

NUCLEAR MAGNETIC RESONANCE STUDY OF ^{59}Co IN SOME Co(III) COMPLEXES

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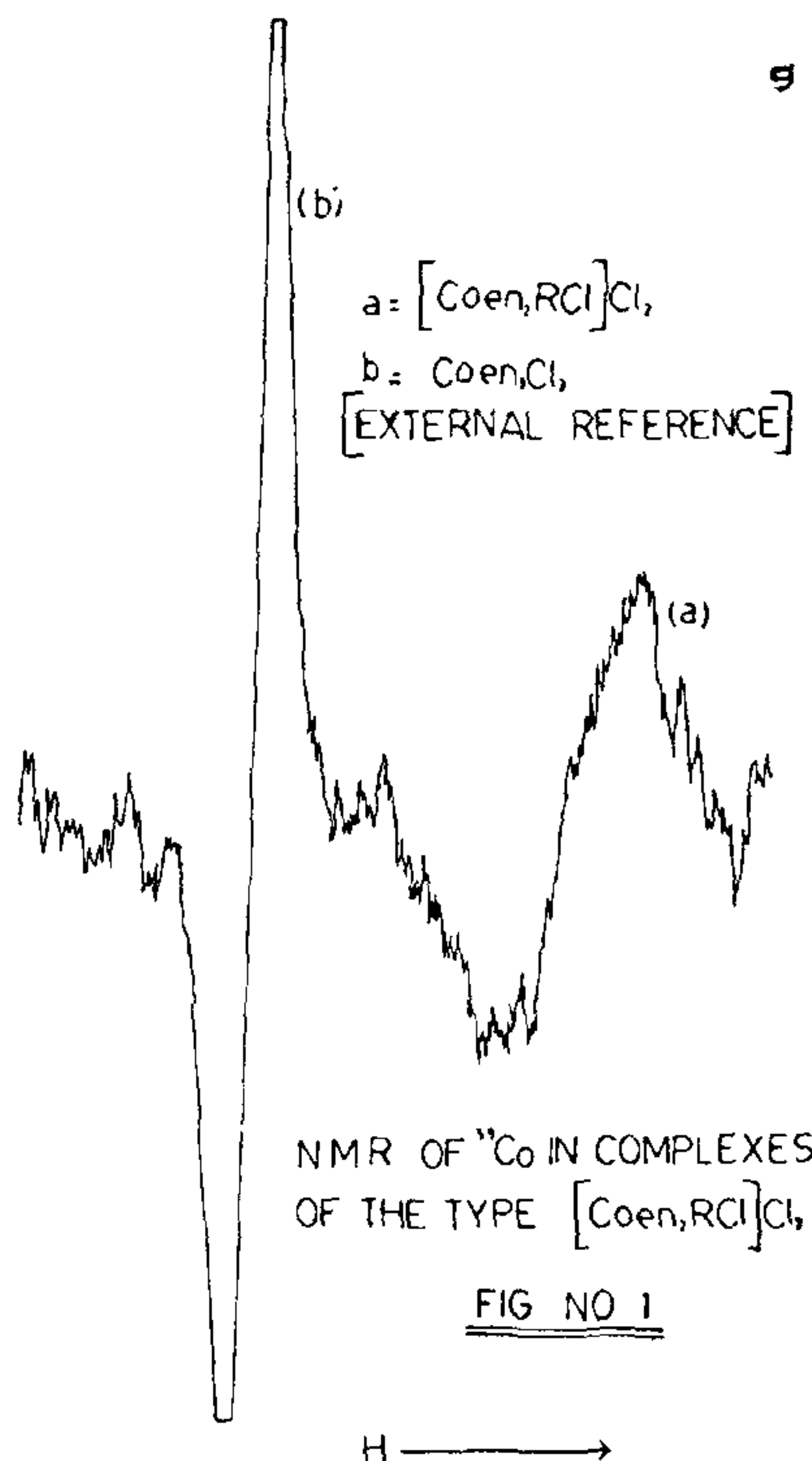
FROM the NMR spectra of ^{59}Co , in Co(III) complexes of the type $[\text{Coen}_2(\text{R})\text{Cl}]\text{Cl}_2$ where en = ethylenediamine R = aliphatic or aromatic amine, the chemical shift values (σ) have been determined. The σ values have been calculated theoretically also using Griffith and Orgel's 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 susceptibility and temperature-independent paramagnetism (t.i.p.), χ_p , values of the Co(III) complexes of the type $[\text{Coen}_2(\text{R})\text{Cl}]\text{Cl}_2$ where R = aliphatic or aromatic amine have been reported by the authors¹ and Patankar and Datar². On the basis of the theory of Griffith and Orgel³, χ_p (t.i.p.) values have been calculated theoretically^{2,4} also. Further ^{59}Co NMR spectra of some of these complexes have been reported by Dodwad and Datar⁵. In the present investigation ^{59}Co NMR spectra of some more similar 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.

Experimental

Concentrated aqueous solution of the complexes was placed in the probe of the varian wide-line spectrometer V-4200 which was coupled with 12 inch electromagnet. Solution of $\text{Co(en)}_3\text{Cl}_3$ was used as an external standard. The stabilities of RF oscillator and the magnetic field were of the order of 1 in 10^5 . The apparatus could give a resolution of about 50 milligauss. The NMR spectra for $[\text{Co(en)}_3\text{Cl}_3]$ and the complex under investigation were recorded by scanning the field over a limited range of 7,000 gauss. A typical spectrum obtained is shown in Fig. 1, where two NMR lines one for the complex and the other for the reference (Coen_3Cl_3) can be seen. Values of $\sigma\%$, were calculated from the separation between the two lines in the spectra. The shifts have been expressed in terms of the dimensionless quantity,

$$\sigma\% = \frac{H_i - H_r}{H_r} \times 100$$



where H_i is the resonance field for the complex under study and H_r that of $(\text{Coen}_3\text{Cl}_3)$. From the values of $\sigma\%$ thus obtained experimentally, $\sigma\%$ values relative to $\text{K}_3\text{Co}(\text{CN})_6$ were calculated and reported in column 4 of Table I.

Discussion of the Results

An examination of the results shows that the observed values of $\sigma\%$ are negative. This is because the resonance occurs at a field lower than that for $\text{K}_3\text{Co}(\text{CN})_6$. Following Griffith and Orgel³ one can assume that the dominant contribution to σ arises from the second order paramagnetism. The observed data thus indicate that the σ para has larger values in these complexes compared to that of reference. Substituting appropriate values of e , h , m and c in the Griffith and Orgel's³ expression we get,

$$\sigma_{\text{para}} = \frac{9.3 \times 10^3}{\Delta E} \times \left(\frac{1}{r^3}\right)$$

using this expression values of $\sigma\%$ for all the complexes studied in this investigation have been theoretically calculated and reported in Table I.

TABLE I
Observed and calculated values of chemical shifts in NMR spectra of Co(III) complexes

| Sl. No. | Formula of the complex (complexing ligand) | Energy of separation (ΔE) cm^{-1} | σ_{para} (%) | | Percentage* deviation |
|---------|--|--|----------------------------|--------|-----------------------|
| | | | Obs. | Calc. | |
| 1. | [Co(en) ₂ (CH ₃ NH ₂)Cl] Cl ₂ (methylamine) | 18870 | -0.801 | -1.073 | 25.35 |
| 2. | [Co(en) ₂ (<i>o</i> -C ₇ H ₇ ONH ₂)Cl] Cl ₂ (<i>o</i> -anisidine) | 19230 | -0.818 | -1.024 | 20.23 |
| 3. | [Co(en) ₂ (<i>p</i> -C ₇ H ₇ NH ₂)Cl] Cl ₂ (<i>p</i> -toluidine) | 19610 | -0.823 | -0.979 | 15.93 |
| 4. | [Co(en) ₂ (<i>p</i> -C ₈ H ₉ ONH ₂)Cl] Cl ₂ (<i>p</i> -phenetidine) | 19040 | -0.826 | -1.048 | 21.18 |
| 5. | [Co(en) ₂ (C ₆ H ₅ NH ₂)Cl] Cl ₂ (aniline) | 19610 | -0.826 | -0.974 | 15.19 |
| 6. | [Co(en) ₂ (<i>o</i> -C ₇ H ₇ NH ₂)Cl] Cl ₂ (<i>o</i> -toluidine) | 18520 | -0.867 | -1.122 | 22.22 |
| 7. | [Co(en) ₂ (C ₂ H ₅ NH ₂)Cl] Cl ₂ (ethylamine) | 19610 | -0.908 | -0.979 | 7.252 |
| 8. | [Co(en) ₂ (C ₃ H ₇ NH ₂)Cl] Cl ₂ (isopropylamine) | 19420 | -0.921 | -0.999 | 7.800 |

$$\left[* \text{ Deviation (\%)} = \frac{\text{obs.} - \text{calc.}}{\text{calc.}} \times 100 \right]$$

Value of $(1/r^3)$ used is that of Co³⁺ ion which is 5.3 angstrom units as done by Griffith and Orgel³ and the energy of separation (ΔE) values required for this purpose were obtained from the optical data and are also reported in Table I.

A comparison between the observed and calculated values shows that the calculated values are lower than the observed ones. Griffith and Orgel³ estimated the probable errors in their calculation of σ and concluded that the theoretical calculation can at best give an agreement within 20% of the observed data. Kanekar and Nipankar⁶ and Dodwad and Datar⁵ have also made similar observations.

The results obtained in the present investigation are within $\pm 20\%$ of the calculated values except for complex at Sr. No. 1 and 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)₃Cl₃.

This is also evident from the ΔE values. ΔE is 21400 cm^{-1} for Co(en)₃Cl₃ whereas it is in the neighbourhood of 19000 cm^{-1} for the complexes under investigation.

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

One of the conclusions of Griffith and Orgel's theory is that χ_0 (t.i.p.) term should decrease as the ligand field strength increases. Considering σ para values as a measure of ligand field strength, the following order of relative ligand field strengths has been established: methylamine > *o*-anisidine > *p*-toluidine > *p*-phenetidine \sim aniline > *o*-toluidine > ethylamine > isopropylamine.

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