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ESR Investigations of the Radicals $\{Li_3[E(N^tBu)_3]_2\}^{\bullet}$ (E = S, Se) and the Radical Anions $SO_x(N^tBu)_{3-x}^{\bullet-}$ (x = 1, 2)

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The air oxidation of the cluster compounds $[Li_2E(N^tBu)_3]_2$ (E = S, Se) in toluene produces deep blue (E = S) or green (E = Se) solutions. The ESR spectra of these solutions consist of a septet (1:3:6:7:6:3:1) of decuplets. The simulation of these spectra shows that the secondary hyperfine splitting results from interaction of the unpaired electron with three equivalent ^{7}Li ions consistent with the formation of the neutral radicals $\{Li_3[E(N^tBu)_3]_2\}^{\bullet}$ (**4a**, E = S, $g = 2.0039$, $a(^{14}N) = 5.69$ G, $a(^7Li) = 0.82$ G; **4b**, E = Se, $g = 2.00652$, $a(^{14}N) = 5.41$ G, $a(^7Li) = 0.79$ G). Over a period of 25 h the seven line pattern of **4b** is replaced first by a five line (1:2:3:2:1) spectrum ($g = 2.009$, $a(^{14}N) = 13.4$ G) and, subsequently, by a three line (1:1:1) spectrum ($g = 2.00946$, $a(^{14}N) = 15.4$ G, $a(^{77}Se) = 4.3$ G), neither of which exhibit ^{7}Li hyperfine splitting. These spectra are tentatively assigned to the radical anions $SeO(N^tBu)_2^{\bullet-}$ and $SeO_2(N^tBu)^{\bullet-}$, respectively. The cluster $\{Li_2[O_2S(N^tBu)]\}_n$ (**3**) is prepared by the reaction of sulfur dioxide with 2 equiv of $LiNH^tBu$ in toluene. The air oxidation of toluene solutions of $\{Li_2[OS(N^tBu)_2]\}_6$ (**2a**) or **3** produces deep blue species. In the former case the initial ESR spectrum is a 1:2:3:2:1 quintet ($g = 2.009$, $a(^{14}N) = 13.3$ G) which, after 16 h, evolves into a 1:1:1 triplet ($g = 2.0088$, $a(^{14}N) = 15.9$ G). The same triplet is observed in the ESR spectrum of oxidized solutions of **3** leading to the assignments $OS(N^tBu)_2^{\bullet-}$ and $O_2S(N^tBu)^{\bullet-}$ for the quintet and triplet, respectively. The disproportionation $2OS(N^tBu)_2^{\bullet-} \rightarrow O_2S(N^tBu)^{\bullet-} + S(N^tBu)_3^{\bullet-}$ is indicated by the changes observed for the ESR spectra of oxidized solutions of **2a**.

Introduction

Chalcogen−nitrogen compounds frequently form long-lived neutral radicals.[1] Some recent examples include both cyclic derivatives, e.g. dichalcogenadithiazolyls $R\overline{CNEEN}^{\bullet}$ (E = S, Se),[2,3] and the acyclic systems $RC(NEPh)_2^{\bullet}$ (R = Ph, E = S, Se;[4] R = H, E = S[5]). A few sulfur−nitrogen *radical anions* have been characterized by ESR spectroscopy. For example, $S_4N_4^{\bullet-}$, generated electrochemically, displays the expected nine line ESR spectrum due to coupling of the unpaired electron with four equivalent N atoms (^{14}N, $I = 1$, 99.6%),[6,7] but the radical anion undergoes ring contraction above 0 °C to give $S_3N_3^-$.[8] Reduction of the sulfur diimide $^tBuN{=}S{=}N^tBu$ with alkali metals in dimethoxyethane produces the corresponding deep purple radical anion, which is stable for several hours at ambient temperature.[9] In the case of a Li^+ counterion the symmetrical five line ESR spectrum (1:2:3:2:1) indicates coupling to two equivalent N atoms, but additional coupling to ^{7}Li ($I = {}^3/_2$, 92.6%) is also observed [$a(^7Li) = 0.72$ G].[9] Recently, Stalke et al. have reported that the oxidation of the dimeric cluster $[Li_2S(N^tBu)_3]_2$ (**1a**) with O_2 or I_2 produces a dark blue radical which was characterized by ESR spectroscopy.[10,11] In a preliminary communication the poorly resolved ESR spectrum of this radical was described as a septet ($a = 8$ G, 1:3:6:7:6:3:1) of *septets* ($a = 0.8$ G, 1:2:3:4:3:2:1) attributed to coupling of the unpaired electron with three equivalent N atoms and "further interaction of the unpaired electron with *two* equivalent ^{7}Li atoms."[10] Subsequent reinvestigation gave a better resolved ESR spectrum, which revealed that the secondary hyperfine splitting is a decuplet ($a = 0.8$ G) resulting from interaction of the unpaired electron with *three* equivalent ^{7}Li nuclei.[11]

We have reported the synthesis of the triazaselenite and triazatellurite ions $E(N^tBu)_3^{2-}$ (E = Se, Te) which, as their dilithium derivatives, have dimeric cyclic ladder structures (**1b**,**c**) analogous to that of the sulfur congener;[12−14] i.e. pyramidal

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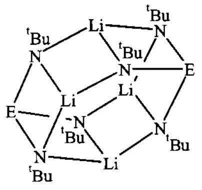
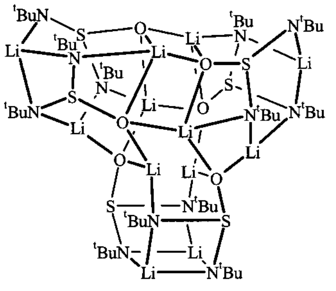
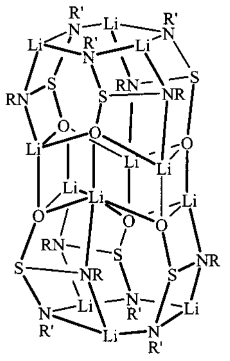


1a (E = S)
1b (E = Se)
1c (E = Te)



2a



2b (R = ^{t}Bu, R' = $SiMe_3$)

$E(N^tBu)_3{}^{2-}$ ions are linked by 4 lithium ions to give a 12 atom $Li_4E_2N_6$ cluster. We have also prepared and structurally characterized the hexamer $\{Li_2[OS(N^tBu)_2]\}_6$ (**2a**) which contains pyramidal diazasulfite ions $OS(N^tBu)_2{}^{2-}$.[15] A different structural arrangement is observed for the hexamer $\{Li_2[OS(N^tBu)(NSiMe_3)]\}_6$ (**2b**).

Both **1b** and **2a** readily form colored radicals in the presence of traces of oxygen. We report here ESR investigations of these systems and further details of the radical derived from **1a**.

Experimental Section

Reagents and General Procedures. The complexes $[Li_2S(N^tBu)_3]_2$ (**1a**),[10] $[Li_2Se(N^tBu)_3]_2$ (**1b**),[12] and $[Li_2OS(N^tBu)_2]_6$ (**2a**)[15] were prepared by literature procedures. ^{t}BuNSeO was obtained by the method of Herberhold et al.[16] Toluene was dried and distilled from Na/benzophenone before use. Liquid SO_2 was stored over P_4O_{10} in a glass vessel equipped with a Teflon needle valve. ^{t}BuNH$_2$ (Aldrich, 98%) was predried over KOH, distilled over CaH_2, and then distilled onto dried molecular sieves. LiHN^{t}Bu was prepared from ^{t}BuNH$_2$ and ^{n}BuLi (Aldrich, 2.5 M in hexanes).[17] SeO_2 (Aldrich) was used as received. Solutions of **1a**,**b**, **2a**, and **3** in toluene were made up in a glovebox. After brief exposure of these solutions to air a series of ESR spectra was recorded at ambient temperature at various time intervals.

Instrumentation. ^{1}H and ^{7}Li NMR spectra were recorded on a Bruker AMX 400 spectrometer operating at 400 MHz and 155.50 MHz, respectively. Chemical shifts are reported relative to Me_4Si in $CDCl_3$ and 4 M LiCl in D_2O, respectively. ESR spectra were recorded at 20 °C on a Bruker ESP 300e spectrometer equipped with a NMR magnetometer, a microwave counter, and a variable-temperature accessory or on Bruker EMX-6 and JEOL TE-200 instruments. Spectral simulations were carried out using the WINEPR SimFonia program provided by Bruker. Elemental analyses were provided by the Analytical Services Laboratory of the Department of Chemistry, University of Calgary.

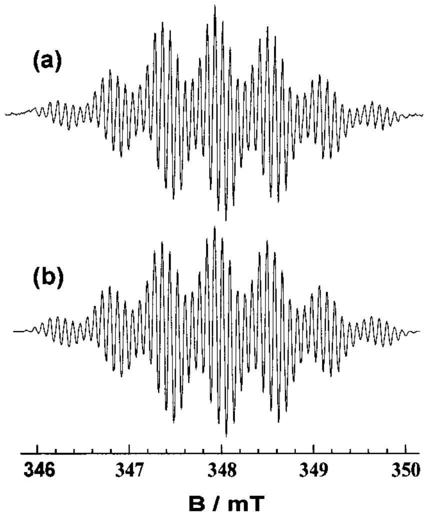


Figure 1. (a) Experimental ESR spectrum of $\{Li_3[S(N^tBu)_3]_2\}^\bullet$ (**4a**) in toluene at 20 °C. (b) Simulated ESR spectrum [includes contribution of ^{6}Li ($I = 1$, 7.5%, $a = 0.31$ G)].

Preparation of $[Li_2SO_2(N^tBu)]_n$ (3). A solution of SO_2 (0.732 g, 11.43 mmol) in toluene (10 mL), prepared by condensing a preweighed amount of SO_2 onto toluene at −196 °C and subsequently warming to 23 °C, was added in aliquots to a stirred slurry of LiHN^{t}Bu (1.807 g, 22.85 mmol) in toluene (10 mL) at −78 °C to give a pale yellow solution. After 0.5 h, the reaction mixture was allowed to warm slowly to 23 °C to give a transparent yellow solution which was stirred for a further 2 h. All volatiles were removed under dynamic vacuum, and the off-white precipitate was washed with cold *n*-hexane (10 mL). The white product was dried under dynamic vacuum. The yield of $[Li_2SO_2(N^tBu)]_n$ was 1.581 g (93%); mp 170 °C (dec). Anal. Calcd for $C_4H_9Li_2NO_2S$: C, 32.23; H, 6.09; N, 9.40. Found: C, 32.43; H, 6.21; N, 9.29. ^{1}H NMR (δ): C_7D_8, 23 °C, 1.31−1.50 (m); C_7D_8, −83 °C, 1.30−2.00 (m). ^{7}Li NMR (δ): C_7D_8, 23 °C, 0.4 to −2.5 (m); C_7D_8, −83 °C, −0.3 to −4.0 (m).

Results and Discussion

ESR Spectra of $\{Li_3[E(N^tBu)_3]_2^\bullet$ (E = S, Se). In order to provide a benchmark for our ESR investigations of the radicals formed upon air oxidation of **1b** and **2a**, we obtained the ESR spectrum of the blue radical generated by oxidation of **1a**. A colorless solution of **1a** in toluene becomes royal blue immediately upon exposure to air. The ESR spectrum of this blue solution consists of a septet (1:3:6:7:6:3:1) consistent with coupling of the unpaired electron with three equivalent ^{14}N nuclei (Figure 1). The *g* value is 2.0039 and $a_N = 5.69$ G. The latter value is significantly different from the value of 8 G reported for the nitrogen hyperfine coupling constant by Stalke et al., who also do not report a *g* value for this radical.[11] There is additional, well-resolved hyperfine splitting ($a = 0.82$ G) for each line of the septet (Figure 1a). The simulation of this spectrum gave the best fit for a radical in which the unpaired electron is interacting with three equivalent $I = 1$ nuclei, i.e. ^{14}N, and three equivalent $I = {}^3/_2$ nuclei, i.e. ^{7}Li. The spectrum obtained in toluene can be simulated accurately (Figure 1b) using a Gaussian line shape (line width 0.5 G) suggesting that the spectrum is inhomogeneously broadened. This is most likely due to the relatively viscous solvent toluene and/or high radical concentration.[18] The previously reported spectrum, recorded in hexane solution,[11] appears more symmetrical consistent with the lower viscosity of the solvent. Thus the oxidation of **1a**

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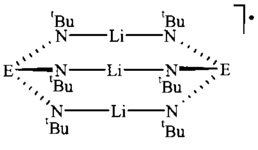
Table 1. ESR Parameters[a]

radical	counterion	g value	$a(^{14}N)$	$a(M)$	$a(^{33}S)$ or $a(^{77}Se)$	ref
$[S(N^tBu)_2]^{\bullet -}$	K^+	2.0071	5.15	~0.05	9.2	9
	Na^+	2.0072	5.10	0.7	9.3	9
	Li^+	2.0071	4.95	0.72	9.5	9
$[S(N^tBu)_3]^{\bullet -}$ [b]	Li^+	not given	8	0.8		11
	Li^+	2.0039	5.69	0.82		*c*
$[Se(N^tBu)_3]^{\bullet -}$	Li^+	2.00652	5.41	0.79	4.3	*c*
$[SO(N^tBu)_2]^{\bullet -}$	Li^+	2.009	13.3			*c*
$[SO_2(N^tBu)]^{\bullet -}$	Li^+	2.0088	15.9			*c*
$[SeO(N^tBu)_2]^{\bullet -}$	Li^+	2.009	13.4			*c*
$[SeO_2(N^tBu)]^{\bullet -}$	Li^+	2.0095	15.4		4.3	*c*
$^tBu_2NO^\bullet$		2.0064	15.4			19
$[^tBuN{=}N^tBu]^{\bullet -}$	K^+	2.0042	8.25			20

[a] *a* values are given in G. [b] The radical anion is present in the neutral complex $\{Li_3[S(N^tBu)_3]_2\}^\bullet$. [c] This work.

appears to involve the removal of one electron and one Li^+ ion from the dimeric 12 atom cluster to give an 11 atom species in which the radical anion $S(N^tBu)_3^{\bullet -}$ is linked to the dianion $S(N^tBu)_3^{2-}$ by three lithium ions, i.e. **4a**. The connectivities of the Li ions in this structure are uncertain, but we note that VT ^1H NMR studies indicate that **1b**,**c** are highly fluxional in solution.[12−14] The fluxionality probably involves the facile stretching and contraction of Li−N interactions.[14] For simplicity the Li ions are represented as two-coordinate in **4a**/**b**. The ESR parameters found for **4a** in this work are very similar to those previously reported for the related radical anion $[S(N^tBu)_2]^{\bullet -}$ (Table 1).[9]



4a, (E = S)
4b, (E = Se)

The oxidation of **1b** gives rise to the analogous Se-containing radical **4b** on the basis of ESR spectroscopic evidence. As indicated below, the radical **4b** is less stable than **4a** which, in the absence of air, persists for several weeks.[11] A pale yellow solution of **1b** in toluene becomes greenish yellow on exposure to air. ESR spectra of this solution at 20 °C were recorded six times over the next 5 h and then again after 26 h. The ESR spectrum of oxidized **1b** undergoes a continuous and informative evolution over this time period. The initial spectrum exhibits a pattern similar to that observed for **4a**, i.e. a septet of decuplets (Figure 2a), and it is, therefore, tentatively attributed to the selenium-containing radical **4b**. The ESR parameters for **4b** are $g = 2.00652$, $a_N = 5.41$ G, and $a_{Li} = 0.79$ G. The simulation of this spectrum using these parameters and a Gaussian line shape with a line-width parameter of 0.40 gives a very good fit for three ^{14}N and *three* ^7Li splittings (Figure 2b).

During the course of 5 h the seven line spectrum of **4b** is replaced first by a five line (1:2:3:2:1) pattern and, finally, by a three line (1:1:1) spectrum. The ESR parameters for the five line spectrum are $g = 2.009$ and $a_N = 13.4$ G, and for the three line spectrum they are $g = 2.00946$, $a_N = 15.4$ G, and $a_{Se} = 4.3$ G. The simulated ESR spectrum confirms the presence of selenium in the radical that gives rise to the three line spectrum. The above observations indicate that the five line pattern is produced by a radical containing two equivalent N atoms and one Se atom, whereas the three line pattern is attributed to a radical involving one N and one Se atom. Significantly, unlike the seven line spectrum, which is attributed to the radical **4b**, no hyperfine splitting by ^7Li is observed for either the five line or the three line spectra. In view of the extremely moisture-sensitive nature of **1b**,[12] it seems reasonable to attribute the changes in the ESR spectra to the sequence depicted in Scheme 1,[21] where the water is provided by atmospheric moisture.

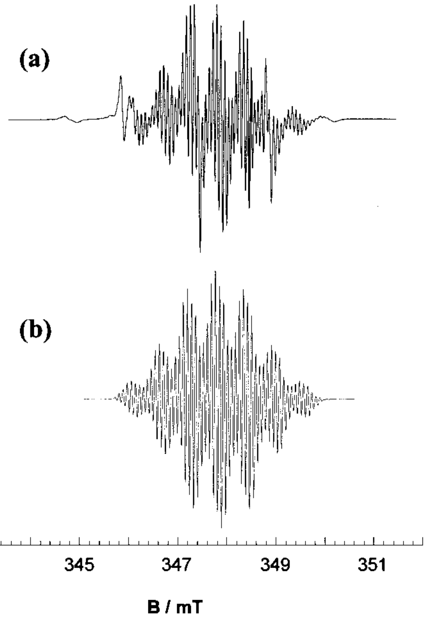
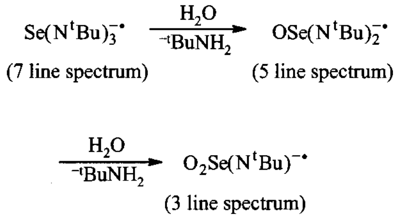


Figure 2. (a) ESR spectrum of an air-oxidized solution of $[Li_2Se(N^tBu)_3]_2$ in toluene at 20 °C after 46 min. (b) Simulated ESR spectrum.

Scheme 1



$$Se(N^tBu)_3^{-\bullet} \xrightarrow[-^tBuNH_2]{H_2O} OSe(N^tBu)_2^{-\bullet} \xrightarrow[-^tBuNH_2]{H_2O} O_2Se(N^tBu)^{-\bullet}$$

In order to provide support for this proposal, we attempted to prepare $\{Li_2[OSe(N^tBu)_2]\}_n$ and $\{Li_2[O_2Se(N^tBu)]\}_n$ by the reactions of 2 equiv of $LiNH^tBu$ with ^tBuNSeO and SeO_2, respectively. However, pure products could not be obtained owing to (a) the thermal instability of ^tBuNSeO[16] and (b) the low reactivity of SeO_2 toward $LiNH^tBu$. Consequently, we turned our attention to the corresponding sulfur-containing clusters $\{Li_2[OS(N^tBu)_2]\}_6$[15] and $\{Li_2[O_2S(N^tBu)]\}_n$.

ESR Spectra of Oxidized $\{Li_2[OS(N^tBu)_2]\}_6$ and $\{Li_2[O_2S(N^tBu)]\}_n$. The hexameric cluster $\{Li_2[OS(N^tBu)_2]\}_6$ (**2a**) is prepared by the reaction of ^tBuNSO with 2 equiv of $LiNH^tBu$.[15] The structure of this 36 atom cluster results from the trimerization of three $Li_4O_2S_2N_4$ hexagonal prisms via their Li_2O_2 faces, while **2b** can be viewed to form from the

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(21) In view of the lack of coupling to ^7Li, the radical anions $OE(N^tBu)_2^{\bullet -}$ and $O_2E(N^tBu)^{\bullet -}$ (E = S, Se) are not depicted as components of cluster structures.

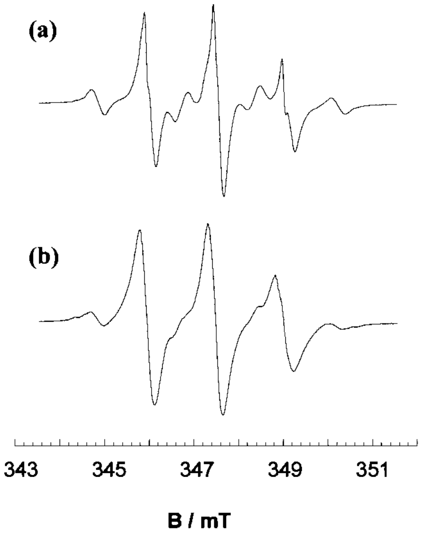
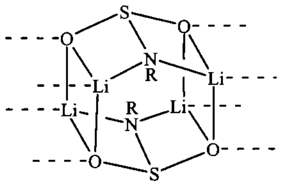


Figure 3. ESR spectra of an air-oxidized solution of $\{Li_2[OS(N^tBu)_2]\}_6$ in toluene at 20 °C after (a) 36 min and (b) 15 h.

Chart 1



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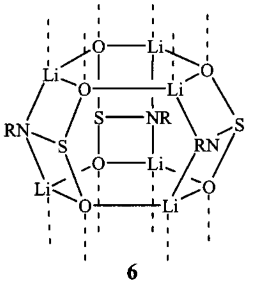

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dimerization of two $Li_6S_3O_3N_6$ clusters via their Li_3O_3 faces. In this work the new complex $\{Li_2[O_2S(N^tBu)]\}_n$ (**3**) was prepared in almost quantitative yield by the reaction of SO_2 with $LiNH^tBu$ (1:2 molar ratio) in toluene. By analogy with the structures of **1a** and **2a**,**b** the basic building block for the complex **3** is likely to be either an $Li_4O_4S_2N_2$ hexagonal prism **5** or the 18 atom $Li_6O_6S_3N_3$ cluster **6**, both of which will lead to highly associated clusters via their Li_xO_x faces (**5**, $x = 2$; **6**, $x = 3$) (see Chart 1) in the solid state. Attempts to obtain crystals of **3** suitable for an X-ray structural determination have been unsuccessful. However, both the ^1H and ^7Li NMR spectra of **3** in C_7D_8 exhibit numerous (8 or 9) resonances over the temperature range 190−295 K suggesting either a structure of low symmetry or, more likely, dissociation into smaller aggregates in solution.

A solution of **2a** in toluene turns blue immediately upon exposure to oxygen. ESR spectra of this solution were recorded at various intervals over a period of 16 h. The initial spectrum (Figure 3a) consists of a five line (1:2:3:2:1) pattern indicating interaction of the unpaired electron with two equivalent nitrogen atoms, i.e. consistent with the formation of $OS(N^tBu)_2^{\bullet-}$.[21] Coupling to ^7Li atoms is not resolved. After 16 h the major component of the ESR spectrum is a 1:1:1 triplet (Figure 3b) suggesting that the dominant radical species now contains only one nitrogen atom, i.e. $O_2S(N^tBu)^{\bullet-}$.[21] Support for this assignment comes from the observation that the oxidation of a toluene solution of $\{Li_2[O_2S(N^tBu)]\}_n$ (**3**) in air yields a blue solution which gives rise to a three line (1:1:1) ESR spectrum with almost identical ESR parameters. The ESR parameters for these new S−N radicals are summarized and compared with those of related radicals in Table 1. The similarity of the ESR parameters for $O_x\,S(N^tBu)_{3-x}^{\bullet-}$ ($x = 1, 2$) and the five line and three line species formed by the degradation of the Se-containing radical **4b** provides support for the identification of these species as $O_x\,Se(N^tBu)_{3-x}^{\bullet-}$ ($x = 1$ and 2, respectively). We note, however, that prolonged exposure of **4a** to air results in the decay of the characteristic ESR spectrum shown in Figure 1 and the formation of a diamagnetic species rather than the radicals $O_x\,S(N^tBu)_{3-x}^{\bullet-}$ ($x = 1, 2$).

Radical dimerizations are widespread in S−N chemistry,[22] and Oakley et al. have shown that unsymmetrical sulfur diimides undergo scrambling via their anion radicals.[23] This disproportionation involves a SOMO−SOMO interaction of two radical anions. Since, the SOMO for $RNSNR^{\bullet-}$ is the π^* orbital located primarily on sulfur, the preferred mode of association is via a S···S interaction; cf. $S_2O_4^{2-}$.[24] A scrambling process has been invoked to account for the formation of sulfur diimides from sulfinylamines in the presence of base or alkali metals.[23] The changes in the ESR spectra observed over time for oxidized solutions of **2a** may be explained by a similar disproportionation (eq 1).

$$2OS(N^tBu)_2^{\bullet-} \rightleftharpoons O_2S(N^tBu)^{\bullet-} + S(N^tBu)_3^{\bullet-} \qquad (1)$$

5 line pattern 3 line pattern 7 line pattern

Conclusions

The air oxidation of $[Li_2Se(N^tBu)_3]_2$ produces a radical which, on the basis of ESR spectra and by analogy with the corresponding S-containing radical, has the composition $\{Li_3[Se(N^tBu)_3]_2\}^\bullet$ in which pyramidal $Se(N^tBu)_3^{2-}$ dianions and $Se(N^tBu)_3^{\bullet-}$ radical anions are linked by three lithium ions. In the presence of air this radical is converted into radical anions containing two and, subsequently, one nitrogen atom tentatively identified as $SeO_x(N^tBu)_{3-x}^{\bullet-}$ ($x = 1$ and 2, respectively). The ESR parameters for these Se-containing radicals are very similar to those of the analogous sulfur radicals $SO_x(N^tBu)_{3-x}^{\bullet-}$ obtained as deep blue solutions by the air oxidation of the clusters $\{Li_2[OS(N^tBu)_2]\}_6$ or $\{Li_2[O_2S(N^tBu)]\}_n$, respectively.

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Supporting Information Available: Figures of ESR spectra of air-oxidized solutions of (a) $[Li_2Se(N^tBu)_3]_2$ in toluene after 26 h and (b) $\{Li_2[O_2S(N^tBu)]\}_n$ in toluene (3 pages). Ordering information is given on any current masthead page.

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