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(1,1,1,5,5,5-Hexafluoro-2,4-pentanedionato-*O,O′*)(1,4,7,10,13-pentaoxapentadecane-κ^5O)sodium

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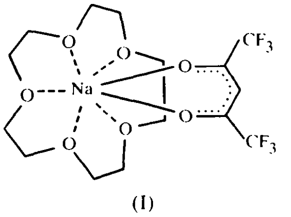
Abstract

The title compound, $[Na(C_5HF_6O_2)(C_{10}H_{20}O_5)]$, contains a seven-coordinate Na$^+$ ion with an irregular coordination geometry. It is bonded to the five crown ether and the two β-diketonate O atoms. The structure contains no unusual features, the conformation of the crown ether being very similar to those in compounds described previously. There are no particularly short intermolecular contacts and the title compound behaves as a discrete molecule, which probably accounts for its relatively high volatility.

Comment

The title compound, (I), sublimes without decomposition at 390 K and a pressure of *ca* 5 Pa, and is thus potentially useful as a precursor for chemical vapour deposition of NaF films. It is also air stable, in contrast to the sodium fluoroalkoxides used in most reported work in this area (Lingg *et al.*, 1992; Samuels *et al.*, 1993, 1994). Furthermore, (I) is of interest as an analogue of the various structurally characterized volatile group 2 metal compounds containing 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfa) and polyether ligands (Motevalli *et al.*, 1996).



(I)

To date, more than 60 structures containing 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) coordinated to an Na$^+$ ion have been described. The Na$^+$ ion is invariably bonded to all five O atoms of the crown ether, and in the vast majority of cases increases its coordination number by either one or two by binding to other (usually hard) donor atoms. In rare cases, as in hexakis(phenylthiolato)tantalum (Koo *et al.*, 1990) or the tetrachloronickel salts (Ruhlandt-Senge & Muller, 1990), the Na$^+$ ion remains five-coordinate.

In complex (I), the Na$^+$ ion is seven-coordinate. The Na—O(crown ether) distances are in the range 2.446 (2)–2.549 (3) Å [mean 2.493 (3) Å] and are substantially longer than the Na—O(diketonate) distances of 2.371 (2) and 2.381 (2) Å. The Na$^+$ ion is displaced by 0.9894 (13) Å from the mean plane described by the crown-ether O atoms. The distances from the mean plane are: O11 −0.0221 (14), O12 0.2972 (14), O13 −0.4832 (15), O14 0.4420 (14) and O15 −0.2339 (14) Å. Thus, the Na$^+$ ion is on the same side of the mean plane as two of the crown-ether O atoms (O12 and O14). The literature compounds most closely related to (I) are (15-crown-5)(4-ethoxybutan-2-one-4-olato-*O,O′*)sodium (Cambillau *et al.*, 1982) and (15-crown-5)[diphenylethyl(diphenylmethyl)cyanoacetonato]sodium (Coleman *et al.*, 1991), both of which contain a six-membered Na—O═C(*R*)C(*R*)C(*R*)═O β-diketonate ring system. For these compounds, the mean Na—O(crown ether) and mean Na—O(ketonate) distances are 2.491/2.309 and 2.478/2.320 Å, respectively.

The coordination geometry of the Na$^+$ ion could be crudely described as a very distorted pentagonal bipyramid, with atoms O1 and O13 in axial positions, but with the remaining five O atoms being far from coplanar. The conformation of the crown ether is similar to that described by Buchanan *et al.* (1994), with all

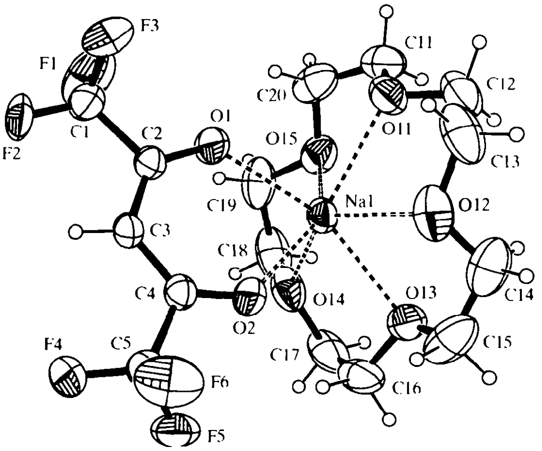


Fig. 1. View of (I) (30% probability displacement ellipsoids). Only the F atoms of the major component of disorder are shown.

the O—C—C—O torsion angles close to 60° and all the C—C—O—C torsion angles close to 180°, with the exception of C12—C13—O12—C14 which has a value of 88.4 (5)° (Table 1).

Both the CF_3 groups in (I) show a non-statistical disorder, which is common for these functional groups, possibly due to very high amplitude librations about the C—C bonds. This disorder was most simply modelled by the use of two sets of F sites for each CF_3 group, in each case approximately related by a 60° rotation. There are no unusually short intermolecular contacts and the title compound behaves as a discrete covalently bonded molecule. This is presumably responsible for its relatively high volatility.

Experimental

Compound (I) was prepared by reacting Hhfa (Fluka, 4.26 mmol), 15-crown-5 (Aldrich, 4.25 mmol) and NaOH (Aldrich electronic grade, 61.0 mmol) in a mixture of water (50 ml) and ethanol (50 ml). After stirring for 15 min at room temperature, a further 150 ml of water were added, and the product was extracted into 50 ml of $CHCl_3$. Following drying of the extract with anhydrous $MgSO_4$, the solvent was removed under reduced pressure. The crude product was washed with 3 × 10 ml portions of pentane and dried at a pressure of *ca* 5 Pa (yield 1.58 mmol). Crystals of (I) were grown at room temperature by diffusion of pentane vapour into a saturated toluene solution. The melting range of recrystallized (I) was 451–455 K. Elemental analysis and spectroscopic characterization gave results consistent with the structure determination.

Crystal data

$[Na(C_5HF_6O_2)(C_{10}H_{20}O_5)]$
$M_r = 450.31$
Triclinic
$P\bar{1}$
$a = 8.7931\ (5)$ Å
$b = 9.2891\ (4)$ Å
$c = 13.2423\ (9)$ Å
$\alpha = 89.657\ (4)°$
$\beta = 73.646\ (7)°$
$\gamma = 82.804\ (5)°$
$V = 1029.21\ (10)$ Å^3
$Z = 2$
$D_x = 1.453$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18.1–19.9°$
$\mu = 0.163$ mm^{-1}
$T = 291\ (2)$ K
Prism
0.50 × 0.40 × 0.37 mm
Colourless

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: none
4868 measured reflections
4034 independent reflections
2771 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0117$
$\theta_{\rm max} = 25.98°$
$h = -1 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$
6 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.055$
$wR(F^2) = 0.175$
$S = 1.045$
4034 reflections
320 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2 + 0.3711P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.291$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.198$ e Å^{-3}
Extinction correction: *SHELXL*97-2
Extinction coefficient: 0.038 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C15—O13	1.462 (5)	O12—Na1	2.446 (2)
O1—Na1	2.371 (2)	O13—Na1	2.498 (2)
O2—Na1	2.381 (2)	O14—Na1	2.478 (2)
O11—Na1	2.494 (2)	O15—Na1	2.549 (3)
O1—Na1—O2	75.09 (7)	O2—Na1—O13	87.30 (7)
O1—Na1—O12	118.81 (10)	O12—Na1—O13	68.78 (10)
O2—Na1—O12	91.81 (9)	O14—Na1—O13	66.20 (9)
O1—Na1—O14	105.20 (9)	O11—Na1—O13	112.98 (8)
O2—Na1—O14	89.82 (8)	O1—Na1—O15	86.40 (8)
O12—Na1—O14	134.81 (10)	O2—Na1—O15	143.41 (8)
O1—Na1—O11	86.10 (8)	O12—Na1—O15	124.77 (9)
O2—Na1—O11	141.68 (8)	O14—Na1—O15	64.62 (9)
O12—Na1—O11	68.29 (10)	O11—Na1—O15	65.41 (8)
O14—Na1—O11	127.67 (9)	O13—Na1—O15	103.88 (8)
O1—Na1—O13	160.68 (8)		
O11—C12—C13—O12	59.1 (5)	C12—C13—O12—C14	88.4 (5)
O12—C14—C15—O13	65.2 (5)	C17—C16—O13—C15	−177.9 (3)
O13—C16—C17—O14	−60.2 (4)	C14—C15—O13—C16	−170.2 (3)
O14—C18—C19—O15	60.3 (4)	C19—C18—O14—C17	−157.3 (3)
O11—C11—C20—O15	−66.2 (3)	C16—C17—O14—C18	163.7 (3)
C13—C12—O11—C11	−179.0 (3)	C11—C20—O15—C19	176.5 (3)
C20—C11—O11—C12	165.5 (3)	C18—C19—O15—C20	177.9 (3)
C15—C14—O12—C13	−171.5 (4)		

The structure was solved by direct methods and refined by full-matrix least squares. H atoms were placed in calculated positions (C—H = 0.96 Å) and refined with a riding model. Calulations were carried out using the *WinGX* package (Farrugia, 1998). Both trifluoromethyl groups were disordered over two positions, with a disorder population of 0.565 (13):0.435 (13) for one group and 0.783 (13):0.217 (13) for the other group. Calculations using *PLATON* (Spek, 1990) indicated that there were no residual voids in the lattice capable of containing solvent molecules.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms & Wocadlo, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *SHELXL*97-2 (Sheldrick, 1997). Molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997). Software used to prepare material for publication: *WinGX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1004). Services for accessing these data are described at the back of the journal.

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(3,7-Diethyl-3,7-diazanonane-1,9-dithiolato-*S*,*N*,*N*′,*S*′)nickel(II)

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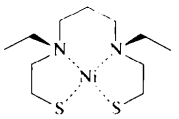
Abstract

The electroneutral title complex, (3,7-diethyl-3,7-diazanonane-1,9-dithiolato-*S*,*N*,*N*′,*S*′)nickel(II), [Ni($C_{11}H_{24}N_2S_2$)], contains a distorted square-planar arrangement of two N- and two S-donor atoms around the Ni^{II} centre in a *cis*-type fashion.

Comment

Nickel(II) complexes with polyfunctional sulfur/nitrogen ligands have been thoroughly investigated (Musie *et al.*, 1996; Darensbourg *et al.*, 1995; Tuntulani *et al.*, 1992; Colpas *et al.*, 1990) because of their importance as starting materials for the synthesis of heterometallic complexes (Osterloh *et al.*, 1996; Drew *et al.*, 1980; Schneider, 1997). Such heterometallic compounds are of current interest as models for the active sites of nickel-containing metalloenzymes (Cammack, 1988).

Crystals of the title compound, (I), consist of discrete (3,7-diethyl-3,7-diazanonane-1,9-dithiolato-*S*,*N*,*N*′,*S*′)-nickel(II) molecules that belong to the point group C_s in their idealized forms. There is no evidence for intermolecular Ni···S or Ni···Ni interactions. The diethyl-3,7-diazanonane-1,9-dithiolate ligand is bonded to the Ni^{II} centre in a tetradentate manner. The coordination of nickel can be described as distorted square planar with significant deviation from planarity, as indicated by the average of all six valence angles (117.2°). The arrangement of the N_2S_2 donor set in a *cis*-type fashion leads to X—Ni—X valence angles that differ by 13.8° on going from X = N to X = S. The N and S atoms define a very flat tetrahedron around the Ni atom. As a result, the planes containing the NiS_2 and NiN_2 fragments subtend an angle of 6.95 (2)°. Due to the tetrahedral distortion of the coordination geometry, the sum of the four acute valence angles around Ni exceeds 360° (experimental value 360.4°). Very similar angular distortions have been observed in the chemically related complex (3,7-dimethyl-3,7-diazanonane-1,9-dithiolato)nickel(II) (Colpas *et al.*, 1990), where the average valence angle of nickel is 117.6°.



(I)

The metal–ligand arrangement is a polycyclic system with five- and six-membered chelate subunits. The six-membered chelate ring is formed by coordination of the propylene-bridged N-donor functions to the Ni centre, and it adopts the chair conformation. The basal plane of the chair is defined by N1, N2, C3 and C5, which are exactly coplanar [within 0.0001 (9) Å], in accordance with the idealized symmetry properties of the molecule. Atoms C4 and Ni are displaced in opposite directions from this plane by 0.722 (2) and 0.730 (2) Å, respectively. Both ethyl groups are on the same side of the plane, resulting in different configurations of the N atoms [N1(*S*) and N2(*R*)]. The title compound thus appears in the *meso* form. The two five-membered chelate rings that contain the S-donor functions adopt envelope-like arrangements with C2 and C6 in the flap positions. The Ni—S and Ni—N bonds (mean bond distances 2.174 and 2.018 Å, respectively) are unexceptional in length and comparable to those of related complexes in the literature (Colpas *et al.*, 1990; Mills *et al.*, 1990).

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