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Proton Magnetic Resonance Spectra of Metal Ammine Complexes. I. Cobalt(III) Pentammine Series

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The proton magnetic resonance spectra have been measured in dimethylsulfoxide on some cobalt(III) complexes of the type $[CoX(NH_3)_5]$. Ammine protons show two peaks, except in a complex with $X=NO_2^-$. The major peak, due to *cis* NH_3, appears downfields and the minor one, due to *trans* NH_3, upfields as compared with the shift in $[Co(NH_3)_6]^{3+}$. In the case of $X=CN^-$, the shift pattern is reversed. For $[Co(NO_2)(NH_3)_5]^{2+}$, the spectrum is a single peak. This chemical shift behavior is explained by a simple model based on Ramsay's theory for chemical shift. It is concluded that the behavior arises primarily from paramagnetic anisotropy of the central cobalt(III) ion. The model used in this work is shown to be applicable also to the assignment of the PMR spectra for complexes of the types *cis*-$[CoX_2(NH_3)_4]$ and *cis*-$[CoX_2(en)_2]$.

Only a few works have been made on the proton magnetic resonance (PMR) spectra of metal–ammine complexes. This is partly due to the paucity of suitable solvents. Cliffton and Pratt[1] may be the first, to our knowledge, to show that the PMR spectra of cobalt(III) ammine complexes can be obtained when dissolved in acidified heavy water. Recently, Jolly and co-workers[2,3] have measured the PMR spectra of pentammine complexes of cobalt(III), rhodium(III), and iridium(III) in sulfuric acid. It is reported that two peaks with an intensity ratio of 4 to 1 can be obtained for cobalt(III) complexes while single peaks are observed in rhodium(III) and iridium(III) complexes. They have suggested that two-peak patterns in cobalt complexes may be explained by taking into consideration the contribution to the proton shift from the paramagnetic anisotropy of the central cobaltic ion. They have not made, however, even qualitative order-of-magnitude estimations and further no clear-cut explanation has been given to the fact that $[Co(CN)(NH_3)_5]^{2+}$ has *trans* ammine protons shifted to lower field than *cis* protons. Other complexes have reversed shift patterns with *trans* protons shifted to higher field.

We have measured the PMR spectra of some pentammine complexes of cobalt(III) in dimethyl sulfoxide. Herein reported are the shift patterns for these complexes and a simple explanation is given to the shift behavior. The model is based on Ramsay's theory of chemical shift. The major contribution to the proton shift is attributed to the anisotropy of temperature-independent paramagnetism of cobalt(III) ion. This model can account for the change in proton chemical shifts of $[CoX(NH_3)_5]$ when X is varied along the spectrochemical series. Further, some applications are given to the assignment of the PMR spectra of *cis*-$[CoX_2(NH_3)_4]$ and *cis*-$[CoX_2(en)_2]$ (en=ethylenediamine).

Experimental

The complexes used in this work are $[Co(NH_3)_6](NO_3)_3$, $[Co(H_2O)(NH_3)_5](NO_3)_3$, $[Co(CN)(NH_3)_5](NO_3)_2$, and $[CoX(NH_3)_5](NO_3)_2$ ($X=NO_2^-$, OH^-, Cl^-, Br^-, HCO^-, $CH_3CO_2^-$, $CH_2ClCO_2^-$, and $CCl_3CO_2^-$). These complexes are prepared after the well-established methods.[4]

All the spectra are recorded on a Varian A-60 spectrometer. Dimethyl sulfoxide of spectrograde or deuterated dimethyl sulfoxide (Merck) as the case may be is used as solvent. Chemical shifts are measured relative to an internal standard of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS).

Results

As illustrated in Fig. 1, the observed PMR spectra of cobalt(III)–pentammine complexes may be grouped into three categories. Category A; most of the complexes investigated belong to this category. The major peak, due to *cis* NH_3, appears downfields and the minor one, due to *trans* NH_3, upfields as compared with the shift of $[Co(NH_3)_6]^{3+}$. Category B; the spectrum of $[Co(NO_2)(NH_3)_5]^{2+}$ is an example. The shift difference between *cis* and *trans* ammine protons is not observed. The single peak lies slightly upfields relative to the hexammine complex. In trifluoroacetic acid, it also shows a single peak. Category C; the spectrum of cyanopentammine complex belongs to this group. The spectrum pattern is reversed in that the major peak is situated at higher field than the minor one.

The PMR data are summarized in Table 1. Note

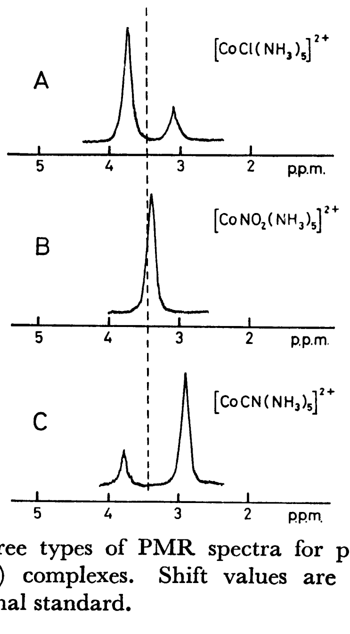

Fig. 1. Three types of PMR spectra for pentammine cobalt(III) complexes. Shift values are relative to DSS internal standard.

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TABLE 1. CHEMICAL SHIFTS (in Hz) OBSERVED FOR PENTAMMINE COBALT(III) COMPLEXES IN DIMETHYLSULFOXIDE SOLUTION

Measurements have been made at 60 MHz with DSS internal standard.

X	*trans* NH_3	*cis* NH_3
CN^-	227	174
NO_2^-	205 (singlet)	
H_2O	173	240
OH^-	175	220
Cl^-	186	222
Br^-	185	$\sim$224
HCO_2^-	a)	230
$CH_3CO_2^-$	a)	227
$CH_2ClCO_2^-$	169	232
$CHCl_2CO_2^-$	173	235
$CCl_3CO_2^-$	174	238
NO_3^-	a)	240
$[Co(NH_3)_6]^{3+}$	207	

a) Overlapped with the methyl signal of dimethylsulfoxide.

that all X's in $[CoX(NH_3)_5]$ of Category A are observed to lie lower in the spectrochemical series than NH_3. Further, the lower in the spectrochemical series the ligand X lies, the greater the shift difference between *cis* and *trans* ammine protons. In $[Co(CN)(NH_3)_5]^{2+}$ of Category C, CN^- is a representative of strong-field ligands and lies highest in the spectrochemical series.

The Model

We assume that three protons of each ammine group are situated at an average position, *i.e.*, at one of the points indicated by open circles in Fig. 2. Figure 2 defines the coordinate axes *x*, *y*, and *z* for complexes $[CoX(NH_3)_5]$. Chemical shift of specific ammine protons of a complex in solution is characterized by

$$\sigma = \frac{1}{3}(\sigma_{xx}+\sigma_{yy}+\sigma_{zz}). \tag{1}$$

Here, σ_{xx}, σ_{yy}, and σ_{zz} are the shielding constants for protons of interest when the magnetic field is applied along the *x*, *y*, and *z* axes, respectively, defined in Fig. 2. These constants consist of two contributions, namely the so-called paramagnetic and diamagnetic terms. It can be shown,[5] however, that diamagnetic terms are at least two orders of magnitude smaller than paramagnetic ones. Thus, we attribute the chemical shift behavior in pentammine cobalt complexes to the paramagnetic shielding constant, σ^P.

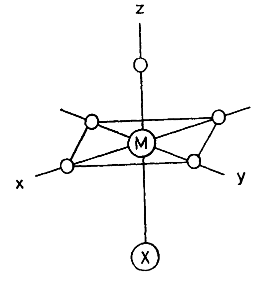

Fig. 2. The definition of the frame of reference for $[CoX(NH_3)_5]$-type complexes. Open circles are assumed to represent the position of ammine protons.

Calculation of the paramagnetic shielding constant for complexes of C_{4v} symmetry has been made by Buckingham and Stephens.[6] They have discussed the PMR spectra of hydride complexes of cobalt and iron. We will follow their procedure. They have modified Ramsay's formula for chemical shift of protons in C_{4v} cobalt complex to the form

$$\sigma^P_{xx} = -\frac{e^2}{2m^2c^2}\frac{1}{E_E-E_{A1}}[\langle{}^1A_1|\sum_j \underset{M}{L_{xj}}|{}^1E_x\rangle\langle{}^1E_x|\sum_k \underset{H}{L_{xk}}/\underset{H}{r_k}^3|{}^1A_1\rangle + \langle{}^1A_1|\sum_k \underset{H}{L_{xk}}/\underset{H}{r_k}^3|{}^1E_x\rangle\langle{}^1E_x|\sum_j \underset{M}{L_{xj}}|{}^1A_1\rangle], \tag{2}$$

and

$$\sigma^P_{zz} = -\frac{e^2}{2m^2c^2}\frac{1}{E_{A2}-E_{A1}}[\langle{}^1A_1|\sum_j \underset{M}{L_{zj}}|{}^1A_2\rangle\langle{}^1A_2|\sum_k \underset{H}{L_{zk}}/\underset{H}{r_k}^3|{}^1A_1\rangle + \langle{}^1A_1|\sum_k \underset{H}{L_{zk}}/\underset{H}{r_k}^3|{}^1A_2\rangle\langle{}^1A_2|\sum_j \underset{M}{L_{zj}}|{}^1A_1\rangle]. \tag{3}$$

We have retained paramagnetic terms only. In the above, $|{}^1A_1\rangle$, and $|{}^1A_2\rangle$ and $|{}^1E_x\rangle$ are the ground and the excited states of the central cobalt(III) ion and E_{A1}, E_{A2}, and E_E are the corresponding energies, respectively (see Fig. 3). L_{xj} and L_{zj} are the x and z components of orbital angular momentum operator for *j*-th electron of cobalt ion. The distance from protons in question to *k*-th electron is denoted by r_k. The summation is over all 3d electrons of cobalt. Operators subscripted with M and H are on the metal and proton centers, respectively.

Figure 3 shows the ground and the low-lying excited states of Co(III) ion under C_{4v} symmetry. Wave functions associated with these levels are given in Table 2. $|{}^1E_x\rangle$ and $|{}^1E_y\rangle$ are degenerate. To a first approximation, we neglect hybridization of 3d with 4s and 4p orbitals and covalency with ligand orbitals.

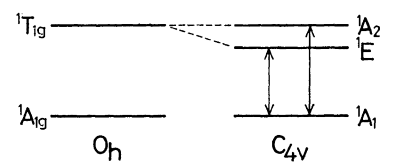

Fig. 3. The ground and the low-lying excited states of Co(III) ion under crystal fields of O_h and C_{4v} symmetries.

TABLE 2. WAVEFUNCTIONS ASSOCIATED WITH THE GROUND AND THE LOW-LYING EXCITED STATES OF Co(III) ION UNDER C_{4v} CRYSTAL FIELD

Superscripts 2, and + and − refer to the fully occupied orbital and orbitals with up and down spins, respectively.

$\vert{}^1A_1\rangle$	$\vert d^2_{yz}d^2_{zx}d^2_{xy}\vert$
$\vert{}^1A_2\rangle$	$\frac{1}{\sqrt{2}}[\vert d^2_{yz}d^2_{zx}d^+_{xy}d^-_{x^2-y^2}\vert - \vert d^2_{yz}d^2_{zx}d^-_{xy}d^+_{x^2-y^2}\vert]$
$\vert{}^1E_x\rangle$	$\frac{1}{\sqrt{2}}[\vert d^+_{yz}d^-_{y^2-z^2}d^2_{zx}d^2_{xy}\vert - \vert d^-_{yz}d^+_{y^2-z^2}d^2_{zx}d^2_{xy}\vert]$
$\vert{}^1E_y\rangle$	$\frac{1}{\sqrt{2}}[\vert d^2_{yz}d^+_{zx}d^-_{z^2-x^2}d^2_{xy}\vert - \vert d^2_{yz}d^-_{zx}d^+_{z^2-x^2}d^2_{xy}\vert]$

Further, contributions can be shown small to be neglected from levels into which T_{2g} state in O_h symmetry is split under the influence of the crystal field of C_{4v} symmetry. Under these simplifying assumptions, calculation of Eqs. (2) and (3) renders Eqs. (4) and (5) for *cis* and *trans* ammine protons, respectively.

$$\sigma_C^P = \frac{1}{3}(\sigma_{xx}^P+\sigma_{yy}^P+\sigma_{zz}^P) = \frac{4e^2\hbar^2}{3m^2c^2}\frac{1}{R^3}\left(\frac{1}{E_{A2}-E_{A1}}-\frac{1}{E_E-E_{A1}}\right). \tag{4}$$

$$\sigma_T^P = \frac{1}{3}(2\sigma_{xx}^P+\sigma_{zz}^P) = \frac{8e^2\hbar^2}{3m^2c^2}\frac{1}{R^3}\left(\frac{1}{E_E-E_{A1}}-\frac{1}{E_{A2}-E_{A1}}\right). \tag{5}$$

Quantities subscripted with C and T refer to *cis* and *trans*, respectively. R is the distance between the protons of interest and the cobalt nucleus. If R and excitation energies are measured in units of a.u. and cm^{-1}, $\sigma_C{}^P$ and $\sigma_T{}^P$ are expressed as dimensionless quantities.

$$\sigma_C^P = \frac{4}{3}\times 11.7\frac{1}{R^3}\left(\frac{1}{E_{A2}-E_{A1}}-\frac{1}{E_E-E_{A1}}\right). \tag{6}$$

$$\sigma_T^P = \frac{8}{3}\times 11.7\frac{1}{R^3}\left(\frac{1}{E_E-E_{A1}}-\frac{1}{E_{A2}-E_{A1}}\right). \tag{7}$$

The above result may be visualized in the following way (see Fig. 4).

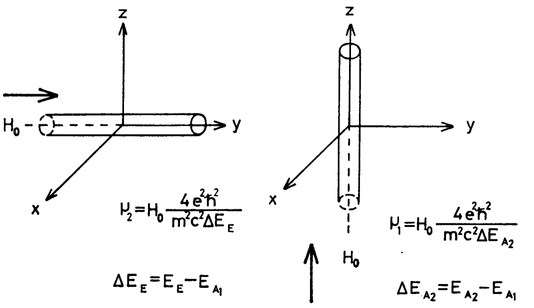

Fig. 4. The schematic presentation of induced paramagnetic moments. All notations have their usual singnificance.

On applying the magnetic field along the, say, x direction, magnetic moment will be induced. This induced moment, μ_2, is known as second-order paramagnetism and in magnetism as temperature-independent paramagnetism or the highfrequency term. This is given by

$$\mu_2 = H_0\frac{4e^2\hbar^2}{m^2c^2}\frac{1}{E_E-E_{A1}}. \tag{8}$$

Induced moments when the magnetic field is applied along the y and z directions are depicted in Fig. 4. These induced moments will be sensed by protons of interest as dipolar fields. Summing up over these dipolar fields, the same result as in Eqs. (6) and (7) is obtained. These reasoning is equivalent to regarding the shift as caused by the anisotropy in paramagnetic moment of Co(III) ion.

Comparison with Experiment

We first note that the energy E_E changes upon substitution of X, while the energy E_{A_2} is unaffected by substitution because the latter energy corresponds to the transition from d_{xy} to $d_{x^2-y^2}$. The ordering of the ligand field levels is determined, from spectroscopic and spectrophotometric studies,[7] as $E_E<E_{A2}$ except for strong-field ligands such as CN^- and NO_2^-, for which the ordering is reversed. Therefore, σ_C^P is generally positive and σ_T^P is negative, which means that *trans* ammine protons are shifted to high fields and *cis* protons to low fields (from the shift of hexammine cobalt(III) ion). This corresponds to the case of Category A. Further, the weaker spectrochemically the ligand X is, we can expect the smaller E_E, and hence, the bigger shift difference between *cis* and *trans* protons. This trend is consistent with experimental results already mentioned. In contrast, when X is a strong-field ligand, *e.g.*, $X=CN^-$, we can expect the shift pattern reversed to that in Category A, as has the case really been observed. So far so good.

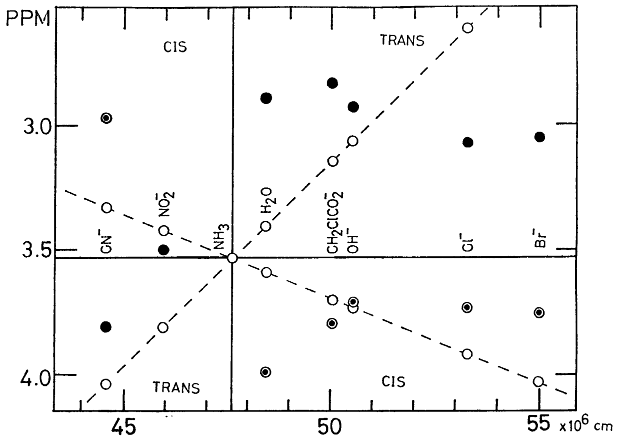

Fig. 5. Comparison of the calculated shift values (○) with observed values (◉ and ●). Shift values are from DSS internal standard and the abscissa is the reciprocal of the excitation energy E_E–E_{A1}.

If we examine more closely the correlation between the experimental results and Eqs. (6) and (7), agreement is not so satisfactory. Setting $R=5.7$ a.u.[8] and using reported values for excitation energies,[9] we can plot the calculated shift values against the reciprocal of the energy difference E_E-E_{A1}. Figure 5 shows the comparison of the calculated and the observed shift values. As seen in Fig. 5, shift patterns of Categories A, B, and C appear to be roughly explained. It seems difficult to explain by using only metal 3d orbitals that the complex with $X=NO_2^-$ goes into Category B.

The model used in this work is applicable also to the interpretation of the PMR spectra of *cis*-[CoX$_2$(NH$_3$)$_4$] and *cis*-[CoX$_2$(en)$_2$]. For these complexes, *trans* (to ligand X) ammine or NH_2 protons and *cis* protons have the same intensity. The assignment is therefore not straightforward. We assume, after Yamatera,[10] that three electronic transitions comprising the first absorption band are approximated, irrespective of the symmetry of the complex in question, by the following transitions under O_h symmetry.

$$d_{xy}\rightarrow d_{x^2-y^2},\ \frac{1}{2}\delta+\Delta \tag{9}$$

$$d_{yz} \rightarrow d_{y^2-z^2}, \quad \frac{1}{4}\delta+\Delta \tag{10}$$

$$d_{zx} \rightarrow d_{z^2-x^2}, \quad \frac{1}{4}\delta+\Delta \tag{11}$$

To the right are given the corresponding transition energies.

δ is the splitting factor defined by Yamatera and Δ the transition energy of the first absorption band in $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$ 11) as the case may be. Substitution of these energies into Eqs. (4) and (5) yields

$$\sigma^P(5,6) = -2\left(\frac{4e^2\hbar^2}{3m^2c^2}\frac{1}{R^3}\right)\left(\frac{1}{\Delta+\delta/2}-\frac{1}{\Delta+\delta/4}\right), \tag{12}$$

$$\sigma^P(2,3) = +\left(\frac{4e^2\hbar^2}{3m^2c^2}\frac{1}{R^3}\right)\left(\frac{1}{\Delta+\delta/2}-\frac{1}{\Delta+\delta/4}\right). \tag{13}$$

Shielding constants $\sigma^P(5,6)$ and $\sigma^P(2,3)$ are for *cis* and *trans* NH_3 or NH_2 protons, respectively. For complexes with weak-field ligand X, δ is negative by definition, rendering $\sigma^P(5,6)$ negative and $\sigma^P(2,3)$ positive. Therefore, we can expect, except for strong-field ligands, that 5- and 6-protons are shifted to low fields and 2- and 3-protons to high fields. For strong-field ligands, such as $X=CN^-$, the situation may be the reverse of the above.

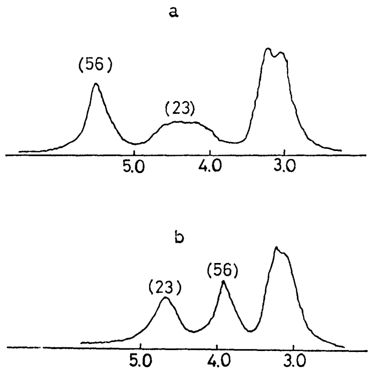

Fig. 6. The PMR spectra of (a) $[CoCl_2(en)_2]^+$ and (b) $[Co(CN)_2(en)_2]^+$ in trifluoroacetic acid. Shift values are from an internal standard of tetramethylsilane. Numbers in parentheses represent the proposed assignments (see text).

Let us illustrate how this result works in actual cases. Figure 6 depicts the PMR spectra of *cis*-$[CoCl_2(en)_2]^+$ and *cis*-$[Co(CN)_2(en)_2]^+$ in trifluoroacetic acid. Chloride ion is a representative of weak-field ligands. Thus, the broader peak situated around 4.4 ppm is assigned as *trans* NH_2 protons and the lowest-field peak as *cis* NH_2. Since CN^- is strong-field ligand, the assignment given in Fig. 6-b will hold.

Conclusion

The PMR spectra of pentammine cobalt(III) complexes can be explained primarily by the paramagnetic anisotropy of the central cobalt(III) ion. The results derived in this work may be summarized as the following rules (see Fig. 7).

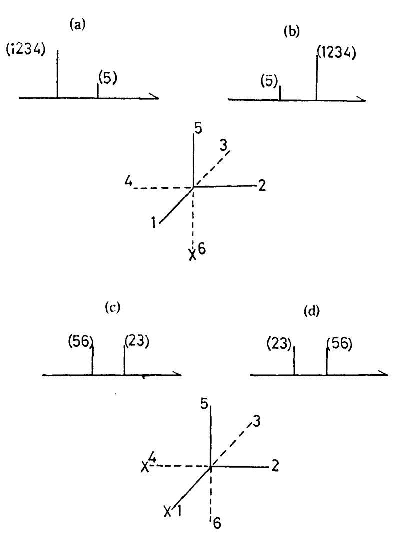

Fig. 7. The predicted behavior of the PMR spectra for $[CoX(NH_3)_5]$ and *cis*-$[CoX_2(NH_3)_4]$ or *cis*-$[CoX_2(en)_2]$. (a) and (b) are for pentammine complexes with weak- and strong-field ligands, respectively. (c) and (d) are for the *cis*-type complexes with weak- and strong-field ligands, respectively.

For $[CoX(NH_3)_5]$;

(1) If X is spectrochemically lower than NH_3, ammine protons *trans* to X appear at high fields (Fig. 7-a).

(2) If X is a strong-field ligand, the reverse is expected (Fig. 7-b).

For *cis*-$[CoX_2(NH_3)_4]$ or *cis*-$[CoX_2(en)_2]$;

(1) If X is a weak-field ligand, the high-field peak is due to 2- and 3-protons (Fig. 7-c).

(2) If X is strong, protons situated at 5- and 6-positions will appear at higher field (Fig. 7-d).

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