$$\text{(EDTA)Co}^{\text{III}}\text{NCFe}^{\text{II}}\text{(CN)}_4\text{L}^{4-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{CoEDTA}^- + \text{Fe(CN)}_5\text{L}^{3-} \tag{5}$$

$$\text{CoEDTA}^{2-} + \text{Fe(CN)}_5\text{L}^{2-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{CoEDTA}^- + \text{Fe(CN)}_5\text{L}^{3-} \tag{6}$$

sphere pathway for the Co(II)–Fe(III) reaction. For the mechanism represented by eq 4 and 5, the value of k_{obsd} (eq 2) is given by $k_2K_1[\text{CoEDTA}^{2-}]/(1 + K_1[\text{CoEDTA}^{2-}])$. For the mechanism represented by eq 4 and 6, $k_{\text{obsd}} = k_3[\text{CoEDTA}^{2-}]/(1 + K_1[\text{CoEDTA}^{2-}])$. Regardless of mechanism, the empirical parameter b in eq 2 is equal to K_1, the equilibrium constant for eq 4. The values of K_1 measured in the present work for bpy and py are listed in Table IV, together with those measured previously for P(C$_6$H$_5$)$_3$ and CN$^-$. The values fall in the narrow range 4.5×10^2–1.5×10^3 and, surprisingly, display no discernible trend with the oxidation potential of the Fe(III) complex. Depending on whether eq 5 or 6 is operative, the physical significance of the empirical parameter a is either k_2K_1 or k_3. Values of k_2 and k_3 are listed in Table IV. Values of k_{-2} or k_{-3}, estimated from the equilibrium constant K_3 for eq 6 (calculated from the appropriate reduction potentials), and the values of k_3 and K_1k_2 are also listed in Table IV. A choice between the two mechanistic interpretations was made previously[4] by comparing the value of k_{-2}, the rate constant for the replacement of one carboxylate of EDTA^{4-} by the N end of a CN in Fe(CN)$_5$L^{3-}, with other values for substitution reactions at a Co(III)–EDTA center. It will be seen that the values of k_{-2} fall in the range 0.03–0.64 M^{-1} s^{-1}, whereas rate constants for substitution of Co(III)–EDTA are in the 2×10^{-3}–3×10^{-6} s^{-1} range.[17-19] The values of k_{-1} appear to be too high for substitution at a Co(III)–EDTA center, and, therefore, we favor the mechanism represented by eq 4 and 6. A similar argument can be applied to the rate constant k_2. These constants fall in the range $(2.1–8.8) \times 10^{-3}$ s^{-1} and measure the loss of the NCFe(CN)$_4$L^{3-} moiety from the coordination sphere of pentadentate Co(III)–EDTA complex. The similar loss of Cl$^-$ from Co(EDTA)Cl^{2-} proceeds with a rate constant of 2.8×10^{-6} s^{-1}. Again this comparison suggests that the values of k_2, calculated on the assumption of eq 5 being operative, are unreasonably high for a substitution process at a Co(III) center. Therefore, eq 6 represents a more attractive alternative.

Additional, indirect support for the outer-sphere interpretation implied in eq 6 comes from calculations of the rate constants for the reactions of Fe(CN)$_5$py^{2-} or Fe(CN)$_5$bpy^{2-} with CoEDTA^{2-} using the Marcus cross relation corrected for electrostatic effects.[20] From the values of the self-exchange rate constants, 4.0×10^5 and 3.5×10^{-7} M^{-1} s^{-1} for Fe(CN)$_5$L$^{2-/3-}$ and CoEDTA$^{-/2-}$,[21-23] respectively, $E°$ values of 0.47, 0.46, and 0.37 V for Fe(CN)$_5$py$^{2-/3-}$, Fe(CN)$_5$bpy$^{2-/3-}$, and CoEDTA$^{-/2-}$,[24] respectively, and radii of 5.0, 5.8, and 4.0 $\times 10^{-8}$ cm for Fe(CN)$_5$py$^{2-/3-}$, Fe(CN)$_5$bpy$^{2-/3-}$, and CoEDTA$^{-/2-}$, respectively,[25,26] we calculate rate constants of 3.8 and 3.2 M^{-1} s^{-1} for the Fe(CN)$_5$py^{2-}–CoEDTA^{2-} and Fe(CN)$_5$bpy^{2-}–CoEDTA^{2-} reactions, respectively. The excellent agreement between these calculated values and the values 4.0 and 6.9 M^{-1} s^{-1} (Table IV) obtained by using experimental measurements and the interpretation embodied in eq 4 and 6 provides strong reinforcement of the outer-sphere interpretation.

Registry No. Fe(CN)$_5$bpy^{2-}, 73295-95-1; Fe(CN)$_5$py^{2-}, 61332-63-6; CoEDTA^{2-}, 14931-83-0; bpyH$_2$[Fe(CN)$_5$bpy], 73295-97-3; Li$_2$Fe(CN)$_5$py, 73295-98-4; (EDTA)Co$^{\text{III}}$NCFe$^{\text{II}}$(CN)$_4$bpy^{4-}, 73308-28-8; (EDTA)Co$^{\text{III}}$NCFe$^{\text{II}}$(CN)$_4$py^{4-}, 73295-99-5; Fe$^{\text{II}}$(CN)$_5$bpy^{3-}, 37475-72-2; Fe$^{\text{II}}$(CN)$_5$py^{3-}, 37475-75-5; Na$_3$[Fe(CN)$_5$NH$_3$], 14099-05-9.

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(22) It is assumed that the self-exchnge rates are equal for L = py or bpy.

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(25) For the nonspherical Fe(CN)$_5$L^{3-} complexes, the radii equivalent to the sphere of equal volume are calculated from $r = 0.5(d_1d_2d_3)^{1/3}$.

(26) The radius of CoEDTA^{2-} is taken to be equal to that of FeEDTA^{2-}.

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Acid–Base Properties of (α,ω-Alkanediamine)pentaamminecobalt(III) Complexes in Aqueous Solution

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Received October 23, 1979

The pK_a values of [Co(NH$_3$)$_5${NH$_2$(CH$_2$)$_n$NH$_3$}]$^{4+}$ (n = 2–8 and 10) have been determined at 25 °C and I = 0.1 M (NaCl). The pK_{a_1} and pK_{a_2} values of both [Co(NH$_3$)$_4${NH$_2$(CH$_2$)$_4$NH$_3$}$_2$]$^{5+}$ and *cis*-[Co(en)$_2${NH$_2$(CH$_2$)$_4$NH$_3$}$_2$]$^{5+}$ have also been determined under the same experimental conditions. The absorption spectrum of [Co(NH$_3$)$_5${NH$_2$(CH$_2$)$_n$NH$_2$}]$^{3+}$ was found to be more intense than that of [Co(NH$_3$)$_5${NH$_2$(CH$_2$)$_n$NH$_3$}]$^{4+}$, especially, in the ultraviolet region. The spectral difference between these two species becomes more significant as the methylenic chain length becomes shorter. The increased ultraviolet absorbance in [Co(NH$_3$)$_5${NH$_2$(CH$_2$)$_n$NH$_2$}]$^{3+}$ was ascribed to the appearance of a charge-transfer band, whose origin was identified as the intramolecular hydrogen bonding between the free amino group and an N–H proton of the coordinated ammines or amino group.

Introduction

Metal complexes containing (2-aminoethyl)ammonium ion (Hen$^+$) are known for cobalt(III),[1-8] platinum(II),[9,10] iron(II),[11] and ruthenium(II) and -(III).[12] Numerous chromium(III) complexes containing Hen$^+$ have also been known.[13]

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Table I. pK_a Values of α,ω-Alkanediammonium (HN-NH^{2+}) at 25 °C and I = 0.1 M (NaCl)

HN-NH^{2+}	pK_{a_1}	pK_{a_2}
H_2en^{2+}	7.15 ± 0.03	9.87 ± 0.04
H_2tn^{2+}	8.71 ± 0.03	10.31 ± 0.04
H_2tmd^{2+}	9.49 ± 0.04	10.67 ± 0.05
H_2pmd^{2+}	9.92 ± 0.04	10.77 ± 0.05
H_2hxn^{2+}	10.12 ± 0.04	10.80 ± 0.05
H_2hepn^{2+}	10.16 ± 0.04	10.88 ± 0.05
H_2ocn^{2+}	10.27 ± 0.04	10.85 ± 0.05
H_2den^{2+}	10.35 ± 0.04	10.94 ± 0.05

These complexes, in which the protonated ethylenediamine acts as a monodentate ligand, have been prepared by thermal and photochemical substitution reactions. It has been inferred that $[PtCl(pn)(pnH)]^{2+}$ is formed as the product of the electron-transfer reaction of $[PtCl_2(pn)_2]^{2+}$ with Cr^{2+}, where pn denotes 1,2-propanediamine.[14] Several examples are known for the complexes containing monodentate α,ω-alkanediamine(s) which have more methylene groups than en (the diamine, $NH_2(CH_2)_nNH_2$, will hereafter be referred to as N-N): *cis*-$[CoCl(en)_2(N\text{-}NH)]^{3+}$,[2,5] $[Co(NH_3)_5(N\text{-}NH)]^{4+}$,[8] $[Co(NH_3)_4(N\text{-}NH)_2]^{5+}$,[8] $[Co(NH_3)_3(N\text{-}NH)_3]^{6+}$,[8] $[Co(en)_2(N\text{-}NH)_2]^{5+}$,[5] $[PtCl_2(Me_2SO)(N\text{-}NH)]^+$,[15] and $[Fe(CN)_5(N\text{-}NH)]^{2-}$.[16] Because of the increasing interest in the complexes containing monodentate N-N's, it was felt worthwhile to examine their chemical properties.

In the present work, the pK_a values of a series of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ complexes were determined systematically (n = 2 (en), 3 (tn), 4 (tmd), 5 (pmd), 6 (hxn), 7 (hepn), 8 (ocn), and 10 (den)) and compared with those of the parent N-N's. The values of pK_{a_1} and pK_{a_2} of $[Co(NH_3)_4(tmdH)_2]^{5+}$ and $[Co(en)_2(tmdH)_2]^{5+}$ were also determined. During the course of this work, the absorption spectrum of $[Co(NH_3)_5(en)]^{3+}$ was found to be much more intense than that of $[Co(NH_3)_5(enH)]^{4+}$, especially, in the ultraviolet region. In order to elucidate the nature of this phenomenon, the absorption spectra of the series of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ complexes and their conjugate bases were measured.

Experimental Section

Materials. The complexes $[Co(NH_3)_5(N\text{-}NH)]X_4$,[8] $[Co(NH_3)_4(tmdH)_2]X_5$,[8] and $[Co(en)_2(tmdH)_2]Br_5\cdot4H_2O$[5] (X = ClO_4^- and/or Br^-) were prepared as reported in the literature. The geometric configuration of $[Co(en)_2(tmdH)_2]^{5+}$ has been determined to be cis by ^{13}C NMR spectroscopy because the spectrum in aqueous solution of the complex which was recorded on a JEOL JNM FX-60 spectrometer showed six signals with almost identical intensities (25.45, 29.08, 40.51, 44.61, 45.26, and 46.19 ppm vs. Me_4Si). In order to obtain diamine dihydrochloride (N-N·2HCl), an aqueous solution of the corresponding N-N (Tokyo Kasei Co.) was neutralized with hydrochloric acid and, then, concentrated in a rotary evaporator. In the cases of ocn·2HCl and den·2HCl, the addition of acetone was needed to complete the precipitation. The crystals deposited were collected and dried in a vacuum desiccator.

Table II. pK_a Values of Metal Complexes Containing (ω-Aminoalkyl)ammonium Ion at 25 °C and I = 0.1 M (NaCl)

complex	pK_a	ref
$[Co(NH_3)_5(enH)]^{4+}$	7.52 ± 0.03	this work
$[Co(NH_3)_5(tnH)]^{4+}$	9.08 ± 0.03	
$[Co(NH_3)_5(tmdH)]^{4+}$	9.67 ± 0.03	
$[Co(NH_3)_5(pmdH)]^{4+}$	10.02 ± 0.03	
$[Co(NH_3)_5(hxnH)]^{4+}$	10.16 ± 0.03	
$[Co(NH_3)_5(hepnH)]^{4+}$	10.28 ± 0.03	
$[Co(NH_3)_5(ocnH)]^{4+}$	10.36 ± 0.03	
$[Co(NH_3)_5(denH)]^{4+}$	10.53 ± 0.03	
$[Co(NH_3)_4(tmdH)_2]^{5+}$	9.34 ± 0.05 (pK_{a_1}) 9.93 ± 0.05 (pK_{a_2})	
cis-$[Co(en)_2(tmdH)_2]^{5+}$	9.30 ± 0.05 (pK_{a_1}) 9.94 ± 0.05 (pK_{a_2})	
cis-$[CoCl(en)_2(enH)]^{2+}$	6.70 ± 0.03	6
cis-$[CoBr(en)_2(enH)]^{2+}$	7.27 ± 0.02	
cis-$[Co(OH)(en)_2(enH)]^{2+}$	7.23	
$[(NH_3)_5CrOCr(NH_3)_4(enH)]^{5+}$	8.42^a	13a
$[Fe(CN)_5(enH)]^{2-}$	10^b	22
$[PtCl_2(enH)_2]^{2+}$	7.92 ± 0.04^c	23
$[PtCl(en)(enH)]^+$	7.96 ± 0.04^c	
$[PtCl_2(Me_2SO)(tmdH)]^+$	10.02^d	15

^{a} At 20 °C and I = 0.1 M (KCl). ^{b} I = 1 M ($NaClO_4$). ^{c} I = 1 M ($LiClO_4$). ^{d} I = 1.2 M ($NaClO_4$).

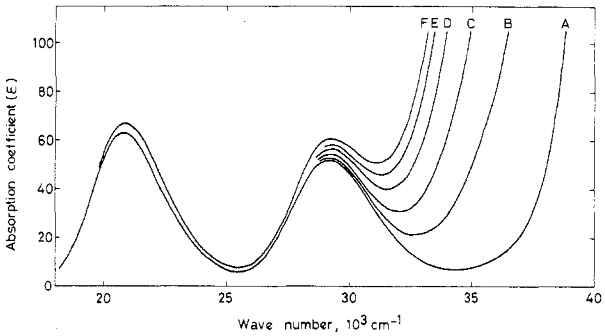

Figure 1. Spectral changes of $[Co(NH_3)_5(enH)]^{4+}$ with changes in hydrogen ion concentrations: $[H^+] = 9.4 \times 10^{-3}$ M (A), 2.86×10^{-7} M (B), 9.9×10^{-8} M (C), 3.20×10^{-8} M (D), 1.01×10^{-8} M (E), and 2.22×10^{-9} M (F).

Determination of pK_a Values. For determination of the pK_a values of N-N·2HCl and cobalt(III) complexes containing HN-N$^+$, pH titrations were made with a standard sodium hydroxide solution under a nitrogen atmosphere at 25 °C and I = 0.1 M (NaCl). The pH values were measured with a Toa HM-20B digital pH meter and a Toa HSS-10A pH stat. The hydrogen ion concentrations were calculated with the activity coefficient of 0.86 for the hydrogen ion.[17] The apparent ion product of water was estimated to be 1.45×10^{-14} from the reported thermodynamic constant[18] and the activity coefficient of 0.81 for hydroxide ion.[17]

Measurement of Electronic Spectra. Electronic spectra were recorded with a Union-Giken SM-401 spectrometer. All complexes used for the measurements were perchlorate salts.[19] Ionic strength was adjusted, if necessary, to 0.1 M with sodium perchlorate. The spectra of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ and $[Co(NH_3)_5(N\text{-}N)]^{3+}$ were measured usually in 1.0×10^{-2} M $HClO_4$ solutions and 5.0×10^{-3} M NaOH solutions, respectively.

Results

The pK_a values of α,ω-alkanediammonium ions (HN-NH^{2+}) are summarized in Table I. Table II gives the pK_a values of

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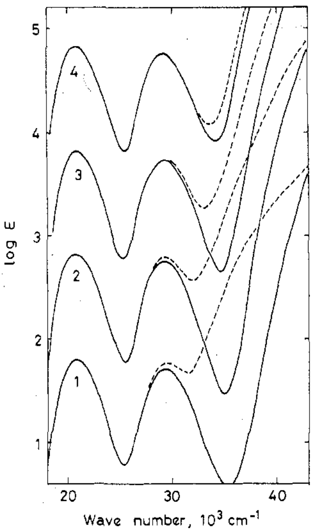


Figure 2. Spectra of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ in 1.0×10^{-2} M $HClO_4$ solution (solid line) and $[Co(NH_3)_5(N\text{-}N)]^{3+}$ in 5.0×10^{-3} M NaOH solution (broken line). N-N = en (curve 1), tn (curve 2), tmd (curve 3), and hxn (curve 4). Curves 2, 3, and 4 are shifted upward by 1, 2, and 3 log ε units, respectively.

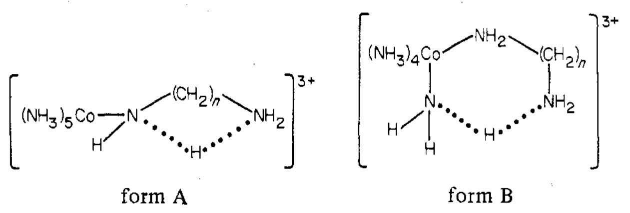
cobalt(III) complexes containing $HN\text{-}N^+$ along with the reported data on the related metal complexes. Figure 1 shows the spectra of $[Co(NH_3)_5(enH)]^{4+}$ at various hydrogen ion concentrations. The absorptions increase markedly in the ultraviolet region with the decrease of hydrogen ion concentrations. The spectra of some $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ ions and their conjugate bases, $[Co(NH_3)_5(N\text{-}N)]^{3+}$, were measured and compared. Figure 2 shows some of them. The numerical data for d–d absorption spectra of the complexes are summarized in Table III.[24]

Discussion

As is expected from the inductive effect of methylene groups, pK_a values of $HN\text{-}NH^{2+}$ given in Table I increase as the methylenic chain becomes longer. The difference between pK_{a_2} and pK_{a_1} approaches the statistically expected value (log 4 = 0.60) with an increase in the number of methylene groups. It has been reported that Hen^+ coordinated to cobalt(III) and platinum(II) has nearly the same acidity as H_2en^{2+} but is a considerably stronger acid than Hen^+.[6,23] Similar relationships are also observed for the other related systems; that is, the effect of a cobalt(III) ion on the pK_a value is similar to that of a proton.[6,25] The "rule" holds for all the pK_a values of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ (see Tables I and II). However, the "rule" seems not to hold for the values of $[Fe(CN)_5(enH)]^{2-}$[22] and probably $[(NH_3)_5CrOCr(NH_3)_4(enH)]^{5+}$[13a] and $[PtCl_2(Me_2SO)(tmdH)]^+$,[15] though the experimental conditions used in measuring them differ. Elucidation of this problem awaits further systematic study.

Both pK_{a_1} and pK_{a_2} values for $[Co(NH_3)_4(tmdH)_2]^{5+}$ are similar to the pK_{a_1} value of H_2tmd^{2+}, and the difference between the pK_{a_2} and pK_{a_1} values of the complex is almost identical with that of the statistical value. This is true also for *cis*-$[Co(en)_2(tmdH)_2]^{5+}$.

Chart I



From the spectral changes given in Figure 1, the pK_a value of $[Co(NH_3)_5(enH)]^{4+}$ was found to be 7.4 ± 0.1 at 25 °C and $I = 0.1$ M ($NaClO_4$). This value is in good agreement with that determined by pH titration (Table II). This fact indicates that spectral changes are attributed to the formation of $[Co(NH_3)_5(en)]^{3+}$. The d–d absorption bands of $[Co(NH_3)_5(en)]^{3+}$ are also somewhat different from those of $[Co(NH_3)_5(enH)]^{4+}$; that is, the wavelengths and molar absorption coefficients (ε) of the absorption maxima are 480 nm (ε = 67) and 340 nm (ε = 61) for $[Co(NH_3)_5(en)]^{3+}$ and 480 nm (ε = 63) and 343 nm (ε = 52) for $[Co(NH_3)_5(enH)]^{4+}$.

Upon the addition of NaOH solutions to the solutions of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, the spectral absorptions in the charge-transfer region are known to increase markedly.[26-30] The spectral changes are considered to be brought about by the presence of an ion pair with hydroxide ion and/or the deprotonated species ($[Co(NH_3)_5NH_2]^{2+}$ if the $[Co(NH_3)_6]^{3+}$ is taken as the example).[31] The deprotonation from an ammine in $[Co(NH_3)_6]^{3+}$ or from an amino group in $[Co(en)_3]^{3+}$ gives double-bond character to the Co–N bond. The hydrogen bonding between the complex ion and hydroxide ion in the ion pair may produce a situation similar to the formation of the deprotonated species; that is, the partial transfer of a hydrogen ion from the coordinated ammine or amino group to the hydroxide ion may increase the order of a Co–N bond to some extent. The observed spectral changes may be attributed primarily to the change in the character of the Co–N bond.

The spectral changes shown in Figure 1 are similar in shape to those observed upon the addition of NaOH solutions to the solutions of $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$. It would be very unlikely that the deprotonation from the ammonium group in $[Co(NH_3)_5(enH)]^{4+}$ affects the electronic state of the cobalt(III) center through the saturated aliphatic bonds, N–C–C–N–Co, and leads to spectral changes as large as those shown in Figure 1. The observed spectral changes may be reasonably understood by considering the appearance of a charge-transfer band due to the intramolecular hydrogen bonding between the free amino group in the conjugate base, $[Co(NH_3)_5(en)]^{3+}$, and an N–H proton in the coordinated ammines or amino ligand. The two modes of hydrogen bonding are possible as shown in Chart I. Transfer of the hydrogen ion in the coordinated amino group of en or ammonia ligand to the free end of en leads to the formation of a coordinated imido or amido ligand, respectively, as an extreme. This is a situation similar to that produced by the interaction of $[Co(NH_3)_6]^{3+}$ or $[Co(en)_3]^{3+}$ with hydroxide ion.

The idea that $[Co(NH_3)_5(en)]^{3+}$ gives a charge-transfer band due to the intramolecular hydrogen bonding is supported by the measurements of electronic spectra of the series of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ complexes. As shown in Figure 2, the

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(24) Supplementary material.

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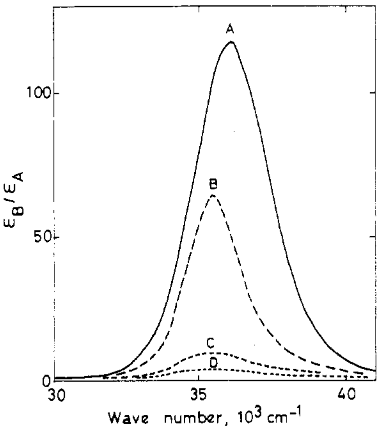

Figure 3. Plots of the ratio of the molar absorption coefficient of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ (ϵ_B) to that of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ (ϵ_A) vs. wavenumber. N-N = en (curve A), tn (curve B), tmd (curve C), and pmd (curve D).

Table IV. Maximum Value and Position of the Ratio of the Molar Absorption Coefficient of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ $(\epsilon_B)^a$ to That of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ (ϵ_A)

	$(\epsilon_B/\epsilon_A)_{max}$	position of $(\epsilon_B/\epsilon_A)_{max}$, 10^3 cm^{-1}
	N-N	
en	120	36.0
tn	65	35.5
tmd	10	35.5
pmd	4.2	35.2
hxn	1.9	35.1
hepn	1.5	36
ocn	1.3	35
den	*b*	*b*
	complex	
$[Co(en)_3]^{3+}$	3.3^c	35.2
$[Co(NH_3)_6]^{3+}$	5.0^c	37.6

[a] The spectrum of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ was measured in 5.0×10^{-3} M NaOH solution. [b] Low solubility of the perchlorate salt prevented accurate measurements. [c] See the text for the definition of ϵ_A and ϵ_B.

spectral difference between $[Co(NH_3)_5(N\text{-}N)]^{3+}$ and $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ in the ultraviolet region decreases with the increase in the number of methylene groups in N-N and the spectrum of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ containing long N-N such as hxn agrees reasonably well with that of the corresponding $[Co(NH_3)_5(N\text{-}NH)]^{4+}$. In order to visualize these differences, the ratios of the absorption coefficient of $[Co(NH_3)_5(N\text{-}N)]^{3+}$ (ϵ_B) to that of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ (ϵ_A) were plotted against the wavenumbers. Typical systems are shown in Figure 3. The maximum values of ϵ_B/ϵ_A are located around 35 000–36 000 cm^{-1}. The numerical data are summarized in Table IV. The value of $(\epsilon_B/\epsilon_A)_{max}$ approaches unity with an increase in the number of methylene groups. This fact suggests that formation of the ring structure in $[Co(NH_3)_5(N\text{-}N)]^{3+}$ becomes more difficult as the methylenic chain of the N-N becomes longer. This is compatible with the instability of medium size rings.[5,8,32,33] Therefore, the spectral changes shown in Figure 2 indicate that the origin of the increased ultraviolet absorbance of $[Co(NH_3)_5\{NH_2(CH_2)_nNH_2\}]^{3+}$ is the intramolecular hydrogen bonding between the free amino group and an N–H proton of the coordinated ammines or amino group. The diminished spectral difference between $[Co(NH_3)_5\{NH_2(CH_2)_nNH_2\}]^{3+}$ and $[Co(NH_3)_5\{NH_2(CH_2)_nNH_3\}]^{4+}$ with increases in the methylenic chain length can be reasonably ascribed to decreases in the fraction of the hydrogen bonded form(s) in $[Co(NH_3)_5\{NH_2(CH_2)_nNH_2\}]^{3+}$. However, the values of $(\epsilon_B/\epsilon_A)_{max}$ for $[Co(NH_3)_5(hxn)]^{3+}$, $[Co(NH_3)_5(hepn)]^{3+}$, and $[Co(NH_3)_5(ocn)]^{3+}$ are still larger than unity. This may be due to the formation of an ion pair of the complex with hydroxide ion (5.0×10^{-3} M) rather than the intramolecular hydrogen bonding between Co–N–H and the free amino group. Because the value of $(\epsilon_B/\epsilon_A)_{max}$ for $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ measured under the same conditions are also larger than unity. These values are given in Table IV, where ϵ_B denotes the absorption coefficient of a complex in 5.0×10^{-3} M NaOH solution and ϵ_A, that of the complex in 5.0×10^{-3} M $HClO_4$ solution. Under the present experimental conditions, it is unlikely that further deprotonation from $[Co(NH_3)_5\{NH_2(CH_2)_nNH_2\}]^{3+}$ contributes to the increased ultraviolet absorbance because the formation of such a species is possible only at extremely high pHs[31] and each pH titration curve of $[Co(NH_3)_5\{NH_2(CH_2)_nNH_3\}]^{4+}$ indicates the existence of only one dissociable proton.

Davies and Hung reported that $[Co(CO_3)_2(HCO_3)(N\text{-}N)]^{2-}$ and $[Co(CO_3)_2(H_2O)(N\text{-}N)]^-$ which contain monodentate N-N (N-N = en, pn, or tn) show unusually strong absorption at the ultraviolet region, while the corresponding complexes containing NH_3, pyridine, or hxn do not.[7] Yasui measured the spectra of $[Co(NH_3)_5(OOCCH_2NH_3)]^{3+}$ at various pHs and observed spectral changes similar to those shown in Figure 1.[34] The spectra of $[Co(H_2NTA)(NH_3)_5]^{2+}$, $[Co(H_2EDTA)(NH_3)_5]^+$, $[Co(HIDA)(NH_3)_5]^{2+}$, and $[Co(H_2EDDA)(NH_3)_5]^{3+}$ vary with the pH of the solution,[35-38] and the spectral changes are especially pronounced in the ultraviolet region and at higher pHs. These observations can be understood by considering the intramolecular hydrogen bonds between the coordinated ammine or amino groups and free amino and carboxylate groups.[39] The complexes studied here may provide a simple model of nonbonding interaction which plays an important role in biological systems.[40]

Acknowledgment. The author wishes to thank the Kurata Foundation for a grant and Dr. Y. Yoshikawa (Nagoya University) for recording the ^{13}C NMR spectra.

Registry No. H_2en^{2+}, 22534-20-9; H_2tn^{2+}, 61696-59-1; H_2tmd^{2+}, 57031-93-3; H_2pmd^{2+}, 57031-94-4; H_2hxn^{2+}, 19513-37-2; H_2hepn^{2+}, 73296-60-3; H_2ocn^{2+}, 49745-06-4; H_2den^{2+}, 49745-07-5; $[Co(NH_3)_5(enH)]^{4+}$, 73309-30-5; $[Co(NH_3)_5(tnH)]^{4+}$, 73309-29-2; $[Co(NH_3)_5(tmdH)]^{4+}$, 73309-28-1; $[Co(NH_3)_5(pmdH)]^{4+}$, 73309-27-0; $[Co(NH_3)_5(hxnH)]^{4+}$, 73309-26-9; $[Co(NH_3)_5(hepnH)]^{4+}$, 73309-25-8; $[Co(NH_3)_5(ocnH)]^{4+}$, 73309-24-7; $[Co(NH_3)_5(denH)]^{4+}$, 73309-41-8; $[Co(NH_3)_4(tmdH)_2]^{5+}$, 73309-40-7; *cis*-$[Co(en)_2(tmdH)_2]^{5+}$, 73346-89-1; $[Co(NH_3)_5(en)]^{3+}$, 64522-00-5; $[Co(NH_3)_5(tn)]^{3+}$, 73309-39-4; $[Co(NH_3)_5(tmd)]^{3+}$, 73309-38-3; $[Co(NH_3)_5(pmd)]^{3+}$, 64522-14-1; $[Co(NH_3)_5(hxn)]^{3+}$, 73309-37-2; $[Co(NH_3)_5(hepn)]^{3+}$, 64522-22-1; $[Co(NH_3)_5(ocn)]^{3+}$, 73309-36-1.

Supplementary Material Available: Table III listing absorption data of $[Co(NH_3)_5(N\text{-}NH)]^{4+}$ and $[Co(NH_3)_5(N\text{-}N)]^{3+}$ (1 page). Ordering information is given on any current masthead page.

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