

Cingi, Guastini, Musatti & Nardelli, 1969) and tris-(thiourea)copper(I) hydrogen *o*-phthalate (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1977b) where the slight rotation of the carboxylic and carboxylate groups on opposite sides by nearly the same angles is determined by a strong intramolecular hydrogen bond.

The chains of the Hpht anion, held together by van der Waals contacts, are arranged through the screw axes at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ in slices parallel to (001) (Fig. 2). K^+ ions, octahedral hexaaquanickel cations and water molecules interpose between these slices linked through $K \cdots O$ interactions and hydrogen bonds that the O atoms of Hpht ions, from different slices, form with the free and Ni-coordinated water molecules.

The authors are indebted to the CNR for financial support.

References

ADIWIDJAJA, G. & KÜPPERS, H. (1976). *Acta Cryst.* B32, 1571–1574.

Acta Cryst. (1984). C40, 58–60

Calcium Naphthionate Octahydrate, $Ca^{2+} \cdot 2C_{10}H_8NO_3S^- \cdot 8H_2O^*$

BY C. J. BROWN, M. EHRENBURG AND H. R. YADAV

Department of Metallurgy and Materials Engineering, City of London Polytechnic, Central House, Whitechapel High Street, London E1 7PF, England

(Received 7 February 1983; accepted 14 September 1983)

Abstract. $M_r = 628.7$, monoclinic, $P2_1/n$, $a = 23.605$ (16), $b = 11.931$ (9), $c = 9.708$ (10) Å, $\beta = 94.0$ (1)°, $V = 2727.42$ Å³, $Z = 4$, $D_m = 1.528$ (1), $D_x = 1.53$ Mg m⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 3.9$ mm⁻¹, $F(000) = 1320$, $R = 0.029$ for 4467 observed reflexions [$I > 3\sigma(I)$]. The Ca^{2+} ion is seven coordinated to water oxygens which are hydrogen bonded to sulphonate oxygens and amino nitrogens. All the bond lengths and inter-bond angles have standard values and there are no geometric peculiarities.

Introduction. The title compound is the neutral calcium salt of naphthionic acid. The crystal structure determination was undertaken because of the similarity of the unit-cell dimensions to those of the sodium salt (Corbridge, Brown & Wallwork, 1966), *i.e.* $a = 11.613$, $b = 12.053$, $c = 10.045$ Å, $\beta = 98.8^\circ$, $P2_1/c$. Comparison

* Calcium 4-amino-1-naphthalenesulphonate octahydrate. (Note that the atomic numbering used throughout corresponds to the alternative description 1-amino-4-naphthalenesulphonate octahydrate.)

ADIWIDJAJA, G., ROSSMANITH, E. & KÜPPERS, H. (1978). *Acta Cryst.* B34, 3079–3083.

BATS, J. W., SCHUCKMANN, W. & FUESS, H. (1978). *Acta Cryst.* B34, 2627–2628.

BIAGINI CINGI, M., GUASTINI, C., MUSATTI, A. & NARDELLI, M. (1969). *Acta Cryst.* B25, 1833–1840.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1977a). *Acta Cryst.* B33, 659–664.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1977b). *Acta Cryst.* B33, 3772–3777.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978a). *Acta Cryst.* B34, 134–137.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978b). *Acta Cryst.* B34, 406–411.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978c). *Acta Cryst.* B34, 412–416.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978d). *Acta Cryst.* B34, 774–778.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1979). *Acta Cryst.* B35, 312–316.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1981). *Acta Cryst.* B37, 2159–2163.

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

SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

of one unit cell of the Ca salt with two of the Na salt shows that for every two Na^+ ions there is only one Ca^{2+} ion, and there was some speculation concerning the environment of the supposedly vacant site. It was thought that the situation might be similar to that found in the structures of lithium and magnesium perchlorates (West, 1934, 1935).

Experimental. Crystals by slow evaporation of a solution of naphthionic acid in 1% calcium hydroxide, equi-dimensional crystals *ca* 0.3 mm, density by flotation in a mixture of organic liquids; accurate lattice parameters by least-squares analysis of the a_1a_2 separations of 75 reflexions taken about **b** and **c** in a 57.3 mm radius camera; $h0l$ absent for $(h+l)$ odd, $0k0$ absent for k odd; intensities by visual estimation, $h0l-h, 12, l$ and $hk0$ on Weissenberg photographs using multiple-film packs, index range h 0–30, k 0–14, $l \pm 12$; no absorption correction, empirical modifications for secondary extinction during refinement for a small number of very intense reflexions; structure solved by

application of Σ_2 relationships in a symbolic addition procedure using computer programs of Ahmed, Hall, Pippy & Huber (1970) implemented on the ICL 1905E computer at the London Polytechnics Computer Unit; three-dimensional E map (Fig. 1) using 794 coefficients ($E \geq 1.5$) clearly indicated the 39 non-H atoms; least-squares refinement based on F , introducing anisotropic thermal parameters and H atoms at appropriate stages, H coordinates calculated either with respect to the naphthalene ring or on the direct line between O or N atoms of the obvious hydrogen bonds; H parameters, including $B_{\text{iso}} = 5.0 \text{ \AA}^2$, not refined; 1149 reflexions had zero or very low intensities, these all had $F_{\text{calc}} < 5.0$; during last cycle of refinement $\Delta < 0.1\sigma$; max. $\Delta\rho$ excursions $\pm 0.1 \text{ e \AA}^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1962); $R = 0.029$, $wR = 0.041$, $w = 1/F_o^2$.

Discussion. The atomic coordinates and isotropic temperature factors are given in Table 1,* and the bond lengths and inter-bond angles in Table 2.

The calcium coordination is sevenfold, the O atoms forming a pentagonal bipyramid with a mean Ca—O distance of 2.411 \AA (*cf.* mean Na—O in Na salt = 2.424 \AA). The coordination of Ca^{2+} may be six, seven or eight with perhaps a preference for eight, especially when hydrated. There are, however, a number of structures where there is sevenfold coordination, with Ca—O between 2.35 and 2.45 \AA , and the O atoms lying at the apices of a pentagonal bipyramid which can distort to a greater or lesser extent (Thompson & Bartell, 1968) with very little energy difference. Comparable structures with Ca^{2+} coordinated sevenfold include CaHPO_4 (MacLennan & Beevers, 1955), $\text{Ca}_4(\text{PO}_4)_2\text{O}$ (Dickens, Brown, Kruger & Stewart, 1973), $\text{CaPO}_3\text{F}\cdot 2\text{H}_2\text{O}$ (Perloff, 1972), $\text{CaHAsO}_4\cdot 2\text{H}_2\text{O}$ (Ferraris, 1969), $\text{CaBr}_2\cdot\beta\text{-D-fructose}\cdot 2\text{H}_2\text{O}$ (Cook & Bugg, 1976), Ca thymidylate (Trueblood, Horn & Luzzati, 1961), $\text{CaCr}_2\text{O}_7\cdot\text{bis}(\text{hexamethylenetetramine})\cdot 7\text{H}_2\text{O}$ (Dahan, 1975), Ca 1-naphthylphosphate. $3\text{H}_2\text{O}$ (Li & Caughlan, 1965) and Ca (*trans*-1,2-cyclohexanediyldinitrilotetraacetato)-aquaferate(III). $8\text{H}_2\text{O}$ (Cohen & Hoard, 1966).

In the naphthalene rings, the C—C distances are not equal, but follow the pattern of naphthalene (Cruickshank, 1957) in which four of the C—C bonds are ~ 1.36 and the other seven are $\sim 1.42 \text{ \AA}$. These agree also with the values found in the Na salt (Brown & Corbridge, 1966). The naphthalene rings are effectively planar, the greatest deviation from the mean planes being $0.040 (4) \text{ \AA}$; for C(1) to C(10) the mean

out-of-plane distance of the C atoms is $0.021 (4) \text{ \AA}$, and for C(11) to C(20) it is $0.013 (4) \text{ \AA}$.* The dihedral angle between the mean planes through the two rings is $16.43 (5)^\circ$.

* Details of mean-plane calculations have been deposited. See deposition footnote.

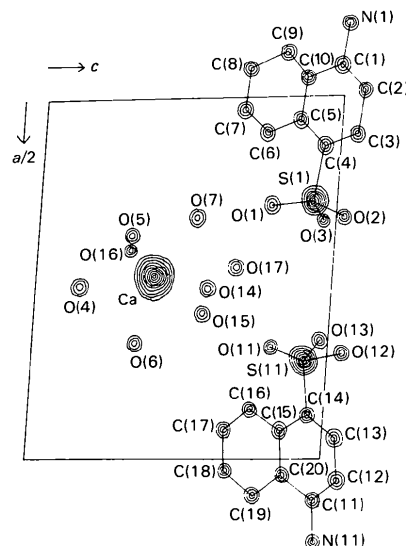


Fig. 1. Superposed sections of the three-dimensional E map, showing the oxygen atoms of the eight water molecules disposed around the Ca^{2+} ion and the numbering of the atoms.

Table 1. Final atomic parameters and *e.s.d.*'s

	x	y	z	$B_{\text{eq}}^\dagger (\text{\AA}^2)$
Ca(1)	0.25135 (1)	0.09974 (4)	0.40147 (4)	2.88 (1)
C(1)	-0.0444 (1)	0.1610 (2)	0.9912 (2)	3.21 (3)
C(2)	-0.0067 (1)	0.2281 (2)	1.0680 (2)	3.35 (3)
C(3)	0.0510 (1)	0.2319 (2)	1.0406 (2)	3.51 (3)
C(4)	0.0709 (1)	0.1683 (2)	0.9365 (2)	2.81 (3)
C(5)	0.0344 (1)	0.0971 (2)	0.8554 (2)	2.80 (3)
C(6)	0.0530 (1)	0.0294 (2)	0.7494 (2)	3.16 (3)
C(7)	0.0142 (1)	-0.0345 (2)	0.6692 (2)	3.86 (4)
C(8)	-0.0436 (1)	-0.0334 (2)	0.6934 (2)	3.85 (4)
C(9)	-0.0628 (1)	0.0303 (2)	0.7967 (2)	3.72 (4)
C(10)	-0.0251 (1)	0.0990 (2)	0.8805 (2)	2.67 (3)
C(11)	0.5586 (1)	0.1473 (2)	0.9760 (2)	3.02 (3)
C(12)	0.5335 (1)	0.2177 (2)	1.0631 (2)	3.52 (3)
C(13)	0.4749 (1)	0.2368 (2)	1.0511 (2)	3.00 (3)
C(14)	0.4409 (1)	0.1851 (2)	0.9511 (2)	2.91 (3)
C(15)	0.4654 (1)	0.1075 (2)	0.8578 (2)	2.54 (3)
C(16)	0.4323 (1)	0.0478 (2)	0.7550 (2)	3.40 (3)
C(17)	0.4570 (1)	-0.0235 (2)	0.6662 (2)	4.25 (4)
C(18)	0.5168 (1)	-0.0393 (2)	0.6782 (2)	4.52 (4)
C(19)	0.5496 (1)	0.0162 (2)	0.7744 (2)	3.52 (4)
C(20)	0.5253 (1)	0.0908 (2)	0.8707 (2)	3.16 (3)
O(1)	0.1518 (1)	0.2041 (2)	0.7722 (2)	4.48 (3)
O(2)	0.1679 (1)	0.2577 (2)	1.0118 (2)	4.10 (3)
O(3)	0.1672 (1)	0.0609 (2)	0.9459 (2)	4.17 (3)
O(4)	0.2585 (1)	0.0783 (2)	1.1549 (2)	4.86 (3)
O(5)	0.1920 (1)	0.2488 (2)	0.3068 (2)	5.36 (3)
O(6)	0.3385 (1)	0.1877 (2)	0.3420 (2)	5.42 (3)
O(7)	0.1735 (1)	0.0562 (2)	0.5402 (2)	6.06 (4)
O(11)	0.3539 (1)	0.2530 (2)	0.8003 (2)	5.53 (3)
O(12)	0.3597 (1)	0.2998 (2)	1.0419 (2)	7.84 (4)
O(13)	0.3387 (1)	0.1123 (2)	0.9702 (2)	5.28 (3)
O(14)	0.2653 (1)	0.2305 (2)	0.5903 (2)	5.17 (3)
O(15)	0.3027 (1)	-0.0218 (2)	0.5587 (2)	5.03 (3)
O(16)	0.2148 (1)	0.0807 (2)	0.3184 (2)	6.08 (4)
O(17)	0.2352 (1)	0.4648 (2)	0.6729 (2)	6.11 (4)
N(1)	0.1014 (1)	0.1612 (2)	1.0195 (2)	4.00 (3)
N(11)	0.6180 (1)	0.1315 (2)	0.9889 (2)	3.87 (3)
S(1)	0.14455 (2)	0.17365 (5)	0.91364 (5)	3.00 (1)
S(11)	0.36828 (2)	0.21722 (5)	0.93898 (5)	3.47 (1)

$$\dagger B_{\text{eq}} = \frac{4}{3}(\beta_{11}/a^2 + \beta_{22}/b^2 + \beta_{33}/c^2).$$

* Lists of structure factors, anisotropic temperature factors, calculated H-atom coordinates, hydrogen-bond distances and least-squares planes data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38870 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°)

Ca—O(4)	2.425 (2)	C(12)—C(13)	1.399 (3)
Ca—O(5)	2.406 (2)	C(13)—C(14)	1.363 (3)
Ca—O(6)	2.415 (2)	C(14)—C(15)	1.444 (3)
Ca—O(7)	2.410 (2)	C(15)—C(16)	1.416 (3)
Ca—O(14)	2.412 (2)	C(15)—C(20)	1.425 (2)
Ca—O(15)	2.375 (2)	C(16)—C(17)	1.370 (3)
Ca—O(16)	2.435 (2)	C(17)—C(18)	1.419 (4)
C(1)—C(2)	1.377 (3)	C(18)—C(19)	1.345 (3)
C(1)—C(10)	1.406 (3)	C(19)—C(20)	1.438 (3)
C(2)—C(3)	1.406 (3)	C(1)—N(1)	1.393 (2)
C(3)—C(4)	1.373 (3)	C(11)—N(11)	1.413 (2)
C(4)—C(5)	1.410 (3)	C(4)—S(1)	1.769 (2)
C(5)—C(6)	1.402 (3)	C(14)—S(11)	1.752 (2)
C(5)—C(10)	1.443 (2)	S(1)—O(1)	1.442 (2)
C(6)—C(7)	1.389 (3)	S(1)—O(2)	1.464 (2)
C(7)—C(8)	1.402 (3)	S(1)—O(3)	1.473 (2)
C(8)—C(9)	1.361 (3)	S(11)—O(11)	1.430 (2)
C(9)—C(10)	1.423 (3)	S(11)—O(12)	1.428 (3)
C(11)—C(12)	1.357 (3)	S(11)—O(13)	1.475 (2)
C(11)—C(20)	1.416 (3)		
C(2)—C(1)—C(10)	119.2 (2)	C(13)—C(14)—S(11)	118.2 (1)
C(2)—C(1)—N(1)	119.3 (2)	C(15)—C(14)—S(11)	122.1 (1)
C(10)—C(1)—N(1)	121.3 (2)	C(14)—C(15)—C(16)	122.7 (2)
C(1)—C(2)—C(3)	120.9 (2)	C(14)—C(15)—C(20)	118.2 (2)
C(2)—C(3)—C(4)	120.5 (2)	C(16)—C(15)—C(20)	119.1 (2)
C(3)—C(4)—C(5)	121.1 (2)	C(15)—C(16)—C(17)	121.2 (2)
C(3)—C(4)—S(1)	117.6 (1)	C(16)—C(17)—C(18)	119.6 (2)
C(5)—C(4)—S(1)	121.3 (1)	C(17)—C(18)—C(19)	120.8 (2)
C(4)—C(5)—C(6)	123.0 (2)	C(18)—C(19)—C(20)	121.3 (2)
C(4)—C(5)—C(10)	117.4 (2)	C(11)—C(20)—C(15)	119.6 (2)
C(6)—C(5)—C(10)	119.5 (2)	C(11)—C(20)—C(19)	122.5 (2)
C(5)—C(6)—C(7)	120.0 (2)	C(15)—C(20)—C(19)	117.9 (2)
C(6)—C(7)—C(8)	120.9 (2)	C(4)—S(1)—O(1)	108.2 (1)
C(7)—C(8)—C(9)	120.5 (2)	C(4)—S(1)—O(2)	105.8 (1)
C(8)—C(9)—C(10)	121.1 (2)	C(4)—S(1)—O(3)	106.6 (1)
C(1)—C(10)—C(5)	120.5 (2)	O(1)—S(1)—O(2)	112.5 (1)
C(1)—C(10)—C(9)	121.2 (2)	O(1)—S(1)—O(3)	111.6 (1)
C(5)—C(10)—C(9)	118.2 (2)	O(2)—S(1)—O(3)	111.8 (1)
C(12)—C(11)—C(20)	120.0 (2)	C(14)—S(11)—O(11)	107.2 (1)
C(12)—C(11)—N(11)	120.1 (2)	C(14)—S(11)—O(12)	106.8 (2)
C(20)—C(11)—N(11)	119.9 (2)	C(14)—S(11)—O(13)	106.0 (1)
C(11)—C(12)—C(13)	121.4 (2)	O(11)—S(11)—O(12)	114.6 (1)
C(12)—C(13)—C(14)	121.0 (2)	O(11)—S(11)—O(13)	111.3 (1)
C(13)—C(14)—C(15)	119.7 (2)	O(12)—S(11)—O(13)	110.5 (1)

There are 19 hydrogen bonds per asymmetric unit, three originating from the amino groups with a mean N(H)···O length of 3.121 (5) Å, and sixteen originating at the water oxygens with a mean O(H)···O length of 2.838 (4) and O(H)···N length of 2.874 (4) Å. All the other bond lengths in the molecule have standard values.

There is a vacant site in the structure, which, taken along with the Ca²⁺ ion, corresponds to the two Na⁺ ions in a double-size unit cell. This vacant site is surrounded by six O atoms, O(1), O(2), O(11), O(14),

O(15') (screw-axis related) and O(17), which form a distorted octahedron. The centre of this is near (0.249, 0.302, 0.845) and the distances between this point and the O atoms lie between 2.59 and 2.67 Å. This polyhedron shares two of its corners with the neighbouring Ca coordinated polyhedra. The radius of this polyhedron is greater than the radii of either the Na or the Ca polyhedra presumably because of its neutral state.

The pentagonal bipyramid around the Ca²⁺ ion is disposed so that O(5) and O(15) lie at the apices, with the angle O(5)—Ca—O(15) 162.6 (1)°. The equatorial atoms are O(4), O(6), O(14), O(7) and O(16), subtending angles at Ca of, in order, 72.0 (1), 80.0 (1), 77.5 (1), 74.2 (1) and 68.1 (1)°, total 371.8° compared with 360° to be expected if these five atoms were exactly co-planar. The eighth water oxygen O(17), is 5.18 Å from Ca, outside the sphere of coordination.

References

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1970). NRC crystallographic programs for the IBM-360 system. National Research Council, Ottawa, Canada.
- BROWN, C. J. & CORBRIDGE, D. E. C. (1966). *Acta Cryst.* **21**, 485–494.
- COHEN, G. H. & HOARD, J. L. (1966). *J. Am. Chem. Soc.* **88**, 3228–3234.
- COOK, W. J. & BUGG, C. E. (1976). *Acta Cryst.* **B32**, 656–659.
- CORBRIDGE, D. E. C., BROWN, C. J. & WALLWORK, S. C. (1966). *Acta Cryst.* **20**, 698–699.
- CRUICKSHANK, D. W. J. (1957). *Acta Cryst.* **10**, 504–508.
- DAHAN, F. (1975). *Acta Cryst.* **B31**, 423–426.
- DICKENS, B., BROWN, W. E., KRUGER, G. J. & STEWART, J. M. (1973). *Acta Cryst.* **B29**, 2046–2056.
- FERRARIS, G. (1969). *Acta Cryst.* **B25**, 1544–1550.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.
- LI, C. T. & CAUGHLAN, C. N. (1965). *Acta Cryst.* **19**, 637–645.
- MACLENNAN, G. & BEEVERS, C. A. (1955). *Acta Cryst.* **8**, 579–583.
- PERLOFF, A. (1972). *Acta Cryst.* **B28**, 2183–2191.
- THOMPSON, H. B. & BARTELL, L. S. (1968). *Inorg. Chem.* **7**, 488–491.
- TRUEBLOOD, K. N., HORN, P. & LUZZATI, V. (1961). *Acta Cryst.* **14**, 965–982.
- WEST, C. D. (1934). *Z. Kristallogr. Teil A*, **88**, 198–204.
- WEST, C. D. (1935). *Z. Kristallogr. Teil A*, **91**, 480–493.

Acta Cryst. (1984). **C40**, 60–62

The Structure of (2,2'-Bipyridine)dichlorozinc(II), Zn(C₁₀H₈N₂)Cl₂

BY MASOOD A. KHAN AND DENNIS G. TUCK

Department of Chemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

(Received 5 April 1983; accepted 2 September 1983)

Abstract. $M_r = 292.5$, triclinic, $P\bar{1}$, $a = 8.922$ (1), $b = 9.054$ (1), $c = 7.587$ (1) Å, $\alpha = 93.94$ (1), $\beta = 94.61$ (1), $\gamma = 111.30$ (1)°, $V = 566.1$ (1) Å³, $Z = 2$,

$D_m = 1.70$ (1), $D_x = 1.716$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 2.50$ mm⁻¹, $F(000) = 292$, 292 K, $R = 0.0274$, $R_{wF} = 0.0305$ for 1643 unique observed

0108-2701/84/010060-03\$01.50

© 1984 International Union of Crystallography