

Table 1. Selected geometric parameters (\AA , $^\circ$)

Zn1—N1	1.998 (5)	Zn1—Cl2	2.230 (2)
Zn1—N3	2.005 (5)	Zn1—Cl1	2.247 (2)
N1—Zn1—N3	111.15 (19)	Cl2—Zn1—Cl1	114.59 (8)
N1—Zn1—Cl2	109.90 (14)	C3—N1—Zn1	128.6 (4)
N3—Zn1—Cl2	106.42 (15)	C1—N1—Zn1	125.4 (4)
N1—Zn1—Cl1	104.56 (15)	C9—N3—Zn1	129.8 (4)
N3—Zn1—Cl1	110.31 (15)	C6—N3—Zn1	123.5 (4)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...Cl1 ⁱ	1.08	1.99	3.071 (7)	176.0
O2—H2...O1 ⁱⁱ	1.05	2.35	2.767 (10)	102.1
O2—H2...O2 ⁱⁱ	1.05	2.41	2.877 (14)	106.1

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $-x, 2 - y, 1 - z$.

Hydroxy H atoms were fixed at positions found in a difference map. Other H atoms were refined using a riding model, with $U(\text{H}) = 0.08 \text{\AA}$.

Data collection: *R3m Software* (Siemens, 1990). Cell refinement: *R3m Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1299). Services for accessing these data are described at the back of the journal.

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Disodium 4,4'-difluoro-3,3'-carbonyl-dibenzenesulfonate hydrofluoride tetrahydrate

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Abstract

The structure determination of the title compound, $2\text{Na}^+ \cdot \text{C}_{13}\text{H}_6\text{F}_2\text{O}_7\text{S}_2^- \cdot \text{HF} \cdot 4\text{H}_2\text{O}$, indicates that intermolecular physical crosslinking through Na^+ ions exists in the crystal so that ionic aggregates are formed.

Comment

Sulfones have received considerable attention owing to their high performance in the membrane separation process (Ueda *et al.*, 1993; Wang *et al.*, 1998). This method of synthesizing sulfonated polymers *via* nucleophilic polycondensation of disodium 4,4'-difluoro-3,3'-carbonyldibenzenesulfonate hydrofluoride tetrahydrate, (I), and bis-phenols is more advantageous than traditional routes of polymer sulfonation, and polymers thus obtained are suitable for gas dehumidification and ion-exchange membranes.

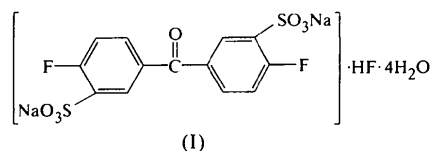


Fig. 1 shows the molecule with the atom-numbering scheme and Fig. 2 illustrates the intermolecular linking through Na^+ ions. The phenyl rings are not coplanar; the torsion angle C9—C8—C3—C4 is $57.2(3)^\circ$, which is larger than the corresponding value of $47.1(1)^\circ$ in 4,4'-difluorobenzophenone (Maginn & Davey, 1994), owing to the introduction of bulky sodium sulfonate groups. It can be seen from Fig. 2 that physical crosslinking through Na^+ ions is present in the compound. The Na^+ ions coordinate with water molecules, O atoms and the hydrofluoride F^- ion. The ionic aggregate is constructed through coordination of the different molecules with Na^+ ions. The water molecules and F^- ion, as main ligands, strengthen the intermolecular forces.

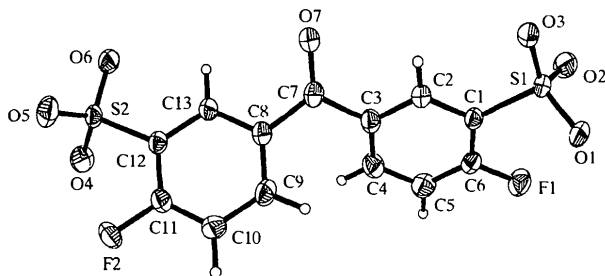


Fig. 1. The structure of the title anion showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

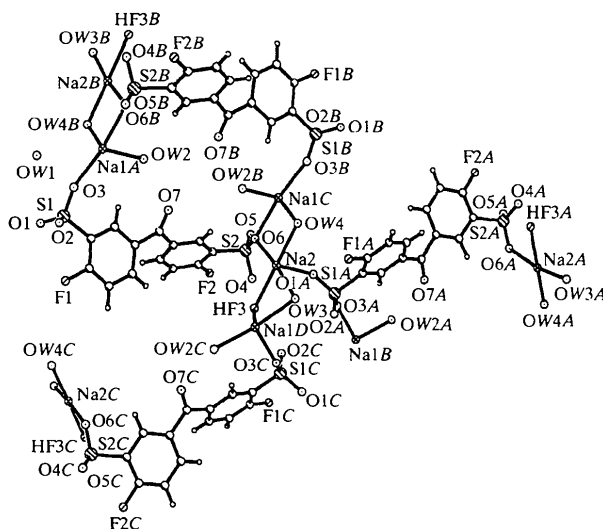
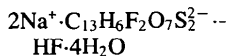


Fig. 2. The linking of anions via Na^+ ions viewed down the c axis.

Experimental

The title compound was synthesized by sulfonation of 4,4'-difluorobenzophenone with fuming sulfuric acid for 10 h at 373 K. The solution was cooled and poured into ice water. The sulfonated compound was neutralized with NaOH, followed by salting-out by NaF (which generated HF). Recrystallization was from methanol/water (9:1 v:v).

Crystal data



$M_r = 514.35$

Monoclinic

$P2_1/c$

$a = 13.702(3) \text{ \AA}$

$b = 14.167(3) \text{ \AA}$

$c = 10.598(2) \text{ \AA}$

$\beta = 97.34(3)^\circ$

$V = 2040.4(7) \text{ \AA}^3$

$Z = 4$

$D_x = 1.674 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 30 reflections

$\theta = 4.89\text{--}10.68^\circ$

$\mu = 0.386 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Needle

$0.50 \times 0.42 \times 0.36 \text{ mm}$

Colourless

Data collection

Siemens P4 four-circle diffractometer

$\omega/2\theta$ scans

Absorption correction: empirical via ψ scans (XSCANS; Siemens, 1994a)

$T_{\min} = 0.26$, $T_{\max} = 0.31$

4685 measured reflections

3559 independent reflections

2732 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 25^\circ$

$h = -16 \rightarrow 16$

$k = -16 \rightarrow 1$

$l = -1 \rightarrow 12$

3 standard reflections

every 100 reflections

intensity decay: 1%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.127$

$S = 1.01$

3559 reflections

304 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0867P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.018$

$\Delta\rho_{\max} = 0.509 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.385 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Na1—Ow2	2.351 (3)	Na1—O3 ⁱⁱⁱ	2.388 (2)
Na2—O1 ⁱ	2.429 (2)	Na2—O5 ^{iv}	2.485 (3)
Na2—F3 ⁱⁱ	2.480 (3)	Ow3—Na1 ⁱⁱⁱ	2.426 (2)
F1—C6	1.354 (4)	S1—O1	1.454 (2)
C1—C2	1.389 (4)	S1—O2	1.448 (2)
C5—C6	1.361 (5)	S1—O3	1.455 (2)
C3—C7	1.496 (4)	S1—C1	1.778 (3)
O7—C7	1.223 (4)	C7—C8	1.489 (4)
Ow2—Na1—F3	113.96 (10)	Na2 ⁱⁱⁱ —F3—Na1	88.63 (9)
O6 ^v —Na1—F3	104.60 (9)	Na1 ⁱ —O6—Na2	89.79 (8)
O3 ⁱⁱⁱ —Na1—Na2 ^v	128.38 (8)	Na2 ^v —Ow4—Na1	93.49 (9)
Ow3 ^{vi} —Na1—Na2 ^{vii}	43.59 (7)	S2—O5—Na2 ^{ix}	122.40 (14)
Ow3 ^{viii} —Na2—O1 ⁱ	85.55 (9)	O5—S2—C12	107.68 (14)
O1 ⁱ —Na2—O5 ^{iv}	170.62 (9)	O6—S2—C12	106.01 (13)
O2—S1—O1	113.10 (13)	O4—S2—C12	103.10 (13)
C1—C2—C3	119.7 (3)	C4—C3—C7	121.9 (3)
C5—C6—C1	123.0 (3)	C2—C3—C7	118.2 (3)
C6—C1—S1	121.3 (2)	F1—C6—C5	118.5 (3)
C2—C1—S1	120.2 (2)	O7—C7—C3	120.6 (3)

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

All atoms were obtained from successive Fourier syntheses. The H atoms were treated by a mixture of independent and constrained refinement; the six H atoms of the anion were refined isotropically. The nine H atoms of the water and HF molecules were not located.

Data collection: P4 (Siemens, 1994b). Cell refinement: XSCANS (Siemens, 1994a). Data reduction: SHELXTL (Sheldrick, 1995). Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1991). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1421). Services for accessing these data are described at the back of the journal.

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An oxamidato-bridged binuclear imidazole–copper(II) complex

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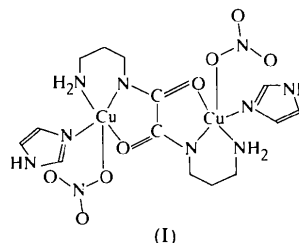
Abstract

The oxpn ligand [oxpn = *N,N'*-bis(3-aminopropyl)oxamide] in the title compound, μ -[*N,N'*-bis(3-aminopropyl)oxamidato(2-)]-*N,N',O':N'',N'''*,*O*-bis[(imidazole-*N*³)(nitrate-*O*)copper(II)], [Cu₂(C₈H₁₆N₄O₂)(NO₃)₂·(C₃H₄N₂)₂], is bis-tridentate in a *trans* conformation, bridging two Cu^{II} ions to form a centrosymmetric binuclear molecule. The symmetry-equivalent central Cu^{II} ions are located in a distorted square-based pyramid, with an O atom from the nitrate ion bonded at the axial site, and a Cu···Cu distance of 5.242 (2) Å.

Comment

As extending bridging ligands transmitting a strong magnetic exchange interaction, oxamidates have played a key role in the design of polymetallic systems (Ojima & Nonoyama, 1988). One of the most important factors for the versatility of the ligands is their easy *cis*–*trans* conformational change to afford symmetric or asymmetric oxamidato bridges. We report here the

crystal structure of a binuclear copper(II) complex with a bridging *N,N'*-bis(3-aminopropyl)oxamide (oxpn) ligand in the *trans* conformation, (I).



The structure of this complex consists of centrosymmetric binuclear molecules, with oxpn acting as a bis-tridentate ligand, in which the Cu^{II} ions are bridged by a *trans*-oxamidato group with an inversion centre in the middle of the C1–C1' bond [symmetry code: (i) 2 – *x*, 1 – *y*, 1 – *z*] (Fig. 1). The Cu^{II} ion is in a distorted square-pyramidal geometry, with three atoms from the oxpn ligand (N1, N2 and O1) and one N atom (N3) from the imidazole in the basal plane, while the axial coordination site is occupied by a nitrate O atom (O2). The four atoms of the coordination plane are almost coplanar, with deviations from the least-squares plane of less than 0.055 Å. The Cu^{II} ion deviates by 0.043 Å towards the O atom belonging to the semicoordinated nitrate anion [Cu–O2 2.673 (2) Å].

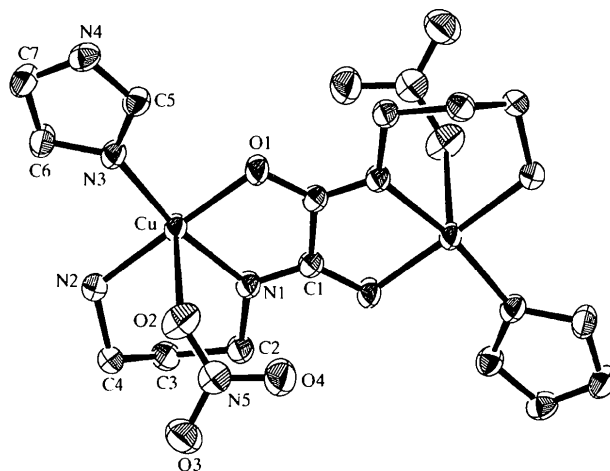


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The bond distances for Cu–N1, Cu–N2 and Cu–N3 [1.967 (2), 2.003 (2) and 1.982 (2) Å, respectively] are close to those observed in parent oxamidato-bridged copper(II) complexes (Chen, Tang & Yu, 1994; Sanz *et al.*, 1996). The significant shortening of the Cu–N1 bond distance is in agreement with the stronger basicity of the deprotonated amide N atom (Chen, Tang