Paddle-Wheel and Trilobate Isomers of the Hexagonal Prisms $\{Li[CE(Nt\text{-}Bu)(n\text{-}Bu)]\}_6$ (E = S, O)

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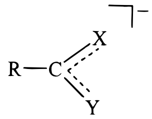
Received June 5, 1998

Current interest in isoelectronic analogues of carboxylate anions RCO_2^- (**1a**) such as amidinates $RC(NR')_2^-$ (**1b**) focuses on the ability of these tunable ligands to generate unusual structures and/or reactivity in both main group and transition-metal chemistry.[1−4] The structures of lithiated oxoamidate anions $[RC(O)(NR')]^-$ (**1c**) are germane for studies of deprotonated oligopeptides.[5] The thioamidate anions $[RC(S)(NR')]^-$ (**1d**) are especially interesting ligands since they combine both hard (N) and soft (S) donor centers. Surprisingly, however, only a few transition-metal complexes of this anion are known and none of them were prepared from **1d** by metathetical reactions.[6] Alkali-metal derivatives of **1d** are unknown.



1a, X = Y = O
1b, X = Y = NR'
1c, X = O, Y = NR'
1d, X = S, Y = NR'
1e, X = Y = S
1f, X = S, Y = O

Here we report the syntheses and structures of the novel anion $[C(S)(Nt\text{-}Bu)(n\text{-}Bu)]^-$ and, for comparison, the oxo analogue $[C(O)(Nt\text{-}Bu)(n\text{-}Bu)]^-$ as their lithium derivatives. Both complexes adopt hexameric $\{Li[CE(Nt\text{-}Bu)(n\text{-}Bu)]\}_6$ structures (**2a**, E = S; **2b**, E = O), based on Li_6E_6 hexagonal prisms.

The reaction of organolithium reagents with carbodiimides provides a versatile route to amidinates (**1b**).[1,3,7] In an extension of this approach to other heteroallenes we disclose that the dropwise addition of *n*-BuLi to a slight excess of *tert*-butylisothiocyanate or *tert*-butylisocyanate in hexane at 0 °C yields the hexamers **2a** and **2b**, respectively, as moisture-sensitive white solids in essentially quantitative yields [eq 1].[8]

$$\underset{(E = S,\, O)}{6t\text{-BuNCE} + 6n\text{-BuLi}} \xrightarrow{\text{hexane}} \underset{\substack{\mathbf{2a},\ E = S\\ \mathbf{2b},\ E = O}}{\{Li[CE(Nt\text{-}Bu)(n\text{-}Bu)]\}_6} \qquad (1)$$

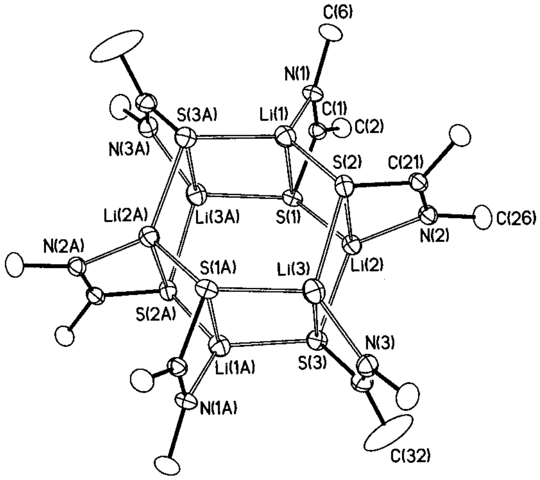


Figure 1. Crystal structure of $\{Li[CS(Nt\text{-}Bu)(n\text{-}Bu)]\}_6$ (**2a**). Only one of the two symmetry-unique, but chemically equivalent, molecules is shown. For clarity only the α-carbon atoms of *n*-Bu and *t*-Bu groups are shown: Li−S (bridged), 2.618−2.660(7) Å; Li−S (unbridged), 2.380−2.425(7) Å; Li−N, 1.973−2.001(7) Å; C−S, 1.763−1.779(4) Å; C−N, 1.254−1.275(5) Å.

The ^1H, ^{13}C, and ^7Li NMR spectra of **2a** and **2b** indicated single environments for $t\text{-}C_4H_9$ and $n\text{-}C_4H_9$ groups as well as the lithium atoms.[8] An X-ray structural determination of **2a** revealed a hexameric aggregate based on a Li_6S_6 hexagonal prism (Figure 1).[9] Although oligomeric structures are common for lithium thiolates,[10] there is only one previous example of a hexagonal prismatic Li_6S_6 arrangement.[11] The structure of **2b** is also composed of a central hexagonal prismatic (Li_6O_6) core (Figure 2).[12] However, there is a significant difference between the

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(8) **2a.** Yield 97%. Mp. 155−156 °C (dec). ^1H NMR (200 MHz, 25 °C, in C_6D_6, TMS in $CDCl_3$): δ = 0.94 (t, 3 H, CH_3), 1.33 (s, 9 H, $C(CH_3)_3$), 1.40 (m, 2 H, CH_2), 2.07 (m, 2 H, CH_2), 2.72 (m, 2 H, CH_2); ^{13}C NMR (200 MHz, 25 °C, in C_6D_6; TMS in $CDCl_3$): δ 185.9 [s, *C*S(N*t*Bu)(*n*Bu)], 56.0 [s, *C*$(CH_3)_3$], 31.7 [s, $C(CH_3)_3$], 43.1, 32.5, 24.0 and 14.6 (all s, $CH_2CH_2CH_2CH_3$). ^7Li NMR (400 MHz, 25 °C, in C_6D_6; standard: 4 M LiCl in D_2O): $\delta = {}^{-}0.31$ (s). Satisfactory, C, H, N analysis. **2b.** Yield 99%. Mp. 141−143 °C (dec). ^1H NMR (200 MHz, 25 °C, in C_6D_6, TMS in $CDCl_3$); δ = 1.04 (t, 3 H, CH_3), 1.31 (s, 9 H, $C(CH_3)_3$), 1.47 (m, 2 H, CH_2), 1.92 (m, 2 H, CH_2), 2.39 (m, 2 H, CH_2); ^{13}C NMR (200 MHz, 25 °C, in C_6D_6; TMS in $CDCl_3$): δ = 175.2 [s, *C*O(N*t*Bu)(*n*Bu)], 50.2 [s, *C*$(CH_3)_3$], 32.8 [s, $C(CH_3)_3$], 36.2, 30.9, 24.2 and 14.7 [all s, $(CH_2)_3CH_3$]; ^7Li NMR (400 MHz, 25 °C, in C_6D_6, standard: 4 M LiCl in D_2O): $\delta = {}^{-}1.56$ (s). Satisfactory, C, H, N analysis.

(9) Crystals of $\mathbf{2a}\cdot C_7H_8$ were obtained from a saturated toluene solution at −20 °C (1 day). Crystal data for $\mathbf{2a}\cdot C_7H_8$: $C_{61}H_{116}Li_6N_6S_6$, M = 1167.60, triclinic, space group $P\bar{1}$, a = 14.466(2) Å, b = 16.454(2) Å, c = 16.454(2) Å, α = 95.025(1)°, β = 90.858(1)°, γ = 105.112(1)°, V = 3763.7(8) Å^3, Z = 2, ρ_{calcd} = 1.030 g cm^{-3}, μ (Mo Kα) = 0.218 mm^{-1}, λ (Mo Kα) = 0.710 73 Å, T = −70(2) °C, F(000) = 1276. Data were collected on a SMART CCD diffractometer on a colorless block (0.4 × 0.4 × 0.4 mm) mounted on a thin glass fiber cooled to −70 °C in the range 1.24° ≤ θ ≤ 25.00° (27 368 reflections collected, 13 032 independent reflections, R_{int} = 0.0813). The structure was solved by direct methods, completed by Fourier synthesis, and refinement, based on F^2, was by full-matrix least-squares procedures. R_1 = 0.0676, wR_2 = 0.1505 for 13 025 unique reflections [$I > 2\sigma(I)$].

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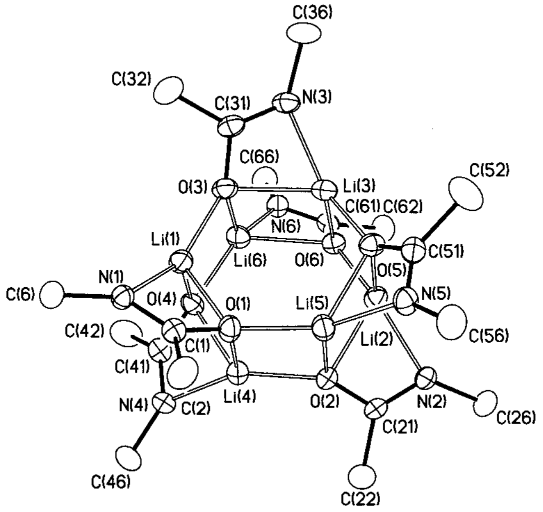

Figure 2. Crystal structure of $\{Li[CO(Nt\text{-}Bu)(n\text{-}Bu)]\}_6$ (**2b**). For clarity only the α-carbon atoms of *n*-Bu and *t*-Bu groups are shown: Li−O (bridged), 2.060−2.103(5) Å; Li−O (unbridged), 1.864−1.875(5) Å; Li−O (connecting Li_3O_3 rings), 1.943−1.981(5) Å; Li−N, 1.989−2.017(5) Å; C−O, 1.309−1.316(4) Å; C−N, 1.275−1.282(4) Å.

orientation of the *n*-BuCN*t*-Bu bridges in the structures of **2a** and **2b**. In the sulfur compound **2a** these units connect the two Li_3S_3 rings in a "paddle-wheel" arrangement with D_{3d} symmetry. By contrast, the hexamer **2b** adopts a "trilobate" structure (D_3) in which three *n*-BuCN*t*-Bu groups span alternating Li−O bonds of the two Li_3O_3 rings. A higher state of aggregation is found for the oxoamidate anion (**1c**) in the unsolvated lithium derivative $\{Li[C(O)(Ni\text{-}Pr)Ph]\}_8$, which adopts an octameric structure involving face-to-face dimerization of two Li_4O_4 cubes.[5a]

Consideration of the metrical parameters for **2a** and **2b** provides a possible explanation for this pronounced difference in molecular architecture. The mean Li−S bond distance in **2a** is 2.405(7) Å *within* the Li_3S_3 rings and 2.638(7) Å for the bridged Li−S bonds (cf. 2.34(2)−2.51(2) Å for $[Li\{SC_6H_4(R)\text{-}CH(Me)NMe_2)\text{-}2\}]_6$ for which the data set is of "rather low quality"[11]). The Li−O distances in **2b** alternate *within* the Li_3O_3 ring with mean values of 2.085(5) and 1.869(5) Å for the bridged and unbridged bonds, respectively. The mean bond length for the Li−O bonds connecting the two Li_3O_3 rings is 1.963(5) Å. Apparently the shorter Li−O compared to Li−S distances result in steric constraints which prevent **2b** from adopting the paddle-wheel conformation.

The mean C−N [1.268(5) and 1.279(4) Å] and Li−N [1.988(7) and 2.004(5) Å] distances in **2a** and **2b**, respectively, are similar. However, the mean C−S bond length of 1.773(5) Å in **2a** is 0.46 Å longer than the corresponding value 1.313(3) Å for d(C−O) in **2b** resulting in a highly distorted, but planar, four-membered ring with mean bond angles of ca. 117.5, 90, 66, and 85° at C, N, Li, and O, respectively. The corresponding mean bond angles in **2a** are ca. 118, 105, 67, and 69.5°. The mean bond angles in the Li_3O_3 ring in **2b** are ca. 118° at oxygen and ca. 119° at lithium. The corresponding values for the Li_3S_3 ring in **2a** are ca. 111° (S) and ca. 106° (Li).

Structural studies of lithium derivatives of amidinates **1b** or dithiocarboxylates **1e** are limited to solvated complexes which form either monomers[13−15] or dimeric step-shaped structures.[16] The formation of the unsolvated hexamers **2a** and **2b** can be visualized as a trimerization of "tub-shaped" dimers. Further discussion of this aggregation process and the ligand behavior of **1d** will be presented in a full paper.

Acknowledgment. We thank the NSERC Canada for financial support.

Supporting Information Available: Crystallographic data (excluding structure factors) for the structures **2a** and **2b** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101375 (**2a**) and CCDC-101374 (**2b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44 (1223) 336 033; e-mail, deposit@chemcrys.cam.ac.uk).

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(12) Crystals of **2b** were obtained by recrystallization of this material from toluene at −20 °C (8 days). Crystal data for **2b**: $C_{54}H_{108}Li_6N_6O_6$, $M = 979.10$, monoclinic, space group $P2_1/n$, $a = 14.1190(8)$ Å, $b = 25.188(2)$ Å, $c = 19.981(1)$ Å, $\beta = 110.690\ (1)°$, $V = 6647.6(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 0.978$ g cm^{-3}, μ (Mo Kα = 0.061 mm^{-1}), λ (Mo Kα = 0.71073 Å), $T = -70(2)$°C, $F(000) = 2160$. Data were collected on a colorless block (0.1 × 0.1 × 0.1 mm) mounted on a thin glass fiber cooled to −70 °C in the range $1.36° \leq \theta \leq 23.50°$ (29 768 reflections collected, 9811 independent reflections, $R_{int} = 0.0941$). The structure was solved and refined as in (9) to $R_1 = 0.0759$, $wR_2 = 0.1979$ for 9625 unique reflections [$I > 2\sigma(I)$].

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