

Structure of Lithium Dimethyldithiocarbamate Tetrahydrate, $\text{Li}[\text{C}_2\text{H}_5\text{NS}_2]\cdot 4\text{H}_2\text{O}$

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Abstract. $M_r = 199.2$, tetragonal, $P4_3$, $a = 8.227(1)$, $c = 15.260(2)$ Å, $V = 1033.0(2)$ Å³, $Z = 4$, $D_m = 1.289(6)$, $D_x = 1.281(1)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.47$ mm⁻¹, $F(000) = 424$, $T = 298$ K. Final $R = 0.038$ for 1970 observed independent reflections. Pairs of distorted tetrahedral $[\text{Li}(\text{H}_2\text{O})_4]^+$ units are linked by O—H...O hydrogen bonds to form chains along *c*. A three-dimensional network, with channels of van der Waals packed dithiocarbamate ions, is formed by O—H...S bridges from the H₂O molecules to the dithiocarbamate S atoms.

Introduction. The geometry of a molecule as observed in the solid state is a compromise between inter- and intramolecular forces. If a particular geometry is observed in crystal structures with different packing arrangements one may conclude that the intermolecular forces are of less importance than the intramolecular ones and the observed geometry is close to that of a 'free' (uncoordinated) molecule. It has previously been shown that for sodium dithiocarbamates, $\text{Na}[\text{S}_2\text{CNR}_2]\cdot n\text{H}_2\text{O}$, there is a strong correlation between the ligand bite and the bulkiness of the substituents *R* (Ymén, 1983*b*). In the series $R_2 = (\text{CH}_2)_4$, $(\text{CH}_3)_2$ and $[\text{CH}(\text{CH}_3)_2]_2$ the angle S—C—S decreases very significantly, 122.3 (1), 120.9 (1) and 118.3 (3)°. The metal–ligand interactions are expected to be small in these compounds. In the corresponding lithium compounds even less metal–ligand interaction is expected and a comparison between the Na⁺ and Li⁺ compounds should give information concerning the effects of hydrogen bonding and packing forces on the geometry of the dithiocarbamate ions. The crystal structure of $\text{Li}[\text{S}_2\text{CN}(\text{CH}_2)_4]\cdot 4\text{H}_2\text{O}$ has been reported previously (Ymén, 1983*a*) and this communication presents the structure of $\text{Li}[\text{S}_2\text{CN}(\text{CH}_3)_2]\cdot 4\text{H}_2\text{O}$.

Experimental. Stoichiometric amounts of $\text{HN}(\text{CH}_3)_2$, CS_2 and LiOH in water and ethanol, tabular single crystals on evaporation at about 1 kPa, crystal $0.16 \times 0.19 \times 0.44$ mm. D_m by flotation, Weissenberg photographs, Laue class $4/m$, systematic extinctions $00l, l \neq 4n$, space group $P4_1$ or $P4_3$. Cell dimensions based on 25 diffractometer θ values [$\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}l})/2$ with $\omega_{\bar{h}\bar{k}l}$ at a negative θ angle]. 6377 symmetry-dependent reflections, $0 \leq h \leq 11$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$, $3 \leq \theta \leq 30^\circ$, averaged to 2580 symmetry-independent reflections; $R_{\text{int}} = 0.030$. CAD-4 diffractometer, ω – 2θ

scan, width = $(0.70 + 0.5 \tan\theta)^\circ$, max. recording time 120 s, $\sigma_{\text{count}}(I)/I < 0.03$ requested in a scan. Four standard reflections, no significant variations. 610 reflections with $I \leq \sigma_{\text{count}}(I)$ unobserved, I and $\sigma_{\text{count}}(I)$ corrected for Lorentz, polarization and absorption effects, transmission factors 0.88–0.93. Direct methods (*MULTAN*, Germain, Main & Woolfson, 1971). Full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma_c^2(I)/4|F_o|^2 + (0.02|F_o|^2)^{-1}]^{-1}$. 1970 reflections in final least-squares cycle, 151 parameters refined. $R(P4_1) = 0.0375$, $R(P4_3) = 0.0367$, $wR(P4_1) = 0.0388$, $wR(P4_3) = 0.0376$, $S(P4_1) = 1.225$, $S(P4_3) = 1.188$; statistical tests on $R' = R(P4_1)/R(P4_3) = 1.022$ and $wR' = wR(P4_1)/wR(P4_3) = 1.032$ resulted in α values $< 10^{-10}$ (Hamilton, 1965; Rogers, 1981), $P4_3$ thus assumed. $(\Delta/\sigma)_{\text{max}} = 0.069$, $(\Delta/\sigma)_{\text{mean}} = 0.009$. $\Delta\rho = -0.28$ – 0.28 e Å⁻³. Corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). No secondary extinction (Zachariasen, 1967). A normal δR plot (Abrahams & Keve, 1971) gave a straight line with slope 1.132 (2), intercept 0.129 (2), correlation coefficient 0.998. Computer programs used described by Svensson (1978).

Discussion. Final atomic parameters are given in Table 1* and distances and angles in Table 2. The structure is depicted in Fig. 1. Lithium coordinates four water O atoms forming a slightly distorted tetrahedron. Chains of $[\text{Li}(\text{H}_2\text{O})_4]^+$ tetrahedra along the fourfold axes are formed by O—H...O hydrogen bonds (Hamilton & Ibers, 1968). There are no Li—S bonds, but instead the dithiocarbamate ions link the chains to a three-dimensional network by hydrogen bonds O—H...S, where S(2) accepts two [S...O range: 3.205 (2)–3.251 (3) Å] and S(1) four [S...O range: 3.240 (3)–3.382 (2) Å] hydrogen bonds from the water molecules. The S...O distances are in the range given by Mereiter, Preisinger & Guth (1979). The dithiocarbamate ions are van der Waals packed along the fourfold axis in channels formed by chains of Li tetrahedra. The shortest van der Waals distance, 2.64 (8) Å, is between H atoms in adjacent methyl groups.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38883 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s for the non-H atoms*

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

| | x | y | z | B(Å ²) |
|------|---------------|---------------|--------------|--------------------|
| S(1) | -0.00395 (8) | 0.44013 (7) | 0.12835 (8) | 3.8 (1) |
| S(2) | 0.26178 (8) | 0.19654 (8) | 0.12600 | 4.6 (1) |
| N | -0.05240 (27) | 0.12081 (23) | 0.12471 (18) | 3.9 (1) |
| C(1) | -0.05726 (29) | 0.23934 (28) | 0.12516 (21) | 3.3 (1) |
| C(2) | -0.00557 (51) | -0.05033 (38) | 0.12101 (39) | 6.0 (1) |
| C(3) | -0.22708 (37) | 0.15204 (44) | 0.12406 (34) | 5.1 (1) |
| O(1) | -0.64136 (31) | 0.79477 (29) | 0.23230 (16) | 4.1 (1) |
| O(2) | 0.63870 (36) | 0.56322 (33) | 0.05851 (23) | 5.3 (1) |
| O(3) | 0.42186 (27) | 0.86092 (25) | 0.06337 (16) | 3.9 (1) |
| O(4) | 0.35906 (27) | 0.57419 (31) | 0.20308 (17) | 5.1 (1) |
| Li | 0.52146 (50) | 0.69676 (49) | 0.13875 (32) | 3.6 (1) |

Table 2. *Selected distances (Å) and angles (°) with e.s.d.'s*

| | | | |
|---------------------------------|-----------|--------------------------------|-----------|
| (a) The dithiocarbamate ion | | | |
| S(1)···S(2) | 2.966 (1) | N—C(2) | 1.461 (4) |
| S(1)—C(1) | 1.728 (2) | N—C(3) | 1.460 (4) |
| S(2)—C(1) | 1.719 (2) | C(2)···C(3) | 2.469 (5) |
| C(1)—N | 1.328 (3) | | |
| S(1)—C(1)—S(2) | 118.8 (1) | C(1)—N—C(2) | 121.9 (3) |
| S(1)—C(1)—N | 120.3 (2) | C(1)—N—C(3) | 122.6 (2) |
| S(2)—C(1)—N | 121.0 (2) | C(2)—N—C(3) | 115.4 (3) |
| S(1)—C(1)—N—C(2) | 179.3 (3) | S(2)—C(1)—N—C(2) | -2.7 (4) |
| S(1)—C(1)—N—C(3) | 2.0 (4) | S(2)—C(1)—N—C(3) | 180.0 (2) |
| (b) The coordination polyhedron | | | |
| Li—O(1) | 1.913 (5) | Li—O(3) | 1.954 (5) |
| Li—O(2) | 1.907 (5) | Li—O(4) | 1.941 (5) |
| O(1)—Li—O(2) | 117.5 (2) | O(2)—Li—O(3) | 103.4 (3) |
| O(1)—Li—O(3) | 111.3 (2) | O(2)—Li—O(4) | 111.9 (2) |
| O(1)—Li—O(4) | 101.3 (3) | O(3)—Li—O(4) | 111.6 (2) |
| (c) The hydrogen bonds | | | |
| S(2)···O(3) | 3.205 (2) | S(1)···O(3) | 3.240 (3) |
| S(2)···O(4) | 3.251 (3) | S(1)···O(4) | 3.382 (2) |
| S(1)···O(1) | 3.266 (3) | O(1)···O(3) | 2.823 (3) |
| S(1)···O(2) | 3.287 (3) | O(2)···O(4) | 2.912 (4) |
| S···H range: 2.36 (4)–2.62 (4) | | O···H range: 2.16 (4)–2.25 (5) | |

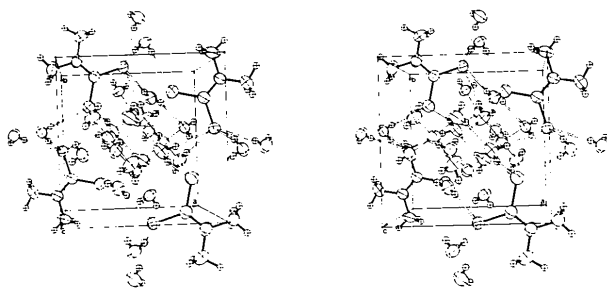


Fig. 1. A stereoscopic view of the structure.

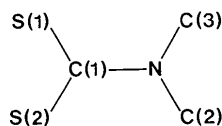


Fig. 2. The numbering of the atoms in the dithiocarbamate ion.

The S₂CNC₂ moiety of the dithiocarbamate ion is close to planar (Table 2). The deviations from the least-squares plane defined by S₂CN are S(1): 4 (8), S(2): 2 (6), C(1): -139 (26), N: 43 (23), C(2): -226 (46) and C(3): -57 (41) × 10⁻⁴ Å. The geometry of the -S₂CN(CH₃)₂ ion in the title compound may be compared to that observed in Na[S₂CN(CH₃)₂].2H₂O (Oskarsson & Ymén, 1983). The C(1)—N, N—C(2) and N—C(3) distances (Fig. 2) are not significantly different in the two compounds. The C—S distances are 1.736 (2) and 1.709 (2) Å in the Na compound and 1.728 (2) and 1.719 (2) Å in the Li compound. This may be the result of different coordination and hydrogen bonding. The S atom in the longer C—S bond in Na[S₂CN(CH₃)₂].2H₂O is coordinated to Na⁺. The influence of coordination and hydrogen bonding on the S₂CNC₂ moiety is also reflected in the different S—C—S angles in the Na⁺ and Li⁺ compounds, 120.9 (1) and 118 (1)°, respectively. Although the two C—S distances are different in the two compounds, the average value $\{[S(1)—C(1) + S(2)—C(1)]/2\}$ is equal, 1.723 (1) Å.

It has been shown previously that for sodium dithiocarbamates the bulkiness of the substituents has a profound influence on the ligand bite (Ymén, 1983*b*). Bulkier substituents force the atoms C(2) and C(3) (Fig. 2) to move apart. This increases the intramolecular steric interaction C—H···S, thus pushing the atoms S(1) and S(2) closer together. Since the ligand bite is 0.026 Å smaller in the title compound than in Na[S₂CN(CH₃)₂].2H₂O the C(2)···C(3) distance should vary in the reverse order. A decrease of 0.014 Å is actually observed, thus supporting the idea of intramolecular steric interactions, C—H···S, in these compounds.

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