Table 2. *Selected bond lengths* (Å) *and angles* (°) *for copper*(II) *chloranilate trihydrate*

E.s.d.'s are given in parentheses.

Cu—O(1)	1.966 (4)	O(1)—Cu—O(2)	78.1 (2)
Cu—O(2)	2.265 (4)	O(1)—Cu—O(3)	179.2 (2)
Cu—O(3)	1.965 (5)	O(1)—Cu—O(4)	102.1 (2)
Cu—O(4)	2.252 (4)	O(1)—Cu—O(5)	91.5 (2)
Cu—O(5)	1.996 (4)	O(1)—Cu—O(6)	88.8 (2)
Cu—O(6)	2.015 (5)	O(2)—Cu—O(3)	101.7 (2)
O(1)—C(1)	1.280 (7)	O(2)—Cu—O(4)	178.9 (2)
O(2)—C(2)	1.241 (8)	O(2)—Cu—O(5)	89.9 (2)
O(3)—C(4)	1.287 (7)	O(2)—Cu—O(6)	87.5 (2)
O(4)—C(5)	1.254 (8)	O(3)—Cu—O(4)	78.1 (2)
$O(7^{iv})$—O(2)	2.931 (7)	O(3)—Cu—O(5)	87.7 (2)
$O(7^{iv})$—O(3)	2.824 (6)	O(3)—Cu—O(6)	92.0 (2)
$O(7^{iv})$—$O(5^{i})$	2.866 (8)	O(4)—Cu—O(5)	91.4 (2)
$O(7^{iv})$—$O(6^{iii})$	2.931 (7)	O(4)—Cu—O(6)	91.2 (2)
		O(5)—Cu—O(6)	177.2 (2)

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

being equal in respect to their affinity to the Cu atom (*cf.* Table 2).

The shortest Cu—Cu distance along the polychelate chains is equal to the unit-cell constant *b*. A shorter distance, 4.991 (2) Å, is found between Cu^{i} and Cu^{iv} across the centre of the *xy* plane. The structure contains one non-coordinated water molecule per Cu atom, O(7), which deviates no more than 0.17 (6) Å from the polychelate layer. $O(7^{iv})$ is almost centred between O(2), O(3), $O(5^{i})$ and $O(6^{iii})$ (*cf.* Table 2). Moreover, there is a slight inclination of O(5) and O(6) towards the next positioned free water molecule. This indicates a possible network of interchain hydrogen bonds (dotted lines in Figs. 1 and 2), similar to the structure of copper squarate dihydrate cited above. Since the crystal structure collapses when the crystals are dried under vacuum at room temperature the presence of non-coordinated water is essential for its stability.

We gratefully thank Mr Th. Müller and Mr M. Pirotta (ETH Zürich) for their experimental assistance. This work was supported by 'Schweizerischer Nationalfonds zur Förderung wissenschaftlicher Forschung' under grant No. 2000-5.478.

References

Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
Cueto, S., Gramlich, V., Petter, W., Rys, F. S. & Rys, P. (1991). *Acta Cryst.* **C47**, 75–78.
Hall, S. R. & Stewart, J. M. (1989). *XTAL 2.6 User's Manual.* Univs. of Western Australia, Australia, and Maryland, USA.
Kanda, S. (1963). *Kogyo Kagaku Zasshi*, **66**, 641–642 [*Chem. Abstr.* (1964), **60**, 3109g].
Kobayashi, H., Haseda, T., Kanda, E. & Kanda, S. (1963). *J. Phys. Soc. Jpn*, **18**, 349–356.
Pierpont, C. G., Francesconi, L. C. & Hendrickson, D. N. (1977). *Inorg. Chem.* **16**, 2367–2376.
Robl, C. (1987*a*). *Z. Naturforsch. Teil B*, **42**, 972–976.
Robl, C. (1987*b*). *Mater. Res. Bull.* **22**, 1483–1491.
Robl, C. & Sheldrick, G. M. (1988). *Z. Naturforsch. Tiel B*, **43**, 733–738.
Robl, C. & Weiss, A. (1986*a*). *Z. Naturforsch. Teil B*, **41**, 1337–1340.
Robl, C. & Weiss, A. (1986*b*). *Z. Naturforsch. Teil B*, **41**, 1341–1345.
Stoe Corporation (1987). *DIF4. Stoe4-Diffractometer Control Program.* Version 7. Stoe, Darmstadt, Germany.
Tinti, F., Verdaguer, M., Kahn, O. & Savariault, J.-M. (1987). *Inorg Chem.* **26**, 2380–2384.
Verdaguer, M., Michalowicz, A., Girerd, J. J., Alberding, N. & Kahn, O. (1980). *Inorg. Chem.* **19**, 3271–3279.
Weiss, A., Riegler, E. & Robl, C. (1986). *Z. Naturforsch. Teil B*, **41**, 1501–1505.

Acta Cryst. (1992). **C48**, 460–465

Structure of the Sodium Salt of 1,4,5,8-Naphthalenetetracarboxylic Acid 4,5-Anhydride Hydrate

By Lawrence J. Fitzgerald, Judith C. Gallucci and Roger E. Gerkin*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, *USA*

(*Received* 17 *June* 1991; *accepted* 17 *September* 1991)

Abstract. Sodium hydrogen 1,3-dioxo-1*H*,3*H*-naphtho[1,8-*cd*]pyran-6,7-dicarboxylate hydrate, $Na[C_{14}H_5O_7].H_2O$, $M_r = 326.2$, triclinic, $P\bar{1}$, $a = 9.520$ (2), $b = 9.549$ (3), $c = 7.860$ (1) Å, $\alpha = 105.88$ (2), $\beta = 110.29$ (1), $\gamma = 100.89$ (2)°, $V = 611.9$ (3) Å^3, $Z = 2$, $D_x = 1.77$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0.71073 Å, $\mu = 1.67$ cm^{-1}, $F(000) = 332$, $T = 295$ K, $R = 0.042$ for 1665 unique reflections having $I > 3\sigma_I$. The organic portion of this structure demonstrates near-*C*2 symmetry with a pseudo-twofold axis coincident with the central C—C naphthalene ring bond. The atoms of the naphthopyran three-ring

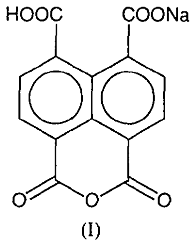
---

* To whom correspondence should be addressed.

0108-2701/92/030460-06$03.00 © 1992 International Union of Crystallography

system deviate by an average of 0.037 (19) Å from the best least-squares plane through the three rings. Each of the carboxyl group planes is substantially inclined to the naphthopyran ring plane, the average dihedral angle measuring 62 (1)°. The Na ion is coordinated by O atoms in a highly distorted octahedral geometry with a mean Na—O distance of 2.49 (12) Å. A short hydrogen bond is formed between a carboxylic acid group and a carboxylate anion; the H···O(acceptor) distance is 1.35 (5) Å and the O···O(acceptor) distance is 2.475 (3) Å. The acid H-atom position is located asymmetrically with respect to the O atoms. The water H atoms are involved in unequal three-centered hydrogen bonds. The molecules are stacked such that the naphthopyran ring portion of the structure is nearly parallel to the *ab* cell face and the stacks are connected by the hydrogen bonds. Inversion centers along the *c* axis relate pairs of coordinated Na ions which lie near this axis. Hydrogen bonding between the carboxylic acid groups occurs perpendicular to the *z* direction and separates from each other the pairs of Na ions created by coordination and related by the inversion centers.

Introduction. Organic acids and their hydrated salts present opportunities to examine a variety of hydrogen-bonding patterns in the organic solid state. The structures of crystalline 1,8-naphthalenedicarboxylic acid (Fitzgerald, Gallucci & Gerkin, 1991*a*) and tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate (Fitzgerald, Gallucci & Gerkin, 1991*b*) have previously been reported. We report here an investigation of the crystalline sodium salt of 1,4,5,8-naphthalenetetracarboxylic acid 4,5-anhydride hydrate (I), a compound closely related to tetrasodium 1,4,5,8-naphthalenetetracarboxylate, which exhibits very short asymmetric hydrogen bonds atypical of acid salts of carboxylic acids. This structure has not previously been described.



(I)

Experimental. Sodium salt of 1,4,5,8-naphthalenetetracarboxylic acid 4,5-anhydride hydrate was produced as a side-product in the purification of 1,4,5,8-naphthalenetetracarboxylic acid. The tetra acid, obtained from Aldrich Chemical Company, was suspended in water and reacted with excess analytical reagent grade NaOH to prepare an aqueous solution of tetrasodium 1,4,5,8-naphthalenetetracarboxylate. The solution was mixed with Norit-A decolorizing carbon and was subsequently filtered. Addition of concentrated HNO_3 then generated a white precipitate which was separated by filtration, rinsed with distilled water and dried in a desiccator. This solid was dissolved in 1/1 acetone/water and the solution was slowly evaporated at room temperature with the production of two crystalline forms. The most abundant crystals (presumably the tetra acid) were colorless thin needles unsuitable for X-ray data collection; the less abundant (title compound) crystals were pale yellow rectangular plates.* The sample used for data collection was a clear rectangular plate having approximate principal dimensions 0.35 × 0.35 × 0.11 mm. This was mounted on a glass rod with epoxy cement. Diffraction data were collected at room temperature with a Rigaku AFC5S diffractometer utilizing graphite-monochromated Mo $K\bar{\alpha}$ radiation.

The crystal system was found to be triclinic. Unit-cell parameters were obtained from a least-squares fit of the setting angles for 25 centered reflections with $28 < 2\theta < 30°$. Intensity data were measured for 2980 reflections (exclusive of standards) with $+h$, $\pm k$, $\pm l$ indices ($h_{\max} = 12$; $k = -12$ to $+12$; $l = -10$ to $+10$) and 2θ values in the range $4 < 2\theta < 55°$. The ω–2θ scan technique was employed with scan widths $(1.15 + 0.35\tan\theta)°$ in ω, and a background/scan time-ratio of 0.5. A variance was assigned to each reflection by means of the formula $\sigma_I^2 = \sigma_{\rm cs}^2(I) + (0.03I)^2$ where $\sigma_{\rm cs}$ is based on counting statistics and I is the integrated intensity. Six standard reflections ($10\bar{1}$, $1\bar{1}2$, $2\bar{2}\bar{1}$, $33\bar{3}$, $5\bar{2}2$, $4\bar{5}2$) were measured after every 150 reflections; over the course of the data collection they showed, on average, a maximum relative intensity variation of ± 3.2%. No decay or absorption correction was applied. Lorentz and polarization corrections were applied. Averaging equivalent reflections gave 2807 independent reflections with $R_{\rm int} = 0.017$.

The direct methods program *MITHRIL* (Gilmore, 1984) in the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1989) was used to generate an E map from which the initial positions of the C and O atoms of the organic portion of the structure were assigned. Fourier difference methods were used to locate the positions of the Na atom, the water O atom and the H atoms. The secondary-extinction coefficient was treated as an adjustable parameter, and full-matrix least-squares refinement was performed (*TEXSAN*; Molecular Structure Corporation, 1989) to minimize the function $\sum\sigma_F^{-2}(|F_o|$

---

* The sensitivity of 1,4,5,8-naphthalenetetracarboxylic acid to anhydride formation (discovered by us subsequent to the preparation of this sample) is discussed by Kofman, Chernysh, Shigalevskii & Vorozhtsov (1988).

Table 1. *Final positional parameters and equivalent isotropic and isotropic displacement parameters* (Å^2) *for the sodium salt of* 1,4,5,8-*naphthalenetetracarboxylic acid* 4,5-*anhydride hydrate*

E.s.d.'s are given within parentheses.

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}/B
Na	0.0232 (1)	0.0873 (1)	0.2371 (2)	2.99 (4)
O(1)	0.2112 (2)	0.0152 (2)	0.5159 (3)	2.67 (6)
O(2)	0.2163 (2)	0.1138 (2)	0.8127 (3)	2.59 (6)
O(3)	−0.0059 (2)	0.2086 (2)	0.5234 (3)	2.41 (6)
O(4)	−0.0016 (3)	0.3291 (2)	0.8132 (3)	3.29 (7)
O(5)	0.8384 (2)	0.6356 (2)	0.7237 (3)	3.05 (7)
O(6)	0.6902 (2)	0.7795 (2)	0.7614 (3)	2.55 (6)
O(7)	0.5552 (3)	0.9378 (2)	0.8049 (3)	3.48 (7)
O(10)	0.1101 (3)	−0.1067 (3)	0.0627 (3)	2.93 (7)
C(1)	0.3724 (3)	0.2681 (3)	0.7074 (4)	1.90 (8)
C(2)	0.5125 (3)	0.2543 (3)	0.7053 (5)	2.45 (10)
C(3)	0.6298 (3)	0.3783 (3)	0.7248 (4)	2.45 (10)
C(4)	0.6034 (3)	0.5163 (3)	0.7427 (4)	1.98 (8)
C(5)	0.4393 (3)	0.6827 (3)	0.7731 (4)	2.09 (8)
C(6)	0.3050 (4)	0.7065 (3)	0.7837 (5)	2.69 (10)
C(7)	0.1861 (4)	0.5841 (3)	0.7650 (5)	2.65 (10)
C(8)	0.1997 (3)	0.4401 (3)	0.7339 (4)	1.95 (8)
C(9)	0.3414 (3)	0.4117 (3)	0.7311 (4)	1.68 (7)
C(10)	0.4623 (3)	0.5376 (3)	0.7506 (4)	1.69 (7)
C(11)	0.2560 (3)	0.1239 (3)	0.6830 (4)	1.95 (8)
C(12)	0.0531 (3)	0.3161 (3)	0.6920 (4)	2.01 (8)
C(13)	0.7202 (3)	0.6415 (3)	0.7440 (4)	2.24 (9)
C(14)	0.5603 (3)	0.8102 (3)	0.7838 (4)	2.35 (9)
H(1)	0.126 (5)	−0.090 (5)	0.504 (7)	9.1 (13)*
H(10)	0.088 (4)	−0.176 (4)	0.099 (5)	4.5 (10)*
H(11)	0.213 (5)	−0.062 (5)	0.125 (6)	6.8 (12)*

* Refined isotropically.

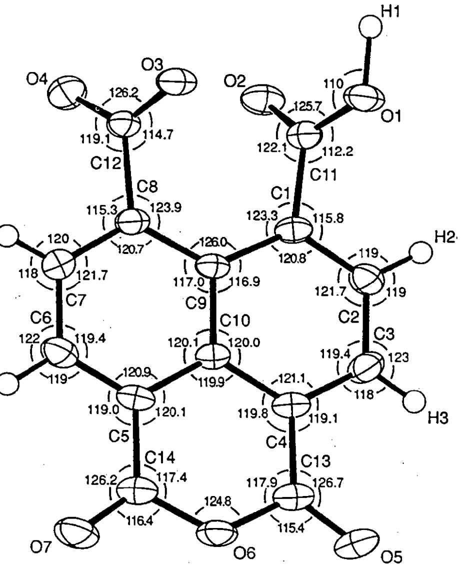


Fig. 1. A view of the 1,4,5,8-naphthalenetetracarboxylic acid 4,5-anhydride anion with our numbering scheme, drawn using *ORTEP*II (Johnson, 1976). Thermal ellipsoids are drawn at 50% probability for all atoms except H for which they have been set artificially small. Bond angles (°) are shown; e.s.d.'s for angles involving C and O atoms are 0.3°, for angles involving H atoms, 3°.

Table 2. *Selected interatomic distances* (Å) *for the organic portion of the title compound* (*angles given in* Fig. 1), *as well as interatomic distances* (Å) *and angles* (°) *for the sodium ion polyhedron and the water molecule*

E.s.d.'s are given within parentheses.

Naphthopyran ring system

C(1)—C(2)	1.369 (4)	C(5)—C(14)	1.470 (4)
C(1)—C(9)	1.433 (4)	C(6)—C(7)	1.400 (4)
C(2)—C(3)	1.398 (4)	C(7)—C(8)	1.368 (4)
C(3)—C(4)	1.367 (4)	C(8)—C(9)	1.432 (4)
C(4)—C(10)	1.416 (4)	C(13)—O(5)	1.199 (3)
C(4)—C(13)	1.466 (3)	C(13)—O(6)	1.381 (3)
C(5)—C(6)	1.366 (4)	C(14)—O(6)	1.381 (3)
C(5)—C(10)	1.417 (4)	C(14)—O(7)	1.197 (3)

Carboxyl groups

C(1)—C(11)	1.514 (3)	C(8)—C(12)	1.517 (3)
C(11)—O(1)	1.297 (3)	C(12)—O(3)	1.283 (3)
C(11)—O(2)	1.224 (3)	C(12)—O(4)	1.224 (3)
O(1)—H(1)	1.13 (4)		

Coordination polyhedron

Na—O(1)	2.656 (3)	Na—O(5)^{iii}	2.605 (2)
Na—O(2)^{ii}	2.522 (2)	Na—O(10)	2.444 (3)
Na—O(3)	2.369 (2)	Na—O(10)^{i}	2.334 (3)
Mean Na—O	2.49 (12)		

O(1)—Na—O(2)^{ii}	91.79 (8)	O(2)^{ii}—Na—O(10)^{i}	91.69 (9)
O(1)—Na—O(3)	73.79 (8)	O(3)—Na—O(5)^{iii}	85.20 (8)
O(1)—Na—O(5)^{iii}	108.84 (8)	O(3)—Na—O(10)	148.57 (9)
O(1)—Na—O(10)	76.08 (8)	O(3)—Na—O(10)^{i}	123.51 (10)
O(1)—Na—O(10)^{i}	162.70 (9)	O(5)^{iii}—Na—O(10)	113.14 (8)
O(2)^{ii}—Na—O(3)	80.58 (8)	O(5)^{iii}—Na—O(10)^{i}	74.93 (9)
O(2)^{ii}—Na—O(5)^{iii}	150.56 (9)	O(10)—Na—O(10)^{i}	86.88 (10)
O(2)^{ii}—Na—O(10)	91.69 (9)		

Water molecule

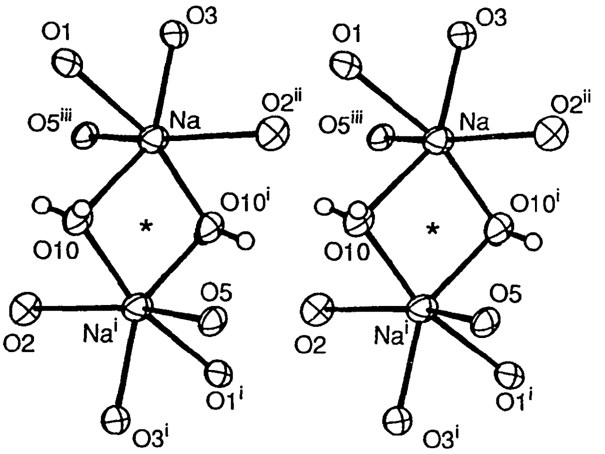
O(10)—H(10)	0.81 (3)	O(10)—H(11)	0.88 (4)
H(10)—O(10)—H(11)	107 (4)		

Symmetry code: (none) x, y, z; (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, y, -1+z$; (v) $-1+x, -1+y, -1+z$.

$-|F_c|)^2$ in which $\sigma_F = \sigma_I/2F\mathrm{Lp}$; non-H atoms anisotropic, H atoms isotropic. Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for C, O and Na; the scattering factor for hydrogen was taken from Stewart, Davidson & Simpson (1965).

The results of the final refinement cycle were: 1665 observations having $I > 3\sigma_I$, 237 variables; $R = 0.042$; $wR = 0.049$; $w = \sigma_F^{-2}$; $S = 1.46$; $(\Delta/\sigma)_{\max} < 0.01$. The optimized secondary-extinction coefficient was 2.4 (4) × 10^{-6}; the maximum extinction correction was 8.4% of $|F_o|$ for the 002 reflection. Max. and min. peaks on the final electron density difference map had values +0.25 and −0.27 e Å^{-3} respectively. The max. peak was located at (0.33, 0.43, 0.25), approximately halfway between C(4) and C(13); the min. peak was located at (0.40, 0.32, 0.22), placing it within the pyran ring, 1.23 Å from O(6). [For the final refinement cycle for 1872 independent observations having $I > \sigma_I$: $R = 0.049$; $wR = 0.052$; $S = 1.45$; $(\Delta/\sigma)_{\max} < 0.02$. Similarly, for the final refinement cycle for 2375 independent observations having $I > 0$: $R = 0.072$; $wR = 0.055$; $S = 1.34$; $(\Delta/\sigma)_{\max} < 0.02$. These latter results are for comparison purposes only.]

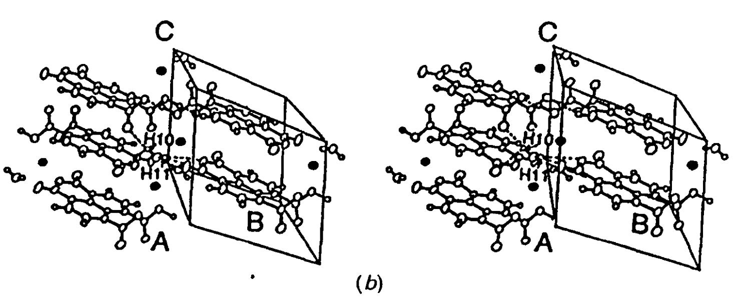
Final atomic coordinates, equivalent isotropic and isotropic displacement parameters and their e.s.d.'s are given in Table 1.* The organic portion of the structure is shown in Fig. 1 along with selected interatomic angles; the sodium atom coordination is shown in Fig. 2(*a*). Table 2 lists selected interatomic distances for the organic portion of the structure and selected distances and angles in the coordination polyhedron of the Na ion.



(*a*)

Discussion. The values given in Fig. 1 and Table 2 indicate that, excepting the carboxyl groups, the organic portion of the structure has near-*C*2 symmetry, with a pseudo-twofold axis coincident with the C(9)—C(10) bond. Angles and distances related in this manner agree within two times their variances except for the O(5)—C(13)—O(6) and O(6)—C(14)—O(7) angles, which agree within four times their variances. The values for bond lengths and angles as well as the near-*C*2 symmetry are very similar to those determined for naphthalic anhydride (Grigor'eva & Chetkina, 1975). The angles around C(1), C(9) and C(8) are typical of naphthalene substituted at the 1 and 8 positions (Fitzgerald, Gallucci & Gerkin, 1991*a*) and take on values that relieve the crowding of the two carboxyl groups. With the formation of the anhydride by the carboxylic acid groups at the 4 and 5 positions the C(1)—C(9)—C(8) angle, 126.0 (3)°, has increased noticeably in comparison with the corresponding angle in the 1,4,5,8-naphthalenetetracarboxylic anion, 122.7 (3)° (Fitzgerald, Gallucci & Gerkin, 1991*b*).

The 13 atoms comprising the naphthopyran three-ring system [C(1)–(10), C(13), C(14) and O(6)] have an average deviation of 0.037 (19) Å from the best least-squares plane describing the three rings. This again is in agreement with results for naphthalic anhydride (Grigor'eva & Chetkina, 1975). O(5) and O(7) are −0.137 (3) and +0.054 (3) Å, respectively, from this best-fit plane, while C(11) and C(12) deviate from it by −0.102 (3) and −0.286 (3) Å, respectively. The planes of the two carboxyl groups make dihedral angles with this best-fit plane of 62.6 (1)° [C(11), O(1), O(2) plane] and 61.2 (1)° [C(12), O(3), O(4) plane], the average dihedral angle being 62 (1)°. These values can be compared to average dihedral-ring angles of 43 (1)° for 1,8-naphthalenedicarboxylic acid (Fitzgerald, Gallucci & Gerkin, 1991*a*) and 54 (2)° for the 1,4,5,8-naphthalenetetracarboxylate anion (Fitzgerald, Gallucci & Gerkin 1991*b*).



(*b*)

Fig. 2. (*a*) A stereoview of the Na ion coordination of the title compound drawn using *ORTEP*II (Johnson, 1976). An inversion center, denoted by an asterisk, is located between the Na ions and water O atoms. Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. (*b*) A unit cell of the title compound with three additional formula units shown, drawn using *ORTEP*II (Johnson, 1976). Hydrogen bonding is indicated by dashed lines; Na atoms have been filled.

---

* Lists of structure factors, anisotropic displacement parameters, least-squares refined coordinates and displacement factors of ring hydrogens, and material relating to best-fit planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54661 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0534]

Table 3. *Hydrogen-bond parameters for the sodium salt of* 1,4,5,8-*naphthalenetetracarboxylic acid* 4,5-*anhydride hydrate*

E.s.d.'s are given within parentheses. See text for details.

Oxygen—acceptor oxygen	Distance (Å)	Proton—acceptor oxygen	Observed distance (Å)	Neutron-adjusted distance (Å)	Observed O—H—O angle (°)	
O(1)—O(3)^{ii}	2.475 (3)	H(1)—O(3)^{ii}	1.35 (5)	—	O(1)—H(1)—O(3)^{ii}	171 (4)
O(10)—O(4)^{ii}	2.745 (3)	H(10)—O(4)^{ii}	1.94 (4)	1.80	O(10)—H(10)—O(4)^{ii}	169 (4)
O(10)—O(5)^{v}	3.012 (3)	H(10)—O(5)^{v}	2.86 (4)	2.86	O(10)—H(10)—O(5)^{v}	93 (3)
O(10)—O(7)^{iii}	2.945 (3)	H(11)—O(7)^{iii}	2.10 (4)	2.02	O(10)—H(11)—O(7)^{iii}	162 (4)
O(10)—O(6)^{iii}	2.975 (3)	H(11)—O(6)^{iii}	2.47 (4)	2.43	O(10)—H(11)—O(6)^{iii}	117 (3)

Symmetry code: (none) x, y, z; (ii) $-x, -y, 1-z$; (iii) $1-x, 1-y, 1-z$; (v) $-1+x, -1+y, -1+z$.

* Neutron diffraction O—H distance taken from Antsyshkina, Dikareva, Porai-Koshits, Fykin, Dudarev & Gusejnov (1982).

The bond lengths and angles for the Na ion coordination polyhedron are given in Table 2. Fig. 2(*a*) depicts the coordination around two Na ions related by an inversion center. The O atoms are arranged in a highly-distorted octahedron with two inversion-related Na atoms sharing two inversion-related water O atoms. The Na—O(10)—Na^{i} angle in this configuration is 93.1 (1)° and the O(10)—Na—O(10)^{i} angle is 86.9 (1)°. The remainder of the O atoms in the coordination polyhedron are supplied by the organic portion of the structure: three carboxylic acid O atoms [O(1), O(3) and O(2)^{ii}] from two molecules and one carbonyl O atom from a third molecule [O(5)^{iii}]. The mean Na—O distance, 2.49 (12) Å, is quite similar to the two mean Na—O distances in tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate: 2.44 (10) and 2.36 (4) Å (Fitzgerald, Gallucci & Gerkin, 1991*b*).

Hydrogen-bond parameters are listed in Table 3; the arrangement of the hydrogen bonds can be seen in Fig. 2(*b*). The acid H atom is involved in a very short hydrogen bond, typical of acid salts (Speakman, 1972). Since the O(1)···O(3)^{ii} distance is 2.475 (3) Å, the possibility of disorder of the acid H atom was evaluated. An electron density difference map showed no evidence of hydrogen disorder. The acid H atom was located approximately 1.0 Å from O(1) and least-squares refinement using this model converged to the *R* values given above, ultimately placing H(1) 1.13 (4) Å from O(1) with an isotropic displacement parameter of 9.1 (13) Å^2. A least-squares refinement for a disordered acid H atom model, consisting of half-occupied H atoms 1 Å from O(1) and O(3)^{ii}, resulted in physically unrealistic displacement parameters. The bond angles and bond lengths within the two carboxyl groups also support the present assignment of H(1). The C(11)—O(1) distance of 1.297 (3) Å is greater than the C(12)—O(3) distance of 1.283 (3) Å and is closer to the typical C—O single-bond distance for aromatic carboxylic acids of 1.305 (20) Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The C(1)—C(11)—O(1) angle, being 112.2 (2)°, is 9.9° smaller than the C(1)—C(11)—O(2) angle of 122.1 (2)°, an arrangement appropriate for carboxylic acids (Speakman, 1972). The difference for the respective angles in the C(12), O(3), O(4) carboxyl group is only 4.4°. Presumably, the short O(1)—O(3)^{ii} distance causes the O(1)—H(1) distance in the present structure to be longer than that which is commonly observed: 1.015 (17) Å (Allen *et al.*, 1987). Nonetheless, the H atom is not symmetrically located nor disordered which is consistent with the fact that the environments of the carboxyl groups are dissimilar: O(1), O(2) and O(3) are involved in coordination with Na, O(4) is not. A short, asymmetric hydrogen bond very similar to that described here has been reported, for example, by Macdonald, Morrison, Murray & Freer (1991) for sodium hydrogen glutarate dihydrate.

The water H atoms, H(10) and H(11), are apparently involved in unequal three-centered hydrogen bonding. H(10) is 1.94 (4) Å from O(4)^{ii} with an O—H···O (acceptor) angle of 169 (4)° but is also 2.86 (4) Å from O(5)^{v} with an O(10)—H(10)···O(5)^{v} (acceptor) angle of 93 (3)°. In addition, H(10) is 0.11 Å from the plane defined by the three O atoms O(10), O(4)^{ii} and O(5)^{v} thus meeting the requirement of near-planarity for three-centered hydrogen bonds described by Jeffrey (1987). Even though the primary interaction with H(10) is provided by O(4)^{ii}, the second oxygen, O(5)^{v}, is also involved. The situation for the other water H atom is similar, with H(11) being 0.19 Å from the plane of the three O atoms, O(10), O(6)^{iii} and O(7)^{iii}; O(7)^{iii} provides the primary interaction while O(6)^{iii} provides the secondary interaction. However, the two proton–acceptor O atom distances for H(11) [2.10(4) and 2.47 (4) Å] are closer in magnitude than the two proton–acceptor O atom distances for H(10), indicating that H(11) interacts more nearly equally with its two O atoms than does H(10).

Fig. 2(*b*) is a stereoview of a unit cell and three additional formula units of the title compound. The naphthopyran three-ring portion of the structure is stacked nearly parallel to the *ab* cell face with alternating layers, related by inversion, offset with respect to each other. The average intermolecular distance between the C and O atoms of the naphthopyran rings related in this manner is 3.5 (1) Å. The layers are connected by pairs of hydrogen bonds formed between the carboxyl groups, as well as those involving the water molecules. Inversion centers along the *c* axis relate pairs of coordinated Na ions which lie near this axis. Hydrogen bonding between the carboxylic acid groups occurs perpendicular to the *z* direction and separates from each other the Na ion pairs created by coordination and related by the inversion centers.

The support by PPG Industries of LJF is gratefully acknowledged, as is the partial support of this research through the purchase of the diffractometer system by an NIH grant.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Antsyshkina, A. S., Dikareva, L. M., Porai-Koshits, M. A., Fykin, L. E., Dudarev, V. Ya. & Gusejnov, M. G. (1982). *Koord. Khim.* **8**, 1256–1260.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1991*a*). *Acta Cryst.* **B47**, 776–782.

Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1991*b*). *Acta Cryst.* **C47**, 2315–2319.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Grigor'eva, L. P. & Chetkina, L. A. (1975). *Kristallografiya*, **20**, 1289–1290.

Jeffrey, G. A. (1987). In *Patterson and Pattersons*, edited by J. P. Glusker, B. K. Patterson & M. Rossi, pp. 193–221. Oxford Univ. Press.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kofman, A. G., Chernysh, G. V., Shigalevskii, V. A. & Vorozhtsov, G. N. (1988). *Zh. Org. Khim.* **24**(9), 1973–1978.

Macdonald, A. L., Morrison, P., Murray, A. & Freer, A. A. (1991). *Acta Cryst.* **C47**, 728–730.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package.* Version 5.0. MSC, The Woodlands, Texas, USA.

Speakman, J. C. (1972). *Struct. Bonding* (*Berlin*), **12**, 141–199.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1992). C**48**, 465–468

Structures of $[(L)(CO)_4ReMo(CO)_3(\eta^5\text{-}C_5H_5)]$ (L = CO, ^{t}BuNC)

By Wayne L. Ingham, S. Don Travlos, Jan C. A. Boeyens, Mark Berry and Neil J. Coville*

Applied Chemistry and Chemical Technology Centre, Department of Chemistry,
University of the Witwatersrand, PO WITS 2050, *Johannesburg, Republic of South Africa*

(*Received* 19 *March* 1991; *accepted* 12 *September* 1991)

Abstract. Octacarbonyl-$1\kappa^5C,2\kappa^3C$-$2(\eta^5)$-cyclopentadienemolybdenumrhenium(*Mo*—*Re*), $[(CO)_5ReMo(CO)_3(\eta^5\text{-}C_5H_5)]$ (*A*), $M_r = 571.2$, monoclinic, $P2_1/c$, $a = 7.046\ (1)$, $b = 24.967\ (2)$, $c = 9.174\ (1)$ Å, $\beta = 107.95\ (2)°$, $V = 1535.2$ Å^3, $Z = 4$, $D_x = 2.47$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.7107$ Å, $\mu = 88.2$ cm^{-1}, $F(000) = 1056.0$, $T = 293$ K, $R = 0.037$ for 2028 unique reflections. (*tert*-Butyl isocyanide-$2\kappa C$)-heptacarbonyl-$1\kappa^4C,2\kappa^3C$-$2(\eta^5)$-cyclopentadienemolybdenumrhenium(*Mo*—*Re*), $[(^tBuNC)(CO)_4ReMo(CO)_3(\eta^5\text{-}C_5H_5)]$ (*B*), $M_r = 626.3$, triclinic, $P\overline{1}$, $a = 7.108\ (4)$, $b = 9.731\ (1)$, $c = 14.240\ (2)$ Å, $\alpha = 90.247\ (6)$, $\beta = 89.969\ (5)$, $\gamma = 87.297\ (5)°$, $V = 983.9$ Å^3, $Z = 2$, $D_x = 1.054$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.7107$ Å, $\mu = 34.3$ cm^{-1}, $F(000) = 593.8$, $T = 293$ K, $R = 0.024$ for 5240 unique reflections. The ^{t}BuNC ligand is found attached to the Re atom in an equatorial site in (*B*). The ^{t}BuNC group in (*B*) is found to influence the *M*—CO bond lengths on *both* the Mo and Re atoms relative to (*A*). In both structures the group(s) on Re closest to the C_5H_5 ring on Mo bends in towards the C_5H_5 ring.

Introduction. Little information is available on the substitution chemistry of mixed metal dimer carbonyl complexes (Roberts & Geoffrey, 1982) and in particular on the site of attachment of an incoming ligand to the metal dimer. While investigating the CO substitution reactions of $[(\eta^5\text{-}C_5H_5)Mo\mathit{M}(CO)_8]$ (M = Mn, Re) with isocyanides we observed that the products obtained were influenced by the Group 7 metal. Thus, reaction with M = Mn (Ingham, Billing,

---

* To whom correspondence should be addressed.

0108-2701/92/030465-04$03.00 © 1992 International Union of Crystallography