Fig. 3. Bond lengths (Å) and angles (°) for CP and ATCB. In CP, the Cl(1)—O(i) lengths are 1·40 (1), 1·44 (2), 1·43 (1) and 1·44 (1) Å for i = 1,2,3 and 4, respectively, and the Cl(2)—O(i) lengths are 1·47 (2), 1·42 (2), 1·40 (3), 1·39 (2) and 1·34 (3) Å for i = 5,6,7,8 and 9, respectively. The O—Cl(1)—O angles range from 106·9 (8) to 111·2 (8)°; for O—Cl(2)—O, the unit-weight O(6) forms essentially tetrahedral angles to O(7), O(8) and O(9) while that to O(5) is large, 121 (1)°.

radiation. It is assumed that there is no relationship between damage and the disorder of the perchlorate group since many other perchlorates are known in which disorder is found, and no comment has been made concerning radiation damage.

The kinetics of imine cyclization, which requires conversion from 2-bonding of the properly substituted tetrazolato ligand to 1-bonding, may occur in solution and has been discussed by Harrowfield & Sargeson (1979). With care, both 2- and 1-bonded substituted tetrazolato materials can be crystallized. The conversion from 1- to 2-bonded (or 2- to 1-bonded) on substituted tetrazolato ligands lacking the cyano group has been examined by Ellis & Purcell (1981). Since CP exhibits 2-bonding to the ring whereas ATCB shows 1-bonding, it appears unlikely that the amidine chelate could form from CP in a solid-state reaction.

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Structure of Lithium 1-Pyrrolidinecarbodithioate Tetrahydrate, Li.C5H8NS2.4H2O

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Abstract. $M_r = 225·25$, monoclinic, $P2_1/n$, $a = 10·279$ (1), $b = 9·989$ (3), $c = 11·291$ (1), Å, $\beta = 93·03$ (1)°, $V = 1158$ (1) Å³, $Z = 4$, $D_m = 1·304$ (5), $D_x = 1·292$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 0·433$ mm⁻¹, $F(000) = 480$, $T = 298$ K, $R = 0·030$, $R_w = 0·041$ for 2680 intensities. Lithium coordinates

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four H_2O molecules forming a slightly distorted tetrahedron. Such coordination polyhedra are connected *via* hydrogen bonds to form chains parallel to the *b* axis. Each dithiocarbamate ion accepts seven S···H—O hydrogen bonds from the water molecules. The dithiocarbamate ions are stacked antiparallel to each other in a channel formed by four chains of polyhedra. The geometry of the $^-S_2CN(CH_2)_4$ moiety is similar to that observed in $NaS_2CN(CH_2)_4.2H_2O$ and $[C_4H_{10}N][S_2-CN(CH_2)_4]$.

Introduction. The geometry of substituted dithiocarbamte ions $^-S_2CNR_2$ is dependent on the nature of the coordinating metal ion (Oskarsson, Ståhl & Ymén, 1982). The most sensitive geometric parameter is the ligand bite angle S—C—S. In compounds with transition-metal ions small ligand bites are observed while main-group metal ions seem to give larger ligand bites. For a certain metal ion the ligand bite decreases in the series $R_2 = (CH_2)_4$, $R' = (CH_3)_2$, $R'' = (C_2H_5)_2$, $R_2''' = [CH(CH_3)_2]_2$, which is probably due to an increasing intramolecular steric interference $(R_2 < R_2' \sim R_2'' < R_2''')$. In order to discriminate between the influence of the metal ion and the substituents R_2 on the geometry of the $>NCS_2$ moiety, crystal structures of compounds with small metal-ligand interactions are investigated. The structures of some sodium compounds have been reported previously (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980; Ymén, 1982, 1983a; Oskarsson & Ymén, 1983). This communication reports the structure of $LiS_2CN(CH_2)_4.4H_2O$ in which less metal–sulphur interaction is expected than in the corresponding sodium compound.

Experimental. Prismatic crystals obtained at reduced pressure from aqueous solution of $(NH_4)S_2CN(CH_2)_4$ and LiOH, D_m by flotation, $0.53 \times 0.30 \times 0.35$ mm, monoclinic, systematic extinctions $h0l$ for $h + l$ odd and $0k0$ for k odd, cell dimensions based on 25 diffractometer θ values $[\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$ with $\omega_{\bar{h}\bar{k}\bar{l}}$ at a negative θ angle], 3526 independent reflections, $3 < \theta \leq 30°$, CAD-4 diffractometer, $\omega-2\theta$ scan, width = $0.70° + 0.5°$ $\tan\theta$, max. recording time 120 s, σ_{count} $(I)/I < 0.01$ requested in a scan, four standard reflections, no significant variations, 846 reflections with $I \leq 3\sigma_{count}(I)$ unobserved, I and $\sigma_{count}(I)$ corrected for Lorentz, polarization and absorption, transmission factors $0.83-0.87$, heavy-atom techniques, full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma_c^2(I)/ 4|F_o|^2 + (0.03|F_o|)^2 + 0.10]^{-1}$, number of reflections in final LS cycle $m = 2680$, number of parameters refined $n = 184$, final $R = 0.030$, $R_w = 0.041$, $S = 0.89$, thermal parameters anisotropic for non-H atoms and isotropic for H atoms, isotropic extinction (Zachariasen, 1967) – ten reflections had corrections larger than 5% in $|F_o|$, maximum 12% for 301,

$g \times 10^{-4} = 0.9(1)$, corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974), δR plot (Abrahams & Keve, 1971) gave a straight line with slope 0.844 (2), intercept 0.057 (2), correlation coefficient 0.988, max. and min. heights in the final ΔF synthesis $= 0.27$ e Å^{-3}, computer programs used described by Svensson (1978).

Discussion. Final positional and isotropic thermal parameters are given in Table 1* and selected distances and angles in Table 2. The structure is depicted in Fig. 1. Lithium coordinates four water O atoms forming a distorted tetrahedron. Such tetrahedra, related *via* a centre of inversion, are kept together in pairs by two equivalent $O(4)\cdots H1(O3)-O(3)$ hydrogen bonds (Hamilton & Ibers, 1968) with $O(4)\cdots O(3) = 2.829$ (2) Å. The pairs of Li tetrahedra are linked into chains, parallel to *b*, by seven O—H···S hydrogen bonds. No Li—S bonds are formed, but instead the dithiocarbamate ion is involved in a S···H—O hydrogen-bond system, where S(1) accepts four [S···O range: 2.309 (2)–3.375 (2) Å] and S(2) three [S···O range: 3.248 (1)–3.329 (2) Å] hydrogen bonds from water molecules. The S···O distances are in the range given by Mereiter, Preisinger & Guth (1979). The dithiocarbamate ions are van der Waals packed antiparallel to each other in the channel formed by four chains of Li tetrahedra. The shortest van der Waals distance, 2.40 (3) Å, is between the hydrogen atoms H1(C4) and H1(C5) in adjacent pyrrolidine rings.

As judged by the shape of the thermal ellipsoids for C(4) and C(5) (Fig. 2), the ligand undergoes a similar type of conformational reorientation as described for $NaS_2CN(CH_2)_4.2H_2O$ (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980). In this case, however, the conformation is best described as a C(5) envelope

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Table 1. *Positional and equivalent isotropic thermal parameters with estimated standard deviations*

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

	x	y	z	$B_{eq}(\text{Å}^2)$
S(1)	0.68941 (3)	0.50585 (3)	0.74633 (3)	3.02 (1)
S(2)	0.40797 (3)	0.58163 (3)	0.75266 (3)	3.28 (1)
N	0.51392 (10)	0.37085 (11)	0.86177 (10)	2.67 (2)
C(1)	0.53463 (12)	0.47651 (11)	0.79490 (11)	2.42 (2)
C(3)	0.61528 (13)	0.27660 (14)	0.90575 (14)	3.19 (3)
C(2)	0.38502 (15)	0.33029 (16)	0.90061 (17)	3.75 (4)
C(5)	0.54055 (23)	0.15427 (26)	0.94022 (36)	6.96 (9)
C(4)	0.41143 (21)	0.20343 (25)	0.97131 (33)	6.36 (8)
O(1)	0.62399 (14)	0.62272 (13)	0.47554 (13)	4.22 (3)
O(2)	0.36747 (12)	0.77798 (16)	0.41005 (12)	4.20 (3)
O(3)	0.62683 (14)	0.93266 (14)	0.38562 (15)	4.77 (4)
O(4)	0.54262 (11)	0.84524 (11)	0.64342 (10)	3.38 (2)
Li	0.54459 (24)	0.79536 (25)	0.47199 (22)	3.36 (5)

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

(a) The dithiocarbamate ligand

S(1)···S(2)	2·995 (1)		
S(1)—C(1)	1·735 (1)	N—C(3)	1·471 (2)
S(2)—C(1)	1·720 (1)	C(2)—C(4)	1·515 (3)
C(1)—N	1·322 (2)	C(3)—C(5)	1·506 (3)
N—C(2)	1·474 (2)	C(4)—C(5)	1·475 (3)

S(1)—C(1)—S(2)	120·16 (7)	S(1)—C(1)—N—C(2)	−175·2 (1)
S(1)—C(1)—N	119·58 (9)	S(1)—C(1)—N—C(3)	3·7 (2)
S(2)—C(1)—N	120·23 (9)	S(2)—C(1)—N—C(2)	2·9 (2)
C(1)—N—C(2)	124·33 (11)	S(2)—C(1)—N—C(3)	−178·2 (2)
C(1)—N—C(3)	124·85 (11)	C(1)—N—C(2)—C(4)	178·6 (2)
N—C(2)—C(4)	104·35 (13)	C(1)—N—C(3)—C(5)	−161·8 (2)
N—C(3)—C(5)	104·17 (14)	C(5)—C(4)—C(2)—N	−17·1 (2)
C(2)—N—C(3)	110·82 (11)	N—C(3)—C(5)—C(4)	−27·4 (2)
C(2)—C(4)—C(5)	106·95 (23)	C(3)—C(5)—C(4)—C(2)	27·9 (3)
C(3)—C(5)—C(4)	105·62 (19)	C(2)—N—C(3)—C(5)	17·2 (2)
		C(4)—C(2)—N—C(3)	−0·4 (2)

(b) The coordination polyhedron

Li—O(1)	1·907 (3)	O(1)—Li—O(2)	108·8 (1)
Li—O(2)	1·923 (3)	O(1)—Li—O(3)	117·4 (1)
Li—O(3)	1·906 (3)	O(1)—Li—O(4)	103·4 (1)
Li—O(4)	2·000 (3)	O(2)—Li—O(3)	108·4 (1)
		O(2)—Li—O(4)	108·5 (1)
		O(3)—Li—O(4)	110·1 (1)

(c) The hydrogen bonds

S(1)···O(1)	3·309 (2)	S(2)···O(1)	3·290 (2)
S(1)···O(2)	3·328 (2)	S(2)···O(3)	3·329 (2)
S(1)···O(2)	3·375 (2)	S(2)···O(4)	3·248 (1)
S(1)···O(4)	3·369 (1)	O(4)···O(3)	2·829 (2)

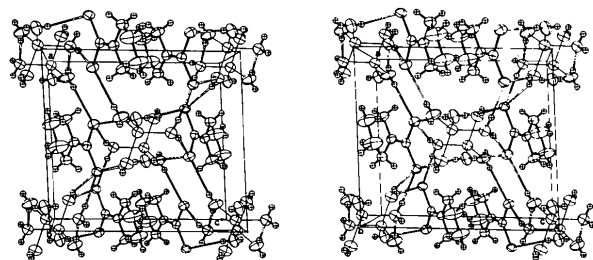S···H range: 2·41 (2)–2·67 (3)   O(4)···H1(O3)   2·02 (3)

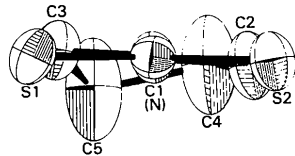Fig. 1. Stereoscopic view of the structure.

Fig. 2. The 1-pyrrolidinecarbodithioate ligand viewed along the C(1)—N bond. The N atom is hidden behind C(1).

(Duax & Norton, 1975). The pseudorotation parameters of Altona, Geise & Romers (1968) are $\Delta = 36\cdot1°$ and $\varphi_{max} = 29\cdot3°$. Significant deviations in Å from the least-squares plane through S(1), S(2), C(1) and N are C(1) 0·013 (1); C(2) −0·098 (2); C(3) 0·042 (2);C(4) −0·118 (3); C(5) −0·454 (3) Å.

The geometry of the pyrrolidinecarbodithioate ion is similar to that observed in other ionic $^-S_2CN(CH_2)_4$ compounds, *i.e.* $NaS_2CN(CH_2)_4.2H_2O$ at 295, 150 and 27 K (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980), $NaS_2CN(CH_2)_4.2H_2O$ by neutron diffraction (Ymén, 1982), $KS_2CN(CH_2)_4.\frac{1}{2}H_2O$ (Ymén, 1983a) and $[C_4H_{10}N][S_2CN(CH_2)_4]$ (Wahlberg, 1979). Typical features of these compounds with small metal–ligand interactions are a large ligand bite angle S—C—S (120–122°) and a large difference between the two S—C(1) distances (in this compound 15σ). This is in contrast to dithiocarbamates of *d* metals. For these the S—C—S angle is much smaller (110–115°) and the difference between the two S—C(1) distances becomes insignificant. The presence of empty *d* orbitals suitable for bonding on the metal seems to be a main factor governing a small ligand bite, *i.e.* a large metal–ligand interaction. Similar effects have been observed for ionic and *d*-metal compounds of $^-S_2CN(CH_3)_2, ^-S_2CN(C_2-H_5)_2$ and $^-S_2CN[CH(CH_3)_2]_2$ (Ymén, 1983b).

Since the metal–ligand interaction must be almost negligible in the present compound the size of the ligand bite angle is mainly affected by the intramolecular steric S···H interaction (Oskarsson & Ymén, 1983). The shortest S···H distances are 2·75 (2) and 2·91 (2) Å, about the same as in $NaS_2CN(CH_2)_4·2H_2O$ and $[C_4H_{10}N][S_2CN(CH_2)_4]$. Hydrogen bonds and packing forces may also influence, but only to a minor extent, as is seen when comparing $LiS_2CN(CH_2)_4·4H_2O$ and $[C_4H_{10}N][S_2CN(CH_2)_4]$. In spite of differences in packing and hydrogen bonding the difference in the angle S—C—S is only 1·5 (1)°.

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