Nuclear Magnetic Resonance Study of $^{59}$Co in Some Co(III) Complexes

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From the NMR spectra of $^{59}$Co in Co(III) complexes of the type [Coen$_2$(R)Cl]$_2$ where en = ethylenediamine and R = dicyandiamide or an aromatic amine, the chemical shift values (σ) have been determined. The σ values have been calculated theoretically also using Griffith and Orgel’s formula. The observed and calculated σ values agree well. Taking σ values as a measure of ligand field strength a decreasing order of ligand field strengths in terms of amine R is reported.

MAGNETIC susceptibilities and temperature-independent paramagnetism (t.i.p.), $\chi_p$, values of the Co(III) complexes of the type [Coen$_2$(R)Cl]$_2$ where R = dicyandiamide or an aromatic amine have been reported by us$^1$. On the basis of the theory of Griffith and Orgel$^2$, we have also calculated the $\chi_p$ (t.i.p.) values theoretically$^3$. In the present investigation $^{59}$Co NMR spectra of the complexes have been recorded. From the spectra, the chemical shift values (σ) have been determined and compared with those calculated using Griffith and Orgel’s formula.

Concentrated aqueous solutions of the complexes were placed in the probe of the Varian wide-line spectrometer, V-4200 which was coupled with a 12 inch electromagnet. Solution of Co(en)$_2$Cl$_2$ was used as an external standard. The stabilities of the Co(III) complexes of the type [Coen$_2$(R)Cl]$_2$ and the complex under examination were recorded by scanning the field over a limited range of 7000 gauss. Values of $\sigma$% were calculated from the separation between the two lines in the spectra of Co(en)$_2$Cl$_2$ and [Co(en)$_2$(R)Cl]$_2$.

From these $\sigma$% values the $\sigma$% values relative to K$_2$Co(CN)$_6$ were calculated (Table 1). Using Griffith and Orgel’s formula, $\sigma$% values were calculated theoretically also. The energy of separation ($\Delta E$) values required for this purpose have also been reported in the same table.

An examination of the results shows that the observed values are negative. This is because the resonance occurs at a field lower than that for K$_2$Co(CN)$_6$. Further, it is seen that the calculated values are lower than the observed ones. Griffith and Orgel estimated the probable errors in their calculation of $\sigma$ and came to the conclusion that the theoretical calculation can at best give an agreement within 20% of the observed data. Kanekar and Nipankar$^4$ and Datar and Patankar$^5$ have also made similar observations.

The results obtained in the present investigation are within $\pm 20\%$ of the calculated values and

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Therefore are in agreement with the conclusions of the theory. From the results it is observed that the energy separation (ΔE) between $A_{1g}$ and $T_{1g}$ states in these complexes must be smaller than the corresponding separation in Co(en)$_3$Cl$_3$.

This is also evident from the ΔE values. ΔE is 21400 cm$^{-1}$ for Co(en)$_3$Cl$_3$ whereas it is in the neighbourhood of 19000 cm$^{-1}$ for the complexes under investigation.

The observed results thus show that the combined ligand field strength of the amine, R, and chlorine in the complexes is lower than that of ethylenediamine.

One of the conclusions reported by Griffith and Orgel is that $\zeta_3$ (t.i.p.) term should decrease as the ligand field strength increases. Considering $\sigma_{\text{para}}$ values as a measure of ligand field strength, the following order of relative ligand field strengths has been established: dicyandiamide > pyridine > m-toluidine > m-anisidine > m-chloroaniline > p-anisidine > p-phenetidine > m-phenetidine > o-phenetidine > o-chloroaniline.

The authors wish to record their deep sense of gratitude to late Prof. C. R. Kanekar of TIFR, Bombay, for providing the facilities to record NMR spectra and for his valuable suggestions and to Dr V. R. Marathe for running the NMR spectra.

References

Reactions of Rhenium Carbonyl with Xenon Difluoride
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Reaction of rhenium carbonyl with xenon difluoride has been carried out in fluorinated hydrocarbons like genetron, perfluoro 1,3-dimethylcyclohexane and perfluoro methyldecaline. The product obtained on washing with tungsten hexafluoride and anhydrous hydrogen fluoride gives a compound of stoichiometry Re(CO)$_6$F$_2$.

The IR and mass spectra of the compound have been reported which indicate a tetrameric structure with fluorine bridges.

Carbonyl halide derivatives of many transition elements are well known and their physical and chemical properties have been studied well$^4$. But only a few reports on such compounds with fluorine as the halogen have been published. Despite the established order of stabilities for carbonyl halides (I > Br > Cl), it seems that given suitable conditions, carbonyl fluorides of some transition elements can be obtained. Peacock et al.$^7$ have been successful in isolating and characterizing ruthenium carbonyl fluoride. Peacock and Marshall$^8$ have carried out the fluorination of osmium carbonyl by xenon difluoride and have characterized osmium carbonyl fluoride. The synthesis and characterization of molybdenum and tungsten carbonyl fluorides have been reported$^9$-10 earlier by me. O'Donnell and Phillips$^11$ have investigated the reaction of rhenium carbonyl and ReF$_6$ and have reported the formation Re(CO)$_6$F$_2$. We report here the results of our studies on the reaction of rhenium carbonyl with xenon difluoride.

Reaction of rhenium carbonyl and xenon difluoride in perfluoro 1,3-dimethylcyclohexane — Rhenium carbonyl (0.239 g) was transferred to a reaction bulb which was maintained at liquid nitrogen temperature. The temperature of the bulb was slowly raised to 0°C when a grey solid started separating from the yellowish solution. This grey solid finally turned yellow. The yellow solid was kept in vacuo overnight to remove unreacted xenon difluoride and any trace of rhenium hexafluoride which might have resulted during the fluorination of rhenium carbonyl. The product obtained weighed 0.26 g [Found: Re, 62.38; F, 12.88. Calc. for Re(CO)$_6$F$_2$: Re, 60.41; F, 12.32%]. $v_{\text{CO}}$: 101

\[\text{TABLE 1 — OBSERVED AND CALCULATED VALUES OF CHEMICAL SHIFTS OF Co(III) COMPLEXES} \]

<table>
<thead>
<tr>
<th>Formula of the complex (complexing ligand)</th>
<th>Energy of separation $\Delta E$ (cm$^{-1}$)</th>
<th>$\sigma_{\text{para}}$ (%)</th>
<th>Deviation (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}$ (dicyandiamide)</td>
<td>20190</td>
<td>-0.713</td>
<td>-0.900</td>
</tr>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}_2\cdot\text{H}_2\text{O}$ (pyridine)</td>
<td>19610</td>
<td>-0.803</td>
<td>-0.984</td>
</tr>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}_2$ (m-toluidine)</td>
<td>19230</td>
<td>-0.818</td>
<td>-1.034</td>
</tr>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}_2$ (p-anisidine)</td>
<td>19610</td>
<td>-0.818</td>
<td>-0.984</td>
</tr>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}_2$ (m-chloroaniline)</td>
<td>19610</td>
<td>-0.821</td>
<td>-1.034</td>
</tr>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}_2$ (o-chloroaniline)</td>
<td>19230</td>
<td>-0.822</td>
<td>-0.984</td>
</tr>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}_2$ (p-phenetidine)</td>
<td>19230</td>
<td>-0.830</td>
<td>-1.034</td>
</tr>
<tr>
<td>[Coen$(\text{C}_2\text{H}_4\text{N}_2)\text{Cl}]\text{Cl}_2$ (o-phenetidine)</td>
<td>19420</td>
<td>-0.871</td>
<td>-1.009</td>
</tr>
</tbody>
</table>

*Deviation (%) = \frac{\sigma_{\text{obs}} - \sigma_{\text{calc.}}}{\sigma_{\text{calc.}}} \times 100.