

## Proton Magnetic Resonance Spectra and Stereochemistry of Ammine Nitrocobalt(III) Complexes

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*Proton magnetic resonance (PMR) spectra in hexadeuterodimethylsulfoxide are reported for a number of ammine nitrocobalt(III) complexes, containing one to four coordinated nitro groups. It is shown that PMR provides a reliable method to determine the stereochemistry of these complexes, contrary to results obtained by other workers. The influence of complex concentration on the spectra has also been investigated.*

### Introduction

Proton magnetic resonance spectroscopy has been applied to diamagnetic ammine cobalt(III) complexes to obtain information about the stereochemistry of these complexes<sup>1–13</sup>.

Recently, Yoneda and Nakashima<sup>10</sup> reported PMR spectra for a number of pentaamminecobalt(III) complexes. They showed that complexes of this type, viz.  $[\text{Co}(\text{NH}_3)_5\text{X}]^{n+}$ , can be grouped in three categories. With  $\text{X} = \text{Cl}^-$ , the major peak due to *cis*  $\text{NH}_3$  appears downfield and the minor one, due to *trans*  $\text{NH}_3$ , upfield as compared to the shift of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (category A). With  $\text{X} = \text{CN}^-$ , the spectrum pattern is reversed (category C). With  $\text{X} = \text{NO}_2^-$ , no shift difference between *cis* and *trans* ammine protons is observed (category B). This would mean that PMR spectroscopy cannot distinguish between isomeric pairs of ammine nitrocobalt(III) complexes.

They further correlated the PMR spectra with the position of the ligand X relative to  $\text{NH}_3$  in the spectrochemical series; because the ligand  $\text{NO}_2^-$  is situated close to  $\text{NH}_3$  in this series, no shift difference should be observed. In the course of a study of the kinetic behaviour of ammine nitrocobalt(III) complexes<sup>14</sup>, we became interested in the stereochemistry of these complexes. We therefore applied the PMR method to a number of ammine nitrocobalt(III) complexes containing one to four coordinated nitro groups. The results of these investigations are presented in this paper.

### Experimental

Most of the complexes used in this work were prepared by standard procedures<sup>15</sup>; the preparation of the new complexes will be published elsewhere<sup>14</sup>.

The PMR spectra were recorded on a Varian A-60 spectrometer. Chemical shifts were measured relative to an internal reference of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS, MERCK).

The solutions were prepared by dissolving the complexes in hexadeuterodimethylsulfoxide ( $\text{DMSO-d}_6$ , MERCK Uvasol); spectra were measured at various concentrations. Spectra were recorded immediately after the solutions had been prepared and were followed in time, in order to see whether or not a reaction did take place. Spectra in the visible and ultraviolet regions were recorded on a Beckman-25 spectrophotometer.

### Results and Discussion

The results of the present investigation are shown in Table I. In this Table the chemical shifts of the ammine protons and the observed intensity ratios are listed for the ammine nitrocobalt(III) complexes and a number of other ammine cobalt(III) complexes of known stereochemistry. The signals due to water are not listed in Table I; they are found in the 4–5 ppm region, as observed before<sup>6</sup>. In Figure 1 a few representative spectra are depicted. In contradiction to the theory developed by Yoneda and Nakashima<sup>10</sup>, a number of ammine nitrocobalt(III) complexes exhibit two PMR peaks, in spite of their neighbouring position in the spectrochemical series (see also ref. 8).

The only exception seems to be  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$  because only one, rather broad signal was observed by us instead of two signals with a 1:4 intensity ratio (*cf.* ref. 10). However, in the case of  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{ClO}_4)_2$  we observed two signals (see Figure 1-c) but we were unable to determine the intensity ratio of the two peaks which theoretically should be 1:4.

TABLE I. Chemical Shifts of the Ammine Protons Observed for Some Cobalt(III) Complexes.<sup>a</sup>

Compound	Chemical shift (ppm)	Intensity ratio
[Co(NH <sub>3</sub> ) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	3.32	—
[Co(NH <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O)](ClO <sub>4</sub> ) <sub>3</sub>	2.83, 3.83	1:4
[Co(NH <sub>3</sub> ) <sub>5</sub> (NO <sub>2</sub> )](ClO <sub>4</sub> ) <sub>2</sub>	3.33, 3.42	b
[Co(NH <sub>3</sub> ) <sub>5</sub> (NO <sub>2</sub> )](NO <sub>3</sub> ) <sub>2</sub>	3.38	—
<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> )	3.32	—
<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> )(H <sub>2</sub> O)](ClO <sub>4</sub> ) <sub>2</sub>	3.73	—
<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl	3.40	—
<i>trans</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O)Cl]Cl <sub>2</sub> <sup>c</sup>	3.33	—
<i>cis</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> )	3.18, 3.45	1:1
<i>cis</i> -[Co(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	3.18, 3.35	1:1
<i>mer</i> -[Co(NH <sub>3</sub> ) <sub>3</sub> (NO <sub>2</sub> ) <sub>3</sub> ]	3.22, 3.62	1:2
<i>trans</i> -K[Co(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>2</sub> ) <sub>4</sub> ]	3.35	—

<sup>a</sup> Measurements were made at 60 MHz in DMSO-d<sub>6</sub> with DSS as internal reference; ammine signals are observed downfield with respect to DSS. <sup>b</sup> Could not be determined; see Figure 1-c. <sup>c</sup> See text.

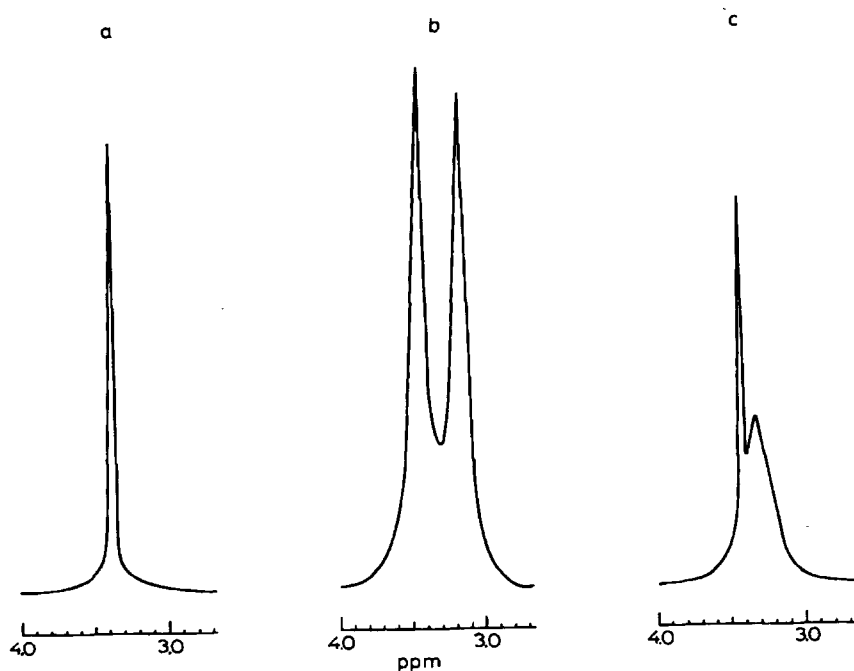


Figure 1. PMR spectra of *trans*-K[Co(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>] (a), *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>) (b), and [Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> (c) in DMSO-d<sub>6</sub> with DSS as internal reference.

In this context it should be remarked that the perchlorato complexes are generally more soluble in DMSO than the corresponding nitrate complexes. We also observed that highly concentrated solutions tend to become viscous and this increases the line-width. Further, experiments with [Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> showed that on dilution the two signals collapse into one broad and asymmetric one. It can therefore be said that an optimum concentration range exists, which may vary from compound to compound, in which resolution is maximal (and line-width minimal).

With respect to the peak separation observed for compounds with non-equivalent NH<sub>3</sub> groups, the following can be said. It follows from the theory of Yoneda and Nakashima<sup>10</sup> that a correlation should exist between the peak separation observed for the complexes *cis*-[Co(NH<sub>3</sub>)<sub>4</sub>X<sub>2</sub>]<sup>3+</sup> and [Co(NH<sub>3</sub>)<sub>5</sub>X]<sup>3+</sup> and the position of the ligand X relative to NH<sub>3</sub> in the spectrochemical series: with increasing difference in ligand-field strength between X and NH<sub>3</sub>, the peak separation should increase. Our results indicate that the case is not that simple: for [Co(NH<sub>3</sub>)<sub>5</sub>X]<sup>3+</sup> the peak

separation with  $X = \text{NO}_2^-$  is smaller than that with  $X = \text{H}_2\text{O}$ ; in the case of  $\text{cis-}[\text{Co}(\text{NH}_3)_4\text{X}_2]^{2+}$ , the situation is reversed.

Nevertheless, it can be concluded that the PMR method can be used for determining the stereochemistry of ammine nitrocobalt(III) complexes: non-equivalent  $\text{NH}_3$  groups show signals with different chemical shifts. An assignment of the observed peaks to a particular  $\text{NH}_3$  class (e.g. *trans* or *cis* with respect to X) is only possible when the intensity ratio differs from 1:1.

A problem arises from the fact that the solvent may react with the complexes and the complexes may isomerize. We investigated these possibilities by following the solutions in time by PMR and UVV spectroscopy. As expected<sup>16</sup>, a slow solvation reaction was observed for the aquo complexes. In the case of  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{ClO}_4)_3$ , for instance, we observed a downfield shift of the *cis*-ammine signal and a larger upfield shift of the *trans*-ammine signal. Simultaneously, the signal due to (coordinated) water was shifted upfield, i.e. in the direction in which the signal due to uncoordinated water is expected.

This can be interpreted as indicating that a slow substitution reaction is taking place in which water is substituted by the solvent,  $\text{DMSO-d}_6$ . This was supported by the results obtained from the UVV spectra. It is interesting to note that only one signal due to  $\text{H}_2\text{O}$  was observed, indicating that fast proton exchange does take place between coordinated and uncoordinated water<sup>17</sup>. We further observed an isomerization reaction in the case of the  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$  compound. In fact, we prepared a solution of the *trans*-species by dissolving the *cis*-complex; we were unable to obtain a spectrum of the original compound. In all other cases, no reaction was observed.

### Conclusion

From the results discussed above, the following conclusions can be drawn:

1. Proton magnetic resonance spectroscopy can be used to determine the stereochemistry of ammine-nitrocobalt(III) complexes.

2. In order to obtain reliable results, experiments must be done at varying concentrations; it is therefore advised to employ perchlorato complexes since these allow the investigation of a more extensive range of concentrations.

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