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Oxidation of Thiocyanate by Thallium(III) in Aqueous Solution Studied by Multinuclear NMR Spectroscopy. Evidence for a $Tl(SCN)^{2+}$ Intermediate

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Thallium(III) in aqueous solution is known to be a strong oxidant.[2,3] The thiocyanate ion forms strong complexes with several metal ions, including d^{10} ions. It is generally assumed that pseudohalide ions, with their reducing properties, cannot exist in solutions containing thallium(III), since they undergo an immediate oxidation. For thiocyanate ion, the following reaction was found to occur:[4]

$$4SCN^- + 3TlCl_3 + 4H_2O \rightleftharpoons HCN + 3TlSCN(s) + SO_4^{2-} + 9Cl^- + 7H^+ \quad (1)$$

About 20 years ago, the kinetics of this redox reaction was studied by means of polarography.[5] On the basis of the dependence of the rate of the reaction on the concentrations of thallium(III) and thiocyanate, Treindl and Fico suggested[5] that the reaction proceeds through a short-lived intermediate with the composition $Tl(SCN)Tl^{5+}$. Species like $Tl_2(SCN)_n^{6-n}$ were also proposed to exist. Recently, Gupta et al.[6] performed a similar kinetic investigation and proposed the existence of the complexes $Tl(SCN)^{2+}$, $Tl(SCN)_2^+$, $Tl_2(SCN)^{5+}$, $Tl_2(SCN)_2^{4+}$ or $\{Tl(SCN)\}_2^{4+}$, and $HTl(SCN)_2^{2+}$. These proposals are surprising, since polynuclear thallium(III) species have never been reported in aqueous solution.[2,3]

Having in our hands the new powerful experimental technique of multinuclear NMR spectroscopy and encouraged by our recent discovery that, contrary to the accepted opinion,[3] thallium(III) cyanide complexes in aqueous solution exist and are extremely strong and stable,[7] we wanted to see if we could find and characterize the suggested[5,6] (or any other) reaction intermediates in the course of the redox reaction between Tl(III) and thiocyanate.

The previous authors[5] used $TlCl_3$ as a source of thallium(III). Chloride ions complicate the chemistry of the system, since their presence may cause formation of several types of complexes, such as $TlCl_n^{3-n}$,[8] $Tl(CN)_mCl_n^{3-m-n}$,[9] etc. In order to simplify the chemical system, our starting solutions contained only $Tl(ClO_4)_3$ in $HClO_4$.

Experimental Section

Materials. The stock solution of 1 M $Tl(ClO_4)_3$ was obtained by anodic oxidation of $TlClO_4$.[10] ^{13}C-enriched NaSCN was prepared by mixing, grinding, and gently fusing 1 mmol of ^{13}C-enriched NaCN (Cambridge Isotope Laboratories, Woburn, MA) with 1 mmol of sulfur and 0.25 mmol of NaSCN. After continued heating in order to remove excess sulfur, the melt was cooled and dissolved in water. This procedure resulted in NaSCN enriched 75% in ^{13}C. ^{15}N-enriched NaSCN (99%) was purchased from MSD Isotopes, Montreal. The stock solution of thallium(III) was then mixed at 0 °C with the appropriate stock solution of sodium thiocyanate (0.040 M) and 3 M $HClO_4$, giving the following concentrations at the beginning of the reaction: $[Tl(III)] = 0.17$ M, $[SCN^-] = 0.025$ M, and $[H^+] = 0.52$ M. The ionic strength was kept approximately constant by means of $LiClO_4$ ($[Li^+] + [H^+] \sim 3$ M).

Analyses. The determination of the concentrations of Tl(I), Tl(III), and H^+ was performed as before.[7] Sulfate was determined as $BaSO_4$(s).

NMR Measurements. All NMR measurements were performed on a Bruker AM400 spectrometer at a probe temperature of 0 (±0.5) °C.

^{205}Tl NMR spectra were recorded at 230.8 MHz with typical NMR parameters: flip angle ~ 15°; spectral window = 125 kHz; pulse repetition time = 0.1 s; 7.5 Hz/point. The chemical shifts are reported in ppm toward higher frequency with respect to an external aqueous solution of $TlClO_4$ extrapolated to infinite dilution.

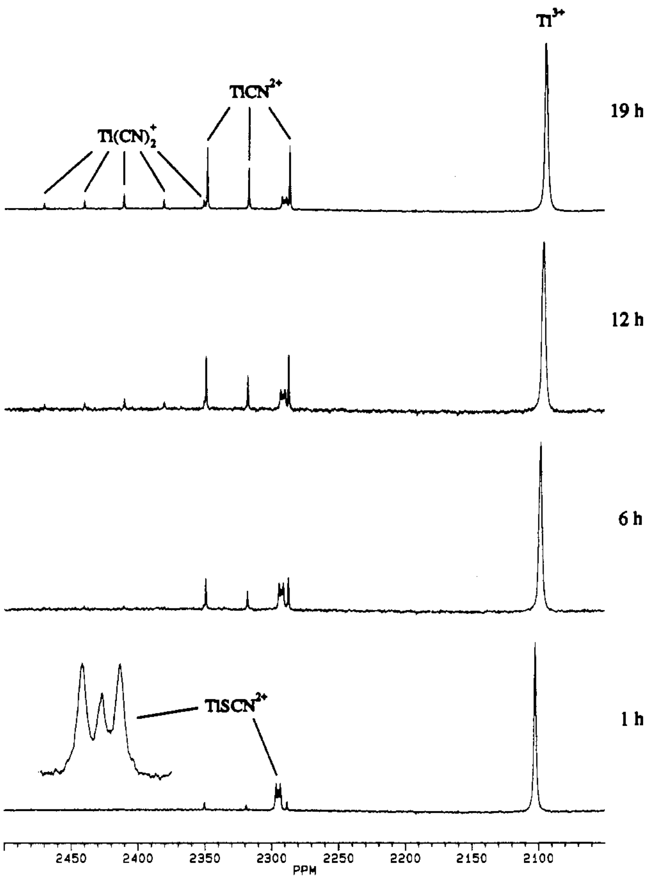

Figure 1. ^{205}Tl NMR spectra of a solution with a starting composition of $[Tl(III)] = 0.17$ M, $[SCN^-] = 0.025$ M, and $[H^+] = 0.52$ M (SCN enriched to about 75% in ^{13}C) as a function of the reaction time (in hours) at 0 °C. The inset shows the expansion of the peak attributed to $Tl(SCN)^{2+}$, showing multiplet structure caused by the spin–spin coupling between ^{205}Tl and ^{13}C in the partially enriched solution. The chemical shifts are reported in ppm toward higher frequency with respect to an external aqueous solution of $TlClO_4$ extrapolated to infinite dilution.

^{13}C NMR spectra were recorded at 100.6 MHz with typical NMR parameters: flip angle ~ 20°; spectral window = 17 kHz; pulse repetition time = 1 s; 2.1 Hz/point. The chemical shifts are reported in ppm toward higher frequency with respect to external TMS.

^{15}N NMR spectra were recorded at 40.55 MHz with typical NMR parameters: flip angle ~ 90°; spectral window = 5 kHz; pulse repetition time = 30 s; 0.15 Hz/point. The chemical shifts are reported in ppm toward higher frequency with respect to an external solution of $NaSC^{15}N$ (32 mM, 0 °C) at 0 ppm, corresponding to +203.5 ppm from neat NH_3 (25 °C). (The signal from an external solution of 32 mM $NaSC^{15}N$ at 25 °C is observed at +1.06 ppm from the same solution at 0 °C).

Results and Discussion

Under the conditions of the present study, chemical analysis shows that the reaction

$$SCN^- + 3Tl^{3+} + 4H_2O \rightleftharpoons HCN + 3Tl^+ + SO_4^{2-} + 7H^+ \quad (2)$$

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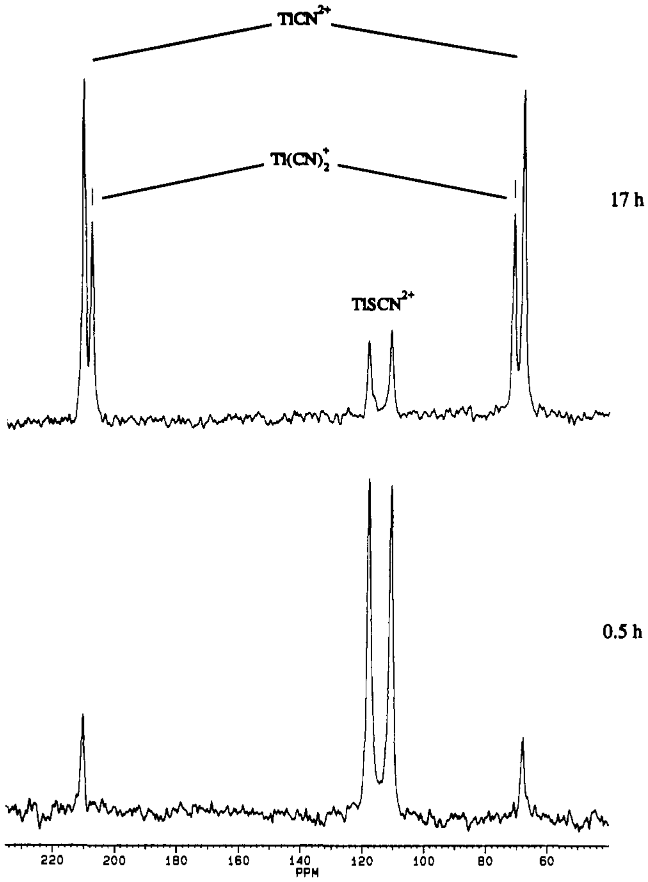

Figure 2. ^{13}C NMR spectra of a solution with the same composition as that in Figure 1 as a function of the reaction time (in hours) at 0 °C. The chemical shifts are reported in ppm toward higher frequency with respect to external TMS.

is quantitative within the experimental error, in agreement with previous studies.[4-6] When excess thiocyanate is added, the reaction is complete within a few minutes at room temperature. When thallium is in excess, the reaction is slightly slower (about 30 min at 25 °C) but takes many hours at 0 °C, thus permitting the recording of NMR spectra. ^{205}Tl and ^{13}C NMR spectra of solutions prepared by mixing a stock solution of thallium(III) perchlorate and ^{13}C-enriched (to about 75% ^{13}C) thiocyanate are shown as a function of the reaction time in Figures 1 and 2.

Equation 2 represents the gross reaction. The starting solution of thallium(III) perchlorate shows only one ^{205}Tl NMR signal, namely that from Tl_{aq}^{3+} at about 2101 ppm. Directly after addition of SCN$^-$ a new peak at roughly -200 ppm can be observed, originating from thallium(I). This peak grows during the course of the reaction (and its chemical shift changes slightly) until all thiocyanate is consumed. The peak of the Tl_{aq}^{3+} broadens and moves slowly to lower frequency and its intensity decreases. These effects are due to (1) formation of thallium(III) sulfate complexes in fast exchange with Tl_{aq}^{3+} (as can be shown by recording separate ^{205}Tl NMR spectra from solutions containing only Tl_{aq}^{3+} and sulfate). These complexes have previously been identified by means of potentiometry[11a] but never observed directly, (2) formation of thallium(III) cyanide complexes[7], and (3) gradual reduction of thallium(III) to thallium(I).

As can be seen in Figure 1, several Tl(III)-containing species are formed in the solution. The species Tl_{aq}^{3+} (at 2101 ppm), $Tl(CN)^{2+}$ (at 2316 ppm, $J_{Tl-C} \sim 14400$ Hz), and $Tl(CN)_2^+$ (at 2410 ppm, $J_{Tl-C} = 13800$ Hz) are known from our earlier studies,[7,8a] but the peak at about 2290 ppm (line width ~180 Hz) showing a spin-spin coupling pattern remains unidentified. This signal can be attributed to the species $Tl(SCN)^{2+}$, and the multiplet is explained by the presence of the species $Tl(S^{12}CN)^{2+}$ (central peak; ~25% of the total SCN concentration) and $Tl(S^{13}CN)^{2+}$ (the two remaining peaks; a doublet arises because of spin-spin coupling to the ^{13}C with spin $^1/_2$; 75% of the SCN). This finding could also be confirmed by means of ^{13}C spectra for the same solution (Figure 2). Besides the signals for the complexes $Tl(CN)_n^{3-n}$ ($n = 1, 2$), the ^{13}C spectra show also a doublet at 114.15 ppm with a $^{13}C-^{205}Tl$ spin-spin coupling constant equal to 733 Hz and a line width of ~100 Hz.

Only a lower limit of the stability constant for $TlSCN^{2+}$ at 0 °C could be estimated from the ^{13}C NMR spectra; $\log K_1 > 2$. A better estimate can be made by the comparison with the corresponding mercury(II) complex. Mercury(II) is isoelectronic to thallium(III), and these two "soft"[3,12] metal ions often show similar behavior toward ligands in solution. For Hg(II), the stability constant for $Hg(SCN)^+$ is $\log K_1 = 9.08$.[11b] Assuming that the difference $\log K_1(Hg) - \log K_1(Tl)$ is similar for the thiocyanate complexes and for the cyanide complexes, we obtain for $Tl(SCN)^{2+}$ $\log K_1 = 5.3$. However, since the cyanide ligand is considered to be softer than thiocyanate, the value of $\log K_1$ for $Tl(SCN)^{2+}$ is probably higher, say about 7.[13]

The thiocyanate ligand is known to exhibit linkage isomerism.[14] Metal ions can be coordinated either via the S or the N atom. For the soft thallium(III) ion,[3,12] we expect S-bonding, as has been found for mercury(II) and other soft metal ions.[14] In order to confirm this assumption, we wanted to determine the spin-spin coupling constant $J(^{205}Tl-^{14}N)$ by means of ^{14}N NMR spectroscopy. However, ^{14}N NMR spectra were not informative. Using ^{15}N-enriched thiocyanate, we were able to determine the spin-spin coupling constant $J(^{205}Tl-^{15}N)$ to be 143 (±3) Hz, using both ^{205}Tl and ^{15}N NMR spectroscopy.

For the Pt(II)-SCN complexes both N-bonding and S-bonding of thiocyanate to the metal has been observed.[15] In the case of N-bonding, the coupling constants $^1J(^{195}Pt-^{15}N)$ are ~550 Hz. In the case of S-bonding, the corresponding constants are ~12 Hz. For comparison with the thallium(III) thiocyanate complex, these values should be multiplied by the ratio between the magnetogyric factors ($\gamma(^{205}Tl)/\gamma(^{195}Pt) = 2.684$). The expected values for the spin-spin coupling constants, $J(^{205}Tl,^{15}N)$, are then ~1500 and ~30 Hz, respectively. However, the thallium thiocyanate complexes are probably stronger than those of platinum (there are no stability constants determined for thallium and platinum thiocyanate complexes, but the chloride and bromide complexes (TlX_n^{3-n}, $n = 1-4$) of thallium are stronger than those of platinum (PtX_n^{2-n}, $n = 1-4$)), and this fact should cause an additional increase of the values of $J(^{205}Tl-^{15}N)$. Thus, our measured value, 143 Hz, supports the assumption that the SCN$^-$ is bonded to Tl(III) through sulfur.

A better way of determining the kind of bonding seems to be ^{15}N NMR chemical shift. As has been shown by Pregosin et al.,[15] N-bonding leads to a lower shift compared to the shift of the free SCN$^-$, whereas S-bonding leads to a moderately higher shift. At 0 °C, the measured ^{15}N shift for the thallium thiocyanate complex is +50.2 ppm (line width ~70 Hz) from 0.032 M $NaSC^{15}N$ (line width = 1.7 Hz), thus showing that the thiocyanate is sulfur-coordinated to thallium(III). This is confirmed by the fact that the ^{13}C-NMR chemical shift for the complex, 114.15 ppm, is in

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the low end of the S-bonded range reported by Burmeister.[16]

The concentration of the $Tl(SCN)^{2+}$ complex is large at the beginning of the redox reaction and decreases gradually with concomitant formation of thallium(III) cyanide complexes[17] and thallium(I). We have not been able to find any other Tl(III)–SCN^--containing species in the investigated solutions.[18] The redox reaction between thallium(III) and thiocyanate was suggested[5] to proceed through a short-lived binuclear intermediate, $Tl(SCN)Tl^{5+}$. Even if we cannot rule out that this species is so short-lived that it escapes discovery by means of NMR spectroscopy, it seems probable that $Tl(SCN)^{2+}$ is the predominant reaction intermediate. This is in agreement with the suggestion of Gupta et al.[6] that the rate of the reaction (2) is proportional to $[Tl(SCN)^{2+}]^2$. However, their conclusions concerning the composition of other Tl(III)–SCN^- species as well as their mechanistic suggestions should probably be modified, since they have not considered the existence of complexes between Tl(III) and cyanide/sulfate.[7,17]

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(17) At 25 °C, ^{15}N NMR parameters for these cyanide complexes are as follows. $TlCN^{2+}$: $\delta = 75.9_4$ ppm (from an external 0.032 M aqueous solution of NaSCN at 0 °C); $^2J(^{205}Tl-^{15}N) = 54$ Hz; line width = ~5 Hz. $Tl(CN)_2^+$: $\delta = 75.8_9$ ppm; $^2J(^{205}Tl-^{15}N) = 108$ Hz; line width = ~6 Hz.

(18) However, at least one more species containing thallium(III) and SCN was observed by means of ^{205}Tl NMR spectroscopy in solutions prepared by mixing a solution containing Tl(III) in the form of $Tl(CN)_2^+$ and $Tl(CN)_3$ and a solution of sodium thiocyanate. This species was assigned to $Tl(CN)_2(SCN)$ and was found to be in fast exchange with $Tl(CN)_2^+$. The redox reaction in such solutions was much slower (several days at room temperature) because Tl(III) is protected by the strong complex formation with cyanide.[7]

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Platinum(II) Binding to the N1 and N7 Ring Nitrogens of Guanosine. Kinetics of Complexation of Aquated Pt^{II}(dien) with 1- and 7-Methylguanosines

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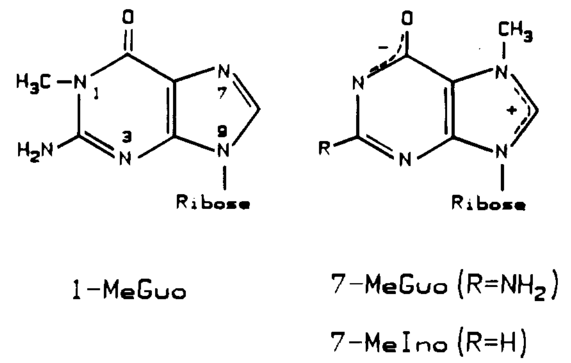
Pt(II) exhibits a marked tendency to bind 6-oxopurine nucleosides through the N7 ring nitrogen, particularly in acidic medium.[1] With increasing pH, however, coordination also to the more basic N1 position becomes possible upon deprotonation of N1H. Despite the intensive study in recent years, no quantitative data appear to exist about the relative binding ability of these sites in the guanine moiety, although this nucleobase represents the main target of anticancer Pt drugs in cellular DNA.[1,2] Recently we have used kinetic approach to study the pH-dependent distribution of mono- and bifunctional Pt(II) between the N1 and N7 ring nitrogens in the hypoxanthine moiety.[3,4] In the case of bifunctional Pt(II), in particular, quantitative estimation of various binding modes becomes rather complicated at higher pH due to the multisite binding behavior of the ligand.[4] On the other hand, blocking of the N1 site with a methyl group considerably simplifies the complexation pattern.[3,4] This observation prompted us to study the kinetically controlled distribution of monofunctional Pt^{II}(dien) in the guanine moiety by employing N1- and N7-methylated guanosines as model compounds (Chart I).[5] The binding of Pt(II) to these ligands can be related to the formation of a 2:1 Pt–guanosine complex from N1- and N7-bound 1:1 complexes. The validity of this assumption is tested by comparing the complexing ability of the corresponding inosine derivatives to the formation of N1,N7-bound Pt–inosine 2:1 complexes from the various 1:1 complexes.[3]

Chart I



1-MeGuo

7-MeGuo (R=NH_2)

7-MeIno (R=H)

Experimental Section

Materials. *N*-Methyl derivatives of guanosine and inosine were purchased from Sigma and were used as received.[6] Aquated Pt^{II}(dien) was prepared as described previously.[3]

Kinetic Measurements. The complexation of aquated Pt^{II}(dien) with *N*-methyl nucleosides in buffered aqueous solution (pH 4.3–8.3) at 298.2 K was followed by HPLC as described earlier.[3,7] During the kinetic runs, signal height was used as the measure of the concentration. With 1-methylguanosine and 7-methylinosine, the complex formation was studied in excess Pt(II) ($[Pt]_T:[L]_T \geq 20:1$), and the time-dependent concentration of the free ligand gave the pseudo-first-order rate constants, $k'_{1,obs}$, for the formation of 1:1 complexes by eq 1. Here $[L]_0$ is the initial

$$\ln [L]_t = -k'_{1,obs}t + \ln [L]_0 \tag{1}$$

ligand concentration and $[L]_t$ is the concentration at time *t*. In the case of 7-methylguanosine, excess of the ligand provided pseudo-first-order conditions for the formation of the 1:1 complex ($[L]_T:[Pt]_T \geq 20:1$), and the rate constants were obtained by employing least-squares fitting to eq 2. Here $[ML]_t$ is the concentration of the complex at time *t*, and $[ML]_T$

$$[ML]_t = [ML]_T(1 - e^{-k'_{1,obs}t}) \tag{2}$$

is the final concentration. A calibration sample prepared from a known amount of ligand in Pt(II) excess was employed to transform the peak heights of ML into concentrations.

Results and Discussion

Chromatographic analysis revealed the formation of a single reaction product in all Pt(II)–nucleoside mixtures, as seen from Figure 1. In the case of 1-methylguanosine, the product is assumed to be the N7-bound 1:1 complex, analogous to that observed earlier with 1-methylinosine.[3] With 7-methylguanosine and -inosine, the reaction products are assumed to be the N1-bound 1:1 complexes. It is known that soft metal species, such as Pt(II), exclusively bind to the N1 ring nitrogen in N7-alkylated, N9-blocked 6-oxopurines.[8] In all cases, Pt(II) coordination to

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(5) Abbreviations used: MeGuo = methylguanosine; MeIno = methylinosine; Ino = inosine.

(6) The 90% purity of commercial 7-methyguanosine confirmed by UV spectroscopy[17] was taken into account in the concentration of this compound.

(7) The ionic strength was adjusted to 0.1 M with $NaClO_4$.

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