

Synthesis and characterization of two novel tetranuclear sodium ketoiminate complexes; structural evidence for formation of dative Na...F and Na-C (olefin) bonding interactions

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Treatment of fluorinated β -ketoiminate ligands MokeimH or AlkeimH with NaH in THF solution afforded the corresponding ketoiminatosodium complexes $[\text{Na}(\text{Mokeim})]_4$ **1** and $[\text{Na}(\text{Alkeim})]_4$ **2**, MokeimH = $(\text{CF}_3)\text{C}(=\text{O})\text{CH}=\text{C}(\text{CF}_3)\text{NH}(\text{CH}_2\text{CH}_2\text{OMe})$ and AlkeimH = $(\text{CF}_3)\text{C}(=\text{O})\text{CH}=\text{C}(\text{CF}_3)\text{NH}(\text{CH}_2\text{CH}=\text{CH}_2)$. These new complexes were characterized by spectroscopic methods, elemental analyses and X-ray diffraction studies. Complex **1** consists of a tetrameric Na_4O_4 cubane core arrangement, of which each sodium atom is surrounded by a tridentate ketoiminato ligand, two oxygen atoms from nearby ketoiminato ligands, and one or two weak Na...F dative interactions. The core structure of **2** is similar, but with formation of the uncommon allyl to sodium π interaction. The stabilization of this Na-C (olefin) bonding interaction is as effective as the Na-O (ether) dative bonding in **1** because **2** shows comparable thermal stability and even an enhanced volatility during sublimation.

As reported in several review articles, metal alkoxides and β -diketonates can be excellent precursors for the chemical vapor deposition of various metal and metal oxide thin film materials.¹ In order to seek more suitable CVD precursors, the corresponding fluorocarbon derivatives have been synthesized because of the greater volatility than that of their non-fluorinated hydrocarbon analogs.² This increased volatility may be due to the combination of strong interatomic repulsion between fluorine lone pairs and low polarizability of the C-F bonds. In addition, after the formation of the metal complexes, the existence of secondary intramolecular bonding interactions between fluorine substituents and electrophilic metal centers would further reduce the intermolecular attraction and thus improve relative volatility.

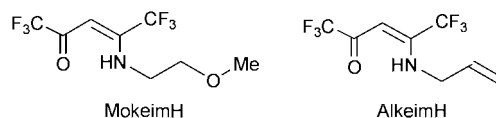
In this paper we report the synthesis of two new fluorine substituted ketoiminato sodium complexes. As these β -ketoiminate ligands are not only closely related to β -diketonate ligands,³ but also possess one more donor functional group that can co-ordinate to the central sodium cation, the structural identification of the new complexes should present important evidence for observed volatility enhancement with respect to the analogous non-fluorinated alkali metal acetylacetonate complexes, the volatilities of which are much lower because of the insufficient number of donor atoms and due to the formation of the zigzag polymeric chain structure.⁴ In addition, for the complex of the allyl substituted derivative, we observed for the first time a novel allylic carbon-carbon double bond to sodium interaction, which is unambiguously revealed by single-crystal X-ray diffraction.

Experimental

General information and materials

All operations were carried out under nitrogen using oven-dried glassware. Solvents were freshly distilled over the appro-

ropriate drying reagents. Ketoimine ligands were prepared from hexafluoroacetylacetone and the appropriate primary amines using literature methods.⁵ The abbreviations used for the β -ketoiminate ligands are as follows: MokeimH = $(\text{CF}_3)\text{C}(=\text{O})\text{CH}=\text{C}(\text{CF}_3)\text{NH}(\text{CH}_2\text{CH}_2\text{OMe})$ and AlkeimH = $(\text{CF}_3)\text{C}(=\text{O})\text{CH}=\text{C}(\text{CF}_3)\text{NH}(\text{CH}_2\text{CH}=\text{CH}_2)$. The ¹H, ¹³C and ¹⁹F NMR spectra



were recorded on a Bruker AM-400 or AMX-300 instrument, mass spectra on a JEOL SX-102A instrument operating in electron impact (EI) mode. TGA Studies were performed on a Seiko SSC 5000 instrument at a heating rate of 10 °C min⁻¹ under 100 cm³ min⁻¹ flowing nitrogen. Elemental analyses were made at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan, Taiwan.

Syntheses

Complex 1. Sodium hydride (0.099 g, 4.14 mmol) was suspended in 20 mL of diethyl ether. To this was added dropwise 1.0 g of MokeimH (3.77 mmol) in ether (10 mL). The mixture was stirred for 4 h until evolution of gas had ceased. Then the solution was filtered, and the solvent removed *in vacuo* to give a light yellow oily material. Recrystallization from hexane (40 mL) at -20 °C afforded 0.82 g of colorless crystalline solid $[\text{Na}(\text{Mokeim})]_4$ **1** (2.84 mmol, 76%). MS (EI, 70 eV, L = C₈H₈F₆NO₂); observed (calculated) {relative abundance} [assignment]: *m/z* 1148 (1148) {0.5} $[(\text{NaL})_4]$, 884 (884) {20.9} $[(\text{NaL})_3 + \text{Na}]$, 861 (861) {0.84} $[(\text{NaL})_3]$, 597 (597) {38.73} $[(\text{NaL})_2 + \text{Na}]$, 574 (574) {33.16} $[(\text{NaL})_2]$, 310 (310) {100} $[(\text{NaL}) + \text{Na}]$, 287 (287) {53.3} $[(\text{NaL})]$, 265 (265) {11.6} [L], 220 (220) {66.4} [L - C₂H₅O], 196 (196) {39.6} [L - CF₃]

Table 1 NMR Data of the ketoimine ligands and their sodium complexes

Compound	^1H , δ (J/Hz)	^{13}C , δ (J/Hz)
MokeymH ^a	2.93 (t, 2 H, $^3J_{\text{HH}} = 5.2$, NCH ₂), 3.08 (t, 2 H, $^3J_{\text{HH}} = 5.2$, OCH ₂), 3.12 (s, 3 H, OCH ₃), 5.98 (s, 1 H, CH), 10.85 (br, m, 1 H, NH)	180.7 (q, $^2J_{\text{CF}} = 34.5$, CO), 154.1 (q, $^2J_{\text{CF}} = 32.1$, CN), 120.2 (q, $^1J_{\text{CF}} = 276.7$, CF ₃), 118.0 (q, $^1J_{\text{CF}} = 286.7$, CF ₃), 86.6 (CH), 70.4 (NCH ₂), 59.2 (OCH ₃), 45.4 (OCH ₂)
1 ^b	3.16 (t, 2 H, $^3J_{\text{HH}} = 4.4$, OCH ₂), 3.19 (s, 3 H, OCH ₃), 3.75 (br, m, 2 H, NCH ₂), 5.96 (s, 1 H, CH)	164.6 (q, $^2J_{\text{CF}} = 28.3$, CO), 156.3 (q, $^2J_{\text{CF}} = 24.6$, CN), 122.5 (q, $^1J_{\text{CF}} = 283$, CF ₃), 119.6 (q, $^1J_{\text{CF}} = 287$, CF ₃), 87.2 (CH), 73.8 (NCH ₂), 59.7 (OCH ₃), 52.8 (OCH ₂)
AlkeimH ^a	3.40 (br, m, 2 H, NCH ₂), 4.97 (d, 1 H, $^3J_{\text{HH}} = 11.0$, =CH ₂), 5.03 (d, 1 H, $^3J_{\text{HH}} = 6.6$, =CH ₂), 5.40 (m, 1 H, CH=CH ₂), 5.98 (s, 1 H, CH), 10.55 (br, s, 1 H, NH)	180.5 (q, $^2J_{\text{CF}} = 35.0$, CO), 154.6 (q, $^2J_{\text{CF}} = 32.0$, CN), 119.8 (q, $^1J_{\text{CF}} = 276.0$, CF ₃), 117.2 (q, $^1J_{\text{CF}} = 286.0$, CF ₃), 132.4 (CH=CH ₂), 119.0 (CH=CH ₂), 86.8 (CH), 48.0 (NCH ₂)
2 ^b	4.14 (d, 2 H, $^3J_{\text{HH}} = 6.0$, NCH ₂), 5.21 (d, 1 H, $^3J_{\text{HH}} = 17.6$ Hz, =CH ₂), 5.27 (d, 1 H, $^3J_{\text{HH}} = 10.3$ Hz, =CH ₂), 5.88 (m, 1 H, CH=CH ₂), 5.93 (s, 1 H, CH)	163.3 (q, $^2J_{\text{CF}} = 28.3$, CO), 156.9 (q, $^2J_{\text{CF}} = 25.0$, CN), 122.4 (q, $^1J_{\text{CF}} = 281$, CF ₃), 119.4 (q, $^1J_{\text{CF}} = 281$, CF ₃), 136.6 (CH=CH ₂), 119.7 (CH=CH ₂), 88.3 (CH), 55.3 (NCH ₂)

^a For spectrum recorded in benzene-d₆. ^b For spectrum recorded in toluene-d₈.

and 69 (69) {20.8} [CF₃]. ¹⁹F NMR (305.5 MHz, toluene-d₈): δ -80.3 (s, 3F) and -93.2 (s, 3F). mp = 218 °C. Calc. for C₈H₈F₆NNaO₂: C, 33.46; H, 3.09; N, 4.88. Found: C, 33.58; H, 2.81; N, 5.00%.

Complex 2. Sodium hydride (0.106 g, 4.45 mmol) was suspended in 20 mL of diethyl ether. To this was added dropwise 1.0 g of AlkeimH (4.04 mmol) in ether (10 mL). The mixture was stirred for 4 h until evolution of gas had ceased. Then the solution was filtered, and the solvent removed *in vacuo* to give a light yellow solid. Recrystallization from hexane (30 mL) at -20 °C afforded 0.65 g of colorless crystalline solid [Na-(Alkeim)]₄ **2** (2.42 mmol, 60%). MS (EI, 70 eV, L = C₈H₆F₆NO); observed (calculated) {relative abundance} [assignment]: *m/z* 1079 (1076) {0.9} [(NaL)₄], 830 (830) {15.4} [(NaL)₃ + Na], 810 (807) {2.8} [(NaL)₃], 561 (561) {49.0} [(NaL)₂ + Na], 541 (538) {10.2} [(NaL)₂], 293 (292) {69.6} [(NaL) + Na], 270 (269) {15.7} [(NaL)], 247 (247) {39.2} [L], 207 (207) {19.5} [L - C₂H₄], 178 (178) {76.4} [L - CF₃] and 69 (69) {100} [CF₃]. ¹⁹F NMR (305.5 MHz, toluene-d₈): δ -81.2 (s, 3F) and -93.8 (s, 3F). mp = 133 °C. Calc. for C₈H₆F₆NNaO: C, 35.70; H, 2.25; N, 5.20. Found: C, 35.43; H, 2.67; N, 5.10%.

X-Ray crystallography

The X-ray diffraction measurement on complex **1** was carried out on a Nonius CAD-4 diffractometer at room temperature. Data were collected using a standard θ - 2θ scan technique with fixed backgrounds at each extreme of the scan. Three standard reflections (4, 0, 0; 0, 6, 0; 0, 0, 7) were monitored every 3600 s, and their intensities decayed 20% during the course of data collection. Single crystal X-ray diffraction data of complex **2** were measured on a Seimens SMART CCD diffractometer. The olefinic carbon atoms C(10) and C(26) were found to display a disorder over two sites, and successfully refined with occupancy factors of 60 and 40%, respectively.

The crystallographic refinement parameters of complexes **1** and **2** are summarized in Table 2, selected bond distances and angles in Tables 3 and 4, respectively.

CCDC reference number 186/1762.

See <http://www.rsc.org/suppdata/dt/a9/a908328f/> for crystallographic files in .cif format.

Results and discussion

Synthesis and characterization

The synthesis of the sodium ketoiminate complex [Na-(Mokeym)]₄ **1** was achieved by deprotonation of the ketoimine MokeymH with an excess of sodium hydride in diethyl ether at room temperature. The unchanged sodium hydride was first removed by filtration under nitrogen. Then, evaporation of solvent under vacuum and subsequent recrystallization in

hexane produced **1** as colorless crystals in 76% yield. The related allyl substituted derivative complex [Na(Alkeim)]₄ **2** was prepared in 60% yield using a similar procedure.

These complexes are water sensitive and soluble in polar organic solvents such as THF, diethyl ether, acetonitrile and acetone, but exhibit only limited solubility in non-polar hydrocarbon solvents like toluene and hexane at lower temperature. As a result, recrystallization was best carried out in the minimum amount of hexane at -20 °C, giving colorless crystalline solids which are sufficiently pure for most analytical purposes.

Complexes **1** and **2** were characterized by various spectral methods. EI Mass analysis (70 eV) shows the formation of a series of sodium-containing cluster cations with approximate molecular formula Na₄L₄⁺, Na₄L₃⁺, Na₃L₂⁺, Na₂L₂⁺, Na₂L⁺ and NaL⁺, L = ketoiminate ligand. In each case, the dinuclear Na₂L⁺ cation fragment is assigned to be the most abundant parent ion, whereas the peak with the highest *m/z* value, corresponding to a tetranuclear aggregate Na₄L₄⁺, is also observed, although the relative intensity is much smaller. This Na₄L₄⁺ ion was subsequently assigned as the molecular ion, as upon reducing the electron ionization energy from 70 to 12 eV its relative intensity increases substantially with respect to those of other sodium-containing ions. The ions Na₄L₃⁺, Na₃L₂⁺ and Na₂L⁺, in which the number of metals is greater than that of the ligand, have also been observed during mass spectrometric analysis of the complex Na(thd), thd = 2,2,6,6-tetramethylheptane-3,5-dionate.⁶

The ¹H, ¹³C and ¹⁹F NMR spectra showed only one set of the expected NMR signals deriving from the ketoiminate ligand and are consistent with formation of the sodium complexes. Of particular interest are the ¹H and ¹³C NMR chemical shifts due to the CH₂CH₂OMe fragment in **1** and the CH₂CH=CH₂ pendant in **2**, which all show substantial downfield movement from those of the "free" ligand (Table 1), suggesting that they possess some kind of bonding interaction with the electro-positive sodium cation. However, as these spectroscopic data did not allow us unambiguously to establish the exact bonding nature between the fluorinated ketoiminate ligand and the sodium metal cation, single crystal X-ray diffraction studies were performed on both compounds to determine their exact molecular structure.

Compound **1** forms a tetranuclear aggregate with a distorted Na₄O₄ cubane configuration, of which three oxygens are co-ordinated intramolecularly to four different sodium atoms (Fig. 1). The Na-O distances within the Na₄O₄ cube range from 2.287(5) to 2.468(5) Å. This is comparable to those previously observed in complexes [Na(HFIP)]₄, [Na(TFTB)]₄ and [Na(PFTB)]₄ (2.298 Å average), HFIP = hexafluoroisopropoxide, TFTB = trifluoro-*tert*-butoxide, PFTB = perfluoro-*tert*-butoxide.⁸

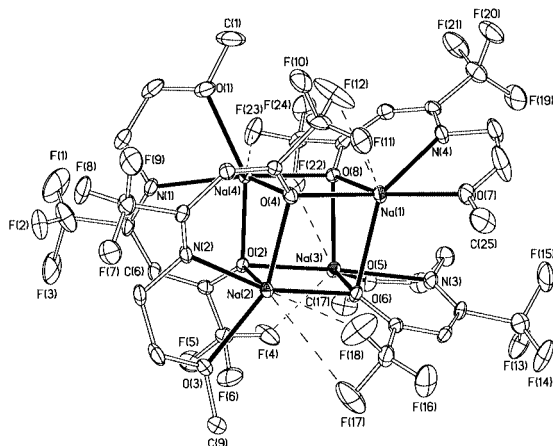
Each sodium atom is co-ordinated by a tridentate ketoiminate ligand and the overall co-ordination sphere consists of

Table 2 X-Ray structural data of complexes **1** and **2**

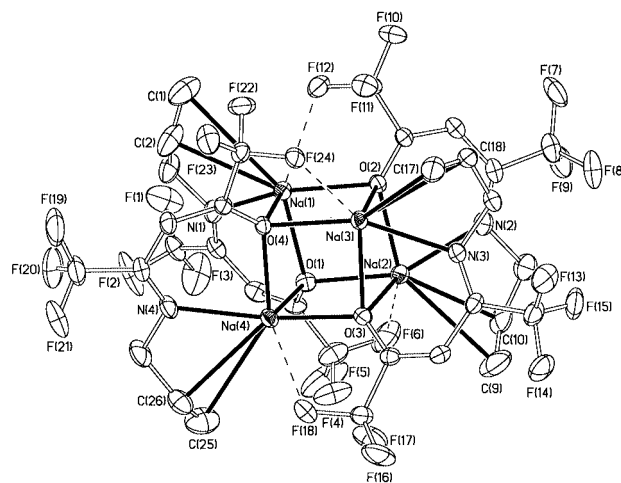
	1	2
Formula	C ₃₂ H ₃₂ F ₂₄ N ₄ Na ₄ O ₈	C ₃₂ H ₂₄ F ₂₄ N ₄ Na ₄ O ₄
<i>M</i>	1148.54	1076.51
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.402(3)	13.6765(2)
<i>b</i> /Å	13.806(3)	21.6103(2)
<i>c</i> /Å	18.819(5)	16.0552(3)
<i>a</i> °	83.85(4)	
<i>β</i> °	77.08(4)	113.605(1)
<i>γ</i> °	70.04(3)	
<i>V</i> /Å ³	2474.5(11)	4348.1(1)
<i>Z</i>	2	4
<i>T</i> /K	295	150
<i>μ</i> (Mo-Kα)/cm ⁻¹	1.96	2.11
No. data in refinement	6452	8771 with <i>R</i> _{int} = 0.0265
No. parameters	649	96, 632
Final <i>R</i> 1, <i>wR</i> 2 indices (<i>I</i> ≥ 2σ(<i>I</i>))	0.072, 0.211	0.056, 0.122

Table 3 Selected bond distances (Å) and angles (°) of complex **1** (e.s.d.s in parentheses)

Na(1)–O(4)	2.419(4)	Na(1)–O(6)	2.468(5)
Na(1)–O(8)	2.287(5)	Na(2)–O(2)	2.404(5)
Na(2)–O(4)	2.363(5)	Na(2)–O(6)	2.345(5)
Na(3)–O(2)	2.429(4)	Na(3)–O(6)	2.329(5)
Na(3)–O(8)	2.390(5)	Na(4)–O(2)	2.288(5)
Na(4)–O(4)	2.363(5)	Na(4)–O(8)	2.389(5)
Na(1)–N(4)	2.465(6)	Na(1)–O(7)	2.349(6)
Na(1)···F(11)	3.22(1)	Na(1)···F(12)	3.05(1)
Na(2)–N(2)	2.426(6)	Na(2)–O(3)	2.385(5)
Na(2)···F(17)	3.31(1)	Na(2)···F(18)	2.88(1)
Na(3)–N(3)	2.464(6)	Na(3)–O(5)	2.424(6)
Na(3)···F(4)	2.59(1)	Na(3)···F(22)	3.14(1)
Na(4)–N(1)	2.402(6)	Na(4)–O(1)	2.341(6)
Na(4)···F(23)	2.65(1)		
O(7)–Na(1)–O(8)	147.5(2)	O(3)–Na(2)–O(4)	147.2(2)
O(5)–Na(3)–O(6)	138.5(2)	O(1)–Na(4)–O(2)	151.9(2)
O(7)–Na(1)–O(4)	123.4(2)	O(7)–Na(1)–O(6)	103.9(2)
O(7)–Na(1)–N(4)	71.5(2)	O(8)–Na(1)–O(4)	87.0(2)
O(8)–Na(1)–O(6)	91.5(2)	O(8)–Na(1)–N(4)	77.1(2)

**Fig. 1** An ORTEP⁷ drawing of the molecular structure of complex **1** with thermal ellipsoids drawn at the 30% probability level.

four oxygen atoms and one nitrogen atom arranged in a distorted trigonal bipyramidal geometry. The oxygen O(8) of the ketoiminato ligand seems to occupy the axial sites with angle O(7)–Na(1)–O(8) 147.5(2)°, showing a great deviation from linearity, while the nitrogen atom N(4) and O(4) and O(6) from neighboring ketoiminato ligands reside on the equatorial plane with the bond angles to the axial Na(1)–O(7) or Na(1)–O(8)

**Fig. 2** An ORTEP drawing of the molecular structure of complex **2**. Details as in Fig. 1.

vectors ranging from 71.5(2) to 123.4(2)° (Table 3). All these unusually large distortions are obviously caused by the geometrical constraint imposed by the ketoiminato ligand. In addition, the co-ordination sphere of sodium is further augmented by several intramolecular Na···F contacts which are less than the sum of the sodium and fluorine van der Waals radii, *r*_{VDW(Na)} (2.30 Å) + *r*_{VDW(F)} (1.50 Å) = 3.80 Å.⁹

For these Na···F interactions, the sodium atoms Na(1), Na(2) and Na(3) each possesses one short and one long Na···F distance from the adjacent trifluoromethyl groups within the range of 2.59(1)–3.31(1) Å. To the fourth sodium atom Na(4), only one Na···F distance of 2.65(1) Å is observed, consistent with the existence of a single Na···F bonding interaction. We speculate that the key function of the Na···F interactions is to compensate for the co-ordinative unsaturation of the sodium metal centers, although we cannot fully eliminate steric origins. The latter is supported by the observation of several Na₄O₄ cubane cluster structures in which the co-ordination number of the Na is even less than that observed here, due to steric protection by relatively bulky substituents.¹⁰ Moreover, Caulton and co-workers⁸ have observed several weak Na···F contacts of 2.774(5)–3.726(5) Å in [Na(TFTB)]₄ and 2.497(4)–3.747(4) Å in [Na(PFTB)]₄, respectively. A related type of bonding interaction has been observed in a few fluorinated alkoxide alkali and alkaline earth metal complexes.¹¹ For example, the complexes Na₂Zr(OCH(CF₃)₂)₂·C₆H₆,^{8a} Rb₂Na(hfac)^{11a} and Ba[Cu(OCMe(CF₃)₂)₂]₃^{11c} exhibit Na···F, Rb···F and Ba···F interactions in the ranges 2.718(4)–3.413(3), 2.80–3.35 and 2.94–3.14 Å, respectively.

In the crystal structure of complex **2** (Fig. 2) the gross Na₄O₄ core structure seems to be related to that of **1**. The bonding parameters within the Na₄O₄ distorted cubane core are essentially identical, except that all four Na–O vectors of the [Na(Alkeim)] monomers are now arranged in a parallel orientation with a *D*₂ point group symmetry which is in sharp contrast to the eclipse configuration of a *S*₄ symmetry observed for **1** (Fig. 3). This difference is probably caused by changing the pendant group of the ketoiminato ligand from methoxyethyl to the slightly shorter allyl, but no satisfactory explanation can be given. In addition to the single Na···F dative interaction from the adjacent CF₃ group, the allylic carbon–carbon double bond was also found to co-ordinate to each Na atom, showing a similar donor capability with respect to that of the CH₂–CH₂OMe group in **1**. The average Na–C (olefin) distance is 3.122 Å, while the average inner Na–C (olefin) distances (≈3.02 Å) is slightly shorter than the average outer Na–C (olefin) distance (≈3.23 Å). Despite this obvious distinction, these Na–C (olefin) distances are all well within the range

Table 4 Selected bond distances (Å) of complex **2** (e.s.d.s in parentheses)

Na(1)–O(1)	2.328(2)	Na(1)–O(2)	2.395(2)
Na(1)–O(4)	2.378(3)	Na(2)–O(1)	2.396(2)
Na(2)–O(2)	2.280(2)	Na(2)–O(3)	2.363(2)
Na(3)–O(2)	2.349(2)	Na(3)–O(3)	2.378(2)
Na(3)–O(4)	2.385(2)	Na(4)–O(1)	2.357(2)
Na(4)–O(3)	2.341(2)	Na(4)–O(4)	2.323(2)
Na(1)–N(1)	2.453(3)	Na(1)–C(1)	3.333(5)
Na(1)–C(2)	2.968(4)	Na(1)···F(12)	2.648(2)
Na(2)–N(2)	2.411(2)	Na(2)–C(9)	3.134(5)
Na(2)–C(10)	2.913(6)	Na(2)···F(6)	2.746(4)
Na(3)–N(3)	2.455(3)	Na(3)–C(17)	3.132(4)
Na(3)–C(18)	3.227(3)	Na(3)···F(24)	2.470(2)
Na(4)–N(4)	2.428(3)	Na(4)–C(25)	3.315(3)
Na(4)–C(26)	2.951(6)	Na(4)···F(18)	2.686(3)

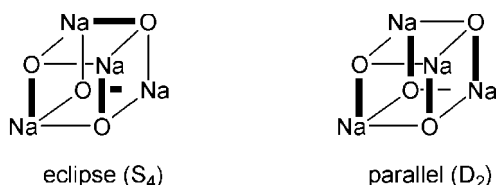


Fig. 3 Schematic representation of tetrameric Na_4O_4 aggregates in which each of the monomeric units is visualized by a bold Na–O vector.

for the benzene complex $\text{Na}_2\text{Zr}(\text{OCH}(\text{CF}_3)_2)_6(\text{C}_6\text{H}_6)_2$, which possesses a benzene to sodium donor interaction (2.980(4)–3.215(4) Å),^{8a} and are slightly longer than the Na–C (olefin) distances of several discrete cyclopentadienylsodium complexes $[\text{NaCp}_2]^+$ (mean value ≈ 2.61 Å)¹² and zigzag polymer of the compound $[\text{NaCp}(\text{tmeda})]_n$ (2.83(1)–3.03(1) Å).¹³ Thus, the data presented in this article provide a new type of bond distance between the non-conjugated olefinic fragment and the cationic sodium center.

Moreover, the longest inner Na–C (olefin) distance of 3.227(3) Å occurs between the atoms Na(3) and C(18). This unusual lengthening may be due to the ineffective competition with that of the strongest $\text{Na}\cdots\text{F}$ dative interaction involving the same sodium atom, $\text{Na}(3)\cdots\text{F}(24)$ 2.470(2) Å. We believe that the latter is expected to cause a large reduction of the electrophilicity of the sodium cation, which would reduce the demand for extensive allyl carbon–carbon double bond to sodium dative bonding.

Volatility studies

Both compounds **1** and **2** can be sublimed with little decomposition at 120–140 °C under a reduced pressure of 400 mTorr. This observation is consistent with the X-ray structural analysis that there was no significant intermolecular attractive interaction between the Na_4L_4 aggregates. To obtain more quantitative information on the relative volatility, studies were performed on freshly sublimed samples using a thermogravimetric analyzer under a nitrogen atmosphere. For complex **1** no change of weight was observed until the temperature was raised to around 170 °C. Then a sudden loss of weight was observed near 240 °C and a small residual weight loss of 9% up to 500 °C (Fig. 4). We speculate that the rapid loss of weight is caused by both sample evaporation and thermally induced decomposition. The latter is supported by the observation of rapid evolution of gas and darkening of the sample at the melting point.

In contrast, complex **2** showed a much lower onset temperature (140 °C) for sample evaporation and underwent a similar type of sudden weight loss at a much lower temperature near 150 °C. As the degree of fluorination as well as the structural complexity are about the same, the reduced molecular weight for **2** (1076.5 vs. 1148.6) and the change in alignment of the monomer within the Na_4O_4 aggregate are probably the two key factors in producing the observed volatility enhancement.

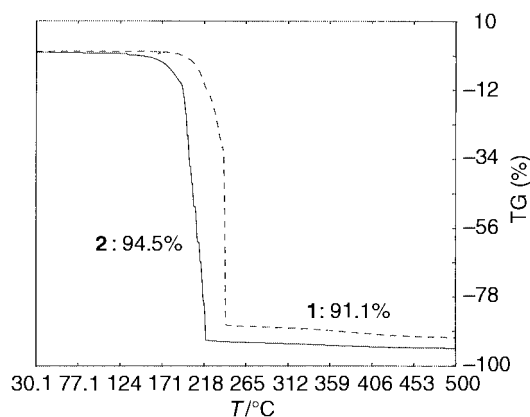


Fig. 4 TGA Diagram of complexes **1** and **2** under N_2 with a temperature ramp of $10^\circ\text{C min}^{-1}$.

General comments

Two sodium ketoiminate compounds have been prepared, and their structural and spectroscopic properties studied. These compounds exist as tetranuclear aggregates, which are typical for alkali metal alkoxide complexes.¹⁴ We suspect that such a tetrameric aggregated structure is maintained intact upon dissolution in hydrocarbon solvents, such as benzene or toluene, as all the ^1H and ^{19}F NMR spectra show no noticeable change of spectral pattern at temperatures between –90 and 25 °C. In addition, the formation of several distinct Na–O (ether) and $\text{Na}\cdots\text{F}$ interactions for **1**, and Na–O (ether) and Na–C (olefin) interactions for **2**, were observed. Similar to that of the Na–O (ether) interactions in **1**, the intramolecular Na–C (olefin) dative bonding in **2** has provided effective reduction of the unsaturation on the sodium cation. This observation is best reflected in its excellent thermal stability under an inert atmosphere.

Moreover, greater volatility has been noted as both complexes can be sublimed without noticeable decomposition at 120 and 140 °C, respectively, at a reduced pressure of 400 mTorr. It is unlikely that complexes **1** and **2** will maintain this tetrameric framework during sublimation as their large molecular masses of 1148.6 and 1076.5 would seem to require severe conditions for this. Thus, it is possible that a process involving facile and reversible dissociation of the tetranuclear aggregate into smaller fragments, such as mononuclear $[\text{NaL}]$, dinuclear $[\text{NaL}]_2$, or even trinuclear $[\text{NaL}]_3$ species, may be the main pathway for effective solid to vapor transport at higher temperatures. The detection of a complete series of smaller sodium-containing cluster cations during the mass spectral analysis provided strong support to this possibility.

Finally, the high volatility of these two complexes makes them optimum precursors for growing sodium fluoride thin films by chemical vapor deposition.¹⁵

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