References

Andersen, E. K. (1967*a*). *Acta Cryst.* **22**, 188–191.
Andersen, E. K. (1967*b*). *Acta Cryst.* **22**, 191–196.
Andre, J. J. & Weill, G. (1971). *Chem. Phys. Lett.* **9**, 27–30.
Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180–182.
Chu, S. S. C., Jeffrey, G. A. & Sakurai, T. (1962). *Acta Cryst.* **15**, 661–671.
Coppens, P., Guru-Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.
Iida, Y. (1971). *Bull. Chem. Soc. Jpn*, **44**, 1777–1780.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Klug, H. P. (1965). *Acta Cryst.* **19**, 983–992.
Konno, M., Ishii, T. & Saito, Y. (1977). *Acta Cryst.* B**33**, 763–770.
Konno, M., Kobayashi, H., Marumo, F. & Saito, Y. (1973). *Bull. Chem. Soc. Jpn*, **46**, 1987–1990.
Mayerle, J. J. & Torrance, J. B. (1981). *Bull. Chem. Soc. Jpn*, **54**, 3170–3172.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
Rees, P. B. (1970). *Acta Cryst.* B**26**, 1304–1311.
Trotter, J. (1960). *Acta Cryst.* **13**, 86–95.
Vegter, J. G., Himba, T. & Kommandeur, J. (1969). *Chem. Phys. Lett.* **3**, 427–429.
Weperen, K. J. van & Visser, G. J. (1972). *Acta Cryst.* B**28**, 338–342.
Zanotti, G., Bardi, R. & Del Pra, A. (1980). *Acta Cryst.* B**36**, 168–171.
Zanotti, G. & Del Pra, A. (1980). *Acta Cryst.* B**36**, 313–316.

Acta Cryst. (1984). C**40**, 238–241

The Sodium Picrate Benzo-15-crown-5 Complex,* $Na^+.C_6H_2N_3O_7^-.C_{14}H_{20}O_5$

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Abstract. $M_r = 519.40$, monoclinic, $P2_1/n$, $a = 11.125$ (3), $b = 13.555$ (4), $c = 14.924$ (5) Å, $\beta = 93.40$ (2)°, $V = 2247$ (3) Å^3, $Z = 4$, $D_x = 1.536$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $\mu(\text{Mo } K\alpha) = 0.975$ cm^{-1}, $F(000) = 270$, $T = 296$ K, $R = 0.061$ for 2786 $[I > 2\sigma(I)]$ of 6588 total unique data. The structural analysis reveals that the Na^+ ion is coordinated to all five crown oxygens [Na—O 2.400 (3) to 2.501 (3) Å] as well as to the phenoxide [Na—O 2.350 (3) Å] and an *ortho* nitro oxygen [Na—O 2.510 (3) Å] of the anion. The Na^+ ion lies out of the cavity of the crown toward the picrate by 0.900 (1) Å.

Introduction. *In vitro* conditions which favor the encapsulation of different alkali and alkaline-earth cations by the macrocyclic ligand benzo-15-crown-5 (B15C5) while the cation is subjected to an anionic effect of diverse organic charge neutralizers [*e.g.* picrate (pic), or 3,5-dinitrobenzoate (3,5-DNB)] have been investigated by one of the authors (NSP) for a number of years. The ultimate aim of this research is to throw some light on the chemical principles which control the hitherto undiscovered mechanism of discrimination of Na^+–K^+ and Mg^{2+}–Ca^{2+} pairs by the cell membrane in biological systems (Williams, 1970).

Earlier X-ray structural work on B15C5 complexes of some alkali and alkaline-earth picrates showed that cations with a higher charge density, Ca^{2+} (Bhagwat, Manohar & Poonia, 1980*a*) and Li^+ (Bhagwat, Manohar & Poonia, 1980*b*), prefer direct bonding with the anion and the solvent (water) molecules while the macrocyclic ligand is hydrogen-bonded to the water molecules in the coordination sphere of the cation. A larger cation, Ba^{2+}, is cooordinated to the anion, the solvent molecule, as well as to the macrocycle (Venkatasubramanian, Poonia, Hackert, Clinger & Ernst, 1983). With a fairly low charge density, K^+ forms charge-separated sandwich complexes $K^+(B15C5)_2$ in which the weakly nucleophilic counterion I^- is separated from the cation by the ligand (Mallinson & Truter, 1972) and in which the strongly chelating picrate anion does not interact with the cation (Bhagwat, Manohar & Poonia, 1981). It was of interest to us to determine whether the Na^+ ion in the $Na^+(B15C5)$ complex is bonded uniquely to the crown ether (as K^+), to the crown ether as well as to the counterion (as Ba^{2+}), or whether there is no direct bonding between the cation and crown ether (as for Li^+ and Ca^{2+}). This led us to undertake the X-ray structural analysis of the complex $Na^+pic^-(B15C5)$.

Experimental. Equimolar amounts (0.04 *M* each) of sodium picrate and B15C5 (Aldrich) were disolved in warm ethanol. The crystalline complex (m.p. 426 K) was obtained upon cooling the solution. It is interesting

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* (6,7,9,10,12,13,15,16-Octahydro-5,8,11,14,17-pentaoxabenzocyclopentadecene)(2,4,6-trinitrophenolato)sodium.

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to note that the yield was lowered by the addition of excess B15C5 which suggests the formation of the $Na^+(B15C5)_2pic^-$ sandwich complex in solution. The infrared spectrum (Nujol) of the complex showed the latter to be anhydrous. Likewise, the characteristic absorption band of the uncomplexed B15C5 at 980 cm^{-1} was absent. Anhydrous product was obtained even when up to 20 vol. % of water was added to the synthesis medium.

Crystal size $0\cdot17 \times 0\cdot25 \times 0\cdot49$ mm; crystal faces [*hkl*, distance (mm) to origin within crystal] (111) 0·128, $(\bar{1}\bar{1}\bar{1})$ 0·120, $(10\bar{1})$ (0·136), $(\bar{1}01)$ 0·115, (001) 0·150, $(00\bar{1})$ 0·128, (101) 0·097, $(\bar{1}0\bar{1})$ 0·076, $(1\bar{1}1)$ 0·145, $(\bar{1}1\bar{1})$ 0·130, $(\bar{1}21)$ 0·193; Picker FACS-I diffractometer, lattice parameters from 13 reflections with $40 < 2\theta < 45°$, absorption correction (Templeton & Templeton, 1973) factors 1·013 to 1·025, $(\sin\theta/\lambda)_{max} = 0\cdot705$ Å^{-1}, $0 \le h \le 15$, $0 \le k \le 19$, $-21 \le l \le 20$, standard reflections (and intensities) 002 (75692·1 to 93296·3), 200 (31851·4 to 35679·6), $02\bar{1}$ (11697·7 to 13120·0); 7168 reflections measured, 6588 unique, $R_{int} = 0\cdot0294$, 3802 unobserved $[I < 2\sigma(I)]$; direct methods [*MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)], refinement on F, calculated H-atom positions, anisotropic non-H atoms, isotropic H atoms, $R = 0\cdot061$, $wR = 0\cdot053$, $S = 1\cdot313$, $w = 1/\sigma_F^2$, $(\Delta/\sigma)_{max} = 0\cdot35$ (non-H), 0·69 (H), final $\Delta\rho$ excursions from 0·67 to $-0\cdot61$ e Å^{-3}; secondary-extinction (Wei & Ward, 1976) value $0\cdot21 \times 10^{-5}$; atomic scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974), computations using DEC PDP 8/I, DEC PDP 11/40, and CDC Cyber 170 Model 750 computers and the programs listed in Table 7 (deposited).

Discussion. Fig. 1 shows the numbering of the atoms and Fig. 2 the structure of the $Na^+pic^-(B15C5)$ complex. Tables 1 to 6 list atomic coordinates, anisotropic thermal parameters, interatomic distances, interatomic angles, least-squares planes, and torsion angles, respectively.*

The structure of the $Na^+pic^-(B15C5)$ complex is similar to that of $Na^+ClO_4^-(B15C5)$ reported by Owen (1980). In our system, the Na^+ ion is coordinated to the five O atoms of the crown as well as to an *ortho* nitro and the phenoxide O atoms of the picrate. The Na—O distances range from 2·350 (3) to 2·510 (3) Å. The O—Na—O angles involving the O atoms of the crown are in the 64·82 (8)–68·77 (10)° range for adjacent pairs and the 112·66 (13)–134·34 (12)° range for opposite pairs; the angles involving a picrate and a crown oxygen range from 83·23 (10) to 147·69 (12)° while the angle involving the two picrate oxygens is 65·83 (10)°. The Na^+ ion lies 0·900 (1) Å towards the picrate ion from the plane of the five O atoms of the crown. The latter are coplanar to within ±0·340 (3) Å. The plane of the five O atoms of the crown makes an angle of 81° with the plane of the Na^+ and the two interacting picrate O atoms, and an angle of 30° with the plane of the benzo group [as compared to 20° found by Owen (1980) in $Na^+ClO_4^-(B15C5)$].

The picrate is practically planar with no C or N atom lying further than 0·107 (4) Å from the least-squares plane through all non-hydrogen atoms. The two nitro groups not involved in interactions with the Na^+ ion are rotated or bent 7 to 8° from the plane of the picrate; the third nitro group is rotated or bent 20°; and the phenolic O atom is displaced 0·276 (3) Å from the plane of the picrate ion. The Na^+ ion lies 1·736 (1) Å from the plane of the picrate; the angle between the plane of the picrate and the plane defined by the Na^+ ion and the two interacting picrate O atoms is 46°.

The Na—O distance with the phenoxide oxygen is shortened reflecting the anionic attraction of Na^+ (Poonia & Bajaj, 1979). Surprisingly, the two oxygens adjacent to the phenyl ring do not form the longest Na^+—O bonds, as has been noted previously for various $M^{n+}(B15C5)$ complexes (Bhagwat, Manohar & Poonia, 1980*a*,*b*, 1981; Venkatasubramanian, Poonia, Hackert, Clinger & Ernst, 1983; Mallinson & Truter, 1972); in fact, one of them [O(1)] forms the shortest of the five cation–ligand bonds [2·399 (3) Å].

A structural comparison of the various $Na^+(B15C5)$ complex structures shows clearly the important role played by the 'nucleophilicity' of the counterion in determining the stoichiometry and the structure of the resulting complexes in the crystalline state. Thus with a 'non-interacting' anion BPh_4^-, a sandwich complex $Na^+(B15C5)_2BPh_4^-$ is obtained (Owen, 1980). With sodium perchlorate, where the anion is *mostly* 'inert', the ion-paired $Na^+ClO_4^-(B15C5)$ as well as the sandwich $Na^+(B15C5)_2ClO_4^-$ complexes are formed (Owen, 1980). In each sandwich the cation is completely separated from the counterion by the crown-ether molecules while the 1:1 complex involves complexation of the cation with five crown ether oxygens as well as with two perchlorate oxygens; the Na^+ ion lies 0·77 Å from the mean plane of the ether oxygens in the $Na^+ClO_4^-(B15C5)$ complex and between 1·52 and 1·65 Å in the sandwich complexes.

In the $Na^+(B15C5)H_2O$ complex, the coordination sphere around the Na^+ ion is in the form of a distorted pentagonal pyramid (Bush & Truter, 1972). The cation is bonded to the five oxygens of the crown ether (lying 0·75 Å from their mean plane) and to the water molecules which also form a hydrogen bond with the I^- ion.

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* Lists of structure factors and Tables 2 to 7 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38927 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Our results provide another example of the influence of the nucleophilic properties of anions on the coordinated properties of the metal ions. The picrate ion readily coordinates to the Na^+ ion and its nucleophilicity is sufficiently high to prevent the formation of a hydrate and, consequently, of a $Na^+—H_2O$ bond.

It should be noted, of course, that the above generalizations apply to the formation of crystalline complexes and cannot be safely extrapolated to their stoichiometry and structures in solutions where solvent–solute interactions are often of great importance. A combination of spectroscopic measurements on the solids and their solutions (*e.g.* NMR or IR), coupled with the knowledge of their crystalline structures, offers an interesting possibility of determining the influence of solvents on the stoichiometry and structure of macrocyclic complexes in solutions. Such studies are currently in progress in our laboratory.

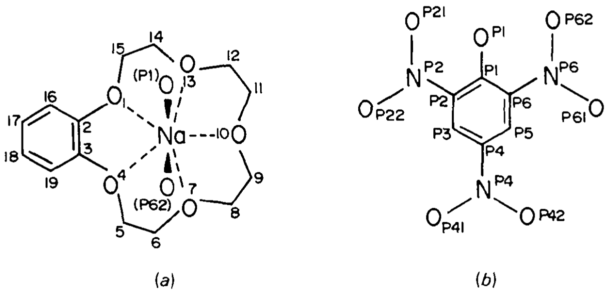

Fig. 1. The numbering of the non-hydrogen atoms. (*a*) Benzo-15-crown-5, including the Na^+ ion and the two interacting O atoms of the picrate ion. (*b*) Picrate ion.

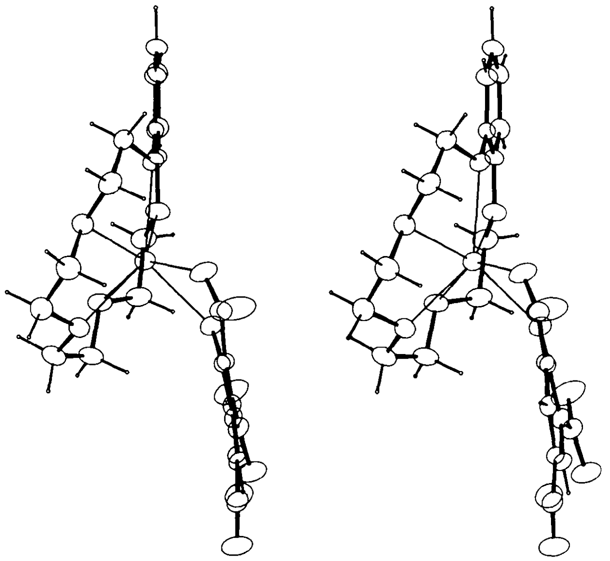

Fig. 2. The structure of the sodium picrate benzo-15-crown-5 complex (*ORTEP*; Johnson, 1965).

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

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} or B(Å^2)
Na(1)	0·8048 (1)	0·9086 (1)	0·21883 (8)	3·10
O(1)	1·0068 (2)	0·9095 (2)	0·2846 (1)	3·35
C(2)	1·1062 (3)	0·9015 (3)	0·2350 (2)	2·88
C(3)	1·0851 (3)	0·9040 (3)	0·1414 (2)	2·85
O(4)	0·9664 (2)	0·9128 (2)	0·1093 (1)	3·18
C(5)	0·9370 (4)	0·8642 (3)	0·0250 (2)	3·52
C(6)	0·8037 (4)	0·8526 (4)	0·0133 (3)	3·86
O(7)	0·7632 (2)	0·8021 (2)	0·0887 (2)	3·44
C(8)	0·6354 (4)	0·7876 (4)	0·0829 (3)	4·39
C(9)	0·6015 (4)	0·7366 (4)	0·1656 (3)	4·55
O(10)	0·6316 (2)	0·8009 (2)	0·2401 (2)	3·81
C(11)	0·6322 (4)	0·7499 (4)	0·3238 (3)	4·57
C(12)	0·7051 (4)	0·8095 (4)	0·3907 (3)	4·13
O(13)	0·8239 (2)	0·8159 (2)	0·3606 (2)	3·69
C(14)	0·8999 (4)	0·8788 (4)	0·4139 (3)	3·98
C(15)	1·0218 (4)	0·8781 (4)	0·3765 (2)	3·82
C(16)	1·2224 (3)	0·8910 (3)	0·2714 (3)	3·65
C(17)	1·3175 (4)	0·8825 (3)	0·2152 (3)	4·21
C(18)	1·2960 (4)	0·8867 (3)	0·1242 (3)	4·61
C(19)	1·1804 (4)	0·8975 (3)	0·0879 (3)	4·04
C(*P*1)	0·6162 (3)	1·0674 (3)	0·2993 (2)	2·48
C(*P*2)	0·5520 (3)	1·0915 (3)	0·3783 (2)	2·75
C(*P*3)	0·4308 (3)	1·1127 (3)	0·3761 (2)	3·09
C(*P*4)	0·3665 (3)	1·1199 (3)	0·2947 (2)	2·85
C(*P*5)	0·4218 (3)	1·1091 (3)	0·2154 (2)	2·95
C(*P*6)	0·5412 (3)	1·0849 (3)	0·2177 (2)	2·69
O(*P*1)	0·7210 (2)	1·0368 (2)	0·3008 (1)	3·47
N(*P*2)	0·6132 (3)	1·0906 (2)	0·4679 (2)	3·46
O(*P*21)	0·7178 (3)	1·0667 (3)	0·4766 (2)	6·09
O(*P*22)	0·5580 (3)	1·1174 (2)	0·5314 (2)	5·16
N(*P*4)	0·2372 (3)	1·1338 (3)	0·2929 (2)	3·82
O(*P*41)	0·1887 (3)	1·1339 (3)	0·3646 (2)	5·57
O(*P*42)	0·1819 (2)	1·1450 (2)	0·2201 (2)	4·91
N(*P*6)	0·5926 (3)	1·0750 (3)	0·1305 (2)	3·53
O(*P*61)	0·5380 (3)	1·1118 (3)	0·0663 (2)	7·12
O(*P*62)	0·6893 (2)	1·0332 (2)	0·1238 (2)	4·57
H(5*A*)	0·977 (3)	0·801 (3)	0·028 (2)	4·0(10)
H(5*B*)	0·965 (3)	0·904 (3)	−0·021 (3)	4·6 (10)
H(6*A*)	0·783 (3)	0·814 (3)	−0·039 (2)	2·8(8)
H(6*B*)	0·759 (3)	0·920 (3)	0·004 (2)	4·0 (9)
H(8*A*)	0·621 (4)	0·751 (3)	0·028 (3)	5·5 (11)
H(8*B*)	0·584 (5)	0·861 (4)	0·072 (3)	8·0 (14)
H(9*A*)	0·649 (4)	0·667 (3)	0·173 (2)	5·5 (11)
H(9*B*)	0·512 (4)	0·722 (3)	0·156 (3)	5·2 (11)
H(11*A*)	0·672 (4)	0·681 (4)	0·316 (3)	8·0 (15)
H(11*B*)	0·551 (3)	0·747 (3)	0·341 (2)	3·4 (9)
H(12*A*)	0·711 (3)	0·780 (3)	0·452 (3)	4·1 (9)
H(12*B*)	0·676 (3)	0·879 (3)	0·400 (2)	4·3 (10)
H(14*A*)	0·902 (3)	0·856 (3)	0·473 (2)	3·3 (8)
H(14*B*)	0·869 (3)	0·945 (3)	0·416 (2)	3·8 (10)
H(15*A*)	1·073 (3)	0·926 (3)	0·410 (2)	3·3 (8)
H(15*B*)	1·060 (4)	0·816 (3)	0·380 (3)	5·2 (11)
H(16)	1·236 (4)	0·888 (3)	0·335 (2)	4·9 (10)
H(17)	1·394 (3)	0·880 (3)	0·242 (2)	3·7 (9)
H(18)	1·364 (4)	0·881 (3)	0·084 (2)	5·2 (10)
H(19)	1·168 (3)	0·902 (3)	0·029 (2)	3·0 (8)
H(*P*3)	0·396 (3)	1·122 (3)	0·425 (2)	3·9 (9)
H(*P*5)	0·375 (3)	1·108 (3)	0·162 (2)	4·6 (10)

References

BHAGWAT, V. W., MANOHAR, H. & POONIA, N. S. (1980*a*). *Inorg. Nucl. Chem. Lett.* **16**, 289–292.

BHAGWAT, V. W., MANOHAR, H. & POONIA, N. S. (1980*b*). *Inorg. Nucl. Chem. Lett.* **16**, 373–375.

BHAGWAT, V. W., MANOHAR, H. & POONIA, N. S. (1981). *Inorg. Nucl. Chem. Lett.* **17**, 207–210.

BUSH, M. A. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 341–344.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2B, p. 99 and Table 2.3.1, p. 149. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794 (revised). Oak Ridge National Laboratory, Tennessee.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,* Univs. of York, England, and Louvain, Belgium.

MALLINSON, P. R. & TRUTER, M. R. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 1818–1823.

OWEN, J. D. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1066–1075.

POONIA, N. S. & BAJAJ, A. V. (1979). *Chem. Rev.* **79**, 389–445.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). *Abstr. Am. Crystallogr. Assoc. Proc. Ser.* 2, **1**, 143.

VENKATASUBRAMANIAN, K., POONIA, N. S., HACKERT, M. L., CLINGER, C. & ERNST, S. R. (1983). *J. Inclus. Phenom.* In the press.

WEI, K.-T. & WARD, D. L. (1976). *Acta Cryst.* B**32**, 2768–2773.

WILLIAMS, R. J. P. (1970). *Q. Rev. Chem. Soc.* **24**, 331–365.

Acta Cryst. (1984). C**40**, 241–243

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

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Abstract. $M_r = 209\cdot25$, triclinic, $P\bar{1}$, $a = 7\cdot710\,(1)$, $b = 8\cdot784\,(3)$, $c = 9\cdot154\,(1)$ Å, $\alpha = 77\cdot88\,(1)$, $\beta = 82\cdot67\,(1)$, $\gamma = 64\cdot93\,(2)^\circ$, $V = 548\cdot5\,(3)$ Å^3, $Z = 2$, $D_x = 1\cdot267\,(1)$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot44$ mm^{-1}, $F(000) = 224$, $T = 298$ K. Final $R = 0\cdot041$ 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, $3 < \theta \le 30^\circ$, $-10 \le h \le 10$, $-12 \le k \le 12$, $0 \le l \le 12$, CAD-4 diffractometer, graphite(002)-monochromatized Mo $K\alpha$, 542 reflections with $I \le 3\sigma_{\text{count}}(I)$, ω–2θ scan, width $= 1\cdot0^\circ + 0\cdot5^\circ \tan\theta$, max. recording time 120s, $\sigma_{\text{count}}(I)/I < 0\cdot033$ 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 $w = [\sigma_{\text{count}}(I)^2/4|F_o|^2 + (0\cdot03|F_o|)^2]^{-1}$. 2573 reflections in final least-squares cycle, 174 parameters;

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