September, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***53****, 2531—2534 (1980)* 2531

Mixed-ligand Complexes of Cobalt(III) with 1-(2-Pyridylazo)-2-naphthol (PAN) and Diethylenetriamine (dien) or Triethylenetetramine (trien)[†]

Katsura Mochizuki and Masatoshi Fujimoto*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received January 14, 1980)

New mixed-ligand complexes [Co^{III}(pan)(dien)](ClO$_4$)$_2$·EtOH and [Co^{III}(pan)(trien)](ClO$_4$)·NaClO$_4$ were synthesized. The ^{1}H NMR and the visible absorption spectra of these complexes were compared with those of the free ligand PAN and [Co^{III}(pan)$_2$]Cl. A remarkable down-field shift observed in the ^{1}H NMR signal for the proton H$_{10}$ of the cobalt(III) complexes reflects the structural changes in the PAN molecule upon chelate-ring formation. The reaction between [Co^{III}Cl$_2$(trien)]Cl and PAN gave two kinds of products, which confirmed a strong tendency for the ligand PAN to behave as a planar terdentate ligand.

In previous papers on the reaction mechanisms of the complex formation of cobalt(II) ion with PAN or its analogs, it was reported that the reaction proceeds in two steps to form a cobalt(III) complex, *i.e.*, the fast formation of a 1:2 cobalt(II) complex followed by the slower oxidation of the central cobalt(II) ion.[1] However, for the elucidation of detailed mechanisms involved in each step further information concerning the coordination fashion of the multidentate ligands like PAN in solution is required.

The complex formation of a terdentate ligand PAN with a metal ion has been assumed to involve predominantly an N,N,O-coordination by the heterocyclic nitrogen, the azo nitrogen, and the phenolic oxygen as revealed by X-ray analysis of [Cu(pan)(OH$_2$)](ClO$_4$)[2] supporting a terdentate structure (Fig. 1). On the other hand, another possibility remains for the terdentate ligand PAN to behave in the metal complex only as a bidentate ligand; two types of N,N-coordination and one N,O-coordination are possible.

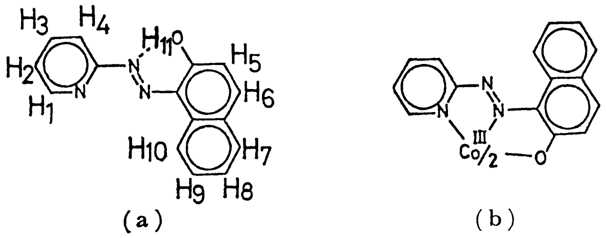

Fig. 1. Structural formulae of (a) PAN with numbering of the protons and (b) its cobalt(III) complex.

In the present study we have synthesized mixed-ligand complexes of cobalt(III) with PAN and a terdentate ligand dien or a qudridentate ligand trien and suggested the possibility for the coordination fashions of PAN as a bidentate or a terdentate ligand in these complexes based on the ^{1}H NMR and the spectral data.

Experimental

Materials. Reagent grade materials were used unless otherwise specified. A commercial specimen of PAN (Dojindo) was used without further purification, the purity being confirmed by elemental analysis. [Co^{III}(pan)$_2$]Cl was prepared as reported in a previous paper.[3)]

[Co^{III}(pan)(dien)](ClO$_4$)$_2$·EtOH was prepared from [Co^{III}Cl$_3$(dien)] in the same manner as in the preparation of [Co^{III}(par)(dien)]Cl·NaCl.[4] Two grams of PAN dissolved in 200 cm^3 of ethanol was added with stirring at 50 °C to 100 cm^3 of an ethanolic suspension, containing 2.1 g of [Co^{III}Cl$_3$(dien)] and 0.6 g of charcoal. Addition of 2.1 cm^3 of a 20% aqueous solution of AgNO$_3$ to the reaction mixture gave a deep green solution. The solution was filtered. The filtrate was evaporated to dryness. The residue was dissolved in a minimum amount of water. After the addition of 0.3 g of NaCl, the solution was filtered. Thirty cm^3 of a saturated solution of NaClO$_4$ was added to the filtrate. The precipitates were recrystallized several times from ethanol to yield crystals with green luster. Found: C, 38.38; H, 4.40; N, 13.00%. Calcd for C$_{19}$H$_{23}$N$_6$O$_9$Cl$_2$Co·C$_2$H$_5$OH: C, 38.49; H, 4.46; N, 12.82%. The elemental analysis shows that the isolated mixed-ligand complex contains one mol of ethanol. The complex is soluble in water.

[Co^{III}(pan)(trien)](ClO$_4$)$_2$·NaClO$_4$ was prepared from *cis*-*α*-[Co^{III}Cl$_2$(trien)]Cl as follows. The reaction mixture obtained by the same treatment as in the synthesis of [Co^{III}(pan)(dien)](ClO$_4$)$_2$·EtOH was passed through a column of a cation-exchange resin SP-Sephadex C-25 in the Na-form (400×30 mm i.d.) and eluted with a 0.2 mol dm^{-3} aqueous solution of NaCl. The chromatogram consisted of two main bands, a red and a green band **A**, which were eluted in this order. The green eluate from the green **A** band evaporated to a small volume at 40—50 °C. Sodium chloride precipitated was filtered off and the filtrate was evaporated to dryness. The residue was extracted with a small amount of ethanol. The extract was filtered in order to remove residual sodium chloride. After the procedure, filtration, evaporation, and extraction, had been repeated, the final extract was dissolved in a small amount of water. To the solution was added 30 cm^3 of a saturated solution of NaClO$_4$ in order to deposit the perchlorate. The crystals were recrystallized several times from ethanol–ether (1:1 v/v). Found: C, 32.74; H, 3.98; N, 12.26%. Calcd for C$_{21}$H$_{28}$N$_7$O$_9$Cl$_2$Co·NaClO$_4$: C, 32.56; H, 3.64; N, 12.66%.

Larger slender plates with green luster were also obtained by slow evaporation of the aqueous solution of the products containing a large amount of NaClO$_4$. Found: C, 30.05; H, 4.02; N, 11.87%. Calcd for C$_{21}$H$_{28}$N$_7$O$_9$Cl$_2$Co·NaClO$_4$·3H$_2$O: C, 30.43; H, 4.14; N, 11.83%. Elemental analysis shows that this complex contains 1 mol of NaClO$_4$ and 3 mol of water.

The red eluate from the red band was treated rapidly in the same manner as mentioned above to remove sodium chloride. The precipitate obtained was immediately subjected to measurements without further recrystallization.

The isolated perchlorates of the mixed-ligand complexes

[†] Presented at the 29th Annual Meeting on Coordination Chemistry, Hamamatsu, October 2, 1979, Abstract, p. 310.

with PAN and trien are soluble in water.

Measurements. 100 MHz ^{1}H NMR spectra were measured with a JEOL spectrometer model PS-100 or FX-100. Tetramethylsilane (TMS) for measurements in $CDCl_3$ or CD_3OD and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for those in D_2O solutions were used as internal standards. The perchlorates of cobalt(III) complexes were converted to the more water-soluble chlorides by passing through a column of an anion-exchange resin in the chloride-form, in order to facilitate measurements. The values of the chemical shifts hardly changed with the concentration of the complexes under the experimental conditions. Absorption spectra were measured at 25 °C with a Hitachi recording spectrophotometer Model EPS-3T.

Results and Discussion

The ^{1}H NMR spectrum of the free ligand PAN in $CDCl_3$ is shown in Fig. 2(a). First-order analysis of the spin-spin coupling constants, values of the chemical shifts, and application of a method of double irradiation allowed the assignment of signals to the protons H_1, H_5, H_6, H_{10}, and H_{11} (*cf.* Fig. 1 as regards the numbering of the protons). The spectra of the free ligand PAN and the PAN coordinated in the complexes were too complicated to attain complete assigments for the other protons of PAN. The assignment of the signals to H_1 and H_{10} was further confirmed by a comparison of the spectrum of the free PAN with that of the coordinated PAN in the cobalt(III) complexes. The values of the chemical shifts for the signals of H_1, H_5, H_6, H_{10}, and H_{11} are summarized in Table 1.

The ^{1}H NMR spectrum of $[Co^{III}(pan)(dien)]^{2+}$ in D_2O at pH *ca.* 5 is shown in Fig. 2(b). The integrated intensities of the signals show the presence of ten aromatic protons and six methylene protons (complex multiplet centered at *ca.* 3.3 ppm) corresponding to the coordinated ligands, PAN and dien, respectively.

The ^{1}H NMR spectrum of $[Co^{III}(pan)_2]^+$ in CD_3OD (Fig. 2(c)) indicates that two ligand molecules in $[Co^{III}(pan)_2]^+$ are both magnetically and chemically equivalent.

A remarkable feature found in the ^{1}H NMR spectra of the cobalt(III)–PAN complexes in comparison with those of the free PAN is a large difference in the chemical shift of the proton H_{10}. The H_{10} signal for the free ligand appeared at 8.19 ppm, while the corresponding signals for the coordinated PAN appeared at 9.37 ppm in $[Co^{III}(pan)(dien)]^{2+}$ and 9.64 ppm in $[Co^{III}(pan)_2]^+$. As shown in Fig. 1, the terdentate planar N,N,O-coordination of PAN molecule is necessarily accompanied by a rupture of the intramolecular hydrogen-bond and an internal rotation of the naphthol ring moiety around the C–N axis by 180 °. The molecular model (Fig. 3) suggests that a fairly close contact takes place between the proton H_{10} and the azo group. The proton H_{10} in such a chemical environment would be susceptible to the effect of the magnetic anisotropy due to the π-electron system of the azo group in addition to the effect of the ring current of the naphthol ring. The location of the

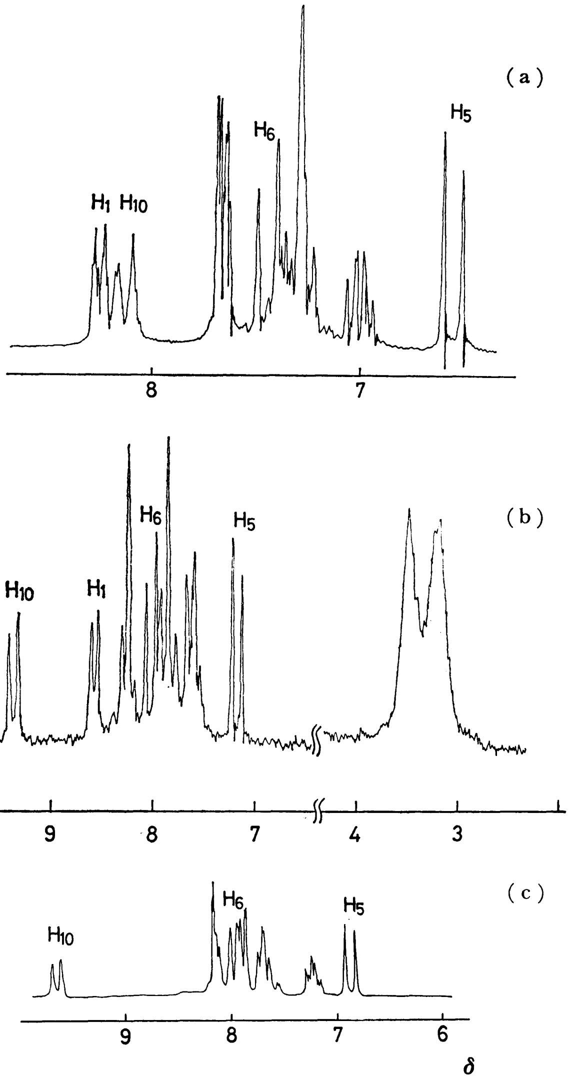

Fig. 2. ^{1}H NMR spectra of (a) PAN in $CDCl_3$, (b) $[Co^{III}(pan)(dien)]^{2+}$ in D_2O at pD *ca.* 5, and (c) $[Co^{III}(pan)_2]^+$ in CD_3OD.

Table 1. Results of chemical shifts in the ^{1}H NMR spectra (in ppm)

	5	6	1	10	11	Solvent	Standard
PAN	6.53	7.46	8.30	8.19	15.70	$CDCl_3$	TMS
$[Co^{III}(pan)(dien)]^{2+}$	7.18	8.03	8.58	9.37	—	D_2O[a]	DSS
	7.14	8.00	8.44	9.41	—	CD_3OD	TMS
$[Co^{III}(pan)_2]^+$	6.88	7.96	b)	9.64	—	CD_3OD	TMS
Red complex[c]	7.09	b)	8.58	b)	—	D_2O[a]	DSS
Green **A** complex[c]	7.18	8.06	8.58	9.46	—	D_2O[a]	DSS

a) pD *ca.* 5. b) In the complex multiplets. c) See text.

proton H_{10} in such an environment causes a down-field shift when the complexes are in the magnetic field. A similar phenomenon was observed in the case of the cobalt(III) complexes with 4-(2-pyridylazo)-resorcinol (PAR) which has a structure similar to that of PAN.[4)]

The resonance signal of the H_1 in $[Co^{III}(pan)_2]^+$ shows a definite up-field shift as compared with that in the free PAN hidden among the complex multiplet appearing at the upper field. On the other hand, no such up-field shift was observed for the H_1 signal for $[Co^{III}(pan)(dien)]^{2+}$ (Fig. 1 and Table 1). We see by inspection of molecular models that the difference in the chemical shift observed for the H_1 is caused by the number of PAN molecule involved. The proton H_1 of one of the PAN molecules in $[Co^{III}(pan)_2]^+$ is disposed close to and above the azo group of the other PAN molecule, only when these two PAN molecules coordinate to the cobalt(III) ion in a planar fashion as terdentate ligands (Fig. 3). Consequently, the observed up-field shift can be explained as being caused by the magnetic anisotropy due to the π-electron system of the azo group in the neighboring ligand PAN. Similar up-field shifts have been observed for the protons in the ortho position to the pyridyl nitrogen in $[Co^{III}(par)_2]$[4)] and other complexes.[5)]

The observed down-field shift of H_{10} signal and the up-field shift of the H_1 signal should give a useful support for the mer configuration also in the similar complex containing ligands with a structure as in Fig. 3 (*e.g.*, the complexes of TAR, TAN, *etc.*).

The data of visible spectra for the cobalt(III) complexes are summarized in Table 2. The positions of absorption bands and the spectral features are essentially the same for these complexes. The values of absorption coefficients for the complexes containing one molecule of PAN, $[Co^{III}(pan)(dien)]^{2+}$ and $[Co^{III}(pan)(trien)]^{2+}$, were about a half of the corresponding absorption coefficients for $[Co^{III}(pan)_2]^+$. The characteristic spectra with three absorption bands at *ca.* 450, 580, and 620 nm were always obtained; in contrast with the case of $[Co^{III}(pan)_2]^+$, for the complexes containing one molecule of PAN the value of absorption coefficient of the absorption band around 580 nm was smaller than that of the absorption around 620 nm. The results indicate that the absorption for these PAN complexes is primarily due to the coordinated PAN molecule and that the PAN molecules in the complexes are in the same electronic state irrespective of the numbers of the ligand.

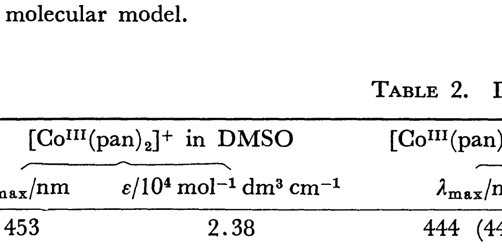

Fig. 3. The mer configuration and the disposition of two PAN molecules in $[Co^{III}(pan)_2]^+$ suggested from a molecular model.

Absence of the pH-dependence in the absorption spectra of these complexes supports the terdentate coordination of the ligand PAN to the central cobalt(III) ion.

Mixed-ligand complexes of cobalt(III) with PAN and trien were synthesized by the reaction of *cis*-α-$[Co^{III}Cl_2(trien)]Cl$ with PAN. Since the coordination sites in the cobalt(III) ion were occupied with a quadridentate triethylenetetramine, only two coordination sites are available for the coordination of the terdentate ligand PAN. If the ligand PAN coordinates to the central cobalt(III) ion as a terdentate ligand, one of the coordination sites in the trien molecule should be dissociated from the cobalt(III) ion.

The data of the ^1H NMR spectra for the red and the green **A** cobalt(III) complex are given in Table 1 (see Experimental for the red and the green **A** complex). The spectral feature and the chemical shifts of the protons H_5, H_6, H_1, and H_{10} in the green **A** complex are very similar to those of $[Co^{III}(pan)(dien)]^{2+}$, which show down-field shift of the resonance for the proton H_{10} and no up-field shift of the resonance for the proton H_1. This suggests that in the green **A** complex the ligand PAN coordinates to the cobalt(III) ion in a planar terdentate fashion and one of the sites of coordination in the ligand trien should be dissociated from the cobalt(III) ion. On the other hand, the spectral feature and the chemical shifts for H_1 and H_{10} of the red cobalt(III) complex differ from those of the green **A** complex, the free PAN, $[Co^{III}(pan)_2]^+$, and $[Co^{III}(pan)(dien)]^{2+}$; in the ^1H NMR spectrum of the red complex no corresponding down-field shift of the resonance for H_{10} was observed, suggesting the possibility of the contribution of some other coordination structure in the ligand PAN.

The visible spectrum of the green **A** complex is essentially the same as that of $[Co^{III}(pan)(dien)]^{2+}$. On the other hand, the spectrum of the red complex differs from that of (1) PAN, $[Co^{III}Cl_2(trien)]^+$, and $[Co^{III}(OH_2)_2(trien)]^{3+}$, (2) the cobalt(III) complex with nitrosonaphthol[6)] which is assumed to be a decomposition product of PAN, and (3) a bivalent cobalt

Table 2. Data of absorption spectra

$[Co^{III}(pan)_2]^+$ in DMSO		$[Co^{III}(pan)(dien)]^{2+}$ in H_2O (DMSO)		$[Co^{III}(pan)(trien)]^{2+}$ in H_2O[a)]	
λ_{max}/nm	$\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}	λ_{max}/nm	$\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}	λ_{max}/nm	$\varepsilon/10^4$ mol^{-1} dm^3 cm^{-1}
453	2.38	444 (448)	1.32 (1.41)	452	1.11
582	2.23	570 (574)	1.08 (1.11)	577	0.90
628	1.93	616 (624)	1.24 (1.39)	625	0.94

a) Green **A** complex (see text).

complex, $[Co^{II}(pan)_2]$.1) The observations suggest the possibility that the ligand PAN in the red complex coordinates to the cobalt(III) ion not in a planar terdentate fashion but in some other way.

Upon standing for a long time or heating with a small amount of 0.1 mol dm^{-3} solution of NaOH, the color of the solution of the red complex turned green, showing the formation of a green complex **B**. The color of the solution of this green **B** complex was not changed reversibly to red under the experimental conditions. The visible spectrum of the solution of the green **B** complex was essentially the same as that of the green **A** complex in the eluate from the ion-exchange column. The ^1H NMR spectra of the green **B** product also showed down-field shift of the H_{10} signal, though the spectra corresponding to the trien in the green **B** complex differ a little from those in the green **A** complex in the eluate.

The results suggest that the multidentate ligand PAN in these two green complexes **A** and **B** coordinates to the cobalt(III) ion in a planar terdentate fashion and the green cobalt(III) complex is more stable than the red cobalt(III) complex. When the synthesis of the mixed-ligand PAN-trien complex of cobalt(III) was carried out in a slightly basic media containing a small amount of NaOH, only the green complexes were obtained, the formation of the red complex was no longer observed.

On the basis of these results, we conclude that the multidentate lignad PAN has a very strong tendency to function as a planar terdentate lignad in the cobalt(III) complexes.

References

1) K. Mochizuki, T. Imamura, T. Ito, and M. Fujimoto, *Chem. Lett.*, **1976**, 1207; *Bull. Chem. Soc. Jpn.*, **51**, 1743 (1978).

2) S. Ooi, D. Carter, and Q. Fernando, *Chem. Commun.*, **1967**, 1301.

3) K. Mochizuki, T. Imamura, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **53**, 1757 (1980).

4) K. Mochizuki, T. Ito, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **52**, 441 (1979).

5) J. D. Milter and R. H. Prince, *J. Chem. Soc.*, **1965**, 3185, 4076; H. Ito, J. Fujita, and T. Ito, *Bull. Chem. Soc. Jpn.*, **44**, 723 (1971); S. Castellano, H. Gunther, and S. Ebersole, *J. Phys. Chem.*, **69**, 4166 (1965); T. Ito and N. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 155 (1970).

6) R. Lundquist, G. E. Markle, and D. F. Boltz, *Anal. Chem.*, **27**, 1731 (1955).