N···Cl sont 3,262 (5) – 3,324 (6) et 3,206 (5) Å. Ces auteurs proposent un modèle de transition de phase dans ce composé et le déduisent des mouvements possibles du cation ammonium, mouvements liés à l'existence d'un ensemble de liaisons hydrogène.

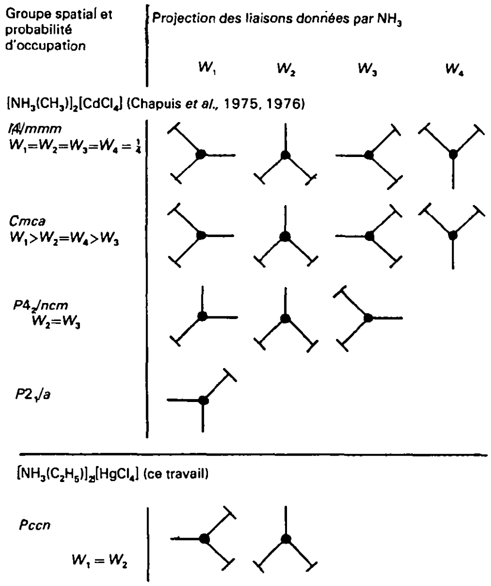

Fig. 5. Liaisons hydrogène pour différentes phases de composés $[NH_3(R)]_2[MCl_4]$. (La liaison avec un chlore equatorial est schématisée par une barre terminale.)

Par comparaison avec leurs résultats, il apparaît donc raisonnable de proposer que les trois atomes d'hydrogène fixés sur l'atome d'azote sont tous engagés dans des liaisons hydrogène N···H···Cl. Mais comme on dénombre six courtes distances N···Cl (< 3,40 Å), dont une un peu plus courte que les autres, d'une part, et que d'autre part, la chaîne C—C du groupement C_2H_5 occupe statistiquement deux positions, ceci laisse penser que deux hydrogènes occupent chacun deux positions avec des distances N···Cl égales à 3,32–3,35 Å pour l'un et 3,37–3,39 Å pour l'autre, le troisième hydrogène restant relativement fixe à distance plus faible, 3,28 Å (Fig. 5).

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Références

Chapuis, G., Kind, R. & Arend, H. (1975). *Phys. Status Solidi A*, **31**, 449–454.

Chapuis, G., Kind, R. & Arend, H. (1976). *Phys. Status Solidi A*, **36**, 285–289.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Mosset, A., Bonnet, J. J. & Galy, J. (1977). *Acta Cryst.* **B33**, 2639–2644.

Peterson, E. R. & Willet, R. D. (1972). *J. Chem. Phys.* **56**, 1879–1882.

Steadman, J. P. & Willet, R. D. (1970). *Inorg. Chim. Acta*, **4**(3), 367–371.

Acta Cryst. (1983). C**39**, 66–68

Structure of Sodium Dimethyldithiocarbamate Dihydrate, $Na[S_2CN(CH_3)_2].2H_2O$

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Abstract. $M_r = 179{\cdot}2$, monoclinic, $P2_1/a$, $a = 11{\cdot}981\ (1)$, $b = 5{\cdot}871\ (2)$, $c = 12{\cdot}878\ (1)$ Å, $\beta = 113{\cdot}62\ (1)°$, $V = 830\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}434\ (2)$ Mg m^{-3}, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}61$ mm^{-1}, $R = \sum|\Delta F|/\sum|F_o| = 0{\cdot}034$ for 1478 reflections. The crystal structure was determined by direct and Fourier methods from X-ray intensities collected with a four-circle single-crystal diffractometer. Na coordinates four water O atoms and two S atoms, forming a distorted octahedron. These polyhedra share edges and corners in layers parallel to the *ab* plane. Along **c** the structure is kept together by van der Waals bonds. Both S atoms form S···H—O hydrogen bonds to the water molecules. The structure is very similar to that of $Na[S_2CN(CH_2)_4].2H_2O$. The most significant difference in the comparable parts of the ligands in the two compounds is the ligand bite angle, 120·9 (1)° in $^-S_2CN(CH_3)_2$ and 122·3 (1)° in $^-S_2CN(CH_2)_4$.

Introduction. Substituted dithiocarbamate ions, $^-S_2CNR_2$, form compounds with a great variety of metal ions (Willemse, Cras, Steggerda & Keijzers, 1976). The geometry of the >NCS_2 moiety is dependent

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on the substituents R_2, as well as the actual coordination environment. In order to elucidate the geometry of dithiocarbamate ions in compounds with weak ligand–metal interactions the crystal structures for a number of alkali-metal dithiocarbamates have been determined. The substituents $R_2 = (CH_2)_4$, $R_2 = (CH_3)_2$, and $R_2 = [CH(CH_3)_2]_2$ have been chosen since the intramolecular steric interference between the substitutents and the S atoms is expected to increase in the order $(CH_2)_4 < (CH_3)_2 < [CH(CH_3)_2]_2$. The crystal structure of $Na[S_2CN(CH_2)_4].2H_2O$ (denoted Na-1Py) has been studied earlier with X-ray (Albertsson, Oskarsson, Ståhl, Svensson & Ymén, 1980) and neutron diffraction (Ymén, 1982) and this paper reports the structure of $Na[S_2CN(CH_3)_2].2H_2O$ (denoted Na-Dim).

Experimental. Stoichiometric amounts of $HN(CH_3)_2$, CS_2 and NaOH in ethanol, plate-like single crystals on evaporation under reduced pressure, recrystallization from aqueous solutions, crystal 0·09 × 0·50 × 0·19 mm; Weissenberg photographs revealed Laue class $2/m$, systematic extinctions $h0l$, h odd and $0k0$, k odd consistent with space group $P2_1/a$, cell dimensions obtained by least squares from 23 θ values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$ with an Enraf–Nonius CAD-4 diffractometer in the bisecting mode and measuring $\omega_{\bar{h}\bar{k}l}$ at a negative θ angle, all 10 526 accessible reflections with $\sin\theta/\lambda < 0{\cdot}70$ Å^{-1}, 6001 reflections with $I < \sigma_c(I)$, Zr-filtered Mo $K\alpha$, ω–2θ scan width = $(0{\cdot}80 + 0{\cdot}3 \tan\theta)^\circ$, $\sigma_c(I)/I$ requested in a scan 0·028, maximum recording time 180s, four standard reflections, no significant variations, I calculated by the Lehmann & Larsen (1974) peak-location method, I and $\sigma_c(I)$ corrected for Lorentz, polarization and absorption effects [$\sigma_c(I)$ based on counting statistics], range of transmission factors 0·90—0·95, agreement between symmetry-related reflections usually better than 10%, averaged before structure determination, 29 weak reflections deleted since only one of the symmetry-related reflections obeyed $I > \sigma_c(I)$, direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and subsequent difference Fourier calculations, full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$ minimized with weights $w = [\sigma_c(I)^2/4|F_o|^2 + (C|F_o|)^2]^{-1}$, C adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2\rangle$ were obtained in different $|F_o|$ and $\sin\theta$ intervals, $C = 0{\cdot}030$, number of reflections in final least-squares cycle $m = 1478$, number of parameters $n = 122$, $R_w = [\sum w(\Delta F)^2/\sum w|F_o|^2]^{\frac{1}{2}} = 0{\cdot}038$, $S = [\sum w(\Delta F)^2/(m-n)]^{\frac{1}{2}} = 0{\cdot}942$, $F(000) = 376$, scattering factors with corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974), no secondary extinction (Zachariasen, 1967); a δR plot (Abrahams & Keve, 1971) resulted in an approximately straight line with slope 0·893 (3), intercept 0·052 (3), correlation coefficient 0·991.

Discussion. Final positional parameters and isotropic thermal parameters are given in Table 1* and selected distances and angles in Table 2. The structure is depicted in Fig. 1. The dithiocarbamate ion acts as a monodentate ligand. Na coordinates four water O atoms and two S atoms forming a distorted octahedron. These polyhedra share edges and corners forming layers parallel to the ab plane. Between these layers the

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

For non-hydrogen atoms $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq} or B(Å^2)
Na	0·57196 (8)	0·74317 (15)	0·48001 (8)	2·8 (1)
S(1)	0·69923 (5)	0·47758 (10)	0·36143 (4)	2·5 (1)
S(2)	0·76842 (6)	0·29198 (12)	0·17862 (5)	3·4 (1)
O(1)	0·62483 (17)	0·42846 (33)	0·61057 (16)	3·1 (1)
O(2)	0·51673 (18)	1·09749 (31)	0·39285 (16)	2·9 (1)
N	0·62251 (18)	0·64399 (36)	0·15222 (16)	3·0 (1)
C(1)	0·69013 (19)	0·48416 (37)	0·22349 (17)	2·2 (1)
C(2)	0·62962 (40)	0·68905 (74)	0·04311 (26)	4·5 (1)
C(3)	0·54219 (35)	0·79873 (66)	0·17879 (30)	4·5 (1)
H1(O1)	0·657 (3)	0·503 (7)	0·668 (3)	4·1 (1·0)
H2(O1)	0·673 (3)	0·344 (7)	0·613 (3)	2·6 (8)
H1(O2)	0·567 (3)	1·173 (6)	0·385 (3)	3·0 (8)
H2(O2)	0·458 (3)	1·121 (6)	0·336 (3)	2·6 (8)
H1(C2)	0·556 (4)	0·689 (9)	−0·011 (5)	8·1 (1·6)
H2(C2)	0·648 (4)	0·564 (8)	0·017 (4)	5·7 (1·2)
H3(C2)	0·646 (4)	0·825 (8)	0·044 (4)	5·6 (1·2)
H1(C3)	0·581 (4)	0·931 (8)	0·218 (4)	6·6 (1·3)
H2(C3)	0·508 (3)	0·728 (5)	0·221 (3)	2·5 (7)
H3(C3)	0·482 (4)	0·845 (7)	0·112 (4)	4·8 (1·0)

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

Symmetry code

(i) $1-x, 1-y, 1-z$
(ii) $\frac{3}{2}-x, \frac{1}{2}+y, 1-z$
(iii) $1-x, 2-y, 1-z$
(iv) $\frac{3}{2}-x, y-\frac{1}{2}, 1-z$
(v) $\frac{1}{2}+x, \frac{3}{2}-y, z$
(vi) $x, y-1, z$

The coordination polyhedron

Na–S(1)	2·992 (1)	Na–O(1^{i})	2·394 (2)
Na–S(1^{ii})	3·015 (1)	Na–O(2)	2·330 (2)
Na–O(1)	2·406 (2)	Na–O(2^{iii})	2·466 (2)

The dithiocarbamate ligand

S(1)–C(1)	1·736 (2)	S(1)–C(1)–S(2)	120·9 (1)
S(2)–C(1)	1·709 (2)	S(1)–C(1)–N	119·4 (2)
C(1)–N	1·335 (3)	S(2)–C(1)–N	119·7 (2)
C(2)–N	1·465 (4)	C(1)–N–C(2)	122·2 (2)
C(3)–N	1·460 (4)	C(1)–N–C(3)	123·5 (2)
S(1)···S(2)	2·997 (1)	C(2)–N–C(3)	114·2 (3)
S(1)···C(3)	3·013 (4)	S(1)–C(1)–N–C(2)	168·6 (3)
S(2)···C(2)	2·987 (4)	S(1)–C(1)–N–C(3)	−7·0 (2)
S(1)···H2(C3)	2·71 (3)	S(2)–C(1)–N–C(2)	−12·5 (2)
S(2)···H2(C2)	2·56 (5)	S(2)–C(1)–N–C(3)	171·9 (3)

C–H: 0·83 (5) –0·92 (4)

The hydrogen bonds

S(1)···O(1^{ii})	3·312 (2)	S(2)···O(1^{iv})	3·283 (2)
S(1)···O(2^{vi})	3·261 (2)	S(2)···O(2^{v})	3·210 (2)

O–H: 0·75 (4) –0·82 (4)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38174 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

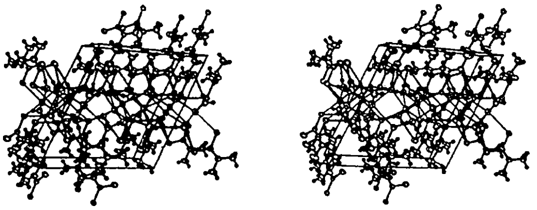
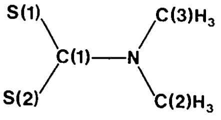


Fig. 1. Stereoscopic view of the structure.

methyl groups are at approximate van der Waals distances, the closest contact between the methyl H atoms being 2·29 (7) Å. The structure of Na-Dim is very similar to that of Na-1Py (Albertsson *et al.*, 1980). The shortening of the *c* axis from 14·008 (2) Å in Na-1Py to 12·878 (1) Å in Na-Dim is consistent with the change from $R_2 = (CH_2)_4$ to $R_2 = (CH_3)_2$.

Each S atom accepts two hydrogen bonds from the water molecules with S···O distances in the range 3·210 (2) – 3·312 (2) Å. The S···H—O hydrogen-bond system in Na-Dim is similar to that in Na-1Py, which has previously been described in detail (Ymén, 1982).

The S(1), S(2), C(1), N part of the dithiocarbamate ion is essentially planar with the two methyl C atoms C(2) and C(3) deviating on each side of the plane [0·27 (1) and 0·15 (1) Å respectively]. The geometry of the organic ligand in Na-Dim may be compared to the corresponding part of the ligand in Na-1Py: S(1), S(2), C(1), N, C(2) and C(3).



In both compounds the distance S(1)—C(1) is about 12 standard deviations longer than S(2)—C(1), but the mean distance is 1·722 (13) Å in both structures. No significant differences are observed in the C(1)—N, N—C(2) or N—C(3) distances. The difference in the angle C(2)—N—C(3), 110·8 (2)° in Na-1Py and 114·2 (3)° in Na-Dim, is due to the change from a strained five-membered ring to two methyl groups. This results in a shorter intramolecular S···H distance in Na-Dim [2·56 (5) Å] than in Na-1Py [X-ray: 2·77 (4) Å; neutron: 2·85 (2) Å]. Raston & White (1976) and Newman & White (1972) have also observed intramolecular S···H interactions in some dithiocarbamate ions. The difference in the ligand bite angle, 122·3 (1)° in Na-1Py and 120·9 (1)° in Na-Dim, is therefore explained by this steric interference. This is further supported by the differences in the torsion angles S—C—N—C in the two ligands [Na-1Py: 1·2 (3) – 2·2 (3)°; Na-Dim: 7·0 (2)–12·5 (2)°]. In Na-Dim some of the steric strain is evidently removed by rotation around the C(1)—N bond. Similar effects are observed in Cs dimethyldithiocarbamate (Wahlberg, 1976) and in dimethylammonium dimethyldithiocarbamate (Wahlberg, 1978).

It is concluded that the only significant difference in the geometry of the moiety $>NCS_2$ in the ions $^-S_2CN(CH_3)_2$ and $^-S_2CN(CH_2)_4$ is the ligand bite angle and this difference is most probably caused by a larger intramolecular S···H interaction in the dimethyldithiocarbamate ion.

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References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

Albertsson, J., Oskarsson, Å., Ståhl, K., Svensson, C. & Ymén, I. (1980). *Acta Cryst.* B**36**, 3072–3078.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Newman, P. W. G. & White, A. H. (1972). *J. Chem. Soc. Dalton Trans.* pp. 2239–2243.

Raston, C. L. & White, A. H. (1976). *Aust. J. Chem.* **29**, 523–529.

Wahlberg, A. (1976). *Acta Chem. Scand. Ser A*, **30**, 433–436.

Wahlberg, A. (1978). *Acta Cryst.* B**34**, 3392–3395.

Willemse, J., Cras, J. A., Steggerda, J. J. & Keijzers, C. P. (1976). *Struct. Bonding* (*Berlin*), **28**, 83–126.

Ymén, I. (1982). *Acta Cryst.* B**38**, 2671–2674.

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