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Thallium-205 NMR Study of Thallium(I) Cryptates in Various Solvents

D. GUDLIN and H. SCHNEIDER
Max-Planck-Institut für biophysikalische Chemie, D-3400 Göttingen, F.R.G.
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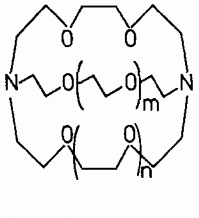
Thallium-205 NMR studies were performed on thallium(I) complexes with cryptands (2,2,1), (2,2,2), and (2,2,2B) in water and in several non-aqueous solvents. The chemical shifts of the complexes were found to be independent of the solvent indicating that the thallium(I) ion is completely shielded by the cryptand.

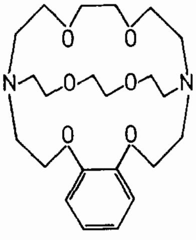
Introduction

The polyoxadiaza macrobicyclic ligands (cryptands) synthesized by Lehn and coworkers [1] form stable complexes with alkali ions and alkaline earth ions. The stability constants of these complexes (cryptates) depend largely on the fit of the metal ions in the ligand cavity and the solvating ability of the solvent.

In the complexation process, the cryptands form inclusion complexes with the metal ions and the ligands entirely surround the cations; the more complete is the enclosure, the better is the relationship between the three dimensional cavity of the cryptand and the diameter of the bare ion. As a result, the solvent is separated from the ion by a cryptand shell and the interaction between the bare ion and the solvent is reduced. Nuclear magnetic resonance (NMR) is a sensitive technique for the study of the shielding of ions by cryptands. The NMR of metal ion nuclei such as ^{7}Li, ^{23}Na, and ^{133}Cs has been found to be solvent independent when the stability constants of the metal ion cryptate complexes are large [2–7].



(2,2,1) : m=1, n=0
(2,2,2) : m=1, n=1



(2,2,2 B)

In this paper we report a ^{205}Tl-NMR study of Tl^+ complexes with the cryptands (2,2,1), (2,2,2), and (2,2,2B) in water and several non-aqueous solvents.

Although the chemical shift range of $^{205}Tl^+$ in different solvents is much larger than that of the alkali metal ions mentioned above, the same solvent independence of the chemical shift of the cryptates has been obtained.

Experimental

TlCl, $TlNO_3$, $TlCH_3CO_2$, Tl_2CO_3, cryptands (2,2,1), (2,2,2), and (2,2,2B) (Merck) were used as purchased. The solvents were dried with molecular sieves and purified by distillation. The water content, determined by a Karl–Fischer titration, was less than 0.01%. All samples were prepared by weighing.

NMR measurements were carried out at 51.9 MHz on a Bruker HFX 90 spectrometer equipped with a ^{205}Tl insert. In order to cover the wide range of ^{205}Tl chemical shifts, the resonance frequency of the spectrometer was modulated by the audio frequency of a Schomandel frequency synthesizer. All spectra were accumulated up to 1012 times using a Fabritek 1074 averager. The temperature was held constant at 25 ± 1 °C. Spinning, 10 mm sample tubes were used with 5 mm o.d. NMR tube inserts which were fixed coaxially by teflon spacers. The 5 mm tubes were filled with tetramethylsilane (TMS) which served as an external reference and as a field-frequency proton lock. No susceptibility corrections were performed because they were found to be insignificant.

Results and Discussion

The NMR chemical shift range of the ions (*i.e.* the sensitivity of the chemical shift of the metal ions nuclei on changing the solvent) increases with their atomic weight. The infinite dilution chemical shifts of $^7Li^+$ both in acetone (AC) and in N,N-dimethylformamide (DMF) differ by –0.98 ppm [8]. With $^{23}Na^+$ the difference is *ca.* 1.3 ppm [9] and with

TABLE I. Chemical Shift of $^{205}Tl^+$ and $\{Tl^+(2,2,1)\}$ at 25 °C.[a]

Solvent	Salt	mol Tl^+/ kg solution	mol (2,2,1)/ mol Tl^+	Chemical shift [kHz] of $\{Tl^+(2,2,1)\}$	(Tl^+)
H_2O	$TlCH_3CO_2$	0.50	1.0	51,948.56	
H_2O	$TlCH_3CO_2$	0.83	0.62	51,948.19	(51,915.15)
methanol	$TlClO_4$	0.260	0.98	52,946.70	
methanol	$TlClO_4$	0.206	1.57	51,946.62	
ethanol	$TlClO_4$	0.251	1.02	51,946.68	
ethanol	$TlClO_4$	0.232	1.44	51.947.04	
formamide	$TlClO_4$	0.483	0.47	51,946.59	(51,919.57)
formamide	$TlClO_4$	0.198	1.26	51,946.60	
NMF	$TlClO_4$	0.635	0.50	51,946.64	(51,922.35)
NMF	$TlClO_4$	0.258	1.41	51,946.35	
DMF	$TlClO_4$	0.166	1.48	51,947.06	
DMF	$TlClO_4$	0.532	0.52	51,947.03	
DMSO	$TlClO_4$	0.587	0.55	51,946.62	(51,933.55)
DMSO	$TlClO_4$	0.249	1.49	51,946.04	
PC	$TlClO_4$	0.255	1.01	51,947.57	
PC	$TlClO_4$	0.175	1.49	51,947.55	
TMP	$TlClO_4$	0.600	0.49	51,947.33	(51.921.06)
TMP	$TlClO_4$	0.216	1.55	51,947.07	
HMPT	$TlClO_4$	0.281	0.94	51,950.04	
HMPT	$TlClO_4$	0.197	1.47	51,947.55	
CH_3CN	$TlClO_4$	0.323	0.98	51,949.17	
CH_3CN	$TlClO_4$	0.219	1.49	51,947.55	
acetone	$TlClO_4$	0.255	0.98	51,947.21	
acetone	$TlClO_4$	0.211	1.54	51,947.20	
NM	$TlClO_4$	0.238	1.05	51.947.51	
NM	$TlClO_4$	0.226	1.29	51,947.49	
$CHCl_3$	$TlNO_3$	0.206	1.09	51,946.91	
$CHCl_3$	$TlCl$	0.195	1.16	51,947.00	

[a] NMF, N-methylformamide; DMF, N,N-dimethylformamide; DMSO, dimethylsulfoxide; PC, propylene carbonate; TMP, trimethylphosphate; HMPT, hexamethylphosphotriamide; NM, nitromethane.

TABLE II. Chemical shift of $^{205}Tl^+$ (2,2,2) at 25 °C.

Solvent	Salt	mol Tl^+/kg solution	mol (2,2,2)/mol Tl^+	Chemical Shift [kHz]
H_2O	$TlCl$	0.235	1.50	51,914.53
H_2O	$TlCl$	0.253	2.92	51,914.42
methanol	$TlClO_4$	0.444	1.31	51,916.56
methanol	$TlClO_4$	0.282	2.18	51,916.48
NMF	$TlClO_4$	0.362	1.19	51,917.05
NMF	$TlClO_4$	0.274	1.61	51,917.00
DMF	$TlClO_4$	0.352	1.93	51,917.42
				51,917.37
DMSO	$TlClO_4$	0.590	1.10	51,918.15
DMSO	$TlClO_4$	0.433	1.58	51,918.09
PC	$TlClO_4$	0.505	1.23	51,917.25
PC	$TlClO_4$	0.434	1.47	51,917.19
TMP	$TlClO_4$	0.205	1.96	51,917.53
CH_3CN	$TlClO_4$	0.486	1.17	51,916.91
CH_3CN	$TlClO_4$	0.287	2.11	51,916.81
acetone	$TlClO_4$	0.342	1.12	51,916.74
NM	$TlClO_4$	0.301	1.34	51,916.72
NM	$TlClO_4$	0.221	1.87	51,916.65

(continued on facing page)

TABLE II. *(continued)*

Solvent	Salt	mol Tl^+/kg solution	mol (2,2,2)/mol Tl^+	Chemical Shift [kHz]
$CHCl_3$	$TlClO_4$	0.213	1.18	51,916.50
$CHCl_3$	$TlNO_3$	0.256	1.00	51,916.48
$CHCl_3$	TlCl	0.222	1.15	51,916.50

TABLE III. Chemical Shift of $^{205}Tl^+$ (2,2,2B) at 25 °C.

Solvent	Salt	mol Tl^+/kg solution	mol (2,2,2B)/mol Tl^+	Chemical Shift [kHz]
formamide	$TlClO_4$	0.179	1.41	51,918.20
NMF	$TlClO_4$	0.207	1.68	51,917.96
DMF	$TlClO_4$	0.250	1.23	51,918.13
DMF	$TlClO_4$	0.191	1.65	51,918.09
DMSO	$TlClO_4$	0.265	1.22	51,918.54
DMSO	$TlClO_4$	0.197	1.68	51,918.51
PC	$TlClO_4$	0.153	1.12	51,918.26
PC	$TlClO_4$	0.109	1.62	51,918.16
CH_3CN	$TlClO_4$	0.318	1.36	51,918.07
NM	$TlClO_4$	0.154	1.61	51,918.02
$CHCl_3$	$TlClO_4$	0.262	0.96	51,917.72

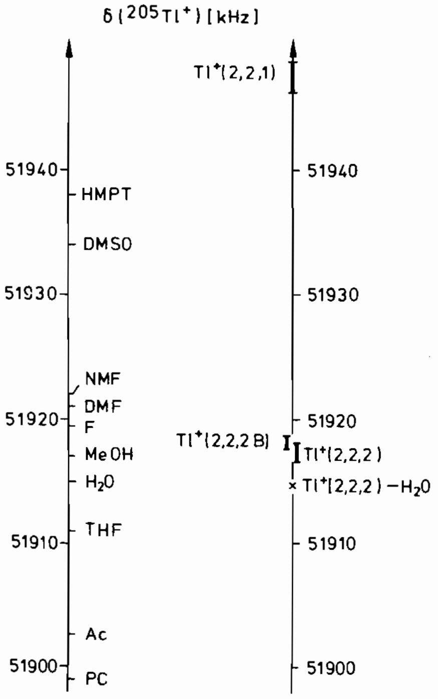


Figure 1. ^{205}Tl chemical shift of solvated Tl^+ and ^+Tl–cryptate complexes.

$^{139}Cs^+$ it increases to 26.3 ppm [10]. The ^{205}Tl nucleus is even more sensitive and the chemical shift difference of thallium(I) ions both in AC and in DMF is >360 ppm. The wide chemical shift range of ^{205}Tl combined with the fact that it has a spin of 1/2 and a not too low NMR sensitivity therefore makes ^{205}Tl-NMR an extraordinarily good tool for the study of Tl^+ cryptates in various protic and aprotic solvents.

Table I contains the chemical shift of $Tl^+(2,2,1)$ as a function of the cryptand/Tl^+ mol ratio in various solvents. The chemical shift is essentially independent of the solvent and the influence of counterions is negligible as is clearly shown by the data for chloroform.

A similar solvent independence of the Tl^+ cryptate chemical shift is found with (2,2,2) (Table II) and (2,2,2B) (Table III). While the resonance frequency of $Tl^+(2,2,1)$ (51,947 kHz) is different from that of $Tl^+(2,2,2)$ (51,917 kHz), the benzene ring in Tl^+ (2,2,2B) only changes the resonance frequency (51,918 kHz) very slightly. The shift of the resonance to higher magnetic fields when the number of oxygen atoms in the ligands increases is also found with complexes of $^7Li^+$ with (2,1,1), (2,2,1), and (2,2,2) [2].

Only in water is the resonance frequency of $^{205}Tl^+$ cryptates 1–2 kHz smaller than the frequencies in all other solvents. Two reasons may be suggested for this: firstly, it is known that hydrophobic solutes are hydrated in a different way from inorganic ions and hydrophilic compounds. The increase of water structure around the hydrophobic surface of cryptates may influence the cation–ligand interaction.

Secondly, water molecules are much smaller than the molecules of the nonaqueous solvents used and may penetrate further into the cryptate shell; this would change the resonance frequency of the ion. It should be mentioned that the line width of the solvated Tl^+ is always more than five times smaller than the width of the cryptate peak.

In general, the Tl^+ cryptate chemical shift is independent of the cryptand/Tl^+ mol ratio (Tables I–III). Mol ratios of less than 1 could only be obtained in basic solvents such as water, formamide (F), DMF, dimethylsulfoxide (DMSO), hexamethylphosphotriamide (HMPT) [11], trimethylphosphate (TMP) and N-methylformamide (NMF) where the solubility of $TlClO_4$ is large enough for the application of c.w. ^{205}Tl-NMR spectroscopy, (Fig. 1). In these solvents the exchange rate is slow and two lines (one from solvated Tl^+ and the other from the cryptate complex), could be observed at room temperature. The temperature was not varied since the determination of rate constants by stopped-flow experiments in aprotic solvents is more accurate [12].

Similar to ^{205}Tl-cryptate NMR (Tables I–III), the resonance frequencies of $^7Li^+(2,1,1)$ and $^{23}Na^+(2,2,2)$ are also almost independent of the solvent. In the case of Li^+ and Na^+ this was confirmed by far i.r. studies on cryptate solutions in several polar solvents [2, 5]. However, the limiting chemical shifts of $^7Li^+(2,2,1)$, $^7Li^+(2,2,2)$, $^{133}Cs^+(2,2,2B)$ and the corresponding $^{133}Cs^+(2,2,2dilactam)$ [7] complex are solvent dependent. The strength of the ion–cryptand interaction (*i.e.* the magnitude of the stability constants of the cryptates) determines whether the central ions' chemical shift changes appreciably from solvent to solvent. In the most stable cryptate complexes the amine nitrogen and the ether oxygen atoms are almost always directed towards the included cation while the ethyl groups alone interact with the solvent. Direct electrostatic ion–solvent interactions are reduced drastically by the thickness of the cryptand shell. Two reasons may be suggested for the solvent independence of the cryptate chemical shifts: a) The interaction between the CH_2-groups of a cryptate and the solvent is considerable and changes with the solvent. The distance between the central ion and the closest solvent molecules is, however, so large that a change in the electron density of the CH_2-groups will not appreciably affect the ion. Furthermore, because of the high stability of the complexes, the ligand's chains are not as free to move against each other around the ion and the influence of the solvent on the ion due to this process may be small. b) The cryptate–solvent interaction is only weak and nonspecific as far as the solvent is concerned.

Since the ^{205}Tl chemical shift is very sensitive to any variation in the environment of the thallium(I) ion [12] and even allows the determination of association constants for solvent-separated ion pairs [11], we propose that b) is responsible for the solvent independence of the cryptate chemical shifts. Stable cryptates may therefore be useful in cases where the determination of single ion free energies and enthalpies of transfer between various solvents (except water) are of importance. Furthermore, in NMR experiments with nuclei which have as yet been used less frequently, the resonance line of the corresponding cryptate complexes can be used as an internal reference.

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