Effect of Aliphatic Amine Bases on the Aggregation of Alkali Metal Salts of 3,5-Di-*tert*-butylsemiquinone (3,5-DBSQ)

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The alkali metal salts (Li$^+$, Na$^+$, K$^+$) of 3,5-di-*tert*-butylsemiquinone anion (3,5-DBSQ) have been prepared in the presence of three amine bases, triethylamine (TEA), tetramethylethylenediamine (TMEDA), and pentameth-yldiethyltriamine (PMDTA), as well as in the absence of amine in two solvents, toluene and THF. EPR spectral evidence shows that for M(3,5-DBSQ), aggregation of the lithium and sodium salts is effectively prohibited by Lewis basic amines PMDTA and TMEDA, with the former being more effective than the latter. The EPR spectra of the least Lewis acidic metal ion, K$^+$, are unaffected by addition of amines. In the absence of amines, the coordinating solvent, THF, is effective at preventing aggregation, while substantial aggregation occurs in the noncoordinating solvent, toluene. The effectiveness of PMDTA is so great that M(3,5-DBSQ) (M = Li$^+$ and Na$^+$) aggregation is prevented even in toluene. The combination of solution and frozen solution spectra is best for determining the presence of aggregates due to aggregation-induced line broadening in solution spectra and fine structure in spectra of $S > 1/2$ species. The results of the frozen solution spectral studies indicates that, for the amines studied, PMDTA is singular in its ability to prevent aggregation and Li$^+$ and Na$^+$ salts are best chelated by PMDTA. Finally, we show the success of this method by preparing a solution of Na$_2$**1** that is stable for several hours and is amenable to EPR spectral characterization.

We have prepared bis(semiquinones), e.g., **1** and **2**, and related species as components of molecule-based magnetic materials.[1,2]

1   **2**
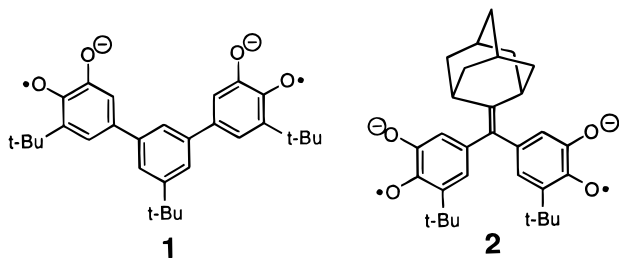
During the course of studying the coordination chemistry of our bis(semiquinones), we desired a source of alkali metal salts that could be used in metathesis reactions. We quickly discovered, however, that alkali metal reduction of the corresponding bis(quinones) in THF or DME gave green precipitates that contained quinone, semiquinone, and catecholate function-alities.[3] The basic semiquinone/catecholate oxygens displace THF and DME from the alkali metal ion, increasing molecular weight and initiating precipitation. Thus, it was desirable to determine the possibility of preventing aggregate formation (and subsequent precipitation) by carrying out the reduction in the presence of nonreducible amines that could bind metal ions.[4] In related work, Tuck and co-workers recently showed that

pyridine, when added to a solution of alkali metal salts of 3,5-di-*tert*-butyl-semiquinone (3,5-DBSQ), suppresses the exchange of semiquinone salts among soluble aggregates of the type [M(3,5-DBSQ)]$_n$ (e.g., dimers, trimers, etc.).[5] As the first step in our studies, we examined the EPR spectra of alkali metal salts of 3,5-DBSQ in the presence of three aliphatic amines and present the results here. In addition, we show the success of this method by preparing a solution of Na$_2$**1** that is stable for several hours and is amenable to EPR spectral characteriza-tion.

EPR spectroscopy is useful for studying soluble aggregates of alkali metal semiquinones. There are three general sce-narios: (1) no aggregation resulting in well-resolved solution phase EPR signals and no fine structure in frozen solution EPR spectra; (2) moderate aggregation that causes minimal line broadening of room-temperature spectra but causes fine structure in frozen solution spectra due to unaveraged dipole−dipole interactions within aggregates of $S \geq 1$ (in addition, a $\Delta m_s = 2$ transition, the spectral signature of an $S \geq 1$ state, can appear);[5,6] (3) extensive aggregation that causes dramatic exchange broadening of fluid solution spectra with loss of hyperfine structure[7−9] and causes exchange narrowing and loss of fine structure in frozen solution spectra.[9] We should point out that these scenarios are simplified, and a detailed analysis of observed spectral features requires knowledge of relaxation phenomenon which, in this case, is complicated due to the presence of multiple species.

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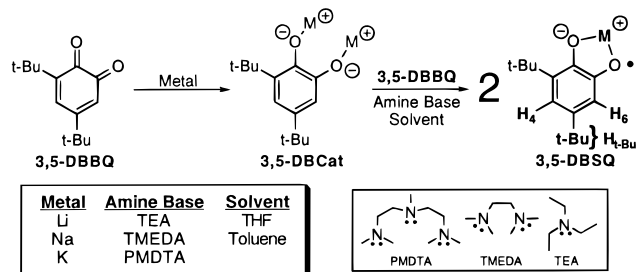
Scheme 1

Table 1. Proton Hyperfine Coupling Constants for Li$^+$, Na$^+$, and K$^+$ Salts of 3,5-DBSQ[a]

metal ion	a_{H_4} (G)	a_{H_6} (G)	$a_{H_{t-Bu}}$ (G)	a_M (G)	line width (G)
Li	3.38	0.61	0.27	0.56 (^{7}Li)	0.11
Na	3.32	0.71	0.28	0.50 (^{23}Na)	0.08
K	3.28	0.79	0.27	*b*	0.09

[a] Hfcc determined by simulation of spectra of 0.83 mM solutions of 3,5-DBSQ in THF containing >200 equiv of PMDTA at 298 K; atom labeling given in Scheme 1. [b] Hyperfine coupling not observed.

The metal semiquinone solutions were prepared in three steps as shown in the Scheme 1: (1) alkali metal reduction of 3,5-DBBQ to the 3,5-di-*tert*-butyl-catecholate dianion (3,5-DBCat); (2) comproportionation of M$_2$(3,5-DBCat) and 3,5-DBBQ to yield 2 equiv of M(3,5-DBSQ) isolated as blue solids; (3) addition of solvent and amine. Since Li$^+$, Na$^+$, and K$^+$ have coordination numbers ranging from 4 to 8,[10−12] a large molar excess of amine was used to ensure coordination saturation and to ensure a high equilibrium concentration of amine-coordinated metal ion, since ether solvents can displace amines.[13]

The EPR spectra of M(3,5-DBSQ) recorded at 298 and 77 K are shown in Figures 1−4 and are similar to those described by Tuck.[5] The proton and alkali metal hyperfine coupling constants (hfcc) for PMDTA-chelated Li(3,5-DBSQ), Na(3,5-DBSQ), and K(3,5-DBSQ) in THF determined by simulation[14] are listed in Table 1. The observation of metal hfcc (except for K$^+$) and the absence of alternating line widths supports the existence of only chelated ions[7] and shows that the amines used do not displace 3,5-DBSQ from the metal ion. The accurate simulations (see Supporting Information) of the spectra ensure that the observed signals are consistent with monomeric alkali metal semiquinones as opposed to an aggregate or byproduct.[15] That it requires at least 8 equiv of amine[16a] to narrow the EPR signals is consistent with the existence of more than one structure in solution. If there were a single, rigid structure, we would expect that addition of more than 1 or 2 equiv of di- or triamine would *not* cause additional spectral resolution *and* we would observe ^{14}N-hfcc from at least some of the amine
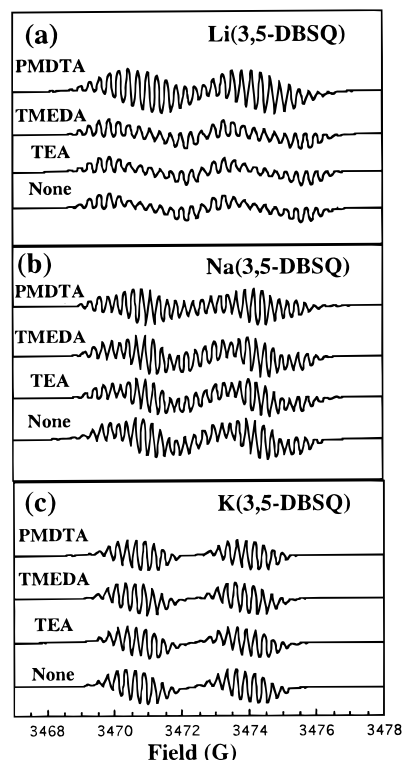
Figure 1. X-band EPR spectra of 0.83 mM M(3,5-DBSQ) in THF at 298 K.

nitrogens. However, an excess of amine is required for maximal spectral resolution and ^{14}N-hfcc is not observed,[16b] suggesting an equilibrium among multiple complexes differing in coordination number and possibly having an amine ligand that is coordinatively fluxional.

Room-Temperature EPR Spectra of M(3,5-DBSQ) in THF. EPR spectra of 0.83 mM THF solutions of M(3,5-DBSQ) in the presence of a 200-fold excess of PMDTA, TMEDA, and TEA, as well as no added amine are shown in Figure 1a−c. As can be seen by the small changes in spectral appearance, only minor changes in hfcc and line widths are observed for Li(3,5-DBSQ) and Na(3,5-DBSQ) in the presence of the different amines, consistent with a minor effect on the solution species. However, the corresponding spectra for K(3,5-DBSQ) are nearly identical. The differences between Li$^+$/Na$^+$ and K$^+$ reflect the relative Lewis acidities. The weakest Lewis acid of the three, K$^+$, cannot distinguish among different amines, nor can it distinguish between amines and ethers; hence, the spectra are nearly identical.

Since the spectra of M(3,5-DBSQ) are satisfactorily simulated[17] as monomeric species even in the absence of amine, THF, a coordinating solvent, effectively prohibits aggregation.

Room-Temperature EPR Spectra of M(3,5-DBSQ) in Toluene. EPR spectra of 0.83 mM toluene solutions of M(3,5-DBSQ) in the presence of a 200-fold excess of PMDTA, TMEDA, and TEA, and no added amine are shown in Figure 2.[16] Since toluene is not a coordinating solvent, open coordination sites exist in the absence of amines; consequently, aggregation can occur and is expected to cause a dramatic broadening of the EPR signals. This broadening and loss of much of the hyperfine coupling information is indeed observed for spectra of M(3,5-DBSQ) in both the absence of amine (only a single, broad resonance is observed) and in the presence of TEA (much

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(14) Fluid solution EPR spectra were simulated using the following: Duling, D. *EPR Calculations for MS-Windows NT/95, Version 0.96*; Public EPR Software Tools; National Institute of Environmental Health Sciences, National Institutes of Health: Research Triangle Park, NC., 1996.
(15) Aggregates with *J* > *a* would have twice as many hyperfine lines. The *J* > *a* spectral type is expected since every metal semiquinone complex exhibits exchange couplings far exceeding the hyperfine couplings reported here; see ref 19.
(16) (a) Addition of more than 8 equiv of amine did not result in further spectral changes. See Supporting Information for a titration plot. (b) ^{14}N hfcc was not observed in Tuck's pyridine coordinated complexes; see ref 5.

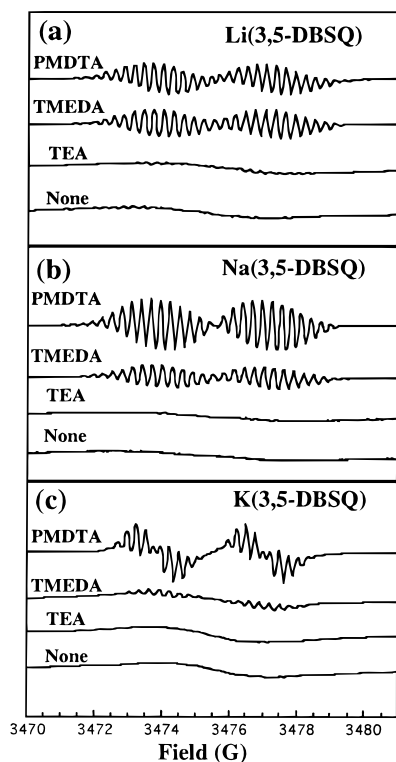(17) Coupling constants from all simulations are available in Supporting Information.

Figure 2. X-band EPR spectra of 0.83 mM M(3,5-DBSQ) in toluene at 298 K.

Figure 3. X-band EPR spectra of 0.83 mM M(3,5-DBSQ) in THF at 77 K.

of the hyperfine coupling is lost). Complexes with the chelating ligands PMDTA and TMEDA have dramatically more resolved EPR signals than observed for TEA or no amine, suggesting far less aggregation with PMDTA and TMEDA. The increased line width of the spectra of M(3,5-DBSQ)/TMEDA sample compared to the M(3,5-DBSQ)/PMDTA sample is consistent with stronger coordination of PMDTA. Fraenkel and co-workers described a similarly strong interaction of PMDTA with Li^+ in studies of neopentyllithium.[18]

We attribute the spectral line broadening of M(3,5-DBSQ)/TEA and M(3,5-DBSQ)/no amine to *J*-modulation since exchange coupling should change dramatically upon aggregation[7,8] and exchange coupling is observed in metal(semiquinone)$_n$ complexes.[19] Consistent with *J*-modulation, we observe narrowed spectra for the TEA/no amine samples at higher temperatures.[20,21] Thus, both PMDTA and TMEDA are effective at stabilizing M(3,5-DBSQ) (M = Li^+, Na^+) with respect to aggregation, and PMDTA is more effective than TMEDA.

Frozen Solution EPR Spectra of M(3,5-DBSQ). The presence of small aggregates (e.g., dimers and trimers) might be determined in frozen solutions if fine structure and/or a $\Delta m_s = 2$ signal is observed in the EPR spectrum. EPR spectra of 0.83 mM THF solutions of M(3,5-DBSQ) in the presence of a 200-fold excess of PMDTA, TMEDA, and TEA, and no added base recorded at 77 K are shown in Figure 3, and the corresponding spectra recorded in toluene are shown in Figure 4. Only spectra recorded in the presence of PMDTA are free of fine structure and free of $\Delta m_s = 2$ transitions (not shown) due to aggregates.
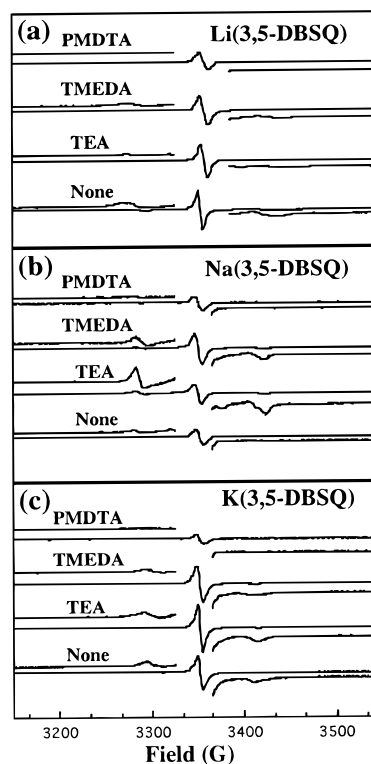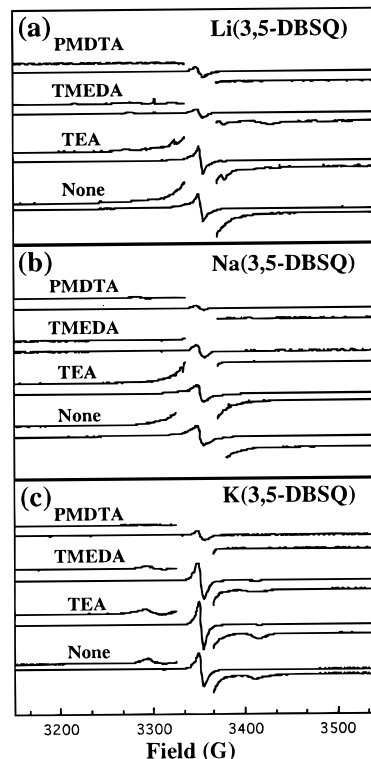

Figure 4. X-band EPR spectra of 0.83 mM M(3,5-DBSQ) in toluene at 77 K.

The picture is slightly more complicated in toluene solutions. Since hyperfine structure is not observed in *fluid* toluene solutions of M(3,5-DBSQ)/TEA and M(3,5-DBSQ)/no added amine, we conclude that aggregation is extensive (trimers and higher-order aggregates), and we expect exchange-narrowed

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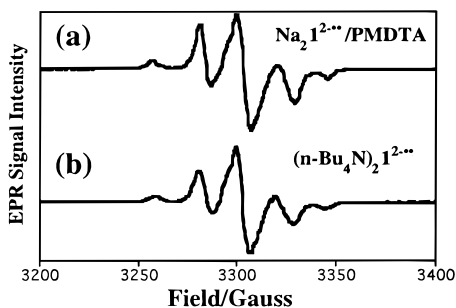(21) Luckhurst, G. R. *Mol. Phys.* **1966**, *10*, 543−550.

Figure 5. X-band EPR spectra of (a) 1 mM Na$_2$**1** at 77 K and (b) 1 mM (*n*-Bu$_4$N)$_2$**1** at 77 K. The signals near 3300 G are doublet monoradical impurities.

frozen solution spectra that lack fine structure. Indeed, fine structure does not appear for Li(3,5-DBSQ)/TEA and Li(3,5-DBSQ)/no added amine in toluene, but $\Delta m_s = 2$ transitions are observed (see Supporting Information), supporting aggregation. However, neither fine structure nor a $\Delta m_s = 2$ transition occurs for Na(3,5-DBSQ) in toluene. We attribute the absence of these spectral features to enhanced exchange narrowing, induced by extensive relaxation within aggregates. This hypothesis is supported by the solution spectra that are among the broadest recorded. Finally, for K(3,5-DBSQ) in toluene, no fine structure is observed in the presence of PMDTA; however, a $\Delta m_s = 2$ transition is observed (see Supporting Information). This observation is consistent with the comparatively low Lewis acidity of K$^+$: PMDTA is least effective for the least Lewis acidic ion. Therefore, aggregation is best prevented using Li$^+$ or Na$^+$ salts in the presence of PMDTA.

Finally, we demonstrate the utility of inhibiting aggregation by successfully preparing a solution of Na$_2$**1**. The EPR signal of Na$_2$**1**/PMDTA observed at 77K is nearly identical to that of a sample prepared by bulk electrolysis,[22] where the counterion is tetra-*n*-butylammonium which cannot be coordinated. These spectra are presented in Figure 5. The lack of precipitation and the nearly identical appearance of the spectra strongly support inhibition of aggregation of Na$_2$**1** by PMDTA.

The solution of Na$_2$**1**/PMDTA is stable for several hours after which precipitation is evident illustrating that the stabilization of Na$_2$**1** by PMDTA is kinetic.

In summary, we have shown EPR spectral evidence that, for M(3,5-DBSQ), aggregation of lithium and sodium salts is effectively prohibited by Lewis basic amines PMDTA and TMEDA, with the former being more effective than the latter. Conversely, the EPR spectra of K(3,5-DBSQ) recorded in THF are unaffected by addition of amines; thus, K$^+$ salts are more

likely to aggregate. In the absence of amines, the coordinating solvent, THF, is effective at preventing aggregation, while substantial aggregation occurs in the noncoordinating solvent toluene. The effectiveness of PMDTA at preventing aggregation is so great that M(3,5-DBSQ) aggregation is prohibited even in toluene, except for the K$^+$ salt. The combination of solution and frozen solution EPR spectra is best for determining the presence of aggregates if aggregation-induced line broadening in solution spectra is observed and if fine structure in frozen solution spectra is observed. The results of the frozen solution spectral studies indicates that, for the amines studied, PMDTA is singular in its ability to prevent aggregation, and PMDTA more effectively chelates Li$^+$ and Na$^+$ than K$^+$. Finally, we demonstrated the success of this approach by preparing a solution of Na$_2$**1** that is stable for several hours and recorded its frozen solution EPR spectrum that shows no evidence for aggregation.

Experimental Section

The preparation of Na$_2$**1**/PMDTA was carried out in a glovebox under a nitrogen atmosphere. A 1 mM solution (1:9 PMDTA/THF, 10 mL) of the bis(quinone) precursor to **1** was stirred for 90 min over a freshly prepared sodium mirror. The initial light green solution darkened and then became colorless. This solution was then filtered through glass wool into a second flask containing another 10 mL of the bis(orthoquinone) solution. This resulted in an immediate color change to a dark green solution. This solution was used immediately for EPR spectroscopy. Precipitation of Na$_2$**1** is observable within a few hours and gives a blue-green solid.

Supporting Information Available: Text giving experimental details and examples of simulated spectra, variable-temperature spectra, an amine titration spectrum, and $\Delta m_s = 2$ transitions, and tabular hfcc data (8 pages). Ordering information is given on any current masthead page.

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(22) See ref 1 for the preparation of **1** and details of the bulk electrolysis.