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A Proton Magnetic Resonance Study of Cobalt(III) Complexes Containing 1,10-Phenanthroline and Ethylenediamine

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The proton magnetic resonance (PMR) spectra of the phenanthroline ligand in $[Co(phen)_3]Cl_3$, $[Co(phen)_2(en)]Cl_3$ (new complex) and $[Co(phen)(en)_2]Cl_3$ were measured in deuterium oxide and analyzed as ABX systems. Significant up-field shifts of signals were observed only for the protons 2 and 9 of $[Co(phen)_3]^{3+}$ and the proton 2 of $[Co(phen)_2(en)]^{3+}$, not for the proton 9 of $[Co(phen)_2(en)]^{3+}$ nor the protons 2 and 9 of $[Co(phen)(en)_2]^{3+}$. The up-field shift was considered to be due to the effect of the ring current of the other phenanthroline ligands, since the protons 2 and 9 of $[Co(phen)_3]^{3+}$ and the proton 2 of $[Co(phen)_2(en)]^{3+}$ lies very close and to above the neighboring aromatic ligand.

The PMR spectra of 1,10-phenanthroline and its diamagnetic tris-complexes of iron(II), ruthenium(II), osmium(II), zinc(II), and cobalt(III) have been well examined.[1,2] Their spectra were analyzed as an ABX system, for the two halves of the ligand are chemically and magnetically equivalent, and no coupling was observed between neighboring protons on different aromatic rings (*e. g.*, H_4 and H_5 in Fig. 1). On the other hand, the spectra of *cis*-$[CoX_2(phen)_2]^{n+}$ were considered to consist of two independent ABX systems (H_2, H_3 and H_4, and H_9, H_8 and H_7) and an AB system (H_5 and H_6).[3] The significant up-field shift of signals corresponding to H_2 and H_9 in $[M(phen)_3]^{n+}$ and to H_2 in $[CoX_2(phen)_2]^{n+}$ was interpreted in terms of a metal-nonbonded hydrogen interaction,[1,2] or the effect of the ring current of the other aromatic ligand.[4,5] In order to clarify the origin of this kind of up-field shift, we have analyzed the PMR spectra of a series of complexes, $[Co(phen)_3]Cl_3$, $[Co(phen)_2(en)]Cl_3$, and $[Co(phen)(en)_2]Cl_3$. These three complexes are terpositive ions surrounded by six nitrogen atoms in pseudo-octahedral positions. Thus, the effect of solvation on the spectra will not be significantly different among these complexes.

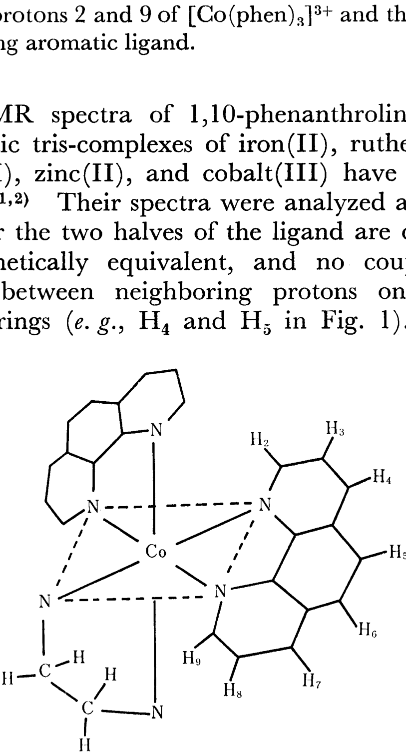

Fig. 1. Numbering of the protons on the phenanthroline ligand.

Experimental

Materials. *Bis(phenanthroline)ethylenediaminecobalt(III) perchlorate,* $[Co(phen)_2(en)](ClO_4)_3$: A mixture of 0.54 g of *trans*-(Cl–Cl)-$[CoCl_2(NH_3)_2(en)]Cl\cdot 0.5H_2O$[6] and 0.78 g of phenanthroline monohydrate in 50 m*l* of water was refluxed at 80°C for about 6 hr. The orange solution was then evaporated on a water bath to about 20 m*l* and cooled to room temperature. A crude complex was precipitated by adding concentrated perchloric acid. The precipitate was filtered off, washed with a small amount of cold water, recrystallized from hot water, and air-dried.

Found: C, 39.36; H, 3.40; N, 10.47%. Calcd for $CoC_{26}H_{24}N_6Cl_3O_{12}$: C, 40.15; H, 3.11; N, 10.80%. For the PMR measurement, the perchlorate was converted into chloride by the anion-exchange method.

The $[Co(phen)_3]Cl_3$ and $[Co(phen)(en)_2]Cl_3$ complexes were obtained by the methods described in the literature.[7,8]

Measurements and Calculation. The PMR spectra were recorded at about 39°C with Varian T 60 and Varian HA 100 spectrometers in a deuterium oxide solution containing sodium trimethylsilylpropanesulfonate (DSS) as the internal standard. The coupling constants, the chemical shifts, and the intensities were calculated with the HITAC 5020E electronic computer at the Computer Center of the University of Tokyo. The Fortran program for Castellano and Waugh's analysis[9] was kindly supplied by Dr. J. Cavanaugh of the Research Department, Socony Mobil Oil Company, Inc., Paulsboro, New Jersey, U.S.A. Since there are some signals which overlap each other, the peak height of the signals was taken as the approximate intensity.

Results and Discussion

The 60 MHz spectra of $[Co(phen)_3]Cl_3$, $[Co(phen)_2(en)]Cl_3$, and $[Co(phen)(en)_2]Cl_3$ in the phenanthroline part are given in Fig. 2.

The spectral pattern of $[Co(phen)(en)_2]^{3+}$ in the

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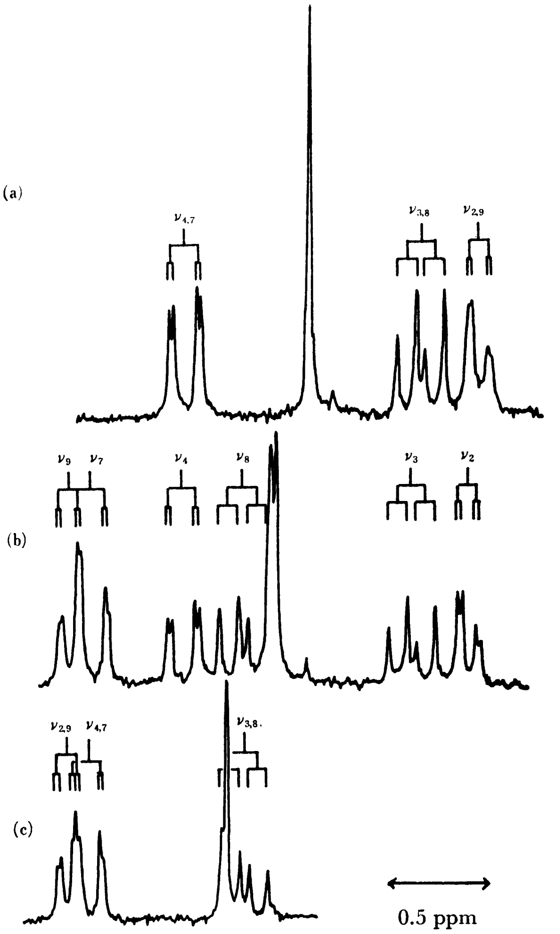

Fig. 2. 60 MHz spectra of $[Co(phen)_3]Cl_3$ (a), $[Co(phen)_2(en)]Cl_3$ (b) and $[Co(phen)(en)_2]Cl_3$ (c) in D_2O. The origin of the abscissa of each complex is arbitrary.

region of the phenanthroline part corresponds well to that of the free ligand,1) although the chemical shifts are slightly different. The signals of all the protons on the chelate appeared at slightly lower fields than those of the corresponding protons on the free ligand,1) this may be due to the deshielding effect of the central metal ion. Thus, the $\nu_{2,9}$, $\nu_{3,8}$, and $\nu_{4,7}$ signals in Fig. 2 of $[Co(phen)(en)_2]^{3+}$ were assigned to $H_{2,9}$, $H_{3,8}$, and $H_{4,7}$ respectively. No up-field shift of the signals corresponding to $H_{2,9}$ is observed in this complex.

The chemical environment of half of the phenanthroline part of $[Co(phen)_2(en)]^{3+}$ is similar to that of $[Co(phen)_3]^{3+}$, and that of the other half, to that of $[Co(phen)(en)_2]^{3+}$ (see Fig. 1). Therefore, the spectrum of $[Co(phen)_2(en)]^{3+}$ may be expected to be similar to the sum of those of $[Co(phen)_3]^{3+}$ and $[Co(phen)(en)_2]^{3+}$. As is shown in Fig. 2, the relative positions of ν_2 and ν_3 signals of $[Co(phen)_2(en)]^{3+}$ are very close to those assigned to $H_{2,9}$ and $H_{3,8}$ respectively for $[Co(phen)_3]^{3+}$.1,2) Thus, these signals can be assigned to the H_2 and H_3 protons respectively (Fig. 1). On the other hand, the resonance of ν_9 and ν_8 appear in the regions of $H_{2,9}$ and $H_{3,8}$ of $[Co(phen)(en)_2]^{3+}$; they are assigned to the H_9 and H_8 signals respectively. The resonances of ν_4 and ν_7 are assigned to H_4 and H_7 respectively for the same reason. These assignments were also confirmed by double-resonance measurements. The 100 MHz spectrum and the double-resonance spectra of $[Co(phen)_2(en)]^{3+}$ are shown in Fig. 3. Upon irradiation at about 9.05 ppm (in the region of H_4), the spectrum in the region of H_2 and H_3 became an AB pattern (Fig. 3(b)), and upon irradiation at about 8.87 ppm (in the region of H_8), the spectrum in the region of H_7 and H_9 changed to a broad doublet (an AB pattern with a small coupling constant) (Fig. 3(c)). In Fig. 3(a), an AB pattern with a coupling constant of 9.1 Hz is observed at 8.73 ppm; this can be assigned to signals of H_5 and H_6.

On the basis of the above assignment, the chemical shifts and the coupling constants were calculated as two independent ABX patterns. Tables 1 and 2 show the calculated values of the chemical shifts and the coupling constants respectively. The calculated and the ob-

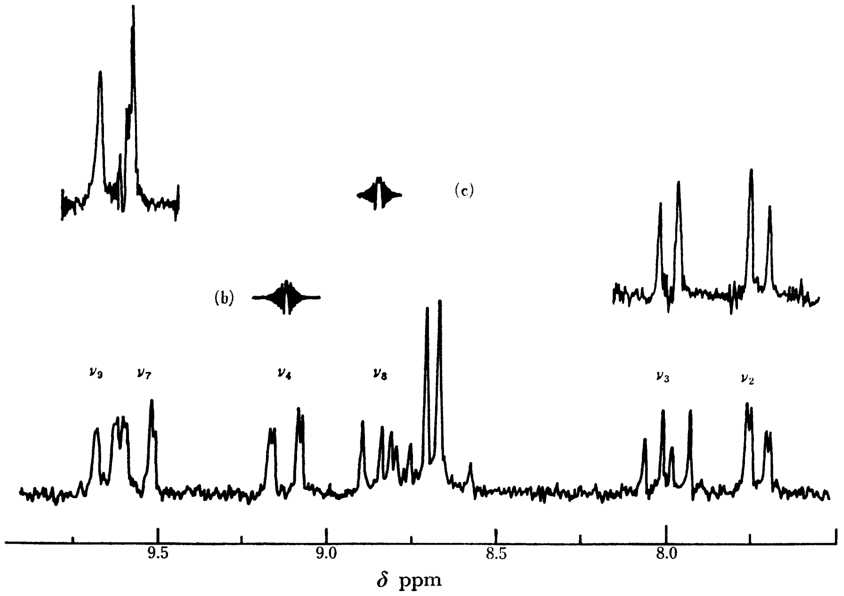

Fig. 3. 100 MHz spectrum of $[Co(phen)_2(en)]Cl_3$ (a), double resonance spectrum irradiated at about 9.05 ppm (b) and double resonance spectrum irradiated at about 8.87ppm (c).

TABLE 1. CALCULATED VALUES OF THE CHEMICAL SHIFT (δ IN PPM RELATIVE TO DSS)

	δ_2	δ_9	δ_3	δ_8	δ_4	δ_7	δ_5	δ_6
[Co(phen)$_3$]Cl$_3$	7.89		8.17		9.35		8.73	
[Co(phen)$_2$(en)]Cl$_3$	7.75	9.68	8.01	8.85	9.14	9.58	8.73	
[Co(phen)(en)$_2$]Cl$_3$	9.25		8.39		9.15		8.47	

TABLE 2. CALCULATED VALUES OF THE COUPLING CONSTANT (IN Hz)

	J_{23}	J_{89}	J_{24}	J_{79}	J_{34}	J_{78}	J_{56}
[Co(phen)$_3$]Cl$_3$	5.6_1		1.1_3		8.4_6		
[Co(phen)$_2$(en)]Cl$_3$	5.2_0	5.6_4	1.1_3	1.0_7	8.1_6	8.5_9	9.1
[Co(phen)(en)$_2$]Cl$_3$	5.6_2		1.0_5		8.2_0		

TABLE 3. CALCULATED AND OBSERVED INTENSITIES

[Co(phen)$_3$]Cl$_3$$^{a,c)}$			[Co(phen)(en)$_2$]Cl$_3$$^{a,d)}$			[Co(phen)$_2$(en)]Cl$_3$$^{b)}$					
Calcd position (Hz)$^{g)}$	Intensities		Calcd position (Hz)$^{g)}$	Intensities		Calcd position (Hz)$^{e,g)}$	Intensities		Calcd position (Hz)$^{f,g)}$	Intensities	
	Obsd	Calcd		Obsd	Calcd		Obsd	Calcd		Obsd	Calcd
−70.46	0.0	0.0	−66.28	0.0	0.0	−110.60	0.0	0.0	−104.28	0.0	0.0
−57.70	1.0	0.9	−22.67	0.8	0.8	−88.70	0.9	0.9	−34.37	0.9	0.9
−56.38	1.1	0.9	−21.55	0.9	1.0	−87.50	0.9	0.9	−33.27	1.0	1.0
−49.42	1.2	1.1	−18.47	1.1	0.9	−80.60	1.2	1.1	−28.77	1.0	0.9
−48.10	1.2	1.1	−17.35	0.9	0.7	−79.40	1.1	1.1	−27.67	1.0	1.2
−35.34	0.0	0.0	−17.15	0.9	0.9	−57.50	0.0	0.0	−25.97	1.1	1.0
10.73	0.8	0.8	−16.03	1.3	1.3	22.10	0.8	0.9	−24.87	1.0	0.8
16.33	1.2	1.4	−10.23	1.3	1.4	27.30	1.1	1.3	−17.37	1.4	1.3
19.01	0.6	0.5	−9.11	0.9	0.9	30.20	0.6	0.7	−16.27	0.9	1.0
24.61	1.2	1.3	26.26	1.3	1.3	35.40	1.1	1.1	42.24	0.0	0.0
31.77	1.1	1.3	27.58	0.0	0.0	52.10	1.2	1.2	45.04	1.1	1.2
33.09	1.1	1.3	31.78	1.0	1.0	53.30	1.2	1.2	50.64	1.0	1.0
37.37	0.7	0.7	34.50	0.9	0.9	57.30	0.9	0.8	53.64	0.9	0.9
38.69	0.6	0.6	38.70	0.0	0.0	58.50	0.8	0.8	59.24	0.7	0.8
105.80	0.0	0.0	40.02	0.7	0.7	168.10	0.0	0.0	62.04	0.0	0.0

a) 60 MHz spectrum; b) 100 MHz spectrum; Negative sign indicates that the shift is lower than c) 508 Hz, d) 536 Hz, e) 830 Hz, and f) 937 Hz (DSS is used as an internal standard); g) These are in good argreement with the observed ones.

served intensities are compared in Table 3. The data for [Co(phen)$_3$]$^{3+}$ and [Co(phen)(en)$_2$]$^{3+}$ are also listed in these tables.

A large difference in the chemical shifts between H_2 and H_9 was observed for [Co(phen)$_2$(en)]$^{3+}$ (1.93 ppm). This could not be explained only by the metal-non-bonded hydrogen interaction suggested by Miller and Prince,[1,2] since no significant difference in distances between Co–H_2 and Co–H_9 can be expected. An explanation by the π-bonding effect was also ruled out,[2] and the effect of the solvation[1,2] is considered to be not very significant, as has been discussed earlier.

The molecular model indicates that the proton 2 lies very close above the plane of the pyridine ring of the other phenanthroline ligand. The distance between the proton 2 and this plane is calculated to be about 2.7 Å on the assumption that the bond lengthes of Co–N, C$=$N, C$=$C, and C–H are 1.97,[10] 1.39, 1.39, and 1.08 Å respectively, and that all the bond angles in the coordinated ligands are 120°. The nitrogen atoms are also assumed to coordinate in the regular octahedral positions. Accordingly, the large up-field shift can reasonably be explained as being caused by the ring current of the neighboring ligand, as has been suggested by Castellano *et al.* for [Fe(bipy)$_3$]$^{2+}$.[4]

The differences in the chemical shifts between H_9 and H_2, H_8 and H_3, and H_7 and H_4 of [Co(phen)$_2$(en)]$^{3+}$ are 1.93, 0.94, and 0.44 ppm respectively. The decrease in the difference in the chemical shift in the above order can be accounted for by the increase in the distances between the proton and the molecular plane of the other phenanthroline ligand.

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