ChemComm

# Synthesis and crystal structure of $[IBa(OBu^t)_4\{Li(thf)\}_4(OH)]$: a mixed ligand heterometallic cluster with an unusual low coordination number for barium

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*Received (in Cambridge, UK) 12th July 2000, Accepted 5th October 2000*
*First published as an Advance Article on the web 25th October 2000*

**The reaction of $[BaI_2(thf)_5]$ with $LiOBu^t$ in THF in the presence of hydroxide yields a volatile mixed alkali and alkaine earth metal cluster with an unusually low coordination number for the alkaline earth cation; due to the presence of the alkoxide groups, the cluster is volatile at temperatures below 200 °C.**

Recently, many organolithium compounds have been structurally investigated, their structure being of interest for the elucidation of possible reaction mecanisms in organic metallation reactions. Thus, it has been shown that metallated organic compounds tend to form aggregated species in the solid state as well as in solution. For example, LiMe, NaMe and $MOBu^t$, M = Rb, K, form tetrahedral tetramers,[1,2] LiEt forms hexameric units[3] and $NaOBu^t$ has been shown to have one hexameric and one nonameric molecule in its structure.[4] $LiOBu^t$ forms a hexameric aggregate in the gas phase as well as in solution and the solid state.[5] We here describe the reaction of this compound with $[BaI_2(thf)_5]$ in THF which yields the mixed metal cluster $[IBa(OBu^t)_4\{Li(thf)\}_4(OH)]$ **1**.†

In our attempts to make alkaline earth metal cluster compounds in analogy to transition metal clusters, we use an alkaline earth metal halide and an alkali metallated organic compound in order to eliminate alkali halide and to enforce aggregation of the alkaline earth compound.[6] Herein, we report on the reaction of $BaI_2$ with $LiOBu^t$ in THF preceded by the synthesis and isolation of $LiOBu^t$.[5]

The reaction of 4 equiv. of $LiOBu^t$ dissolved in THF under partial hydrolysis or directly in the presence of LiOH with a THF-solution of 1 equiv. of $BaI_2$ containing $[BaI_2(thf)_5]$[7] at −20 °C yields colorless blocks of **1** [eqn. (1)], suitable for single crystal X-ray analysis.[8]

$$[BaI_2(thf)_5] + 4\,[Li(OBu^t)] + OH^- \longrightarrow [IBa(OBu^t)_4\{Li(thf)\}_4(OH)]\ \mathbf{1} + I^- \quad (1)$$

The compound crystallises in the tetragonal space group *P*4/*nmm* (No. 129) with two molecules per unit cell. The structure can be described as a square antiprism formed by four Li atoms in one plane and four O atoms of the $OBu^t$ ligands in the other square plane, the Li-face being capped by an OH-group and the O-face by a Ba–I unit leading to an overall almost spherical entity. Its formation can be explained by the successful substitution of one iodide and five thf molecules of $[BaI_2(thf)_5]$ by a $[LiOBu^t]_4$-unit and a $\mu_4$-capping OH-group (Fig. 1), the latter being introduced by partial hydrolysis of the THF solution of $LiOBu^t$ or LiOH. In fact, compound **1** can be obtained in a yield of up to 65% when the reaction is carried out in the presence of 1 equiv. of LiOH relative to $BaI_2$. The coordination sphere of barium is built up by the one remaining iodide and four $OBu^t$-groups to give a tetragonal pyramidal geometry. Barium has thus a coordination number of five which is unusually low for such a big cation (ionic radius of 1.36 Å for a coordination number of 6)[9] and only possible by the steric protection by the $OBu^t$-ligands. The four thf molecules, each one coordinating a lithium ion to yield a tetrahedral coordination sphere for the alkali metal, form a calix[4]arene-like cavity of an average diameter of 7.5 Å, this diameter taking into account the disorder positions of the thf molecules. The $\mu_4$-capping OH-group presents an oxygen with five bonding partners.

The alkaline earth cation Ba lies on a crystallographic 4*mm* site $(0, \frac{1}{2}, z\ (c))$ as do the halide I and the O3-hydroxy group. The Li-atom is found on a crystallographic mirror plane *m* $(y, 0, -z\ (i))$, the oxygen atom O1 of the $OBu^t$-groups are on a crystallographic mirror plane *m* $(-x+\frac{1}{2}, x, -z\ (j))$ together with the attached C1 atom and one of the three methyl groups C2. The main symmetric features of the molecule are thus the four-fold axes through I, Ba and O3 as well as the two mirror planes through Li and O1. In the crystal, the neutral clusters are arranged along the $C_4$-axis with rather long I–O3(H3) hydrogen bonds of 3.935 Å.[6]

The terminal Ba–I distance at 3.344(2) Å is extremely short due to the low coordination number of barium and even shorter than the smallest Ba–I distance in solid $BaI_2$ of 3.38 Å.[10] In $[BaI_2(thf)_5]$,[7] the terminal Ba–I distances are 3.374(2) and 3.3822(2) Å for a coordination number of seven for the barium. The Ba–O distances in **1** are 2.597(6) Å and thus shorter than in the six-coordinate $[Ba(OBu^t)_2(HOBu^t)_2]_4$ (2.673(8) Å).[11] The four $OBu^t$-groups form, together with the four Li(thf) units a square antiprism, the two square faces being twisted by 41.85° to each other. The Li–Li contacts at 2.716(18) Å are shorter than in elemental lithium (3.0390 Å), but longer than in similar

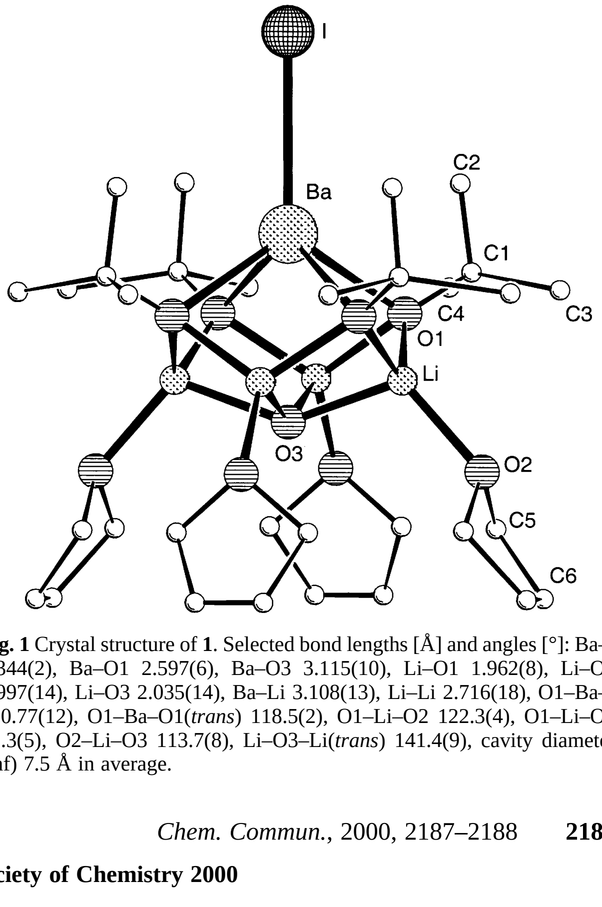

**Fig. 1** Crystal structure of **1**. Selected bond lengths [Å] and angles [°]: Ba–I 3.344(2), Ba–O1 2.597(6), Ba–O3 3.115(10), Li–O1 1.962(8), Li–O2 1.997(14), Li–O3 2.035(14), Ba–Li 3.108(13), Li–Li 2.716(18), O1–Ba–I 120.77(12), O1–Ba–O1(*trans*) 118.5(2), O1–Li–O2 122.3(4), O1–Li–O3 91.3(5), O2–Li–O3 113.7(8), Li–O3–Li(*trans*) 141.4(9), cavity diameter (thf) 7.5 Å in average.

DOI: 10.1039/b005638n

compounds like $[Ph_2P(NSiMe_3)]_2CLi_2$[12] with 2.393–2.410 Å. The enlargement relative to the literature data is probably due to the short Ba–O3 contact of 3.115(10) Å in which the alkaline earth cation strongly attracts the $OH^-$ anion which caps the $Li_4$-square. This also leads to the formation of the very flat square antiprism in which the plane containing the four Li atoms is only 1.115 Å apart from the plane containing the oxygen atoms of the $OBu^t$ groups. Thus, the O3 atom is 0.672 Å above the $Li_4$ plane, and the Ba atom is 1.328 Å below the $O_4$ plane. For the Li–O3 and the Li–O2 bonds, bond lengths of 2.035(14) Å and 1.997(14) Å, respectively are observed.

Similar structures containing a square arrangement of four alkali metals are the above mentioned $[Ph_2P(NSiMe_3)]_2CLi_2$,[12] $[Na_4][P\{Si(F)R_2\}(SiPr^i_3)]_2$, (R = 2,4,6-$Pr^i_3C_6H_2$),[13] $[(LiOBu^t)_{10}(LiOH)_6]$,[14] $[Me_2C(CH_2)_3CMe_2NLi]_4$,[15] $[\{Li(NBu^t)_3S\}_2]$[16] or $[Li_4L\cdot LiOH\cdot 4hmpa]$, ($H_4L$ = *tert*-butylcalix[4]arene)[17] as well as $[(Bu^tO)_8Li_4K_4]$.[18] In the $[(LiOBu^t)_{10}(LiOH)_6]$ structure, one can also find the square $Li_4O_4$-antiprism which is capped on one side by an HO ligand. This fragment shows similar Li–$OBu^t$ and Li–OH bond lengths to **1** at 1.877(10)–2.063(9) and 1.905(11)–2.066(10) Å, respectively.

Similar low coordination spheres for barium are known for instance in the sterically hindered molecule $[(thf)Ba_3(\mu_4\text{-}PSiBu^t_3)_2\{\mu_2\text{-}P(H)SiBu^t_3\}_2]_2$[19] where coordination numbers 5 and 4 for Ba are stabilised by THF or agostic interactions with $Bu^t$-groups respectively. In the case of **1**, one can also discuss agostic interactions with neighbouring $Bu^t$-groups since the Ba–(C2)$CH_3$ distances are in the range of 3.41(3) Å. Other examples for the stabilized low coordination number of 5 for barium are the compounds $[\{BaNP(NMe_3)_2NP(NMe_2)_2NSiMe_3\}_4]$,[20] $[Ba_2\{(C_6H_{11})NC(Me)CHC(Me)N(C_6H_{11})\}_3\{(SiMe_3)_2N\}]$,[21] $[(Et_3PO)_2Ba_2Cu_4(OBu^t)_8]$[22] and $[H_3Ba_6(O)(OBu^t)_{11}(OCEt_2CH_2O)(thf)_3]$[23] for which the Ba–O($\mu_3$-$OBu^t$) distances at 2.76(1) Å are much longer than in **1**. An even lower coordination sphere of 4 in $[BaY_2\{\mu\text{-}OCH(CF_3)_2\}_4(thd)_4]$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionato),[24] $[Ba\{N(SiMe_3)_2\}_2(thf)_2]$ and $[Ba\{N(SiMe_3)_2\}_2(thf)]_2$[25] or 3 in $[Ba\{N(SiMe_3)_2\}]$[25] for the alkaline earth metal cation is observed. Another molecular cluster compound combining lithium and barium is the $\{[Ba_6Li_3O_2][OC(CH_3)_3]_{11}(OC_4H_8)_3\}$ in which an oxygen-centered $Ba_6$-octahedron is fused *via* one triangular face to an oxygen-centered $Li_3Ba_3$-prism.[26]

As compound **1** is volatile in vacuum at temperatures lower than 200 °C due to the presence of alkoxide groups, its potential application as a barium source in *chemical vapour deposition* processes in order to synthesise high temperature superconductors will be tested. The syntheses of further mixed metal clusters are also under current investigation.

This work was financed by the Swiss National Foundation and the University of Geneva. The authors are grateful to Professor A. F. Williams and Professor C. Piguet for their support, Dr E. Rivara-Minten for $^7Li$ NMR measurements.

## Notes and references

† *Experimental* : $BaI_2$ was dried under vacuum at 200 °C and the reaction carried out under nitrogen atmosphere. 20 ml of a 0.2 M (4 mmol) solution of $Bu^tOLi$ in THF was added to 0.391 g (1 mmol) of $BaI_2$ and 0.024 g (1 mmol) of LiOH dissolved in 20 ml freshly dried and distilled THF in order to yield a milky white solution after 30 min of stirring. The solution was cooled to −20 °C to give colorless crystals of **1**. Yield: 65% (for $BaI_2$). $^1H$ NMR ($d_8$-THF, 20 °C) $\delta$ 1.147 (s, $CH_3$), 1.78 (m, thf), 3.62 (m, thf), 4.5 (s, OH); $^{13}C$ NMR ($d_8$-THF, 20 °C) $\delta$ 31.78 ($CH_3$); $^7Li$ NMR ($d_8$-THF, 20 °C, LiCl 1M/$D_2O$) $\delta$ 0.84, T1 = 1.8 s. $\nu$/cm$^{-1}$ (CsI, Nujol) 3584(s, sharp), 3050(vs, Nujol), 1596(s, Nujol), 1440(s, Nujol), 1374(s, Nujol), 1260(m), 1100(w), 1020(w), 802(m), 497(s, broad), 275(s), 238(w). MS: EI (low resolution): ($M^+$) = 889 (6%), ($M^+ - Bu^tOH$) = 815 (8%), ($M^+ - 2Bu^tOH$) = 741 (7%), plus degradation compounds at 355 (10%), 281 (56%), 207 (100%), 133 (16%), 73 (38%) and 59 (3%).

1 E. Weiss and E. A. C. Lucken, *J. Organomet. Chem.*, 1964, **2**, 197; E. Weiss and G. Hencken, *J. Organomet. Chem.*, 1978, **21**, 265.

2 J. E. Davies, J. Kopf and E. Weiss, *Acta Crystallogr., Sect B*, 1982, **38**, 2251.

3 D. Seebach, Proceedings of the Robert A. Welch Foundation. Conferences on Chemical Research XXVII. Stereospecificity in Chemistry and Biochemistry, Houston, TX, 1984.

4 E. Weiss, H. Alsdorf, H. Kühr and H. F. Grützmacher, *Chem. Ber.*, 1968, **101**, 3777.

5 M. Braun, D. Waldmüller and B. Mayer, *Angew. Chem., Int. Ed.*, 1989, **28**, 895, (see ref. 4 within); G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, 1966, **5**, 1257; J. D. Kahn, A. Haag and P. v. R. Schleyer, *J. Phys. Chem.*, 1988, **92**, 212; V. Halaska, L. Lochmann and D. Lim, *Collect. Czech. Chem. Commun.*, 1968, **33**, 3245; R. D. Thomas, S. G. Bott, P. W. Gravelle and H. D. Nguyen, *Abstracts of Papers of the American Chemical Society*, 1998, **215**, 291.

6 K. M. Fromm, *Chem. Commun.*, 1999, 1659.

7 K. M. Fromm, *Angew. Chem.*, 1997, **24**, 2876; K. M. Fromm, *Angew. Chem., Int. Ed. Engl.*, 1997, **24**, 2799.

8 *Single crystal data* for **2**: $C_{32}H_{69}O_9BaILi_4$, $M$ = 889.87 g mol$^{-1}$, tetragonal, space group $P4/nmm$ (No. 129), $a$ = 15.574(2), $c$ = 10.395(2) Å, $V$ = 2521.5(7) Å$^3$, $Z$ = 4, $T$ = 200 K, $\mu(Mo_{Ka})$ = 1.435 mm$^{-1}$, 4721 reflections of which 1313 unique and 1313 observed, 86 parameters refined, $R$(int) = 0.1139, $R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.0807$, $wR2 = 0.2014$ for $I > 2\sigma$ and $R1 = 0.1138$, $wR2 = 0.2343$ for all data. Crystals of **2** were measured on an ENRAF-NONIUS four-circle diffractometer on a crystal of 0.3 × 0.3 × 0.65 mm and with an absorption correction by analytical integration. The structure was solved with direct methods and refined by full matrix least squares on $F^2$ with the SHELX-97 package.[27] Disorder was observed for the thf molecules bound to Li as well as for the methyl groups of the *tert*-butanolate ligands. All heavy atoms of the cluster could be refined anisotropically. CCDC 182/1803. See http://www.rsc.org/suppdata/cc/b0/b005638n/ for crystallographic files in .cif format.

9 R. D. Shannon, *Acta Crystallogr., Sect. A.*, 1976, **32**, 751.

10 E. B. Brackett, T. E. Brackett and R. L. Sass, *J. Phys. Chem.*, 1963, **67**, 2132.

11 B. Borup, J. A. Samuels, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1994, **33**, 994.

12 A. Kasani, R. P. Kamalesh Babu, R. McDonald and R. G. Cavell, *Chem. Commun.*, 1999, **38**, 1483.

13 M. Driess, H. Pritzkow, M. Skipinski and U. Winkler, *J. Am. Chem. Soc.*, 1998, **120**, 10774.

14 C. Lambert, F. Hampel, P. v. R. Schleyer, M. G. Davidson and R. Snaith, *J. Organomet. Chem.*, 1995, **487**, 139.

15 R. E. Mulvey, *Chem. Soc. Rev.*, 1998, **27**, 339 (see ref. 30 within).

16 R. Fleischer and D. Stalke, *Coord. Chem. Rev.*, 1998, **176**, 431 (see ref. 31 and 32 within).

17 M. G. Davidson, J. A. K. Howard, S. Lamb and C. W. Lehmann, *Chem. Commun.*, 1997, 1607.

18 W. Clegg, A. M. Drummond, S. T. Liddle, R. E. Mulvey and A. Robertson, *Chem. Comm.*, 1999, 1569.

19 M. Westerhausen, M. H. Digeser, M. Krofta, N. Wiberg, H. Nöth, J. Knizek, W. Ponikwar and T. Seifert, *Eur. J. Inorg. Chem.*, 1999, 743.

20 S. K. Pandey, A. Steiner, H. W. Roesky and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1993, **34**, 596.

21 W. Clegg, S. J. Coles, E. K. Cope and F. S. Mair, *Angew. Chem., Int. Ed.*, 1998, **37**, 796.

22 B. Borup, J. C. Huffman and K. G. Caulton, *J. Organomet. Chem.*, 1997, **536**, 109.

23 K. G. Caulton, M. H. Chisholm, S. R. Drake and K. Folting, *J. Chem. Soc., Chem. Commun.*, 1990, 1349.

24 F. Labrize, L. G. Hubert-Pfalzgraf, J.-C. Daran and S. Halut, *J. Chem. Soc., Chem. Commun.*, 1993, 1556.

25 M. Westerhausen, *Inorg. Chem.*, 1991, **30**, 96; B. A. Vaartstra, J. C. Huffman, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 121.

26 H. Bock, A. John, C. Näther and Z. Havlas, *J. Am. Chem. Soc.*, 1995, **117**, 9367.

27 G. M. Sheldrick, SHELX-97, University of Göttingen, Göttingen 1997.