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Proton Magnetic Resonance Spectra of Cobalt(III) Hexammine-type Polyamine Complexes[1]

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The proton magnetic resonance spectra of [Co *en*$_3$]Cl$_3$, [Co *tn*$_3$]Cl$_3$, [Co *pn*$_3$]Cl$_3$ and [Co *den*$_2$]Cl$_3$ (*den*=diethylenetriamine) dissolved in trifluoroacetic acid were measured. All of the observed spectra consist of broad bands, which were assigned on the basis of intensity considerations and by comparing them with the spectra of the corresponding deuterated species. In case of the ethylenediamine complex, the double-resonance method was applied, measurements at different temperatures were made, and the origin of the breadth of the bands was discussed. The NH$_2$ signals of the ethylenediamine and trimethylenediamine complexes show AB-type features. This was confirmed by comparing the spectra obtained at 60 Mc. and at 100 Mc. The AB-type features of the NH$_2$ signal were explained in terms of the crystal structure of the complex.

Although the study of Werner-type complexes by the use of the proton magnetic resonance technique is an attractive subject to the coordination chemist, relatively few works have been reported. This is because most of Werner-type complexes are not soluble in ordinary organic solvents, and because in aqueous solutions, the strong signal of water prevents the observation of the signals of ligands and, moreover, rapid proton exchange makes it difficult to pick up the signals of ligands separately. To avoid this difficulty, Clifton and Pratt[2] measured the proton magnetic resonance spectra of several cobalt(III) ammine complexes dissolved in acidified heavy water; they thus succeeded in obtaining fairly satisfactory results.

Recently we found that an acid itself, if it is a liquid and dissolves a sample, could be used for the NMR measurement of the complex.[3] Among the several acids we tried, trifluoroacetic acid proved to be the most suitable for this purpose. In this paper we should like to report on several interesting features of the NMR spectra of cobalt(III) polyamine complexes.

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[1] A part of this article was presented at the 15th Symposium of Coordination Chemistry, Kanazawa University, October, 1965.

[2] P. Clifton and L. Pratt, *Proc. Chem. Soc.*, **1963**, 339. S. Hayashi made the same kind of measurements using heavy water; *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **85**, 256 (1964); **86**, 364 (1965).

[3] During this work we learned that W. L. Jolly, A. D. Harris and T. S. Briggs had reported the use of concentrated sulfuric acid as a solvent for NMR studies of cobalt(III) ammine complexes; *J. Inorg. Chem.*, **4**, 1064 (1965).

Experimental

The complexes used in the measurement were tris-ethylenediamine cobalt(III) chloride $[\mathrm{Co}\ en_3]\mathrm{Cl}_3$, tris-trimethylenediamine cobalt(III) chloride $[\mathrm{Co}\ tn_3]\mathrm{Cl}_3$, tris-propylenediamine cobalt(III) chloride $[\mathrm{Co}\ pn_3]\mathrm{Cl}_3$ and bis-diethylenetriamine cobalt(III) chloride $[\mathrm{Co}\ den_2]\mathrm{Cl}_3$. The spectra of the free ethylenediamine as well as of its trifluoroacetic acid salt were also measured. The trifluoroacetic acid used in the measurement is of the spectrograde (Merck Company).

The apparatus used was a Varian A60 Analytical NMR spectrometer. In some cases, a Varian HR100 NMR spectrometer was also used. Tetramethylsilane was used as the internal standard throughout the measurements.

Results and Discussion

The NMR spectrum of the free ethylenediamine dissolved in carbon tetrachloride consists of two sharp signals of an equal intensity; the peak appearing in the higher field (-64 c. p. s.) is assigned to the NH_2 protons, and the other, in the lower field (-156 c. p. s.), to the CH_2 protons. (The NH_2 protons of alkylamine dissolved in carbon tetrachloride have their signals in higher fields than the CH_3 and CH_2 protons.) However, this situation is reversed in the case of the protonated ethylenediamine dissolved in an acid. By protonation the NH_2 group becomes the $\mathrm{NH}_3{}^+$ group, and its signal is shifted to -459 c. p. s. On the other hand, the CH_2 signal is shifted to -237 c. p. s. (The assignment of the signals can easily be made from intensity consideration.) The spectrum of the $[\mathrm{Co}\ en_3]^{3+}$ complex is expected to have a character intermediate between those of the free and protonated ethylenediamine species. Actually, it has two signals of an equal intensity. While the signal in the higher field (-190 c. p. s.) shows no fine structure, the other in the lower field, has a doublet structure (-292 and -310 c. p. s.), and each doublet component carries a shoulder. In order to assign these signals, the spectrum of the amino-deuterated complex was also measured. In the deuterated complex, the NH_2 group is converted to the ND_2 group, and the signal due to the NH_2 protons should disappear. In the actual deuterated complex, the signal in the lower field disappears. Therefore, this is assigned to the NH_2 protons. Consequently, the signal in the higher field is assigned to the CH_2 protons. The general features of the spectrum are rather coloser to those of the protonated ethylenediamine than to those of the free ethylenediamine. Therefore, we assume that the nature of the coordinated ethylenediamine is closer to that of the protonated ethylenediamine.

In Fig. 1, the NMR spectra of $[\mathrm{Co}\ tn_3]\mathrm{Cl}_3$, $[\mathrm{Co}\ pn_3]\mathrm{Cl}_3$ and $[\mathrm{Co}\ den_2]\mathrm{Cl}_3$ are also shown. Of these, the spectrum of $[\mathrm{Co}\ tn_3]\mathrm{Cl}_3$ is similar to that of $[\mathrm{Co}\ en_3]\mathrm{Cl}_3$. The signal on the left-hand side (-282 and -267 c. p. s.) has a doublet structure and disappears in the deuterated species. Therefore, it is assigned to NH_2. The middle one (-170 c. p. s.) and the one on the right-hand side in the spectrum (-130 c. p. s.) are assigned to the CH_2 adjacent to NH_2 and to the middle CH_2 respectively. The spectrum of the $[\mathrm{Co}\ pn_3]^{3+}$ complex has five bands which correspond to CH_3 (-92 c. p. s.), CH_2 (-185 c. p. s.), CH (-210 c. p. s.), and two kinds of NH_2 (ca. -280 and ca. -310 c.p.s.). The spectrum of the $[\mathrm{Co}\ den_2]^{3+}$ complex has the most diffuse pattern among the four complexes. From intensity considerations, the bands are assigned to CH_2 (-205 c. p. s.), NH_2 (-280 and -310 c. p. s.), and the middle NH (-435 c. p. s.).

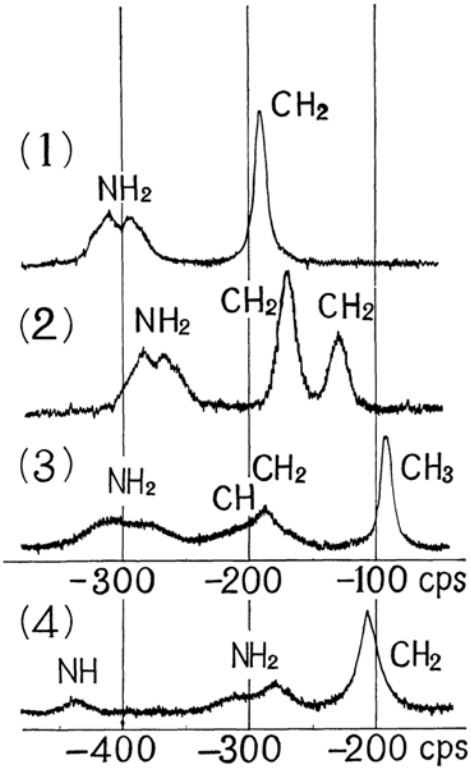

Fig. 1. NMR spectra of four complexes.
(1) $[\mathrm{Co}\ en_3]\mathrm{Cl}_3$, (2) $[\mathrm{Co}\ tn_3]\mathrm{Cl}_3$, (3) $[\mathrm{Co}\ pn_3]\mathrm{Cl}_3$, (4) $[\mathrm{Co}\ den_2]\mathrm{Cl}_3$

All these spectra consist of broad bands. This seems to be characteristic of polyamine complexes. In polyamine complexes, there are several kinds of possibilities which cause signal broadening. To obtain a deeper insight, further experiments were made involving the $[\mathrm{Co}\ en_3]^{3+}$ complex. First, the NMR spectra of the complex at 70 and 10°C were measured. Though the temperature effect is very small within this temperature range, we can clearly observe a definite tendency for the bands to be broadened at low temperatures and to be sharpened at high temperatures. Secondly,

TABLE I. NH_2 SIGNALS OF [Co *en*$_3$]Cl_3 AND [Co *tn*$_3$]Cl_3 MEASURED AT 60 AND 100 Mc. (c. p. s. UNIT)

		Shoulder	Main peaks		Shoulder
[Co *en*$_3$]Cl_3	60 Mc.	−284	−292	−310	−319
	100 Mc.	−476.5	−485	−520.6	−529
		Coupling constant 8.5 c. p. s.			
		Chemical shift 0.43 p. p. m.			
[Co *tn*$_3$]Cl_3	60 Mc.	−257	−267	−282	−292
	100 Mc.	−431	−440	−473	−483
		Coupling constant 9.5 c. p. s.			
		Chemical shift 0.40 p. p. m.			

the double resonance technique was applied to the pair of CH_2 and NH_2 signals (more exactly, a component of the NH_2 signal). The irradiation of either signal causes a slight sharpening of the other. In the case of the CH_2 band, the value of the half-width decreases to nearly 60% of the original. (Similarly, a sharpening of the CH_2 band takes place in the deuterated [Co *en*$_3$]$^{3+}$ complex. In this case, the value of the half-width is approximately one half of the original.) Therefore, the spin-spin coupling between the CH_2 and NH_2 protons is one of the origins of the band-broadening. In addition, in polyamine complexes, many protons which are magnetically different and crowded around the central metal ion and fixed in a relatively rigid, cage-like framework. The situation is somewhat like that in a solid. Therefore, a complete time-averaging of local fields is not realized. The authors should like to regard this situation as the main origin of band-broadening. The tendency of the temperature effect is consistent with this view. In the case of the NH_2 signal, the irradiation of the CH_2 signal does not change the essential features of the band. Consequently, the diffuse pattern may be attributed mainly to the quadrupole relaxation of the nitrogen nucleus.

The NH_2 signal of the [Co *en*$_3$]$^{3+}$ and [Co *tn*$_3$]$^{3+}$ complexes seems to have the characteristics of the AB-type pattern. To confirm this point, the NMR spectra of both the complexes at 100 Mc. were also measured. The results are listed, along with those obtained at 60 Mc., in Table I. As expected, at 100 Mc. the separation between the main peaks of the doublet components increases, while the separation between the main peak and its shoulder is kept constant. This is characteristic of the AB-type. Thus, it has been proved that two kinds of magnetically-unequivalent protons exist in the NH_2 group.

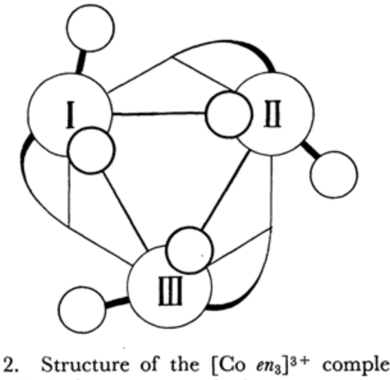

Fig. 2. Structure of the [Co *en*$_3$]$^{3+}$ complex.
Small circles represents hydrogens.
Large circles represents nitrogens.

The structure of the [Co *en*$_3$]$^{3+}$ complex was analyzed by Nakatsu et al.[4] According to their report, the complex has a threefold axis, and all three ethylenediamine ligands coordinated to the cobalt(III) ion have a nonplanar twisted structure of optically the same configuration.[5] In this structure, if we assume the nitrogen atom to have a regular tetrahedral configuration, we can easily distinguish two kinds of protons attached to it. The situation is illustrated in Fig. 2, which shows the upper part of the complex viewed along the threefold axis. Among the six N–H bonds in Fig. 2, three are directed upwards from the N(I)-N(II)N(III) plane and the other three outwards nearly perpendicularly to the threefold axis. In this way the upper three H(A) atoms form a regular triangle, while the lower three H(B) atoms form a larger, regular triangle. The same situation holds in the lower part of the complex. Although the structure of the [Co *tn*$_3$]$^{3+}$ complex has not yet been elucidated by X-ray analysis, a similar situation may be assumed. Here it is worth noting that this kind of doublet pattern does not appear in an aqueous solution. In an acidified aqueous solution, the NH_2 signal appears as a broad single band with no fine structure. This indicates that

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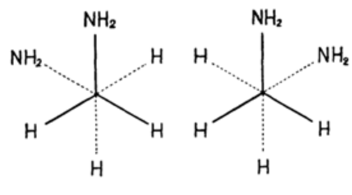
[4] K. Nakatsu, Y. Saito and H. Kuroya, This Bulletin, **29**, 428 (1956); **30**, 158 (1957).

[5] When the ethylenediamine molecule takes a twisted structure, two optically-isomeric forms are possible, as is shown below. These are figures viewed along the C–C axis. The full lines represent the upper side of the molecule, the dotted lines, the lower side.



k form *k'* form

a frequent flipping[6] of the coordinated ethylenediamine takes place, through which all the NH_2 protons are magnetically equalized. Such a flipping is presumed to be eased by proton dissociation from the NH_2 group. The feature of the NH_2 signal in an aqueous solution can thus be understood. On the contrary, neither proton dissociation nor proton exchange takes place in trifluoroacetic acid solution (the spectrum of the deuterated complex in trifluoroacetic acid solution does not show a time-change). Therefore, no flipping of the coordinated ethylenediamine occurs.

Last, it must be added that two kinds of the CH_2 protons also exist in the above-mentioned stereomodel of the $[Co\ en_3]^{3+}$ complex. Therefore, the doublet pattern of the CH_2 signal should be observed. However, this is not the case. This is probably either because the relative chemical shift is too small to be observed, or because all the CH_2 protons are equalized through the rocking motion of the CH_2 group.

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[6] By "flipping" we mean that the coordinated ethylenediamine turns over from the k form to k', and vice versa, keeping its two coordination positions fixed.