Contribution from the Service d'Hydrometallurgie et de Chimie des Transuraniens, C.E.N. de Fontenay-aux-Roses, 92269 Fontenay-aux-Roses, France, and Service de Chimie Physique, C.E.N. de Saclay, 91190 Gif-sur-Yvette, France

^{13}C, ^{14}N, and ^{15}N Nuclear Magnetic Resonance and Relaxation Study of the Binding of Thiocyanate to Trivalent Lanthanide Ions

CLAUDE MUSIKAS,[1a] CHRISTINE CUILLERDIER,[1a] and CLAUDE CHACHATY*[1b]

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The binding of thiocyanate ions to trivalent lanthanides in aqueous solutions has been studied by ^{13}C, ^{14}N, and ^{15}N NMR for a SCN$^-$ concentration range of 0.05–3 M. The ratio of the ^{13}C and ^{15}N dipolar relaxation rates induced by Gd^{3+} yields N–Gd $\simeq$ 2.5 Å for Gd(SCN)$^{2+}$, Gd(SCN)$_2^+$, and Gd(SCN)$_3$ aquo complexes showing that SCN$^-$ is in the first coordination sphere of the metal. The T_{1e} and T_{2e} electron relaxation times in these Gd^{3+} complexes have been deduced from ^{14}N and ^{13}C transverse relaxation rates and ESR line width measurements between 278 and 353 K. At 300 K one finds $T_{1e} = 2.9 \times 10^{-9}$ s and $T_{2e} = 3.2 \times 10^{-10}$ s for $H_0 = 23.5$ kG. The ^{13}C and ^{14}N paramagnetic shifts in aqueous thiocyanate complexes of Ln^{3+} (Ln^{3+} = Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Yb^{3+}) are dominated by the contact effect. Their dependence upon [SCN$^-$] as well as the relevant 2s spin densities suggests that we are dealing with inner-sphere complexes as in the case of Gd^{3+}. This conclusion is well supported by UV and laser Raman experiments on europium(III) thiocyanate aqueous solutions.

I. Introduction

Aqueous thiocyanato complexes of trivalent lanthanides and actinides have received considerable attention in the last 15 years because of the use of thiocyanate solutions for group separation between the ions of the 4f and 5f families.[2] A review of the formation constants of the thiocyanato complexes of these ions has been done by Khopkar and Mathur.[3] It appears that thiocyanato complexes of trivalent ions of the f series are weak compared to analogous complexes of the d transition-metal ions. The formation constants of lanthanide and actinide complexes are of the same order and it is difficult on the basis of their values to understand why the trivalent ions of the two series can be separated from thiocyanate solutions. Several authors[3-6] have suggested that this difference results from the nature of the complexes formed in the separation process. They claim that monothiocyanates are outer-sphere complexes whereas the dithiocyanates have a more pronounced inner-sphere character, especially for the actinides. These assumptions are essentially based on the grounds of the thermodynamic constants of complexation (ΔG, ΔH, ΔS). In order to elucidate the nature of the thiocyanato complexes of trivalent lanthanides ions (Ln^{3+}) we used NMR, EPR, UV, and Raman spectroscopies. The three latter methods were used as subsidiary techniques to support some conclusions drawn from NMR experiments, which are in disagreement with previous works.

II. Experimental Section

1. Magnetic Resonance Experiments. The ^{13}C and ^{14}N NMR measurements were done on D$_2$O solutions of lanthanide perchlorates and NaSCN 0.05–3 M at pD 6.0–6.5. The ^{15}N NMR experiments were performed on 95% enriched samples of KSC^{15}N provided by the Service des Molécules Marquées of Saclay. Some ^{13}C experiments at high dilutions were done with ^{13}C-enriched KSCN samples of the same origin. The molar ratios $p = [\mathrm{Ln}^{3+}]/[\mathrm{SCN}^-]$ were generally taken between 10^{-3} and 5×10^{-2} to obtain a linear dependence of paramagnetic shifts and relaxation rates upon p. The ^{13}C shifts were measured with respect to an internal reference of dioxane which was also used to estimate the outer-sphere contribution to observed relaxation rates. This contribution was found to be negligibly small under our experimental conditions. No internal references were needed in ^{14}N and ^{15}N experiments because of the magnitude of relaxation rates and paramagnetic shifts. The latter were measured with respect to the carrier frequency of the Fourier transform.

All NMR experiments were performed in the Fourier transform mode at 20 and 25.2 MHz for ^{13}C and 7.2 and 10.13 MHz for ^{14}N and ^{15}N, respectively, with Varian XL100 (H_0 = 23.5 kG) and CFT20 (H_0 = 18.7 kG) spectrometers. The ^{13}C and ^{15}N T_1 relaxation times were determined by inversion recovery (180°, τ, 90° sequences). The T_2 relaxation times were obtained from line widths ($\pi\Delta\nu_{1/2} = T_2^{-1}$) after correction for instrumental contributions and for quadrupolar broadening in the case of ^{14}N and ^{13}C coupled to ^{14}N, using blank Ln^{3+}-free thiocyanate solutions.

The ESR spectra of gadolinium(III) thiocyanate solutions were recorded with a Varian E9 X-band spectrometer operating at 9.25 GHz with a 100-kHz modulation of the magnetic field. The Gd^{3+} concentration was $\sim 5 \times 10^{-4}$ M to avoid the exchange broadening. The magnetic field was calibrated by means of a Varian F8 NMR magnetometer connected to a frequency counter.

2. Optical Spectroscopy Experiments. The UV and visible absorption measurements were performed with a Cary 17 spectrophotometer using Suprasil 1-, 2-, 5-, and 10-mm cells.

For Raman spectroscopy experiments a spectrophotometer, Coderg LRT 800, with triple monochromator has been used. The light source was a 1-W Spectra Physics krypton laser. The Raman spectra reported in this work were obtained by use of the main line of the laser at 647.1 nm.

III. Results and Discussion

1. Magnetic Resonance of Thiocyanate–Gadolinium(III) Complexes. Among the lanthanide ions, Gd^{3+} has the property in its $^8S_{7/2}$ ground state to form magnetically isotropic complexes with a large variety of ligands, giving rise to paramagnetic shifts due only to the Fermi contact effect. Moreover, the electron spin relaxation time of Gd^{3+} is comparatively long, of the order of 10^{-9} s or more at room temperature, so that this ion behaves as a very efficient nuclear relaxation reagent.

These two properties have been used in the study of the binding of thiocyanate ions to Gd^{3+} allowing in particular the determination of whether we are dealing with first or second coordination sphere complexes. For that purpose, we have measured the paramagnetic shifts as the longitudinal and transverse relaxation rates of ^{13}C, ^{14}N, and ^{15}N induced by Gd^{3+} in aqueous solutions of SCN$^-$.

The contact shift $\Delta\nu_{\mathrm{m}}{}^{\mathrm{k}}$ of a nucleus k in the metal coordination sphere is[7]

$$\frac{\Delta\nu_{\mathrm{M}}{}^{\mathrm{k}}}{\nu_0{}^{\mathrm{k}}} = -\frac{2\pi A_{\mathrm{k}} g_{\mathrm{e}} \beta_{\mathrm{e}} S(S+1)}{3kT\gamma_{\mathrm{k}}} \qquad (1)$$

where $\nu_0{}^{\mathrm{k}}$ is the spectrometer frequency, A_{k} is the hyperfine coupling constant (in hertz), γ_{k} is the nuclear magnetogyric ratio, $S = {}^7/_2$ the total electron spin of Gd^{3+}, and $g_{\mathrm{e}} \simeq 2$ the relevant electron spectroscopic splitting factor. The longitudinal and transverse nuclear relaxation rates induced by a

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Table I. Paramagnetic Shifts and Relaxation Rates in Aqueous Gadolinium(III) Thiocyanate Complexes

		$[SCN^-]$, mol L^{-1}						
		0.05	0.1	0.3	0.5	1	2	3
^{13}C	$\Delta\nu_{obsd}/\nu_0 p$,[a] ppm	50	71	163	260	329	525	631
	$(T_1^{-1}{}_{obsd}/p) \times 10^{-3}$, s	0.185	0.463	0.810	1.330	1.692	2.817	3.269
	$(T_2^{-1}{}_{obsd}/p) \times 10^{-4}$, s	0.165	0.298	0.515	0.895	1.233	1.697	2.358
	q[c]	0.17 ± 0.03	0.32 ± 0.04	0.60 ± 0.02	0.99 ± 0.05	1.30 ± 0.13	(2)[b]	2.50 ± 0.24
^{15}N	$(T_1^{-1}{}_{obsd}/p) \times 10^{-3}$, s			1.33	1.74	2.84	4.84	
^{14}N	$\Delta\nu_{obsd}/\nu_0 p$,[a] ppm			2427	2604	3334	6333	7861
	$(T_2^{-1}{}_{obsd}/p) \times 10^{-4}$, s			4.9	6.13	8.80	19.48	27.33
	q[c]			0.60 ± 0.14	0.72 ± 0.10	1.04 ± 0.13	(2)[b]	2.64 ± 0.22

[a] Upfield shifts. [b] Reference value (see the text and Figure 1). [c] Mean values obtained from paramagnetic shifts and relaxation rates for ^{13}C and ^{14}N + ^{15}N.

paramagnetic ion are given, in the case where $T_{1e} \neq T_{2e}$, by modified forms[8] of the Bloembergen and Solomon equations[9,10]

$$(T_{1M}^{-1})_k = \frac{2}{15}S(S+1)(\gamma_s\gamma_k\hbar)^2 r_k^{-6}\left[\frac{3\tau_{c_1}}{1+\omega_k^2\tau_{c_1}^2} + \frac{7\tau_{c_2}}{1+\omega_s^2\tau_{c_2}^2}\right] + \frac{2}{3}S(S+1)A_k^2\frac{\tau_{e_2}}{1+\omega_s^2\tau_{e_2}^2} \quad (2)$$

$$(T_{2M}^{-1})_k = \frac{1}{15}S(S+1) \times (\gamma_s\gamma_k\hbar)^2 r_k^{-6}\left[4\tau_{c_1} + \frac{3\tau_{c_1}}{1+\omega_k^2\tau_{c_1}^2} + \frac{13\tau_{c_2}}{1+\omega_s^2\tau_{c_2}^2}\right] + \frac{1}{3}S(S+1)A_k^2\left[\tau_{e_1} + \frac{\tau_{e_2}}{1+\omega_s^2\tau_{e_2}^2}\right] \quad (3)$$

where γ_s is the electron magnetogyric ratio, ω_k and ω_s are the nuclear and electron spin Larmor frequencies, and r_k is the distance of nucleus k to the metal. τ_{c_1}, τ_{c_2}, τ_{e_1}, and τ_{e_2} are correlation times defined by

$$\tau_{c_{1,2}} = \left(\tau_R^{-1} + \tau_{e_{1,2}}^{-1}\right)^{-1} \quad (4)$$

$$\tau_{e_{1,2}} = (T_{1,2e}^{-1} + \tau_h^{-1})^{-1} \quad (5)$$

where τ_R is the reorientation correlation time of the complex, T_{1e} and T_{2e} are the electron spin longitudinal and transverse relaxation times, and τ_h is the residence time of the ligand in the metal coordination sphere. From the estimates of the different correlation times which are given below, it is easily shown that simplified forms of eq 2 and 3 may be used

$$(T_{1M}^{-1})_k = 6.3(\gamma_s\gamma_k\hbar)^2 r_k^{-6}\tau_r \quad (6)$$

$$(T_{2M}^{-1})_k = 7.35(\gamma_s\gamma_k\hbar)^2 r_k^{-6}\tau_r + 5.25A_k^2 T_{1e} \quad (7)$$

In eq 2, 3, and 7 A_k is expressed in rad s^{-1}.

Under fast exchange conditions of a ligand between the solution and the complex, any observable Δ_M, i.e., $\Delta\nu_M$, T_{1M}^{-1}, or T_{2M}^{-1}, is related to a directly measured value Δ_{obsd} by

$$\Delta_{obsd} = \Delta^*_{obsd} - \Delta_0(1 - pq) = \Delta_M pq \quad (8)$$

where Δ^*_{obsd} is the value of Δ_{obsd} before correction for the contribution Δ_0 of the free ligand and q its coordination number in the complex. In the present case, several complexes of general formula $Gd(SCN)_n(H_2O)_{9-n}$ exist simultaneously, and it is easily shown that eq 8 must be rewritten as

$$\Delta_{obsd} = p\,\frac{\sum_1^n i\Delta_{Mi}\beta_i X^i}{1 + \sum_1^n \beta_i X^i} \quad (9a)$$

where $X = [SCN^-]$, β_i is the product $K_1K_2...K_i$ of the stepwise formation constants, and Δ_{Mi} is the value of Δ_M for $q = i$.

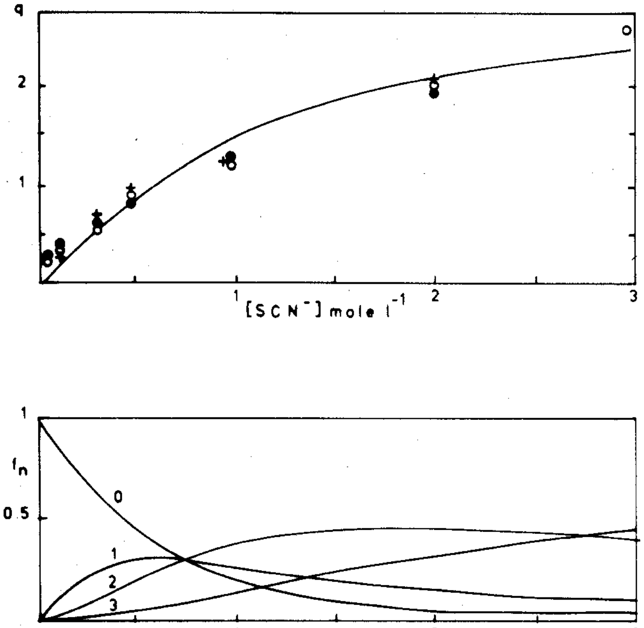

Figure 1. Dependence upon $[SCN^-]$ for the apparent coordination number q and for the molar fraction f_n of $Eu^{3+}[SCN^-]_n\cdot(9-n)H_2O$ complexes with n = 0, 1, 2, and 3. The diagrams are calculated with stability constants $\beta_1 = 1.36$, $\beta_2 = 1.93$, and $\beta_3 = 0.73$ given in ref 3 and confirmed by optical spectroscopy measurements (section III-2). In the upper diagram the experimental points are the mean of the q values obtained from magnetic resonance experiments of aqueous thiocyanate complexes of Gd^{3+} (○), Tb^{3+} (●), and Pr^{3+} (+) (see Tables I and II).

Assuming that Δ_{Mi} is not very dependent upon i, one can define an effective coordination number by

$$q = \frac{\Delta_{obsd}}{\Delta_M p} = \frac{\sum_1^n i\beta_i X^i}{1 + \sum_1^n \beta_i X^i} \quad (9b)$$

The validity of this assumption is proved by the fact that q is nearly independent of the nature of the observable Δ_M (see Table I). In the present study where $X \leq 3$ mol L^{-1}, it may be estimated from the formation constants of some lanthanide and actinide thiocyanate complexes[3] that $n \leq 3$ (Figure 1).

With the ^{13}C and ^{15}N longitudinal relaxations being governed by hyperfine dipolar interactions, the ligand-to-metal distance is obtained from the ratio

$$\frac{r_C}{r_N} = \left(\frac{\gamma_C}{\gamma_N}\right)^{1/3}\left[\frac{(T_{1M})_C}{(T_{1M})_N}\right]^{1/6} \quad (10)$$

Assuming that S–C–N–Gd is linear with C–N = 1.18 Å as in $[U(SCN)_8]^{4-}$[11] one finds N–Gd = 2.52 ± 0.04 Å for 0.3

$< [SCN^-] < 2$ M (Table I), showing that SCN^- forms an inner-sphere complex with Gd^{3+} in this concentration range.

An approximate value of the apparent coordination number q is obtained from eq 6 and 9 where τ_R is given by the Stokes–Einstein relation

$$\tau_R = \frac{4\pi\eta R^3}{3kT} \qquad (11)$$

where R is the mean radius of the complex. $R \simeq 3.2$ Å for $Gd(H_2O)_9{}^{3+}$ at 298 K[12] and may be estimated to 3.6 Å for $q = 2$, taking S–Gd = 4.3 Å. For a 2 M solution of NaSCN in D_2O at 300 K where $\eta = 0.85$ cP, $\tau_R \simeq 4 \times 10^{-11}$ s, and $(T_1{}^{-1}{}_{obsd}/p)_{^{13}C} = 2817$ s^{-1} one finds $q = 1.84$ in reasonable agreement with the value of $q \simeq 2$ calculated from formation constants of some lanthanide and actinide thiocyanate complexes.[3] We have therefore adopted $q = 2$ for $[SCN^-] = 2$ M as a reference value in all our determinations of coordination numbers (Figure 1).

The dependence of the observed paramagnetic shifts and NMR line widths upon the residence time τ_h of the ligand under study is provided by the Swift and Connick equations[13]

$$\Delta\omega_{obsd} = 2\pi(\Delta\nu_{obsd}) = \frac{pq(\Delta\omega_M)}{\tau_h{}^2[(T_{2M}{}^{-1} + \tau_h{}^{-1})^2 + \Delta\omega_M{}^2]} \qquad (12)$$

$$\pi(\Delta\nu_{1/2})_{obsd} = pq\tau_h{}^{-1}\left[\frac{T_{2M}{}^{-1}(T_{2M}{}^{-1} + \tau_h{}^{-1}) + \Delta\omega_M{}^2}{(T_{2M}{}^{-1} + \tau_h{}^{-1})^2 + \Delta\omega_M{}^2}\right] \qquad (13)$$

To eq 12 and 13 correspond the fast-exchange conditions $\tau_h{}^{-1} >> \Delta\omega_M$ and $(\tau_h T_{2M})^{-1} >> \Delta\omega_M{}^2$, respectively. The first condition is well verified under our experimental conditions where most of the measurements have been performed at 300 K. The ^{13}C paramagnetic shifts in parts per million at spectrometer frequencies of 20 and 25 MHz are indeed equal and those of ^{14}N and ^{15}N are likewise nearly equivalent in a field of 23.5 kG (Figure 2). The verification of the second condition is more difficult because of the restricted temperature range ($278 < T < 353$ K), and the residence time τ_h was not determined. Between 300 and 353 K, however, the ratio $(\Delta\nu_{M1/2})_{^{15}N}/(\Delta\nu_{M1/2})_{^{14}N} = 1.9 \pm 0.3$ is close to its upper limit $\gamma_{^{15}N}{}^2/\gamma_{^{14}N}{}^2 = 1.97$ expected in fast-exchange conditions (Figure 2). The calculated dependence of the line width ratios of ^{15}N and ^{14}N upon τ_h using eq 13 (Figure 2) suggests that $\tau_h < 10^{-6}$ s at 300 K and above. The fast-exchange condition $\tau_h << T_{1M}$ is therefore also verified for longitudinal relaxation time measurements.

The dependence of q upon the concentration of thiocyanate from 0.05 to 3 M has been derived from ^{13}C, ^{14}N, and ^{15}N longitudinal and transverse relaxation rates as well as contact shift measurements (eq 9). In this whole concentration range, all methods yield nearly the same values. In particular the ratios of ^{13}C and ^{14}N T_{2M} and $\Delta\nu_M$ are constant from 0.3 to 3 M confirming that the same kind of complexes, namely, inner-sphere complexes, exist at these concentrations. Below $[SCN^-] = 0.3$ M where ^{14}N and ^{15}N NMR measurements become inaccurate, the ratios T_{1M}/T_{2M} and $\Delta\nu_M/T_{2M}$ obtained for ^{13}C are nearly the same as for higher concentrations where the formation of inner-sphere complexes is unambiguously demonstrated (Table I).

The comparison of ^{15}N $T_{1M}{}^{-1}$ and $T_{2M}{}^{-1}$ relaxation rates (Table I) indicates that the dipolar contribution to $T_{2M}{}^{-1}$ is only of ca. 3% and therefore that the transverse relaxation of ^{15}N is dominated by the scalar term (eq 7). The electron spin relaxation time T_{1e} is then given by

$$T_{1e} \simeq 3[T_{2M}S(S + 1)A_k{}^2]^{-1} \qquad (14)$$

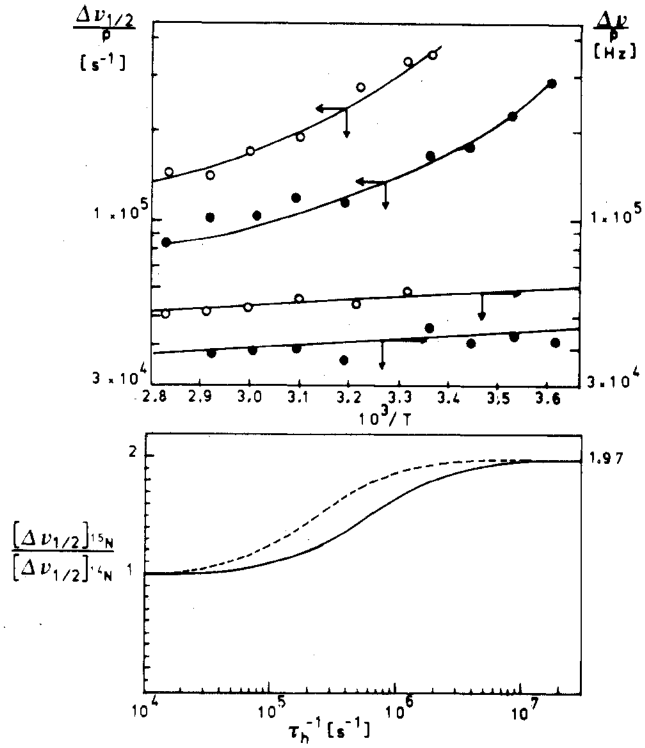

Figure 2. Upper diagram: temperature dependence of observed ^{15}N (○) and ^{14}N (●) paramagnetic shifts and line widths for $[SCN^-] = 2$ M in the presence of Gd^{3+}. Lower diagram: calculated dependence of the ratio of ^{15}N to ^{14}N line widths upon $\tau_h{}^{-1}$ assuming that $q = 2$ and $(T_{2M}{}^{-1})_{^{14}N} = 3 \times 10^5$ s^{-1} (—) and 3×10^4 s (---) which correspond to the boundary values expected for $T_{2M}{}^{-1}$. The curves have been calculated by eq 13 taking $\Delta\nu_M{}^{^{14}N} = 2 \times 10^4$ Hz.

On the other hand T_{2e}, which is not given by nuclear relaxation measurements, has been derived from the ESR line widths of the complexes under study between 278 and 353 K in a magnetic field of 3.3 kG

$$T_{2e}{}^{-1} = \pi\sqrt{3}\Delta\nu_{ms} \qquad (15)$$

where $\Delta\nu_{ms}$ is the peak to peak separation of the derivative of the Gd^{3+} single absorption line, expressed in hertz. When $S > {}^1/_2$, the electron spin relaxation rates, depending on the modulation of the zero field splitting tensor with a correlation time τ_v, are given by[14]

$$T_{1e}{}^{-1} = K\left[\frac{2\tau_v}{1 + \omega_s{}^2\tau_v{}^2} + \frac{8\tau_v}{1 + 4\omega_s{}^2\tau_v{}^2}\right] \qquad (16)$$

$$T_{2e}{}^{-1} = K\left[3\tau_v + \frac{5\tau_v}{1 + \omega_s{}^2\tau_v{}^2} + \frac{2\tau_v}{1 + 4\omega_s{}^2\tau_v{}^2}\right] \qquad (17)$$

with $K = D^2[4S(S + 1) - 3]$, D being the zero field splitting parameter, and ω_s the electron Larmor frequency equal to 4.13×10^{11} rad s^{-1} in NMR experiments ($H_0 = 23.5$ kG) and to 5.80×10^{10} rad s^{-1} in ESR experiments ($H_0 = 3.3$ kG). The $T_{1e}{}^{-1}$ and $T_{2e}{}^{-1}$ vs. T^{-1} curves given in Figure 3 have been fitted to experimental data taking $\tau_v = 1.76 \times 10^{-14} \exp(3950/RT)$ s and $K = 1.18 \times 10^{20}$ s^{-2} ($D = 7.4 \times 10^{-3}$ cm^{-1}). The values of these parameters are of the same order of magnitude as those reported by Reuben[15] for other Gd(III) complexes in aqueous solution. For a magnetic field of 23.5 kG eq 16 and 17 yield $T_{1e} = 2.9 \times 10^{-9}$ s and $T_{2e} = 3.2 \times 10^{-10}$ s so that the use of simplified expressions 6 and 7 of the Bloembergen–Solomon equations is fully justified. The ^{13}C relaxation measurements at 20 MHz ($H_0 = 18.7$ kG) for concentrations of SCN^- between 0.05 and 3 M yield $T_{1e} = (2.6 \pm 0.5) \times 10^{-9}$ s at 300 K.

2. NMR of Other Lanthanide Thiocyanate Complexes. We have investigated the binding of SCN^- to other lanthanide ions

Table II. Concentration Dependence of Observed Paramagnetic Shifts $\Delta\nu_{\text{obsd}}/p\nu_0$ (ppm) in Aqueous Terbium(III) and Praseodymium(III) Thiocyanate Complexes

		[SCN⁻], mol L⁻¹					
		0.05	0.1	0.3	0.5	1	2
Tb^{3+}	^{13}C	47	73	160	210	306	509
	^{14}N		1295	1886	2454	3545	5667
	q	0.19	0.38 ± 0.12	0.65 ± 0.03	0.85 ± 0.03	1.23 ± 0.04	(2)[b]
Pr^{3+}	$^{13}C^a$		−9.2	−16.0	−21.3	−34.5	−51
	$^{14}N^a$			−183	−212	−289	−498
	q		0.36	0.68 ± 0.07	0.85 ± 0.01	1.26 ± 0.13	(2)[b]

[a] The negative sign correspond to a downfield shift. [b] Reference value.

such as Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Yb^{3+}. The straightforward relaxation method reported for Gd^{3+} complexes to show that SCN^- is in the first coordination sphere does not hold for other lanthanide ions which do not enhance sufficiently nuclear relaxations because of their very short electron spin relaxation times (T_{1e}, $T_{2e} < 10^{-12}$ s at room temperature).

The ^{14}N and ^{13}C paramagnetic shifts induced by Tb^{3+} are close to those found for gadolinium(III) thiocyanate complexes while those of Pr^{3+} complexes are different in magnitude and sign. However, the paramagnetic shift measurement performed on the typical examples of Tb^{3+} and Pr^{3+} for thiocyanate concentrations ranging from 0.05 to 2 M yield virtually the same dependence of q upon SCN^- as in the case of Gd^{3+} (Table II, Figure 1). Moreover the concentration-independent ratios of ^{14}N to ^{13}C paramagnetic shifts are nearly the same for Gd^{3+} (12 ± 2.0), Tb^{3+} (11.5 ± 0.3), and Pr^{3+} (9.9 ± 1.2). That seems to us an evidence that, most likely, all the lanthanide ions examined here form inner-sphere complexes with SCN^- under our experimental conditions. The differences nevertheless observed between the ratio $\Delta\nu_{^{14}N}/\Delta\nu_{^{13}C}$ of the complexes under study may be attributed to variable contributions of the pseudocontact shift $\Delta\nu_2$ which is given by[16]

$$\frac{\Delta\nu_2^{\,k}}{\nu_0^{\,k}} = -\frac{[g^2\beta^2 J(J+1)(2J-1)(2J+3)]}{60(kT)^2 r_k^{\,-3}}F \qquad (18)$$

with $F = D_z[3\cos^2\theta - 1] + (D_x - D_y)\sin^2\theta\cos^2\theta$ where $D_{x,y,z}$ are the principal values of the zero field splitting tensor and θ is the angle between the metal nucleus vector and the z axis. In the present case where ^{13}C, ^{14}N, and the metal ions are aligned, the angular factor F is the same for both nuclei and we have

$$\frac{\Delta\nu_2^{\,N}}{\Delta\nu_2^{\,C}}\,\frac{\nu_0^{\,C}}{\nu_0^{\,N}} = \left(\frac{r_C}{r_N}\right)^3 = R_2 \qquad (19)$$

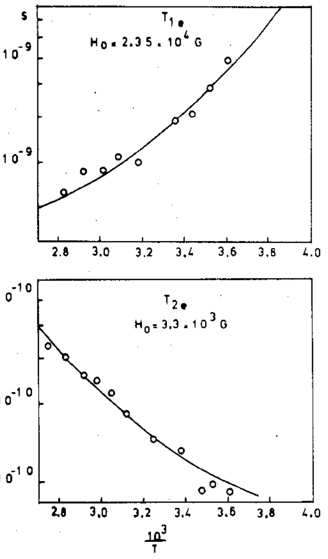

Figure 3. T_{1e} and T_{2e} electron spin relaxation times determined from ^{14}N line widths (eq 14) and ESR line widths (eq 15) for Gd^{3+} with $[SCN^-] = 2$ M. The curves are calculated by means of eq 16 and 17 with parameters given in the text.

The contact and pseudocontact contributions to the ^{14}N and ^{13}C paramagnetic shifts have been tentatively separated using the same procedure as Reuben and Fiat in their study of the coordination of water to lanthanide ions.[17] R_1 being the ratio of contact shifts $(\Delta\nu_1^{\,N}/\Delta\nu_1^{\,C})(\nu_0^{\,C}/\nu_0^{\,N})$, we have

$$\Delta\nu_M^{\,C} = \Delta\nu_1^{\,C} + \Delta\nu_2^{\,C} \qquad \Delta\nu_M^{\,N} = \Delta\nu_1^{\,N} + \Delta\nu_2^{\,N}$$

$$\frac{\Delta\nu_2^{\,C}}{\nu_0^{\,C}} = \frac{\Delta\nu_M^{\,N}/\nu_0^{\,N} - R_1\Delta\nu_M^{\,C}/\nu_0^{\,C}}{R_2 - R_1} \qquad (20)$$

$$\Delta\nu_2^{\,N}/\nu_0^{\,N} = \frac{\Delta\nu_M^{\,C}/\nu_0^{\,C} - (1/R_1)(\Delta\nu_M^{\,N}/\nu_0^{\,N})}{R_2^{\,-1} - R_1^{\,-1}}$$

We have taken $R_1 = 12$ and $R_2 = 3.2$ ($N{-}Ln^{3+} = 2.5$ Å) as in the case of Gd^{3+}. The results obtained in standard conditions ($[SCN^-] = 2$ M, $T = 300$ K) for all the lanthanides under study are given in Table III. It appears that ^{14}N and to a less extent ^{13}C paramagnetic shifts are dominated by the contact term which, in the case where quantum numbers S and J are different, is given by

$$\frac{\Delta\nu_1^{\,k}}{\nu_0^{\,k}} = -\frac{2\pi\beta A_k g(g-1)J(J+1)}{3kT\gamma_k} \qquad (21)$$

In the case of Eu^{3+} where $J = 0$ in the ground state the observed shifts result from the admixture of $J = 1$ and $J = 2$ excited states.[16] For the other lanthanides, only the ground state is populated at room temperature and the spin densities

Table III. Paramagnetic Shifts (ppm), Hyperfine Coupling Constants, and Spin Densities in $[Ln(SCN)_2]^+$ Aquo Complexes[a]

	Pr^{3+}	Nd^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Yb^{3+}
$\Delta\nu_{\text{obsd}}{}^{13}C/\nu_0 p$ (overall)	−51[c]	−79[c]	177	525	509	390	254	23
$\Delta\nu_{\text{obsd}}{}^{13}C/\nu_0 p$ (contact)	−36	−50	144	525	454	390	300	27
$A\,^{13}C$, MHz	−0.081	−0.073		−0.119	−0.103	−0.099	−0.096	−0.075
$\rho_{2s}\,^{13}C \times 10^4$	−1.71	−1.75		−2.21	−2.76	−3.93	−4.06	−1.40
$\Delta\nu_{\text{obsd}}{}^{14}N/\nu_0 p$ (overall)	−488	−695	1845	6333	5667	4720	3480	314
$\Delta\nu_{\text{obsd}}{}^{14}N/\nu_0 p$ (contact)	−440	−602	1739	6333	5491	4720	3627	327
$A\,^{14}N$, MHz	−0.28	−0.25		−0.42	−0.36	−0.35	−0.33	−0.26
$\rho_{2s}\,^{14}N \times 10^3$	−1.24	−1.25		−1.63	−2.40	−2.92	−2.93	−1.01
$\rho_{2s}\,^{17}O \times 10^3$ in $Ln^{3+}(H_2O)_9$[b]	−1.45	−1.34		−1.07	−1.94	−2.10	−2.39	−0.86

[a] Obtained from 2 M [SCN⁻] solutions at 300 K, assuming that $q = 2$. [b] Given in ref 17. [c] The negative sign corresponds to downfield paramagnetic shifts.

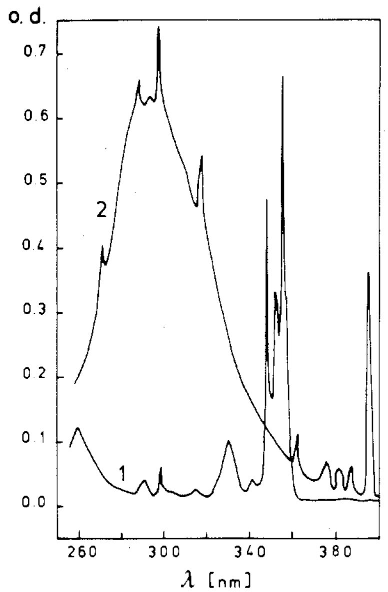

Figure 4. UV absorption spectra: (1) [Nd^{3+}] 0.12 M and [SCN^-] 0.23 M; (2) [Eu^{3+}] 0.25 M and [SCN^-] 0.062 M.

in carbon and nitrogen 2s orbitals are related to the hyperfine coupling constants by[18]

$$\rho_{2s} = 2JA_k/A_{2s}^{k} \qquad (22)$$

with $A_{2s}^{^{14}N} \simeq 1800$ MHz and $A_{2s}^{^{13}C} \simeq 3760$ MHz.[19] The sign of A_k depends upon $g - 1$ and corresponds to negative spin densities in carbon and nitrogen 2s orbitals. The s spin density on carbon is only 10% that of nitrogen and possibly less on sulfur if, as it seems likely, the delocalization of the electron spin in the thiocyanate ligand occurs through σ bonds. It may be pointed out in Table III that the spin densities on nitrogen are of an order of magnitude comparable to those reported[17] for the oxygen of water coordinated to the same lanthanide ions, showing that there are no significant differences between the covalent character of the binding of H_2O and SCN^- to Ln^{3+}. This is further evidence that thiocyanate ions form inner-sphere complexes with Ln^{3+}. The substitution of H_2O (or D_2O) by SCN^- in the first coordination sphere seems therefore to result mainly from Coulombic interactions.

3. UV and Raman Spectroscopy. In order to confirm the results of our NMR study showing that lanthanide thiocyanate complexes are mostly inner sphere, we have investigated the Eu^{3+}–SCN^- complexes by UV and laser Raman spectroscopies.

It has been shown that charge-transfer bands appear in the near-UV region of the spectra of inner-sphere halide complexes of lanthanides.[20-22] The energies at which the bands are observed have been correlated to the oxidation potentials of the Ln^{3+}–Ln^{2+} couple.[20,23] For a given ligand, the most easily reducible trivalent ion will have the charge-transfer band of lowest energy. It appears therefore that among the lanthanide ions the most easily observable charge-transfer band of inner-sphere complexes will be that of europium. One of the recorded UV spectra of europium(III) thiocyanic solutions is shown in Figure 4 together with the spectrum of Nd^{3+} in favorable conditions for charge transfer. We can see a band attributable to charge transfer only in the Eu^{3+} spectrum. This band may be assigned to the hydrated $Eu(SCN)^{2+}$ species because of the excess of Eu^{3+} with respect to SCN^- ions and of the value of the formation constant of the dithiocyanate complex deduced from extraction data.[3] The formation constant of $Eu(SCN)^{2+}$ has been determined from the charge-transfer band intensities according to the method reported by Ahrland.[24] We found thus $\beta_1 = 1.3 \pm 0.3$ in agreement with the value obtained by solvent extraction.[3] The latter method, giving the overall stability constant, is further evidence that the $Eu(SCN)^{2+}$ complex is mostly inner sphere.

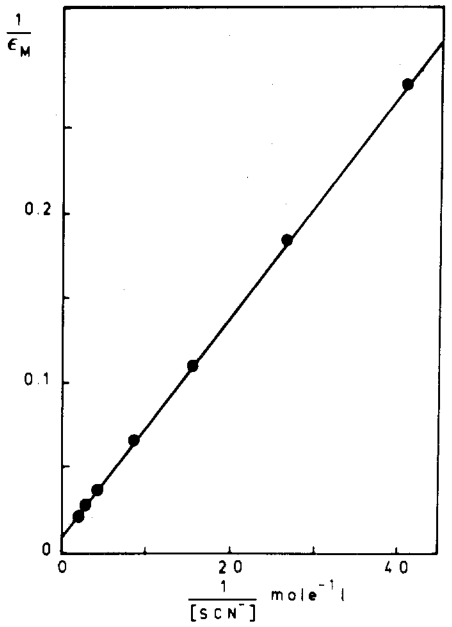

Figure 5. Benesi–Hildebrand plot for the Eu^{3+}–SCN^- charge-transfer band.

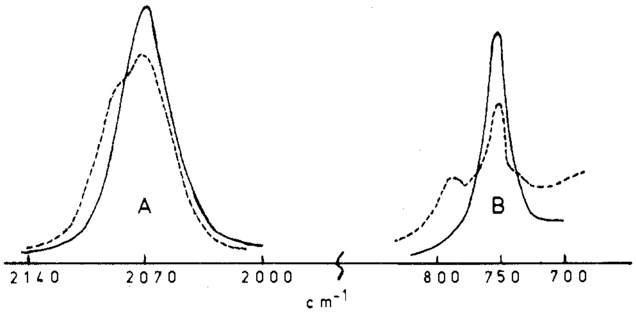

Figure 6. Raman spectra of free and coordinated SCN^- ions: solid lines, 0.5 M NaSCN; dotted lines, 0.5 M NaSCN + 0.5 M $Eu(ClO_4)_3$; A, C≡N stretching; B, C—S stretching.

In order to verify that the contact charge transfer[25] is negligible, we made a Benesi–Hildebrand plot of $1/\epsilon_M$ vs. $1/X$, where ϵ_M is the apparent molar extinction coefficient of Eu for the charge-transfer band and X is the concentration of free SCN^- ions (Figure 5). The fact that the straight line does not pass through the origin may be attributed to the complex charge transfer. In addition, we verified that ϵ_M decreases slowly with temperature as expected from the weak negative value of the enthalpy of formation of the complex.[6] Between 278 and 313 K, ϵ_M decreases by about 2% whereas it would be likely to increase if the contact charge transfer would be responsible for the absorption band.[25]

It may be safely assumed that the energies of C≡N or C—S stretching will be affected differently by the formation of outer- or inner-sphere thiocyanate complexes.[26] We recorded therefore laser Raman spectra of europium(III) thiocyanate solutions with a large excess of Eu^{3+} to have only the $Eu(SCN)^{2+}$ complex in solution (Figure 6). The deconvolution of these spectra shows that $Eu(SCN)^{2+}$ has two emission bands at 2088 and 787 cm^{-1} attributable to C≡N and C—S stretching, respectively. For free SCN^- solutions these bands are located at 2068 and 752 cm^{-1}.

For the complex under study the wavenumbers of the stretching bands are quite comparable to those found in the case of the inner-sphere $Eu(SCN)_6^{3-}$ complex[27] which is stable in nonaqueous solutions. From the results of the deconvolution of the spectra obtained for different values of [Eu^{3+}]/[SCN^-], we obtained $\beta_1 = 1.0 \pm 0.5$ for the formation constant of $Eu(SCN)^{2+}$ in agreement with the results of solvent extraction[3] and UV spectroscopy. In the complex, the C–S stretching band is shifted to higher wavenumbers compared to free SCN^-. This behavior has been correlated with the coordination of SCN^- through the nitrogen.[28] When S is the donor atom, the C–S stretching is observed at lower wavenumbers.

IV. Conclusion

The NMR, UV, and Raman experiments reported in this work concur to show that the binding of thiocyanate ions to trivalent lanthanide ions gives rise to inner-sphere complexes. The NMR spectroscopy indicates in particular that the spin density delocalized from the metal ions to the directly bonded nitrogen atom of the SCN^- ligand is of the same order as that found for oxygen in the water solvation molecules.[17] A similar situation was found in the case of cobalt(II) aqueous thiocyanate complexes[29] except that the spin density transferred from Co(II) to nitrogen is of an order of magnitude higher than that reported here for Ln(III) SCN^- complexes.

The disagreement between the conclusions of this work and those of other authors[3–6] concerning the nature of lanthanide(III) thiocyanate complexes is possibly due to the difficulty to deduce this nature from the variation of thermodynamic constants. In the case of thiocyanato complexes, these constants are indeed very small ($\Delta H = 0.8$ kcal mol^{-1}, $\Delta S = 4.6$ cal deg^{-1} mol^{-1} [6]) and the experimental uncertainties are probably important as shown by the discrepancies between the values reported in different works.[3,6] Moreover, the variations of thermodynamic constants result from a large number of effects so that the semiempirical rules[30] relating the sign of these constants to the nature of the complexes are not necessarily valid in the case of the weak thiocyanate complexes.

Registry No. $[Pr(SCN)_2(H_2O)_7]^+$, 67905-00-4; $[Nd(SCN)_2(H_2O)_7]^+$, 67905-01-5; $[Eu(SCN)_2(H_2O)_7]^+$, 67905-02-6; $[Gd(SCN)_2(H_2O)_7]^+$, 67905-03-7; $[Tb(SCN)_2(H_2O)_7]^+$, 67905-04-8; $[Dy(SCN)_2(H_2O)_7]^+$, 67905-05-9; $[Ho(SCN)_2(H_2O)_7]^+$, 67905-06-0; $[Yb(SCN)_2(H_2O)_7]^+$, 67905-07-1; ^{13}C, 14762-74-4; SCN^-, 302-04-5.

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Contribution from the Departments of Chemistry, Southern Illinois University at Carbondale, Carbondale, Illinois,
and University of Vermont, Burlington, Vermont 05401

Comparison of the Electrochemical Properties and Electron Spin Resonance Spectra of Thio and Imino Chelates

FRED C. SENFTLEBER and WILLIAM E. GEIGER, JR.*

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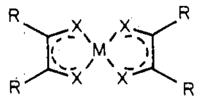
Electrochemical reduction and oxidation of square-planar nickel, palladium, and platinum complexes of the bidentate ligand $(NH)_2C_2(CN)^{2-}$ have been accomplished. The general electron-transfer series $MN_4^+ \rightleftharpoons MN_4^0 \rightleftharpoons MN_4^- \rightleftharpoons MN_4^{2-}$ is detected, where N_4 stands for 2 mol of the ligand. Cyclic voltammetry and phase-selective ac polarography establish the electron-transfer steps as rapid and reversible. Visible and near-IR spectra of the anions are greatly similar to those observed previously for the corresponding MS_4^- complexes, in which sulfur replaces NH in the chelate structure. Electron spin resonance spectra of the anions show that the half-filled orbital is highly delocalized over the chelate structure, and metal hyperfine splittings suggest that, in PtN_4^-, the unpaired electron is more *ligand localized* than in PtS_4^-. An unequivocal determination of the electronic ground states of these complexes could not be made, but the ESR spectra are more consistent with the ^2A_g ground state than with the $^2B_{2g}$ ground state formed for the analogous dithiolate chelates.

Square-planar metal dithiolate complexes which undergo reversible electron-transfer reactions have been widely studied.[1] Syntheses of analogous chelates with other donor groups (e.g., O or NH) have been reported,[2–8] but characterization of the electron-transfer properties and electronic structures of these complexes has been less complete. Reductions of imino or oxo complexes are more difficult to achieve since these complexes have a lower electron affinity than the thio chelates[2–4] and at



1, X = NH
2, X = S
3, X = O

* To whom correspondence should be addressed at the University of Vermont.