solution changed color from purple to dark blue. The solvent was then removed by evaporation, and the resulting solid was extracted with toluene. Cooling resulted in the isolation of a blue solid. This solid was reacted with HCl in order to protonate the remaining methyl groups (see Scheme IV) and generate methane and an analytically pure sample. This blue solid was reacted with 1.1 equiv of HCl in THF and allowed to stir for 1-2 h. Toepler pump and GC measurements were consistent with the generation of a nonstoichiometric amount of methane (0.2 equiv). Evaporation of solvent and recrystallization from diethyl ether gave **13** with an overall yield of 43%. ^{1}H NMR (C_6D_6): δ 14.08 (br, 2.6 H, fwhm = 100 Hz), −12.68 (br, 2 H, fwhm = 120 Hz), −36.4 (br, 15 H, fwhm = 520 Hz), −41.4 (br, 15 H, fwhm = 700 Hz). IR (KBr, cm^{-1}): 3070 (w), 2982 (m), 2942 (s), 2855 (sh), 1585 (s), 1566 (s), 1492 (m), 1442 (s), 1431 (s), 1378 (s), 1361 (m), 1246 (m), 1116 (w), 1071 (w), 1026 (s), 767 (m), 747 (w), 700 (s), 646 (s), 589 (w), 481 (m), 411 (s). Anal. Calcd for $C_{28}H_{38}Cr_2NCl_3$: C, 56.17; H, 6.41; N, 2.34; Cl, 17.77. Found: C, 56.59; H, 6.61; N, 2.24; Cl, 17.39. MS (CI): 599 (M^+, 9%). Magnetic measurements (diamagnetic correction = -398×10^{-6} emu/g-atom): antiferromagnetically coupled, $J = -44$ cm^{-1}. $j = 4.0$ cm^{-1}, $P = 2.5 \times 10^{-3}$, $\chi_0 = 1.3 \times 10^{-3}$ cmu/mol, $\mu_{eff}(300\ K) = 4.1\ \mu_B$.

Reaction of 1 with Excess 2-Butyne (C_4H_6). Synthesis of Poly-2-butyne and (η^5-Pentamethylcyclopentadienyl)(η^6-hexamethylbenzene)chromium(I) {Cp*Cr(η^6-C(CH_3)$_6$)} (14). A solution of **1** (0.25 g, 0.53 mmol) in about 25 mL of toluene was charged on the vacuum line with approximately 20 mmol of 2-butyne. The reaction flask was then placed in a 60 °C oil bath for 3 days. At the end of this time the solution had changed color from a dark purple to green with a colorless insoluble solid. Filtration and washing of the solid with THF afforded 0.06 g of poly-2-butyne identified by its characteristic IR (2969 (s), 2923 (s), 2849 (s), 2711 (m), 1438 (s), 1366 (s), 1092 (s), 1028 (s), 698 (w), 526 (br, w)) and ^{1}H NMR ($CDCl_3$, 1.8 ppm) resonances;[16] mp >355 °C. Anal. Calcd for $(C_4H_6)_x$: C, 88.80; H, 11.20. Found: C, 85.49; H, 10.88. Evaporation of the solution and extraction of the solid residue with pentane gave a brown solution of **14** and a green solid (0.088 g recrystallized, 32% yield) which was identified as **5** by its IR and ^{1}H NMR signals. Cooling the pentane solution to −30 °C resulted in the isolation of **14** (0.111 g, 30% yield); mp >310 °C. ^{1}H NMR (C_6D_6): δ −12.6 (br, fwhm = 1080 Hz). IR (KBr, cm^{-1}): 2900 (s), 2943 (s), 2715 (m), 1440 (m), 1378 (s), 1283 (w), 1066 (m), 1024 (s), 493 (m), 440 (m). MS (CI): 349 (M^+, 19%), 350 ($[M + 1]^+$, 100%). Electrochemistry (vs Cp_2Fe/Cp_2Fe^+ in THF): reversible oxidation −1.3 V, irreversible oxidation −0.3 V, reversible reduction −3.0 V (see Figure 3). Anal. Calcd for $C_{22}H_{33}Cr$: C, 75.59; H, 9.54. Found: C, 75.97; H, 9.42. Magnetic measurements (diamagnetic correction = -257×10^{-6} emu/g-atom): $\mu_{eff}(296\ K) = 1.9\ \mu_B$.

Thermal Decomposition of 14. A sample of **14** (10 mg) in C_6D_6 was heated to 200 °C in a polyethylene glycol bath, and the decomposition of **14** was monitored by ^{1}H NMR. Over the next 7 days the solution took on a green color, and resonances for free hexamethylbenzene (δ 2.12) and Cp^*_2Cr (δ −6.37) appeared and continued to grow in intensity. At the end of this time the integrated ratios of hexamethylbenzene, Cp^*_2Cr, and **14** were 11:1:23.

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Supplementary Material Available: Tables of X-ray structure determination of **13** including fractional coordinates and thermal parameters, anisotropic thermal parameters, crystal data, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

Thermodynamics of Solvation of Lithium Compounds. A Combined MNDO and ab Initio Study

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The solvation of the lithium cation and of (monomeric) methyllithium has been studied by semiempirical MNDO calculations for a large range of different nitrogen and oxygen bases. In addition, ab initio calculations have been performed for the solvation of methyllithium with ammonia and water. Enthalpies, entropies, and free enthalpies of solvation at different temperatures have been obtained by statistical thermodynamics at the MNDO level. General trends are discussed. The performance of MNDO has been checked against experimental values and high-level ab initio calculations. Where such comparisons are available, MNDO provides reasonable thermodynamic data. Semiempirical calculations of this type are suggested for use in the design of "optimum" solvents.

Introduction

Quantum chemical calculations[1] are a rapidly growing source of fundamental quantitative data in chemistry. They have been used, e.g., to predict structures and energies[2,3] or to gain insights into reaction pathways[4] that are otherwise hard to obtain. Because of the tremendous developments in computing power, it is possible to obtain

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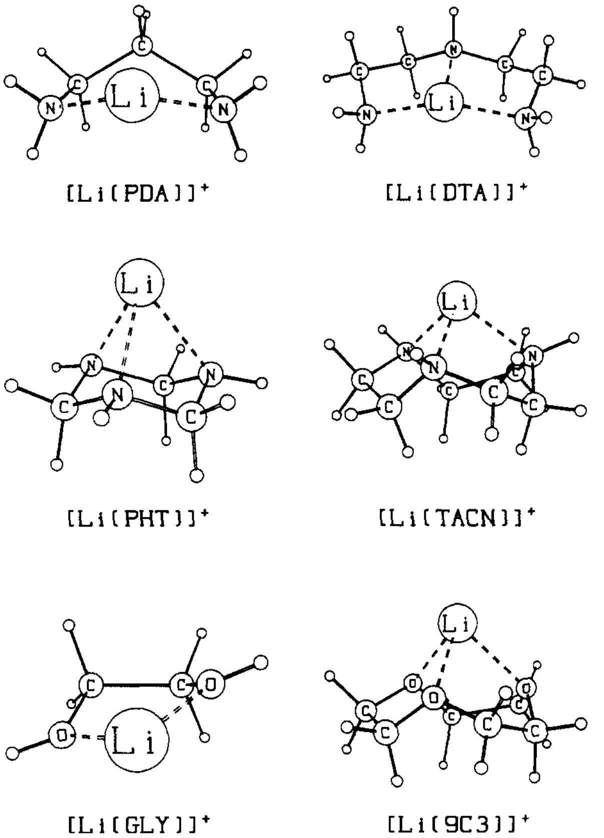
Table I. Abbreviations of Solvents Studied

NMe_3	trimethylamine
EDA	ethylenediamine = 1,2-diaminoethane
TMEDA	*N,N,N′,N′*-tetramethyl-ethylenediamine = 1,2-bis(dimethylamino)ethane
PDA	propanediamine = 1,3-diaminopropane
TMPDA	*N,N,N′,N′*-tetramethyl-propanediamine = 1,3-bis(dimethylamino)propane
DTA	diethylenetriamine = bis(2-aminoethyl)amine
PMDTA	*N,N,N′,N″,N″*-pentamethyl-diethylenetriamine = bis(2-(dimethylamino)ethyl)methylamine
PHT	perhydrotriazine = 1,3,5-triazacyclohexane
TMPHT	*N,N′,N″*-trimethyl-perhydrotriazine = 1,3,5-trimethyl-1,3,5-triazacyclohexane
TACN	1,4,7-triazacyclononane
TMTACN	1,4,7-trimethyl-1,4,7-triazacyclononane
Me_2O	dimethyl ether
Et_2O	diethyl ether
THF	tetrahydrofuran
GLY	ethylene glycol = 1,2-dihydroxyethane
9C3	9-crown-3 = 1,4,7-trioxacyclononane

calculational data with accuracies comparable to those of sophisticated experiments.[1,5,6] The size of systems practicable for theoretical treatments is increasing rapidly. However, most calculations have been restricted to isolated species. "Real chemistry" occurs in solution. Although much information can be obtained by gas-phase calculations, consideration of solvent effects is necessary for a more detailed understanding. One approach is to calculate supermolecules that represent the inner solvation sphere (which is assumed to be dominant) of the species in question. This approach should be especially useful for the calculation of molecules exhibiting strong interactions with the solvent. Because of their highly ionic character,[5] lithium compounds in polar solvents belong to this category. In a previous paper[7] we have shown by ab initio calculations that the interaction energies involved are nearly independent of the groups attached to lithium, provided there are no adverse steric effects. The model solvents used were ammonia and water. This paper extends the solvation studies to larger, more realistic nitrogen and oxygen bases by using the semiempirical MNDO[8] method. The results for equilibria between solvated methyllithium oligomers of different sizes have been encouraging.[5] We now report an attempt to evaluate both energetic and entropic aspects of lithium solvation as well as steric effects for a large range of different solvents. Abbreviations used for some solvents are listed in Table I. Some of the corresponding complexes with Li^+ are shown in Figure 1. The performance of MNDO is checked against experimental data and high-level ab initio calculations. Some of the latter have been carried out in this work and others taken from the literature.



$[Li[PDA]]^+$ $[Li[DTA]]^+$

$[Li[PHT]]^+$ $[Li[TACN]]^+$

$[Li[GLY]]^+$ $[Li[9C3]]^+$

Figure 1. Complexes of the lithium cation with selected nitrogen and oxygen bases. For the abbreviations used, see Table I. The drawings are not to the same scale.

Method of Calculation

All semiempirical calculations used the MNDO[8] approximation and various versions of the MOPAC and AMPAC program packages.[9] The latest calculations were done with the vectorized VAMP[10] version on a Convex C120 computer. Geometries were fully optimized and symmetry constraints applied if possible. Thermodynamic functions (enthalpy, *H*; entropy, *S*) were obtained by frequency analysis and by using the standard statistical formulae contained in the above programs. Sometimes the calculations proved to be difficult because finding a minimum required the consideration of several conformations. In some cases, following the imaginary vibrational modes of nonminimum structures was necessary several times. Since frequency analyses are very large calculations, huge amounts of computer time were necessary.

The MNDO heats of formation, ΔH_f, and entropies, *S*, are given in Table II. They correspond to gas-phase molecules at 298 K. The data were converted to reaction enthalpies, ΔH, entropies, ΔS, and free enthalpies, $\Delta G = \Delta H - T\Delta S$, at three different temperatures (250, 298, and 350 K). The results are shown in Tables V–VIII. Some of the species calculated had very low-lying vibrational modes, mostly internal rotations. Although these cause errors in the absolute values (especially for entropies), relative values and trends should be reliable. A more detailed analysis has been done for the clustering of Li^+ with NH_3 and H_2O where the internal rotations have been explicitly considered by an extension of the thermody-

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Table II. MNDO Heats of Formation, ΔH_f (kcal/mol), and Entropies, S (cal K^{-1} mol^{-1}), at 298 K

species[a]	point group	ΔH_f	S	species[a]	point group	ΔH_f	S
Li^+	K_h	156.7	31.8	$[Li(TMPHT)]^+$	C_{3v}	126.8	97.6
CH_3Li	C_{3v}	−1.4	53.7	$[Li(TACN)]^+$	C_3	95.9	89.3
NH_3	C_{3v}	−6.0	45.8	$[Li(TMTACN)]^+$	C_3	116.2	112.5
NMe_3	C_{3v}	−2.5	72.5	$[Li(H_2O)]^+$	C_{2v}	64.4	53.9
EDA	C_{2h}	−5.7	71.5	$[Li(H_2O)_2]^+$	D_{2d}	−25.0	78.7
TMEDA	C_{2h}	7.7	106.1				77.0[b]
PDA	C_{2v}	−10.6	79.4	$[Li(H_2O)_3]^+$	D_3	−109.9	92.5
TMPDA	C_{2v}	2.6	111.9				89.1[b]
DTA	C_s	−3.7	96.0	$[Li(H_2O)_4]^+$	S_4	−188.4	113.6
PMDTA	C_s	15.6	139.4				107.8[b]
PHT	C_{3v}	13.8	73.1	$[Li(Me_2O)]^+$	C_{2v}	74.2	74.9
TMPHT	C_{3v}	20.2	96.1	$[Li(Me_2O)_2]^+$	D_{2d}	−4.2	114.2
TACN	C_3	17.3	93.0	$[Li(Et_2O)]^+$	C_{2v}	55.0	89.9
TMTACN	C_3	32.3	115.9	$[Li(THF)]^+$	C_{2v}	64.8	79.0
H_2O	C_{2v}	−60.9	44.9	$[Li(GLY)]^+$	C_2	−0.8	74.3
Me_2O	C_{2v}	−51.2	64.8	$[Li(GLY)_2]^+$	D_2	−145.2	110.5
Et_2O	C_{2v}	−62.0	81.0	$[Li(9C3)]^+$	C_3	−19.6	90.9
THF	C_{2v}	−59.3	69.9	$CH_3Li(NH_3)$	C_{3v}	−27.2	81.1
GLY	C_2	−106.2	73.8	$CH_3Li(NH_3)_2$	C_s	−46.6	103.2
9C3	C_3	−119.9	87.2	$CH_3Li(NH_3)_3$	C_3	−60.1	111.2
$[Li(NH_3)]^+$	C_{3v}	115.8	54.0	$CH_3Li(NMe_3)$	C_{3v}	−21.1	110.9
$[Li(NH_3)_2]^+$	D_{3h}	78.0	81.5	$CH_3Li(EDA)$	C_1	−35.4	97.3
			77.8[b]	$CH_3Li(EDA)_2$	C_1	−46.1	131.8
$[Li(NH_3)_3]^+$	C_{3h}	46.0	105.1	$CH_3Li(TMEDA)$	C_1	−18.0	127.1
			90.0[b]	$CH_3Li(TMPHT)$	C_{3v}	5.6	127.1
$[Li(NH_3)_4]^+$	T_d	21.0	107.6	$CH_3Li(TACN)$	C_3	−15.8	110.7
			102.5[b]	$CH_3Li(TMTACN)$	C_3	4.4	127.8
$[Li(NMe_3)]^+$	C_{3v}	119.5	86.4	$CH_3Li(H_2O)$	C_s	−79.3	82.4
$[Li(NMe_3)_2]^+$	D_{3d}	87.0	133.6	$CH_3Li(H_2O)_2$	C_s	−152.0	97.5
$[Li(EDA)]^+$	C_2	90.8	73.7	$CH_3Li(H_2O)_3$	C_3	−220.0	109.4
$[Li(EDA)_2]^+$	D_2	40.2	106.0	$CH_3Li(Me_2O)$	C_s	−67.4	101.8
$[Li(EDA)_3]^+$	D_3	27.1	135.8	$CH_3Li(Et_2O)$	C_1	−82.5	110.5
$[Li(TMEDA)]^+$	C_2	107.0	105.8	$CH_3Li(THF)$	C_s	−75.1	108.8
$[Li(PDA)]^+$	C_s	82.8	87.4	$CH_3Li(THF)_2$	C_1	−141.4	147.4
$[Li(TMPDA)]^+$	C_s	98.8	115.6	$CH_3Li(GLY)$	C_1	−129.4	101.4
$[Li(DTA)]^+$	C_s	73.2	92.6	$CH_3Li(GLY)_2$	C_1	−240.3	130.5
$[Li(PMDTA)]^+$	C_s	98.7	132.3	$CH_3Li(9C3)$	C_3	−138.0	111.4
$[Li(PHT)]^+$	C_{3v}	113.9	74.8				

[a] For the abbreviations used, see Table I. [b] Calculated including internal rotations of the solvent molecules.

Table III. Total (−au), Zero-Point Vibrational (kcal/mol), and Solvation Energies (kcal/mol)[a]

species	point group	3-21G//3-21G	6-31G*//6-31G*	MP2/6-31G*//6-31G*	6-31+G*//6-31G*	MP2/6-31+-G*//6-31G*	ZPE[b]
$CH_3Li(NH_3)$[c]	C_{3v}	102.677 84 (33.4)	103.238 24 (24.1)	103.558 35 (26.8)	103.242 23 (22.1)	103.566 85 (23.6)	47.59 (0) (21.3)[d]
$CH_3Li(NH_3)_2$	C_s	158.583 50 (21.0)	159.445 21 (14.2)	159.938 13 (16.4)	159.451 26 (12.3)	159.951 96 (14.1)	72.14 (1) (12.4)[d]
$CH_3Li(NH_3)_3$	C_{3v}	214.479 85 (15.2)					96.46 (0)
$CH_3Li(H_2O)$[c]	C_s	122.394 14 (35.0)	123.059 72 (21.0)	123.395 03 (23.3)	123.065 51 (19.0)	123.406 84 (19.8)	38.12 (0) (18.0)[d]
$CH_3Li(H_2O)_2$	C_s	198.022 54 (26.6)	199.094 49 (15.1)	199.620 80 (18.7)	199.102 92 (12.4)	199.638 83 (14.6)	54.35 (1) (12.3)[d]
$CH_3Li(H_2O)_3$	C_3	273.651 82 (27.2)					70.95 (2)

[a] The values in parentheses are the association energies at the corresponding levels. [b] Zero-point energy at 3-21G; number of imaginary frequencies in parentheses. [c] Reference 7. [d] Final estimate at MP2/6-31+G*//6-31G* + ZPE, see text.

namics part of the program.[11] Replacing low-frequency vibrations by internal rotations generally results in lowering the entropy by about 1–5 cal K^{-1} mol^{-1} per degree of freedom.

Ab initio calculations were performed with standard basis sets (3-21G, 6-31G*, 6-31+G*)[1a] incorporated in the Gaussian 82 program package.[12] Electron correlation was estimated by using Møller–Plesset theory[13] carried out to second-order keeping the core electrons frozen. Zero-point energies (ZPE) were obtained by frequency analysis at 3-21G. Total energies and ZPEs as well as ab initio solvation energies are listed in Table III. The final estimates of reaction energies given in Table IV have been evaluated at the same high level previously used (MP2/6-31+G*/

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[11] The *molecular* partition function for a free internal rotation is $z = 8\pi^3IkT)^{1/2}/(\sigma\hbar)$. The *molar* thermodynamic functions are then $U = RT^2(\partial \ln z)/\partial T = {}^1/_2RT$, $H = U$, and $S = U/T + R \ln z$. Abbreviations: I, reduced moment of inertia; k, Boltzmann's constant; T, absolute temperature; σ, symmetry factor; $\hbar$, Planck's constant; R, gas constant.

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Table IV. Comparison of Experimental and Calculated (ab Initio and MNDO) Thermodynamic Parameters of the Lithium Cation (R = "+") and Methyllithium (R = CH_3) Solvation, $[RLi(S)_n]^+ + S \rightarrow [RLi(S)_{n+1}]^+$

species, solv	$-\Delta H$				$-\Delta S$		
n, $n + 1$	exptl	ab initio[a]	MNDO[b]	MNDO[c]	exptl	MNDO[b]	MNDO[c]
Li^+, S = NH_3[d]							
0, 1	39.1 ± 2[e]	39.7	34.8	34.8	23.5[e]	23.6	23.6
1, 2	33.1 ± 1.3		31.8	31.2	29.7 ± 2.1	18.4	20.7
2, 3	21.0 ± 0.3		25.9	25.7	25.3 ± 0.5	22.2	33.2
3, 4	16.5 ± 0.3		19.0	18.9	32.6 ± 0.7	43.4	33.1
Li^+, S = H_2O[f]							
0, 1	34.0 ± 2	34.1	31.3	31.3	23.0	22.8	22.8
1, 2	25.8		28.4	27.8	21.1	20.1	20.4
2, 3	20.7		24.0	23.8	24.9	31.1	32.4
3, 4	16.4		17.6	17.4	29.9	23.8	25.9
CH_3Li, S = NH_3							
0, 1		21.3	19.8			18.4	
1, 2		12.4	13.3			23.7	
2, 3			7.5			37.8	
CH_3Li, S = H_2O							
0, 1		18.0	17.0			16.2	
1, 2		12.3	11.7			29.9	
2, 3			7.0			33.0	

[a] At MP2/6-31+G*//6-31G* + ZPE, see the text. [b] Data at 298 K considering no internal rotations. [c] Data at the temperatures of the measurements considering internal rotations. [d] Experimental values from ref 15. [e] From ref 17. [f] Experimental values from ref 16.

Table V. Thermodynamic Parameters for the Solvation of the Lithium Cation with Nitrogen Bases at Different Temperatures[a]

	250 K			298 K			350 K		
base[b]	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$
monodentate									
NH_3	34.7	23.3	28.9	34.8	23.6	27.8	34.8	23.8	26.5
2 NH_3	31.9	18.6	27.2	31.8	18.4	26.4	31.7	18.0	25.4
3 NH_3	26.0	22.5	20.3	25.9	22.2	19.2	25.8	21.9	18.1
4 NH_3	19.1	43.8	8.2	19.0	43.4	6.1	18.9	43.0	3.8
NMe_3	34.6	17.9	30.2	34.7	17.9	29.3	34.6	17.9	28.4
2 NMe_3	30.1	25.9	23.6	30.0	25.4	22.4	29.8	24.8	21.1
bidentate									
EDA	60.1	29.2	52.8	60.2	29.6	51.4	60.3	29.9	49.8
2 EDA	44.9	39.4	35.1	44.9	39.1	33.2	44.8	38.8	31.2
3 EDA	7.5	42.4	-3.1	7.4	41.8	-5.1	7.2	41.2	-7.2
TMEDA	57.3	31.8	49.4	57.4	32.0	47.9	57.4	32.1	46.2
PDA	63.2	23.4	57.3	63.3	23.8	56.2	63.4	24.0	55.0
TMPDA	60.4	27.9	53.5	60.5	28.1	52.1	60.5	28.2	50.6
tridentate acyclic									
DTA	79.6	34.6	71.0	79.8	35.2	69.3	79.9	35.6	67.4
PMDTA	73.5	38.6	63.8	73.6	38.9	62.0	73.6	39.1	60.0
tridentate cyclic									
PHT	56.4	29.7	49.0	56.5	30.0	47.6	56.6	30.3	46.0
TMPHT	50.1	30.2	42.6	50.1	30.3	41.1	50.1	30.3	39.5
TACN	78.0	35.0	69.2	78.1	35.5	67.5	78.2	35.9	65.7
TMTACN	72.8	34.8	64.0	72.8	35.2	62.4	72.9	35.3	60.5

[a] MNDO calculation. Heats (ΔH) and free enthalpies (ΔG) of reaction in kcal/mol; reaction entropies (ΔS) in cal K^{-1} mol^{-1}. [b] Data correspond to successive addition of *one* molecule of base. For the abbreviations used, see Table I.

Table VI. Thermodynamic Parameters for the Solvation of the Lithium Cation with Oxygen Bases at Different Temperatures[a]

	250 K			298 K			350 K		
base[b]	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$
monodentate									
H_2O	31.2	22.5	25.6	31.3	22.8	24.5	31.4	23.0	23.3
$2H_2O$	28.5	20.4	23.4	28.4	20.1	22.4	28.3	19.8	21.4
$3H_2O$	24.1	31.4	16.2	24.0	31.1	14.7	23.9	30.8	13.1
$4H_2O$	17.7	24.3	11.6	17.6	23.8	10.5	17.4	23.4	9.2
Me_2O	31.3	21.7	25.9	31.3	21.7	24.8	31.3	21.6	23.7
$2Me_2O$	27.4	26.0	20.8	27.2	25.4	19.6	27.0	24.8	18.3
Et_2O	39.7	23.0	34.0	39.7	23.0	32.9	39.7	22.9	31.7
THF	32.6	22.7	26.9	32.6	22.7	25.8	32.6	22.6	24.7
bidentate									
GLY	51.2	31.0	43.5	51.3	31.3	42.0	51.4	31.5	40.3
2GLY	38.2	38.1	28.7	38.1	37.7	26.9	38.0	37.2	25.0
tridentate cyclic									
9C3	56.3	27.9	49.3	56.3	28.0	48.0	56.4	28.1	46.5

[a] MNDO calculation. Heats (ΔH) and free enthalpies (ΔG) of reaction in kcal/mol; reaction entropies (ΔS) in cal K^{-1} mol^{-1}. [b] Data correspond to successive addition of *one* molecule of base. For the abbreviations used, see Table I.

Table VII. Thermodynamic Parameters for the Solvation of Methyllithium with Nitrogen Bases at Different Temperatures[a]

	250 K			298 K			350 K		
base[b]	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$
monodentate									
NH_3	19.9	18.8	15.2	19.8	18.4	14.3	19.7	18.0	13.4
$2NH_3$	13.3	24.0	7.3	13.3	23.7	6.2	13.1	23.4	5.0
$3NH_3$	7.6	38.2	-1.9	7.5	37.8	-3.8	7.4	37.4	-5.7
NMe_3	17.4	15.9	13.4	17.2	15.3	12.7	17.1	14.7	11.9
bidentate									
EDA	28.4	28.2	21.3	28.3	27.9	20.0	28.2	27.6	18.5
2EDA	5.2	37.4	-4.2	5.0	37.0	-6.0	4.9	36.6	-7.9
TMEDA	24.4	33.1	16.1	24.3	32.7	14.6	24.2	32.2	12.9
tridentate cyclic									
TMPHT	13.4	23.3	7.6	13.2	22.7	6.5	13.0	22.1	5.3
TACN	31.8	36.2	22.8	31.8	36.0	21.0	31.7	35.7	19.2
TMTACN	26.6	42.1	16.1	26.5	41.8	14.0	26.4	41.4	11.9

[a] MNDO calculation. Heats (ΔH) and free enthalpies (ΔG) of reaction in kcal/mol; reaction entropies (ΔS) in cal K^{-1} mol^{-1}. [b] Data correspond to successive addition of *one* molecule of base. For the abbreviations used, see Table I.

Table VIII. Thermodynamic Parameters for the Solvation of Methyllithium with Oxygen Bases at Different Temperatures[a]

	250 K			298 K			350 K		
base[b]	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$
monodentate									
H_2O	17.1	16.6	12.9	17.0	16.2	12.1	16.8	15.8	11.3
$2H_2O$	11.8	30.2	4.3	11.7	29.9	2.8	11.6	29.5	1.3
$3H_2O$	7.1	33.3	-1.2	7.0	33.0	-2.8	6.9	32.6	-4.5
Me_2O	15.0	17.3	10.6	14.8	16.7	9.8	14.6	16.1	9.0
Et_2O	19.3	24.8	13.1	19.2	24.2	11.9	19.0	23.7	10.7
THF	14.6	15.4	10.8	14.4	14.8	10.0	14.3	14.2	9.3
2THF	7.2	31.8	-0.8	7.1	31.3	-2.3	6.9	30.8	-3.9
bidentate									
GLY	21.9	26.5	15.3	21.8	26.1	14.0	21.7	25.7	12.7
2GLY	4.8	45.1	-6.5	4.7	44.8	-8.6	4.6	44.4	-10.9
tridentate cyclic									
9C3	16.8	30.0	9.3	16.7	29.5	7.9	16.5	29.0	6.4

[a] MNDO calculation. Heats (ΔH) and free enthalpies (ΔG) of reaction in kcal/mol; reaction entropies (ΔS) in cal K^{-1} mol^{-1}. [b] Data correspond to successive addition of *one* molecule of base. For the abbreviations used, see Table I.

/6-31G* + ZPE).[7] The differences in ZPE have been scaled by the empirical factor 0.9.[14]

Performance of MNDO Method

In order to evaluate the performance of the MNDO method for calculating heats and entropies of solvation, two comparisons have been made. One source of data are measurements of gas phase complexation equilibria of the lithium cation with a variety of bases[15–17] by means of high-pressure mass spectrometry (HPMS) and ion cyclotron resonance (ICR) spectroscopy. Some studies also dealed with larger clusters of ammonia and water about the lithium cation. The other sources of data for comparison are ab initio calculations at sufficiently high levels to provide reliable energetic data. This is the only approach possible for solvated organolithium compounds since experimental data are not available.

Table IV shows experimental heats and entropies of solvation for the clustering of the lithium cation with ammonia and water, together with calculated ab initio and MNDO data. The latter have been evaluated both at 298 K without any corrections and at the temperatures of the measurements with additional consideration of the free internal rotations of the solvent molecules. The same temperatures as for the ammonia clusters[15] have been applied for the water clusters, since these data were not obtainable from the literature.[16] The temperatures chosen were 298, 640, 540, and 360 K for the first through fourth clusters, respectively.[18] There is reasonable agreement between calculated and experimental enthalpies of solvation. The temperature dependence is rather small (maximum change 0.6 kcal/mol). MNDO underestimates the complexation energies of the smaller clusters and overestimates those of the larger clusters by up to 4.7 kcal/mol.

The MNDO and ab initio solvation energies of methyllithium with ammonia and water agree within 1.5 kcal/mol (Table IV). The ab initio level used (MP2/6-31+G*//6-31G* with zero-point energy corrections) has been shown to be sufficient[7] for obtaining reliable data. No attempt has been made to correct the ab initio data to 298 K since the temperature dependence of the enthalpies is rather small. Although the second and third clusters of methyllithium with water are not local minima (they are unstable with respect to hydrolysis; i.e., there is no barrier and optimization without symmetry restrictions leads to the formation of methane and hydrated lithium hydroxide), the energetic data can be used for comparison. The imaginary frequency of the monoammonia solvate $CH_3Li(NH_3)$ corresponds to the internal rotation of the

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methyl and NH_3 groups. Because of the size of the systems, the trisolvated methyllithium species have only been calculated at 3-21G. The data are included in Table III for completeness. It is interesting to note that the C–Li distances in $CH_3Li(H_2O)_3$ and $CH_3Li(NH_3)_3$ are elongated by 0.32 and 0.20 Å, respectively. Similar effects due to solvation are commonly noted in crystal structures.[19] The lithium cation in the trihydrate and its surrounding, the three oxygens of the water molecules, are nearly in the same plane, indicating the beginning of solvent-separation ion pair formation. The approach toward planarity of the $Li(N)_3$ moiety in the triammoniate is less pronounced. Since MNDO overestimates the strength of the C–Li bond,[5] its elongation due to solvation occurs to a smaller extent with this method. However, interactions of lithium with N and O bases, which are the scope of this study, are given as well (see discussion above).

Entropies calculated by statistical thermodynamics are quite reliable for rigid systems. Free internal rotations (which are characterized by very low wavenumbers in a frequency analysis) also can be treated properly. Problems arise, however, for low-frequency vibrations, where the harmonic approximation fails. This results in calculated entropies that are too large. In the Li^+/NH_3 system the internal rotations are well separated from the rest of the molecular vibrations. Table IV shows essentially perfect agreement with experiment for the first and the fourth cluster if the data are evaluated at the middle of the temperature range used for the measurements and as long as the free internal rotations of the bound ammonia molecules within the clusters are considered. Entropy data involving the linear $[Li(NH_3)_2]^+$ cluster are inaccurate because of the very low-frequency degenerate bending motions. These interact strongly with rotations of the bent molecule. Assuming similar entropy changes (about 4 cal K^{-1} mol^{-1}/degree of freedom) when considering these two pseudo internal rotations, the entropy changes for the formation of the second and the third clusters are 28.7 and 25.2 cal K^{-1} mol^{-1}, respectively. These estimates are in excellent agreement with the experimental data (29.7 and 25.3 cal K^{-1} mol^{-1}). Calculated entropy data for the third and fourth water clusters are less satisfactory. In the case of $[Li(H_2O)_4]^+$ there are only two true internal rotations; the other two are mixed with vibrations of the $Li(O)_4$ skeleton. This leads to errors in the treatment.

Such detailed analyses have not, however, been made for most of the other systems, but the data should be sufficiently accurate for the comparisons of different solvents where the relatively small errors in entropies are expected to cancel. Calculated entropies should be most accurate for the formation of rigid systems with no additional internal rotations and no "floppy" vibrational modes, i.e., for most of the monosolvated lithium cations.

We conclude that MNDO calculations seem to be a practical tool for the investigation of solvation of lithium compounds by donor solvents. This is also shown by an increasing number of structures of solvated lithium compounds that have been predicted correctly by MNDO.[2,20] With a reparametrization of lithium within the PM3 method,[21] which is in progress,[22] results may be even better. By using MNDO or PM3, "designing" a lithium solvent for special purposes should be possible. Recently, there has been much interest in the selective complexation of lithium and the other alkali metals.[23] We believe semiempirical calculations to be useful in this area of research.

Results and Discussion

Data for the solvation of the lithium cation by nitrogen and oxygen bases (Table I summarizes the abbreviations used) are given in Tables V and VI, respectively, while those for methyllithium are listed in Tables VII and VIII, respectively. The *negative* of all values is given. First, we will discuss some general trends. As expected, solvation enthalpies are much larger for the lithium cation than for methyllithium. The differences are about 12–18 and 13–17 kcal/mol per solvation site for nitrogen and oxygen bases, respectively. Nitrogen bases in general have larger solvation enthalpies than the analogous oxygen bases (e.g., NH_3 vs H_2O, EDA vs GLY, etc.). This has also been shown by ab initio calculations on the complete set of lithium first-row compounds.[7] Replacing the hydrogens at a basic nitrogen or oxygen by methyl groups results in a lowering of the association enthalpy by about 1–2 kcal/mol per basic center. This is a steric effect of the chelates (e.g., EDA vs TMEDA, PHT vs TMPHT, etc.) since the association enthalpies of NH_3 and NMe_3 (and also of H_2O and Me_2O) with Li^+ are almost identical.

Unless stated otherwise, the following discussion refers to solvation at the standard temperature of 298 K.

Lithium Cation Solvates. We note some interesting details. Comparing the bidentate nitrogen bases, it appears that a six-membered chelate ring is better than a five-membered ring: PDA and TMPDA have 3 kcal/mol larger solvation enthalpies for Li^+ than EDA and TMEDA, respectively. The entropy terms also are more favorable (smaller) for PDA and TMPDA by 6 and 4 cal K^{-1} mol^{-1}, respectively. These result in ΔG differences of about 4.5 kcal/mol. The "best" tridentate ligand investigated is the acyclic DTA which has nearly the same solvation entropy but a 1.8 kcal/mol larger free enthalpy of solvation than those of the cyclic nine-membered TACN. However, its N-methylated counterpart, PMDTA, is 7.3 kcal/mol "worse" than DTA. The six-membered ring species PHT and TMPHT cannot compete with the other tridentate ligands: they are over 20 kcal/mol less favorable. The analogous oxygen compound to TMTACN, 9-crown-3, has much less "solvating power"; $-\Delta G$ of solvation is only 48 kcal/mol compared to 62 kcal/mol for TMTACN. However, the entropy term is more favorable by 7 cal K^{-1} mol^{-1}.

The N-methylated species are more "realistic" solvents for highly basic lithium compounds; i.e., they have no acidic N-bound hydrogens. Although the acyclic tridentate ligand PMDTA has a 0.8 kcal/mol higher solvation enthalpy than its cyclic counterpart TMTACN, the more favorable entropy term makes the cyclic system the better solvent with $\Delta\Delta G = 0.4$ kcal/mol. Recently, Fraenkel[24] has used TMTACN to prepare monomeric organolithium compounds. This chelate effect of TMTACN becomes more pronounced at higher temperatures and is also seen in the comparison of ammonia with ethylenediamine. Attaching $2NH_3$ to Li^+ is 6.4 kcal/mol more exothermic

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than complexation with one molecule of EDA, but the difference in ΔG is only 2.8 kcal/mol. Occupying all four solvation sites at the lithium cation even results in a reversal of stabilities: $-\Delta G$ is 5.1 kcal/mol larger for adding 2EDA than $4NH_3$. This effect also leads to the possibility of a 6-fold coordinated lithium cation, in contrast to the normal 4-fold solvation; ΔG for the addition of a third molecule of EDA to Li^+ is only slightly positive at lower temperatures. Indeed, there is an X-ray structure of this type, LiI·3EDA.[25] It is of interest to compare the binding energy of the lithium cation with EDA calculated by Ikuta[26] (66.3 kcal/mol at 6-31G*//3-21G) with the MNDO value (60.2 kcal/mol). Inclusion of electron correlation, zero-point energy corrections, and diffuse functions in the basis set to eliminate basis set superposition errors (BSSE) is expected to reduce Ikuta's value by at least 5 kcal/mol[7] to about 61 kcal/mol. The latter value should be a good estimate for the "true" solvation energy, in excellent agreement with MNDO.

The chelate effect is not as pronounced with the oxygen bases (Table VI). Solvation by two water molecules is 4.9 kcal/mol more exergonic than by one molecule of ethylene glycol. This difference is smaller, 3.2 kcal/mol, with $4H_2O$ vs 2glycol, but still solvation by water is better. Dimethyl ether also is better than glycol. Thus, ethylene glycol seems to be a rather ineffective solvent for the *lithium cation*. (The situation is quite different for *methyllithium*, see below.) The entropy terms are almost the same for diethyl ether and for tetrahydrofuran, but the enthalpy (and thus, free enthalpy) are more negative by 7 kcal/mol for Et_2O. This is due to an agostic interation[5] of Li^+ with the terminal methyl hydrogens of diethyl ether in the W conformation. As a consequence, the C–O–C angle in the Et_2O moiety is widened by 6.6°, and the C–C–O angle is reduced by 3.8°, thus bringing the hydrogens closer to the lithium cation.[27] The Li–H agostic stabilization is expected to be smaller for more sterically hindered organolithium compounds (e.g., for methyllithium, see below). This should favor THF relative to Et_2O, especially when aggregates are involved.

Methyllithium Solvates. The steric requirements of the solvates are higher for methyllithium than for the lithium cation. In contrast to Li^+, the solvation enthalpies with NMe_3 and Me_2O are 2–3 kcal/mol less than those with NH_3 and H_2O, respectively. The chelate effect also is more pronounced for methyllithium. The difference in ΔG for $2NH_3$ and EDA is only 0.5 kcal/mol (Li^+, 2.8 kcal/mol). The same is true for $2H_2O$ vs GLY: $\Delta\Delta G$ = 0.9 vs 4.9 kcal/mol. Thus, glycol (and its derivatives) should be better solvents for organolithium compounds than for free Li^+. The difference between the solvating powers of Et_2O and THF, observed for Li^+ (see above), also becomes smaller for CH_3Li. The solvation enthalpy with THF is only 4.8 kcal/mol smaller than with Et_2O. Together with the much better solvation entropy (−14.8 vs −24.2 cal K^{-1} mol^{-1}), THF is now only 1.9 kcal/mol worse than Et_2O. With a second solvent molecule attached, THF should be even better than Et_2O. However, Table VIII shows that a second molecule of THF is only weakly bound (ΔG = +2.3 kcal/mol). Thus, the superior solvating ability of THF taken advantage of by experimentalists appears to be due to its better solvating power for organolithium compounds and aggregates rather than for the free Li^+ cation.

The attachment of a third ammonia or water molecule to methyllithium is endergonic by 3.8 and 2.8 kcal/mol, respectively. A 5-fold lithium coordination in methyllithium does not appear to be possible: ΔG for a second molecule of EDA or GLY is +6.0 or +8.6 kcal/mol, respectively. In contrast to Li^+ there is not much difference between the solvating powers of the bidentate TMEDA and the tridentate TMTACN; ΔH and ΔG of solvation are about 25 and 14 kcal/mol, respectively, for both solvents.

Temperature Dependence of Solvation. An inspection of Tables V–VII shows that the solvation enthalpies are rather unaffected by temperature changes. The maximum changes for ΔH occurring in the temperature range 250–350 K are 0.4 kcal/mol. In general, $-\Delta H$ increases for the first solvation of Li^+ and decreases for CH_3Li with increasing temperature. However, this subtle effect should not be overemphasized.

The temperature dependence of solvation entropies also is rather small (maximum changes of 1.2 cal K^{-1} mol^{-1}). In most cases, ΔS becomes more negative with increasing temperature for the first solvent molecule attached. For the larger clusters, however, the solvation entropy increases (i.e., becomes more favorable) with increasing temperature. This is due to the more dominant vibrational terms in the larger clusters that have more vibrational modes. The addition of a third molecule of EDA to Li^+, e.g., reveals an entropy change of −42.4 cal K^{-1} mol^{-1} at 250 K and of −41.2 cal K^{-1} mol^{-1} at 350 K. However, the positive temperature dependence of $-T\Delta S$ is not overcome by this effect.

Of course, the free enthalpies of solvation, $\Delta G = \Delta H - T\Delta S$, are most affected by temperature changes. In general, $-\Delta G$ *decreases* (i.e., becomes less favorable) with *increasing* temperature, as expected. A reverse temperature dependence has been observed for the solvent-induced dissociation of alkyllithium tetramers into dimers[5] where the solvation is coupled with a change in the number of solvated species.

Conclusions

The semiempirical MNDO method is a valuable tool for investigating lithium–solvent interactions. This has been shown by comparison with experimental and high-level ab initio data. Solvation enthalpies and entropies as well as steric effects are accessible. MNDO may be used for designing the "optimum solvent" for special purposes, e.g., to obtain monomeric lithium compounds[24] or free anions. The influence of solvation on lithium reactions also should be addressable. The accuracy of the entropy calculations can be improved considerably for molecules having free internal rotations when these are included explicitly in the statistical treatment. The best results with the standard program (treatment of internal rotations is not possible)[9,10] can be obtained for rigid systems. Entropy calculations are especially useful for quantifying the "chelate effect".

Nitrogen bases in general have larger solvation enthalpies than the analogous oxygen compounds. With nitrogen bases, lithium prefers six-membered chelate rings over five-membered rings. Ethylene glycol (and its derivatives) and 9-crown-3 are better solvents for methyllithium than for a free lithium cation. With strong chelating agents, e.g., with ethylenediamine, higher coordination numbers than the normally observed maximum number of four can be achieved.

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(27) Indeed, the solvation enthalpy calculated with Et_2O in the U conformation that excludes the agostic interaction is almost the same as that for THF. Presumably, the Li–H agostic stabilization is somewhat overestimated by MNDO.

dustrie, the Stiftung Volkswagenwerk, and Convex Computer GmbH.

Registry No. EDA, 107-15-3; TMEDA, 110-18-9; PDA, 109-76-2; TMPDA, 110-95-2; DTA, 111-40-0; PMDTA, 3030-47-5; PHT, 110-90-7; TMPHT, 108-74-7; TACN, 4730-54-5; TMTACN, 96556-05-7; THF, 109-99-9; GLY, 107-21-1; 9C3, 27725-91-3; Li^+, 17341-24-1; CH_3Li, 917-54-4; NH_3, 7664-41-7; NMe_3, 75-50-3; H_2O, 7732-18-5; Me_2O, 115-10-6; Et_2O, 60-29-7; $[Li(NH_3)]^+$, 52472-72-7; $[Li(NH_3)_2]^+$, 43415-98-1; $[Li(NH_3)_3]^+$, 68011-04-1; $[Li(NH_3)_4]^+$, 44013-01-6; $[Li(NMe_3)]^+$, 87311-90-8; $[Li(NMe_3)_2]^+$, 122677-10-5; $[Li(TMPHT)]^+$, 122677-11-6; $[Li(TACN)]^+$, 122677-12-7; $[Li(TMTACN)]^+$, 122677-13-8; $[Li(H_2O)]^+$, 63313-34-8; $[Li(H_2O)_2]^+$, 30051-05-9; $[Li(H_2O)_3]^+$, 43567-59-5; $[Li(H_2O)_4]^+$, 40791-36-4; $[Li(Me_2O)]^+$, 53259-64-6; $[Li(Me_2O)_2]^+$, 53259-69-1; $[Li(Et_2O)]^+$, 44387-74-8; $[Li(THF)]^+$, 53307-59-8; $[Li(GLY)]^+$, 122677-14-9; $[Li(GLY)_2]^+$, 122677-15-0; $[Li(9C3)]^+$, 122677-16-1; $CH_3Li(NH_3)$, 63448-35-1; $CH_3Li(NH_3)_2$, 122677-17-2; $CH_3Li(NH_3)_3$, 122677-18-3; $CH_3Li(NMe_3)$, 63448-39-5; $CH_3Li(EDA)$, 122677-19-4; $CH_3Li(EDA)_2$, 122677-20-7; $CH_3Li(TMEDA)$, 106563-74-0; $CH_3Li(TMPHT)$, 122677-21-8; $CH_3Li(TACN)$, 122677-22-9; $CH_3Li(TMTACN)$, 122677-23-0; $CH_3Li(H_2O)$, 117317-80-3; $CH_3Li(H_2O)_2$, 122677-24-1; $[Li(EDA)]^+$, 82268-60-8; $[Li(EDA)_2]^+$, 110556-22-4; $[Li(EDA)_3]^+$, 122677-25-2; $[Li(TMEDA)]^+$, 45651-70-5; $[Li(PDA)]^+$, 89960-63-4; $[Li(TMPDA)]^+$, 122677-26-3; $[Li(DTA)]^+$, 122677-27-4; $[Li(PMDTA)]^+$, 57444-53-8; $[Li(PHT)]^+$, 122677-28-5; $CH_3Li(H_2O)_3$, 122677-29-6; $CH_3Li(Me_2O)$, 122677-30-9; $CH_3Li(Et_2O)$, 122677-31-0; $CH_3Li(THF)$, 122677-32-1; $CH_3Li(THF)_2$, 122677-33-2; $CH_3Li(GLY)$, 122677-34-3; $CH_3Li(GLY)_2$, 122677-35-4; $CH_3Li(9C3)$, 122677-36-5.

Reaction of Organoaluminum Species with Macrocyclic and Open-Chain Tetradentate Amines: Synthesis and Molecular Structure of $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ and $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$. An Examination of Aminoalanes Containing Six-Coordinate Aluminum Atoms

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Reaction of diethylaluminum chloride with *N*,*N*′-bis(3-aminopropyl)ethylenediamine in a toluene/methylene chloride mixture affords the crystalline product $[Cl_2Al{\cdot}C_8H_{20}N_4][Al(C_2H_5)_2]$ (I). I crystallizes in the monoclinic space group $C2/c$ with unit-cell parameters $a = 17.056$ (4) Å, $b = 10.855$ (3) Å, $c = 11.050$ (4) Å, $\beta = 116.77$ (2)°, $V = 1826.6$ (9) Å^3, and $D_{calcd} = 1.29$ g cm^{-3} for $Z = 4$. Least-squares refinement based upon 970 observed reflections (1354 collected reflections; 1200 unique reflections; $R_{int} = 0.018$) with intensities $I > 3\sigma(I)$ in the range $3.50 < 2\theta < 45.0°$ converged at $R = 0.044$ ($R_w = 0.059$). The two terminal primary amine nitrogen atoms of *N*,*N*′-bis(3-aminopropyl)ethylenediamine are bridged by a dichloroaluminum unit and a diethylaluminum unit, thereby constituting a planar Al_2N_2 four-membered ring with an Al···Al contact of 2.819 (2) Å. The mean Al–N bond distance in I is 1.97 (3) Å while the independent Al–Cl distance is 2.394 (1) Å. Additionally, I contains a crystallographic 2-fold axis coincident with Al(1) and Al(2). The crystalline product $[Al(CH_3)_2][ClAl{\cdot}C_{10}H_{21}N_4{\cdot}OCH_3][ClAl(CH_3)]$ (II) is obtained from reaction of the methanol adduct of cyclam, $C_{10}H_{24}N_4{\cdot}CH_3OH$, trimethylaluminum, and $ZrCl_4$. II crystallizes in the triclinic space group $P\bar{1}$ with unit-cell parameters $a = 9.234$ (3) Å, $b = 10.681$ (3) Å, $c = 15.021$ (5) Å, $\alpha = 96.23$ (3)°, $\beta = 108.78$ (3)°, $\gamma = 97.34$ (3)°, $V = 1373.3$ (8) Å^3, and $D_{calcd} = 1.30$ g cm^{-3} for $Z = 2$. Least-squares refinement based on 2976 observed reflections (3887 collected reflections; 3616 unique reflections; $R_{int} = 0.017$) with intensities $I > 3\sigma(I)$ in the range $3.50 < 2\theta < 45.0°$ converged at $R = 0.056$ ($R_w = 0.074$). II also contains an Al_2N_2 four-membered ring with an Al···Al contact of 2.889 (2) Å. The central aluminum atom of both I and II are six-coordinate residing in octahedral environments. The coordination sphere of the octahedral aluminum atom in I consists of the four nitrogen atoms of the open-chain amine in addition to two chloride atoms residing on either side of the equatorial N_4 plane. The coordination sphere of the core aluminum atom in II consists of the four nitrogen atoms of the macrocycle, one chlorine atom, and a μ-bridging methoxide fragment. The mean Al–N distance in II is 1.98 (4) Å while Al–Cl distances of 2.368 (1) and 2.130 (3) Å were observed. The mean Al–O bond distance in the Al_2ON four-membered ring in II is quite short at 1.88 (6) Å.

Introduction

The interactions of aluminum species with amines represents one of the most extensively investigated facets of organoaluminum chemistry. Investigations may be traced to 1930 when Krause and Dittmar[1] reported the synthesis of $H_3N{\cdot}Al(p\text{-tolyl})_3$ and $H_3N{\cdot}AlPh_3$. In terms of more recent studies, seminal work has been reported concerning both aluminum–nitrogen oligomers[2-10] and poly(*N*-alkylimino)alanes.[11-25] Although these studies often resulted

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