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Disodium Fluorescein Octahydrate

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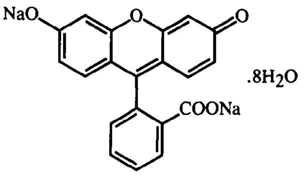
Abstract

The molecular structure of disodium fluorescein octahydrate, $2Na^+.C_{20}H_{10}O_5^{2-}.8H_2O$, exhibits a quinonoid form [sodium 2-(3-oxo-6-sodioxy-3*H*-xanthen-9-yl)-benzoate]. The crystal structure includes eight water molecules in an asymmetric unit in the cell. Two Na—O(hydroxy) distances are 2.568 (4) (Na2—O2) and 2.343 (3) Å (Na1—O4).

Comment

Various spectroscopic investigations have been carried out in order to determine the structural formula of sodium fluorescein (Tamura, Morioka, Maeda & Tsuji, 1994). Although this compound was assigned to be a lactanoid species in JPXII (1995), the results derived from the above experiments indicated that sodium fluorescein exists in a quinonoid form (Tamura, 1994) in the crystalline state. However, since the compound is powdery and hygroscopic in the solid state, a single crystal is difficult to obtain. Fortunately, by gradual evaporation of an aqueous solution, the compound solidified into a large efflorescent single crystal, part of which was used for X-ray analysis. The X-ray crystallographic study confirmed the structure of sodium fluorescein, (I).



(I)

The molecule of (I) consists of planar xanthene and benzoate groups, as shown in Fig. 1. They are linked by a C—C single bond of length 1.500 (6) Å and twisted around the C7—C14 bond by 98.2 (5)°. The two C—O bond lengths of 1.297 (5) (O2—C11) and 1.285 (5) Å (O3—C3) in the xanthene group suggest a partial quinonoid form in the respective phenol groups. This electronic effect, as well as the geometric parameters, are almost consistent with those found in sulfonefluorescein (Kanazawa, Senga, Tamura & Iitaka, 1994). Eight water molecules are included in the asymmetric unit in the crystal, which is probably caused by the extremely slow evaporation of the highly concentrated solution necessary to obtain the crystal of this compound. Na—O distances of 2.343 (3) and 2.568 (4) Å were observed for Na1—O4 and Na2—O2, respectively.

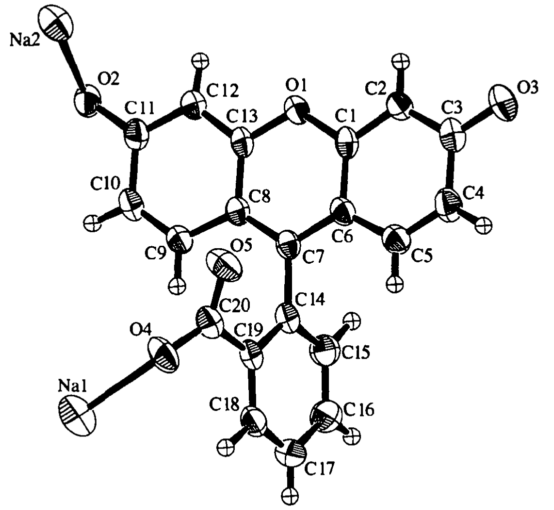


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of sodium fluorescein. Ellipsoids are drawn at the 50% probability level and isotropic H-atom displacement parameters are represented by spheres of arbitrary size.

Experimental

Crystals of the title compound were obtained by gradual evaporation of an aqueous solution.

Crystal data

$2Na^+.C_{20}H_{10}O_5^{2-}.8H_2O$
M_r = 520.40
Monoclinic
$P2_1/a$
a = 13.636 (2) Å
b = 12.597 (2) Å
c = 13.794 (1) Å
β = 97.875 (9)°
V = 2347.0 (5) Å^3
Z = 4
D_x = 1.512 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 21.9–23.0°
μ = 1.402 mm^{-1}
T = 296.2 K
Prismatic
0.48 × 0.40 × 0.28 mm
Red

Data collection

Rigaku AFC-5*S* diffractometer

2720 reflections with $I > 1.5\sigma(I)$

ω–2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.411$, $T_{\max} = 0.675$
3857 measured reflections
3685 independent reflections

$R_{\text{int}} = 0.0215$
$\theta_{\max} = 60°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections every 150 reflections intensity decay: 12.5%

Refinement

Refinement on F
$R = 0.0637$
$wR = 0.0777$
$S = 2.114$
2720 reflections
316 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.00016|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.0756$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Na1—Na2^{i}	3.596 (3)	Na2—O10^{v}	2.356 (4)
Na1—O4^{ii}	2.343 (3)	Na2—O12	2.352 (4)
Na1—O7^{iii}	2.401 (4)	O1—C1	1.378 (5)
Na1—O9^{iv}	2.498 (4)	O1—C13	1.371 (4)
Na1—O10	2.517 (4)	O2—C11	1.297 (5)
Na1—O11^{v}	2.709 (4)	O3—C3	1.285 (5)
Na1—O13	2.342 (5)	O4—C20	1.251 (5)
Na2—O2	2.568 (4)	O5—C20	1.256 (5)
Na2—O4^{i}	2.433 (4)	C7—C14	1.500 (6)
Na2—O8^{iii}	2.439 (4)	C19—C20	1.509 (6)

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (ii) $1 + x, y, z$; (iii) $x, y, z - 1$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z - 1$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

The ω-scan width was $(1.3 + 0.14\tan\theta)°$ and the scan speed was 32° min^{-1}. Refinement was by full-matrix least-squares methods. The H atoms associated with the O13 water molecule were not located.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetracarbonyl-1κ²*C*,2κ²*C*-μ-diphenylphosphido-*P*:*P*-μ-iodo-bis(triphenylphosphine)-1κ*P*,2κ*P*-diosmium(*Os*—*Os*) Benzene Solvate

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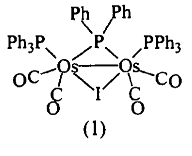
Abstract

In the title compound, $[Os_2I(C_{12}H_{10}P)(C_{18}H_{15}P)_2(CO)_4].C_6H_6$, the Os—Os bond distance is unusually short [2.781 (1) Å]. The two Os atoms are symmetrically bridged by both an iodo and a phosphido ligand. Two carbonyl groups and a triphenylphospine moiety complete the Os-atom coordination spheres. There are only two other reported structures with an iodo ligand bridging two Os atoms [Sutton, Nivin & Moss (1983). *Inorg. Chim. Acta*, **70**, 207–210; Geoffroy, Rosenberg, Herlinger & Rheingold (1986). *Inorg. Chem.* **25**, 2916–2919].

Comment

The coordination geometries about the Os atoms in the title compound, (1), are octahedral, with distortions probably due to steric factors. The compound is diamagnetic with the octadecet count being completed by an unusually short Os—Os bond [2.781 (1) Å]. The asymmetric unit contains a severely distorted solvent molecule that according to the synthesis and recrystallization information should be benzene, but toluene cannot be ruled out. The solvent molecule is statistically disordered over two positions with a 63/37% occupancy distribution.



(1)

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