

Fig. 1. View of the complex showing the nickel coordination and the atomic numbering.

References

- BEHM, H. & BEURSKENS, P. T. (1985). *Z. Kristallogr.* **170**, 10.
- BEURSKENS, P. T., BOSMAN, W. P., DOESBURG, H. M., VAN DEN HARK, TH. E. M., PRICK, P. A. J., NOORDIK, J. H., BEURSKENS, G., GOULD, R. O. & PARTHASARATHI, V. (1982). *Conformation in Biology*, edited by R. SRINIVASAN & R. H. SARMA, pp. 389–406. New York: Adenine Press.
- GARCÍA-GRANDA, S. & GÓMEZ-BELTRÁN, F. (1986). *Acta Cryst.* **C42**, 33–35 and references therein.
- GRANT, D. F. & GABE, E. J. (1978). *J. Appl. Cryst.* **11**, 114–120.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
- MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
- NARDELLI, M. (1983). *Comput. Chem.* **7**, 95–98.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1987). **C43**, 41–43

Structure of Sodium 1,1-Dicyanoethylene-2,2-dithiolate Trihydrate

BY HANS-ULRICH HUMMEL

Institut für Anorganische Chemie der Universität Erlangen–Nürnberg, Egerlandstrasse 1, D-8520 Erlangen, Federal Republic of Germany

(Received 25 March 1986; accepted 31 July 1986)

Abstract. $\text{Na}_2\text{C}_4\text{N}_2\text{S}_2 \cdot 3\text{H}_2\text{O}$, $M_r = 240.21$, monoclinic, $I2/m$, $a = 8.750$ (1), $b = 7.588$ (1), $c = 14.479$ (2) Å, $\beta = 91.00$ (2)°, $V = 961.2$ Å³, $Z = 4$, $D_m = 1.70$, $D_x = 1.66$ Mg m⁻³, $\lambda(\text{Ag K}\alpha) = 0.5591$ Å, $\mu = 0.26$ mm⁻¹, $F(000) = 488$, room temperature, $R = 0.045$ for 650 observed reflections up to $(\sin\theta)/\lambda = 0.5527$ Å⁻¹. The 1,1-dicyanoethylene-2,2-dithiolate ligand (dedt) is planar with symmetry C_s . The structure contains two crystallographically different Na^+ ions at the centres of distorted octahedra, $\text{NaO}_2\text{N}_2\text{S}_2$ and NaO_4NS . The water molecules are involved in two approximately linear O–H...S hydrogen bonds (H...S = 2.25 and 2.50 Å) and one O–H...N hydrogen bond (H...N = 1.94 Å).

Introduction. This study was stimulated by the fact that the polydentate ligand dedt is thought to be a planar delocalized system while the geometry in the solid state is affected by various intermolecular and packing effects. In the series $M(\text{dedt}) \cdot n\text{H}_2\text{O}$ ($M = \text{Ca}, \text{Sr}, n = 5$; $M = \text{Ba}, n = 3$) dedt shows considerable deviations

from planarity (Hummel & Wolf, 1985) while in $\text{K}_2(\text{dedt}) \cdot \text{H}_2\text{O}$ the ligand has approximate C_{2v} symmetry (Hummel, 1985). It might be expected that deviations from planarity of the $(\text{S}_2\text{C}_4\text{N}_2)^{2-}$ anion should increase with decreasing size of the counterion although this trend is not observed in the series of compounds with alkaline-earth cations.

Experimental. Single crystals of $\text{Na}_2(\text{dedt}) \cdot 3\text{H}_2\text{O}$ from ethanol (Söderbäck, 1963). Crystal $0.08 \times 0.08 \times 0.08$ mm. D_m determined pycnometrically. Precession photographs. Monoclinic, Laue class $2/m$, systematic extinctions hkl , $h + k + l = 2n + 1$, space group $I2/m$. PW 1100 four-circle diffractometer, graphite-monochromatized Ag K α radiation, ω scan, scan width $(1.00 + 0.20 \tan\theta)^\circ$. Cell dimensions based on 25 high-indexed diffractometer-measured intensities ($7 \leq \theta \leq 12^\circ$). 2833 symmetry-dependent reflections ($-16 \leq h \leq 16$, $-8 \leq k \leq 8$, $-9 \leq l \leq 9$; $2 \leq \theta \leq 18^\circ$) averaged to give 722 symmetry-independent reflections, $R_{\text{int}} = 0.030$. Three standard reflections, no significant

deviations from their initial intensities. Corrections for Lorentz and polarization effects, no absorption correction applied. Structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971). 650 observed reflections [$I > 1.5\sigma(I)$] in full-matrix least-squares refinement; 86 parameters; H atoms as parts of rigid H_2O molecules with $H \cdots H = 1.560(5)$ and $O-H = 0.960(5)$ Å, and common isotropic temperature factor; $\sum w|F_o| - |F_c|^2$ minimized; $w = 0.1 \times [\sigma^2(F_o) + 7 \times 10^{-4}F_o^2]^{-1}$; *SHELX76* system (Sheldrick, 1976); $(\Delta/\sigma)_{\max} = 0.0091$, $(\Delta/\sigma)_{\min} = 0.001$, $(\Delta/\sigma)_{\text{ave}} = 0.0012$; $\Delta\rho = -0.57$ to $0.36 e \text{ \AA}^{-3}$, correction for empirical isotropic extinction $F^* = F(1 - 3 \times 10^{-8}F^2/$

$\sin\theta)$. Final refinement converged to $R = 0.045$, $wR = 0.043$, $S = 2.1$. Scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1,* and selected distances and angles in Table 2. The structure is depicted in Fig. 1. The dedt ions are situated on the mirror planes with $y = 0, 0.5$ and correspond to approximate C_{2v} symmetry. All observed intramolecular bond lengths clearly reflect the delocalized π system of dedt (Hummel, 1985). The deviation of the angle $C3-C2-C4$ from 120° seems to be caused by repulsive forces of the S atoms and is observed in many other salts of dedt (Hummel & Wolf, 1985). There are two crystallographically different sodium ions in the

Table 1. Final atomic coordinates and equivalent isotropic temperature factors

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j \text{ (average e.s.d.} = 0.005 \text{ \AA}^2\text{)}.$$

Site	symmetry	x	y	z	$U_{eq}(\text{\AA}^2)$
Na1	1	0.25	0.25	0.25	0.035
Na2	m	0.1750(2)	0.0	0.4581(1)	0.038
S1	m	0.3515(2)	0.0	0.6296(1)	0.032
S2	m	0.5118(2)	0.0	0.8155(1)	0.027
C1	m	0.3478(6)	0.0	0.7473(3)	0.021
C2	m	0.2059(6)	0.0	0.7911(3)	0.022
C3	m	0.0648(6)	0.0	0.7422(3)	0.024
C4	m	0.1939(6)	0.0	0.8881(4)	0.025
N3	m	0.9453(5)	0.0	0.7072(3)	0.035
N4	m	0.1778(5)	0.0	0.9667(3)	0.041
O1	1	0.8426(3)	0.2803(4)	0.8995(2)	0.036
O2	2	0.5	0.2772(5)	0.0	0.033
H11	1	0.939(2)	0.341(3)	0.900(2)	
H12	1	0.848(3)	0.184(3)	0.943(2)	
H2	1	0.529(4)	0.204(3)	0.051(1)	

Table 2. Selected distances (Å) and angles ($^\circ$) with e.s.d.'s in parentheses

(a) The Na^+ ions

Na1-S2	2.985 (1) (2 \times)	Na2-S1	2.901 (2)
Na1-O1	2.309 (3) (2 \times)	Na2-O2	2.367 (3) (2 \times)
Na1-N3	2.634 (3) (2 \times)	Na2-O1	2.386 (3) (2 \times)
		Na2-N3	2.598 (5)

O1-O1'	3.334 (4) ⁱⁱ
O1-O1''	4.254 (4) ⁱ

(b) The dedt ion

S1...S2	3.013 (2)	S1-C1-S2	122.8 (3)
S1-C1	1.705 (5)	S1-C1-C2	118.9 (4)
S2-C1	1.728 (5)	S2-C1-C2	118.3 (3)
C1-C2	1.404 (7)	C1-C2-C3	123.1 (4)
C2-C3	1.412 (7)	C1-C2-C4	122.1 (5)
C2-C4	1.410 (7)	C3-C2-C4	114.8 (4)
C3-N3	1.155 (7)	C2-C3-N3	176.1 (5)
C4-N4	1.149 (7)	C2-C4-N4	177.2 (6)

(c) The hydrogen bonds

O1-N4	2.885 (4)	H12-N4	1.94 (2)
O1-S1	3.188 (3)	H11-S1	2.25 (2) (2 \times)
		O1-H12-N4	170 (2)
		O1-H11-S1	167 (3)
		H11-S1-H11'	65.1 (7) ⁱ
		H12-N4-H12'	93 (1) ⁱ
O2-S2	3.403 (3)	H2-S2	2.50 (2) (2 \times)
		O2-H2-S2	156 (3)
		H2-S2-H2'	76.3 (7) ⁱ

Symmetry code: (i) x, y, z ; $x, -y, z$; (ii) x, y, z ; $x, 1-y, z$.

* Lists of structure factors, anisotropic thermal parameters and intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43301 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

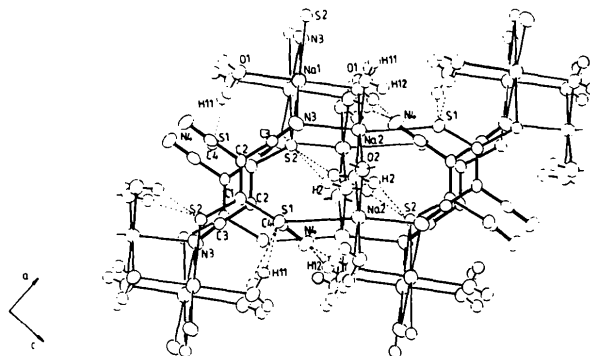


Fig. 1. A projection of $Na_2S_2C_4N_2 \cdot 3H_2O$ on the ac plane. The dedt anions are situated on mirror planes with $y = 0.0$ and 0.5 .

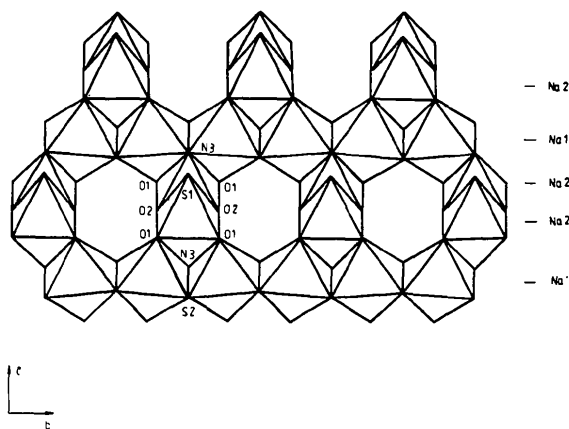


Fig. 2. The polyhedron layer in $Na_2(\text{dedt}) \cdot 3H_2O$.

structure; Na1 with site symmetry $\bar{1}$ and Na2 on *m*. Na1 is surrounded by two S, two N and two water O atoms forming a distorted octahedron. These polyhedra share edges N3–S2 forming chains $\infty[\text{NaO}_2\text{N}_{2/2}\text{S}_{2/2}]$ parallel to [010]. Each dedt links two different chains *via* the *trans*-positioned S2 and N3 atoms. Na2 coordinates four water O atoms ($2 \times \text{O1}$, $2 \times \text{O2}$), one S1 and one N3 atom. Na2 polyhedra form pairs by edge-sharing [O(2)–O(2)] and these pairs are connected with the Na1 octahedra *via* common O1 and N3 atoms (Fig. 2).

As a result, short and long O1–O1 distances alternate along [010]. The Na–O and Na–N distances correspond to usually observed bond lengths (Colapietro, Domenicano & Vaciago, 1968). A sodium–sulfur coordination is mainly found in inorganic compounds with Na–S distances in the range 2.8–3.1 Å (Mereiter, Preisinger & Guth, 1979).

There are two crystallographically different water molecules (site symmetries 1 and 2) interspersed between the layers of dedt ions which build up a symmetric set of hydrogen bonds with respect to the mirror planes. The molecule H₂O(1) connects two dedt ions in $y = 0$ and $y = 0.5$ *via* an unusually short S...H contact (S1...H11 = 2.25 Å) and an N–H hydrogen bridge (N4...H12 = 1.94 Å), while H₂O(2) is associated with two anions within the same layer ($y = 0$ or 0.5) *via* H2...S2 contacts with H...S = 2.50 Å. The distances O...X (X = S2, N4) are in the range given by Kuleshova & Zorkii (1981) and Chiari & Ferraris (1982) while the O1...S1 distance is at the low end of usually observed values (3.23–3.31 Å).

It is expected that hydrogen bonds as well as the charge and size of a metal cation in the salts of dedt (Table 3) will lead to deviations from planarity of the ligand. Nevertheless no systematic trend within the

Table 3. *Maximum deviations from planarity of dedt in some ionic compounds (Å)*

Compound	Δ	Reference
Ba(dedt).3H ₂ O	0.10	Hummel & Wolf (1985)
Sr(dedt).5H ₂ O	0.04	Hummel & Wolf (1986)
Ca(dedt).5H ₂ O	0.10	Wolf & Hummel (1985)
K ₂ (dedt).H ₂ O	0.03	Hummel (1985)

known compounds is observed. Although the metal cation in the present species is small ($r_{\text{Na}^+} = 0.97$, $r_{\text{Ba}^{2+}} = 1.34$ Å; Shannon & Prewitt, 1969), dedt is situated on a mirror plane and forms an effective and symmetric set of hydrogen bonds.

References

- CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* B38, 2331–2341.
 COLAPIETRO, M., DOMENICANO, A. & VACIAGO, A. (1968). *J. Chem. Soc. Chem. Commun.* pp. 572–573.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
 HUMMEL, H. U. (1985). *Acta Cryst.* C41, 1591–1592.
 HUMMEL, H. U. & WOLF, C. (1985). *Z. Naturforsch. Teil B*, 40, 1638–1643.
 HUMMEL, H. U. & WOLF, C. (1986). *Z. Naturforsch.* In the press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KULESHOVA, L. N. & ZORKII, P. M. (1981). *Acta Cryst.* B37, 1363–1366.
 MEREITER, K., PREISINGER, A. & GUTH, H. (1979). *Acta Cryst.* B35, 19–25.
 SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B25, 925–946.
 SHELDRIK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
 SÖDERBÄCK, E. (1963). *Acta Chem. Scand.* 17, 362–376.
 WOLF, C. & HUMMEL, H. U. (1985). *J. Chem. Soc. Dalton Trans.* pp. 43–45.

Acta Cryst. (1987). C43, 43–46

Di- μ -hydroxo-[tetrakis(tetrahydrothiophene 1-oxide)]diplatinum(II) Nitrate

BY F. D. ROCHON AND FRANCE GUAY

Département de chimie, Université du Québec à Montréal, CP 8888, succ. A, Montréal, Canada H3C 3P8

(Received 19 August 1985; accepted 5 August 1986)

Abstract. $[\text{Pt}_2(\text{OH})_2(\text{C}_4\text{H}_8\text{OS})_4](\text{NO}_3)_2$, $M_r = 964.82$, triclinic, $P\bar{1}$, $a = 6.036$ (2), $b = 10.848$ (5), $c = 11.737$ (10) Å, $\alpha = 69.97$ (6), $\beta = 75.63$ (5), $\gamma = 80.30$ (3)°, $V = 696.4$ (8) Å³, $Z = 1$, $D_x = 2.300$, $D_m = 2.29$ (2) Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 10.479$ mm⁻¹, $F(000) = 460$, $T = 295$ K,

$R = 0.043$, and $wR = 0.041$ for 3044 unique observed reflections. The hydroxo-bridged dimer has a center of symmetry. The coordination around the Pt^{II} atom is square-planar. The Pt–S bond distances are 2.203 (2) and 2.209 (2) Å and the Pt–O distances are 2.045 (5) and 2.050 (5) Å. The Pt–O–Pt' angle is 100.0 (3)°