Table 2. *Bond lengths* (Å) *and angles* (°)

Pd—P(1)	2·360 (1)	C(11)—C(15)	1·524 (4)
Pd—P(2)	2·359 (1)	C(12)—C(13)	1·495 (5)
Pd—C(1)	2·085 (3)	C(12)—C(14)	1·516 (5)
Pd—C(20)	2·083 (3)	C(12)—C(15)	1·528 (4)
P(1)—C(31)	1·829 (3)	C(15)—C(16)	1·491 (4)
P(1)—C(37)	1·828 (3)	C(16)—C(17)	1·519 (4)
P(1)—C(38)	1·816 (3)	C(16)—C(20)	1·520 (4)
P(2)—C(21)	1·839 (3)	C(17)—C(18)	1·524 (4)
P(2)—C(27)	1·832 (3)	C(17)—C(19)	1·508 (4)
P(2)—C(28)	1·816 (4)	C(17)—C(20)	1·529 (4)
C(1)—C(2)	1·537 (4)	C(21)—C(22)	1·385 (5)
C(1)—C(5)	1·527 (4)	C(21)—C(26)	1·390 (5)
C(2)—C(3)	1·503 (5)	C(22)—C(23)	1·404 (5)
C(2)—C(4)	1·520 (5)	C(23)—C(24)	1·361 (7)
C(2)—C(5)	1·511 (4)	C(24)—C(25)	1·365 (6)
C(5)—C(6)	1·494 (4)	C(25)—C(26)	1·400 (5)
C(6)—C(7)	1·520 (4)	C(31)—C(32)	1·397 (5)
C(6)—C(10)	1·522 (4)	C(31)—C(36)	1·383 (5)
C(7)—C(8)	1·520 (5)	C(32)—C(33)	1·393 (6)
C(7)—C(9)	1·510 (4)	C(33)—C(34)	1·380 (7)
C(7)—C(10)	1·512 (4)	C(34)—C(35)	1·363 (7)
C(10)—C(11)	1·490 (4)	C(35)—C(36)	1·404 (6)
C(11)—C(12)	1·518 (4)		
P(1)—Pd—P(2)	93·6 (1)	C(6)—C(10)—C(7)	60·1 (2)
P(1)—Pd—C(1)	168·5 (1)	C(6)—C(10)—C(11)	115·0 (2)
P(1)—Pd—C(20)	87·5 (1)	C(7)—C(10)—C(11)	125·4 (2)
P(2)—Pd—C(1)	87·6 (1)	C(10)—C(11)—C(12)	126·0 (2)
P(2)—Pd—C(20)	168·0 (1)	C(10)—C(11)—C(15)	115·5 (2)
C(1)—Pd—C(20)	93·7 (1)	C(12)—C(11)—C(15)	60·3 (2)
Pd—C(1)—C(2)	120·0 (2)	C(11)—C(12)—C(13)	122·8 (3)
Pd—C(1)—C(5)	135·5 (2)	C(11)—C(12)—C(14)	115·4 (3)
C(2)—C(1)—C(5)	59·1 (2)	C(13)—C(12)—C(14)	112·4 (3)
C(1)—C(2)—C(3)	118·0 (3)	C(11)—C(12)—C(15)	60·0 (2)
C(1)—C(2)—C(4)	120·7 (3)	C(13)—C(12)—C(15)	121·5 (3)
C(3)—C(2)—C(4)	113·1 (3)	C(14)—C(12)—C(15)	115·3 (3)
C(1)—C(2)—C(5)	60·1 (2)	C(11)—C(15)—C(12)	59·6 (2)
C(3)—C(2)—C(5)	118·2 (3)	C(11)—C(15)—C(16)	117·8 (2)
C(4)—C(2)—C(5)	117·0 (3)	C(12)—C(15)—C(16)	119·7 (2)
C(1)—C(5)—C(2)	60·8 (2)	C(15)—C(16)—C(17)	123·9 (2)
C(1)—C(5)—C(6)	129·1 (2)	C(15)—C(16)—C(20)	128·5 (2)
C(2)—C(5)—C(6)	123·9 (2)	C(17)—C(16)—C(20)	60·4 (2)
C(5)—C(6)—C(7)	120·3 (2)	C(16)—C(17)—C(18)	117·8 (2)
C(5)—C(6)—C(10)	118·5 (2)	C(16)—C(17)—C(19)	117·1 (2)
C(7)—C(6)—C(10)	59·6 (2)	C(18)—C(17)—C(19)	112·8 (2)
C(6)—C(7)—C(8)	116·4 (3)	C(16)—C(17)—C(20)	59·9 (2)
C(6)—C(7)—C(9)	121·3 (3)	C(18)—C(17)—C(20)	118·3 (2)
C(8)—C(7)—C(9)	112·1 (2)	C(19)—C(17)—C(20)	121·2 (3)
C(6)—C(7)—C(10)	60·3 (2)	Pd—C(20)—C(16)	133·5 (2)
C(8)—C(7)—C(10)	116·0 (3)	Pd—C(20)—C(17)	119·6 (2)
C(9)—C(7)—C(10)	121·7 (3)	C(16)—C(20)—C(17)	59·8 (2)

is probably due to a conjugative effect induced by the unsaturated character of the cyclopropyl groups.

The nonbonding distance between the two α-C atoms C(1) and C(20) [3·039 (4) Å] is *ca* 0·3 Å shorter than the sum of the van der Waals radii. The comparable transannular distances C(5)—C(16) and

C(6)—C(15) are 3·696 (4) and 3·291 (4) Å respectively. This indicates a preferred interaction between C(1) and C(20) which facilitates the reductive elimination of the hydrocarbon part of the molecule. It is interesting to know that in the case of (III) reductive elimination can be achieved even in boiling diethyl ether while (IIa) and (IIb) eliminate only at *ca* 473 K with a comparable rate.

Unusually short intermolecular distances were not observed.

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Structure of Lithium Diisopropyldithiocarbamate Trihydrate, $Li^+.C_7H_{14}NS_2^-.3H_2O$

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Abstract. $M_r = 237·3$, triclinic, $P\bar{1}$, $a = 6·143$ (1), $b = 8·488$ (1), $c = 12·796$ (1) Å, $\alpha = 95·71$ (1), $\beta = 101·32$ (1), $\gamma = 93·73$ (1)°, $V = 648·5$ (1) Å³, $Z = 2$, $D_m = 1·224$ (5), $D_x = 1·215$ (1) Mg m⁻³, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 3·5$ mm⁻¹, $F(000) = 256$, $T = 295$ K, $R = 0·047$ for 920 reflections. Pairs of distorted tetrahedra $[Li(H_2O)_4^+]_2$ are formed by edge sharing and these polyhedra are connected to layers parallel to the

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ab plane by O—H⋯S hydrogen bonds. Along **c**, the structure is kept together by van der Waals forces between the hydrophobic parts of the dithiocarbamate ions.

Introduction. The structure of the title compound was determined as part of a research project dealing with the geometry of dithiocarbamate ions in compounds with small metal–ligand interactions. Comparisons of corresponding Na^+ and Li^+ compounds should give information about the effect of packing and hydrogen bonding on the geometry of the dithiocarbamate ions. The crystal structures of three sodium (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980; Oskarsson & Ymén, 1983; Ymén, 1983*b*) and two lithium dithiocarbamates (Ymén, 1983*a*, 1984) have been studied previously and this communication reports the structure of $LiS_2CN[CH(CH_3)_2]_2.3H_2O$.

Experimental. Stoichiometric amounts of CS_2, $HN[CH(CH_3)_2]_2$ and LiOH in H_2O, efflorescent needle-shaped single crystals on evaporation at about 1 kPa; crystal $0.44 \times 0.10 \times 0.02$ mm in sealed capillary, CAD-4 diffractometer, Laue class $\bar{1}$, $P1$ or $P\bar{1}$, $P\bar{1}$ assumed, D_m by flotation, cell dimensions based on 32 diffractometer θ values $|\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$ with ω_{hkl} at a negative θ angle|, 1424 independent reflections with $3 < \theta \le 50°$, 504 with $I \le \sigma_{count}(I)$ unobserved, $\omega-2\theta$ scan, width = $(1.0 + 0.5\tan\theta)°$, $\sigma_{count}(I)/I < 0.01$ requested in a scan, max. recording time 180 s, four standard reflections (intensity decreased 40% as a linear function of the exposure time, corrected), I and $\sigma_{count}(I)$ corrected for Lorentz, polarization and absorption, transmission factors $0.69–0.93$, direct methods (*MULTAN*; Germain, Main & Woolfson, 1971) and subsequent ρ_{diff}, $\sum w(\Delta F)^2$ minimized, $w = |\sigma_c^2(I)/4|F_o|^2 + (0.05|F_o|)^2|^{-1}$, number of reflections in final LS cycle $m = 920$, number of parameters refined $n = 209$, $R = 0.047$, $wR = 0.057$, $S = 1.003$, max. and min. $\Delta\rho$ excursions in final ΔF synthesis = 0.55 e Å^{-3}, max. and mean Δ/σ 0.221 and 0.033, respectively, scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974), isotropic extinction (Zachariasen, 1967), max. 15% for $\bar{1}02$, $g \times 10^{-4} = 0.7$ (2); a full normal δR plot comparing calculated and observed structure-factor amplitudes (Abrahams & Keve, 1971) gave a straight line with slope 0.879 (1), intercept 0.055 (1), correlation coefficient 0.999; 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 distorted tetrahedron. Pairs of such tetrahedra are formed by sharing the edge O(2)–O(2^i) (Table 2). No Li–S bonds are formed. The pairs of tetrahedra are connected to layers parallel to the *ab* plane by six O—H⋯S hydrogen bonds. The S⋯O distances are in the range given by Mereiter, Preisinger & Guth (1979). Along **c**, the structure is held together by van der Waals forces between the non-polar ends of the dithiocarbamate ions. The shortest intermolecular van der Waals distance, 2.42 (16) Å, is between two atoms H(C2B) in adjacent molecules.

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* Lists of structure factors, positional and isotropic thermal parameters for H atoms and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38817 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters with e.s.d.'s*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(Å^2)$
S(1)	0.6668 (3)	0.4929 (2)	0.7508 (1)	2.7 (1)
S(2)	0.4378 (3)	0.1928 (2)	0.6323 (1)	3.3 (1)
N	0.7542 (9)	0.2072 (5)	0.8111 (4)	2.3 (2)
C(1)	0.6327 (11)	0.2863 (7)	0.7381 (5)	2.1 (2)
C(2)	0.7546 (12)	0.0228 (7)	0.8027 (6)	3.0 (2)
C(2A)	0.8371 (17)	−0.0421 (10)	0.7071 (7)	4.4 (3)
C(2B)	0.5419 (17)	−0.0505 (10)	0.8237 (9)	4.4 (3)
C(3)	0.9070 (12)	0.2931 (9)	0.9073 (5)	3.1 (2)
C(3A)	0.8398 (20)	0.2499 (13)	1.0084 (7)	4.7 (3)
C(3B)	1.1491 (15)	0.2680 (12)	0.9066 (10)	5.1 (3)
Li	0.1086 (20)	0.6315 (13)	0.5685 (9)	3.2 (3)
O(1)	0.1663 (12)	0.5937 (8)	0.7125 (5)	3.6 (2)
O(2)	0.2143 (8)	0.4469 (5)	0.4837 (4)	2.9 (2)
O(3)	0.2204 (12)	0.8233 (8)	0.5294 (6)	5.6 (2)

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

Symmetry code
(i) $-x, 1 - y, 1 - z$
(ii) $1 + x, y, z$
(iii) $1 - x, 1 - y, 1 - z$
(iv) $x, y - 1, z.$

(*a*) The dithiocarbamate ligand

S(1)⋯S(2)	2.948 (2)	C(2)–C(2A)	1.501 (12)
S(1)–C(1)	1.740 (6)	C(2)–C(2B)	1.513 (12)
S(2)–C(1)	1.709 (6)	C(3)–C(3A)	1.504 (12)
C(1)–N	1.341 (8)	C(3)–C(3B)	1.518 (12)
N–C(2)	1.508 (8)	C(2)⋯C(13)	2.518 (10)
N–C(3)	1.486 (9)		

S(1)–C(1)–S(2)	117.5 (3)	N–C(3)–C(3A)	110.8 (7)
S(1)–C(1)–N	119.8 (4)	N–C(3)–C(3B)	111.9 (7)
S(2)–C(1)–N	122.7 (4)	C(2A)–C(2)–C(2B)	116.7 (7)
C(1)–N–C(2)	124.4 (5)	C(3A)–C(3)–C(3B)	112.4 (8)
C(1)–N–C(3)	121.1 (5)	C(2)–N–C(3)	114.5 (5)
N–C(2)–C(2A)	113.8 (6)		
N–C(2)–C(2B)	112.3 (6)		

S(1)–C(1)–N–C(2)	−174.0 (5)	C(1)–N–C(3)–C(3A)	119.1 (7)
S(1)–C(1)–N–C(3)	4.3 (8)	C(1)–N–C(3)–C(3B)	114.7 (7)
S(2)–C(1)–N–C(2)	7.4 (9)	C(2A)–C(2)–N–C(3)	116.2 (7)
S(2)–C(1)–N–C(3)	−174.3 (5)	C(2B)–C(2)–N–C(3)	108.5 (7)
C(1)–N–C(2)–C(2A)	62.2 (9)	C(3A)–C(3)–N–C(2)	62.5 (8)
C(1)–N–C(2)–C(2B)	73.1 (8)	C(3B)–C(3)–N–C(2)	63.8 (8)

(*b*) The coordination polyhedron

Li–O(1)	1.870 (13)	Li–O(2^i)	2.011 (13)
Li–O(2)	2.031 (12)	Li–O(3)	1.877 (13)

O(1)–Li–O(2)	107.2 (6)	O(2)–Li–O(2^i)	92.9 (5)
O(1)–Li–O(2^i)	103.6 (6)	O(2)–Li–O(3)	109.2 (6)
O(1)–Li–O(3)	119.9 (7)	O(2^i)–Li–O(3)	120.2 (6)

(*c*) The hydrogen bonds

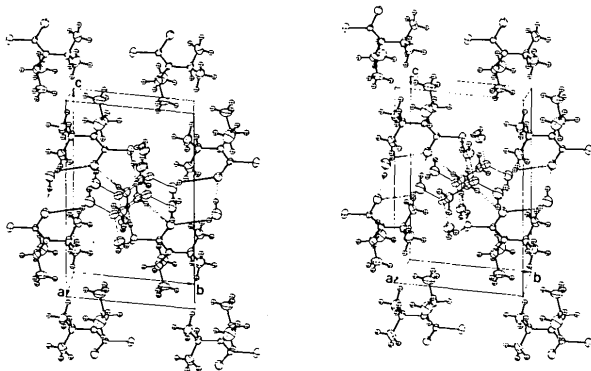|			
S(1)⋯O(1)	3.203 (7)	S(2)⋯O(2)	3.214 (5)
S(1)⋯O(1^{ii})	3.274 (7)	S(2)⋯O(3^{iv})	3.362 (7)
S(1)⋯O(2^{iii})	3.303 (5)	S(2)⋯O(3^{iii})	3.224 (8)
S⋯H range: 2.22 (11)–2.91 (12)			

Fig. 1. Stereoscopic view of the structure.
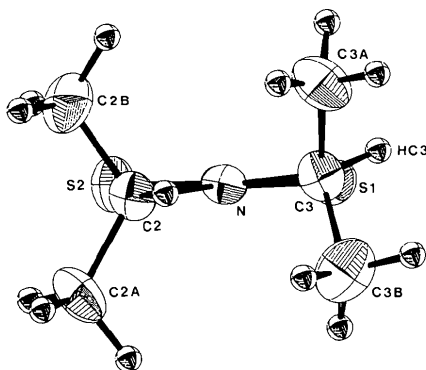
Fig. 2. The diisopropyldithiocarbamate ion viewed along the N—C(1) bond. The atom C(1) is hidden by the atom N.

Fig. 3. S(1)⋯S(2) = f[C(2)⋯C(3)]. Squares represent $^-$S$_2$CN(CH$_2$)$_4$, triangles $^-$S$_2$CN(CH$_3$)$_2$, circles $^-$S$_2$CN{CH(CH$_3$)$_2$}$_2$, open symbols Li$^+$ and filled symbols Na$^+$ compounds. Data are taken from Albertsson et al. (1980), Oskarsson & Ymén (1983) and Ymén (1983a,b, 1984).

The observed conformation of the dithiocarbamate ion (Fig. 2) is similar to that observed in NaS$_2$CN[CH(CH$_3$)$_2$]$_2$.5H$_2$O (Ymén, 1983b). In the title compound, however, the S$_2$CNC$_2$ moiety is less planar. The deviations from the LS plane defined by S(1), S(2), C(1) and N are S(1) 2 (17), S(2) 2 (18), C(1) 26 (51), N −93 (60), C(2) −1346 (71), C(3) 1199 (73) ×10^{-4} Å. A similar twist around the C(1)—N bond is observed in [H$_2$N{CH(CH$_3$)$_2$}$_2$][S$_2$CN{CH(CH$_3$)$_2$}$_2$] (Wahlberg, 1978). Bond distances and angles are not significantly different in the Li$^+$ and Na$^+$ compounds.

It has been shown previously that for sodium dithiocarbamates the ligand bite decreases as the substituents R_2 in $^-$S$_2$CNR_2 become bulkier (Ymén, 1983b). This was interpreted as the result of steric intramolecular interactions, C—H⋯S, between the substituents and the S atoms. Since the steric interaction produces a variable number of S⋯H interactions it is not easily described by a single parameter. Further evidence may be obtained from a study of the correlation between the distances S⋯S and C⋯C in the studied Na$^+$ and Li$^+$ compounds (Fig. 3). For $^-$S$_2$CH(CH$_3$)$_2$ and $^-$S$_2$CH{CH(CH$_3$)$_2$}$_2$ a decrease in the S⋯S distance results in an increase of the C⋯C distance. This is not the case for $^-$S$_2$CN(CH$_2$)$_4$ since the five-membered ring restricts the C⋯C distance to about 2·425 Å. Excluding LiS$_2$CN(CH$_2$)$_4$.4H$_2$O (Ymén, 1983a), the resulting five points are linearly correlated with a weighted coefficient of 0·950. Since NaS$_2$CN(CH$_2$)$_4$.2H$_2$O (Albertsson et al., 1980) fits the line very well there may be a small steric interaction in this compound. In conclusion, a highly significant correlation between the S⋯S and C⋯C distances in dithiocarbamates strongly supports the idea of intramolecular steric interferences, C—H⋯S, in these compounds.

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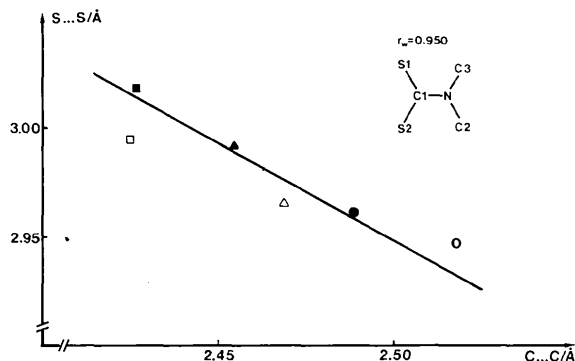ZACHARIASEN, W. H. (1967). Acta Cryst. 23, 558–564.