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Structure of Lithium Diethyldithiocarbamate Trihydrate, $Li[C_5H_{10}NS_2].3H_2O$

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Abstract. $M_r = 209{\cdot}25$, triclinic, $P\bar{1}$, $a = 7{\cdot}710\,(1)$, $b = 8{\cdot}784\,(3)$, $c = 9{\cdot}154\,(1)$ Å, $\alpha = 77{\cdot}88\,(1)$, $\beta = 82{\cdot}67\,(1)$, $\gamma = 64{\cdot}93\,(2)°$, $V = 548{\cdot}5\,(3)$ Å^3, $Z = 2$, $D_x = 1{\cdot}267\,(1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}44$ mm^{-1}, $F(000) = 224$, $T = 298$ K. Final $R = 0{\cdot}041$ for 2573 observed intensities. Pairs of distorted $[Li(H_2O)_4^+]$ tetrahedra are formed by edge-sharing. Such pairs are linked to a three-dimensional network by six O—H···S hydrogen bonds. The non-polar ends of the dithiocarbamate ions are packed with van der Waals contacts in channels parallel to the *a* axis.

Introduction. The magnetic properties of tris(dithiocarbamato)iron(III) compounds, $Fe(S_2CNR_2)_3$, are dependent on the nature of the substituents R_2. Fe^{III} compounds of $^-S_2CN(CH_2)_4$, $^-S_2CN(CH_3)_2$, $^-S_2CN(C_2H_5)_2$ and $^-S_2CN[CH(CH_3)_2]_2$ exhibit high-spin, cross-over, cross-over and low-spin behaviour, respectively (Ewald, Martin, Sinn & White, 1969; Ståhl, 1983). The most obvious ways in which the substituents may influence the magnetic behaviour are through inductive effects, cooperative effects and steric interference with the S_2CNC_2 moiety. In order to elucidate steric effects in the ligands given above, their geometries in the solid state have been studied by diffraction methods. Li^+ and Na^+ dithiocarbamates have been used in this study, since small metal–ligand interactions are expected in these compounds so that the observed geometry may be approximated to that of an uncoordinated ('free') ligand. The crystal structures of three sodium and three lithium compounds have been reported previously $\{NaS_2CN(CH_2)_4.2H_2O$ (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980); $NaS_2CN(CH_3)_2.2H_2O$ (Oskarsson & Ymén, 1983); $NaS_2CN[CH(CH_3)_2]_2.5H_2O$ (Ymén, 1983*b*); $LiS_2CN(CH_2)_4.4H_2O$ (Ymén, 1983*a*); $LiS_2CN(CH_3)_2.4H_2O$ (Ymén, 1984); $LiS_2CN[CH(CH_3)_2]_2.3H_2O$ (Oskarsson & Ymén, 1984)$\}$. This paper reports the structure of $LiS_2CN(C_2H_5)_2.3H_2O$, which is the last compound in this series.

Experimental. Prismatic, hygroscopic crystals obtained at about 1 kPa from aqueous solution of $HN(C_2H_5)_2$, CS_2 and LiOH; triclinic, $P\bar{1}$ assumed in calculations. Cell dimensions obtained from 44 diffractometer θ values. 3115 independent reflections, $3 < \theta \le 30°$, $-10 \le h \le 10$, $-12 \le k \le 12$, $0 \le l \le 12$, CAD-4 diffractometer, graphite(002)-monochromatized Mo $K\alpha$, 542 reflections with $I \le 3\sigma_{\text{count}}(I)$, ω–2θ scan, width $= 1{\cdot}0° + 0{\cdot}5°\tan\theta$, max. recording time 120s, $\sigma_{\text{count}}(I)/I < 0{\cdot}033$ requested in a scan. Four standard reflections, no significant variations. I and $\sigma_{\text{count}}(I)$ corrected for Lorentz and polarization effects, no absorption correction due to loss of the crystal. Direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and subsequent ρ_{diff}, $\sum w\Delta F^2$ minimized with weights $w = [\sigma_{\text{count}}(I)^2/4|F_o|^2 + (0{\cdot}03|F_o|)^2]^{-1}$. 2573 reflections in final least-squares cycle, 174 parameters;

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$R = 0.041$, $wR = 0.056$, $S = 1.585$. Max. height in final $\rho_{\text{diff}} < 0.8$ e Å^{-3}. $(\Delta/\sigma)_{\text{max}} = 0.28$, $(\Delta/\sigma)_{\text{mean}} = 0.028$. Scattering factors with corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). A full normal δR plot (Abrahams & Keve, 1971) comparing observed and calculated structure amplitudes resulted in an approximately straight line with slope 1·452(5), intercept 0·101(5), correlation coefficient 0·990. Computer programs used given 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. Li^+ coordinates four water O atoms forming a distorted tetrahedron. Pairs of such tetrahedra are formed by edge-sharing. These pairs are connected to a three-dimensional network by six O—H···S hydrogen bonds from water molecules to the dithiocarbamate ions. The S···O distances are in the range given by Mereiter, Preisinger & Guth (1979). Within the hydrogen-bond network channels are formed along **a**. These channels contain dithiocarbamate ions, packed with their non-polar ends at approximate van der Waals distances (Bondi, 1964). The shortest intermolecular van der Waals distance, 2·44 (5) Å, is between two H(C5) atoms.

The observed conformation of the dithiocarbamate ion is similar to that in $NaS_2CN(C_2H_5)_2.3H_2O$ (Colapietro, Domenicano & Vaciago, 1968; Mereiter & Preisinger, 1983) and $[NH_2(C_2H_5)][S_2CN(C_2H_5)_2]$ (Wahlberg, 1978), *i.e.* the atoms C(4) and C(5) deviate 1·236(2) and −1·391(2) Å on each side of the least-squares plane defined by S(1), S(2), C(1) and N. Other significant deviations from this plane are observed for C(1) [0·019(1) Å] and C(2) [0·105(2) Å].

It has previously been shown that the ligand bite decreases as the substituents R_2, in $^-S_2CNR_2$, become bulkier (Oskarsson & Ymén, 1984) and this was interpreted as the result of intramolecular steric interactions, C—H···S. If steric interactions are of importance in determining the spin state of Fe^{3+} in tris(dithiocarbamato)iron(III) compounds, the steric effect in $^-S_2CN(CH_3)_2$ and $^-S_2CN(C_2H_5)_2$ should be of similar strength, since the corresponding Fe^{3+} compounds exhibit almost identical cross-over behaviour (Ståhl, 1983; Ewald *et al.*, 1969). A comparison of the geometry of the S_2CNC_2 moiety (Fig. 2) in $LiS_2CN(CH_3)_2.4H_2O$ and $LiS_2CN(C_2H_5)_2.3H_2O$ shows no significant differences, except for the angle C(2)—N—C(3) [115·4(2) and 114·0(1)° respectively] and the averages of the N—C(2) and N—C(3) distances

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

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

	x	y	z	B_{eq}(Å^2)
S(1)	0·14258 (5)	0·76945 (4)	0·90265 (4)	2·5 (1)
S(2)	0·44543 (5)	0·76240 (5)	0·66577 (5)	3·1 (1)
N	0·14068 (15)	0·70546 (14)	0·63157 (14)	2·3 (1)
C(1)	0·23204 (17)	0·74468 (14)	0·72262 (15)	2·0 (1)
C(2)	0·21676 (23	0·66831 (19)	0·48188 (18)	2·8 (1)
C(3)	−0·04121 (20)	0·68787 (20)	0·67572 (20)	2·8 (1)
C(4)	0·12619 (31)	0·81967 (26)	0·35923 (22)	3·9 (1)
C(5)	−0·01197 (29)	0·50905 (25)	0·75324 (25)	3·9 (1)
O(2)	0·69611 (15)	0·98494 (14)	−0·00248 (14)	2·7 (1)
O(1)	0·56534 (26)	0·86909 (22)	0·31313 (18)	4·7 (1)
O(3)	0·60094 (24)	0·65912 (18)	0·02524 (22)	5·4 (1)
Li	0·54784 (39)	0·85258 (34)	0·11283 (33)	3·1 (1)

Table 2. *Selected distances* (Å), *valence angles and torsion angles* (°) *with e.s.d.'s in parentheses*

(*a*) The dithiocarbamate ligand			
S(1)···S(2)	2·966 (1)	N—C(3)	1·472 (2)
S(1)—C(1)	1·724 (1)	C(2)—C(4)	1·517 (3)
S(2)—C(1)	1·722 (1)	C(3)—C(5)	1·515 (3)
C(1)—N	1·336 (2)	C(2)···C(3)	2·464 (2)
N—C(2)	1·466 (2)		
S(1)—C(1)—S(2)	118·8 (1)	C(1)—N—C(3)	122·8 (1)
S(1)—C(1)—N	120·2 (1)	C(2)—N—C(3)	114·0 (1)
S(2)—C(1)—N	120·9 (1)	N—C(2)—C(4)	112·6 (1)
C(1)—N—C(2)	123·1 (1)	N—C(3)—C(5)	112·7 (1)
S(1)—C(1)—N—C(2)	−174·6 (1)	C(1)—N—C(2)—C(4)	−100·0 (2)
S(1)—C(1)—N—C(3)	2·4 (2)	C(1)—N—C(3)—C(5)	−87·8 (2)
S(2)—C(1)—N—C(2)	2·5 (2)	C(5)—C(3)—N—C(2)	89·5 (2)
S(2)—C(1)—N—C(3)	179·6 (1)	C(4)—C(2)—N—C(3)	82·7 (2)
(*b*) The coordination polyhedron			
Li—O(2)	2·019 (3)	Li—O(1)	1·895 (3)
Li—O(2$^{\text{i}}$)	2·049 (3)	Li—O(3)	1·897 (3)
O(2)—Li—O(1)	102·2 (1)	O(2$^{\text{i}}$)—Li—O(1)	118·8 (2)
O(2)—Li—O(3)	109·4 (2)	O(2$^{\text{i}}$)—Li—O(3)	97·7 (1)
O(2)—Li—O(2$^{\text{i}}$)	96·6 (1)	O(1)—Li—O(3)	130·4 (2)
(*c*) The hydrogen bonds			
S(1)···O(2$^{\text{ii}}$)	3·254 (1)	S(2)···O(1)	3·295 (2)
S(1)···O(2$^{\text{iii}}$)	3·229 (1)	S(2)···O(1$^{\text{iii}}$)	3·248 (2)
S(1)···O(3$^{\text{iv}}$)	3·391 (2)	S(2)···O(3$^{\text{v}}$)	3·452 (2)
S···H range:	2·44 (2)–2·71 (4)		

Symmetry code: (i) $1 - x, 2 - y, -z$; (ii) $x - 1, y, z + 1$; (iii) $1 - x, 2 - y, 1 - z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $x, y, 1 + z$.

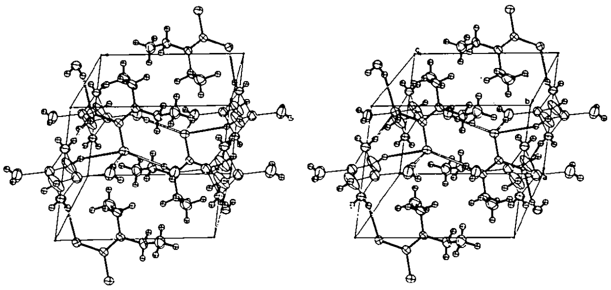

Fig. 1. A stereoscopic view of the structure.

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* Lists of structure factors, anisotropic thermal parameters and H atom positional and isotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38907 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

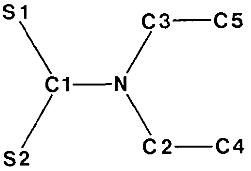

Fig. 2. Denotations of the atoms in the dithiocarbamate ion.

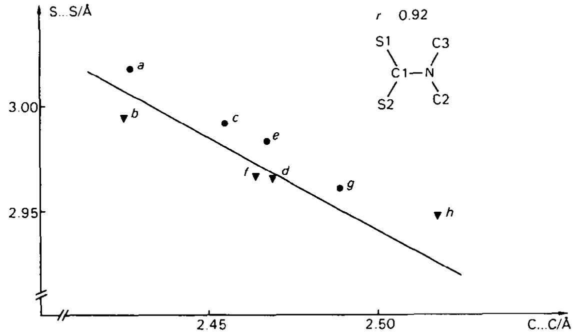

Fig. 3. $S(1)\cdots S(2) = f[C(2)\cdots C(3)]$. Circles represent Na^+ and triangles Li^+ compounds. Data are taken from (*a*) Albertsson *et al.* (1980); (*b*) Ymén (1983*a*); (*c*) Oskarsson & Ymén (1983); (*d*) Ymén (1983*b*); (*e*) Mereiter & Preisinger (1983); (*f*) this paper; (*g*) Ymén (1984) and (*h*) Oskarsson & Ymén (1984). Point (*b*) was excluded from the calculation of the correlation coefficient, *r*, for reasons discussed by Oskarsson & Ymén (1984). Points (*d*) and (*f*) represent $LiS_2CN(CH_3)_2.4H_2O$ and $LiS_2CN(C_2H_5)_2.3H_2O$ respectively.

[1·460(4) and 1·469(2) Å respectively]. These parameters are important for the intramolecular steric interference and their combined effect is reflected in the distance $C(2)\cdots C(3)$, which only differs by 0·005 Å in the two compounds. It has been proposed previously that the steric interactions are reflected in the distance $S(1)\cdots S(2)$ as a function of the distance $C(2)\cdots C(3)$ (Oskarsson & Ymén, 1984). The steric interference increases as the distance $C(2)\cdots C(3)$ increases (Fig. 3). As expected the points for $LiS_2CN(CH_3)_2.4H_2O$ and $LiS_2CN(C_2H_5)_2.3H_2O$ almost coincide in the middle of the graph, showing that the intramolecular steric interference in these two ligands is of similar strength (further support is provided by the two points observed for the corresponding Na^+ compounds).

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Acetatobis(1,10-phenanthroline)copper(II) Tetrafluoroborate, $[Cu(C_{12}H_8N_2)_2(C_2H_3O_2)]BF_4$

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Abstract. $M_r = 569{\cdot}81$, triclinic, $P\bar{1}$, $a = 15{\cdot}087$ (3), $b = 10{\cdot}615$ (2), $c = 8{\cdot}443$ (2) Å, $\alpha = 106{\cdot}43$ (2), $\beta = 76{\cdot}67$ (2), $\gamma = 109{\cdot}40$ (2)°, $U = 1209{\cdot}37$ Å^3, $Z = 2$, $D_m = 1{\cdot}52$ (5), $D_x = 1{\cdot}564$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 9{\cdot}22$ cm^{-1}, $F(000) = 577{\cdot}98$, $T = 296$ K. Final $R = 0{\cdot}036$ for 3287 unique observed reflections. The structure involves $[Cu(phen)_2(O_2CCH_3)]^+$ cations and BF_4^- anions; the cation

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