Rhodium(III) Complexes with Cyanide and Sulfur-donor Ligands: Rhodium-103 Nuclear Magnetic Resonance Chemical Shift Correlations

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The ^{103}Rh NMR chemical shifts for hexa(cyano-κ*C*)-, hexa(thiocyanato-κ*S*)-rhodate(III) and tris(*O,O'*-diethyl dithiophosphato-κ^2*S,S'*)rhodium(III) have been determined in aqueous solution. Two-bond spin–spin coupling is observed between ^{103}Rh and ^{31}P in the ^{103}Rh NMR spectrum of $[\mathrm{Rh\{S_2P(OEt)_2\}_3}]$, $^2J(\mathrm{Rh{-}P}) = 13$ Hz. A value for the nephelauxetic ratio ($\beta = 0.29 \pm 0.05$) was obtained for the $[\mathrm{Rh(SCN)_6}]^{3-}$ ion from a correlation between the ^{103}Rh NMR chemical shifts of octahedral rhodium(III) complexes and the ligand-field parameter ratio, $\beta/\Delta E(^1\mathrm{A}_{1g}{-}^1\mathrm{T}_{1g})$. Comparison with the nephelauxetic ratios of other S- and N-bonded complexes shows S-bonding between rhodium(III) and the thiocyanate ligand. An empirical correlation is demonstrated between the metal NMR chemical shift and the logarithm of the overall thermodynamic formation constant ($\log \beta_6$), for a range of octahedral rhodium(III) and cobalt(III) complexes, thus allowing the formation constants $\log \beta_6 = 47 \pm 4$ and 35 ± 3 to be estimated for $[\mathrm{Rh(CN)_6}]^{3-}$ and $[\mathrm{Rh(SCN)_6}]^{3-}$, respectively. The stability of the aquafluororhodium(III) species is discussed. The thermodynamic basis for the dissolution of rhodium metal in aqueous solution using cyanide or thiocyanate is examined.

Catalytic converters containing platinum, rhodium and palladium metal are widely used to remove carbon monoxide, hydrocarbons and nitrous oxides from car exhaust fumes. The recycling methods used to recover these platinum-group metals from used catalysts can be divided into two groups, (1) hydrometallurgical and (2) pyrometallurgical processes.[1] The requirements for a successful hydrometallurgical leaching process are first an oxidant which is capable of oxidising the metal particles on the catalyst surface, and secondly a complexing agent or ligand which can stabilize the metal ions thereby decreasing the oxidation potential of the metal in aqueous solution.

Modern exhaust catalysts contain typically 0.3 g rhodium and 1.5 g platinum and/or palladium metal per catalytic converter, where the rhodium content represents about 50% of the recycling value.[2] Concentrated nitric and hydrochloric acid mixtures have previously been used to leach platinum and palladium from used catalysts.[3] However, the rate of dissolution of rhodium in *aqua regia* is slow and new reagent combinations are therefore required which are more environmentally acceptable, less corrosive and give good yields of all three platinum metals. For example, leaching with aqueous cyanide solutions has recently been investigated,[4] a technique which is widely used in the hydrometallurgical processing of gold. In a patent application,[5] recoveries of 97% Pd, 94% Pt and 98% Rh are claimed by autoclaving used catalysts at around 160 °C with 5% (1 mol dm^{-3}) solutions of sodium cyanide.

Owing to the difficulties of leaching rhodium metal in chloride-based systems we have previously[6] investigated the aquabromorhodium(III) complexes using ^{103}Rh NMR spectroscopy. The stability of the bromochlororhodium(III) species has also been determined,[7] showing that the hexabromorhodate(III) ion ($\log \beta_6 = 13.0$) is more stable than hexachlororhodate(III) ($\log \beta_6 = 8.44$). In this paper we investigate the complex formation between rhodium(III) and (1) cyanide, (2) ambidentate thiocyanate (SCN$^-$ may be either S- or N-bonded), and (3) the bidentate sulfur donor *O,O'*-diethyl dithiophosphate.

An effective hydrometallurgical leaching agent should primarily be capable of forming strong complexes in aqueous solution, thus lowering the oxidation potential required to convert rhodium metal into rhodium(III) species. The kinetic inertness of the rhodium(III) ion, and thus the time required to establish equilibrium has, however, hindered the measurement of formation constants of complexes with all but a few ligands.[7,8] There are, therefore, little thermodynamic data available for the assessment of different leaching reagents. In this work we correlate the metal NMR chemical shifts of some octahedral d^6 cobalt(III) and rhodium(III) complexes with their respective formation constants, thus allowing the stability of complexes such as hexa(thiocyanato-κ*S*)- and hexa(cyano-κ*C*)-rhodate(III) to be assessed. On this basis we discuss the applicability of cyanide and thiocyanate in the hydrometallurgical recovery of used car exhaust catalysts.

Experimental

Preparations.—$\mathrm{K_3[Rh(CN)_6]}$. Attempts to prepare this compound by treating aqueous solutions of hexaaquarhodium(III) with KCN resulted in precipitation of rhodium hydroxide in the resulting basic solutions. In acidic solutions the rate of anation was very slow due to the low concentration of 'free' cyanide ions. Successful preparations were achieved using Schmitdke's method[9] in which $\mathrm{RhCl_3{\cdot}}n\mathrm{H_2O}$ (2.5 g, Johnson Matthey, 42.39% Rh) was dissolved in distilled water (20 cm^3). After warming at 60 °C for 1 h, KCN (4.3 g, Merck) was added in small portions to give a stoichiometric ratio Rh : CN$^-$ = 1 : 6.4. After the final addition the solution was allowed to stand for 1 h at 60 °C to ensure complete reaction. It was adjusted to pH ≈ 1 with 2 mol dm^{-3} HCl and air was bubbled through to remove any excess of HCN. The solution was evaporated to 8 cm^3 and white crystals of KCl filtered off. The filtrate was diluted to a total volume of 15 cm^3 with distilled water and ethanol (50 cm^3) was added. White crystals of KCl were again filtered off from the oily yellow product which was dissolved in distilled water (40 cm^3) and allowed to evaporate at 60 °C until crystals of the white solid $K_3[Rh(CN)_6]$ started to form. After further crystallisation at 0 °C the product (0.70 g, yield 22%) was filtered off from the yellow supernatant.

Solid $K_3[Rh(CN)_6]$ (0.5 g) was dissolved in 1 mol dm^{-3} $HClO_4$ (3 cm^3). After cooling to 0 °C the precipitated $KClO_4$ was filtered off and the solution used for ^{103}Rh NMR measurements (solution I). A solution of $K_3[Rh(CN)_6]$ (0.1 g) in distilled water (1 cm^3) was used for Raman and IR measurements (solution Ia).

$K_3[Rh(SCN)_6]$. The compound $RhCl_3{\cdot}nH_2O$ (1.0 g) was dissolved in distilled water (20 cm^3). After warming at 60 °C for 1 h, KSCN (2.4 g, Merck) was added in small portions ($Rh:SCN^- = 1:6.1$). After the final addition the solution was allowed to stand for 1 h at 60 °C to ensure complete reaction. Ethanol (50 cm^3) was added and the resulting KCl crystals filtered off. The solution was evaporated to dryness giving red-orange crystals of $K_3[Rh(SCN)_6]$[9] which were dissolved in distilled water (3 cm^3) for ^{103}Rh NMR measurements (solution II).

$[Rh\{S_2P(OEt)_2\}_3]$. *O,O'*-Diethyl dithiophosphoric acid (Merck, 1.45 cm^3) was dissolved in distilled water (10 cm^3) and warmed to 60 °C. The compound $RhCl_3{\cdot}nH_2O$ (0.25 g) was added in small portions to the stirred acidic solution. After 30 min a red-brown precipitate was filtered off and recrystallised from warm ethanol. The dark red crystals of $[Rh\{S_2P(OEt)_2\}_3]$ (0.76 g, yield 56%) are monoclinic with $a = 14.26$, $b = 13.59$, $c = 14.28$ Å, $\beta = 90.62°$. The UV/VIS spectrum of the complex in ethanol agreed with that previously observed,[10] having $\lambda_{max} = 470$, 413, 319 and 257 nm. The complex (0.6 g) was dissolved in chloroform (2.5 cm^3) for ^{103}Rh NMR measurements (solution III).

NMR Measurements.—All spectra were recorded on a Bruker AM400 spectrometer at 298 K. The ^{103}Rh NMR spectra of solutions I–III were recorded at 12.64 MHz and 298 K in 10 mm NMR tubes. A pulse width of 10 μs, representing a flip-angle $\alpha \approx 13°$ for ^{103}Rh in aqueous $[Rh(H_2O)_6]^{3+}$, was used with a pulse repetition time of 1.5 s.[6] Spectra were referenced to $\Xi = 3.16$ MHz using the high-frequency positive-shift sign convention. The ^{13}C NMR spectra of solutions I and II were recorded at 100.6 MHz and 298 K, the chemical shifts being reported to high frequency of external $SiMe_4$.

Vibrational Spectroscopy.—Raman spectra were recorded using the 514.5 nm line of an argon-ion laser on a Dilor Z24 triple monochromator. A spectral bandwidth of 3 cm^{-1} gave adequate resolution for the broad bands of the complexes when measured in aqueous solution. Mid-IR spectra of aqueous solutions were recorded on a Perkin-Elmer 1760X spectrometer. Barium fluoride windows were used and a path length of approximately 25 μm was maintained with a polyethylene spacer. The IR spectra were corrected for solvent background by subtraction of a spectrum of pure water using the Lab Calc® software package.[11]

Thermodynamic Calculations.—Calculations to model the leaching of rhodium metal from exhaust catalysts were conducted using the SED program which is a modification of the SOLGASWATER program for equilibrium calculations.[12] The concentrations of dissolved rhodium(III) species in equilibrium with metallic rhodium were calculated as a function of the solution redox potential (E), in the presence of (1) a 1 mol dm^{-3} total concentration of cyanide and (2) a 1 mol dm^{-3} total concentration of thiocyanate, at 298 K. The redox potential is expressed as $pE = EF/RT \ln 10$, where $p = 59.16$ mV at 298 K.

Results

Infrared and Raman Spectroscopy.—The Raman spectrum of solution I exhibited cyanide C≡N stretching frequencies at 2166 (ν_1, polarised) and 2147 cm^{-1} (ν_3, depolarised). A C≡N stretching frequency was observed in the mid-IR spectrum at 2133 cm^{-1} (ν_6). These bands are fully compatible with other reports and assignments[13] for $[Rh(CN)_6]^{3-}$ in octahedral (O_h) symmetry, where the totally symmetric ν_1 (A_{1g}) and the antisymmetric ν_3 (E_g) modes are Raman active, and ν_6 (F_{1u}) is IR active. The Rh–C symmetric (A_{1g}) and asymmetric (E_g) stretching modes for aqueous solutions of $K_3[Rh(CN)_6]$ were previously reported at 445 (ν_2, polarised) and 435 cm^{-1} (ν_4, depolarised), respectively.[13] In our Raman spectrum a broad and asymmetric band was observed at 438 cm^{-1}. By subtracting the ν_4 band at 435 cm^{-1}, which remained in the perpendicularly polarised spectrum, we obtained a value of 441 ± 2 cm^{-1} for the ν_2 (A_{1g}) Rh–C stretching mode of the hexa(cyano-κ*C*)-rhodate(III) ion. The ^{103}Rh and ^{13}C NMR spectra provide evidence that only the $[Rh(CN)_6]^{3-}$ ion is present in solution I.

Solution I containing the supposed hexa(thiocyanato-κ*S*)-rhodate(III) ion gave a single sharp band in the mid-IR region at 2110 cm^{-1} which may be assigned to the C≡N stretching frequency of the thiocyanate ligands co-ordinated to rhodium(III).[14] The intense orange-brown colour of solution II prevented the measurement of Raman spectra using the 514.5 nm laser line.

NMR Investigations.—The ^{13}C NMR spectrum of solution I exhibited a doublet at δ 132.9, $^1J(^{13}C-^{103}Rh) = 34.4$ Hz, resulting from spin–spin coupling between ^{103}Rh ($I = \frac{1}{2}$) and co-ordinated $^{13}CN^-$ ligands. This is in good agreement with a previous observation[15] of the $[Rh(CN)_6]^{3-}$ ion and confirms the symmetric arrangement of cyanide carbons around rhodium(III). There was no evidence for the existence of free CN^- or HCN in solution I, on the basis of the ^{13}C NMR spectra in the chemical shift range $\delta \approx 110$–170.[15,16] The ^{13}C NMR spectrum of solution II exhibited a singlet at δ 128.4 due to the $[Rh(SCN)_6]^{3-}$ ion. No two-bond coupling was observed between ^{103}Rh and co-ordinated $S^{13}CN^-$ ligands. The ^{13}C signal due to 'free' thiocyanate was observed at δ 137.1 in a 1 mol dm^{-3} aqueous solution of KSCN.

The measured ^{103}Rh NMR chemical shifts of $[Rh(CN)_6]^{3-}$, $[Rh(SCN)_6]^{3-}$ and $[Rh\{S_2P(OEt)_2\}_3]$ are given in Table 1. The ^{103}Rh NMR spectrum of the latter, shown in Fig. 1, consisted of a quadruplet signal with the intensity ratio 1:3:3:1. The multiplet results from two-bond spin–spin coupling between a central rhodium nucleus (^{103}Rh, 100% abundance, $I = \frac{1}{2}$) and three phosphorus nuclei (^{31}P, 100% abundance, $I = \frac{1}{2}$), present in the three-co-ordinated phosphate ligands. The observed coupling pattern, with $^2J(Rh-P) = 13$ Hz, provides conclusive evidence that the $[Rh\{S_2P(OEt)_2\}_3]$ complex is present in solution III.

Table 1 Summary of ^{103}Rh NMR chemical shifts at 298 K and ligand-field parameters (β and Δ*E*, see text) for octahedral rhodium(III) complexes

Complex	δ	β	$\Delta E(A_{1g}-T_{1g})/cm^{-1}$
$[Rh(H_2O)_6]^{3+}$	9 924[a,b]	0.73[c]	25 500[d]
$[RhCl_6]^{3-}$	8 025[b,e]	0.49[c]	19 300[d]
$[RhBr_6]^{3-}$	7 051[a,b]	0.40[c]	18 100[d]
$[Rh(NO_2)_6]^{3-}$	5 580[f]	0.59[f]	29 900[f]
$[Rh(NH_3)_6]^{3+}$	4 776[a]	0.60[c]	32 700[d]
$[Rh\{S_2P(OEt)_2\}_3]$	3 665[g]	0.29[c]	21 300[h]
$[Rh(SCN)_6]^{3-}$	2 726[g]	0.29[g]	19 600[i]
$[Rh(CN)_6]^{3-}$	340[g]	0.49[g]	44 400[j]

[a] Ref. 6. [b] Extrapolated to 298 K, see text. [c] Ref. 17. [d] Ref. 18. [e] Ref. 19. [f] Ref. 20. [g] This work; SCN^- extrapolated and CN^- estimated, see text. [h] Ref. 10. [i] Ref. 9. [j] Ref. 21.

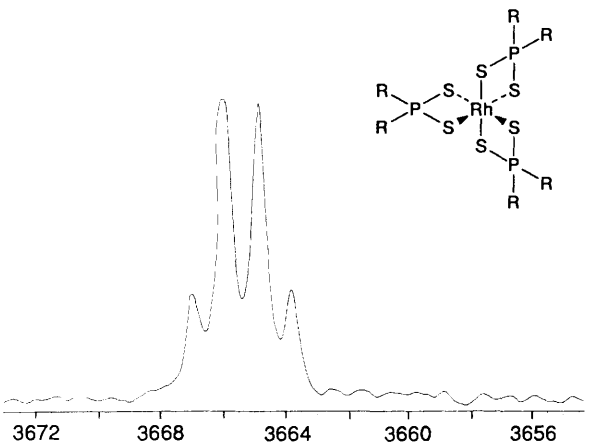

Fig. 1 Rhodium-103 NMR spectrum of a 0.3 mol dm^{-3} solution of [Rh{$S_2P(OEt)_2$}$_3$] in $CHCl_3$ (solution III), recorded at 12.64 MHz and 298 K (R = OEt)

The Ramsey equation for paramagnetic nuclear shielding is given in a simplified form in the first part of equation (1),[22,23]

$$\delta = \delta_{dia} + \frac{K}{\langle r_d{}^3\rangle \Delta E} = \delta_{dia} + \frac{K'\beta}{\Delta E(^1A_{1g}\text{–}^1T_{1g})} \quad (1)$$

where δ_{dia} is the chemical shift due to diamagnetic shielding, $\langle r_d{}^3\rangle$ is the average cubic distance of the 4d valence electrons from the rhodium nucleus, and ΔE is the energy difference between the ground and excited states responsible for the paramagnetic shielding. This equation has been successfully parametrised in terms of experimentally observable ligand-field parameters for a range of cobalt(III)[20] and rhodium(III)[6,20] complexes. Linear correlations are observed between the ^{59}Co or ^{103}Rh NMR chemical shifts of complexes in octahedral (O_h) symmetry and their ligand-field parameter ratios, $\beta/\Delta E(^1A_{1g}\text{–}^1T_{1g})$. The nephelauxetic ratio (β), which is calculated from the ligand-field spectrum of the complex, describes the interelectronic repulsion between d electrons and thus gives a measure of the radial extent of the d-orbital electron density in the complex, *i.e.* it is assumed that $\beta \propto 1/\langle r_d{}^3\rangle$. The energy difference (ΔE) is equated with the energy of the $^1A_{1g}$–$^1T_{1g}$ electronic transition in O_h symmetry;[20] K and K' are positive constants. In this work we have included the $[Rh(CN)_6]^{3-}$ ion in an attempt to extend the previous correlation for rhodium(III) complexes. The ligand-field data are also given in Table 1.

The chemical shifts have been extrapolated to 298 K where appropriate, using the temperature coefficient +2 ppm K^{-1}.[6,23] The nephelauxetic series of ligands[24] indicates that the nephelauxetic influence of the cyanide ligand is approximately equal to that of chloride, independent of the central metal ion. However, this comparison is based only on data for $[CrCl_6]^{3-}$ ($\beta = 0.56$) and $[Cr(CN)_6]^{3-}$ ($\beta = 0.58$) and should therefore be treated with some caution. Since no value of the nephelauxetic ratio was available for the hexa(cyano-κ*C*)rhodate(III) ion, this was approximated by $\beta = 0.49$[17] determined from the ligand-field spectrum of the hexachlororhodate(III) ion. The correlation between ^{103}Rh NMR chemical shifts and $\beta/\Delta E(^1A_{1g}\text{–}^1T_{1g})$ is shown in Fig. 2. The data for the [Rh{$S_2P(OEt)_2$}$_3$] complex were not included in the least-squares fitted line.

The diamagnetic shift due to the core-electron density is estimated by extrapolation such that $\beta/\Delta E(^1A_{1g}\text{–}^1T_{1g}) = 0$. From this work we obtain δ_{dia} −5000 ± 1000, which is not significantly different from our previous estimate.[6] Furthermore, for the $[Rh(SCN)_6]^{3-}$ ion (see Table 1), we can estimate a value of the nephelauxetic ratio $\beta = 0.29 \pm 0.05$ from the ^{103}Rh NMR chemical shift measured in this work and the known energy of the $^1A_{1g}$–$^1T_{1g}$ electronic transition.[9]

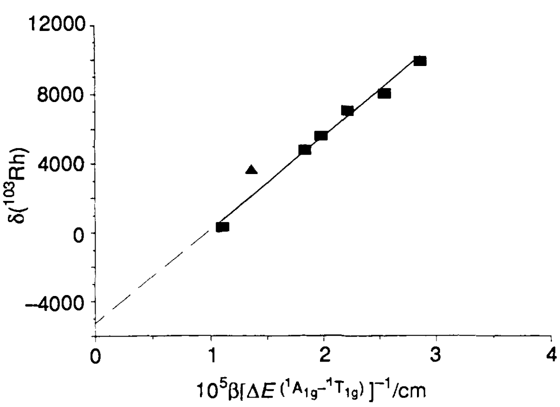

Fig. 2 Variation of the ^{103}Rh NMR chemical shift of six-co-ordinated rhodium(III) complexes $[ML_6]$ (L = CN^-, NH_3, NO_2^-, Br^-, Cl^- or H_2O) denoted by ■, and [Rh{$S_2P(OEt)_2$}$_3$] by ▲, with the ligand-field parameter ratio $\beta/\Delta E(^1A_{1g}\text{–}^1T_{1g})$

The linear correlation between the metal NMR chemical shifts of some octahedral rhodium(III) and cobalt(III) complexes and their respective overall formation constants is shown in Fig. 3. The equilibrium constants (log β_6) refer to the general complex-formation reaction (2) and are given for measurements

$$[M(H_2O)_6]^{3+} + 6\,L^{n-} \rightleftharpoons [ML_6]^{(3-6n)+} + 6\,H_2O \quad (2)$$

at 298 K, where possible. No corrections for the effects of different ionic media were made in these empirical correlations. The data are summarised in Table 2.

Discussion

The cyanide ion is one of the strongest ligands in the spectrochemical series,[24] hence it is not surprising on the basis of equation (1) that it has one of the lowest ^{103}Rh NMR chemical shifts of the symmetrically six-co-ordinated rhodium(III) complexes (Table 1). The good fit of the $[Rh(CN)_6]^{3-}$ complex to the correlation line in Fig. 2 confirms the assumption of near equivalence between the Cl^- and CN^- ligands in the nephelauxetic series.[24] There has been some discussion as to the correctness of extrapolating ^{103}Rh (or ^{59}Co) NMR chemical shift correlations to $\beta/\Delta E(^1A_{1g}\text{–}^1T_{1g}) = 0$, in order to obtain the shift due to diamagnetic shielding, δ_{dia}.[20,27] It has been proposed[27] that as $1/\Delta E(^1A_{1g}\text{–}^1T_{1g}) \longrightarrow 0$, *i.e.* as $\Delta E(^1A_{1g}\text{–}^1T_{1g}) \longrightarrow \infty$, the core-electron distribution will be affected thus invalidating the extrapolated shift. The reasonably linear correlation between the ^{103}Rh NMR chemical shift and $\beta/\Delta E(^1A_{1g}\text{–}^1T_{1g})$ tends to support the argument[20] that the core-electron distribution remains undisturbed even when the central metal ion is complexed by very strong spectrochemical ligands such as the cyanide ion. Extrapolation from experimental data to obtain δ_{dia} should thus be valid. Indeed, constant effective core potentials are often used to describe the core-electron distribution in quantum-chemical calculations involving heavy elements.[28] A value of the diamagnetic shift due to the rhodium core-electron density (δ_{dia} −4500 ± 1000) has recently been obtained from similar correlations involving rhodium(I) complexes.[22] The similarity with our value (δ_{dia} −5000 ± 1000) determined for rhodium(III) implies that the ligand-field parametrisation of the Ramsey equation for nuclear shielding is valid for different oxidation states of rhodium, as well as for ligands with a wide range of spectrochemical and nephelauxetic strengths.

The ^{103}Rh NMR chemical shift of the [Rh{$S_2P(OEt)_2$}$_3$] complex in chloroform (δ 3665) deviates somewhat from the correlation in Fig. 2. The NMR chemical shifts of ^{103}Rh and other transition-metal complexes are solvent dependent due to a range of interactions such as hydrogen bonding between the ligand and solvent, ion pairing and outer-sphere complex

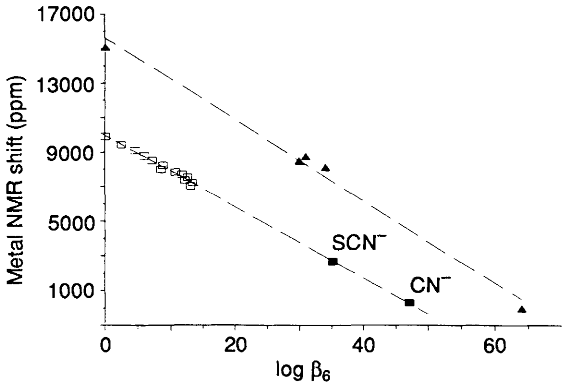

Fig. 3 Correlation of ^{103}Rh (□) and ^{59}Co (▲) NMR chemical shifts of octahedral rhodium(III) and cobalt(III) complexes in aqueous solution with their respective overall formation constants (log β_6). The extrapolated points for the $[Rh(SCN)_6]^{3-}$ and $[Rh(CN)_6]^{3-}$ complexes are indicated by ■

Table 2 Summary of the available overall stability constants (log β_6) and corresponding metal NMR chemical shifts (δ) for rhodium(III) and cobalt(III) complexes in aqueous solution

Complex	log β_6	$\delta(^{103}Rh)$ or $\delta(^{59}Co)$
$[Rh(H_2O)_6]^{3+}$	0	9 880[a]
$[RhCl(H_2O)_5]^{2+}$	2.45[b]	9 440[c]
$[RhCl_2(H_2O)_4]^{+}$	4.55[b]	9 121[c,d]
$[RhCl_3(H_2O)_3]$	5.93[b]	8 798[c,e]
$[RhCl_4(H_2O)_2]^{-}$	7.09[b]	8 536[c,d]
$[RhCl_5(H_2O)]^{2-}$	8.76[b]	8 246[c]
$[RhCl_6]^{3-}$	8.44[b]	7 981[c]
$[RhBrCl_5]^{3-}$	10.6[f]	7 848[g]
$[RhBr_2Cl_4]^{3-}$	11.7[f]	7 710[d,g]
$[RhBr_3Cl_3]^{3-}$	12.5[f]	7 559[e,g]
$[RhBr_4Cl_2]^{3-}$	12.1[f]	7 406[d,g]
$[RhBr_5Cl]^{3-}$	13.3[f]	7 243[g]
$[RhBr_6]^{3-}$	13.0[f]	7 007[g]
$[Co(H_2O)_6]^{3+}$	0	15 110[h]
$[CoCl(NH_3)_5]^{2+}$	31[b]	8 790[h]
$[CoBr(NH_3)_5]^{2+}$	30[b]	8 540[h]
$[Co(NH_3)_6]^{3+}$	34[b]	8 173[h]
$[Co(CN)_6]^{3-}$	64[b]	0[h]

[a] Ref. 6. [b] Ref. 8. [c] Ref. 19. [d] Average $\delta(^{103}Rh)$ for *cis* and *trans* isomers. [e] Average $\delta(^{103}Rh)$ for *mer* and *fac* isomers. [f] Ref. 7. [g] Ref. 25. [h] Ref. 26.

formation.[26] Medium effects are expected to cause changes principally in the electronic excitation-energy term[20] (ΔE) of equation (1), and thus the measured NMR shift. The UV/VIS spectra of $[Rh\{S_2P(OEt)_2\}_3]$ were recorded in ethanol and chloroform solutions. The shift in the wavelength of the $^1A_{1g}$–$^1T_{1g}$ transition was 5 nm from λ = 470 (EtOH) to 465 nm ($CHCl_3$). From Fig. 2 the expected ^{103}Rh NMR shifts are thus δ 2107 and 2037 in ethanol and chloroform, respectively. Unfortunately, this complex is insoluble in water, and only sparingly soluble in ethanol, thus preventing corresponding ^{103}Rh NMR measurements. However, it is unlikely that medium effects alone can explain the observed deviation of the measured ^{103}Rh NMR chemical shift. Distortion from a regular octahedral co-ordination for the bidentate *O,O'*-diethyl dithiophosphate ligand may also be a contributing factor.[10]

Qualitatively, the relative effect of different ligand donor atoms on the overall ^{103}Rh NMR chemical shift for six-co-ordinated rhodium(III) complexes is as follows: $\delta(^{103}Rh)$: $F^- > H_2O > Cl^- > Br^- >$ N (NH_3, NO_2^-) > S [$S_2P(OEt)_2^-$, SCN^-] > CN^-. Not surprisingly, an identical ordering is observed for the ^{59}Co NMR shifts of the analogous cobalt(III) complexes, and has been explained in terms of the relative nephelauxetic and spectrochemical strengths of the ligands.[27] This comprehensive series allows us to predict the composition of unknown rhodium(III) species on the basis of: (1) their ^{103}Rh NMR chemical shifts and (2) by assuming approximate additivity of the metal NMR chemical shift with the number of co-ordinating ligands. Near additivity of the ^{103}Rh NMR shifts for octahedral rhodium(III) complexes has previously been observed for the aquachloro-,[19] aquabromo-[6] and mixed bromochloro-rhodium(III) species.[7,25]

The CN stretching frequencies of SCN^- ligands which are S-bonded to the central metal are observed at about ν = 2100 cm^{-1}, whilst N-bonding normally gives rise to frequencies near and below ν 2050 cm^{-1}.[14] Our observation of a CN stretching band at 2110 cm^{-1} provides further evidence for S-bonding in $[Rh(SCN)_6]^{3-}$. The rhodium(III) ion has a strongly polarising effect on its environment due to a high charge : radius ratio. This effect gives rise to a highly ordered second hydration sphere around ions such as hexaaqua-rhodium(III) and -chromium(III) in aqueous solution, for example.[29,30] Theoretical *ab initio* calculations on the hexaaqua-rhodium(III) complex show a high degree of charge transfer even for the 'hard' aqua ligand.[31] The bonding to the 'soft' or more polarisable end of the thiocyanate ligand is thus expected to give a relatively high degree of covalency in the Rh^{III}–S bonds.

Further evidence for S-bonding in $[Rh(SCN)_6]^{3-}$ can be found from the ^{13}C NMR shift of the thiocyanate ligands. For a range of metal-bonded thiocyanates[32] the ^{13}C NMR shift difference, relative to 'free' thiocyanate (at Δδ 0.00) is found to range from Δδ +12.4 to −3.80 for N-bonded and from −3.30 to −17.7 for S-bonded complexes. The ^{13}C NMR shift difference, Δδ −8.70, measured for the hexa(thiocyanato-κ*S*)rhodate(III) ion in solution II thus supports S-bonding.

The estimated nephelauxetic ratio for the hexa(thiocyanato-κ*S*)rhodate(III) ion ($\beta = 0.29 \pm 0.05$) is another indication that the SCN^- ligand is S-bonded in this complex. For example, the nephelauxetic ratio is $\beta = 0.20$ when rhodium(III) is surrounded by six sulfur donors in the $[Rh\{S_2P(OEt)_2\}_3]$ complex, whilst for $[Ir\{S_2P(OEt)_2\}_3]$ $\beta = 0.24$.[17,27] In contrast, $\beta = 0.60$ and 0.59 for rhodium(III) surrounded by six nitrogen donors as in $[Rh(NH_3)_6]^{3+}$ and $[Rh(en)_3]^{3+}$ (en = ethylenediamine), respectively.[17,27] Similar differences are found in the β values of N- and S-bonded octahedral chromium(III) complexes.[17,27] We propose that the magnitude of the nephelauxetic ratio is a useful indicator of the bonding mode of the thiocyanate ligand, when used in combination with other experimental information.

Correlation of Metal Chemical Shifts with Complex Stability.—The kinetic inertness of the rhodium(III) ion has hindered the measurement of complex-formation constants by classical methods such as potentiometric titration due to the length of time required to reach equilibrium. Other methods are therefore required to assess the thermodynamic stability of rhodium(III) complexes with different ligands.

In the above, and in previous discussions,[6,20] the metal NMR chemical shifts of d^6 transition-metal ions such as cobalt(III) and rhodium(III) have been shown to be inversely proportional to the product of the ligand-field strength and the average cubic distance of the 4d electrons from the rhodium nucleus in the complex, *i.e.* $\delta \propto 1/\langle r_d^{\,3}\rangle \Delta E$, in accordance with the Ramsey theory of paramagnetic nuclear shielding. Both terms in the Ramsey equation can, in turn, be connected to the strength of the metal–ligand bond and thus the complex stability. We have therefore investigated possible correlations between the metal NMR chemical shifts of these ions and the stability of their six-co-ordinated complexes in aqueous solution.

A comprehensive search of the literature yielded overall stability constants (log β_6) for the complexes $[RhBr_nCl_{6-n}]^{3-}$ and $[RhCl_n(H_2O)_{6-n}]^{3-n}$, where n = 0–6 (Table 2), which have also been investigated by ^{103}Rh NMR spectroscopy. For comparison similar data are also included for the cobalt(III) complexes $[Co(H_2O)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$, $[CoBr(NH_3)_5]^{2+}$, $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$.[8,26] The correlations between the measured ^{103}Rh and ^{59}Co NMR chemical shifts and the overall stability constants of each complex are illustrated in Fig. 3. It is interesting that the fitted lines for these two metal ions have similar slopes, and that the displacement may simply be related to the difference in the diamagnetic contribution to the NMR chemical shift for these d^6 metal ions.

Although the range of log β_6 values is limited in the case of rhodium(III) complexes, the similarities both in terms of chemistry and nuclear shielding give us confidence in our extrapolation of the stability constants for rhodium(III) complexes with low metal NMR chemical shifts. The formation constants for $[Rh(CN)_6]^{3-}$ (log $\beta_6 = 47 \pm 4$) and $[Rh(SCN)_6]^{3-}$ (log $\beta_6 = 35 \pm 3$) were extrapolated from their measured ^{103}Rh NMR chemical shifts (see Table 1 and Fig. 3), with the 95% confidence limits estimated from a linear regression analysis of the data.

As discussed previously[6] the ^{103}Rh NMR chemical shift of the hexafluororhodate(III) complex may be estimated from the ligand-field parameter ratio $[\beta/\Delta E(^1A_{1g}-{}^1T_{1g}) = 3.00 \times 10^{-5}$ cm] of solid $K_3[RhF_6]$, hence from Fig. 2 we estimate $\delta(^{103}Rh) \approx 10\,990$. From Fig. 3 we can conclude that the thermodynamic stability of this species must be low, *i.e.* log $\beta_6 < 0$. On the basis of ^{19}F NMR spectroscopy a range of complexes of type $[RhF_n(H_2O)_{6-n}]^{3-n}$, where $n = 0$–6, have been proposed to exist in equilibrated solutions of $K_3[RhF_6]$ dissolved in HF.[33] The ^{103}Rh NMR spectra of solutions prepared by treating freshly precipitated $Rh(OH)_3$ with concentrated HF indicate the presence of hydrolytic oligomers of rhodium(III)[34] and also show a doublet at δ 10 595, ^1J(Rh–F) = 230 Hz. The coupling pattern indicates that this signal arises from $[RhF(H_2O)_5]^{2+}$. Eight doublets were observed in the ^{19}F NMR spectrum of this solution due to coupling between rhodium and complexed fluoride, with the dominant doublet signal at δ −382 and ^1J(Rh–F) = 230 Hz being attributed to the $[RhF(H_2O)_5]^{2+}$ complex. The low thermodynamic stability, coupled with the low 'free' fluoride concentration in acidic solutions containing F^-, and the weak *trans* activating effect of F^- explain our failure to observe higher aquafluororhodium(III) species in aqueous solution by using the rather insensitive ^{103}Rh NMR method.

The observed empirical correlation between the stability of rhodium(III) and cobalt(III) complexes and their metal NMR chemical shifts may be understood, at least qualitatively, by considering the factors that determine the metal NMR chemical shift and their effect on metal–ligand bonding. As a first approximation we have assumed that the entropy effects on replacing six H_2O by six L ligands in the general complex-formation reaction (2) are approximately equal, and that the complex stability is determined primarily by the enthalpy of formation of the metal–ligand complex. For this reason no attempt has been made to estimate the formation constant of $[Rh\{S_2P(OEt)_2\}_3]$ from its measured chemical shift. The 'chelate effect' may be expected additionally to stabilise[35] this species which contains three bidentate sulfur-donor ligands, as compared to the hexa(thiocyanato-κ*S*)rhodate(III) ion with six monodentate sulfur-donor ligands.

If we consider the hexaaquarhodium(III) ion, the replacement of H_2O ligands by first chloride to give $[RhCl_6]^{3-}$ and secondly bromide to give $[RhBr_6]^{3-}$ leads to a reduction in the ligand-field splitting energy (ΔE) due to the increasing metal–ligand bond length and a subsequent decrease in the repulsion between occupied metal d orbitals and the ligand electrons. However, the NMR chemical shift is lower for $[RhCl_6]^{3-}$ and even lower for $[RhBr_6]^{3-}$, whilst the thermodynamic stability increases for these complexes (Table 2).

The decrease in the metal NMR chemical shift implies that the d-orbital radial term, $\langle r_d{}^3\rangle$, must increase significantly on going from $[Rh(H_2O)_6]^{3+}$ to $[RhBr_6]^{3-}$ in order to counteract the effects of decreasing ΔE, according to equation (1). The decrease in the repulsion between occupied metal d orbitals and the ligand electrons is reflected in a decrease in the inter-electronic repulsion between metal d electrons as expressed by the nephelauxetic ratio, β.

Regarding the increasing complex stability, the decreasing ligand-field stabilisation energy in these complexes must be counteracted by some other stabilisation of the metal–ligand bond, and for these ligands an increasing covalency is expected. However, it is not possible directly to relate an increase in covalent bonding to an increase in the apparent radii of the d orbitals. For low-spin d^6 rhodium(III) the filled 4d orbitals belong to the t_{2g} species in O_h symmetry and are thus expected to participate in π back bonding to ligand p orbitals. For the CN^- ion, which is a very strong ligand in the spectrochemical series, the ligand-field splitting energy is large resulting in the formation of stable complexes, and also in low metal NMR chemical shifts. The cyanide complex is further stabilised due to metal to ligand π back bonding, an effect which can be expected to increase the average cubic distance of the 4d electrons from the nucleus $\langle r_d{}^3\rangle$, leading to a somewhat lower metal NMR chemical shift (Table 2).

Thermodynamic Basis for leaching Rhodium with CN^- *or* SCN^-.—Using our estimates for the formation constants of the hexa(cyano-κ*C*)- and hexa(thiocyanato-κ*S*)-rhodate(III) ions we have made thermodynamic equilibrium calculations in order to illustrate the cyanide-leaching process for the recovery of rhodium from used exhaust catalysts,[4,5] and to investigate the viability of the thiocyanate ligand which would be preferable from *e.g.* safety considerations. Obviously, the results of a leaching process will be primarily dependent on the kinetics of dissolution, however thermodynamic calculations of this type may provide insight into the required experimental conditions, *e.g.* the effects of ligand, redox potential, *etc.* The speciation was calculated for solutions containing 1 mol dm^{-3} total CN^- or SCN^- at self pH, in equilibrium with solid rhodium metal at 298 K, as a function of the redox potential (E), expressed as $pE = EF/RT \ln 10$. The equilibrium constant for reaction (3)

$$Rh^{3+} + 3e^- \rightleftharpoons Rh(s) \qquad (3)$$

was taken as log $K = 38.44$.[8] For the cyanide system the oxidation of cyanide to cyanogen according to reaction (4) was

$$2CN^- \rightleftharpoons (CN)_2 + 2e^- \qquad (4)$$

also included, log $K = -9.13$.[36] Analogously, in the thiocyanate system, oxidation of thiocyanate to dithiocyanogen was included with log $K = -26.03$.[36] All calculations were performed using the SED program[12] and the results are given in Fig. 4.

The advantage of using a strongly complexing ion such as CN^- is obvious from Fig. 4 (upper) and explains the promising results of leaching experiments using it with only dissolved air as the oxidising agent. From these thermodynamic arguments, thiocyanate could also be expected to dissolve rhodium metal at moderate redox potentials. However, in the experiments of Atkinson and co-workers[4,5] only millimolar rhodium concentrations were achieved in the final leach solutions. The redox potentials required to reach *e.g.* 1 mmol dm^{-3} solutions of dissolved rhodium with CN^- and SCN^- are $pE \approx -4$ and ≈ 0, respectively (Fig. 4). An advantage of thiocyanate illustrated in Fig. 4 is that stronger oxidising agents may be used before oxidation to thiocyanogen occurs.

Cyanide and to a lesser extent thiocyanate have thermodynamic advantages when compared to chloride and bromide in the dissolution of rhodium metal in aqueous solution. Furthermore, the cyanide ion also has a particularly strong kinetic *trans*-labilising effect as demonstrated in the square-planar complexes of platinum(II).[35] The formation of higher cyano complexes of rhodium(III) after dissolution of the metal is thus also kinetically favoured.

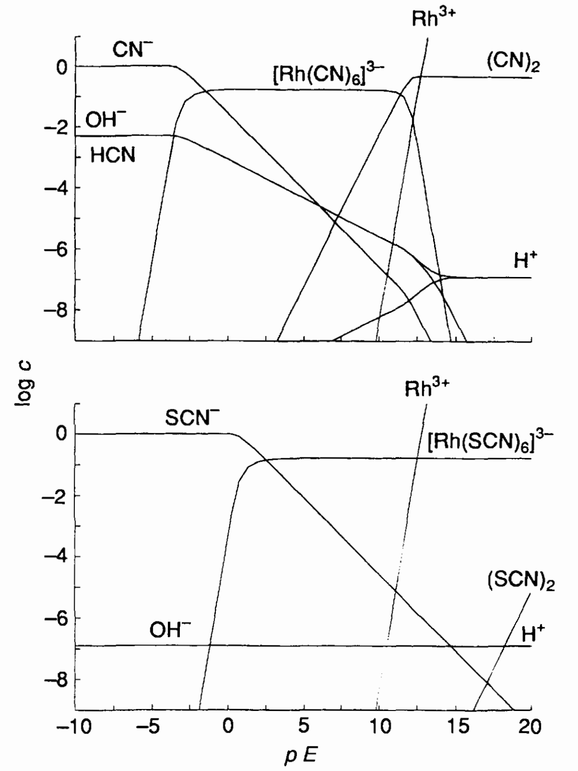

Fig. 4 Speciation of aqueous solutions containing 1 mol dm^{-3} total CN^- (upper) and 1 mol dm^{-3} total SCN^- concentration (lower), in equilibrium with solid rhodium metal as a function of the redox potential (*E*) of the system (p = 59.16 mV at 298 K)

Conclusion

Rhodium-103 NMR spectroscopy has been used to characterise complexes of rhodium(III) with sulfur-donor ligands and with cyanide. The low metal NMR chemical shifts of these, and other octahedrally co-ordinated, complexes, may be understood in terms of parameters determined from the ligand-field spectra. An almost linear correlation is found between the metal NMR shift and the formation constants of rhodium(III) complexes, thus allowing the stability of strong complexes such as $[Rh(CN)_6]^{3-}$ and $[Rh(SCN)_6]^{3-}$ to be assessed. Thermodynamic model calculations indicate that SCN^-, as well as CN^-, may be useful in the hydrometallurgical recovery of rhodium from *e.g.* used car exhaust catalysts.

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