DALTON
FULL PAPER

A novel example of self-assembly in lanthanide chemistry: synthesis and molecular structure of $[Na(EtOH)_6][Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8\{\mu\text{-}\eta^2\text{-}MeC(O)CHC(O)OEt\}_8\{\eta^2\text{-}MeC(O)CHC(O)OEt\}_8]$ †

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The reaction between yttrium nitrate pentahydrate and the sodium salt of allyl acetatoacetate afforded nonanuclear cluster anions $[Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8\{MeC(O)CHC(O)Z\}_{16}]^-$, the functional group Z being the initial allyl one $OCH_2CH{=}CH_2$ or an ethoxide depending on the experimental conditions.

The diversity of applications of hybrid organic–inorganic materials has motivated increasing interest in this class of materials.[1] Depending on the strategy used for their elaboration, hybrid materials of class I or of class II are obtained.[2] Materials of class II usually display better properties in terms of homogeneity, stability toward leaching, *etc.* but require the organic moiety to be covalently bonded to the inorganic network and thus the preparation of designed precursors.[3] If the hybrid materials are based on organic as well as inorganic networks inorganic precursors having polymerizable ligands in the metal co-ordination sphere are needed.[4] A large number of such derivatives have been developed for silicon, the functionality being introduced *via* a silicon–carbon bond.[5] The hydrolytic stability of the Sn–C bond has permitted tin derivatives to be obtained accordingly.[6] However, for most non-silicon systems and especially for transition metals, the functional group modifying the network properties needs to be introduced *via* non- or poorly reactive M–O bonds namely carboxylates, β-diketonates or related ligands. A number of derivatives with polymerizable ligands have been reported for tin,[7] titanium,[8] zirconium[9] and niobium.[10] The selected ligands are mainly acrylates, methacrylates, or β-ketoesterates such as allyl acetatoacetate (HAAA) or 2-(acetoacetoxy)ethyl methacrylate (HAAEMA). Allyl acetatoacetate was used to modify aluminium and zirconium alkoxides.[11] In the case of aluminium, copolymerization reactions with silicon derivatives were achieved. A zirconium oxohydroxide cluster $Zr_{10}(\mu\text{-}O)_6(\mu\text{-}OH)_4(O^nPr)_{18}(AAA)_6$ resulting from hydrolysis reactions could be structurally characterized.[12]

No derivatives based on such ligands have, to the best or our knowledge, been reported for yttrium or lanthanides.[13] Derivatives with unsaturated ligands are essentially based on enolates[14] or cyclopentadienyl type ligands with an unsaturated pendant arm.[15] We report herein the result of our investigations with allyl acetatoacetate.

Experimental

All reactions were achieved under an inert atmosphere using Schlenk tubes and vacuum line techniques. Solvents were dried and purified by distillation. Allyl acetatoacetate was dried over molecular sieves. The ^1H NMR spectra were run on a Bruker AC-200 spectrometer, FT-IR spectra as Nujol mulls on a Perkin-Elmer Paraggon 500 spectrometer. Analyses were obtained from the Centre de Microanalyses du CNRS.

Syntheses

$[Na(EtOH)_6][Y_9O_2(OH)_8\{MeC(O)CHC(O)OEt\}_{16}]$ 1. The salt Na(AAA) was obtained by treating 0.39 g (9.75 mmol) of NaOH dissolved in 20 ml of ethanol and 1.39 g (9.79 mmol) of HAAA in 15 ml of ethanol. After 1 h, a solution of 1.19 g (3.27 mmol) of $Y(NO_3)_3\cdot 5H_2O$ in 10 ml of ethanol was added. Precipitation was observed. Filtration was achieved after 2 h. The filtrate was evaporated to dryness and the crude product redissolved in 8 ml of ethanol at reflux; 0.46 g (40%) of colorless needles of complex **1** were isolated at room temperature after 12 h. Found: C, 38.22; H, 5.45; Na, 0.76. Calc. for $C_{108}H_{188}NaO_{64}Y_9$: C, 38.93; H, 5.64; Na, 0.69%. FT-IR [cm^{-1}]: 3274m (νOH); 1735 (sh), 1645s, 1614s, 1551s, 1525s (νC=O, νC=C); 1415w, 1299w, 1264s; 1169s, 1093w, 1057m, 1014m, 965m, 858w (νC–O, νC–C); 784s, 602w, 562w, 458w, 405m, 363w (νM–O). ^1H NMR ($CDCl_3$, 20 °C): δ 1.1 [td, $J_t = 7.08$, $J_d = 2.07$ Hz, 38 H, Me of OEt], 1.2–1.4 [m, t, $J = 7.14$, 28 H, Me of OEt], 1.6 (s, 24 H, MeCO), 1.8 (s, 24 H, MeCO), 3.85–4.5 (m and q, $J_q = 7.1$, 36 H, OCH_2), 4.25 (q, $J = 7.14$ Hz, 8 H, OCH_2), 4.75 (s, 8 H, CH) and 5.0 (s, 8 H, CH).

$[Na(EtOH)_6][Y_9O_2(OH)_8\{MeC(O)CHC(O)OCH_2CH{=}CH_2\}_{16}]$ 2. The same procedure was applied to 0.36 g (8.95 mmol) of NaOH in 10 ml ethanol, 1.27 g (8.93 mmol) of HAAA in 5 ml ethanol and 1.84 g (5.03 mmol) of $Y(NO_3)_3\cdot 5H_2O$ in 10 ml ethanol. The filtrate was concentrated and cooled to −20 °C, giving parallelepipedic crystals of complex **2** (0.83 g, 45%) after 24 h. Found: C, 41.85; H, 5.14; Na, 0.63; Y, 21.20. Calc. for $C_{124}H_{188}NaO_{64}Y_9$: C, 42.26; H, 5.33; Na, 0.55; Y 22.70%. FT-IR [cm^{-1}]: 3270m (νOH); 1644s, 1615s, 1550s, 1514s (νC=O, νC=C), 1262s, 1167s, 1095w, 1058m, 995m, 932m, 919m (νC–O, νC–C); 783s; 600m, 560m, 455m, 404m, 361w (νM–O). ^1H NMR ($CDCl_3$, 20 °C): δ 1.1 [td, $J_t = 7.01$, $J_d = 3.7$ Hz, 18 H, Me of OEt], 1.6 (s, 24 H, MeCO), 1.8 (s, 24 H, MeCO), 4.0 (m, 12 H, OCH_2), 4.4 [m, 32 H, CH_2CH], 4.8 [m, 8 H, C(O)CHC(O)O], 5.2 [m, 48 H, $CH{=}CH_2$ and C(O)CH-C(O)O] and 5.7 [m, 16 H, $CH{=}CH_2$].

$[Na(EtOH)_6][Ln_9O_2(OH)_8\{MeC(O)CHC(O)OCH_2CH{=}CH_2\}_{16}]$ (Ln = Er 3 or Yb 4). Complexes **3** and **4** were obtained

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4127/

by using a procedure similar to that for **2**, giving 51% of pink crystals and 50% colorless crystal respectively. Complex **3**. Found: C, 35.02; H, 4.07; Er, 37.05; Na, 0.60. Calc. for $C_{124}H_{188}Er_9NaO_{64}$: C, 35.21; H, 4.44; Er, 36.59; Na, 0.54%. FT-IR [cm^{-1}]: 3282m (νOH); 1643s, 1615s, 1551s, 1519s (νC=O, νC=C); 1262s, 1167s, 1096w, 1060m, 998m, 932m (νC–O, νC–C); 795s; 600w, 560w, 460m, 405m, 370m (νM–O). Complex **4**. Found: C, 34.39; H, 4.05; Na, 0.50; Yb, 35.96. Calc. for $C_{124}H_{188}NaO_{64}Yb_9$: C, 34.76; H, 4.39; Na, 0.54; Yb, 36.38%. FT-IR [cm^{-1}]: 3260m (νOH); 1644s, 1614s, 1550s, 1519s (νC=O); 1263s, 1166s, 1096w, 1058m, 994m, 918m (νC–O, νC–C); 783s; 600w, 560w, 460m, 405m, 360m (νM–O).

All products were soluble in ethanol and toluene.

Crystallography of complex 1

Suitable crystals could only be obtained from the reaction medium. 13602 Data of which 12945 were unique were collected at room temperature. A decrease of 16% was observed in the intensities of two checked reflections during data collection and reflections were scaled accordingly. Some crystallographic information is given in Table 1. Computations were performed by using the PC version of CRYSTALS.[16] The structure was solved by direct methods (SHELXS 86).[17] 3728 Reflections ($F_o^2 > 3\sigma F_o^2$) used for the refinement by full-matrix least squares (585 variables). Only atoms with relatively small isotropic displacement parameters were anisotropically refined. Since most of the carbon atoms were not well located, hydrogen atoms were not introduced. Only some of the oxygen atoms were found around the sodium atom. Unfortunately many attempts to resolve this problem failed.

CCDC reference number 186/1700.

See http://www.rsc.org/suppdata/dt/1999/4127/ for crystallographic files in .cif format.

Results and discussion

Synthesis

Synthetic routes to yttrium and lanthanide derivatives with the unsaturated β-ketoester allyl acetoacetate (HAAA) were first evaluated under conditions similar to those reported for the synthesis of 2,2,6,6-tetramethylheptane-3,5-dionates.[18] Yttrium nitrate pentahydrate was allowed to react in a 1 : 3 stoichiometry with the sodium salt of the allyl acetatoacetate in ethanol at room temperature. After filtration and elimination of sodium nitrate, crystallization of the crude product in hot ethanol afforded compound **1**. Its spectral data indicate a modification of the initial β-ketoesterate ligand. The main feature is the absence in the ^1H NMR spectrum of the multiplets around δ 5.95 and 5.2 characteristic of the $CH=CH_2$ groups as well as that at δ 4.5 attributed to the methylene protons in α position to the unsaturation. On the other hand, the spectrum shows signals due to ethoxide groups. These resonances are found at δ 3.95 and 4.25 for the CH_2 groups with an integration ratio between the resonances of the CH and the CH_2 (ethoxide) groups of 16 : 22. The FT-IR spectrum contained an absorption band due to hydroxyl vibrations at 3274 cm^{-1}. The absorption bands due to the νC=O stretching vibrations are observed at 1645, 1614, 1551 and 1525 cm^{-1} and are thus significantly shifted to lower wavenumbers with respect to those of the "free" ligand (1745 and 1719 cm^{-1}).

A different work-up, namely rapid crystallization at −20 °C directly from the reaction medium without thermal treatment after elimination of sodium nitrate, afforded compound **2**. By contrast with **1**, the allyl acetoacetate ligands appear unmodified in **2**. Indeed, the ^1H NMR spectrum shows multiplets at δ 5.2 and 5.7 (integration 3 : 1) attributed respectively to the CH_2 (overlapping with the CH of the chelate ring) and the CH groups of the unsaturated moiety. On the other hand, resonances are found at δ 4.0 for CH_2 of ethoxide groups with an integration ratio of 12 : 16 [OEt : $CH=CH_2$]. The FT-IR spectrum of **2** is similar to that of **1** since the absorption bands due to the νC=C stretching are obscured by those due to the C=O groups at 1644 and 1615 cm^{-1}. Nevertheless compounds **1** and **2** can be differentiated by their IR pattern but in the 900–950 cm^{-1} region. Comparison of the spectra shows that loss of the C=C double bond of the β-ketoesterate ligand results in the disappearance of the absorption bands at 919 and 932 cm^{-1}. Erbium and ytterbium compounds, **3** and **4** respectively, were isolated by rapid crystallization using the procedure for the synthesis of **2**. Absorption bands at 932 and 918 cm^{-1} were observed in their FT-IR spectra supporting the presence of the allyl functionality, whereas their paramagnetic nature precluded characterization by ^1H NMR. Thus, FT-IR as well as analytical data are in favour of a formulation $[Na(EtOH)_6][M_9O_2(OH)_8\{MeC(O)CHC(O)OCH_2CH=CH_2\}_{16}]$ (M = Yb or Er).

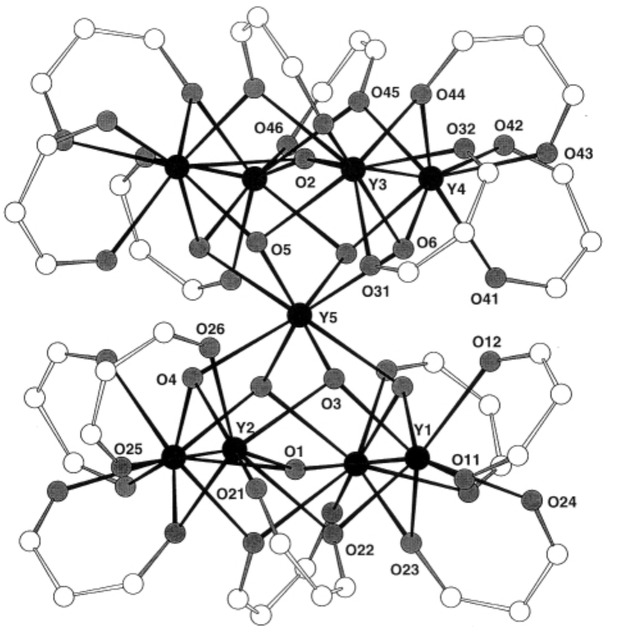


Fig. 1 Molecular structure of the anion of compound **1** showing the atom numbering scheme. The substituents (Me and OEt) have been omitted for clarity; they are linked to the carbon atoms close to the metal and the peripheral one respectively.

Molecular structure of $[Na(EtOH)_6][Y_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8\{\mu\text{-}\eta^2\text{-}MeC(O)CHC(O)OEt\}_8\{\eta^2\text{-}MeCOCHC(O)OEt\}_8]$

The identity of compound **1** was established by X-ray diffraction (Fig. 1). It is actually an ionic species based on a nonanuclear anion associated to a $Na(EtOH)_6^+$ which acts as a discrete counter ion. The surrounding of the sodium atom could only be poorly defined and the structure is thus only partially reported here. The nonanuclear anion can be seen as two square pyramidal pentanuclear units assembled *via* the apical metal center. The basic structural pentanuclear units are related to the Y_5O_{14} core of $[Y_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(OR)_5]$[19] (R = Pr^i) although one can notice some differences. The presence of the bidentate β-ketoesterate ligands increases the co-ordination number of the basal (peripheral) yttrium atoms to eight. The same co-ordination number is observed for Y(5) corresponding to the junction of the elementary building blocks. However, the Y(5) center displays a square antiprismatic geometry while the other yttrium atoms have a surrounding corresponding to a distorted dodecahedron. The most striking feature is the presence of β-ketoesterate ligands MeC(O)-CHC(O)OEt different from the initial allyl acetatoacetate. These ligands show two types of co-ordination behaviour: eight are terminal-chelating whereas eight others are bridging-chelating connecting the peripheral metal atoms. The Y–O

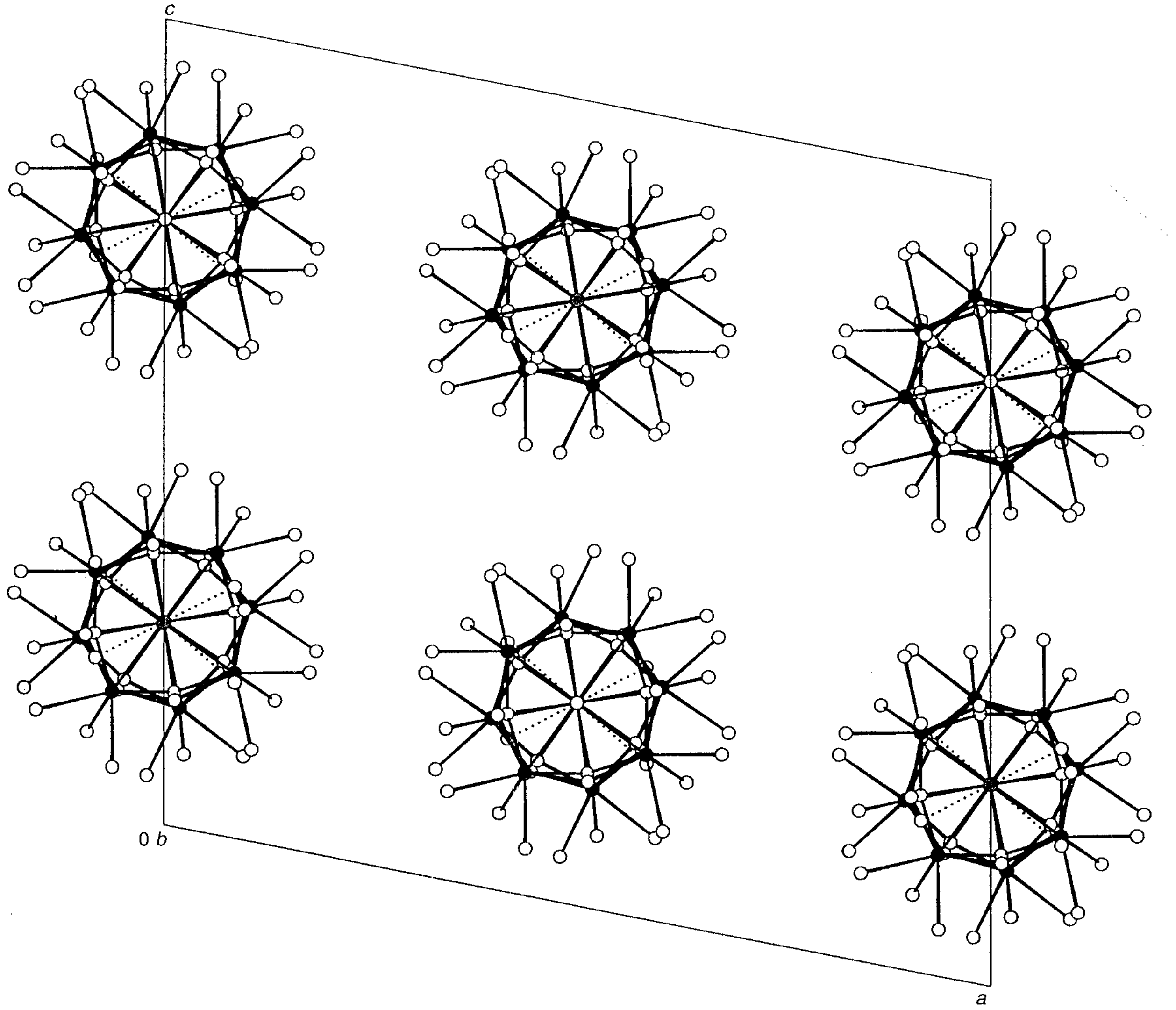


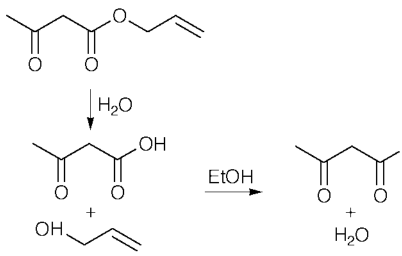
Fig. 2 Packing of compound **1** along the *ac* plane showing the symmetry of the nonanuclear anion. Dotted lines correspond to the bonding between Na and EtOH.

bond lengths spread over the range 2.27(1) to 2.554(3) Å and follow the order Y–η^2-OCMeCHC(O)OEt ≈ Y–μ_3-OH < Y–μ-OCMeCHC(O)OEt < Y–μ_4-O. The hydroxo ligands are trigonal and cap the various faces of the square pyramids. The yttrium–hydroxo bond distances are in agreement with the values reported for $[Y_4(\mu_3\text{-}OH)_2(acac)_{10}]$.[20] The Y···Y distances range from 3.560(3) to 3.680(3) Å, longer than observed for $[Y_5O(OPr^i)_{13}]$ [3.30(1)–3.47(1) Å].[19] The same observation applies to the yttrium–oxo bond distances, 2.54(3) *vs.* 2.35 Å (average). The distances between Y(5) and the oxo ligands are longer (average 2.92(2) Å). The oxo ligand O(1) is thus essentially of type μ_4 and planar. A planar μ_4-oxo ligand was also observed for instances for $[Er_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(thd)_{10}]$ (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione), a by-product of the synthesis of $Er(thd)_3$.[21] The structure is highly symmetrical (Fig. 2) and no intermolecular interactions were found in the solid state. The number of alcohol molecules of the $Na(EtOH)_6$ cation was determined by ^1H NMR and analytical data, since only some of the oxygens could be located by X-ray diffraction due to disorder phenomena (Na–O distances of 2.30 and 2.70 Å). The presence of alternative ligands such as water molecules around sodium was excluded on the basis of the NMR spectra. These observations are in agreement with the literature data, sodium being essentially either four-[22] or six-co-ordinate.[23,24]

The various compounds were obtained in reasonable yields (≈45%). The modification of the initial allyl acetatoacetate ligand, actually by a transesterification reaction, is favoured by the basicity of the reaction medium. A new β-ketoesterate ligand MeC(O)CHC(O)OEt is formed by reaction with the solvent ethanol, eqn. (1). The modification of the initial ligand is slow with respect to its co-ordination to the metal and continues to proceed during the isolation of the lanthanide species. The oxocluster anion appears more stable than neutral species such as $Y(AAA)_3$ or $[Y_4(\mu_3\text{-}OH)_2(AAA)_{10}]$ for instance. Eight-co-ordination has been observed for yttrium, especially when non-bulky β-diketonates such as acetylacetonate are present in the co-ordination sphere, *e.g.* $[Y_3(acac)_4(OC_2H_4OMe)_5]$[25] and $[M_4(OH)_2(acac)_{10}]$[20,26] (M = Y or Nd).

Table 1 Crystal data for $[Na(EtOH)_6][Y_9O_2(OH)_8\{MeC(O)CHC(O)OEt\}_{16}]$

Formula	$C_{108}H_{188}NaO_{64}Y_9$
M	3354
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	24.484(4)
b/Å	26.086(4)
c/Å	23.553(3)
β/°	101.44(1)
V/Å^3	14744(4)
μ/cm^{-1}	36.06
Diffractometer	CAD4 Enraf-Nonius
Radiation	Mo-Kα (λ = 0.71069 Å)
T/K	298
R	0.0837
R′	0.0919



(1)

Although nonaclusters are less common than hexanuclear or octanuclear ones, a number of such clusters have been reported, *e.g.*. $Na_9(O^tBu)_9$,[27] $[Ti_9O_8(OPr^n)_4(CH_2CMeCO_2)_{16}]$,[28] $[M_9(OC_2H_4OMe)_{18}(HOC_2H_4OMe)_2]$ (M = Ca[29] or Cd[30]), $[Ni_9(\mu_3\text{-}OH)_2(chp)_{16}(MeCN)_2]$[31] (Hchp = 6-chloro-2-hydroxypyridine) and manganese derivatives.[32] They display quite different frameworks, cyclic for the titanium species, more compact structures for the others. The metal–oxygen core of the calcium and cadmium species for instance mimics a portion of the CdI_2 layer. The Ni_9 species is based on vertex and face-sharing adamantane units. Heteronuclear nonaclusters such as $[Al_3Nd_6(\mu_3\text{-}Cl)_6(\mu\text{-}Et)_9Et_5(OPr^i)_7]$[33] or $[Ln_4(\mu_4\text{-}O)(NHPh)_3(OSiMe_2NPh)_6Na_5(THF)_7]$[34] have been reported as well. For the latter, sodium atoms are linked to the nitrogens forming a second co-ordination sphere.

The formation of compound **1** corresponds to a novel example of "self-assembly" in yttrium and organolanthanide chemistry[35] for which tri-, tetra-, penta-,[13] hexa-,[19,36a] octa-,[37] deca-,[38] dodeca-[36b] and tetradeca-[39]nuclear clusters have been reported.

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