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Hexameric Lithium Phenolate. Crystal Structures and ^{7}Li Quadrupole Coupling in Solid and Solution Phases

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Abstract: Whereas lithium phenolate in dioxolane coexists as a mixture of comparable amounts of a hexamer and tetramer, together with minor amounts of less aggregated species, in THF the predominant species is the tetramer. Two crystalline forms of lithium phenolate have been obtained from THF and THF/hexane solutions, and X-ray crystallographic studies show that they consist of very similar hexagonal prismatic hexamers of lithium phenolate with one THF molecule bound to each lithium cation. The ^{7}Li nuclear quadrupole coupling constant (QCC = e^2Qq_{zz}/h = 67 ± 1 kHz) and the asymmetry parameter ($\eta = 0.77 \pm 0.05$) have been obtained from line shape analysis of the powder spectrum of one of the crystalline samples. Proton decoupling was used to remove ^{1}H/^{7}Li dipole–dipole interactions, and samples diluted with ^{6}Li were employed to estimate the contribution of the ^{7}Li/^{7}Li interaction to the line shape. These data give a value (73 kHz) for the quadrupole splitting constant [QSC = $(1 + \eta^2/3)^{1/2}(e^2Qq_{zz}/h)$] in agreement with that (72 ± 10 kHz) determined for hexameric lithium phenolate in dioxolane from spin–lattice relaxation data. The values of QSC for the tetrameric species in THF and dioxolane are 46 ± 0.5 and 59 ± 6 kHz, respectively. CP-MAS ^{13}C NMR spectroscopy is of limited value for characterizing solid samples of the aggregates.

The reactions of organic lithium compounds with electrophiles in weakly polar aprotic solvents are known to be influenced by the state of aggregation of the lithium reagent. Those compounds in which lithium is bound to oxygen most commonly exist as dimers and/or tetramers. More recently, however, the formation of hexamers has been established and, in one case at least, a hexamer has been shown to be the primary reactant.[1] In this paper, we present a full characterization of the hexameric lithium phenolate (LiOPh·Solv)$_6$ in the solid state (Solv = THF) and in solution (Solv = dioxolane), which we regard as archetypal hexamers. The study includes X-ray structures as well as characterization of the species in both the solid state and solution by ^{13}C and ^{7}Li NMR spectroscopy.

Several hexameric lithium enolates have previously been characterized in the crystalline state.[2] The unsolvated hexamer of lithium enolate derived from pinacolone generated with LDA in heptane has a hexagonal prismatic structure.[2a,b] A similar structure has been found for the lithium enolate of ethyl *N,N*-diethylglycinate, in which the five-membered chelate rings stabilize the hexamer.[2c] Lithium *N*-isopropylbenzamide forms the same type of hexameric crystals in THF/hexane when 1 equiv of TMEDA is added.[2d,e] This aggregate, which contains three THF molecules but no TMEDA, is also stabilized by chelation. Hexamers of (hexamethylenimido)lithium have tricyclic ladder-type structures.[3]

Our earlier studies of solution species revealed the existence of hexameric lithium phenolates in the weakly polar aprotic solvent dioxolane. For example, in dioxolane at low temperatures, both lithium phenolate and its 3,5-dimethyl homologue coexist as the tetramer and hexamer, which exchange slowly on the ^{13}C and ^{7}Li NMR time scale.[4] A close similarity between all the ^{13}C chemical shifts for the tetramer and the hexamer implies similar π-electron distributions in the two species. This is expected since, in both cases, the phenolate oxygen atoms are each surrounded by three lithium cations as is found in the solid-state structures. The stoichiometry for this equilibrium is tetramer $\rightleftharpoons$ $^2/_3$ hexamer, and the related thermodynamic parameters, ΔS and ΔH, indicate that the hexamer is more highly solvated than the tetramer.[4]

A useful parameter for the characterization of lithium salts in solution is the ^{7}Li quadrupole splitting constant (QSC), which is a function of the electrical environment of the Li nucleus. QSC is derived from values of ^{7}Li and certain ^{13}C spin–lattice relaxation times in solution and involves some assumptions about molecular geometry and motion.[5] The current study includes the measurement of QCC and the asymmetry parameter (η), and hence QSC, for (LiOPh·THF)$_6$ in the crystalline state, thereby allowing us to examine the validity of these assumptions.

Experimental Section

Materials. Solvents were purified as previously described.[1,6,7] All phenols were obtained from Aldrich Chemical Co. They were recrystallized from dry hexane and sublimed twice before use. Butyllithium in hexanes (1.6 M, 2.5 M) and 1,10-phenanthroline were obtained from Aldrich Chemical Co. ^{6}Li metal was obtained from Oak Ridge National Laboratory.

NMR Sample Preparation. Lithium phenolate samples used for the solution NMR study were prepared by previously described vacuum line techniques.[4a]

Preparation of Crystalline Lithium Phenolate. Lithium phenolate crystals were prepared using a slight modification of the previously described vacuum line technique.[8] The phenol solution was titrated with butyllithium to the end point with the indicator, 1,10-phenanthroline, and then back-titrated with a very small quantity of phenol to ensure the

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slight excess of the latter. After removal of all the solvents and any phenol by prolonged pumping under high vacuum, the salt was washed with freshly distilled THF transferred over calcium hydride and the solvent was again removed. The recrystallization solvent, either THF or a mixture of THF/hexane (1:4), was introduced into the flask by vacuum transfer. The reaction vessel was removed from the vacuum manifold by glass-sealing it. Repeated crystallizations were carried out as previously described.[9] The solid material was collected on the frit, and the bulb containing the mother liquor was then removed by sealing off. The side arm of the vessel containing the solid was open in a glovebox and the pure lithium phenolate removed. This crystalline material was used directly for the solid-state NMR experiments and to obtain crystals of suitable X-ray crystallography.

Preparation of Single Crystals of the [(Lithium Phenolate·THF)$_3$]$_2$ Complex (1).[10] Solid lithium phenolate was added to hexane/THF (60:40) to produce a saturated solution, and the solution was sealed in a glass tube. The phenolate was dissolved by warming the solution to 40 °C. Single crystals were obtained by slowly cooling the solution to room temperature. A suitable crystal was chosen and mounted on the X-ray diffractometer, and the X-ray data were collected at approximately −80 °C.

Preparation of Single Crystals of the (Lithium Phenolate·THF)$_6$ Complex (2).[11] Solid lithium phenolate was added to pure THF to produce a saturated solution, and the solution was sealed in a glass tube. The solution became homogeneous when the solution was warmed to 40 °C. Single crystals were obtained by slowly cooling the solution to room temperature. A suitable crystal was chosen and mounted in a 0.5-mm (i.d.) glass capillary tube, and the tube was flame-sealed under argon. The X-ray data were collected at approximately 22 °C. (These crystals became opaque and eventually powdered when cooled to −80 °C.)

X-ray Crystallography. X-ray crystallographic data were collected using a Siemens P4 crystallographic system (Mo K$_\alpha$ radiation, $\lambda = 0.710\,69$ Å, graphite monochromator, θ–2θ scans). Intensity measurements were corrected for Lorentz and polarization effects. The structures were solved by direct methods using the SHELXS-86[12] program. Full-matrix least-squares (SHELXTL v. 4.2, Unix version) refinement of atomic positional and thermal parameters (at first isotropic, then anisotropic) followed. During the later least-squares iterations, hydrogen atoms were placed at their calculated positions, allowed to ride with the atom to which they are attached, and given a fixed isotropic thermal parameter of 80×10^{-3} Å^2. Crystallographic calculations were performed on an IBM RS/6000 computer system (SHELXS-86, SHELXTL v. 4.2, Unix version). Detailed X-ray crystallographic data for complexes **1** and **2** have been included as supplementary material.

[^{6}Li]Lithium Phenolate. ^{6}Li metal (0.43 g) was weighed under an inert atmosphere and washed many times with dry hexane. An excess of dry methanol (25 mL) was added slowly with vigorous stirring. After the metal had dissolved, the solvent was completely removed and replaced by dry methanol (25 mL) under a nitrogen atmosphere to afford a 2.86 M solution. The lithium phenolate was prepared using vacuum line techniques, where the phenol (2 g) was titrated partially with [^{6}Li]lithium methoxide and with regular butyllithium to afford the 80% [^{6}Li]lithium phenolate. No indicator was used, and a large excess of phenol was left in the reaction mixture which was stirred overnight. The reaction was completed as previously described.

NMR Spectroscopy. Solution NMR data were obtained using Bruker WM-360 and AM-500 instruments. ^{13}C chemical shifts are reported relative to the internal C_6D_{12} (26.40 ppm) or THF (26.50 ppm). ^{7}Li chemical shifts are referenced internally and referred to ^{7}Li in 0.3 M LiCl/MeOD (0.00 ppm) containing 5% TMS at 22 °C using a previously described technique.[4b] Temperatures were calibrated using neat methanol.[13]

Table I. NMR Parameters for Lithium Phenolate in THF

	δ(^{13}C), ppm						
temp, °C	C(1)	C(2)	C(3)	C(4)	T_1(^{13}C), s	T_1(^{7}Li), s	QSC, kHz
+30	168.1	120.0	129.8	114.6	0.74	1.76	46 ± 0.5
−67	167.8	119.9	128.8	114.5	0.19	0.58	40 ± 2

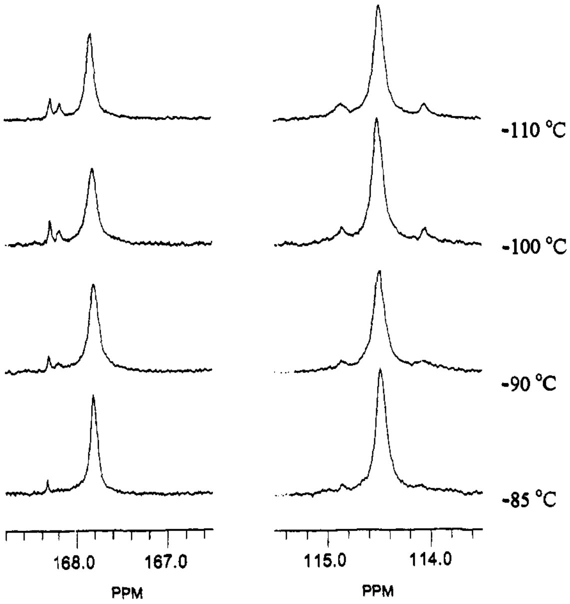

Figure 1. Partial ^{13}C NMR spectrra (125.78 MHz) of lithium phenolate (0.45 M) in THF.

The ^{13}C and ^{7}Li relaxation times were determined using the inversion–recovery method, and the Bruker three-parameter nonlinear least-squares program was used for the extraction of the relaxation times.

Solid-state NMR spectra were obtained using a Chemagnetics CMX-300 instrument. The probe used for both ^{13}C and ^{7}Li was the Chemagnetics pencil probe. The crystalline powder was ground in the drybox under a nitrogen atmosphere and loaded into the zirconium rotor.

^{13}C (74.8 MHz) spectra were obtained using CP-MAS, and the suppression of the spinning sidebands was implemented by the TOSS sequence.[14] Hexamethylbenzene (HMB) (132.21 ppm) was used as the chemical shift reference. The magic angle was adjusted with KBr.

^{7}Li (115.6 MHz) powder patterns were obtained using ($\pi/2$–τ–$\pi/2$–τ–acq.) or ($\pi/2$–τ–$\pi/4$–τ–acq.) quadrupolar spin echo pulse sequences with decoupling during acquisition. The pulse delay used was 300–1200 s. Decoupled spectra were obtained using both CW decoupling and also COMARO-2-decoupling.[15,16]

The solvation number of lithium phenolate crystals in THF was established using solution ^{1}H NMR. The salt was dissolved in D_2O, and the proton peaks associated with the phenolate residues and the solvent were carefully integrated. This procedure was repeated with increasing relaxation delays until no change in the area was observed.

Simulation of Static ^{7}Li Powder Patterns. The first- and second-order perturbation terms of the ^{7}Li powder pattern were performed on a Microvax using the FTNMR software package developed by Hare Research Inc. The program[17] calculates the line shape of a nonspinning solid; the resonance frequency is numerically integrated over a large number of different orientations in the magnetic field.[18] This program requires the input of the spin number I, the transition m to $m-1$ computed, the number of iterations (orientations), the spectrometer frequency, the number of data points, and estimates of QCC and η. A series of computations were made for different values of QCC and η to obtain the best visual fit with the experimental spectrum. The precision indices for

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(10) Crystal data for $C_{60}H_{78}Li_6O_{12}$ (**1**): triclinic system; space group, $P\bar{1}$; $a = 11.358(5)$ Å; $b = 12.628(4)$ Å; $c = 25.069(11)$ Å; $\alpha = 58.79(3)°$; $\beta = 79.27(4)°$; $\gamma = 72.12(3)°$; from 23 orientation reflections, $22 < 2\theta < 30°$; $V = 2925(2)$ Å^3; $Z = 2$; $d_{\text{calcd}} = 1.17$ g cm^{-3}; μ (Mo K$_\alpha$) = 0.78 mm^{-1}. Intensity data h,k,l: 701 parameters refined using 5958 nonequivalent reflections ($\theta_{\max} = 45°$); $R = 0.096$ ($R_w = 0.094$, GOF = 2.27) over 3552 reflections with $I > 3.0\,\sigma(I)$.

(11) Crystal data for $C_{60}H_{78}Li_6O_{12}$ (**2**): triclinic system; space group, $P\bar{1}$; $a = 13.080(5)$ Å; $b = 13.026(4)$ Å; $c = 19.424(8)$ Å; $\alpha = 93.68(3)°$; $\beta = 94.52(3)°$; $\gamma = 112.34(3)°$; from 24 orientation reflections, $22 < 2\theta < 26°$, $V = 3045(2)$ Å^3; $Z = 2$; $d_{\text{calcd}} = 1.13$ g cm^{-3}; μ (Mo K$_\alpha$) = 0.75 mm^{-1}. Intensity data h,k,l: 661 parameters refined using 7972 nonequivalent reflections ($\theta_{\max} = 45°$); $R = 0.105$ ($R_w = 0.108$, GOF = 2.59) over 2842 reflections with $I > 4.0\sigma(I)$.

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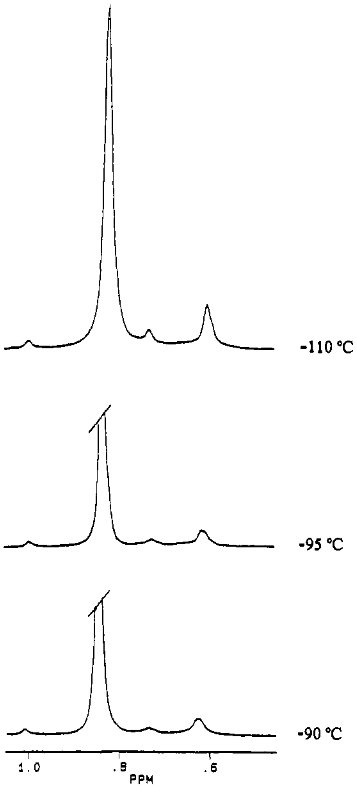

Figure 2. ^{7}Li NMR spectra (194.37 MHz) of lithium phenolate (0.45 M) in THF.

the parameters are taken to be the differences between their high and low values, which were visually recognizable as providing inferior fits.

Results and Discussion

Aggregates of Lithium Phenolate in Solution. We have previously investigated the species present in solutions of lithium phenolate in dioxolane, dimethoxyethane, and pyridine[4a,6] but not in THF. Arnett and Moe[19] have established, using vapor pressure osmometry, that lithium phenolate is tetrameric in THF at 37 °C. We now show (Table I) that over the temperature range 30 to -70 °C the ^{13}C chemical shifts for the phenolate are essentially constant, and we conclude that the tetramer is the predominant species present in this temperature range. At and below -70 °C, peaks corresponding to small amounts of new species are apparent in both the ^{13}C (Figure 1) and ^{7}Li (Figure 2) NMR spectra. These new resonances are undoubtedly due to the formation of other aggregates since their relative intensities are dependent on the total lithium phenolate concentrations. The concentrations of these new species relative to the tetramer are, however, too low to permit their stoichiometric relation to the latter to be established. We have also examined lithium phenolate in dioxolane at concentrations lower than those used in our earlier studies,[4b] and we find similar evidence in the ^{7}Li (Figure 3) spectra for two less aggregated species, which are probably a trimer and dimer or possibly *E* and *Z* isomers of the latter.

A very useful parameter for characterizing aggregates of organic lithium compounds is the ^{7}Li quadrupole splitting constant (QSC) defined in eq 1.[5] This quantity can be determined from

$$\mathrm{QSC} = (1+\eta^2/3)^{1/2}(e^2Qq_{zz}/h)\ \ (\mathrm{kHz}) \qquad (1)$$

^{7}Li and ^{13}C spin-lattice relaxation times. In the case of tetrameric lithium phenolate, which will undergo isotropic rotational diffusion in the extreme narrowing range, QSC is given by eq 2, provided $T_1(^{13}\mathrm{C})$ refers to the para atom.

$$\mathrm{QSC} = 70[T_1(^{13}\mathrm{C}_{para})/T_1(^7\mathrm{Li})]^{1/2}\ \ (\mathrm{kHz}) \qquad (2)$$

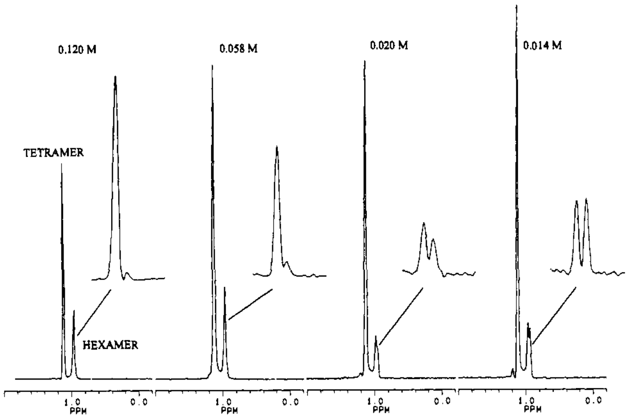

Figure 3. ^{7}Li NMR spectra (194.37 MHz) of lithium phenolate in dioxolane at -48 °C. Gaussian resolution enhancement was performed on both the spectra (GB = 0.05; LB = -4.3) and the expansions (GB = 0.1; LB = -7.5).

Table II. QSCs for ^{7}Li of Tetrameric Lithium Phenolates in Various Solvents

substituents	solvent	temp, °C	QSC, kHz	$-\Delta H°$ (BF_3),[a] kJ mol^{-1}
3,5-$(CH_3)_2$	HMPA/Et_2O[b]	-114	35	117.5
none	pyridine[c]	30	39	128.1
none	THF	30	46	90.3
3,5-$(CH_3)_2$	diethyl ether[d]	-50	51	78.7
3,5-$(CH_3)_2$	dioxolane[d]	-57	57	68.6[e]

[a] Reference 20a. [b] Reference 21. [c] Reference 6. [d] Reference 4b. [e] Reference 20b.

The values of QSC are recorded in Table II. It is expected that the magnitude of the effective negative charge associated with the lone pair of electrons involved in coordination of the solvent to lithium will be directly related to the Lewis basicity of the solvent. We have previously noted that there is a good correlation between the Lewis basicity of the solvent, as measured by its heat of reaction with boron trifluoride,[20] and QSC for a given aggregate.[5,21] The value for tetrameric lithium phenolate in THF fits in well with this trend.

X-ray Structures of Lithium Phenolate·THF Solvates. Although the overwhelming predominant aggregate of lithium phenolate in THF is the tetramer, the only crystalline materials that we could obtain from this solvent (with or without hexane as cosolvent) were hexasolvated hexamers. Two crystallographically-distinguishable forms, **1** and **2** (see the Experimental Section) have been characterized.

The solid-state structure of the [(lithium phenolate·THF)$_3$]$_2$ complex (**1**) is shown in Figure 4. Two crystallographically-independent lithium phenolate·THF trimers were observed in the asymmetric unit of **1**. (See the supplementary material.) The two hexamers illustrated in Figure 4 result when the crystallographically-imposed symmetry is applied. The structural differences in the two trimers (from which the hexamers are generated) are shown in Figure 5. Although there are slight differences between the two trimers, in each, the planes that pass through the carbon atoms of the phenyl groups are essentially perpendicular to the six-member Li–O rings of the hexameric core. More noticeable differences are observed when one compares the positions and conformations of the THF molecules in the two trimers. The Li–O interatomic distances in the hexameric core range from 1.911(21) to 1.990(22) Å (mean 1.959 Å), while the Li–O interatomic distances involving the coordinated THF molecules range from 1.940(15) to 2.016(23) Å (mean 1.970 Å). The Li–O–Li and O–Li–O bond angles in the four-member rings of the hexameric Li–O core range from 80.1(8) to 85.4(7)° (mean 83.3°) and 94.2(8) to 100.2(9)° (mean 96.6°), respectively. The Li–O–Li and O–Li–O bond angles of the six-member Li–O

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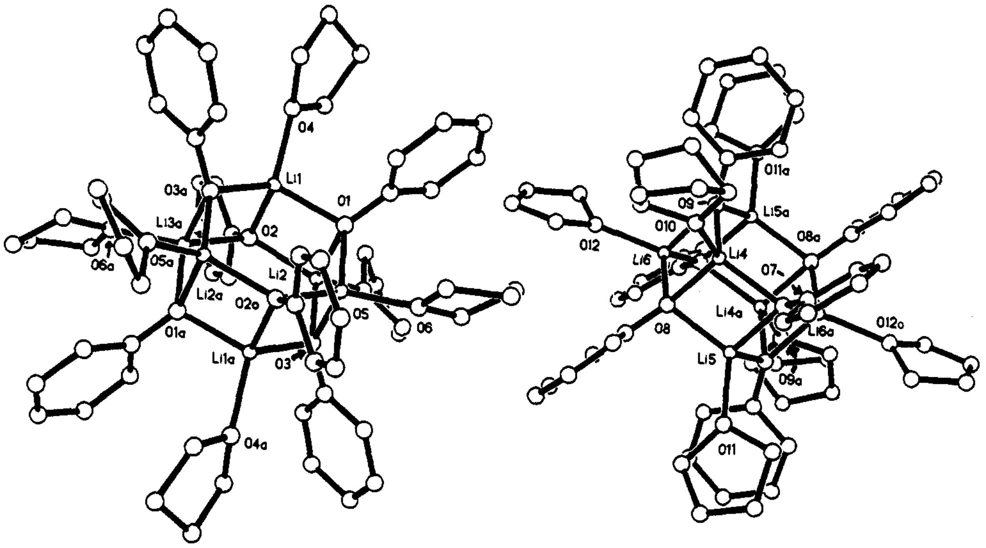

Figure 4. Computer-generated diagram for the [(lithium phenolate·THF)$_3$]$_2$ complex (1). Hydrogen atoms have been omitted for clarity. See supplementary material for the X-ray crystallographic data.

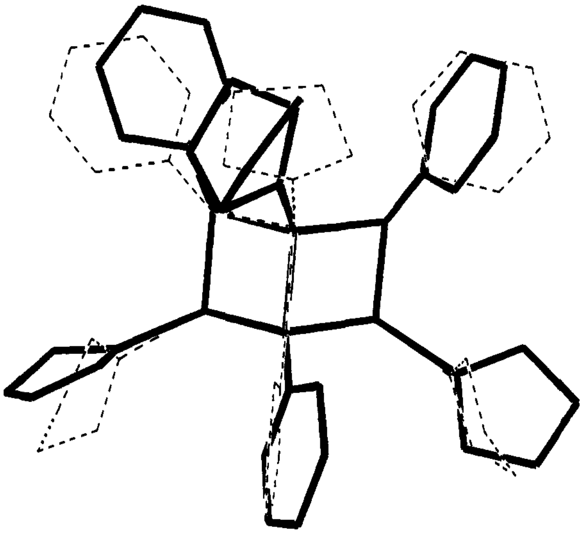

Figure 5. Computer-generated diagram illustrating the differences in the two trimers contained in the asymmetric unit of crystalline 1. This plot was generated by constraining only the lithium and oxygen atoms of the Li–O core to have the same crystallographic coordinates.

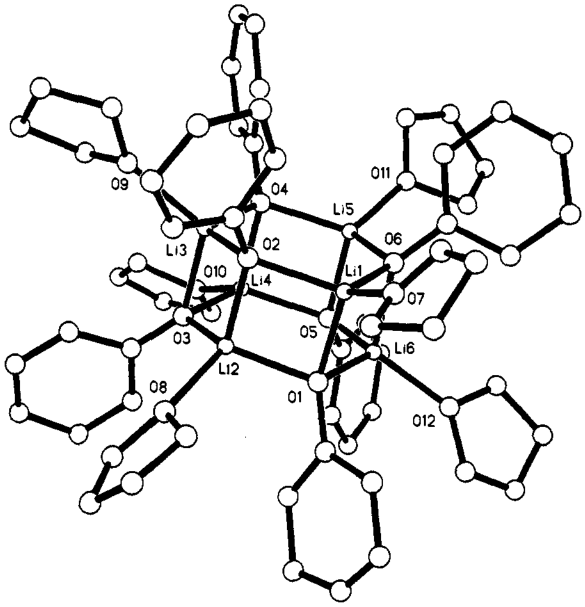

Figure 6. Computer-generated diagram for the (lithium phenolate·THF)$_6$ complex (2). Hydrogen atoms have been omitted for clarity. See supplementary material for the X-ray crystallographic data.

rings of the hexamers range from 116,6(9) to 120.9(10)° (mean 118.6°). The O(THF)–Li–O(phenolate) bond angles range from 106.3(10) to 118.9(9)° (mean 113.9°).

The solid-state structure of the (lithium phenolate·THF)$_6$ complex (2) is shown in Figure 6. Complex 2 has a hexameric structure similar to that of 1, except that the crystals only contain one hexamer. The Li–O interatomic distances in the hexameric core range from 1.895(21) to 1.992(22) Å (mean 1,955 Å), while the Li–O interatomic distances involving the coordinated THF molecules range from 1.950(21) to 2.046(27) Å (mean 1.986 Å). The Li–O–Li and O–Li–O bond angles in the four-member rings of the hexameric Li–O core range from 81.0(9) to 86.2(9°) (mean 83.8°) and 94.9(10) to 99.2(11)° (mean 97.1°), respectively. The Li–O–Li and O–Li–O bond angles of the six-member Li–O rings of the hexamers range from 116.0(12) to 141.9(10°) (mean 120.1°). The O(THF)–Li–O(phenolate) bond angles range from 109.3(12) to 118.4(13)° (mean 114.4°).

The two hexamers of 1 and the hexamer of 2 are very similar in structure, except for very small differences in the conformations of the phenyl and THF groups relative to the Li–O hexameric core. Furthermore, these hexamers have the same general structural features as other solid-state hexamers reported for lithium enolates,[2] alkoxides,[22] and amides.[23] The hexamers of 1 and 2 can be pictured as two six-member Li–O rings (or cyclic trimers) stacked upon one another. In these hexamers, the six-member rings are not planar. Instead, they have conformations that somewhat resemble the chair conformation of cyclohexane. (See Figure 7 and also ref 23 for other examples).

It is not clear why the crystals grown from a hexane/THF solution contain two crystallographically-independent hexamers whereas those grown from pure THF contain only one. The two crystalline materials do, however, have different physical characteristics, since single crystals of 2 were not stable at -80 °C and the X-ray data had to be collected at ambient temperature.

CP-MAS ^{13}C NMR Spectra. In this section we examine the potential of solid-state ^{13}C NMR for the characterization of lithium phenolate aggregates in crystalline samples.

The CP-MAS spectra of crystalline (LiOPh·THF)$_6$ obtained at room temperature and at -50 °C are reproduced in Figure 8. Interesting features of the room-temperature spectrum are the

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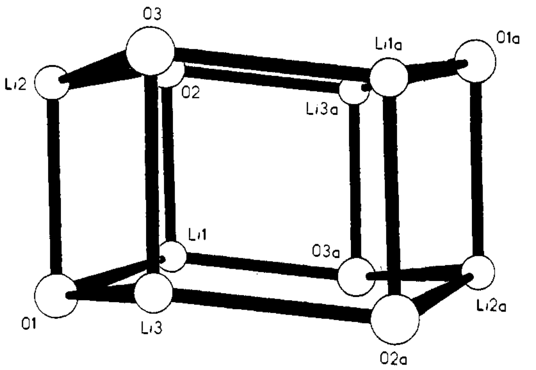

Figure 7. Computer-generated diagram illustrating the nonplanarity of the six-member Li–O rings of hexameric lithium·THF complexes. If planes defining the upper and lower six-membered rings are generated from (O3, O2, Li1a, Li3a) and (Li3, Li1, O3a, O2a), atoms Li2, O1a, O1, and Li2a deviate from these planes by 0.31(2) Å.

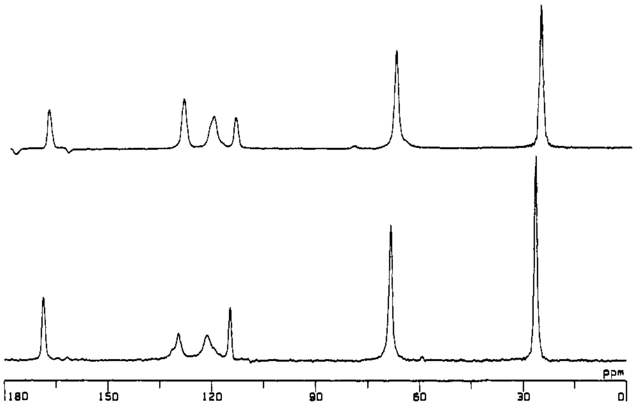

Figure 8. CP-MAS ^{13}C NMR spectra (74.8 MHz), with TOSS, of (lithium phenolate·THF)$_6$ (2) at -50 (upper selection) and 27 (lower spectrum) °C.

Table III. Comparison of ^{13}C Chemical Shifts of Lithium Phenolate Aggregates in Solid and Solution Phases

			$\delta(^{13}C)$, ppm			
phase	species	temp, °C	C(1)	C(2)	C(3)	C(4)
solid[a]	(LiOPh·THF)$_6$	+25	168.6	121.1	129.4	114.6
solid[a]	(LiOPh·THF)$_6$	–50	168.6	120.9	129.7	114.5
THF[b]	tetramer	–70	167.8	119.9	128.8	114.5
dioxolane[b,c]	hexamer	–80	167.7	121.2	130.5	116.2
	tetramer	–80	167.6	120.1	130.5	115.5

[a] Referenced to the β-resonance of THF(δ, 26.5 ppm). [b] Solution. [c] Reference 18.

distorted and broadened line shapes of the ortho and meta resonances. At approximately -50 °C, these resonances are much sharper and more nearly Lorentzian. Apparently, there is some dynamic disorder involving the orientations of the phenyl residues at room temperature that is removed by cooling. Crystallographic disorder in phenyl groups is not disordered in the X-ray structure, which is based on the data obtained at -80 °C.

The chemical shifts, referenced to the β-carbon resonance in THF (δ, 26.5 ppm), are given in Table III. The shifts for the solid hexamer are within 1 ppm of the corresponding value for the tetramer in THF solution. This is consistent with earlier findings that the chemical shifts of the hexamer and tetramer in dioxolane are very similar. We conclude that it is not possible to distinguish between a hexamer and a tetramer on the basis of ^{13}C CP-MAS NMR spectroscopy.

We have also tried to characterize the crystalline materials obtained from dioxolane, a solvent of substantially lower Lewis basicity.[20b] Crystalline material could be obtained from dioxolane/hexane mixtures and was shown to be a 1:1 solvate by proton NMR of its solution in deuterium oxide. However, grinding the sample for CP-MAS caused loss of 20% of dioxolane (determined by solution ^1H NMR) and all the solvent was removed by heating to 70 °C at high vacuum. The ^{13}C CP-MAS spectra before and after this treatment are shown in Figure 9. Some resonances characteristic of the 1:1 solvate can be assigned, and their chemical shifts correspond to either the hexamer or the tetramer. The facile loss of solvent may be the reason why crystals suitable for X-ray crystallography could not be obtained.

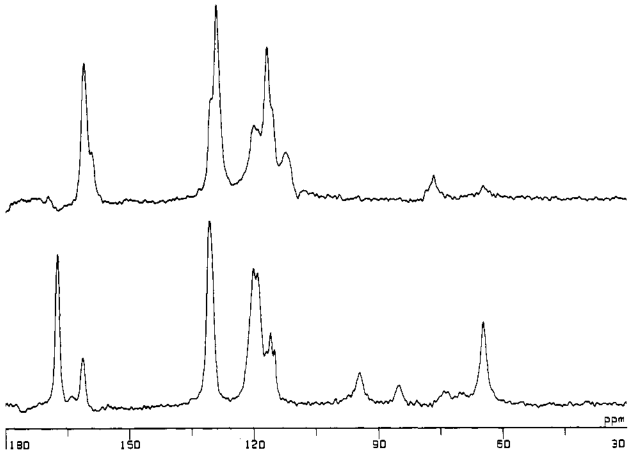

Figure 9. Room-temperature CP-MAS ^{13}C NMR spectra (74.8 MHz), with TOSS, of lithium phenolate·dioxolane solvate before (lower spectrum) and after (upper spectrum) pumping at 70 °C.

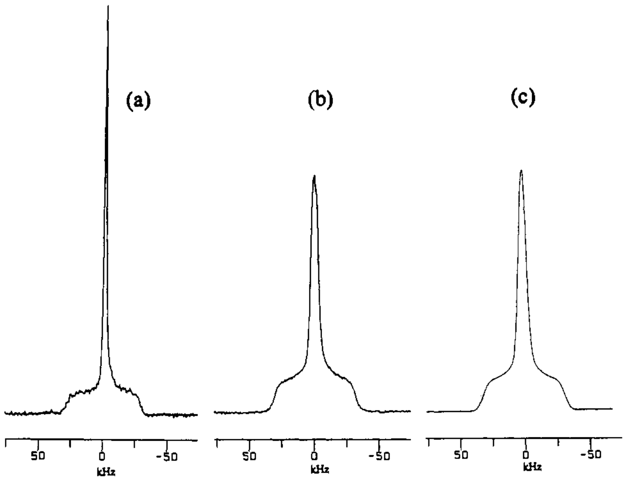

Figure 10. ^7Li NMR powder spectra (115.6 MHz) of crystalline (lithium phenolate·THF)$_6$ (2). (a) Isotopically enriched sample (^7Li:^6Li = 1:4). (b) ^7Li natural abundance sample. (c) Computed line shape (see text).

Solid-State ^7Li NMR Spectra. We have seen that it is difficult to distinguish between the tetramer and the hexamer on the basis of ^{13}C chemical shifts but that the ^7Li QSC values for these species in solution are apparently sufficiently different to do so. However, there are assumptions involved in calculating QSCs from spin-lattice relaxation data[7] and, furthermore, the degrees of solvation of the solution species are unknown. Since we had available crystalline samples of the THF hexamer, we determined the ^7Li quadrupole coupling constant and its asymmetric parameter for (LiOPh·THF)$_6$ in the solid state from the ^7Li NMR powder pattern.

The solid-state ^7Li spectra are presented in Figure 10. Since $^7Li/^1H$ dipole–dipole interactions contribute significantly to the line shapes, they were removed by high-power proton single frequency decoupling. Under these conditions, the central transition ($m = -^1/_2$ to $m = +^1/_2$) still has a line width of about 7 kHz which arises from $^7Li/^7Li$ near-neighbor dipole–dipole interactions. We have confirmed this by taking advantage of the much smaller magnetogyric ratio of ^6Li. Thus the line width of the central transition is reduced from 7 to 2.5 kHz for a sample diluted with 80% ^{6}Li (Figure 10a). We have simulated the line shapes using the FT51 software package (see the Experimental Section). The ^{7}Li/^{7}Li dipole–dipole contribution was taken into account by using a 7.3-kHz line broadening. The experimental spectrum and those calculated using QCC = 67 ± 1 kHz and η = 0.77 ± 0.05 are essentially superimposable. The spectrum was also obtained at about -50 °C and yielded values of 64 kHz and 0.80, respectively, for these quantities. The room-temperature values correspond to a QSC of 73 kHz, which agrees nicely with the value of 72 ± 10 kHz found from relaxation times in solution for the hexamer in dioxolane.[24]

We note that, in contrast to the ^{13}C chemical shifts, the differences between the QSCs for tetramers and hexamers are sufficiently large (46 and 73 kHz, respectively, in THF) to provide a method of characterizing the two species in solution, subject of course to the validity of the assumptions[5,26] regarding the use of ^{13}C relaxation times for estimating the reorientation times of the principal field gradients at the lithium nucleus.

Conclusions

(1) Lithium phenolate exists in THF solution predominantly as a tetramer but crystallizes as a hexamer.

(2) In the solid state, the hexameric lithium phenolate·THF solvate has a hexagonal prismatic structure with each lithium cation surrounded by three phenolates and one solvent oxygen atom.

(3) ^{13}C chemical shifts cannot be used to distinguish between tetrameric and hexameric lithium phenolates.

(4) For lithium phenolates, the assumptions made in determining ^{7}Li QSCs from ^{13}C and ^{7}Li spin–lattice relaxation times appear to be justified.

(5) The values of ^{7}Li QSCs can be used to distinguish between the tetrameric and hexameric structures of lithium phenolates.

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Supplementary Material Available: Tables of crystallographic data, non-hydrogen atomic fractional coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, hydrogen atom fractional coordinates and isotropic thermal parameters, interatomic distances and angles, and selected tortional angles, together with figures showing atomic numbering schemes, for compounds **1** and **2** (55 pages). Ordering information is given on any current masthead page.

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[24] **Note Added in Proof:** Johnels[25] has recently published a study of monomeric, dimeric, and tetrameric phenyllithium solvates in which he also shows that QSC values derived from solid-state data agree well with those obtained from relaxation times for the same species in solution.

[25] Johnels, D. *J. Organomet. Chem.* **1993**, *445*, 1.

[26] Consideration of the overall shape of the hexamer indicates that the anisotropy of its rotational diffusion can be neglected. The effects of anisotropyare only significant for highly prolate or oblate spheroidal rotors.[5]