Complexes of Tris((2-pyridyl)alkyl)amines with Lithium and Sodium Salts[†]

Sydney K. Brownstein,[*] Pierre-Yves Plouffe, Corinne Bensimon, and John Tse

Institute for Environmental Chemistry and Steacie Institute for Molecular Sciences,
National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

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Tris((2-pyridyl)methyl)amine forms complexes with sodium and lithium ions. The enthalpy of formation of the lithium iodide complex in deuterioacetone was found to be 8.0 ± 0.3 kcal/mol from proton resonance spectroscopic determination of exchange rates as a function of temperature. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.077(4)$ Å, $b = 12.221(11)$ Å, $c = 26.613(7)$ Å, and $\beta = 94.642(24)°$, with $Z = 4$ and $R_w = 0.083$. Tris(2-(2-pyridyl)ethyl)amine forms a weaker complex with lithium ions but does not complex sodium ions. Theoretical calculations of the structure of the lithium complex were in good agreement with the results of the X-ray structure determination.

Introduction

Both Cu(I) and Cu(II) complexes have been reported with tris((2-pyridyl)alkyl)amine ligands.[1] In the course of the synthesis of chain-substituted ligands we found that these ligands also strongly complex lithium. Since strong complexes with lithium ions are less common than for other metallic cations,[2] it was decided to further investigate these complexes. The significant selectivity of these compounds for lithium over sodium is also not very common.[2] This selectivity may be useful in some special applications currently under investigation. The crystal structure and an ab initio theoretical calculation were obtained for the lithium complex of tris((2-pyridyl)methyl)amine, TMPA. In addition nuclear magnetic resonance spectroscopic investigations of exchange between free and complexed ligands were conducted in deuterioacetone and D_2O for the lithium and sodium complexes of TMPA and tris(2-(2-pyridyl)ethyl)amine, TEPA.

Experimental Section

The X-ray diffraction data were collected at −120 °C on a Rigaku diffractometer with Mo Kα radiation using the ω–2θ scan technique to a maximum 2 θ value of 50.

A plate crystal of $C_{41}H_{46}N_8Li_2I_2O$ having approximate dimensions of 0.4 × 0.2 × 0.3 mm was mounted in a capillary tube. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 24 reflections in the range $40 < 2\theta < 50$ corresponded to a monoclinic cell with dimensions as follows: $a = 13.077(4)$ Å, $b = 12.221(11)$ Å, $c = 26.613(7)$ Å, and $\beta = 94.642(24)°$. For $Z = 4$ and fw = 934.55, the calculated density is 1.464 g/cm.[3] On the basis of the systematic absences, the space group was determined to be $P2_1/c$. A total of 7833 reflections were collected. The unique set contains only 7481 reflections. Three standards were measured after every 150 reflections. No crystal decay was noticed. The data were corrected for Lorentz and polarization effects.[3] A ψ-scan Gaussian absorption correction was made. The minimum and maximum transmission factors are 0.919451 and 0.989704.

The structure was solved by direct methods. All the atoms were refined anisotropically except the solvent molecule and the hydrogens. The hydrogen atoms are in calculated positions. The final cycle of full-matrix least-squares refinement was based on 4303 observed reflections ($I > 2.5\sigma(I)$) and 463 variable parameters. Weights based on counting statistics were used. The refinement converged with $R = 0.094$ and $R_w = 0.083$. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.37 and −1.79 e/Å^3, respectively.

Table 1. Crystallographic Data for $Li_2(CH_2NC_5H_4)_3N(CHCH_3NC_5H_4)(CH_2NC_5H_4)_2NI_2{\cdot}THF$

chem formula: $C_{41}H_{46}N_8Li_2I_2O$	fw = 934.55
space group: $P2_1/c$	$T = -120$ °C
$a = 13.077(4)$ Å	$\lambda = 0.709\ 30$ Å
$b = 12.221(11)$ Å	$\rho_{calcd} = 1.464$ g cm^{-3}
$c = 26.613(7)$ Å	μ(Mo Kα) = 15.1 cm^{-1}
$\beta = 94.642(24)°$	$R^a = 0.094$
$V = 4239(4)$ Å^3	$R_w{}^b = 0.083$
$Z = 4$	

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

There are 2 molecules per asymmetric unit. The difference between the 2 molecules is the presence of a methyl group in one of the molecules (C20). There is also a molecule of the solvent, tetrahydrofuran, in the unit cell. The last Fourier map shows some big residues around the two I ions. Since the crystal was mounted in a capillary tube, the glass all around the crystal makes the correction of absorption quite difficult.[4]

All the calculations were performed using the NRCVAX crystallographic software package.[5] The crystal data are listed in Table 1.

Ab *initio* calculations for the model compound $LiN(CH_2CHNH_2)_3$ were performed using the program GAMESS,[6] and the electronic properties were examined with natural orbital analysis.[7] The extended 6-31G* basis sets[8] were used for all the heavy atoms. The geometry optimization was performed with full analytical gradient C_{3v} symmetry.

All magnetic resonance spectra were obtained with a Bruker AM 400 spectrometer operating at a proton frequency of 400.13 MHz. Spectra were normally obtained at room temperature in either deuterioacetone, deuteriochloroform, or deuterated water as solvent. Proton spectra were collected with a spectral width of 4000 Hz and a 16K data table. All results are reported for Fourier transformation of the free induction decay without apodization. In some cases to aid spectral interpretation the free induction decay was apodized to narrow the spectral peaks. In these cases the data table was increased to 32K. A pulse width of 1.0 μs (8.0°) and a delay of 0.5 s between pulses were employed to ensure that there was no saturation. Carbon-13 spectra were collected with a spectral width of 20 000 Hz and a 16K data table. Apodization corresponding to a line broadening of 1.0 Hz was employed. Two power level proton

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[*] Author to whom correspondence may be addressed.

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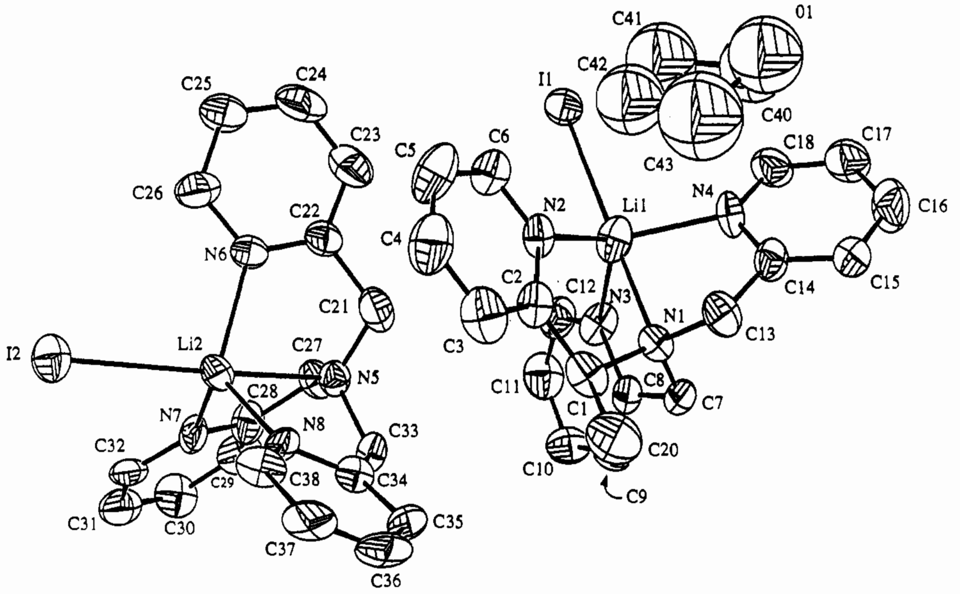

Figure 1. ORTEP drawing of TMPA–LiI adduct containing a tetrahydrofuran molecule of solvation (probability level 50%). Hydrogens are omitted for clarity.

decoupling was employed to minimize dielectric heating of the sample. A pulse width of 5.0 μs (72°) and a delay of 5.0 s between pulses were used to avoid saturation. Proton–carbon one-bond connectivities were obtained from two-dimensional spectra using a modified HETCOR sequence[9] with a final data table of 4K points in the carbon frequency domain of 19 900 Hz and 512 points in the proton domain of 3000 Hz. Longer range proton–carbon connectivities were determined using the COLOC sequence[10] with 4K data points in the carbon frequency domain of 19 900 Hz and 512 data points in the proton domain of 2760 Hz. All chemicals shifts are referred to tetramethylsilane as reference in deuterioacetone and deuteriochloroform and to DSS in D_2O. Lifetimes for exchange were obtained by matching experimental spectra with theoretical ones calculated for particular lifetimes and chemical shifts using a stochastic procedure.[11]

All experiments were performed under nitrogen in appropriately sized three-neck flasks. Tetrahydrofuran (THF) was distilled over sodium/benzophenone under nitrogen just before use. The complex tris((2-pyridyl)methyl)amine (TMPA) was prepared by the method of Anderegg and Wenk.[12] The complex tris(2-(2-pyridyl)ethyl)amine (TEPA) was prepared on the basis of a partial preparation reported from Karlin et al.[13] Solvents and liquid reagents were transferred by means of an appropriately sized glass syringe. The compound 2-picoline chloride hydrochloride was purchased from Aldrich and recrystallized from hot acetone before use. Vinylpyridine, 2-(aminomethyl)pyridine, methyllithium, and methyl iodide were purchased from Aldrich and used as received.

Ultraviolet spectra were recorded in water on a Varian Cary 210 via auxiliary computer control. Melting points were measured in sealed tubes on a Gallenkamp melting point apparatus and are uncorrected.

Electrospray experiments were performed on an atmospheric–pressure ionization triple quadrupole mass spectrometer (SCIX, TAGA, Model 6000E), which has an upper m/z limit of approximately 1400. For electrospray studies, the corona discharge assembly was removed and replaced with a laboratory-built electrospray probe, which was fabricated from a 3-cm long capillary stainless steel tube (Hamilton, 33-gauge, ~100-μm i.d.) previously attached to an approximately 5-cm × $^1/_{16}$-in. o.d. stainless steel tube (typically used in gas chromatography). The probe tip was electropolished prior to use. The optimum probe tip position was established from time to time but was generally found to be about 1–2 cm from the interface plate with the spray off-axis from the orifice.

Table 2. ^1H NMR Data for TMPA, TMPA–Me, TEPA, and BEPA[a]

	NH	CH_3	CH_2	Py
TMPA			$3.883^{b,c}$	$7.14\ (H_\beta)^{d,e}$
				$7.59\ (H_\delta)^{d,e}$
				$7.66\ (H_\gamma)^{d,e}$
				$8.56\ (H_\alpha)^{d,e}$
TMPA–Me		$1.583^{e,f,g}$	$3.658\ (CH_aH_b)^{f,h,j}$	$7.21\ (H_\delta,H_{\delta'},H_\beta,H_{\beta'})^{c,d}$
			$3.767\ (CH_cH_d)^{f,i,j}$	$7.13\ (H_{\gamma'})^{d,j}$
			$3.807\ (CH_cH_d)^{f,i,u}$	$7.65\ (H_\gamma)^{d,l}$
			$3.925\ (CHM_e)^{g,j,k}$	$9.38\ (H_\alpha)^{d,j}$
			$4.070\ (CH_aH_b)^{f,h,j}$	$9.44\ (H_{\alpha'})^{d,j}$
TEPA			$2.905\ (CH_2\theta)^{c,d}$	$7.00\ (H_\delta)^{d,e}$
			$2.985\ (CH_2{}^\psi)^{c,d}$	$7.09\ (H_\beta)^{d,e}$
				$7.52\ (H_\gamma)^{d,e}$
				$8.52\ (H_\alpha)^{d,e}$
TEPA·4HCL[a]			$3.713\ (CH_2{}^\theta)^{c,d}$	$8.03\ (H_\beta)^{d,e}$
			$3.930\ (CH_2{}^\psi)^{c,d}$	$8.10\ (H_\delta)^{d,e}$
				$8.61\ (H_\gamma)^{d,e}$
				$8.78\ (H_\alpha)^{d,e}$
BEPA	$2.28^{l,m}$		$2.978^{d,n}$	$7.12\ (H_\beta)^{d,l}$
			$3.042^{d,n}$	$7.15\ (H_\delta)^{d,l}$
				$7.58\ (H_\gamma)^{d,l}$
				$8.49\ (H_\alpha)^{d,l}$

[a] In $CDCl_3$: reported in ppm relative to TMS as internal reference. [b] Singlet. [c] 6H. [d] Multiplet. [e] 3H. [f] Doublet. [g] $J_{H-H} = 7.04$ Hz. [h] $J_{H-H} = 15.26$ Hz. [i] $J_{H-H} = 15.85$ Hz. [j] 1H. [k] Quartet. [l] 2H. [m] Broad. [n] 4H. [o] In D_2O: reported in ppm relative to DSS.

Polarization of the spray probe was achieved via a 50 MΩ current-limiting resistor in series with a high-voltage power supply (Tennelec, Model TC950) set typically at 2.5–3.5 kV. The electrospray current was monitored by a laboratory-built microammeter that could be floated above ground; typical values were between 0.1 and 0.2 μA.

The sample solutions were continuously infused into the spray probe by means of a syringe pump (Harvard Apparatus, Model 22) at a typical flow rate of 20 μL/min. Electrical isolation of the pump from the probe was achieved by using polytetrafluoroethylene (Teflon) connection tubing.

The lens and quadrupole voltages were optimized for electrospray. Mass spectra were acquired with a typical measurement time of 50 ms per m/z unit at unit mass resolution or better.[14]

Preparation of Tris(2-(2-pyridyl)ethyl)amine (TEPA).[13] A solution of ammonium acetate (4.00 g, 51.9 mmol) in methanol (100 mL) was prepared in a 250-mL three-neck flask fitted with a condenser. To that solution, vinylpyridine (60 mL, 556.4 mmol) was added. The mixture was brought to reflux and maintained for 8 days. After that time, the solution was reduced to dryness under vacuum. The residue was extracted

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Table 3. Atomic Parameters for TMPA–LiI Adduct

	x	y	z	B_{iso},[a] (Å^2)		x	y	z	B_{iso},[a] (Å^2)
I1	0.15873(14)	0.27529(15)	0.47258(6)	3.66(7)	C17	0.556(3)	0.202(3)	0.4847(11)	5.0(16)
I2	0.67568(15)	0.31311(17)	0.75053(7)	4.18(8)	C18	0.4577(23)	0.207(3)	0.4954(11)	4.6(14)
N1	0.3595(14)	0.1287(15)	0.6297(7)	2.5(7)	Li1	0.273(3)	0.190(4)	0.5627(18)	3.7(19)
N2	0.2204(14)	0.2920(18)	0.6164(7)	2.8(8)	C20	0.362(3)	0.146(3)	0.7236(13)	6.0(18)
N3	0.2223(15)	0.0242(17)	0.5605(7)	3.0(8)	C21	0.9747(21)	0.165(3)	0.6238(11)	4.2(13)
N4	0.4229(15)	0.2007(19)	0.5411(8)	3.5(8)	C22	0.9068(19)	0.2592(21)	0.6048(10)	3.2(10)
N5	0.9180(14)	0.0839(17)	0.6508(7)	2.8(8)	C23	0.9248(25)	0.316(3)	0.5622(12)	4.7(13)
N6	0.8346(16)	0.2885(17)	0.6352(7)	3.0(8)	C24	0.865(3)	0.406(3)	0.5495(13)	5.4(15)
N7	0.7334(15)	0.0405(16)	0.6875(9)	3.3(9)	C25	0.7877(23)	0.436(3)	0.5783(10)	4.2(12)
N8	0.9463(14)	0.1642(17)	0.7493(7)	2.7(7)	C26	0.7744(23)	0.3760(24)	0.6223(12)	4.2(12)
O1	0.551(3)	0.585(3)	0.6122(15)	10.9(10)	C27	0.8492(20)	0.0156(23)	0.6196(9)	3.4(11)
C1	0.2967(21)	0.1530(24)	0.6724(9)	3.6(11)	C28	0.7588(20)	−0.0240(23)	0.6454(11)	3.7(12)
C2	0.2421(18)	0.2613(21)	0.6646(9)	2.9(9)	C29	0.7103(24)	−0.119(3)	0.6330(11)	4.4(13)
C3	0.2148(25)	0.322(3)	0.7062(11)	4.8(15)	C30	0.6286(22)	−0.152(3)	0.6614(12)	4.4(13)
C4	0.156(3)	0.416(3)	0.6933(14)	5.6(16	C31	0.6013(22)	−0.087(3)	0.7020(12)	4.6(13)
C5	0.133(3)	0.449(3)	0.6453(14)	5.7(16)	C32	0.6528(19)	0.0110(20)	0.7119(9)	3.0(9)
C6	0.1664(19)	0.3857(24)	0.6073(9)	3.5(10)	C33	0.9865(17)	0.0231(21)	0.6896(8)	2.7(9)
C7	0.3699(20)	0.0079(23)	0.6204(12)	4.0(12)	C34	1.0159(17)	0.0860(9)	0.7375(9)	2.7(9)
C8	0.2755(20)	−0.0385(24)	0.5979(11)	3.9(12)	C35	1.1038(20)	0.0632(25)	0.7664(10)	3.7(11)
C9	0.2400(23)	−0.1435(22)	0.6051(11)	3.9(12)	C36	1.1212(24)	0.119(3)	0.8129(10)	4.5(13)
C10	0.1553(24)	−0.1850(23)	0.5814(12)	4.3(13)	C37	1.0542(24)	0.196(3)	0.8249(9)	4.7(14)
C11	0.1041(24)	−0.122(3)	0.5427(13)	4.9(14)	C38	0.9690(21)	0.2168(23)	0.7923(8)	3.5(11)
C12	0.1388(22)	−0.0181(25)	0.5343(13)	4.4(14)	Li2	0.818(3)	0.187(4)	0.6980(14)	3.1(16)
C13	0.4561(20)	0.1856(23)	0.6298(10)	3.7(11)	C40	0.510(4)	0.512(5)	0.5774(21)	9.7(14)
C14	0.4952(19)	0.1874(23)	0.5783(10)	3.5(11)	C41	0.395(5)	0.523(5)	0.5771(23)	10.9(16)
C15	0.5976(22)	0.180(3)	0.5699(11)	4.2(12)	C42	0.392(4)	0.549(5)	0.6323(21)	9.5(14)
C16	0.630(3)	0.189(3)	0.5224(13)	5.7(17)	C43	0.491(6)	0.559(7)	0.654(3)	14.3(23)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 4. Bond Distances and Angles Involving the Li Atoms in the TMPA–LiI Adduct

Li1–I1	2.91(5)	Li2–I2	2.87(4)
Li1–N1	2.17(5)	Li2–N5	2.27(4)
Li1–N2	2.06(5)	Li2–N6	2.11(4)
Li1–N3	2.13(5)	Li2–N7	2.10(5)
Li1–N4	2.09(5)	Li2–N8	2.10(5)
I1–Li1–N1	178.9(23)	I2–Li2–N5	174.7(20)
I1–Li1–N2	100.2(18)	I2–Li2–N6	100.5(17)
I1–Li1–N3	100.5(17)	I2–Li2–N7	99.8(15)
I1–Li1–N4	100.4(19)	I2–Li2–N8	105.7(16)
N1–Li1–N2	79.5(17)	N5–Li2–N6	77.6(14)
N1–Li1–N3	80.6(19)	N5–Li2–N7	77.1(16)
N1–Li1–N4	78.9(17)	N5–Li2–N8	79.6(16)
N2–Li1–N3	118.5(24)	N6–Li2–N7	118.9(21)
N2–Li1–N4	121.5(23)	N6–Li2–N8	117.5(21)
N3–Li1–N4	110.5(21)	N7–Li2–N8	111.1(21)

with toluene, dried with magnesium sulfate, and reduced to dryness under vacuum. The residue was dissolved in the minimum of diethyl ether, chromatographed over activated alumina (20 mm × 250 mm), and eluted with diethyl ether. The brown band was collected, and the eluent was changed to 20% (v/v) methanol in diethyl ether thereby eluting a red band. Both bands were reduced to dryness under vacuum to give a golden oil for band 1 (TEPA, 6.96 g, 20.96 mmol, 11%) and a dark red oil for band 2 (bis(2-(2-pyridyl)ethyl)amine, BEPA, 0.58 g, 2.56 mmol, 4.9%). UV: λ_{max} = 261 nM; ϵ = 1025 M^{-1} cm^{-1}. Electrospray mass spectrometry of TEPA: *m/z* 334.

Preparation of Tris(2-(2-pyridyl)ethyl)amine Tetrahydrochloride (TEPA·4HCL). The compound TEPA (7.8 g, 23 mmol) was dissolved in 9 N HCl (20 mL). To this solution, ethanol (300 mL) was slowly added. The powder was filtered out, washed with ethanol, and air dried for 1 h. The yield was quantitative. Mp: 213–215 °C. Anal. Calc: 52.74, C; 5.90, H; 11.71, N; 29.7, Cl. Found: 51.90, C; 5.69, H; 11.16, N; 29.8, Cl. UV: λ_{max} = 261 nM; ϵ = 1260 M^{-1} cm^{-1}.

Preparation of Bis((2-pyridyl)methyl)(1-(2-pyridyl)ethyl)amine (TMPA-Me). The complex TMPA (0.23 g, 0.79 mmol) was dissolved in THF (5 mL), and the solution was cooled to −78 °C in an ethanol/dry ice bath. To the cooled solution, methyllithium (0.56 mL, 1.4 M in ether, 0.79 mmol) was added dropwise. After stirring for 5 min, methyl iodide (0.60 mL, 9.6 mmol) was added dropwise, and the mixture was stirred for 10 min. The product was warmed to room temperature and stirred for 1 h. Upon exposure to air, the residual pink color disappeared. The solution was reduced to dryness and extracted with CH_2Cl_2 and filtered. The yellow filtrate was collected, and hexanes was added until turbid. Crystallographic grade crystals (0.2126 g) were collected and dried under vacuum. X-ray crystallography indicates a 1:1:1 crystal of desired product, TMPA and THF. Therefore, the yield is 0.23 mmol (29%) as a mixture with 0.23 mmol (29%) TMPA and THF. Mp: 211–218 °C.

The magnetic resonance parameters for these compounds are listed in Table 2.

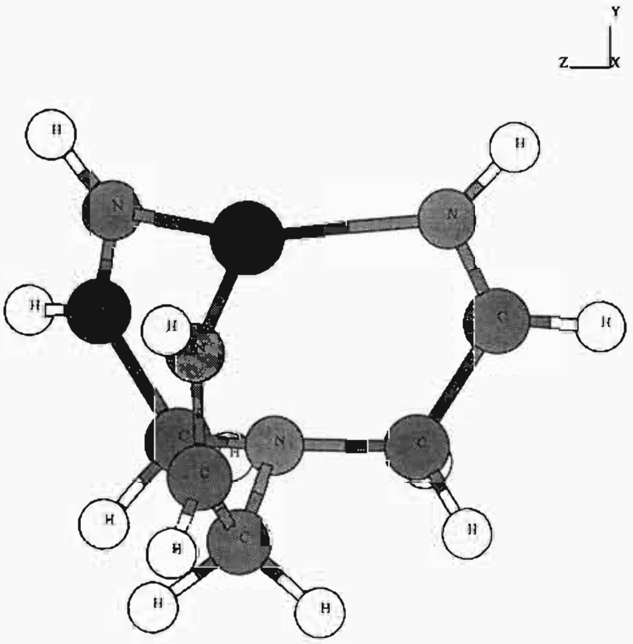

Figure 2. Calculated structure of $LiN(CH_2CHNH_2)_3$.

Results

A synthesis was attempted to put a methyl group in place of a hydrogen on one of the CH_2 groups of TMPA. Crystals were obtained containing equal quantities of TMPA and methylated TMPA, both complexed to a lithium cation with iodide as the counterion. An ORTEP drawing of the complexes is shown in Figure 1, and the atom coordinates are listed in Table 3. All bond distances and angles are normal.[15] The lengths and angles of the bonds to lithium are listed in Table 4. Complete listings

Table 5. Nuclear Magnetic Resonance Parameters (ppm, Hz) for TMPA and Two of Its Complexes

	solvent					
	deuterioacetone			D_2O		
	TMPA	(TMPA)Li$^+$	(TMPA)Na$^+$	TMPA	(TMPA)Li$^+$	(TMPA)Na$^+$
θ H	3.833	3.998	3.888	3.724	3.721	3.74
θ C	60.74	59.07	59.07	61.86	61.89	61.86
α H	8.487	8.850	8.687	8.32	8.32	8.33
α C	149.8	150.7	150.7	149.4	149.5	149.4
β H	7.204	7.366	7.311	7.40	7.40	7.40
β C	122.8	123.8	123.3	124.5	124.5	124.6
γ H	7.736	7.844	7.795	7.69	7.68	7.69
γ C	137.1	138.7	138.9	139.4	139.4	139.5
δ H	7.669	7.459	7.432	7.23	7.22	7.24
δ C	123.5	123.9	124.4	125.8	125.8	125.9
ϵ C	160.5	159.4	159.3	159.3	159.3	159.1
$J_{\alpha-\beta}$	4.85	5.03		5.04	5.01	4.28
$J_{\alpha-\gamma}$	1.81	1.75		1.76	1.73	1.63
$J_{\alpha-\delta}$	0.98	0.91		0.86	0.87	
$J_{\beta-\gamma}$	7.50	7.79		7.73	7.72	7.78
$J_{\beta-\delta}$	1.38	1.79		1.09	1.13	
$J_{\gamma-\delta}$	7.65	7.79		7.73	7.72	7.78

Table 6. Lifetimes for Exchange between Equal Concentrations of Free and Li-Complexed TMPA in Deuterioacetone

	τ (s)			τ (s)	
T (K)	H_α	H_θ	T (K)	H_α	H_θ
313.5	2.13×10^{-4}		258.0	4.30×10^{-3}	4.30×10^{-3}
295.0	4.80×10^{-4}		237.0	2.03×10^{-2}	1.77×10^{-2}
278.0	1.52×10^{-3}	1.80×10^{-3}	215.0	7.05×10^{-2}	

of bond lengths and angles along with thermal parameters and structure factors are available from the authors. The three pyridyl nitrogens form a plane with the Li atoms 0.39 Å from the planes away from the amino nitrogen. Within 3σ, there is no significant difference in the nitrogen–lithium bond lengths. These are essentially the same length as was found for the adducts of other lithium pyridine complexes, 2.05–2.16 Å.[15]

The optimized geometry for $LiN(CH_2CHNH_2)_3$ is shown in Figure 2. The Li atom is found to be strongly bound to the three pyridyl nitrogen atoms (N_p) with a Li–N_p distance of 2.023 Å but only interacts weakly with the amino nitrogen atom (N_a) with a longer Li–N_a separation of 2.310 Å. The Li atom is slightly displaced from the plane of the three pyridyl nitrogen atoms toward the amine nitrogen. This is a result of steric constraint. The N_a–Li–N_p angle is 82.3°, and the N_p–Li–N_p angle is 118.2°. The valence C–N_p–Li and H–N_p–Li angles of 114.98 and 132.27° are normal for a pyridyl nitrogen atom. Moreover, the interatomic separation between the pyridyl nitrogen atoms is 3.742 Å, which is substantially larger than the separation between the pyridyl and the amine nitrogen atoms of 2.859 Å. A bond indices analysis confirms this observation. The calculated bond indices between the Li atom and the pyridyl nitrogen is 0.194, which is substantially larger than that with the amino N of 0.068. Natural orbital analysis also suggests that the Li–N interactions are fairly ionic. The natural electron configuration for Li is $2s^{0.13}2p^{0.01}$, for N_a is $2s^{1.25}2p^{4.35}$, and for N_p is $2s^{1.46}2p^{4.30}$.

Proton and carbon chemical shifts and some proton–proton spin coupling constants for TMPA and its adducts with lithium and sodium iodides in deuterioacetone and D_2O are listed in Table 5. Values for the adducts are only listed for conditions in which adduct formation is essentially complete. The chemical shifts are temperature sensitive, and the tabulated values are for 25 °C. Since the corresponding atoms for each radical attached to the amino nitrogen are magnetically and chemically equivalent, a simplified numbering scheme is used to describe the chemical shifts of Table 5. The α position corresponds to atoms C6, C12, and C18; the β position to C5, C11, and C17; the γ position to C4, C10, and C16; the δ position to C3, C9, and C15; the ϵ position to C2, C8, and C14; and the θ position to C1, C7, and C13. The proton signals were assigned to particular nuclei on the basis of their spin coupling patterns and change in shift upon alkali metal complexation. The carbon resonance signals were then assigned by the correlations found in a HETCOR experiment.[9] In some cases the proton signals were not sharp enough to get good values for spin coupling constants.

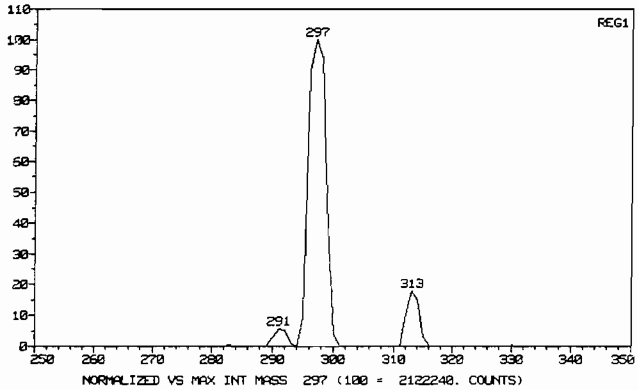

Figure 3. Electrospray mass spectrum of the TMPA–LiI adduct in D_2O.

In deuterioacetone it was noted that sharp signals were obtained at room temperature located midway between the signals for TMPA and its adduct when only 0.5 equiv of the alkali iodide was present. This strongly suggested a rapid exchange of TMPA between the free and complexed forms. Separate signals were observed for Hα and Hθ at 215 K for the lithium adduct in deuterioacetone. It was therefore possible to calculate the lifetimes of the two species as a function of temperature. These are listed in Table 6.

From a least squares analysis of the temperature dependence of the lifetimes an enthalpy of activation of 8.0 ± 0.3 kcal/mol was calculated for the exchange reaction. Since there are four nitrogens coordinated to the lithium, we believe that it is very unlikely that exchange could occur by displacement on lithium of a bound TMPA ligand by one which is not complexed. Rather, it would appear that exchange is effected by dissociation of the TMPA-Li$^+$ complex followed by complexing between Li$^+$ and another TMPA molecule. If this is the exchange mechanism, it follows that the enthalpy of activation for exchange is equal to the heat of formation of the complex.[16] Although the effects of exchange upon the proton resonance spectrum of a TMPA solution

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Table 7. Nuclear Magnetic Resonance Parameters (ppm, Hz) for TEPA and Its Li^+ Complex

	solvent			
	deuterioacetone		D_2O	
	TEPA	$(TEPA)Li^+$	TEPA	$(TEPA)Li^+$
θ H	2.848	2.907	3.01	2.93
θ C	36.8	38.0	35.1	
ψ H	2.958	2.964	3.14	2.93
ψ C	54.7	54.8	54.4	
α H	8.480	8.562	8.37	8.35
α C	149.9	149.9	149.9	
β H	7.096	~7.25	7.25	7.25
β C	124.1	124.5	125.7	
γ H	7.592	7.727	7.76	7.71
γ C	136.7	137.6	139.7	
δ H	7.136	~7.25	7.19	7.19
δ C	121.8	122.2	123.7	
ϵ C	161.8	161.9	160.6	
$J_{\alpha-\beta}$	4.85	3.99		
$J_{\alpha-\gamma}$	1.80	1.87		
$J_{\alpha-\delta}$	0.94			
$J_{\beta-\gamma}$	7.64	7.68		
$J_{\beta-\delta}$	1.88			
$J_{\gamma-\delta}$	7.64	7.68		

containing 0.5 equiv of NaI were observable at low temperature, the exchange rates were too rapid to allow accurate calculations of the lifetimes. Since the Na adduct exchanges much more rapidly than that of Li, it is quite likely that a weaker complex is formed with sodium ion.

It is worth nothing that in D_2O as solvent there is essentially no difference in the chemical shifts found for TMPA in the presence or absence of Li or Na cations. This could arise either because there is no complex formation with the metal cation or because TMPA forms a complex with a water molecule in D_2O alone. An electrospray mass spectrometry analysis of a 1:1 solution of TMPA and LiI in D_2O clearly showed a peak from the Li adduct as illustrated in Figure 3. Although this technique is not quantitative,[17] a strong peak attributed to the TMPA–Li^+ adduct and a small peak due to TMPA–H^+ suggest that TMPA is mostly present in the TMPA–Li^+ complexed form.

Proton and carbon chemical shifts and some proton–proton spin coupling constants for TEPA and its adduct with lithium iodide in deuterioacetone and D_2O are listed in Table 7. The designation of the atoms is the same as for TMPA with the θCH_2 being that next to the pyridine ring and the ψCH_2 being that next to the amino nitrogen. These signals were distinguished by a COLOC experiment[10] in which the long-range interaction of ϵC is assumed to be with θH.

From the proton and carbon resonance shifts there is no evidence for complex formation between TEPA and Na^+ in deuterioacetone. There is complexing with Li^+ and there is also rapid exchange between complexed and free TEPA. The exchange rate is reduced at 214 °K but is still too fast to observe separated peaks from the exchanging species so quantitative studies were not attempted. However, the increased exchange rate for the Li TEPA complex, compared to LiTMPA, and the lack of formation of a NaTEPA complex, show that TMPA is a better complexing agent than TEPA for both Na and Li.

Supplementary Material Available: Tables listing additional crystallographic data, including bond distances, bond angles, torsional angles, equations for the least squares planes, and dihedral angles for $C_{41}H_{46}N_8Li_2I_2O$ (8 pages). Ordering information is given on any current masthead page.

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