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Investigation into the Nature and Chemistry of $(NSCl)_n$ (n = 1, 3) in Solution Using ^{14}N NMR Spectroscopy, a Useful Routine Tool for the Characterization of Small Sulfur–Nitrogen-Containing Compounds

Sir:

The nature of the $(NSCl)_3/NSCl$ system has been an enigma to workers in the field for many years.[1,2] A recent paper illustrating the complex nature of $(NSCl)_3$ in solution, concluded with the statement "This study draws attention to the need for a better understanding of the species formed from $(NSCl)_3$ in warm solvent. A ^{15}N NMR study of ^{15}N-enriched $(NSCl)_3$ in various solvents at different temperatures should be informative."[3] We describe below such a study, but using routine ^{14}N NMR spectroscopy, and we establish for the first time in solution approximate thermodynamic quantities governing equilibrium 1. We show

$$(NSCl)_3 \rightleftharpoons 3NSCl \qquad (1)$$

$$\Delta H = 65 \pm 13 \text{ kJ mol}^{-1} \qquad \Delta S = 206 \pm 20 \text{ J mol}^{-1} \text{ deg}^{-1}$$

that both the forward and reverse reactions are very kinetically hindered. We discovered that impure $(NSCl)_3$ readily dissociates in solution, and we propose that an impurity acts as a "facilitating agent" for the monomerization of the trimer but not the trimerization of the monomer. Thus, pure $(NSCl)_3$ dissolves in CCl_4 to give 100% trimer, whereas impure $(NSCl)_3$ gives 30% monomer and 70% trimer. This implies that the chemistry of $(NSCl)_3$ in solution is very dependent on its purity, as well as other factors. Therefore, we have established the grounds for the systematic and facile exploration of the chemistry of both the trimer and monomer in solution, both of which are very important reagents in sulfur–nitrogen chemistry.[1,2] In addition, we show by ^{14}N NMR spectroscopy that NSCl undergoes simple cycloaddition reactions with some dienes in SO_2 solution but that it does not form the NS^+ cation, on addition of Ag^+, as has been proposed.[4]

NMR spectroscopy has played only a minor role in sulfur–nitrogen chemistry. This is one of several reasons progress in this fascinating and important area has been relatively slow, despite many recent notable advances.[5-7] There has been some important work on compounds enriched with ^{15}N,[8,9] but this work is by no means routine. Early ^{14}N studies found sulfur–nitrogen-containing compounds gave broad peaks,[10] and various reports have implied a pessimistic future for the utility of ^{14}N NMR in sulfur–nitrogen chemistry.[2,6,8,11] More recently Belton and Woolins, using a high-field instrument, obtained ^{14}N spectra of various sulfur–nitrogen compounds and were able to readily distinguish between chemically different nitrogen atoms.[12] They predicted that ^{14}N (and ^{33}S) NMR would make useful contributions to the study of sulfur–nitrogen chemistry. This work confirms their prediction with respect to ^{14}N NMR. However, ^{15}N studies will be needed when ^{14}N peaks are very broad and when detailed structural information is required from couplings to nitrogen.

The ^{14}N NMR chemical shifts of a variety of chemically important, small sulfur–nitrogen compounds, obtained in nonviscous solvents, are given in Table I. The nitrogen NMR spectra of these compounds have not been previously reported, with the exception of that of $(NSCl)_3$.[8] Characteristic chemical shift ranges were observed for a wide variety of examples of $R\overline{CSNSCR}^+$ ($-14 \leq \delta \leq 16$), $R_2\overline{CSNSCR_2}^+$ ($120 \leq \delta \leq 148$), $R_2\overline{C(CR_2)SNSCR_2}\text{-}\underline{(CR_2)}^+$ ($-307 \leq \delta \leq -286$), and $S{\equiv}N$ ($180 \leq \delta \leq 350$). Solid $S_3N_2(AsF_6)_2$ (0.467 g, 0.93 mmol), containing the $S_3N_2^{2+}$ cation (from vibrational spectra),[13] dissolved in SO_2 (2.19 g) to give a ^{14}N NMR spectra containing only resonances due to NS^+ and SNS^+ in a 1:1 ratio. Thus, the $S_3N_2^{2+}$ cation completely dissociates to NS^+ and SNS^+ at room temperature in SO_2 solution, the process favored by entropy. Relatively large samples (1–5 mmol) are needed for accumulation times of 1 or 2 h. For samples that have only broad resonances ($\Delta\nu \geq 500$ Hz) the accumulation times can be much reduced by shortening the pulse width from 40 to 15 μs. The large samples are not a disadvantage, as we use spinnable 10-mm NMR tubes equipped with a O-ringette type, J. Young, Teflon-in-glass valve as the reaction vessel. Thus, we are able to add and remove reagents and also continually monitor the whole sample in situ.

Our ^{14}N NMR studies were initiated in order to follow the course of our previously reported reaction of $(NSCl)_3$ and $AgAsF_6$ in SO_2 solution,[14] giving $NSAsF_6$ quantitatively. We therefore obtained the ^{14}N NMR spectra of $(NSCl)_3$[26] in CCl_4, $CHCl_3$, and SO_2 solutions, and some of the results are given in Table I. The ^{14}N NMR spectra of $(NSCl)_3$ of high purity (mp 92 °C) at 22

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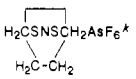
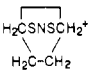
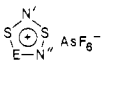
Table I. Chemical Shifts (δ) and Line Widths ($\Delta\nu_{1/2}$) of Sulfur–Nitrogen Compounds[a]

compd	comment	solvent; concn,[b] mmol mL^{-1}	signal to noise ratio[c]	δ	$\Delta\nu^{1/2}$, Hz	assignt[d] (integration, % of signal obsd)
$NSAsF_6$[e]		SO_2; 1.05	90	202	240	NS^+
$SNSAsF_6$[f]		SO_2; 1.14	500	−91	8	SNS^+
NSF[g]		SO_2; 1.05	90	196	48	NSF (80)
NSCl[h]		SO_2; 1.05	40	323	60	NSCl
$N(SCl)_2AsF_6$[i]		SO_2; 0.74	65	19	470	$ClSNSCl^{\bullet}$
$HCSNSCHAsF_6$[j]		SO_2; 0.86	50	−5	350	$HCSNSCH^+$
$H_2CSNSCH_2AsF_6$[k]		SO_2; 0.66	15	134	680	$H_2CSNSCH_2^+$
		SO_2; 0.66	10	−298	600	
	E = SF[l]	SO_2; 0.39	30	−27	350	N′ (~50)
				−173	370	N″ (~50)
	E = SCl[m]	SO_2; 1.12	35	−40	260	N′ (~50)
				−176	470	N″ (~50)
	E = CCH_3[j]	SO_2; 1.86	60	−27	480	N′ (~50)
				126	530	N″ (~50)
	E = $CN'''(CH_3)_2$[n]	SO_2: 0.70	60	−17	236	N′ (33)
				−101	131	N″ (33)
				−266	211	N‴ (33)
$(NSCl)_3$[26]	mp 92 °C	CCl_4; 0.26	20	−262	260	$(NSCl)_3$
		CCl_4; 0.26 (52 °C)[o]	25	−264	199	$(NSCl)_3$ (99)
				350		(NSCl) (1)
		SO_2; 0.28	40	−260	210	$(NSCl)_3$ (65)
				323	60	NSCl (35)
$(NSCl)_3$[27]	mp 75–76 °C	CCl_4; 0.25	40	−264	220	$(NSCl)_3$ (70)
				348	70	NSCl (30)
		CCl_4; 0.25 (70 °C)[o,p]	75	−263	260	$(NSCl)_3$ (30)
				352	80	NSCl (70)
		SO_2; 0.25	400	−259		$(NSCl)_3$ (20)
				323	61	NSCl (80)

[a] The spectra were recorded at 14.450 MHz on a Varian XL-200 spectrometer operating in the FT mode. Chemical shift values are reported on the δ scale with neat nitromethane at 22 °C as an external reference (high-frequency direction positive). Useful spectra could usually be obtained with 20 000 scans (approximately 1 h), a pulse width of 40 μs, 10K data points, and a spectral width of 30 kHz. A line-broadening routine was not applied. The signal to noise ratio could be improved by doing so. [b] Unless stated in parentheses, the experimental temperature was 22 °C. [c] Signal to noise ratio = 2.5[(intensity of strongest peak)/(average intensity of noise)]. [d] Assignments are based on comparison of observed resonance (δ and $\Delta\nu_{1/2}$) with published spectra and by comparison with the other spectra reported above. [e] Prepared according to ref 14. [f] Prepared according to ref 22. [g] Prepared according to ref 13. The ^{14}N NMR spectrum also indicated the presence of five minor resonances (<20% of total ^{14}N signal observed). The ^{19}F NMR spectrum also showed that NSF was the major product in SO_2 solution. [h] Prepared in situ by reaction of $NSAsF_6$ and CsCl in SO_2. [i] Prepared according to ref 23. [j] Prepared according to ref 24. [k] Prepared according to ref 25. [l] Prepared quantitatively from the reaction of $SNSAsF_6$, $NSAsF_6$, and CsF in SO_2 to give a red-black crystalline solid upon solvent removal identified as $S_3N_2FAsF_6$ from elemental analysis and comparison of the IR and ^{19}F NMR spectra with published[20] and unpublished spectra. [m] Prepared quantitatively from the reaction of $SNSAsF_6$ and $(NSCl)_3$ in SO_2 to give a soluble red-brown solid identified as $S_3N_2ClAsF_6$ from elemental analysis and comparison of the IR spectrum with published[20] and unpublished spectra. [n] Prepared quantitatively from the reaction of $SNSAsF_6$ and $(CH_3)_2NCN$ in SO_2 to give a colorless crystalline solid identified as $(CH_3)_2NCSNSNAsF_6$ from elemental analysis and comparison of the IR and NMR spectra with other published spectra.[24] [o] Spectra obtained at room temperature after the solution was held at the stated temperature for not less than 1 h. [p] The IR spectrum of the solid $(NSCl)_3$ recovered on removal of the solvent after the heating cycle was identical with that of the starting material.

°C in CCl_4 and $CHCl_3$ showed only one resonance at −264 and −260 ppm, respectively, in agreement with the reported ^{15}N NMR spectra of $(NSCl)_3$ in $CHCl_3$.[8] A slightly impure sample of $(NSCl)_3$[27] (mp 75 °C), with an IR spectrum of the solid essentially identical with that of purer $(NSCl)_3$, gave a ^{14}N NMR spectrum in CCl_4 solution consistent with the presence of $(NSCl)_3$ (70%) and NSCl (30%) and an IR spectrum in CCl_4 solution that showed peaks attributable to both $(NSCl)_3$ (1017 (vs), 702 (sh), 518 cm^{-1} (m)) and substantial amounts of NSCl (1323 cm^{-1} (s)).[16] From the relative concentrations of monomer and trimer of the less pure $(NSCl)_3$[27] in CCl_4 solution as a function of temperature, the thermodynamic values for reaction 1 in solution were obtained. These values are in general agreement with those obtained by Jolly[17] in the gas phase, although a direct comparison of data obtained in the two phases cannot be made. The extent of monomerization of $(NSCl)_3$ in solutions of recrystallized $(NSCl)_3$[26] in CCl_4 gradually increased from zero to 20%, when the solutions stood for 1 month at room temperature (by ^{14}N NMR). This indicates that the monomerization process is kinetically hindered and that an impurity in the less pure $(NSCl)_3$[27] is acting as a "facilitating agent" for the monomerization process. The extent of monomerization in $(NSCl)_3$[27] solutions decreased very slowly (1–2 weeks) after heating, as observed by Heal.[16] Thus, the monomerization facilitating agent does not speed up the slow trimerization of NSCl. The identity of the facilitator has not yet been established, although we have ruled out Cl^-, NH_4^+, and Cl_2.

Fresh solutions of slightly impure $(NSCl)_3$[27] in SO_2 contained largely NSCl (80%) whereas purer $(NSCl)_3$[26] solutions consisted of $(NSCl)_3$ (60%) and NSCl (40%). These solutions decomposed over time (55% decomposition in 5 h). Stable solutions were formed by the addition of chlorine (20% decomposition in 14 days). Presumably the decomposition involves the dechlorination of $S_3N_3Cl_3$ as observed for $S_3N_2Cl_2$.[18] A third resonance that could be assigned to the dimer $(NSCl)_2$ was not observed in these spectra, in agreement with other work[17] and a recent theoretical study.[19] The reported green color that has been associated with solutions of $(NSCl)_3$[1,2,17] at high temperature was occasionally observed (SO_2 at 22 °C; CCl_4 and $CHCl_3$ at $50 \le T \le 70$ °C), but no additional ^{14}N NMR resonances were apparent.

Relatively large concentrations of NSCl are present in solutions of both pure and less pure $(NSCl)_3$ (see Table I) in SO_2 solution.

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Therefore, it might reasonably be predicted that the chemistry of the mixture would be dominated by the chemistry of NSCl. This is true, in some cases. Thus $(NSCl)_3$[27] and 3 $SNSAsF_6$ react in SO_2 quantitatively to give $ClSSNSNAsF_6$ (see Table I). The reaction likely proceeds by the symmetry-allowed cycloaddition of NSCl with SNS^+, as is observed for $SNSAsF_6$ and NSF leading to $FSSNSNAsF_6$.[20] Solutions of $(NSCl)_3$[27] (0.244 g, 1.01 mmol) in SO_2 (3.37 g) react with the perfluoro diene $F_2CCFCFCF_2$ (0.496 g, 3.06 mmol) to give $ClSCF_2CFCFCF_2N$ quantitatively (^{19}F NMR;[21] ^{14}N NMR δ −263, $\Delta\nu_{1/2}$ = 230 Hz). Presumably the reaction proceeds via the symmetry-allowed Diels–Alder type cycloaddition reported for NSF and the same diene.[21]

In view of the above, it would be reasonable to expect that a mixture of $(NSCl)_3$ in SO_2 (essentially NSCl in SO_2) and 3 $AgAsF_6$ would lead to the rapid formation of 3 AgCl (insoluble in SO_2) and 3 $NSAsF_6$ in solution at room temperature as described by eq 2. In fact, this does not occur. Addition of $AgAsF_6$

$$(NSCl)_3 + 3AgAsF_6 \rightarrow 3AgCl\downarrow + 3NSAsF_6 \qquad (2)$$

to solutions of $(NSCl)_3$ in SO_2 gave a mixture that did not contain $(NSCl)_3$, NSCl, or NS^+ (^{14}N NMR). Only on removal of the solvent and heating of the solid is reaction 2 completed and $NSAsF_6$ generated (^{14}N NMR and ref 14).

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(26) $(NSCl)_3$ freshly recrystallized from less pure $(NSCl)_3$ according to ref 5; mp 92 °C. However, similar results were obtained from $(NSCl)_3$ that melted at 86 °C.
(27) $(NSCl)_3$ taken directly from preparation of $(NSCl)_3$ according to ref 15, without recrystallization; mp 76–77 °C.

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cis-Diamminediaquaplatinum(II) Selectivity for GpG: Influence of the Adjacent Base on the First Platination Step

Sir:

One important point characterizing the binding of the anticancer drug *cis*-diamminedichloroplatinum(II) ("cisplatin") to DNA is the drug's high affinity for d(GpG) sites.[1] From studies on nucleosides and nucleotides, it is known that guanine N7 atoms are the best DNA ligands for Pt(II).[2] But in vitro[3] as well as in vivo[4] experiments have shown that cisplatin binds to d(GpG) sites with a frequency exceeding the statistical probability, assuming all guanines to be equireactive. Calculations of molecular potentials have revealed that the negative potential at the N7 atom of a guanine is enhanced in the presence of an adjacent guanine at both the 5′- and 3′-sides.[5] These effects are, however, small and not likely to explain solely the observed GpG affinity of cisplatin. We present here conclusive evidence that, for single-stranded ribodinucleotides, interactions of the platinum ligands with the adjacent base are an important factor making GpG more reactive toward *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$, the aquated form of cisplatin, which seems to be the active compound forming the adducts with the dinucleotides.[6] Although dinucleotides are not necessarily good models for DNA, the selective GpG (or d(GpG)) binding could have the same origin in both cases. Since platinum binding to DNA is controlled kinetically,[7] the binding site is determined by the first platination step. Thus, we measured and analyzed the rate constants for the first platination of XpG and GpX dinucleotides (X = G, A, C) by *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ (cation of **1**) and interpreted them by molecular mechanics modeling of the pentacoordinated reaction intermediate, which we expect to have a geometry similar to that of the transition state, since H_2O is a good leaving group.[8] A set of analogous experiments using $[Pt(NH_3)_3(H_2O)]^{2+}$ (cation of **2**) was done to reveal the role of the nonleaving H_2O ligand of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$.

Table I. Rate Constants of the First Platination Step of Dinucleotides by *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$ (**1**) and $[Pt(NH_3)_3(H_2O)](NO_3)_2$ (**2**)[a]

		k_1, $M^{-1}\cdot s^{-1}$	
		1	**2**
$k_1(3')$	GpG	5.7 ± 1.0	0.61 ± 0.02
$k_1(3')$	ApG	1.7 ± 0.1	0.40 ± 0.02
$k_1(3')$	CpG	2.2 ± 0.1	0.52 ± 0.05
$k_1(5')$	GpG	2.8 ± 0.5	0.31 ± 0.02
$k_1(5')$	GpA	0.8 ± 0.1	0.31 ± 0.02
$k_1(5')$	GpC	0.95 ± 0.1	0.44 ± 0.05

[a] The kinetic studies were done under pseudo-first-order conditions, with **1** or **2** (0.1 to 0.4 mM) and the dinucleotide (0.01 mM) at pH 5.2 and 20 °C. UV data were recorded for the disappearance of the dinucleotide and appearance of the monocoordinated complex (λ = 280 nm). Differential UV monitoring of the reactions clearly showed two isosbestic points. The rate constants were obtained from the analysis of the UV absorbance data by nonlinear regression with the Marquardt algorithm,[12] as previously reported for the platination of ApG and GpA by **1**.[13] The rate constants obtained from the data of HPLC monitoring of the reactions (**1** or **2**, 10–15 mM; dinucleotide, 1 mM) were in good agreement with the UV results.

The kinetic data are summarized in Table I. They show that, for the diaqua complex **1**, (i) the presence of a 5′-guanine favors the platination of the 3′-guanine by a factor of $\simeq$3 ($\simeq$5.7/1.7 $\simeq$ 5.7/2.2) relative to the case where the 5′-neighbor is A or C and (ii) the presence of a 3′-guanine, instead of 3′-A or 3′-C, favors the platination of the 5′-guanine also by a factor of $\simeq$3 ($\simeq$2.8/0.8

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(6) When ApG reacts with an aqueous solution of cisplatin containing mainly *cis*-$[PtCl(NH_3)_2(H_2O)]^+$, no *cis*-$[PtCl(NH_3)_2(ApG\text{-}N7(2))]^+$ intermediate can be detected by HPLC, whereas a little amount of the aqua intermediate is present. Moreover, we have shown that the rate-determining step for the chelation reaction of the monochloro complex is the aquation of the chloride ligand (to be submitted for publication).
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