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Proton Magnetic Resonance Spectra of Some Rhodium(III) and Iridium(III) Pentaammines[1]

YUKIYOSHI MORIMOTO

Research Laboratories, Fujisawa Pharmaceutical Co. Ltd., Kashima-2-chome, Yodogawa-ku, Osaka 532, Japan

USHIO SAKAGUCHI and HAYAMI YONEDA*

Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

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Recently, it has been shown that proton chemical shifts of ammine groups coordinated to a cobalt(III) ion are governed by the anisotropy in the second-order paramagnetism of the central cobalt(III) ion [2]. For pentaammine ions, $[Co(NH_3)_5(X)]^{n+}$, the shift values were nicely accounted for by the theory based on the magnetic anisotropy and by cobalt-59 chemical shift data. Small but significant discrepancies were noted, however, between the calculated and the observed shift values for the *trans* ammine hydrogens of the cyano- and nitro-pentaammines. Here *trans* hydrogens mean the hydrogens on the nitrogen atom *trans* to the substituent X. These hydrogens are more shielded and resonated at higher magnetic fields than does the theory predict, suggesting increased electron densities on these hydrogens. The suggestion appeared to be substantiated by the measurement of hydrogen–deuterium exchange rate in deuterium oxide [3]; these hydrogens exchanged with deuterium more slowly than the *cis* hydrogens whereas the opposite was observed for complexes with weak-field X ligands.

To examine factors which affect the ammine proton chemical shifts, we here measured the PMR spectra of some rhodium(III) and iridium(III) pentaammine complexes. The results are discussed in relation to the result of cobalt(III) pentaammines.

Experimental

The complexes were prepared by the literature methods with some modifications [4, 5]. The identity of the complexes was confirmed by infrared spectra [6] and chemical analysis. *Anal.* Calcd. for $[Rh(NH_3)_5(CN)](NO_3)_2$: C, 3.55; H, 4.47; N, 33.14%. Found: C, 3.66; H, 4.38; N, 32.77%. Calcd. for $[Rh(NH_3)_5(CN)]Cl_2$: C, 4.21; H, 5.31; N, 29.49; Cl, 24.88%. Found: C, 4.37; H, 5.27; N, 29.51; Cl, 24.63%. Calcd. for $[Rh(NH_3)_5(NO_2)](NO_3)_2 \cdot 0.5H_2O$: H, 4.39; N, 30.53%. Found: H, 4.30; N, 30.41%. Calcd. for $[Rh(NH_3)_5(Cl)](NO_3)_2$: H, 4.35; N, 28.21; Cl, 10.20%. Found: H, 4.25; N, 27.98; Cl, 10.04%. Calcd. for $[Rh(NH_3)_6](NO_3)_3$: H, 4.64; N, 32.23%. Found: H, 4.39; N, 32.16%. Calcd. for $[Ir(NH_3)_5(NO_2)]Cl_2$: H, 3.83; N, 21.31; Cl, 17.98%. Found: H, 3.74; N, 21.38, Cl, 17.86%. Calcd. for $[Ir(NH_3)_5(NO_2)](NO_3)_2 \cdot 0.5H_2O$: H, 3.53; N, 24.55%. Found: H, 3.43; N, 24.68%. Calcd. for $[Ir(NH_3)_6]Cl_3$: H, 4.53; N, 20.97; Cl, 26.54%. Found: H, 4.43; N, 20.88; Cl, 26.27%.

The PMR spectra were obtained on a JEOL PS-100 spectrometer at ambient probe temperature (*ca.* 25 °C) and 100 MHz. Unless otherwise stated, the dimethylsulfoxide-d_6(DMSO-d_6) solutions of the nitrate salts were used. The chemical shifts were referenced to internal tetramethylsilane (TMS) for DMSO-d_6 solutions or internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for sulfuric acid solutions.

The spectra of rhodium complexes are given in Figs. 1 and 2 and the spectra of iridium compounds in Fig. 3. The chemical shift values obtained for DMSO-d_6 solutions are summarized in Table I, along with the data of cobalt pentaammines. The hexaammines show only one signal, as expected. The nitro pentaammines of both rhodium and iridium exhibit two well-resolved peaks with an intensity ratio of 1:4, from which the assignment to *cis* and *trans* ammines follows immediately. The *trans* ammine group of $[Rh(NH_3)_5(Cl)](NO_3)_2$ appears as a shoulder to the low-field side of the *cis* peak (Fig. 1b). Unfortunately, the *trans* peak of $[Rh(NH_3)_5(CN)](NO_3)_2$ is obscured by the overlap of the H_2O resonance with the ammine peak(s) of this compound. The shoulder to the high-field side of Fig. 1d is due to H_2O in the DMSO-d_6 solvent. In sulfuric acid solution, the cyano rhodium compound gives rise to two well-resolved signals.

Previously, Hendrickson and Jolly [4] obtained the PMR spectra of $[M(NH_3)_5(X)]^{n+}$ type of complexes in concentrated sulfuric acid, where X = Cl^-, Br^-, HSO_4^-, and NH_3 for M = Rh(III), and X = Cl^-, NCS^-, H_2O, and HSO_4^-, for M = Ir(III). It is reported that these complexes show only one peak. The two-peak pattern observed here is certainly brought about by the higher spectrometer frequency (100 MHz) compared with 60 MHz, and by the use of different solvent (DMSO-d_6 *vs.* conc. H_2SO_4). The effect of solvent upon the spectrum of $[Rh(NH_3)_5(CN)]^{2+}$ is seen from Figs. 1 and 2. Of particular interest in Figs. 1 to 3 is that the shift pattern of the rhodium and iridium pentaammines is similar to each other but drastically different from that of the corresponding

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*Author to whom correspondence should be addressed.

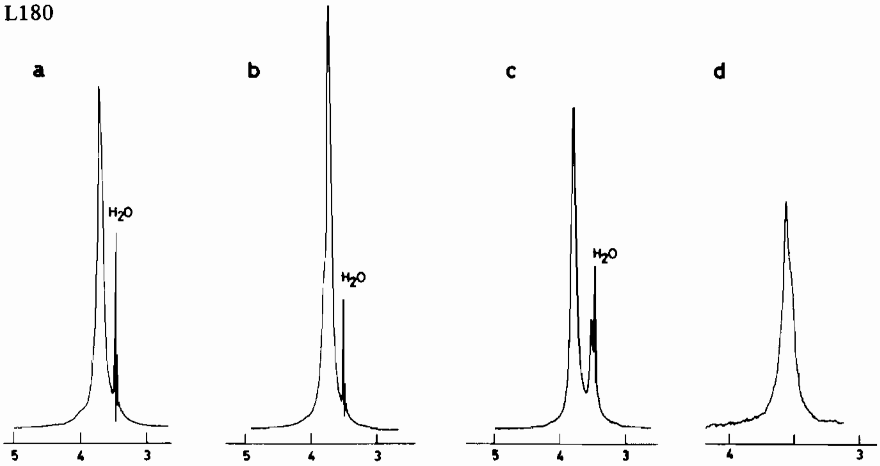

Fig. 1. The PMR spectra of rhodium ammine complexes in DMSO-d_6. (a) $[Rh(NH_3)_6](NO_3)_3$; (b) $[Rh(NH_3)_5(Cl)](NO_3)_2$; (c) $[Rh(NH_3)_5(NO_2)](NO_3)_2$; (d) $[Rh(NH_3)_5(CN)](NO_3)_2$.

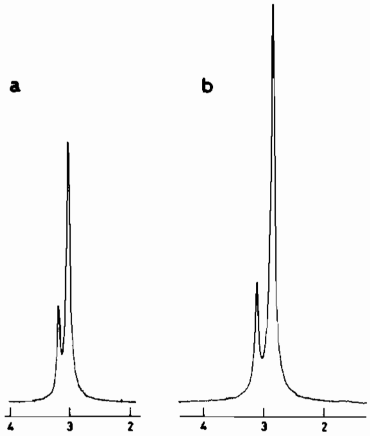

Fig. 2. The PMR spectra of $[Rh(NH_3)_5(CN)]Cl_2$ in (a) 50% and (b) 98% sulfuric acid.

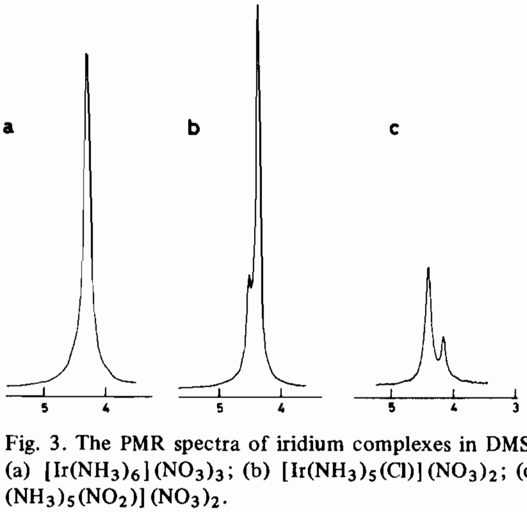

Fig. 3. The PMR spectra of iridium complexes in DMSO-d_6. (a) $[Ir(NH_3)_6](NO_3)_3$; (b) $[Ir(NH_3)_5(Cl)](NO_3)_2$; (c) $[Ir(NH_3)_5(NO_2)](NO_3)_2$.

TABLE I. Ammine Chemical Shifts of $[M(NH_3)_5(X)](NO_3)_{2\text{ or }3}$ in DMSO-d_6.

M X	Rh(III) *cis*	 *trans*	Ir(III) *cis*	 *trans*	Co(III)[a] *cis*	 *trans*
NH_3	3.72	3.72	4.31	4.31	3.45	3.45
CN	3.54	b			2.90	3.78
NO_2	3.80	3.52	4.41	4.16	3.42	3.42
Cl	3.74	3.78[c]	4.38	4.52	3.70	3.10

[a]Data taken from Ref. 2. [b]Overlapped with the H_2O resonance. [c]Shoulder.

cobalt compounds (Table I). The *trans* ammine hydrogens of $[Co(NH_3)_5(Cl)]^{2+}$ resonated upfield of *cis* ones [2, 3b], whereas the corresponding rhodium and iridium compounds show the *trans* hydrogens at lower magnetic fields than *cis* ones. Likewise, the $[Co(NH_3)_5(NO_2)]^{2+}$ complex showed only one resonance in many solvents, including DMSO-d_6 [2], concentrated sulfuric acid [4], deuterium oxide [3b], and DMSO-d_6/D_2O mixed solvents [3a], while the rhodium and iridium nitropentaammines give two well-resolved peaks. A direct consequence of these observations is that the ammine chemical shifts of rhodium and iridium complexes are not governed by the effect of the second-order paramagnetism of the metal ions. Otherwise, a similar shift pattern should be obtained for all the cobalt triad pentaammines. The result is not unexpected since the magnitude of the second-order paramagnetism depends inversely upon the exciting energies between the ground state and low-lying excited states [2]. While the trivalent cobalt ions have excited states of low enough energy to give rise to sizable residual paramagnetism, the rhodium(III) and iridium(III) ions do not. The energies of the $^1A_{1g}$ to $^1T_{1g}$ octahedralparentage transitions for the latter two ions are greater than those of the former by a factor of about two [7]. Further, increased metal-to-ligand bond covalency and increased orbital reduction factors for the latter two ions [8] would work to diminish the second-order paramagnetism. Instead, the results seem to be better understood in terms of the electron-donating and electron-withdrawing effect of the sixth ligand. Namely, if we postulate that the nitrite ion, for example, coordinates more strongly or more covalently than ammine to metal(III) ion and weaken the *trans* M(III)–NH_3 bond, it will result in an increased electron density on the hydrogens on this ammine group [8b]. The net effect is that the hydrogens on the nitrogen atom *trans* to the nitrite are more shielded than *cis* ones. Experimentally this is what we observed for the nitropentaammine rhodium and iridium complexes. For cobalt compounds, a shielding contribution from this effect is overridden or partially offset by the second-order paramagnetism depending on the sixth ligand [3a, 9]. Similarly, it appears that the chloride ion coordinated to rhodium and iridium tends to strengthen the M(III)–NH_3 bond *trans* to itself and confer a more covalent character on this bond, which will reduce the electron densities on the *trans* hydrogens. For both rhodium(III) and iridium(III) compounds, the chemical shifts of the *cis* peak appear less sensitive to the variation of the sixth ligand and close to that of the hexaammines. In this context, the single peak observed for the $[Rh(NH_3)_5(CN)]^{2+}$ ion in DMSO-d_6 was unexpected. In sulfuric acid solvent, this compound gives two peaks. The peak positions move to high fields as the sulfuric acid content increases. A similar behavior was reported by Fung *et al.* [10] for the amino hydrogens of *mer*-tris(glycinato)cobalt(III) in sulfuric acid.

Comparison of the chemical shifts of the cobalt triad ammine complexes reveals that the rhodium ammine resonances appear upfield of the corresponding iridium ammine resonances and cobalt ammine resonances upfield of the rhodium ammine resonances. This general trend was first reported by Hendrickson and Jolly [4]. A similar trend can be recognized for the amine resonances of the bis(ethylenediamine) complexes of these metal ions [11]. The shift difference for the corresponding rhodium and iridium compounds is about 0.60 to 0.74 ppm and appears almost insensitive to the sixth ligand. The trend noted for the cobalt triad amine and ammine complexes may be explained as follows. The rhodium-amine bonds generally assume a more covalent character than the cobalt-amine bonds, and iridium complexes become still more covalent than the corresponding rhodium complexes [8]. Thus, the electron density on the nitrogen bound to iridium is likely to be reduced compared with that on the nitrogen bound to rhodium and cobalt.

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