3112 | | (3100) | 3108 | 3112 | |
| | 2 | (804) | 834[c)] | | (770) | 780 | | |
| | 3 | 1105 | 1105 | ≈0 | (1105) | 1109 | 1114 | ≈0 |
| | 4 | 303 | 306 | 0.22 | (220) | 255 | 245 | 0.33 |
| $A_{2u}$ | 8 | 3085 | 3095 | | 3075 | 3090 | 3100 | |
| | 9 | 811 | 809 | | 773 | 776 | 763[c)] | |
| | 10 | 1103 | 1107 | | 1110 | 1102 | 1111 | |
| | 11 | 478 | 476 | | 355 | 420[d)] | 355 | |
| $E_{1g}$ | 12 | 3085 | | | (3085) | 3102 | | |
| | 13 | 1010 | 1006 | | (1010) | 1002 | | |
| | 14 | (800) | 816[c)] | | (770) | | | |
| | 15 | 1408 | 1417 | | (1425) | 1426 | | |
| | 16 | 388 | 390 | 0.73 | (275) | 208 | 198 | 0.70 |
| $E_{1u}$ | 17 | 3075 | 3095 | | 3075 | 3078 | 3100 | |
| | 18 | 1002 | 1004 | | 1000 | 997 | 1006 | |
| | 19 | 834 | 830 | | 800 | 840 | 794[c)] | |
| | 20 | 1411 | 1410 | | 1430 | 1404 | 1424 | |
| | 21 | 492 | 490 | | 355 | 490[d)] | 355 | |
| | 22 | 170 | | | (125) | | | |

a) Data from Ref. 4. b) Data from Ref. 5. c) Observed in crystal. d) See text. ( ) Estimated value in Ref. 4. $\rho$ Depolarization ratio.

$k_1$ is determined by the electronic wavefunction of the ground state at equilibrium configuration $\psi_0{}^0$, so that its value for the Ni–Cp may be considerably smaller than that of the Fe–Cp owing to the anti-bonding electrons occupying $(e_{1g}^*)$ orbitals. $k_2$ represents the relaxation of vibrational potential due to the vibronic mixing of excited state wavefunctions $\psi_i{}^0$ into the ground state. $k_2$ may not be very important for other metal–Cp vibrations than $\nu_{16}(e_{1g})$, since the electronic spectra as well as theoretical studies[6,9,11)] show that the excited states with $a_{1g}$, $a_{2u}$, $e_{1u}$, and $e_{2u}$ symmetries, which can couple with the ground state through those vibrational perturbations, are all located at high energy, *viz.*, >40000 $cm^{-1}$ in $Fe(Cp)_2$ and >30000 $cm^{-1}$ in $Ni(Cp)_2$. On the other hand, there are several low-lying excited states of $e_{1g}$ symmetry in both metallocenes, which have been assigned to the $(a_{1g})\rightarrow(e_{1g}^*)$ and $(e_{2g})\rightarrow(e_{1g}^*)$ excitations and are located at 22000 $cm^{-1}$—30000 $cm^{-1}$ in $Fe(Cp)_2$ and at 14000 $cm^{-1}$—23000 $cm^{-1}$ in $Ni(Cp)_2$, respectively. Thus the force constant of $\nu_{16}(e_{1g})$ may be considerably reduced from the $k_1$ value, which approximately corresponds to the classical valence force field, due to a large $k_2$ term involving these lower $e_{1g}$ states. This is supported by the observation that the $\nu_{16}$ frequency is always considerably smaller than the related $\nu_{21}(e_{1u})$ ring tilt frequency.

The above fact is equally described as the vibrationally induced mixing of the $(e_{1g}^*)$ orbital into the $(e_{2g})$ and $(a_{1g})$ orbitals. Such a mixing may modify the latter non-bonding orbitals so as to relieve the strain energy of the molecule (Fig. 1). This effect may be enhanced further on the $(a_{1g})$ orbital by the presence of $3d(z^2)$-4s hybridization, shown to be appreciable by an ESR study.[12)] In $Ni(Cp)_2$, the above vibronic mixing effect on the force field may be partly cancelled by the opposite behavior of half-filled $(e_{1g}^*)$ orbitals, but the $k_2[Ni(Cp)_2]$ may still be comparable to or even greater than that of $Fe(Cp)_2$ since the mixing orbitals are much closer to each other in energy than in $Fe(Cp)_2$.[10)] On the other hand, the outer electron shell may be much less flexible for other modes, since each occupied MO can find partners of mixing only at very high energy.

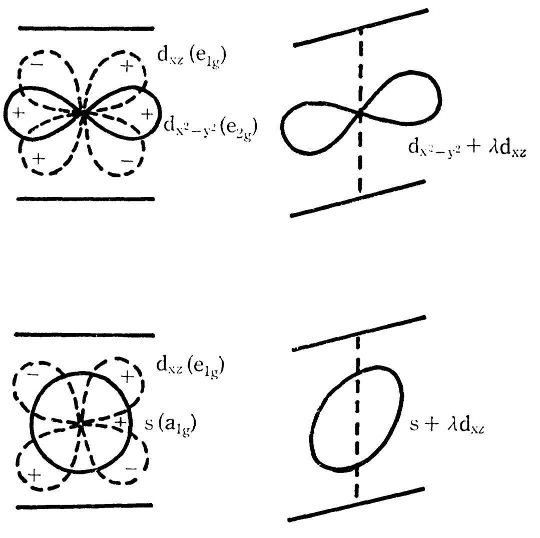

Fig. 1. Changes of the $3d(x^2-y^2)$ and the 4s orbital lobes due to a mixing 3d(xz) caused by $\nu_{16}(e_{1g})$ Cp-tilt vibration.

In order to have an approximate idea, we consider a very simplified case in which $k_2$ is deliberately assumed to be significant only for the $\nu_{16}$ mode with equal values in both metallocenes. Then, $k_1$ of $Ni(Cp)_2$ may be

Table 2. Ratio of force constants between $Ni(Cp)_2$ and $Fe(Cp)_2$ for metal–Cp modes

| Mode$^{a)}$ | $\nu_4(a_{1g})$ | $\nu_{11}(a_{2u})^{b)}$ | $\nu_{16}(e_{1g})$ | $\nu_{21}(e_{1u})^{b)}$ |
|---|---|---|---|---|
| $\frac{k[Ni(Cp)_2]}{k[Fe(Cp)_2]}$ | 0.64 | 0.57 | 0.26 | 0.53 |

a) Each mode was assumed to be of entirely metal-Cp character without the contribution of Cp-internal motions. b) Considerably higher $Ni(Cp)_2$ frequencies chosen in Ref. 5 give the ratios close to unity.

Table 3. Vibrational intensities of $Fe(Cp)_2$ and $Ni(Cp)_2$

| Mode | | $Fe(Cp)_2$ | $Ni(Cp)_2$ |
|---|---|---|---|
| IR | $\nu_8$, $\nu_{17}$ | $4.06\times10^6$ cm/M | $3.13\times10^6$ cm/M |
| | $\nu_{20}$ | 1.07 | 1.10 |
| | $\nu_{10}$ | 4.16 | 0.35 |
| | $\nu_{18}$ | 4.56 | 8.53 |
| | $\nu_{21}$ | 5.17 | 1.26 |
| | $\nu_{11}$ | 3.00 | |
| Raman$^{a)}$ | $\nu_4$ | 1.0 | 5.6 |
| | $\nu_{16}$ | 0.2 | 1.5 |

a) Relative intensities.

estimated at about 60% of the $Fe(Cp)_2$ value from Table 2. Subsequently, we get the small $k[Ni(Cp)_2]/k[Fe(Cp)_2]$ value for $\nu_{16}$ in the table if we assume the common $k_2$ to be equal to 0.45 times of $k_1[Fe(Cp)_2]$. The essential fact is that the negative contribution from vibronic mixing, $-k_2$, affects the force constant of $Ni(Cp)_2$ more profoundly, since $k_1$ of $Ni(Cp)_2$, the minuend of the above equation, is considerably smaller than $k_1[Fe(Cp)_2]$.

A few remarks should be added to the results shown in Table 3. Most striking in the infrared is the extreme difference of $\nu_{10}$ ($a_{2u}$ ring breathing) intensities between both metallocenes. The transition moment of this mode may mostly originate from the electron vibration[13] between Cp-rings *via* metal. Therefore, the observed difference indicates a much greater importance of charge transfer effect in the Fe–Cp bindings than in the Ni–Cp. As for Raman intensities, $Ni(Cp)_2$ is by far surpassing as far as the measured bands are concerned. On the basis of Raman intensity theory,[14] it may be understood as due to the fact that the allowed excited states of $Ni(Cp)_2$ are located at considerably lower energy than $Fe(Cp)_2$.

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