The proton nmr spectrum in $CDCl_3$ consisted of two singlets at τ 5.37 (C_5H_5) and 5.50 (CH_3CO), and two broad signals at τ 7.8–8.85 (C_6H_{10}) and 6.0–6.4 (C_6H).

Reaction of Dicarbonyl-π-cyclopentadienylbenzyliron with *tert*-Butyl Isocyanide.—By the procedures similar to those described above, π-$C_5H_5Fe(CO)(CNC(CH_3)_3)CH_2Ph$ (0.43 g, 39%; mp 55–57° dec) was prepared from the treatment of π-$C_5H_5Fe(CO)_2$-$CH_2C_6H_5$ (0.95 g, 3.6 mmol) with cyclohexyl isocyanide (0.4 g, 4.8 mmol) in refluxing THF for 12 hr. *Anal.* Calcd for $C_{15}H_{21}$-NOFe: C, 66.89; H, 6.55; N, 4.33. Found: C, 66.57; H, H, 6.41; N, 4.16.

Reaction of Dicarbonyl-π-cyclopentadienylbenzyliron with Cyclohexyl Isocyanide in a 1:4 Molar Ratio.—π-$C_5H_5Fe(CO)_2$-CH_2Ph (0.6 g, 2.24 mmol) was treated with cyclohexyl isocyanide (0.98 g, 9.0 mmol) in refluxing THF for 20 hr. The solvent was removed almost to dryness under reduced pressure. The residue was chromatographed on alumina, using hexane–benzene, benzene, and benzene–THF as eluents. The yellow hexane–benzene layer gave unconverted starting material (0.05 g), the benzene one gave [π-$C_5H_5Fe(CO)_2$] (0.03 g), and the reddish-brown layer gave π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3(CH_2Ph)]$ (0.64 g, 51%).

Reaction of Dicarbonyl-π-cyclopentadienyl-*p*-chlorobenzyliron with Cyclohexyl Isocyanide in a 1:1 Molar Ratio.—π-C_5H_5Fe-$(CO)_2CH_2C_6H_4Cl$-*p* (0.52 g, 1.72 mmol) and cyclohexyl isocyanide (0.22 g, 2.0 mmol) in THF (2 ml) and benzene (3 ml) was charged in a sealed tube and kept in a water bath at 50° for 20 hr. By the procedures similar to those described above, π-$C_5H_5Fe(CO)[(C{=}NC_6H_{11})_3(CH_2C_6H_4Cl$-*p*)] (0.057 g, 5.5%) was obtained.

Reaction of Dicarbonyl-π-cyclopentadienyl-*p*-chlorobenzyliron with Cyclohexyl Isocyanide in a 1:2 Molar Ratio.—π-C_5H_5Fe-$(CO)[(C{=}NC_6H_{11})_3(CH_2C_6H_4Cl$-*p*)] (0.23 g, 22%) was obtained from the reaction of π-$C_5H_5Fe(CO)_2CH_2C_6H_4Cl$-*p* (0.52 g, 1.72 mmol) and cyclohexyl isocyanide (0.4 g, 3.68 mmol) in 2 ml of THF and 3 ml of benzene.

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Nitrogen-15 Chemical Shifts in Cobalt(III)–Pentaammine Complexes

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Among diamagnetic transition metal complexes, cobalt(III) complexes have some unique features in their nuclear magnetic resonance (nmr) spectra. For example, the ^{59}Co chemical shifts are unusually large.[2–4] The ^{14}N shifts in the ligands are also quite appreciable.[5] In cobalt(III)–pentaammine complexes, $Co(NH_3)_5X^{n+}$, the trans amine protons have a chemical shift different from that of the cis amine protons,[6,7] a phenomenon which is not observed in rhodium(III) and iridium(III) pentaammine complexes.[8] The origin of the chemical shifts of ^{59}Co and the ligand nuclei is the presence of low-lying paramagnetic states in the cobalt(III) complexes.[2–5,8]

In view of the difference in the trans and cis amine protons in cobalt(III)–pentaammine complexes, one may expect that the trans and cis nitrogens would also have different chemical shifts. However, the ^{14}N resonance absorption is broad and the different absorption signals would be difficult to resolve. Cobalt(III) complexes with $^{15}NH_3$ as ligand can be prepared and the proton nmr shows clearly resolved ^{15}N coupling.[9] By irradiating at the ^{15}N resonance frequency and observing the proton spectrum, namely, performing $\{^{15}N\}$–^{1}H double resonance, it is possible to determine the ^{15}N chemical shift.

The proton nmr spectra of $[Co(^{15}NH_3)_5X]^{n+}$ complexes showed well-resolved sharp lines. The ^{15}N–H coupling constants are 70 ± 1 Hz for both cis and trans groups and do not vary with the trans ligand X. The ^{59}Co–H coupling did not show up in the spectra because of rapid ^{59}Co quadrupole relaxation. A typical spectrum is shown in Figure 1. In contrast to the pentaammine complexes, $[Co(^{15}NH_3)_6]^{3+}$ showed two broad proton peaks, because the quadrupole relaxation is slow in this highly symmetrical species and the ^{59}Co–H coupling is not completely averaged out. Consequently, the ^{15}N resonance frequencies obtained from the $\{^{15}N\}$–^{1}H double-resonance experiments were more accurate and reproducible for the pentaammine complexes than for the hexaammine complex. In the latter case, the result was taken from the average of a large number of data.

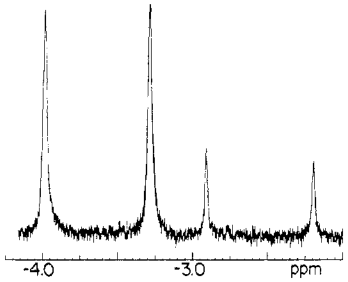

Figure 1.—Proton nmr spectrum of $[Co(^{15}NH_3)_5(H_2O)](ClO_4)_3$ in 20% H_2SO_4–D_2O solution at 100 MHz and 30°.

The ^{15}N and ^{1}H chemical shifts of the $[Co(^{15}NH_3)_5$-$X]^{n+}$ complexes with respect to $[Co(^{15}NH_3)_6]^{3+}$ are listed in Table I. The proton shifts are slightly different from those listed in ref 8 because of the difference in the solvent composition.

TABLE I

CHEMICAL SHIFTS (PPM) OF COBALT(III)–PENTAAMMINE COMPLEXES FROM HEXAAMMINECOBALT(III) IN SOLUTIONS OF 20% H_2SO_4 IN D_2O

	^{15}N		^{1}H	
	Cis	Trans	Cis	Trans
$[Co(^{15}NH_3)_5H_2O]^{3+}$	3.4	30.9	0.40	−0.69
$[Co(^{15}NH_3)_5NO_3]^{2+}$	2.8	30.4	0.41	−0.79
$[Co(^{15}NH_3)_5HSO_4]^{2+}$	3.3	31.0	0.32	−0.77
$[Co(^{15}NH_3)_5Cl]^{2+}$	3.2	18.0	0.01	−0.60
$[Co(^{15}NH_3)_5Br]^{2+}$	5.2	10.6	−0.06	−0.64

The data in Table I show that the ^{15}N chemical shifts for both the cis and the trans nitrogens in the pentaammine complexes are both upfield (lower in frequency) from the hexaammine complex, in contrast to the proton

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chemical shifts. In an earlier paper[10] it was argued that the proton chemical shifts in Co(III) complexes can be explained by the magnetic anisotropy of the Co–N and Co–X bonds. Now we examine this postulation quantitatively by considering both the ^{15}N and proton chemical shifts.

The point-dipole approximation for the chemical shift due to magnetic anisotropy leads to the equation[11,12]

$$\Delta\sigma = \frac{1}{3N_0R^3}(3\cos^2\theta - 1)\Delta\chi \qquad (1)$$

where N_0 is Avogadro's number, R is the distance between the center of the anisotropy and the nucleus concerned, θ is the angle between R and the symmetry axis, and $\Delta\chi$ is the anisotropy in magnetic susceptibility.

As an example, a calculation on the trans proton chemical shift in $Co(NH_3)_5Cl^{2+}$ was made based upon the assumption that the changes in ^{15}N chemical shifts (Table I) are solely due to magnetic anisotropy. By using suitable bond lengths[13] it was found that $\Delta\chi = 620 \times 10^{-6}$ cgsu, and the center of anisotropy situates at 0.74 Å away from the chlorine nucleus on the Co–Cl bond. If it is assumed that the Co–N–H bond angle is 110° and the N–H distance is 1.01 Å, the calculated trans proton shift is +11.8 ppm. This has both the wrong sign and magnitude compared with the experimental data in Table I. Even if an allowance on the effect of reduced positive charge (from $Co(NH_3)_6^{3+}$ to $Co(NH_3)_5Cl^{2+}$) on the ^{15}N chemical shift is made, the calculated trans proton shift does not come close to the experimental value. Therefore, the point-dipole approximation of magnetic anisotropy is too much a simplification to account for the chemical shifts in Co(III) complexes. The cis protons change their R and θ during rotation; the calculation is less straightforward and was not performed.

The shielding constant for the ligands in cobalt(III) complexes with D_{4h} or C_{4v} symmetry, as in any other compounds, can be expressed as the sum of a diamagnetic term and a paramagnetic term.[14] The diamagnetic part depends upon ground-state wave functions only. The two components in the paramagnetic term involve excited state wave functions $d_{x^2-y^2}$ and d_{z^2} for the pentaammine complexes and are inversely proportional to the ligand field splittings $\Delta E_1(^1A_1 \rightarrow {}^1E)$ and $\Delta E_2(^1A_1 \rightarrow {}^1A_2)$, respectively. The values of ΔE_1 and ΔE_2 can be obtained from visible–ultraviolet spectra and are listed in Table II for the complexes studied.

TABLE II
LIGAND FIELD SPLITTINGS OF
COBALT(III)–PENTAAMMINE COMPLEXES (CM^{-1})

	ΔE_2	ΔE_1
$[Co(NH_3)_5H_2O]^{3+}$	29,000	20,200
$[Co(NH_3)_5NO_3]^{2+}$	29,000	19,900
$[Co(NH_3)_5HSO_4]^{2+}$	29,000	19,100
$[Co(NH_3)_5Cl]^{2+}$	27,400	18,900
$[Co(NH_3)_5Br]^{2+}$	~20,800	18,200

The data in Tables I and II show that the ^{15}N shifts for the trans amine and ΔE_2 both change very little when the sixth ligand in the pentaammine complex is coordinated to cobalt *via* an oxygen. However, $1/\Delta E_2$ and the trans ^{15}N shifts for the oxygen, chloride, and bromide complexes change in opposite directions. Therefore, in contrast to the ^{59}Co chemical shifts,[1-3] there is no simple way to correlate the ligand field splittings to the ^{15}N shifts. Because of a lack of knowledge for the wave functions in different complexes, we have not attempted to perform quantitative calculations. It would be of interest to see whether the ^{15}N shifts in cobalt(III)–tetraammine complexes are additive, as for the proton shifts.

Experimental Section

$[Co(^{15}NH_3)_5Cl](ClO_4)_2$ was prepared by a modification of the standard method[15] for $[Co(NH_3)_5Cl]Cl_2$, using $^{15}NH_4Cl$ and NaOH to generate aqueous $^{15}NH_3$. Optimum yields from $^{15}NH_4Cl$ were obtained with about 80% excesses of the ^{15}N reagents, though the yield from cobaltous chloride was thereby reduced from over 90 to 71%.

The nitrato, aquo, and bromo complexes were obtained from ligand exchange of the chloro complex. The sulfato complex was obtained when the aquo complex was dissolved in 20% sulfuric acid and let stand for a few hours, but the product was not isolated.

Measurement of ^{15}N Chemical Shifts.—Solutions of the four cobalt–pentaammine compounds and the nitrogen-15–hexaammine complex in 20% H_2SO_4–D_2O were prepared just prior to use in each case. Measurements of ^{15}N chemical shifts using an internal H_2SO_4 lock signal were made by the "spin-tickling" technique, using a Schomandl frequency synthesizer to generate the ^{15}N resonant frequencies and a Varian HA-100 nmr spectrometer to observe the proton spectra. In most cases, only the two deeper minima (of four expected) were measured, since reproducible frequency values for the other two were difficult to obtain. Chemical shifts for cis and trans amino group nitrogens were then calculated using a resonant frequency value halfway between the corresponding frequencies of the minima.

Absorption spectra were taken with a Perkin-Elmer 202 spectrophotometer.

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