Diamagnetic Behaviour of High-resolution Nitrogen-14 Nuclear Magnetic Resonance Spectra for Co-ordinated Nitrogens in Paramagnetic Chromium(III) Diamine Complexes

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Diamagnetic behaviour in the chemical shift and linewidth of high-resolution nitrogen-14 NMR spectra for paramagnetic chromium(III) diamine complexes was investigated in comparison with that for the corresponding diamine dihydrochlorides and the diamagnetic cobalt(III) complexes. The NMR signals can be assigned to each inequivalent nitrogen ligating atom of unsymmetric diamines in the chromium(III) complexes. The ^{14}N NMR spectra are affected by the diamine chelate ring conformations of the tris(diamine) complexes, but hardly sensitive to the ligand replacement in *trans*- and *cis*-$[CrX_2(diamine)_2]$ type complexes.

Although chromium(III) complexes with organic ligands such as amino acids have attracted much attention as models of the glucose tolerance factor,[1] their structural characterization has been hampered by the inability to employ NMR spectroscopy owing to their paramagnetic properties. Recently, the ^2H NMR spectra of chromium(III) complexes with various kinds of deuteriated ligands have been found to be useful in the study of stereochemistry and electronic properties.[2] Nevertheless, such NMR study often suffers from the tedious and expensive deuteriation of the ligands. Nitrogen-14 NMR spectroscopy of chromium(III) complexes is expected to overcome this disadvantage and may afford more straightforward and valuable information on their co-ordination environment by extending the pioneering work of McGarvey and Pearlman[3] on some chromium(III) amine complexes in such a way as to improve the chemical shift accuracy and the ability to resolve the different ^{14}N NMR shifts. However, so far there has been no systematic investigation.

In this paper, we report ^{14}N NMR spectra for several chromium(III) diamine complexes and examine their chemical shifts and linewidths to obtain information on stereochemistry and/or electronic structure in comparison with those of related diamagnetic compounds.

Experimental

Measurements.—The ^{14}N NMR spectra were recorded at 36.13 MHz on a JEOL GX-500 FT spectrometer at 300 K. The data were collected on aqueous solutions ranging in concentration from 0.2 to 1 mol dm^{-3} of the complexes in 10 mm tubes under the following conditions; pulse width 15 μs; pulse repetition time 0.3 s; spectral width 50 000 Hz; scanning time 30–60 min; 16 K data points. The external standard of 1 mol dm^{-3} $Na^{14}NO_3$ in deuterium oxide solution was assigned a chemical shift of δ 0.0. Note that downfield shifts are defined as positive.

Preparation of the Complexes.—All the diamines used were commercially available and the corresponding diamine dihydrochlorides were obtained from aqueous solutions by neutralizing the diamines with 2 mol dm^{-3} HCl. They were identified by elemental analysis. Chromium(III) and cobalt(III) complexes were synthesised by the literature methods and identified by elemental analysis and UV/VIS absorption spectra: $[Cr(NH_3)_6]Cl_3\cdot H_2O$,[4] $[Co(NH_3)_6]Cl_3$,[5] $[Cr(en)_3]Cl_3\cdot 3H_2O$ (en = ethane-1,2-diamine),[6] $[Co(en)_3]Cl_3\cdot 3H_2O$,[7] $[Cr(tn)_3]Cl_3\cdot 4H_2O$ (tn = propane-1,3-diamine),[8] $[Co(tn)_3]Cl_3$,[9] Δ-*lel*$_3$- and Λ-*ob*$_3$-$[Cr\{(R)pn\}_3]Cl_3\cdot 1.5H_2O$ (pn = propane-1,2-diamine),[10] Δ-*lel*$_3$-$[Cr\{(R,R)chxn\}_3]Cl_3\cdot 1.5H_2O$ (chxn = *trans*-cyclohexane-1,2-diamine),[10] Δ-*lel*$_3$-$[Co\{(R,R)chxn\}_3]Cl_3\cdot 1.5H_2O$,[11] Δ-*lel*$_3$-$[Co\{(R)pn\}_3]Cl_3$,[12] $[Cr(diamine)_2(H_2O)_4]^{3+}$ [13] [diamine = en, pn or isobutane-1,2-diamine (ibn)], *cis*-$[CrCl_2(en)_2]Cl\cdot H_2O$,[14] *cis*-$[CrF_2(en)_2]I$,[15] *cis*-$[Cr(CN)_2(en)_2]Cl\cdot H_2O$,[16] *cis*-$[Cr(NCS)_2(en)_2]HSO_3\cdot 0.5H_2O$,[17] *trans*-$[CrF_2(diamine)_2]ClO_4$[18] [diamine = en, pn, ibn, *N*-methylethane-1,2-diamine (men) or *N*,*N*-dimethylethane-1,2-diamine(dmen)], *trans*-$[CrCl_2(en)_2]Cl\cdot H_2O$,[19] *trans*-$[CrBr_2(en)_2]Br\cdot H_2O$,[19] *trans*-$[Cr(NCS)_2(en)_2]Cl\cdot H_2O$,[20] *trans*-$[CrF_2(en)_2(H_2O)]Cl$,[21] *trans*-$[Cr(en)_2(H_2O)_2]Br_3$,[22] *cis*-$[Co(en)_2(H_2O)_2]Br_3$,[23] $[Cr(nta)(H_2O)_2]$ (nta = nitrilotriacetate)[24] and $[Co_2(OH)_2(en)_4]Cl_4\cdot 5H_2O$.[25] The complex *trans*-$[Cr(OH)_2(en)_2]^+$ was prepared by adjusting an aqueous solution of the diaqua complex to pH 10 with sodium hydroxide.[22] The complex *trans*-$[CrCl(F)(en)_2]Cl$ was prepared from the perchlorate[26] in order to obtain sufficient concentration for NMR measurement. The dinuclear complexes $[(nta)Cr(OH)_2M(en)_2]Cl\cdot nH_2O$ (n = 3.5 and 2.5 for M = Cr and Co, respectively) were synthesised by the literature method.[27]

Results and Discussion

General Features of ^{14}N *NMR Spectra.*—As shown in Figs. 1 and 2 and Tables 1–3, the remeasurement of the ^{14}N NMR spectra of several diamine chromium(III) complexes revealed that the chemical shifts and linewidths tend to behave similarly to those previously observed,[3] but that the spectral quality is sufficiently improved to allow a more systematic examination of stereochemistry or electronic structure. The chemical shifts of the chromium(III) complexes are similar to each other and to those of the corresponding diamine dihydrochlorides, but to lower field than those of the corresponding free diamines and their cobalt(III) complexes. The linewidths are narrower than those (600–900 Hz) of the free diamines and the corresponding cobalt(III) complexes, but a few times as broad as those of the dihydrochlorides. The sharp linewidths of the diamine dihydrochlorides result from the slow quadrupolar relaxation of the ^{14}N nucleus, because of the decreased electric field gradient

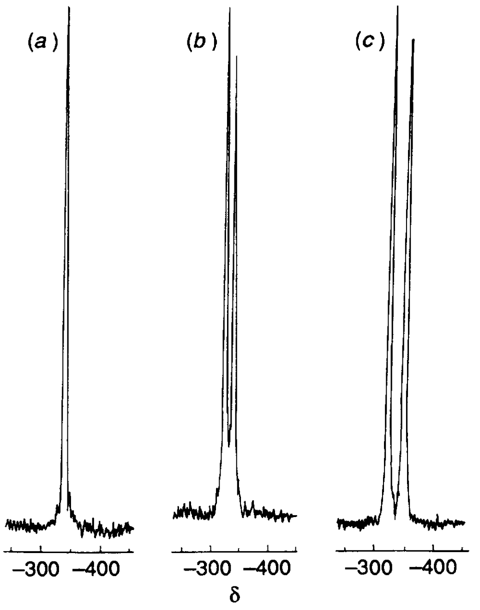

Fig. 1 The ^{14}N NMR spectra for $[Cr(diamine)(H_2O)_4]^{3+}$ complexes in water. Diamine = en (*a*), (*R*)pn (*b*) and ibn (*c*)

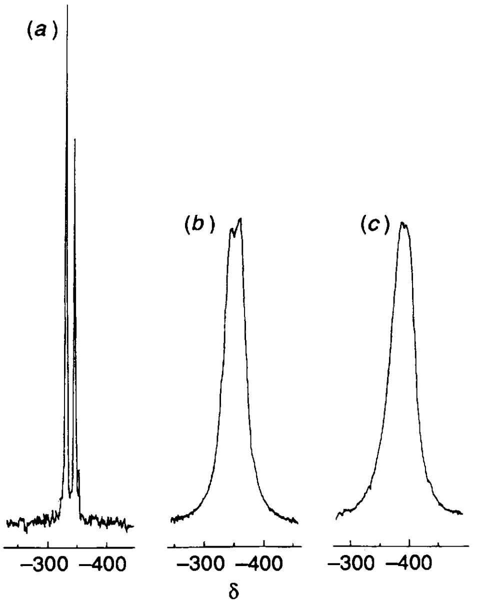

Fig. 2 The ^{14}N NMR spectra for (*R*)pn complexes in aqueous solution: (*a*) Δ-*lel*$_3$-$[Cr\{(R)pn\}_3]^{3+}$; (*b*) (*R*)pn; (*c*) Δ-*lel*$_3$- $[Co\{(R)pn\}_3]^{3+}$

around it.[28] On the other hand, the broadening of the linewidths of the cobalt(III) complexes may be due to the spin–spin coupling $[^1J(^{59}Co–^{14}N)]$ between the ^{14}N (99.7%, $I = 1$) and ^{59}Co nuclei (100%, $I = \frac{7}{2}$).[29]

The ^{14}N NMR spectra of the nitrogen ligators are found to be hardly affected by the unpaired electrons in the chromium(III) complexes, as observed by McGarvey and Pearlman,[3] although the resonances are anticipated to exhibit large shifts and line broadening upon the fast paramagnetic relaxation due to the unpaired electrons. No temperature dependence of the ^{14}N NMR shifts was observed for *trans*-$[CrF_2(en)_2]^+$. This fact besides the chemical shift and linewidths substantiates its diamagnetic behaviour. In this case there is no contribution from the pseudo-contact shift due to the negligibly small magnetic anisotropy of Cr^{3+} ($^4A_2$ ground state), nor from the contact shift due to a small density of the unpaired electron spin on the nitrogen nucleus; there is no nitrogen s-orbital character in the t_{2g} orbitals as explained by McGarvey and Pearlman.[3]

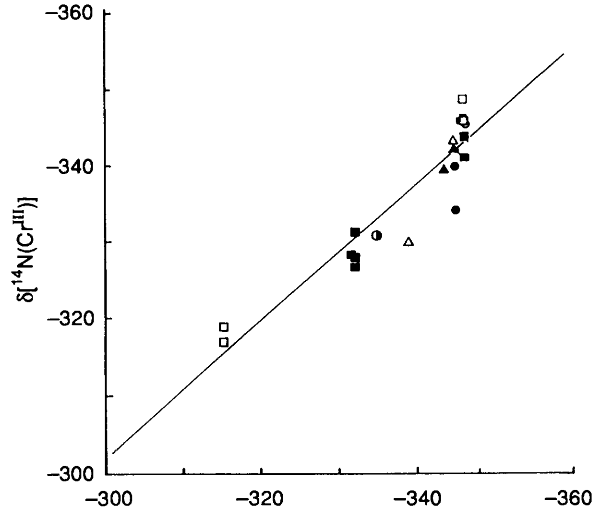

Fig. 3 Plot of δ $[^{14}N(Cr^{III})]$ *vs.* δ $[^{14}N$(diamine dihydrochloride)] in aqueous solution: (○), en; (●), tn; (■), pn; (□), ibn; (◐), chxn; (▲), men; (△), tmen

Stereochemistry.—For Δ- and Λ-$[Cr\{(R)pn\}_3]^{3+}$, *trans*-$[CrF_2(diamine)_2]^+$ and $[Cr(diamine)(H_2O)_4]^{3+}$ complexes with unsymmetrical diamine ligands having two inequivalent nitrogen atoms (pn, ibn and men) two well resolved signals are observed (see Figs. 1 and 2 and Table 1). This shows the significant advantage of the present high-resolution (δ ± 0.17) measurement by a strong magnetic field (12 T) Fourier-transform NMR spectrometer over the previous poor-resolution (δ ± 10) of McGarvey and Pearlman[3] who observed only one signal for $[Cr(pn)_3]^{3+}$ using a low magnetic field (0.95 T) wide-line NMR spectrometer.

A similar tendency in spectral shift was observed for the chromium(III) complexes and the corresponding diamine dihydrochlorides. A plot of the ^{14}N NMR shifts of $[Cr(diamine)_3]^{3+}$, *trans*-$[CrF_2(diamine)_2]^+$ and $[Cr(diamine)(H_2O)_4]^{3+}$ against those of the corresponding diamine dihydrochlorides gives a linear correlation as expressed by the equation δ(complex) = 0.888 δ(diamine dihydrochloride) −35.5, with a correlation coefficient $r = 0.924$ (Fig. 3). Therefore, the substituent shifts for the complexes are additive as is also the case for the ^{15}N NMR chemical shifts of saturated aliphatic amine hydrochlorides where the regular shifts are observed according to the numbers and/or kinds of the substituent groups.[30] For $[Cr(diamine)(H_2O)_4]^{3+}$ and *trans*-$[CrF_2(diamine)_2]^+$ (Fig. 1 and Table 1), the intervals between two well resolved signals increase with increasing number of the branches at the α-carbons or with the number of β-carbons. For one and two branches in the pn and ibn complexes, respectively, the observed intervals of δ 14 and 27–32 are almost coincident with those predicted according to the additive substituent parameters for the ^{15}N NMR shifts of various kinds of the amine hydrochlorides.[30] For *trans*-$[CrF_2(men)_2]^+$ and the corresponding dmen complex, on the other hand, the intervals between the ^{14}N NMR chemical shifts for the inequivalent nitrogens are much smaller than those of the pn and ibn complexes. This behaviour is also in line with the ^{15}N NMR shifts for the corresponding secondary and tertiary amine hydrochlorides.[30] On this basis, the almost unshifted signals at higher field around δ −340 can be assigned to the primary amine nitrogens adjacent to the methylene groups (Table 1). On going from primary amine nitrogens adjacent to a methine group and from the secondary to the tertiary amine nitrogens, the ^{14}N NMR signals for the pn, ibn, men and dmen complexes

Table 1 Nitrogen-14 NMR data for [CrN$_6$]$^{3+}$, [Cr(diamine)(H$_2$O)$_4$]$^{3+}$ and *trans*-[CrF$_2$(diamine)$_2$]$^{+}$ type complexes and diamine dihydrochlorides

Compound	$\delta(\nu_{\frac{1}{2}}/\mathrm{Hz})$	
[Cr(NH$_3$)$_6$]$^{3+}$	−336.2[a] (130.8)	
[Cr(en)$_3$]$^{3+}$	−322.7[a] (292.1)	
[Cr(en)$_3$]$^{3+}$ [b]	−323.1[a] (280.3)	
[Cr(en)(H$_2$O)$_4$]$^{3+}$	−338.4[a] (142.9)	
trans-[CrF$_2$(en)$_2$]$^{+}$	−346.8[a] (119.7)	
en	−358.2[a] (621.5)	
en·2HCl	−345.2[a] (45.2)	
[Cr(tn)$_3$]$^{3+}$	−334.2[a] (202.0)	
[Cr(tn)$_3$]$^{3+}$ [b]	−334.5[a] (190.5)	
trans-[CrF$_2$(tn)$_2$]$^{+}$	−340.5[a] (170.2)	
tn	−353.5[a] (622.9)	
tn·2HCl	−344.8[a] (81.0)	
Δ-*lel*$_3$-[Cr{(*R*)pn}$_3$]$^{3+}$	−345.9[a] (124.3)	−328.0[c] (111.7)
Λ-*ob*$_3$-[Cr{(*R*)pn}$_3$]$^{3+}$	−345.9[a] (116.1)	−331.0[c] (100.6)
[Cr(pn)(H$_2$O)$_4$]$^{3+}$	−341.1[a] (155.5)	−327.1[c] (155.4)
trans-[CrF$_2$(pn)$_2$]$^{+}$	−344.5[a] (162.8)	−328.1[c] (144.3)
pn	−357.8, −344.7 (1486[d])	
pn·2HCl	−346.4[a] (80.9)	−332.5[c] (74.8)
Δ-*lel*$_3$-[Cr{(*R*,*R*)chxn}$_3$]$^{3+}$		−331.3[e] (155.4)
(*R*,*R*)chxn		−342.1[e] (640.1)
(*R*,*R*)chxn·2HCl		−335.0[e] (70.5)
[Cr(ibn)(H$_2$O)$_4$]$^{3+}$	−346.5[a] (161.6)	−319.7[f] (161.6)
trans-[CrF$_2$(ibn)$_2$]$^{+}$	−349.1[a] (149.2)	−317.0[f] (155.8)
ibn	−327.4, −361.1 (2237[d])	
ibn·2HCl	−346.0[a] (75.9)	−315.1[f] (60.5)
trans-[CrF$_2$(men)$_2$]$^{+}$	−342.7, −339.2 (250.0[d])	
men	−359.2 (630.5[d])	
men·2HCl	−344.8, −343.5 (118.0[d])	
trans-[CrF$_2$(dmen)$_2$]$^{+}$	−343.1[a] (160.1)	−330.9[g] (140.5)
dmen	−360.3 (880.1)	
dmen·2HCl	−344.7[a] (71.6)	−338.6[g] (62.3)

[a] CH$_2$NH$_2$ nitrogen. [b] In 0.3 mol dm^{-3} Na$_2$SeO$_3$ aqueous solution. [c] CH(CH$_3$)NH$_2$ nitrogen. [d] Linewidth for unresolved signals. [e] CHNH$_2$ nitrogen. [f] C(CH$_3$)$_2$NH$_2$ nitrogen. [g] CH$_2$N(CH$_3$)$_2$ nitrogen.

Table 2 Nitrogen-14 NMR data for [CoN$_6$]$^{3+}$ and *cis*-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ type complexes

Complex	$\delta(\nu_{\frac{1}{2}}/\mathrm{Hz})$
[Co(NH$_3$)$_6$]$^{3+}$	−420.3 (372.9)
[Co(en)$_3$]$^{3+}$	−392.1[a] (668.1)
[Co(en)$_3$]$^{3+}$ [b]	−405.6[a] (477.5)
[Co(tn)$_3$]$^{3+}$	−406.3[a] (747.7)
[Co(tn)$_3$]$^{3+}$ [b]	−405.6[a] (472.5)
Δ-*lel*$_3$-[Co{(*R*)pn}$_3$]$^{3+}$	−387.6, −380.3 (1703[c])
Δ-*lel*$_3$-[Co{(*R*,*R*)chxn}$_3$]$^{3+}$	−380.6[d] (505.0)
cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$	−386, −403 (1260[c])
cis-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ [e]	−380, −396 (1880[c])
[Co$_2$(OH)$_2$(en)$_4$]$^{4+}$	−387, −408 (1800[c])
[(nta)Cr(OH)$_2$Co(en)$_2$]$^{+}$	−433 (2480)

[a] CH$_2$NH$_2$ nitrogen. [b] In 0.3 mol dm^{-3} Na$_2$SeO$_3$ solution. [c] Linewidth for unresolved signals. [d] CHNH$_2$ nitrogen. [e] With addition of an equimolar amount of paramagnetic [Cr(nta)(H$_2$O)$_2$] (see text).

Table 3 Nitrogen-14 NMR data for *cis*- and *trans*-[CrX$_2$(en)$_2$]$^{n+}$ complexes

Complex	$\delta(\nu_{\frac{1}{2}}/\mathrm{Hz})$
cis-[CrF$_2$(en)$_2$]$^{+}$	−338.8 (92.1)
cis-[CrCl$_2$(en)$_2$]$^{+}$	−338.8 (140.2)
cis-[Cr(NCS)$_2$(en)$_2$]$^{+}$	−340.0 (102.8)
cis-[Cr(CN)$_2$(en)$_2$]$^{+}$	−336.4 (245.7)
[(nta)Cr(OH)$_2$Cr(en)$_2$]$^{+}$	−329.8 (81.0)
trans-[Cr(OH)$_2$(en)$_2$]$^{+}$	−347.0 (136.8)
trans-[CrF$_2$(en)$_2$]$^{+}$	−346.8 (119.7)
trans-[Cr(en)$_2$(H$_2$O)$_2$]$^{3+}$	−348.1 (132.4)
trans-[Cr(NCS)$_2$(en)$_2$]$^{+}$	−333.9 (122.9)
trans-[CrBr$_2$(en)$_2$]$^{+}$	−333.0 (123.1)
trans-[CrCl$_2$(en)$_2$]$^{+}$	−335.4 (120.8)
trans-[CrF(en)$_2$(H$_2$O)]$^{2+}$	−341.1 (130.1)
trans-[CrCl(F)(en)$_2$]$^{+}$	−340.4 (125.6)

are shifted to lower field as summarized in Table 1. Such a parallel behaviour of ^{14}N NMR spectra between the diamine chromium(III) complexes and the corresponding diamine dihydrochlorides manifests the intrinsic diamagnetic properties of the former.

In view of this NMR behaviour in *trans* bis(unsymmetrical diamine) complexes, ^{14}N NMR spectroscopy cannot distinguish between *cis* and *trans* geometrical isomers with respect to the relative position of the substituted groups in the diamines.

The ^{14}N NMR chemical shifts and the linewidths of [CrN$_6$]$^{3+}$ type complexes together with those for the corresponding [CoN$_6$]$^{3+}$ are shown in Tables 1 and 2. The shifts for the chromium(III) complexes range from δ −322.7 to −345.9 similar to those observed for the free diamine ligands.

The linewidth of the ^{14}N NMR signal for the tris(ethane-1,2-diamine)chromium(III) complex is about one third as broad as that for the corresponding cobalt(III) complex. Moreover, $\Delta(\lambda\lambda\lambda)$-*lel*$_3$- and $\Lambda(\delta\delta\delta)$-*ob*$_3$-[Cr{(*R*)pn}$_3$]$^{3+}$ * containing the unsymmetrical pn ligand also give two well separated ^{14}N NMR signals (Fig. 3). The linewidths of these two signals are much narrower than those of the corresponding diamine dihydrochlorides and the cobalt(III) complexes.

There exist *mer* and *fac* geometrical isomers with respect to the position of the methyl groups in Δ-*lel*$_3$- and Λ-*ob*$_3$-[Cr{(*R*)pn}$_3$]$^{3+}$ complexes. Although at most four ^{14}N NMR signals are expected for a mixture of the geometrical isomers, only two signals with the intervals δ 14.9–17.9 are observed as in the case of the *trans* bis(pn) complexes. These signals may be assigned to unsymmetrical diamine nitrogen ligators, the higher- and the lower-field signals being due to the 1- and 2-amino nitrogens, respectively, in [Cr{(*R*)pn}$_3$]$^{3+}$ complexes in accordance with the results for the mono- and bis-diamine complexes as mentioned above.

As to the ^{14}N NMR spectra of the Δ-*lel*$_3$ and Δ-*ob*$_3$ diastereoisomers of [Cr{(*R*)pn}$_3$]$^{3+}$ complexes (Table 1), there is no significant change in the chemical shifts irrespective of the difference in geometry or conformation. The linewidths of the Λ-*ob*$_3$ isomer are narrower than those of the Δ-*lel*$_3$ one. This difference may reflect the subtle geometrical or conformational changes of the diamine chelates in the *lel*$_3$ and *ob*$_3$ isomers as mentioned above for the tris(en) complex.

The complex [Cr(en)$_3$]$^{3+}$ gives a broader ^{14}N NMR line than Δ-*lel*$_3$-, Λ-*ob*$_3$-[Cr{(*R*)pn}$_3$]$^{3+}$ and Δ-*lel*$_3$-[Cr{(*R*,*R*)-chxn}$_3$]$^{3+}$ (Table 1). The linewidths of [Cr(en)$_3$]$^{3+}$ and [Co(en)$_3$]$^{3+}$ in 0.3 mol dm^{-3} Na$_2$SeO$_3$ solution are narrower than those in aqueous solution. The complexes [Cr(tn)$_3$]$^{3+}$ and [Co(tn)$_3$]$^{3+}$ in 0.3 mol dm^{-3} Na$_2$SeO$_3$ solution also give narrower signals than those in aqueous solution. These facts also suggest that the linewidth of ^{14}N NMR signals for paramagnetic tris(diamine) complexes is affected by the distribution of the conformational isomers, which is affected by the formation of an outer-sphere ion pair with selenite ion.[31–33] This is in line with the corresponding diamagnetic cobalt(III) complexes where a decrease of *ca.* 30% in linewidths upon ion pairing is observed (Table 2).

cis- *and* trans-[CrX$_2$(en)$_2$]$^{n+}$ *Complexes*.

—Although there are two inequivalent nitrogen atoms *cis* and *trans* to the X

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* For tris(ethane-1,2-diamine) complexes, the chelate rings in which the C–C bonds are parallel to the C_3 rotation axis of the complex form the collective *lel* conformation, whereas the ring C–C bonds which are obliquely inclined form the overall *ob* conformation.[31]

ligand in *cis*-$[CrX_2(en)_2]^+$ type complexes, only one sharp signal is observed for all the complexes (Table 3). Thus, such inequivalent nitrogen atoms cannot be distinguished even by the present high-resolution ^{14}N NMR spectrometer, in contrast to the large splitting observed for *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ (Table 2). In addition, the variation of the ligand field for ligands X results in only small chemical shift changes (δ 4), whereas their linewidths vary from 91 to 246 Hz.

For *trans*-$[CrX_2(en)_2]^+$ complexes, the linewidths in the ^{14}N NMR spectra change only within 20 Hz. However one signal changes by *ca.* 15 ppm with variation of the axial ligands, the highest- and lowest-field signals being for the OH^- and Br^- ligands, respectively (Table 3). The shift range for the *trans* bis(diamine) complexes is larger than that for the *cis* ones. This suggests that the magnetic anisotropy in the temperature-independent paramagnetic term is operative for this type of complex as predicted for ^{14}N, ^{15}N and/or ^{13}C NMR chemical shifts of $[CoX(NH_3)_5]^{n+}$,[34,35] $[Co(ox)_x(gly)_y(en)_z]$ (ox = oxalate, gly = glycinate),[36] *cis*-$[CoX_2(en)_2]^{n+}$ [37] and $[CoX(CN)_5]^{n-}$ [38] type complexes.

The Dinuclear Complexes.—The ^{14}N NMR spectra of the ethane-1,2-diamine ligand in the di-μ-OH dinuclear complexes $[(nta)Cr(OH)_2M(en)_2]^+$ (M = Cr or Co) were examined to compare with those of the mononuclear Cr(III) complexes. The signal for the en ligands in the dichromium complex is observed at almost the same position as, and becomes even narrower than, that of the mononuclear *cis*-bis(en) chromium(III) complexes (Table 3). The spectrum is little influenced by the $(nta)Cr^{III}$ moiety. On the other hand, one signal of the en ligand observed for the $Co(en)_2$ moiety of the chromium–cobalt complex is shifted to higher field and broader than for mononuclear *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ and dinuclear $[Co_2(OH)_2(en)_4]^{4+}$ (Table 2). Therefore, the chemical shift and linewidth of this complex do not result, respectively, from the co-ordination shift and the line broadening due to the enhanced rotation-correlation time. Moreover, the coexistence of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ in an equimolar amount (0.5 mol dm^{-3}) with the paramagnetic complex $[Cr(nta)(H_2O)_2]$ results in a lower-field shift together with the line broadening for the ^{14}N NMR signals (Table 2) as observed for $[NBu_4]_2[CoX_4]$.[39] This small lower-field shift caused by adding the chromium(III) complex is in contrast to the large higher-field one for the chromium–cobalt complex which exhibits the expected pseudo-contact shift with paramagnetic relaxation line broadening. Accordingly, the contribution from the Cr(nta) moiety to the $Co(en)_2$ one in this complex may originate from the contact shift, but is quite different from that to the paramagnetic $Cr(en)_2$ in the dichromium complex. The almost unshifted ^{14}N NMR signal even with line narrowing for the $Cr(en)_2$ moiety in this complex is unexpected from the intrinsic diamagnetic properties of the ^{14}N NMR spectra of mononuclear chromium(III) complexes. It should provide clues to the peculiar diamagnetic behaviour of chromium(III) complexes.

Conclusion

By remeasurement of the high-resolution ^{14}N NMR spectra of paramagnetic chromium(III) amine complexes, their diamagnetic properties were substantiated to be intrinsic more evidently than previously by McGarvey and Pearlman.[3] The chemical shifts of the diamine nitrogen nucleus attached directly to octahedral six-co-ordinate Cr^{III} are slightly affected by ligand replacement in *cis*- and *trans*-$[CrX_2(diamine)_2]$, but are susceptible to variation of the substituent groups in the diamines as found for ^{15}N NMR chemical shifts of the amine hydrochlorides. The linewidths for the tris(diamine) complexes are sensitive to conformational change in the diamine chelates. Such anomalous ^{14}N NMR behaviour is expected to afford steric information through the conformational effect of diamine chelates in chromium(III) complexes as revealed for the cyclic amines.[40]

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