Correlation of ^{13}C, ^{15}N and ^{59}Co Nuclear Magnetic Resonance Chemical Shifts with Ligand-field Parameters for Pentacyanocobaltate(III) Complexes

Takashi Fujihara and Sumio Kaizaki *

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

The ^{13}C, ^{15}N and ^{59}Co NMR spectra of 15 pentacyanocobaltate(III) complexes revealed a common tendency for the chemical shift to vary with the identity of the sixth co-ordinated ligand. These chemical shifts were found to correlate with ligand-field parameters, including the nephelauxetic ratio, among them the reduction parameter having a significant effect.

Since the nuclear shielding in ^{59}Co was reported[1] as being closely related to the temperature-independent paramagnetism (t.i.p.) of cobalt(III) ions, there have been a number of investigations concerning the correlation of ^{59}Co NMR chemical shifts with ligand-field parameters in various cobalt(III) complexes.[2–4] Among them, a series of pentaammine complexes was considered to be suitable for such ^{59}Co NMR spectroscopic studies because the absorption spectra of complexes of general formula $[CoX(NH_3)_5]^{n+}$ have been examined in detail in terms of ligand-field theory. Recently, a monotonic linear relation was obtained between the ^{59}Co NMR chemical shifts and the ligand-field parameters in the pentaamminecobaltate(III) complexes by introducing the nephelauxetic ratio β into the Ramsey equation.[4] Soon after, the linear relation between the ^{1}H and ^{14}N NMR chemical shifts of the ammine ligands of these complexes and the ligand-field parameters was found to be improved by including the anisotropic nephelauxetic effect[5] into the magnetic anisotropy of the t.i.p. term of Nakashima's formulation,[6] which had included only the long-range magnetic terms in the screening constant of the central cobalt(III) ion. The small but often unobservable interval between the split components of the first ligand-field transition ($^1T_1 \longleftarrow {}^1A_1$) may make it disadvantageous to estimate the t.i.p. contribution from each tetragonal split component in the pentaammine complexes. However, a series of pentacyano complexes is expected to provide more rigorous information as such split components can be more easily observed, especially at longer wavelengths where the degenerate component is located.[7] Furthermore, it will be invaluable to compare the contribution of the nephelauxetic effect to the chemical shifts through the t.i.p. between the ammine and cyano complexes. Only scattered data, however, using ^{13}C and ^{15}N NMR spectroscopy[8] and a brief discussion on ^{59}Co NMR shifts for a limited number of pentacyanocobaltate(III) complexes,[9,10] have been reported with no systematic study on ^{13}C, ^{15}N and ^{59}Co NMR chemical shifts for these complexes.

This paper deals with the correlations of ^{13}C, ^{15}N and ^{59}Co NMR chemical shifts for 15 pentacyanocobaltate(III) complexes, $[CoX(CN)_5]^{n-}$, with the ligand-field parameters in a modified manner to those for the pentaammine complexes.

Results and Discussion

Ligand-field Absorption Spectra.—Absorption data for the pentacyanocobaltate(III) complexes are listed in Table 1. Only the lower energy degenerate ^1E_a component is observed, as the higher energy non-degenerate component $^1A_1$ overlaps with the intense charge-transfer absorption bands in the short-wavelength region. The deviation of the observed values for the ^1E_a component [$\sigma_{obs}(^1E_a)$] from the values predicted by Yamatera's rule[11] are eliminated by introducing the empirical reduction parameter α. This has been proposed by Shimura[12] to improve the prediction by Yamatera's rule of the first ligand-field absorption band components of the low-spin d^6 metal complexes and was later elucidated by Kaizaki[13] on the basis of theoretical and empirical approaches in terms of the angular overlap model parameterization. As shown in Table 1, by adopting the reduction parameter, the predicted values of the ^1E_a component agree with the observed ones. On the other hand, the predicted values by Yamatera's rule for the $^1A_2$ component [$d(CN^-)$] correspond to the first absorption maxima of hexacyanocobaltate(III), $[Co(CN)_6]^{3-}$. Since the position of the non-degenerate component is also found to shift by the same amount as the reduction parameter value for the degenerate component, $\sigma_{calc}(^1A_2) = \alpha d(CN^-)$ as used in Table 1 and in the following discussion.

Table 1 Observed and calculated first d–d band positions (10^3 cm^{-1}) for the $[CoX(CN)_5]^{n-}$ complexes; py = pyridine

X	$\sigma_{obs}(^1E_a)$	$\sigma_{calc}(^1E_a)$[a]	α[b]	$\sigma_{calc}(^1A_2)$
CN^-	32.09	32.01	1.00	32.01
Cl^-	25.63	25.57	0.94	30.16
Br^-	25.20	25.11	0.93	29.84
I^-	24.3 (sh)	24.22	0.92	29.52
NH_3	28.82	28.28	0.955	30.65
H_2O	26.32	26.51	0.94	30.16
NO_2^-	29.6 (sh)	29.57	0.955	30.65
N_3^-	26.30	26.31	0.955	30.65
SO_3^{2-}	29.87	29.62	0.955	30.65
OH^-	26.67	26.83	0.94	30.16
py	28.5 (sh)	28.86	0.955	30.65
CH_3^-	31.45	—	1.00	32.01
$[(CN)Co(NH_3)_5]^{2+}$	31.95	—	1.00	32.01
$[(NC)Co(NH_3)_5]^{2+}$	29.15	—	0.955[c]	30.65

[a] Calculated using equation (1) or (2) in ref. 12. [b] $\sigma_{calc}(^1A_2) = \alpha d(CN^-)$. Values for α and $d(CN^-)$ are taken from ref. 12. [c] Assuming the nitrogen to be ligating.

General Characteristics of NMR Spectra.—Cobalt-59 NMR chemical shifts and linewidths are shown in Table 2. The ^{59}Co NMR spectra were remeasured for seven of the complexes

(X = CN, Br, I, NH_3, H_2O, NO_2 or OH) whose NMR data have already been reported, and those for the remaining complexes were newly obtained. Although most of the data are close to the literature values, the complex $[Co(NO_2)(CN)_5]^{3-}$ gives different chemical shifts and linewidths from those of Au-Yeung and Eaton,[10a] but similar ones to Yamasaki *et al.*[9a] In view of the ^{59}Co NMR chemical shifts for the nitroammine complexes,[3] our value seems to be appropriate. As is usually observed for other cobalt(III) complexes, a variation in the ligand X results in differing ^{59}Co NMR chemical shifts.

Table 3 shows the variation of the natural abundant ^{13}C and ^{15}N NMR chemical shifts by changing the ligand X. The complexes $[CoX(CN)_5]^{3-}$ (X = CN, CH_3 or I) exhibit an octet in their ^{13}C NMR spectra due to ^{59}Co–^{13}C coupling (J = 126.4, 123.2 and 126.7 Hz, respectively) (Fig. 1) in accordance with the value (126.0 Hz) obtained from the ^{59}Co NMR spectrum for ^{13}C-enriched $[Co(CN)_6]^{3-}$.[14] The ^{15}N NMR spectra of these complexes are also similar, the equivalent nitrogens giving rise to only one signal. For the remaining complexes in Table 3, two ^{13}C and two ^{15}N NMR signals corresponding to inequivalent cyanide ligands are observed with an intensity ratio *ca.* 4 : 1 (Fig. 2). In view of their intensities, the NMR signals are assigned as follows. The stronger signals, *ca.* δ 139–145 and δ −86 to −91 for the ^{13}C and ^{15}N NMR spectra, respectively, are due to the four equivalent cyanide ligands which are *cis* to X, the weaker signals, *ca.* δ 126–141 and δ −78 to −89, respectively, are assigned to the cyanide ligand which is *trans* to X. The range in chemical shift is thus greater when the nuclei are at the *trans* position (δ 14 and 11) than at the

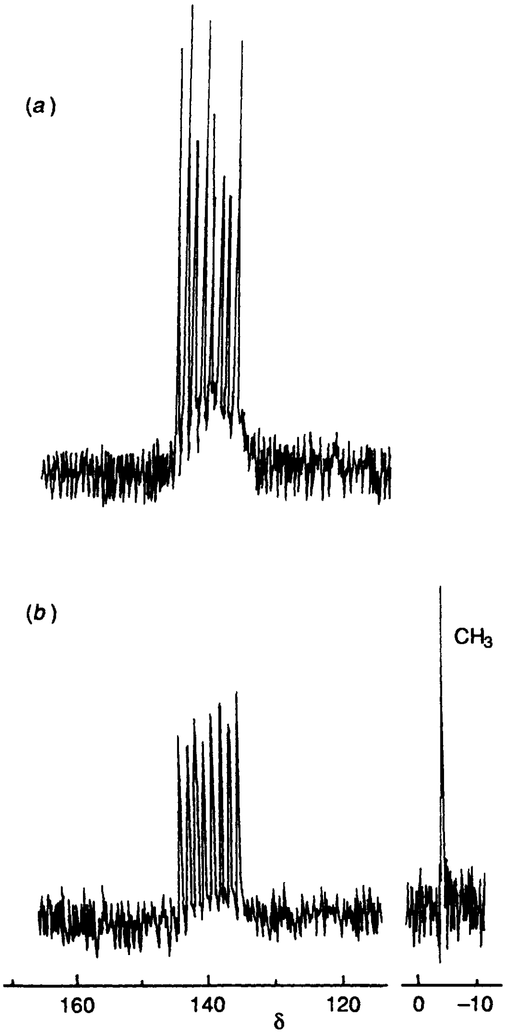

Fig. 1 Carbon-13 NMR spectra of $[CoI(CN)_5]^{3-}$ (*a*) and $[Co(CH_3)(CN)_5]^{3-}$ (*b*)

Table 2 Cobalt-59 NMR chemical shifts and linewidths for the $[CoX(CN)_5]^{n-}$ complexes

X	δ	$\nu_{\frac{1}{2}}$/Hz
CN^-	0	110.2
Cl^-	1 470	12 130
Br^-	1 300	11 260
I^-	860	9 150
NH_3	1 155	3 560
H_2O	1 840	5 250
NO_2^-	1 364	6 650
N_3^-	1 484	6 650
SO_3^{2-}	601	3 420
OH^-	1 820	6 200
py	1 371	7 937
CH_3^-	−5	385
$[(CN)Co(NH_3)_5]^{2+}$	3	917
	8 129 (CoN_6)	2 349
$[(NC)Co(NH_3)_5]^{2+}$	1 343	7 077
	6 714 (CoN_5C)	8 644
$[(NC)Fe(CN)_5]^{4-}$	1 338	15 560

Table 3 Carbon-13 and ^{15}N NMR chemical shifts and shift differences[a] and ^{13}C NMR linewidths for the cyanide ligands in the $[CoX(CN)_5]^{n-}$ complexes

	^{13}C				^{15}N		
	δ ($\nu_{\frac{1}{2}}$/Hz)				δ		
X	*trans*	*cis*	Δδ	$^1J(^{59}Co–^{13}C)$/Hz	*trans*	*cis*	Δδ
CN^{-} [b]	140.0		0	126.4	−87.6		0
Cl^-	139.1 (50.3)	141.7 (42.7)	−2.6		−83.8	−87.2	3.4
Br^-	139.6 (40.2)	141.9 (37.7)	−2.3		−84.3	−86.4	2.1
I^{-} [b]	139.6		0	126.7	−86.5		0
NH_3	128.2 (159)	139.1 (136)	−10.9		−83.2	−88.5	5.3
H_2O	132.0 (80.7)	144.0 (75.2)	−12.0		−78.3	−90.8	12.5
NO_2^-	128.2 (94.3)	141.1 (62.8)	−12.9		−81.7	−87.8	6.1
N_3^-	127.2 (72.7)	141.6 (86.0)	−14.4		−79.3	−88.1	8.8
SO_3^{2-}	140.7 (176)	144.5 (126)	−3.8		−88.3	−90.0	1.7
py	126.5 (76.3)	142.5 (73.1)	−16.0		−81.4	−87.6	6.2
CH_3^{-} [b]	140.3		0	123.2	−87.5		0
$[(NC)Fe(CN)_5]^{4-}$ [c]	127.1 (30.2), 127.3 (30.5) (*cis*) (Co moiety) 140.1 (35.2), 140.6 (25.1) (*trans*) 173.7, 173.8, 175.6, 177.0 (Fe moiety) 178.3, 178.7 (bridging CN)		−13.2 (av)		−80.8, −86.5, −85.6, −90.0 (br)		—

[a] $\Delta\delta = \delta_{trans} - \delta_{cis}$. [b] Carbon-13 NMR linewidths for these multiplet signals are omitted. [c] Assignments for $\delta(^{15}N)$ are tentative (see text).

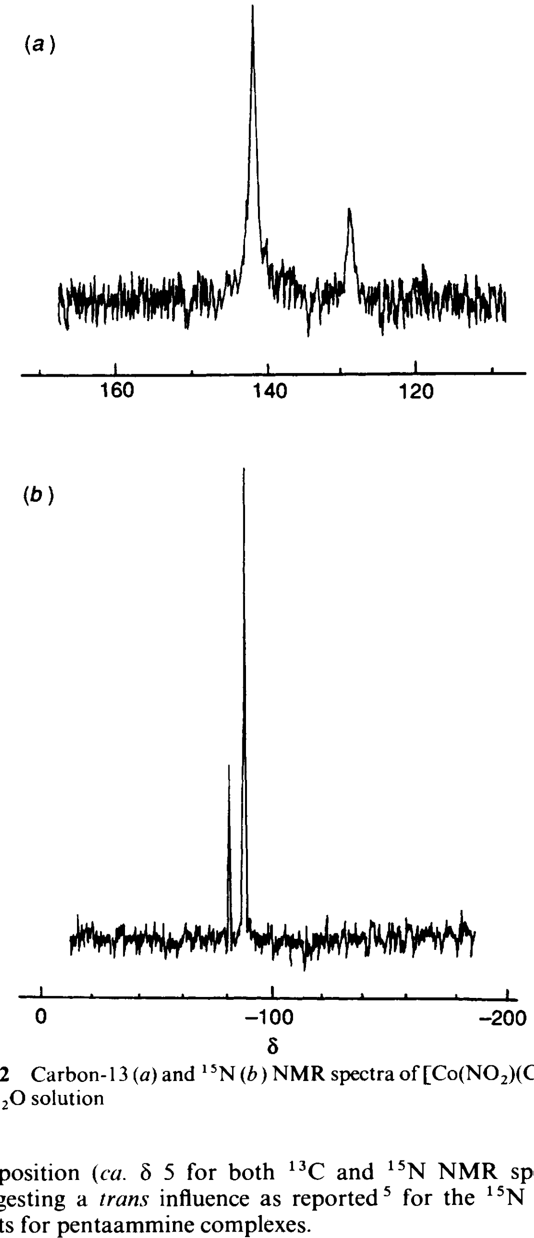

Fig. 2 Carbon-13 (*a*) and ^{15}N (*b*) NMR spectra of $[Co(NO_2)(CN)_5]^{3-}$ in D_2O solution

cis position (*ca.* δ 5 for both ^{13}C and ^{15}N NMR spectra), suggesting a *trans* influence as reported[5] for the ^{15}N NMR shifts for pentaammine complexes.

The ^{59}Co NMR chemical shifts and the ^{13}C and ^{15}N NMR shift differences between the *trans* and *cis* positions of the ligand X ($\Delta\delta = \delta_{trans} - \delta_{cis}$) vary in a similar manner, according to the ligands. This suggests that the three NMR shifts arise from a common origin. It is noted that the ^{13}C and ^{15}N NMR signals of the cyanide ligand at the *cis* position of the ligand X appear at lower and higher fields, respectively, than those at the *trans* positions irrespective of the nature of the ligand X. This reverse tendency for the ^{13}C and ^{15}N NMR shifts lends support to the presence of cyanocobalt(III) π back-bonding as revealed in cyanocobaloximes.[15]

Juranić *et al.*[16] reported that a relationship exists between the linewidths ($\nu_{\frac{1}{2}}$) in the ^{59}Co and ^{15}N NMR spectra for cobalt(III) aminoacidato complexes through the ^{59}Co–^{15}N coupling (J), $\nu_{\frac{1}{2}}(^{15}N) = 21\ J^2/\nu_{\frac{1}{2}}(^{59}Co)$. The log–log plots of the linewidths of the ^{59}Co and ^{13}C NMR signals of the present cyano complexes are found to give a good correlation with a slope of −1.02 and a correlation coefficient of 0.951 (Fig. 3). From the intercept of the least-squared line, the coupling constant $[J(^{59}Co–^{13}C)]$ is estimated to be *ca.* 156 Hz according to the equation $\log J(^{59}Co–^{13}C) = \frac{1}{2}[\log \nu_{\frac{1}{2}}(^{13}C) + 1.02 \log \nu_{\frac{1}{2}}(^{59}Co) - \log 21] = \frac{1}{2}(5.71 - \log 21)$. It should be noted that this value is comparable to the ^{59}Co–^{13}C coupling constant (126.4 Hz) in $[Co(CN)_6]^3$ as mentioned above. The trend in variation of the linewidth with the ligand ($CN^- < NH_3 < N_3^- < I^- < Br^- < Cl^-$) is in accordance with the order of the broadening parameter proposed by Au-Yeung and Eaton[10a] excluding H_2O and OH^- for which the linewidths are sharper for the present complexes than expected.[10a]

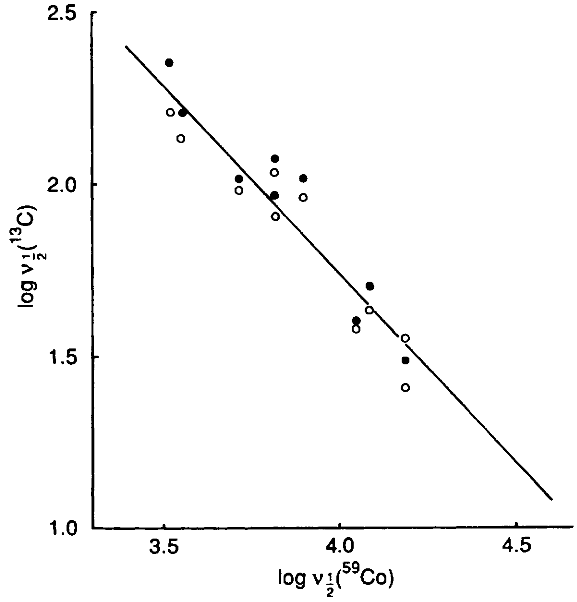

Fig. 3 Correlation between log $\nu_{\frac{1}{2}}(^{13}C)$ and log $\nu_{\frac{1}{2}}(^{59}Co)$ for ^{13}C and ^{59}Co NMR spectra of the $[CoX(CN)_5]^{n-}$ complexes: (●) CN *trans* to X, (○) CN *cis* to X. Line shown is the least-squared fit

Three cyano-bridged dinuclear complexes are examined on the basis of the above results. The complexes $[(CN)_5Co(NC)$-$Co(NH_3)_5]$ and $[(CN)_5Co(CN)Co(NH_3)_5]$ are linkage isomers and their structures have already been determined by X-ray crystal structure analyses.[17] In the absorption spectra, there are two bands corresponding to the first absorption bands for each chromophore. Two ^{59}Co NMR signals due to two different chromophores were also observed. Owing to the low solubilities of these complexes, we could not obtain a sufficient concentration to measure ^{13}C and ^{15}N NMR spectra. For $K_6[(NC)_5Fe(CN)Co(CN)_5]\cdot 6H_2O$, on the other hand, ^{13}C, ^{15}N and ^{59}Co NMR spectra can be observed. This complex gives a more complicated ^{13}C than ^{15}N NMR spectrum. The ^{13}C NMR signal for each carbon is a doublet of almost equal intensity. This is not attributed to coupling between ^{15}N and ^{13}C nuclei owing to their low natural abundance. In the ^{15}N NMR spectrum (Table 3) each signal is not split and the one ^{59}Co NMR signal suggests that there exists only one species. Thus, there is no possibility of the existence of a linkage isomeric pair for the complex $[(NC)_5Fe(NC)Co(CN)_5]^{6-}$ in solution. So far, there seems to be no assignable isomer except two rotational isomers (rotamers) which exist in solution, *i.e.* one staggard and one eclipsed with respect to the two sets of four in-plane Co–CN bonds perpendicular to the Co–NC–Fe axis. In the ^{13}C NMR spectrum signals at δ 127–140 are assigned to the $Co(CN)_5$ moiety by comparison with those of the $[CoX(CN)_5]^{n-}$ complexes. The two highest-field signals at δ 127 and 140 are due to the carbons in the $Co(CN)_5$ moiety which are *cis* and *trans*, respectively, to the $Fe(CN)_5$ moiety. The remaining lower-field signals at δ 173–178 are assigned to the $(NC)_5Fe(CN)$ moiety by comparison with our ^{13}C NMR observation of $[Fe(CN)_6]^{4-}$ (δ 177.2). The lowest field signal at δ 178 may be due to the bridging cyano ligand which, by bridging to the Co^{3+} ion, causes a decrease in the electron density.

NMR chemical shifts and ligand-field parameters. Cobalt-59 NMR. In addition to the recent reformulation of the relation between the ^{59}Co NMR chemical shifts and the optical spec-

Table 4 Ligand-field parameters obtained from ^{59}Co NMR spectra

X	$\{\beta[(CN)_3X]/\sigma_{obs}(^1E_a)\}$/nm [a]	$\{\beta[(CN)_4]/\alpha\sigma_{calc}(^1A_2)\}$/nm	β(X)	*h*(X) [b]
CN^-	131.1	131.1	0.420 [c]	1.76
Cl^-	156.1	139.3	0.340 [d]	2.00
Br^-	148.9	140.8	0.241 [d]	2.30
I^-	140.8	142.3	0.109 [d]	2.70
NH_3	157.9	137.0	0.560 [c]	1.33
H_2O	183.5	139.3	0.670 [c]	1.00
NO_2^-	162.0	137.0	0.660	1.03
N_3^-	165.9	137.0	0.484	1.55
SO_3^{2-}	137.3	137.0	0.380	1.88
OH^-	175.6	139.3	0.612	1.18
py	161.8	137.0	0.580	1.27
CH_3^-	120.8	131.1	0.260	2.24
$[(CN)Co(NH_3)_5]^{2+}$	121.1	131.1	0.288	2.16
$[(NC)Co(NH_3)_5]^{2+}$	161.4	137.0	0.620	1.15
$[(NC)Fe(CN)_5]^{4-}$	161.2	137.0	—	—

[a] $\beta[(CN)_3X] = \frac{1}{4}\{3\beta[(CN)_4] + \beta(X_6)\}$. [b] Nephelauxetic ligand parameter.[18] [c] Ref. 18(*a*). [d] Ref. 18(*b*).

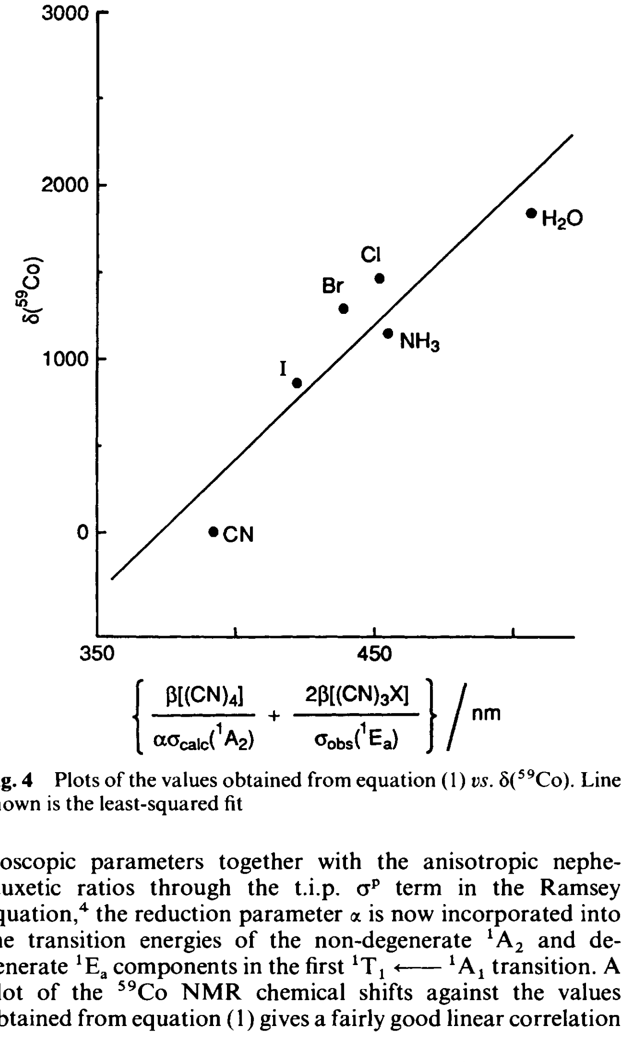

Fig. 4 Plots of the values obtained from equation (1) *vs.* $\delta(^{59}Co)$. Line shown is the least-squared fit

troscopic parameters together with the anisotropic nephelauxetic ratios through the t.i.p. σ^p term in the Ramsey equation,[4] the reduction parameter α is now incorporated into the transition energies of the non-degenerate $^1A_2$ and degenerate ^1E_a components in the first $^1T_1 \longleftarrow {}^1A_1$ transition. A plot of the ^{59}Co NMR chemical shifts against the values obtained from equation (1) gives a fairly good linear correlation

$$\delta \propto \left\{\frac{\beta[(CN)_4]}{\alpha\sigma_{calc}(^1A_2)} + \frac{2\beta[(CN)_3X]}{\sigma_{obs}(^1E_a)}\right\} \qquad (1)$$

(correlation coefficient $r = 0.921$) (Fig. 4), where $\beta[(CN)_4]$ is the nephelauxetic ratio for $[Co(CN)_6]^{3-}$ and $\beta[(CN)_3X]$ is the weighted average for the β values between $[Co(CN)_6]^{3-}$ and $[CoX_6]$, $\frac{1}{4}\{3\beta[(CN)_4] + \beta(X_6)\}$, corresponding to the $^1E_a \longleftarrow {}^1A_1$ transition within the $CoX(CN)_3$ plane. If the reduction parameter is not introduced (*i.e.* $\alpha = 1$), the correlation coefficient is worse ($r = 0.871$). The first and second terms of equation (1) refer to the $^1A_1$ and $^1E_a \longleftarrow {}^1T_1$ transitions primarily depending on the cyano and X ligands, respectively. The transition energy in the first term is also affected by α which, in turn, is dependent on X as in Table 1.

Using equation (1), we can estimate unknown β values from the ^{59}Co NMR chemical shifts and the ligand-field parameters evaluated from the absorption spectra (Table 4). The order of these estimated (italicised ligands) and known[18] β values as positioned in the nephelauxetic series is as follows: $I^- < Br^- < \mathit{CH_3^-} < \mathit{[(CN)Co(NH_3)_5]^{2+}} < Cl^- < \mathit{SO_3^{2-}} < CN^- < \mathit{N_3^-} < NH_3 < \mathit{py} < \mathit{OH^-} < \mathit{[(NC)Co(NH_3)_5]^{2+}} < \mathit{NO_2^-} < H_2O$. This is supported by the good linear relation obtained between the ^{13}C and ^{15}N NMR shifts and the ligand-field parameters employing both estimated and known β values as discussed below. The β value for the N_3^- ligand is close to that estimated by Siebert and Macht.[19]

*Carbon-*13 *and* ^{15}*N NMR.* By incorporating the reduction parameter into equation (6) in ref. 5, a proportional relationship is established [equation (2)] for the ^{13}C and ^{15}N NMR

$$\delta \propto \left\{\frac{\beta[(CN)_4]}{\alpha\sigma_{calc}(^1A_2)} - \frac{\beta[(CN)_3X]}{\sigma_{obs}(^1E_a)}\right\}\frac{(3\cos^2\theta - 1)}{3r_i^3} \qquad (2)$$

chemical shifts for the nuclei at the *cis* and *trans* positions of ligand X (θ = 90 and 180°, respectively). Equation (3) may, therefore, be obtained assuming that the distance from a Co^{III} ion to each ^{13}C or ^{15}N nucleus is virtually invariant for both the *cis* and *trans* positions. Plots of the shift difference $\Delta\delta$ ($\delta_{trans} - \delta_{cis}$) against the value obtained from equation (3) are shown in

$$\Delta\delta \propto \left\{\frac{\beta[(CN)_4]}{\alpha\sigma_{calc}(^1A_2)} - \frac{\beta[(CN)_3X]}{\sigma_{obs}(^1E_a)}\right\} \qquad (3)$$

Fig. 5. For the complexes with unknown β values, estimated values from the ^{59}Co NMR chemical shifts as mentioned above were used. The linear correlation is good with $r = 0.849$ and 0.972 for $\Delta\delta(^{13}C)$ and $\Delta\delta(^{15}N)$, respectively. The ^{13}C and ^{15}N NMR spectral behaviour of $[CoI(CN)_5]^{3-}$ which exhibits similar patterns to those of $[Co(CN)_6]^{3-}$ can be reproduced (Fig. 5), if the reduction parameter is included in equation (3). Its omission ($\alpha = 1$) leads to a shift difference for both the ^{13}C and ^{15}N NMR signals which is estimated to be large (*ca.* 5 ppm) enough to be detectable. Therefore, the involvement of the reduction parameter has a significant implication in the elucidating of NMR results. The ^{13}C NMR shifts give a more scattered correlation with the values obtained from equation (3) than the ^{15}N NMR ones. This suggests that the Co–C distances

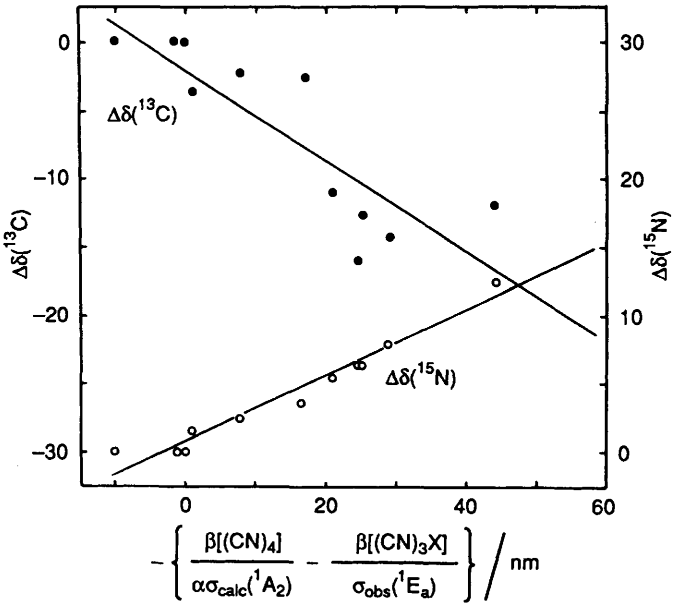

Fig. 5 Plots of the values obtained from equation (3) *vs.* the NMR shift differences $\Delta\delta(^{13}C)$ (●) and $\Delta\delta(^{15}N)$ (○). Lines shown are the least-squared fits

vary at the *cis* and *trans* positions with a change in the ligand X in contrast to the Co–N distances which are almost invariant owing to the fact that the Co–C bond stretch is compensated by the C–N bond contraction and *vice versa*.

Conclusions

The present mutual linear relation between the ^{59}Co, ^{13}C and ^{15}N NMR chemical shifts and the ligand-field parameters are improved by incorporating Shimura's reduction parameter into the t.i.p. term and further make it possible to obtain the nephelauxetic ratio β which is not available from the electronic spectra.

Experimental

Preparations of the Complexes.—The complexes $K_3[CoX(CN)_5]$ (X = CN,[20] Cl,[21] I,[22] Br,[22] NO_2[7] or CH_3[23]), $K_3[Co(N_3)(CN)_5]\cdot 2H_2O$,[7] $K_4[Co(SO_3)(CN)_5]$,[7] $[Co(H_2O)(CN)_5]^{2-}$,[4] $[Co(OH)(CN)_5]^{3-}$,[24] $K_2[CoX(CN)_5]$ (X = py[24] or NH_3[25]), $[(NC)_5Co(CN)Co(NH_3)_5]$,[26] $[(NC)_5Co(NC)Co(NH_3)_5]$[27] and $K_6[(NC)_5Co(CN)Fe(CN)_5]\cdot 6H_2O$ (synthesized by a modified method of ref. 28) were prepared using the literature methods and identified by elemental analyses and UV/VIS absorption spectra.

Measurements.—Absorption spectra were measured by a Hitachi 330 spectrophotometer in aqueous solutions at room temperature. Cobalt-59 NMR and natural abundant ^{15}N, ^{13}C NMR spectra were measured using a JEOL JNM-GSX-400 FT NMR spectrometer at 25 °C. The concentrations of the samples for the ^{59}Co and ^{15}N, ^{13}C NMR spectra were 0.02 and *ca.* 1 mol dm^{-3} in D_2O solutions, respectively. The external standards used were $K_3[Co(CN)_6]$ $[\delta(^{59}Co) = 0]$, $Na^{15}NO_3$ $[\delta(^{15}N) = 0.0]$ and dioxane $[\delta(^{13}C) = 67.4]$, with the downfield shifts defined as positive.

References

1 W. G. Proctor and F. C. Yu, *Phys. Rev.*, 1951, **81**, 20.
2 J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 1957, **53**, 601; R. Freeman, G. P. Murray and R. E. Richards, *Proc. R. Soc. London, Ser. A*, 1957, **242**, 455.
3 R. G. Kidd and R. J. Goodfellow, *NMR and the Periodic Table*, eds. R. K. Harris and B. E. Mann, Academic Press, New York, 1978, ch. 8, pp. 225–244; N. Juranić, *Coord. Chem. Rev.*, 1989, **96**, 253 and refs therein.
4 R. Bramley, M. Brorson, A. M. Sargeson and C. E. Schäffer, *J. Am. Chem. Soc.*, 1985, **107**, 2780.
5 R. Bramley, M. Brorson, A. M. Sargeson and C. E. Schäffer, *Inorg. Chem.*, 1987, **26**, 314.
6 Y. Nakashima, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 766; Y. Nakashima, U. Sakaguchi and H. Yoneda, *Chem. Lett.*, 1974, 503; Y. Nakashima, M. Muto, I. Takagi and K. Kawano, *Chem. Lett.*, 1975, 1075; Y. Nakashima, M. Muto, K. Kawano, Y. Kyogoku and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2455.
7 J. Fujita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 1281.
8 M. Shporer, G. Ron, A. Loewenstein and G. Navon, *Inorg. Chem.*, 1965, **4**, 358; B. R. McGarvey and J. Pearlman, *J. Magn. Reson.*, 1968, **1**, 178; B. M. Fung and S. C. Wei, *J. Magn. Reson.*, 1970, **3**, 18; R. Bramley, B. N. Figgis and R. S. Nyholm, *J. Chem. Soc. A*, 1967, 861.
9 (*a*) A. Yamasaki, F. Yajima and S. Fujiwara, *Inorg. Chim. Acta*, 1968, **2**, 39; (*b*) N. A. Matwiyoff and W. E. Wageman, *Inorg. Chim. Acta*, 1970, **4**, 460.
10 (*a*) S. C. F. Au-Yeung and D. R. Eaton, *Can. J. Chem.*, 1983, **61**, 2431; (*b*) S. C. F. Au-Yeung and D. R. Eaton, *J. Magn. Reson.*, 1987, **52**, 351.
11 H. Yamatera, *Bull. Chem. Soc. Jpn.*, 1958, **31**, 95.
12 Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 693.
13 S. Kaizaki, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3198.
14 P. C. Lauterbur, *J. Chem. Phys.*, 1965, **42**, 799; A. Loewenstein and M. Shporer, *Mol. Phys.*, 1965, **9**, 289.
15 K. L. Brown and S. Satyanarayana, *Inorg. Chem.*, 1992, **31**, 1366.
16 N. Juranić, R. L. Richter, M. B. Ćelap, M. J. Malinar and P. N. Radivojša, *Inorg. Chim. Acta*, 1982, **62**, 131.
17 B. Wang, W. P. Schaefer and R. E. Marsh, *Inorg. Chem.*, 1971, **10**, 1492; F. R. Fronczek and W. P. Schaefer, *Inorg. Chem.*, 1974, **13**, 727.
18 C. K. Jørgensen, *Oxidation Numbers and Oxidation States*, Springer, Berlin, Heidelberg, New York, 1969, ch. 5, (*a*) p. 100; (*b*) p. 106.
19 H. Siebert and R. Macht, *Z. Anorg. Allg. Chem.*, 1982, **489**, 77.
20 J. H. Bigelow, *Inorg. Synth.*, 1946, **2**, 225.
21 R. Tsuchida, H. Yoneda and S. Kida, *Mukibushitsu Seihou*, Nikkan Kogyo Shinbunsha, Tokyo, 1962, p. 319.
22 A. W. Adamson, *J. Am. Chem. Soc.*, 1956, **78**, 4260.
23 J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, 1964, **86**, 2311.
24 R. Barca, J. Ellis, M. Tsao and W. K. Wilmarth, *Inorg. Chem.*, 1967, **6**, 243.
25 P. B. Chock, R. B. K. Dewar, J. Halpern and L. Wang, *J. Am. Chem. Soc.*, 1971, **91**, 82.
26 R. A. de Castelló, C. P. Mac-Coll and A. Haim, *Inorg. Chem.*, 1971, **10**, 203.
27 R. A. de Castelló, C. P. Mac-Coll, N. B. Egen and A. Haim, *Inorg. Chem.*, 1969, **8**, 699.
28 A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, 1961, **83**, 509.

Received 24*th July* 1992; *Paper* 2/03981H