or hydroxide is also ascribed to replacement of a coordinated water molecule.

In contrast to the above stabilities, $K_{\mathrm{MLF}}^{\mathrm{F}}$ of Th-EGTA-F^- is exceptionally large. Recent X-ray crystal structural studies have shown that Ca-EGTA, Cd-EGTA, and Mn-EGTA have a distorted dodecahedral coordination sphere utilizing the ligand's octadentate chelating ability.[17] The bond distances of M-O(ether) are shorter than those of M-N for calcium, whereas for transition-metal ions the reverse trend is found. Since thorium has an ionic radius (Å) between those of the other metal ions (Th, 1.08; Ca, 1.12; Cd, 1.10; Mn, 0.96), Th-EGTA is expected to have a quite similar structure. Two weak Th-O(ether) bonds in the parent complex are easily broken by coordination of the first fluoride, and the resultant mixed-ligand complex has EGTA of hexadentate chelation together with fluoride and water molecules. The second stability constant ($10^{3.45}$) is comparable to that of Th-EDTA or -CDTA, and the reaction is assigned as the usual displacement of a water molecule with fluoride. In Th-EGTA, the ligand can coat the thorium ion to disturb the coordination of water molecules to the metal center, and this is the reason for the exceptionally high affinity of this complex to the first fluoride.

Formation of the mixed-ligand complexes was monitored also by ^{1}H NMR spectroscopy at 200 MHz (Figure 2). The parent Th-EDTA complex has a singlet pattern for both acetate and ethylene protons with reasonable chemical shifts compared to those of other EDTA complexes.[18] The reaction with fluoride does not cause change in the chemical shift, although slight splitting into an A-B quartet is observed for acetate protons. In contrast, the parent Th-EGTA has an A-B quartet for acetate protons, two triplets for ethylene protons between ether and amino groups, and a singlet for ethylene protons between ether groups. Increase in the chemical shift for the ethylene protons between ether groups (4.0 ppm) compared to that of the free ligand (3.7-3.8 ppm)[19] indicates the coordination of ether groups. The reaction with fluoride decreases the chemical shift ($\sim$3.9 ppm), although the spectrum is broadened and complicated. This change supports the uncoordination of ether oxygen atoms in the mixed-ligand complex as proposed above.

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Pressure and Temperature Effects on the Coordination Equilibrium of a Cobalt(III) [Co(N)$_4$Cl] System

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Paramagnetic cobalt(III) complexes are relatively rare. Complexes having a spin-triplet ground or close-lying excited state have been characterized, including square-planar,[1] five-coordinate trigonal-bipyramidal,[2] and five-coordinate square-pyramidal[3] complexes.

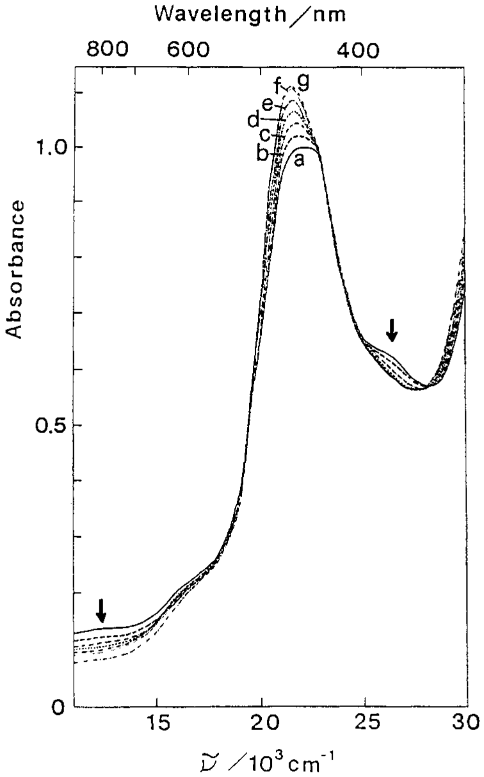
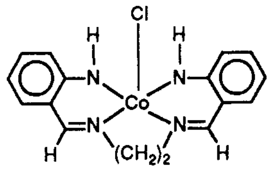


Figure 1. High-pressure spectra of 9.5 × 10^{-5} M [Co(aben)Cl] in pyridine at 19.3 °C (optical path length 16 mm): (a) 0.001 kbar; (b) 0.5 kbar; (c) 1.0 kbar; (d) 1.5 kbar; (e) 2.0 kbar; (f) 2.5 kbar; (g) 3.0 kbar.

The paramagnetic (S = 1) five-coordinate cobalt(III) compound [Co(aben)Cl] (I; aben = 1,2-bis(*o*-iminobenzylideneamino)ethane) has been reported[3b,c] to be in equilibrium with the diamagnetic (S = 0) six-coordinate complex in pyridine solution (eq 1). The



I

$$[\mathrm{Co(N)_4Cl}] + \mathrm{py} \rightleftharpoons [\mathrm{Co(N)_4Cl(py)}] \qquad (1)$$

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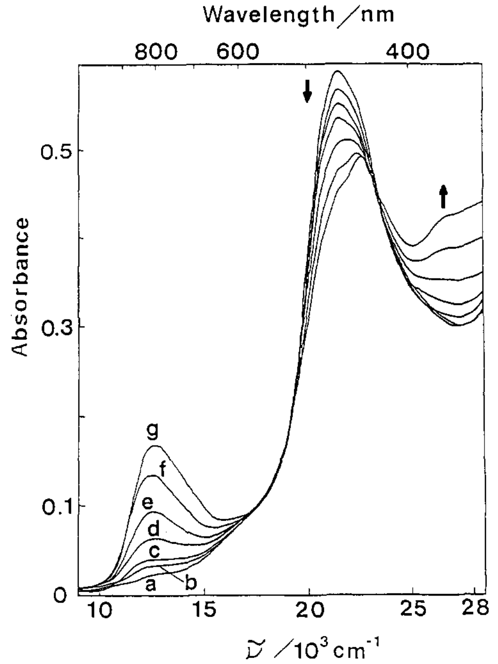

Figure 2. Spectra of 9.5 × 10^{-5} M [Co(aben)Cl] in pyridine at various temperatures and at atmospheric pressure (optical path length 10 mm): (a) 10.0 °C; (b) 20.0 °C; (c) 30.0 °C; (d) 40.0 °C; (e) 50.0 °C; (f) 60.0 °C; (g) 65.0 °C.

equilibrium (1) is, to our knowledge, the first example of a Co(III) complex that shows a coordination–spin equilibrium.[4]

We report here our results of an electronic spectral study of the pressure and temperature effects on the equilibrium (1).

Experimental Section

The compound [Co(aben)Cl] was prepared by the literature method[3b] and identified by elemental analysis, the magnetic moment, and the electronic spectrum. Sample solutions were prepared by dissolving the compound in pyridine just before spectroscopic measurements.

High-pressure electronic spectra were recorded on a Hitachi 340 spectrophotometer fitted with a clamp-type optical cell.[5] The change in the optical path length with pressure was found to be negligible. Variable-temperature spectra were determined on a Shimadzu MPS-50L spectrophotometer equipped with thermostated quartz cells.

Results and Discussion

Figures 1 and 2 show the visible spectra of [Co(aben)Cl] in pyridine solutions at high pressures and at various temperatures, respectively. The absorbances in both figures are uncorrected for compression or thermal expansion of the solution. The peaks and shoulders are observed at 26 300, 22 600, 21 500, 16 400, and 12 300 cm^{-1} under atmospheric pressure and at room temperature, being in agreement with the results in the literature.[3b] By comparison with the previous data[3b], it is found that the peaks of 26 300 and 12 300 cm^{-1} are due to the five-coordinate species [Co(aben)Cl] and the 21 500-cm^{-1} peak is due to the six-coordinate species [Co(aben)Cl(py)]. From the changes in the intensities of these peaks with pressure and temperature in Figures 1 and 2, it is clear that the equilibrium (1) is shifted to the six-coordinate-species side at high pressures but to the five-coordinate-species side at elevated temperatures.

In general, the pressure and temperature parameters of an equilibrium yield the volume change $\Delta V = -RT\mathrm{d}\ln K/\mathrm{d}P$ and the enthalpy change $\Delta H = -R\mathrm{d}\ln K/\mathrm{d}(1/T)$, respectively. For the reaction (1), $\mathrm{d}\ln K/\mathrm{d}P$ can be estimated by $\mathrm{d}\ln (A_{21\,500}/A_{12\,300})/\mathrm{d}P$, and $\mathrm{d}\ln K/\mathrm{d}(1/T)$ by $\mathrm{d}\ln (A_{21\,500}/A_{12\,300})/\mathrm{d}(1/T)$. From the slope of the linear plots of $\ln (A_{21\,500}/A_{12\,300})$ vs pressure, ΔV for eq 1 is found to be −21.8 cm^3 mol^{-1} in the range 0.001–1.5 kbar. In a similar manner, ΔH is evaluated to be −51.8 kJ mol^{-1} in the range 10.0–65.0 °C.

The spin-state change in eq 1 may be expected to contribute to the ΔV of −21.8 cm^3 mol^{-1} through volume changes for complexes [Co(N)$_4$Cl(py)] and [Co(N)$_4$Cl]. It has been reported[1j,6] for Fe(II), Fe(III), and Co(II) octahedral complexes, all of which show spin-state changes without changes in coordination number, that the transition from the low-spin to the high-spin state results in lengthening of the metal–ligand bonds and a consequent increase in the volume of the complex by 4–23.6 cm^3 mol^{-1}. On the other hand, in a Co(II) complex system showing no spin-state change, we obtained the value of ΔV = −41 cm^3 mol^{-1} for the addition reaction of two pyridine molecules, $[\mathrm{Co(py)_2Cl_2}] + 2\mathrm{py} \rightleftharpoons [\mathrm{Co(py)_4Cl_2}]$.[7] Although this reaction cannot be compared directly with eq 1 because it is not merely the addition reaction of pyridines but is accompanied by the tetrahedral–octahedral transformation, the ΔV value per one molecule of pyridine for this reaction is close to the ΔV value of −21.8 cm^3 mol^{-1} for eq 1 obtained in the present study. Thus, it is considered in the present stage that in reaction 1 the contribution of the spin-state change to ΔV is not as large as to be expected.

The reaction in which ΔH can be compared directly with the value of −51.8 kJ mol^{-1} for eq 1 has not been studied so far. However, ΔH for related systems are mentioned below. Concerning the coordination–spin equilibrium, the values has been determined as −76.5 kJ mol^{-1} in water or −97.4 kJ mol^{-1} in ethanol for the reaction of Co(III) complex[1m,n] [Co(η^4-HMPA-DMP)]$^-$ (square-planar, S = 2) + 2py $\rightleftharpoons$ [Co(η^4-HMPA-DMP)(py)$_2$]$^-$ (six-coordinate, S = 0), where H$_4$HMPA-DMP denotes 2,4-bis(2-hydroxy-2-methylpropanamido)-2,4-dimethyl-3-oxopentane. On the other hand, ΔH for the coordination equilibrium without the spin-state change has been reported for the addition reaction of amine bases such as pyridine. We obtained[7] the ΔH value of −57.3 kJ mol^{-1} for the above-mentioned reaction $[\mathrm{Co(py)_2Cl_2}] + 2\mathrm{py} \rightleftharpoons [\mathrm{Co(py)_4Cl_2}]$. For cobalt(II) porphyrins having a low-spin ($S = {}^1/_2$) ground state, the ΔH values have been evaluated[8] to be −25.1 to −48.1 kJ mol^{-1} for the reaction of CoP + B $\rightleftharpoons$ CoP·B, where CoP is a four-coordinate cobalt porphyrin and B represents an amine base.

Further discussion of the effects of the spin-state change on ΔV and ΔH for eq 1 will be possible if the data are obtained for coordination reactions of diamagnetic five-coordinate Co(III) complexes[9] such as chloro(*meso*-tetraphenylporphyrinato)cobalt(III), [Co(tpp)Cl].

In order to estimate the concentration of the five-coordinate paramagnetic species [Co(aben)Cl] at atmospheric pressure and at room temperature, the absorbances in Figure 1 are corrected for changes in pyridine density with pressure.[10] Since the corrected absorbances of the 21 500-cm^{-1} peak increase with pressure in the low-pressure region and then become saturated at 3 kbar (not shown), the six-coordinate species [Co(aben)Cl(py)] exists predominantly in solution at 3 kbar. Assuming that the molar

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extinction coefficient[11] for [Co(aben)Cl(py)] is independent of pressure, the concentration of the five-coordinate species [Co(aben)Cl] is found to be 7.7% at atmospheric pressure, being larger than the previous value of 4%.[3c] Moreover, the thermodynamic parameters for the equilibrium (1) are calculated with [py] = 12.41 M as follows: $K = 0.96\ M^{-1}$, $\Delta G = 0.099$ kJ mol^{-1}, and $\Delta S = -0.18$ kJ mol^{-1} K^{-1}.

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Registry No. py, 110-86-1; [Co(aben)Cl], 36433-98-4.

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(11) The molar extinction coefficients are estimated to be 4290 M^{-1} cm^{-1} at 21 500 cm^{-1} for [Co(aben)Cl(py)] and 3450 M^{-1} cm^{-1} at 12 300 cm^{-1} for [Co(aben)Cl].

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Amination of Coordinated Nitriles: Synthesis of Metal Complexes of Amidines and Guanidines

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Coordination by nitriles to electron-withdrawing metal ions results in considerable enhancement in the electrophilicity of the nitrile carbon center. This is demonstrated[1] by the 10^6–10^8-fold increase in the rate of base-catalyzed hydration of nitriles when bound to $(NH_3)_5M^{3+}$ (M = Co(III), Rh(III), Ru(III)), although metal ions such as Ru(II) (which are strongly metal-to-ligand π-bonding) have little influence on this reactivity.[1] The susceptibility of coordinated nitriles to attack by other nucleophiles (e.g. CN^-, N_3^-, and CO_3^{2-})[2-5] prompted the present work, where we have used liquid NH_3 to aminate nitriles, including a substituted cyanamide, providing a synthesis of metal complexes of unidentate amidines and of a (substituted) guanidine. We were particularly interested in comparing the acid/base properties and solution structures of such complexes with those of their isoelectronic N- and O-bonded urea and amide complexes.[6] This study may be relevant to the in vivo coordination chemistry of arginine residues, which contain protonated guanidine derivatives as potential ligands for bio-constituent metal ions.

Results and Discussion

The series of yellow nitrile complexes $[(NH_3)_5Co\text{-}NCR]^{3+}$ (R = NH_2, $N(CH_3)_2$, CH_3, $CH_2{=}CH$, C_6H_5, $o\text{-}NO_2\text{-}C_6H_4$, $p\text{-}F\text{-}C_6H_4$) were prepared by the reaction of $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ with the appropriate nitrile, either as the neat compound or in acetone.[2,7] When dissolved in NH_3(l), they undergo a slow reaction (minutes at −76 °C), evidenced by the distinct color change from yellow to burgundy (R = $N(CH_3)_2$) or yellow-orange; the R = NH_2 derivative merely deprotonates at the exo NH_2 and does not aminate. The solvent was evaporated, giving quantitative yields of amination products, which were recrystallized (water) and characterized by microanalyses and NMR (^{1}H, ^{13}C) and absorption spectra.

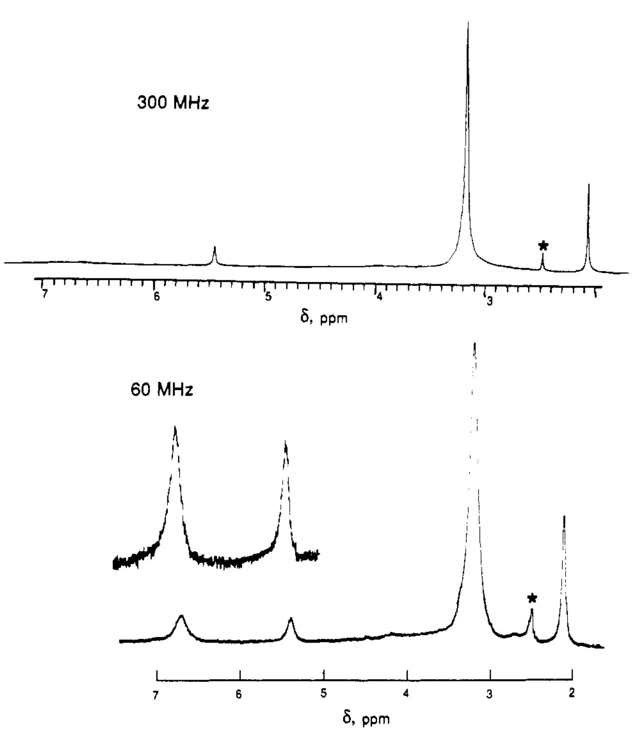

Figure 1. 60-MHz (35 °C, bottom) and 300-MHz (20 °C, top) ^{1}H NMR spectra of $[(NH_3)_5CoNH{=}C(NH_2)CH_3]^{3+}$ in Me_2SO showing the collapse of the exo-NH_2 signal at the higher field strength. These spectra were run with the same sample but are not on the same scale; the asterisk represents residual $Me_2SO\text{-}d_5$ in the solvent.

Amidines. The aqueous recrystallization of products obtained from either alkyl or aryl nitrile complexes in NH_3, with use of either Tris/$NaClO_4$ (pH ca. 9) or $HClO_4$, gave yellow-orange crystals with identical properties (for a particular nitrile). Each material gave the correct analysis for addition of 1 mol of NH_3, $[(NH_3)_5CoNCRNH_3](ClO_4)_3\cdot xH_2O$, and the cation-exchange behavior (Sephadex C25 resin) indicated a 3+ ion. The 60-MHz ^{1}H NMR spectrum of the prototype $[(NH_3)_5Co{-}NH{=}C(NH_2)CH_3]^{3+}$ in $Me_2SO\text{-}d_6$ (Figure 1, bottom) shows coincident cis- and trans-NH_3 signals (δ 3.26 ppm, 15 H), not uncommon for CoN_6 species,[6] lattice water (δ 3.42 ppm, 4 H), the methyl signal (δ 2.12 ppm, 3 H), and broad signals at δ 6.68 (2 H) and 5.39 (1 H) ppm, typical[8] of imine (NH=C) protons. None of these signals corresponds to residual free NH_3 or NH_4^+ or unreacted nitrile complex (δ 3.70 ppm, cis NH_3; δ 3.33 ppm, trans NH_3; δ 2.60 ppm, CH_3). These data allow formulation of the product as $[(NH_3)_5Co{-}NH{=}C(NH_2)CH_3](ClO_4)_3\cdot 2H_2O$, and similar considerations apply to the other amidine complexes (Table I). The ^{13}C NMR data confirmed the presence of the amidine ligands and the purity of the complexes (Table II).

These results indicate that at least up to pH 10 the amidine ligands are uncharged, and the complexes are stable in neutral or acid solution for many hours, although slow aquation (amidine release) ultimately occurs ($t_{1/2} > 10$ h). There seems to be no hydrolysis of the ligand to produce (initially) the N-bonded amide, $[(NH_3)_5CoNH{=}C(OH)R]^{2+}$. Above ca. pH 11, deprotonation can be observed spectrophotometrically, and indeed brown-orange deprotonated forms can be readily crystallized from 0.1 M OH^- (although prolonged exposure to strong base (1 M) results in decomposition). These revert to the protonated amidine species

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