

Understanding the Formation of New Clusters of Alkali and Alkaline Earth Metals: A New Synthetic Approach, Single-Crystal Structures, and Theoretical Calculations

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Abstract: A new synthetic approach, reacting alkaline earth metal iodides with butyllithium, lithium hydroxide, and/or lithium butoxide under salt elimination, is presented, giving access to some interesting clusters of calcium, strontium, and barium, partially in combination with lithium. The so far largest calcium cluster $\text{Li}[\{\text{Ca}_7(\mu_3\text{-OH})_6(\text{thf})_{12}\}_2(\mu_2\text{-I})]\cdot 3\text{THF}$, **4**, and the new strontium compound $[\text{Sr}_3\text{I}_3(\text{OH})_2(\text{thf})_9]\text{I}$, **5**, are shown to feature common building blocks of OH-capped M_3 triangles. On the basis of mainly electrostatic interactions, these clusters are not volatile. By introducing LiO^tBu , the two clusters $[\text{M}(\text{O}^t\text{Bu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]$ (**6**, $\text{M} = \text{Sr}$; **7**, $\text{M} = \text{Ba}$) are prepared, **7** exhibiting volatility as an important physical property, which makes it a potential precursor for chemical vapor deposition. The structural relationship between **4**, **5**, **6**, and **7** and their respective starting materials is shown, and possible reaction mechanisms are proposed. Exhibiting surprising and new structural motifs, the bonding modes of these clusters are investigated by the electron localization function as well as by ab initio calculations.

Introduction

Group 1 and 2 metal ions show similarities with group 11 metals, especially concerning the reactivity and structure of organo-lithium and organo-copper compounds.¹ We therefore wanted to investigate the similarities in their cluster chemistries. Previously, a number of lithium clusters were observed, mainly as unexpected intermediates or byproducts in organic metalation reactions, whose constitution resembles that of some copper clusters. Since then, investigation of their structure and related reactivity has helped to understand the mechanisms of fundamental reactions that still surprise us from time to time with unusual reaction products, such as $[(\text{Ph}_2\text{NLi})\cdot\{\text{Ph}(\text{C}_6\text{H}_4\text{Li})\text{-NLi}\}_2\cdot(\text{BuLi})_2(\text{Et}_2\text{O})_4]$.² Clusters of lithiated phosphanes and arsanes are among the most important nucleophilic transfer reagents in the organo-element chemistry of phosphorus and arsenic. Soluble molecular derivatives of such compounds are

found to possess cage-like structures such as $[(\text{RE})_{12}\text{Li}_{26}\text{O}]$, $[(\text{REH})_6(\text{RE})_6\text{Li}_{20}\text{O}]$, $[(\text{RE})_8\text{Li}_{18}\text{O}]$, or $[(\text{RE})_{10}\text{Li}_{16}]$ ($\text{E} = \text{P}, \text{As}$; $\text{R} = \text{silyl groups}$).³ In the same context, some rare alkaline earth metal aggregates such as $\{(\text{THF})_2\text{Ca}_6[\text{P}^t\text{Bu}_3]_4[\text{P}(\text{H})\text{Si}^t\text{Bu}_3]_4\}$ are known.⁴ Bock, Lehn, et al. have published a Na_{14} cluster, $[(\text{Na}_8\text{O})\text{Na}_6(\text{bpy})_6(\text{tmeda})_6]$, which is structurally very similar to the general transition metal cluster geometry with a cluster core and some protecting ligands.⁵ Most of the cage compounds involve the smaller alkali metals, whereas similar clusters for the heavier group 1 metals are almost unknown.^{6,7} Heteroalkali and alkaline earth metal organic compounds are of great interest because they can exhibit reactivity superior to conventional organo-lithium compounds. The investigation of their structures is interesting insofar as it might help to understand why they are more reactive. A review by Mulvey surveys the recent developments in this field including mixed alkali and alkaline earth compounds.⁸

In the quest for new volatile alkaline earth metal compounds in the context of CVD for synthesising oxide materials, alkaline

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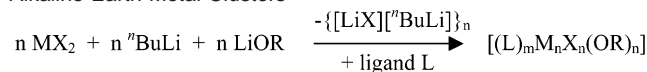
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Scheme 1. General Reaction Scheme for the Synthesis of Alkaline Earth Metal Clusters



X = halide, pseudo-halide; R = H, ^tBu; M = Ca, Sr, Ba; n, m = 1, 2, ...

earth metal alkoxides have been studied and were found to form higher aggregates in aprotic organic solvents. A CdI₂ core geometry was observed for a calcium cluster with nine metal centers, [Ca₉(OCH₂CH₂OMe)₁₈(HOCH₂CH₂OMe)₂].⁹ Turova et al. reported the Ca₆(O)₂(OEt)₄ system, which consists of two heterocubanes fused via one face.¹⁰ Higher cage compounds are unknown so far. Another interesting field of application for alkali and alkaline earth metal clusters is homogeneous catalysis. Thus, a Ba₂ compound was found to be active in the supra-molecular catalysis of the lysis reaction of esters and amides.¹¹ Alkaline earth metal clusters have also proved to be good precursors for the formation of sol-gels at low temperature: the compound [{BaNP(NMe₂)₂NP(NMe₂)₂NSiMe₃}]₄, which consists of a RN-capped Ba tetrahedron, forms, on hydrolysis, a white gel of composition Ba(OH)₂·xH₂O.¹² Further investigations have not been carried out on this subject, but an interesting application in this context could be the synthesis of precursors for BaO as an ingredient for high-Tc superconductors.

Results

Whereas the synthesis for group 11 clusters is by now well established,¹⁴ no systematic approach to alkali and alkaline earth metal clusters is known so far. The aim was therefore to find a reaction that forces aggregation of the metal ions. As the clusters would probably not be the most thermodynamically stable products, the formation of a secondary, very stable product seemed to be necessary as the driving force of the reaction. For the synthesis of alkaline earth metal clusters, we therefore envisaged a reaction pathway starting with a group 2 metal halide, which was to be reacted with an organo-lithium compound in order to eliminate a salt (Scheme 1).

From this reaction scheme, we decided to use the alkaline earth metal iodides as starting material, because of their good solubility in organic solvents. The solvent had to be chosen judiciously, as it had to be polar enough to dissolve the starting material without leading to the formation of charge-separated ionic species, totally coordinating the cation. THF was found to be best in this context, yielding species such as [Ca(thf)₄I₂] **1**¹⁵ and [M(thf)₅I₂] (**2**, M = Sr; **3**, M = Ba),^{16,17} which can be isolated from solution and present linear (**1**) or quasi linear I–M–I motifs (**2**, **3**). As the reaction partner and organo-lithium

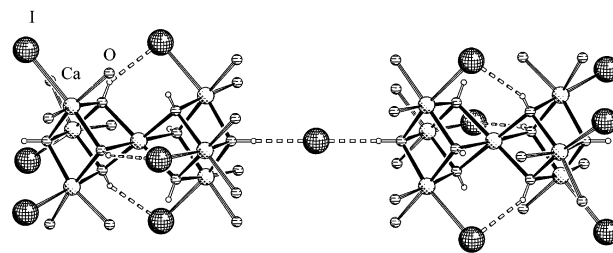


Figure 1. Cluster dimer of **4**. C and H atoms of the THF ligands are omitted for clarity.

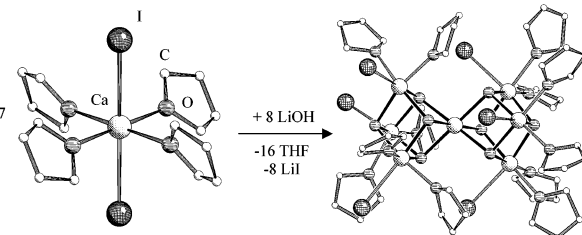


Figure 2. Possible reaction scheme for the formation of **4** from **1**.

compound ⁿBuLi was our first choice to verify our reaction scheme. To compensate for the missing charges once the iodide was partially eliminated, the reactions were carried out in the presence of LiOH, obtained via partial hydrolysis of ⁿBuLi.

The first example of reactions was carried out in THF in the presence of LiOH with a ratio of CaI₂:ⁿBuLi 1:1. As a result, the cluster compound Li[{Ca₇(μ₃-OH)₈I₆(thf)₁₂]₂(μ₂-I)·3THF, **4**, was reproducibly obtained. Compound **4** is also obtained, but in lower yield, if fewer equivalents of ⁿBuLi/LiOH are used. As the structure has already been described in a short communication elsewhere,¹⁸ it will only be summarized in the following. The molecule consists of two neutral Ca₇ clusters of composition [Ca₇(μ₃-OH)₈I₆(thf)₁₂] **4a**, linked together by μ₂-bridging iodide ions which form hydrogen bonds to one OH group of each cluster unit (Figure 1), yielding an anionic Ca₁₄ unit. The negative charge is compensated by a Li⁺ cation in the structure. To the authors' knowledge, this compound is still unique in its structural motif for this kind of cluster.

A structural relationship is found between **1** and **4** for the outer Ca ions, in which half of the initial molecules of [CaI₂(thf)₄] **1** are maintained (Figure 2).

μ₃-capped Ca₃ triangles such as those in **4** can be found in the alkoxide aggregate [Ca₉(OCH₂CH₂OMe)₁₈(HOCH₂CH₂OMe)₂],⁹ in which the coplanar Ca atoms occupy octahedral holes between two close-packed oxygen layers. A similar tetrahedral feature like those in the building units for **4** was found in the compound [Ba(μ₃-O'Bu)(O'Bu)(^tBuOH)₂]₄,¹⁹ where the tetrahedron is formed by Ba atoms, and the triangle-capping OH groups are formally replaced by O'Bu. The same ligand, once protonated and deprotonated, acts as a terminal ligand on the alkaline earth metal, whereas in **4** different ligands are found on almost each position.

The similar reaction, but with SrI₂ as starting material instead of CaI₂, reproducibly yields a new, different, and smaller cluster compound, [Sr₃I₃(μ₃-OH)₂(thf)₉]I **5**. It crystallizes at room temperature in the trigonal space group *R*(-3) (No. 148) in the form of colorless blocks. Attempts to synthesize **5** from a

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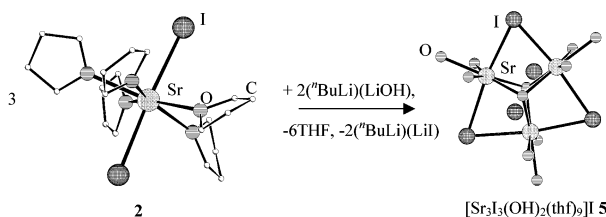


Figure 3. Possible reaction scheme for the formation of **5** from **2**, and molecular structure of **5**. H and C atoms of THF are omitted for clarity.

reaction of SrI₂ with LiOH failed, probably due to the stability and low solubility of the latter in THF. The molecule consists of a triangular cluster of strontium, the three vertexes of the triangle being μ_2 -bridged by one iodide each. Above and below the plane formed by these six ions, two μ_3 -functional OH groups coordinate the three strontium cations. To complete the cationic +1 charged cluster, each strontium atom is coordinated by three THF molecules (Figure 3). The counterion to this cluster is μ_2 -bridging iodide, linking the clusters together to form linear chains through hydrogen bonding to the OH groups.

This cluster can be structurally derived from the fusion of three of the species [SrI₂(thf)₅] **2**, with elimination of half of the iodide and two of the five THF molecules in each, the latter being replaced formally by two OH groups in total (Figure 3).

The Sr–Sr distance (3.733(3) Å) in the triangle is shorter than the shortest metal–metal contacts in the γ -form of strontium metal (4.2 Å), as expected for cationic species. The Sr–I distances are 3.349(2) and 3.353(2) Å long, which is slightly shorter than the sum of their ionic radii by Shannon,²⁰ but 0.13 Å longer than the Sr–I bonds in [SrI₂(thf)₅] **2**.¹⁶ The I–Sr–I angle in **2** is 176.37(5)°, 4° wider than the one in **5** (172.30(6)°). The Sr–I–Sr angle in **5** is very acute at 67.70–(6)° and compares to the ones found in other compounds with μ_2 -bridging iodide.²¹ The Sr–O(thf) distances in **5** vary between 2.57(2) and 2.61(2) Å compared to 2.561(6)–2.619(9) Å in **2**. The bond lengths of the metal cation to the anionic OH groups in **5** are, as expected, shorter, being 2.483(10) and 2.495(12) Å.

With these two results being new and showing interesting structures, we wanted to improve the physical properties of such clusters in order to be able to use them in CVD methods, i.e., the volatility of the compound. Bearing in mind the high volatility of alkoxide materials, substitution of the LiOH in Scheme 1 by LiO^tBu seemed judicious with the aim not only to introduce the structure of LiO^tBu into the product but also to impart volatility. A reaction carried out with SrI₂ under these conditions leads to the isolation of the uncharged, mixed-metal cluster compound [ISr(O^tBu)₄{Li(thf)₄(OH)}], **6**. This compound crystallizes from the mother liquor in THF and at room temperature after several days in the form of colorless cubic crystals in the tetragonal space group *P4/n* (No. 85). Traces of LiOH were found even in freshly opened commercial solutions of LiO^tBu, which accounts for the OH group in the product. The structure can be described as a square anti-prism formed by four Li atoms in one plane and four O atoms of the O^tBu ligands in the other square plane, the Li face being capped by an OH group and the O face by a Sr–I unit, leading to an overall almost spherical entity.

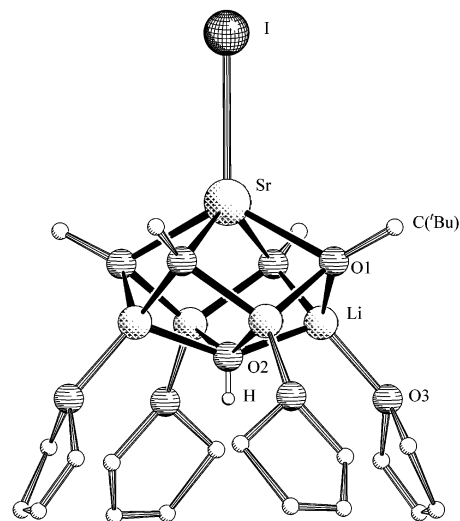


Figure 4. Molecular structure of **6**. C and H atoms of ^tBu groups as well as H atoms of THF are omitted for clarity.

The Sr–I distance is 3.223(2) Å, 0.13 Å shorter than in **5** due to the fact that the coordination number for Sr is lower in **6** than in **5** and that the iodide acts as terminal ligand. The Sr–O(O^tBu) bonds are 2.482(4) Å long, the Sr–Li distances are 2.972(11) Å, and the Sr–O(OH) distance is 2.935(11) Å long. The structure can thus be interpreted as insertion of a [(THF)–LiO^tBu]₄ unit into the Sr–OH bond of a linear I–Sr–OH fragment (Figure 4). In fact, the bond valence sum for Sr would be 1.8 if the Sr–O(OH) bond was not taken into account, whereas it is 2.0 if it is included.²²

Using BaI₂ as the starting material under exactly the same conditions as for the synthesis of **6**, we were able to isolate a mixed-metal cluster compound of exactly the same composition, except that the strontium was replaced by barium, [IBa(O^tBu)₄{Li(thf)₄(OH)}], **7**. Its structure was communicated before,²³ so that we here refer to a short summarized description. The compound crystallizes in the tetragonal space group *P4/nmm* (No. 129) with two molecules per unit cell. Its structure is analogous to the strontium one with all bonds involving barium elongated compared to the strontium compound, which is in accordance with the larger ionic radius of the heavier alkaline earth cation compared to strontium. The valence bond sum for barium is 2.1 without taking into account the Ba–O(OH) bond, and therefore the coordination number for barium in **7** can be considered as five, whereas it is six for strontium in compound **6**. Unlike **4** and **5**, which are not volatile at all, a molecular peak of **7** was observed in the mass spectrum under mild conditions, leading to the conclusion that this mixed-metal cluster is volatile under vacuum and up to temperatures of 200 °C. Decomposition is observed only at temperatures > 250 °C without melting. We can thus conclude that the goal of introducing volatility has been reached.

Discussion

A comparison of the most important structural parameters of the starting material as well as the clusters is given in Table 1.

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Table 1. Comparison of the Most Important Structural Parameters between **1** and **4**, **2** and **5**, and **3**, **6**, and **7**

	1	4	2	5	3	6(7)
coord no.	6	6	7	7	7	6(5)
coord geom	octahedral	octahedral	distorted pentagonal bipyramid	distorted pentagonal bipyramid	distorted pentagonal bipyramid	square pyramid
M ²⁺ –I	3.106(2) Å	3.147(2)–3.153(2) Å	3.2279(8) Å 3.2280(8) Å	3.349(2)–3.353(2) Å	3.378(2) Å av	3.223(2) Å (3.344(2) Å)
M ²⁺ –O(thf)	2.34(1) Å av	2.42(1) Å av	2.586(6) Å av	2.585(2) Å av	2.728(8) Å av	2.482(4) Å (2.597(6) Å) (OtBu)
M ²⁺ –O(R)		2.323(2) Å av		2.488(9) Å av		2.935(11) Å (3.115(10) Å) (OH)
I–M ²⁺ –I	180°		176.37(5)°	172.30(6)°	178.61(3)°	
M ²⁺ –M ²⁺		3.566(3) Å av		3.733(3) Å		
M ²⁺ –M ⁺						2.972(11) Å (3.108(13) Å)

It can be seen from Table 1 that for the calcium and strontium compounds **1** and **4**, and **2** and **5**, respectively, similar coordination spheres and the same coordination numbers are maintained. Both cluster compounds, **4** and **5**, possess a C₃-axis dominating the structure. Aggregation is in each case due to partial elimination of both the iodide and coordinating THF molecules in **1** and **2**, respectively. To account for the charge deficit by this elimination, the much smaller OH[−] is included in the cluster structures, acting as clamp on three metal ions within the cluster. The M²⁺–I distances get longer when passing from the monomer to the cluster compound, increasing from 3.106(2) Å in **1** to 3.150(2) Å on average in **4**, and from 3.228(8) Å in **2** to 3.351(2) Å in **5**. In the calcium compound, this is probably due to the fact that the metal ion is linked to only two anions in **1**, but to four anions in **4**. In **5**, this same effect is reinforced by the fact that the iodide anions change from terminal ligands in **2** to bridging ligands in **5**.

A common feature to most of the alkaline earth metal clusters known so far seems to be the μ₃-OR-bridged triangles of metal cations.^{18,24–27} For both clusters **4** and **5**, we observed the formation of a white sol of M(OH)₂(H₂O)_n (M = Ca, Sr) on partial or total hydrolysis which remains stable for several days. The measurement of the particle size of the sol formed upon hydrolysis shows a narrow distribution around 1000 nm for the particle diameter. Due to the organic solvent in which the sols can be generated and its low vapor pressure, THF would be an ideal medium for deposition experiments via dip-coating. Thermal treatment of these sols leads then to halide-free oxide materials.

The mixed-metal clusters **6** and **7** present a very similar molecular structure, and the bond lengths vary as expected when going from the smaller strontium to the larger barium cation for the M²⁺–O(tBu) and the M²⁺–I distances. However, the Sr–OH bond in **6** is shorter than the Sr–Li distance, whereas in **7**, the Ba–OH bond is longer than the intermetallic Ba–Li distance. This can be explained by the higher charge concentration on Sr²⁺ compared to Ba²⁺, leading to a stronger attraction of the anion OH[−] and a stronger repulsion of the Li⁺ cations for strontium than for barium. The difference in valence bond sums shows indeed that the Sr–OH bond cannot be neglected.

The mixed-metal strontium and lithium cluster **6** still contains a Sr–I bond similar to the ones in **2**, but none of the coordinating THF molecules in **2** have been maintained, so that the structural resemblance is less evident. The same is true for the mixed-metal cluster compound **7** and its starting compound **3**. Instead of being longer as for the calcium and strontium compounds **4** and **5**, the Sr–I (Ba–I) bond in **6** (**7**) is 0.005 (0.04) Å shorter than in its precursor molecule **2** (**3**). This can be explained by the lower coordination number of six for strontium in **6** and five for barium in **7**, compared to seven in **2** and **3** due to steric protection by the *tert*-butyl groups of the cluster. The insertion of the four LiOtBu units changes the coordination geometry around the strontium and barium ions completely, from a pentagonal bipyramid to a distorted square bipyramid for strontium in **6** and a square pyramid for barium in **7**. At the same time, the physical properties change from nonvolatile to volatile. To understand the bonding situation in these cluster compounds, as to whether they are covalent or ionic, some theoretical investigations were undertaken for the compounds **4**, **5**, **6**, and **7**.

Theoretical Investigations. General Conditions. The calculations have been performed using the density functional theory²⁸ within the Kohn–Sham formalism.²⁹ Both the LDA (local density approximation) functional (VWN³⁰) and GGA (generalized gradient approximation) functionals (Becke’s functional for exchange (B88)³¹ and Perdew’s functional for correlation (P86)³²) were used. The ADF package³³ was used to calculate the wave function necessary for the Mulliken and Hirshfeld charge analysis as well as for the plot of the molecular orbitals (MO). The basis sets are a combination of three Slater-type orbitals (triple-ζ) with a polarization function added on the heavy atoms (i.e., all atoms except the hydrogens). For the electron localization function (ELF)³⁴ calculation, the ToPMoD suite of programs³⁵ has been used in conjunction with the

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Table 2. Calculated Structure Parameters (bond lengths in Å and Bond Angles in deg), Mulliken and Hirshfeld Charges of $[\text{Sr}_3\text{I}_3(\text{OH})_2(\text{H}_2\text{O})_9]^+$, and AIM Analysis

	structural parameters		exp
	NR	R	
Sr–Sr	3.761	3.775	3.733(3)
I–I	6.724	6.750	6.693(3)
Sr–I	3.370	3.383	3.349(2)/3.353(2)
Sr–O(H)	2.566	2.551	2.495(12)
Sr–I–Sr	67.9	67.8	67.70(6)
I–Sr–I	172.2	172.2	172.30(6)

	charge analysis		AIM analysis (electron population on atoms)
	Mulliken	Hirshfeld	
Sr	1.36	0.47	1.8 (36.2)
I	−0.51	−0.33	−0.8 (53.8)
O(OH)	−1.17	−0.45	−1.6 (9.6)
O(H ₂ O)	−0.77	−0.23	(9.2 < p^a < 10.0)

^a p = electron population.

Gaussian98 package,³⁶ as well as the *elf* program adapted at the University of Fribourg (Switzerland), and which utilizes information from an ADF calculation.

Depending on the structures, the following conditions were applied for the theoretical investigations.

For the Ca cluster **4**, the crystallographic coordinates were used to calculate the wave function. Furthermore, the 12 THF molecules were substituted by water molecules for which the H–O–H angle was fixed at the C–O–C angle value of THF. As the strontium cluster **5** is the smallest one and has a high symmetry (D_3), geometrical parameters have been partially optimized using the VWN functional, i.e., the coordinates of the Sr and the I atoms as well as those of the (OH) groups have been relaxed. Similarly to structure **4**, the THF molecules were substituted by water molecules and were not taken into account in the structural minimization. For the optimization procedure, both nonrelativistic (NR) and relativistic (R) calculations were performed, the latter ones using the Pauli Hamiltonian.³⁷ The mixed-metal cluster **7** belongs to the C_{4v} symmetry group. Similarly to structure **4**, crystallographic coordinates were used, and the calculations were performed using the complete molecule, i.e., retaining the O'Bu and the THF molecules, to calculate the MO. Furthermore, relativistic effects have been taken into account. For the ELF calculations, THF molecules and O'Bu groups have been modeled using H₂O molecules and methoxy groups, respectively.

Results

As most calculations have been carried out systematically for the Sr₃ cluster, we first describe results obtained for structure **5**. When compared to the experimental structure, the optimized parameters (Table 2) are in relatively good agreement, at both the nonrelativistic and relativistic levels, at least for the Sr–Sr and Sr–I bonds.

The mean deviation amounts to 0.025 and 0.04 Å, respectively, at the nonrelativistic (NR) level. The relativistic (R) effects increase these bond lengths, hence slightly worsening the agreement with experiment. On the other hand, the calculated Sr–O(H) are too long by 0.07 and 0.06 Å according to R and NR calculations, respectively, leading to a less accurate description of the bond length. Contrary to previous results, relativistic effects decrease the Sr–O(H) bond length. It is finally noteworthy that the bond angles are exceptionally well reproduced by the calculations, whatever approach was used. We notice therefore that the bond lengths are too long compared to experiment, whereas the bond angles are well reproduced. Crystal packing forces could be responsible for the difference in bond lengths, although they may not necessarily modify them in the right way. The lack of accuracy of the bond lengths may be better ascribed to failures in the exchange–correlation functionals which have been parametrized on covalent systems and which are therefore less suitable for the description of ionic systems. Indeed, when GGA corrections are added to LDA functionals, an increase of bond lengths is usually obtained (bonds involving H atoms excepted), whereas the bond angles, although involving less energy than bond lengths, are often almost unchanged. In addition, we conclude that the structure is better described without taking into account the relativistic effects. In Table 2 are gathered the Mulliken and the Hirshfeld charges. It can be noticed that the Hirshfeld charges are smaller (in absolute value) than the Mulliken ones. Furthermore, relativistic effects in general decrease those charges, except for iodine. Consequently, conclusions on the bonding nature of this structure are contradictory whether we use Mulliken or Hirshfeld charges. According to the former, we expect the structure to be strongly ionic; according to the latter, it is more covalent. It is worth mentioning that it is well-known that Mulliken charges are, unlike Hirshfeld charges, very basis set dependent, although both of them can be used to get trends in the ionicity of the bonds. Therefore the AIM analysis as implemented in TopMoD has been calculated (Table 2). This analysis clearly indicates that the structure is strongly ionic, in agreement with the Mulliken charges, as the charges on the strontium, iodine, and oxygen atoms are roughly +2, −1, and −2, respectively. The molecular orbitals (MO) of the $[\text{Sr}_3\text{I}_3(\text{OH})_2(\text{H}_2\text{O})_9]^+$ cluster are depicted in Figure 5. The electronic state is $|a_2^2e_1^4a_2^2e_1^4a_1^0e_1^0a_2^0;^1A_1\rangle$. As expected, the MO near the Fermi level mainly accommodates the iodine electron pairs. Virtual orbitals are located on the THF ligands.

Finally, the ELF of the $[\text{Sr}_3\text{I}_3(\text{OH})_2(\text{H}_2\text{O})_9]^+$ cluster has been calculated for the plane containing both the Sr and I triangles. To study if such structures could exist with other alkali or alkaline earth metal cations as well as other halides, the ELF for a series of compounds of the composition $[\text{Sr}_3\text{X}_3(\text{OH})_2(\text{H}_2\text{O})_9]^+$ (X = Cl[−], Br[−], and I[−], respectively) were calculated and are depicted in Figure 6a. As can be seen, the ELF contours around the halides become larger from Cl to I atoms, clearly showing the shell structure of these atoms. Even though the spatial extent of the ELF becomes more important from Cl to I, no attractors can be localized between the halide and the Sr atoms. Obviously, the sphericity of the ELF around the halide is distorted, therefore suggesting an ionic bond with Sr. On the

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98* (Revision A.7); Gaussian, Inc.: Pittsburgh, PA, 1998.

(37) (a) Snijders, J. G.; Baerends, E. J. *Mol. Phys.* **1978**, *36*, 1789. (b) Snijders, J. G.; Baerends, E. J. *Mol. Phys.* **1979**, *38*, 1909.

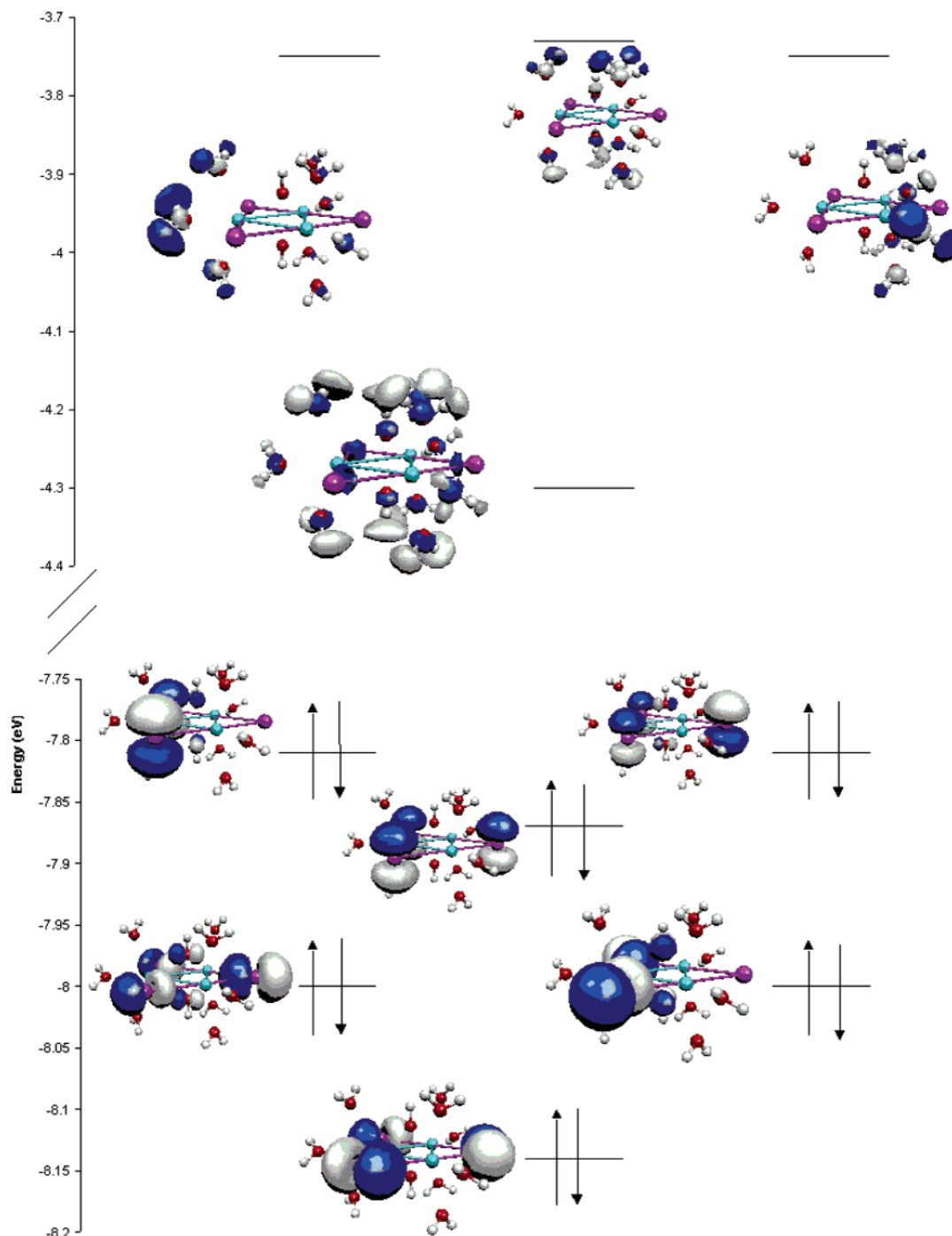


Figure 5. Molecular orbitals of structure 5.

other hand, in the region of the water molecules, we may undoubtedly assign the OH bond from the hydrogenated disynaptic basin near the oxygen atom. As for the series of clusters $[M_3I_3(OH)_2(H_2O)_9]^n$ ($M = K^+, Rb^+, Cs^+; n = 2^-; Ba^{2+}, Sr^{2+}, and Ba^{2+}; n = +$) for the group 1 metal cations and alkaline earth metal cations, the ELF's similarly show an ionic metal–halide bond. Finally, a 3D plot of the ELF of $[Sr_3I_3(OH)_2(H_2O)_9]^+$ (on-top view) is presented in Figure 6b. The three big spheres forming a triangle are assigned to the iodine basins. The three smaller ones correspond to the strontium basins. The central surfaces correspond to the OH bonds, and the remaining surfaces are assigned to H_2O molecules. Both the absence of an attractor between the core regions of the Sr,

I, and O(H) atoms and the shape of the Sr and I spheres confirm that the structure is mainly ionic.

It can thus be concluded that the metal–halide bonds in these and similar clusters are ionic, which corresponds well to the properties observed for compound 5.

The Mulliken and Hirshfeld charge analyses of the $Ca_7I_6(OH)_8(H_2O)_{12}$ cluster used as a model for structure 4 are shown in Figure 7a,b, in which, for the sake of clarity, hydrogen atoms are not depicted. The representation corresponds to the Ca_7 unit on the right of Figure 1. Interestingly, the description of the charge distribution in this cluster is very different depending on the analysis. From the Mulliken analysis, an asymmetry between both sides of the material is observed. This is

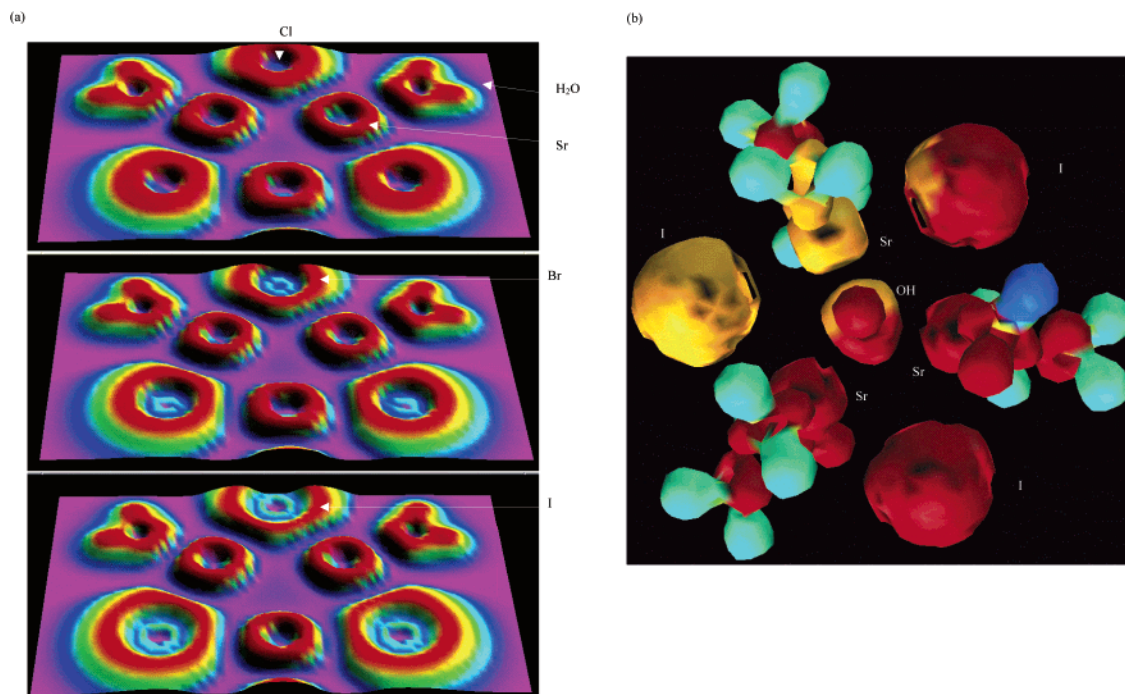


Figure 6. ELF plot of structure 5. (a) Sr^{2+} with halide series; (b) on-top view of the ELF of $[\text{Sr}_3\text{I}_3(\text{OH})_2(\text{H}_2\text{O})_9]^+$ (contour map 0.8).

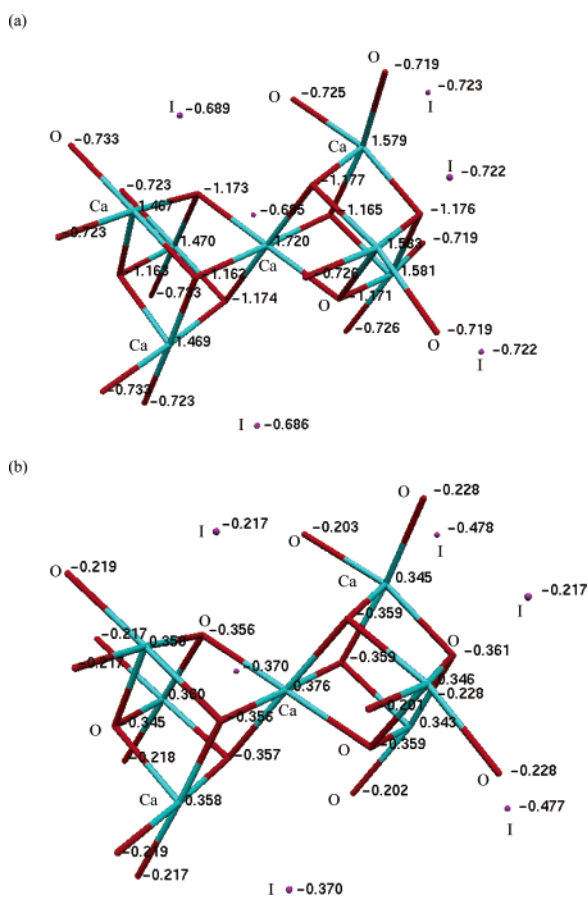


Figure 7. Mulliken (a) and Hirshfeld (b) charges of the $\text{Ca}_7\text{I}_6(\text{OH})_8(\text{H}_2\text{O})_{12}$ cluster.

particularly evident for the iodine charges: on the left-hand side, the iodine atoms are poorer in electrons than on the right-hand side of the cluster. Additionally, one may observe a strongly charged central cation (Ca^{2+}).

This would account for the polarity of such a single cluster. It is also evident that the central Ca atom should be charged more positively than the others, as it is surrounded by six OH anions, whereas the others have only four negatively charged neighbors. According to the Hirshfeld analysis however, we cannot observe the left-right separation, though some iodide ions are poorer in electrons than others. Furthermore, the central cation is only slightly more charged than the other Ca^{2+} cations.

The molecular orbitals of this cluster are depicted in Figure 8. The occupied orbitals, near the HOMO, mainly accommodate the iodine nonbonding electron pairs. As to the vacant orbitals (LUMO and upper orbitals), they are localized on the water molecules (σ^* -antibonding orbitals) with which the THF molecules were replaced.

The electron localization function has been calculated in three different planes. The results are depicted in Figure 9a–c. As expected, no covalent bonds can be seen between the Ca and O atoms which form the heterocubanes. As for the iodide ions which can be considered as ligands, ionic interactions with the Ca atoms are observed. Consequently, the ELF function shows that this structure exhibits an ionic character.

Concerning the $\text{BaLi}_4(\text{OH})(\text{O}^t\text{Bu})_4(\text{THF})_4$ cluster (structure 7), the charge analysis is represented in Table 3.

Similarly to structure 5, the Hirshfeld charges of structure 7 are in general smaller (in absolute value) than the Mulliken ones, except for the Li one, suggesting a less ionic structure. The AIM analysis confirms the ionic structure (see Table 4), as the global charges on the Sr, I, O, and Li atoms are roughly +2, -1, -2, and +1, respectively. Note that the AIM charges correspond to the $\text{SrLi}_4(\text{OH})(\text{OCH}_3)_4(\text{H}_2\text{O})_4$ model cluster, as no accurate all-electron basis set could be found for Ba. It can however be assumed that similar qualitative results would be obtained for the $\text{BaLi}_4(\text{OH})(\text{OCH}_3)_4(\text{H}_2\text{O})_4$ compound. The molecular orbitals MO of structure 6 are depicted in Figure 10. The electronic structure near the Fermi level is $|a_1^2e^4a_1^2a_1^0e^0a_1^0;^1A_1\rangle$. The valence orbitals of the material are

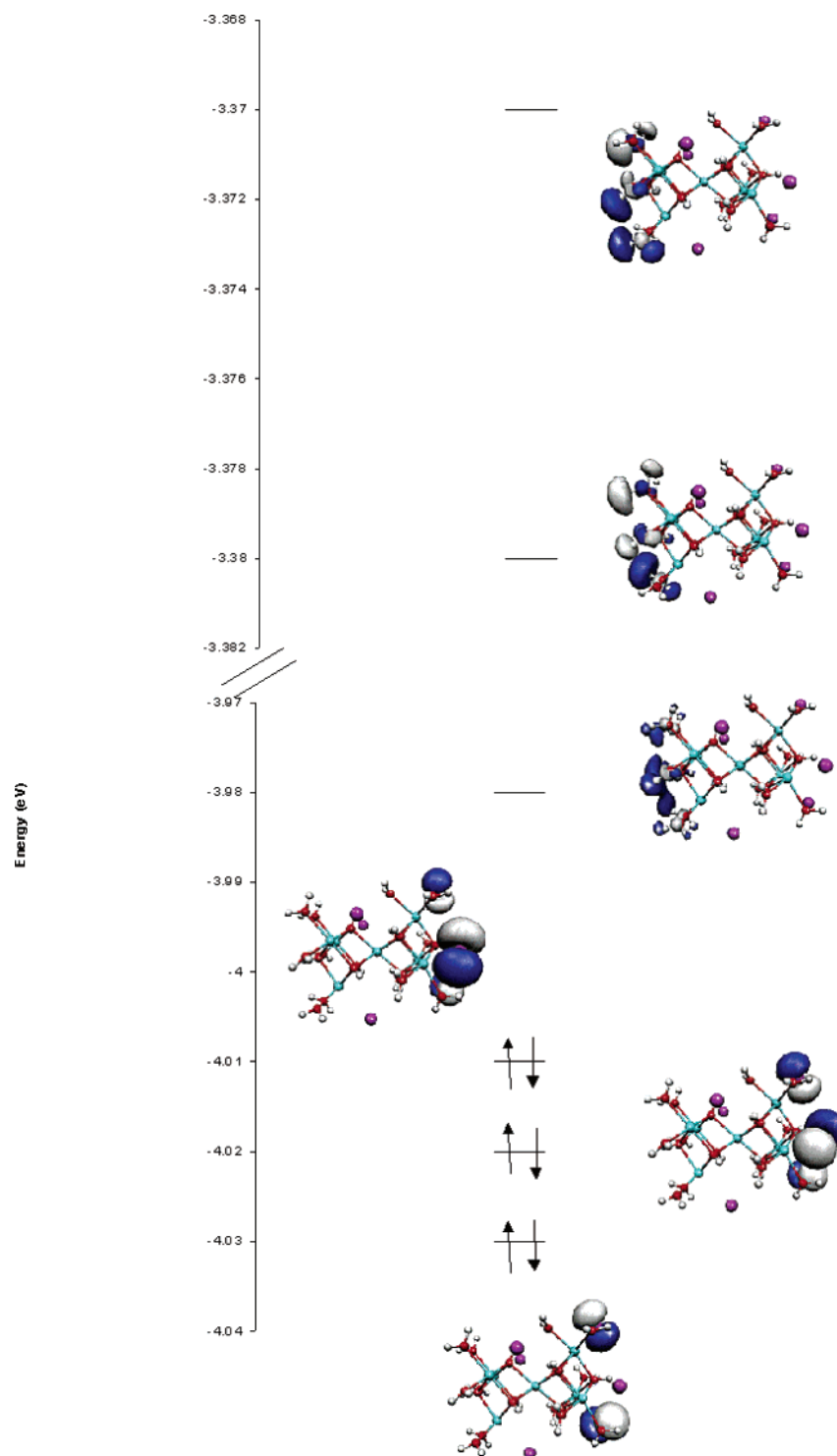


Figure 8. Molecular orbitals of the $\text{Ca}_7\text{I}_6(\text{OH})_8(\text{H}_2\text{O})_{12}$ cluster.

situated on the electron-rich atoms, namely, the I and O atoms. The HOMO corresponds to a π -nonbonding orbital of the central oxygen atom. As to the unoccupied orbitals, the LUMO and higher orbitals are mainly localized on the THF molecules. It is worth mentioning that the LUMO is a mixing of the π^* -nonbonding orbital of the central oxygen atom and the σ^* -antibonding orbitals of the THF molecules.

Finally, the ELF of the $\text{SrLi}_4(\text{OH})(\text{OCH}_3)_4(\text{H}_2\text{O})_4$ structure is depicted in Figure 11. The core regions of the I, Sr, and Li atoms can easily be identified. Nevertheless, no attractor can

be located between those atoms, therefore suggesting an ionic bonding in the core of this substructure. The same statement can be made for the I–Sr–O(CH_3) plane, where no covalent bonds can be seen between the I, Sr, and O atoms. However, the O–C(H_3) and C–H bonds are clearly identified as covalent in this figure, featuring an attractor between these atoms (remember that the tBu groups have been substituted by CH_3 groups). Again, only ionic interactions for the core are shown on the map. Unfortunately, the barium analogue could not be calculated due to unsatisfactory basis sets for the metal cation.

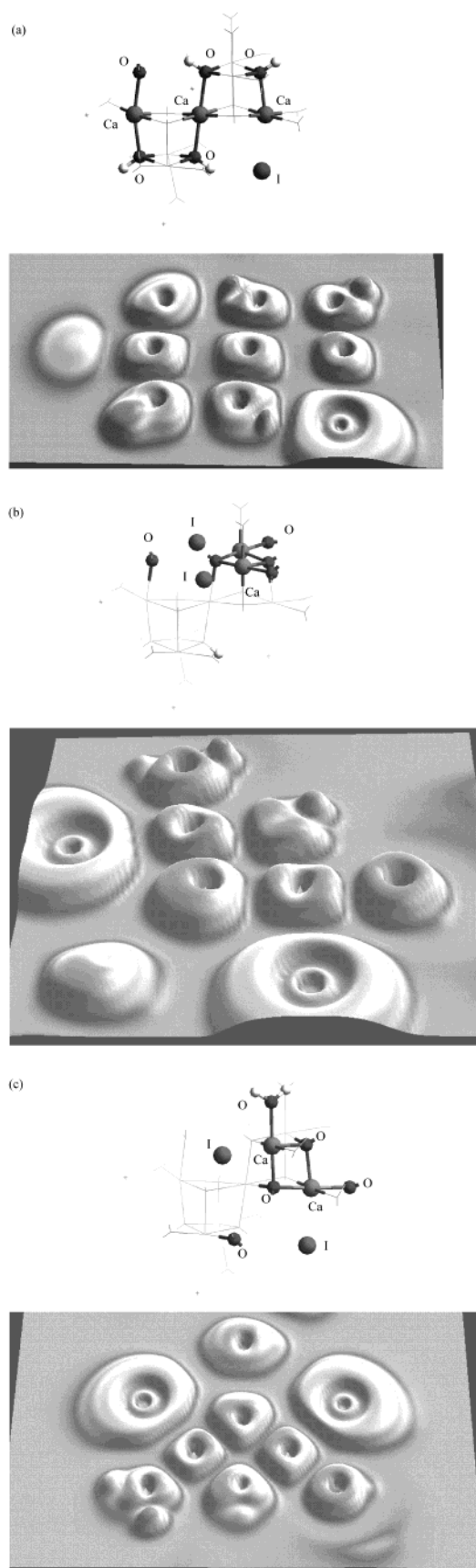


Figure 9. ELF of the $\text{Ca}_7\text{I}_6(\text{OH})_8(\text{H}_2\text{O})_{12}$ cluster calculated in three different planes. The “+” symbols correspond to the position of the I atoms.

Potential Applications. The compounds are of interest concerning their potential application as precursors for oxide

Table 3. Mulliken and Hirshfeld Charges of the $\text{BaLi}_4(\text{OH})\text{O}(\text{Bu})_4(\text{THF})_4$ Cluster **7**

	Mulliken	Hirshfeld		Mulliken	Hirshfeld
Ba	2.09	0.56	O	-0.84	-0.32
I	-0.87	-0.50	O(Bu)	-0.85	-0.32
Li	0.04	0.13	O(THF)	-0.61	-0.08

Table 4. AIM Analysis for the $\text{SrLi}_4(\text{OH})(\text{OCH}_3)_4(\text{H}_2\text{O})_4$ Model Cluster

basins	charge (population)	basins	charge (population)
I	-0.8 (53.8)	O(H_2O)	-1.1 (9.15)
Sr	1.5 (36.5)	H(H_2O)	0.6 (0.4)
O(H)	-1.5 (9.5)	O(OCH_3)	-1.2 (9.2)
H(OH)	0.6 (0.4)	C(OCH_3)	0.1 (5.9)
Li	0.9 (2.1)	H(OCH_3)	0.1 (0.9)

materials such as high Tc superconductors. Whereas compounds **4** and **5** are not volatile, they show however the formation of stable sol-gels on partial and total hydrolysis with “ $\text{Ca}(\text{OH})_2(\text{H}_2\text{O})_n$ ” and “ $\text{Sr}(\text{OH})_2(\text{H}_2\text{O})_n$ ” as products, and a particle size distribution with a maximum at 1000 nm, leading to halide-free oxide materials.

From the electron impact mass spectrum of the mixed-metal clusters **6** and **7**, the mass peak for the complete cluster of **7** and fragments of the strontium compound could be found. This suggests that compound **7** is volatile under the experimental conditions, whereas **6** is not. However, before testing such an expensive method as chemical vapor deposition, we first investigated if **7** yields the desired barium oxide upon the thermal treatment used in the synthesis of high Tc superconductors. Therefore, the cluster was brought onto a SrTiO_3 wafer of dimensions 0.5×0.5 cm via a THF solution of **7**. A surface analysis via scanning electron microscopy (SEM) and an Auger electron analyzer provided evidence for the presence of all elements Ba, I, O, and C, whereas lithium cannot be detected with this method. After thermal annealing at 600°C for several hours, all organic material was eliminated, and the remaining thin film shows a regular distribution of grains containing only Ba and O (Figure 12). This is in accordance with the expected formation of BaO from this starting material, given the fact that the $\text{LiO}(\text{Bu})$ itself is volatile even though the Li–O bonds are considered as ionic.

With the fact that compound **7** was observed to be volatile, it can be concluded that (i) the volatility appears as a new property by introduction of $\text{LiO}(\text{Bu})$ fragments to yield cluster **7**, and (ii) the compound can be used as a precursor for halide-free BaO as an ingredient for high Tc superconductors. As it is reasonable from these results to expect very similar behavior for the strontium analogue, the latter is under investigation in our laboratories.

Conclusions

This paper clearly shows an innovative synthetic pathway for the generation of new alkaline earth metal clusters with surprising structural motifs. Homometallic alkaline earth metal clusters are shown to form stable sols on hydrolysis. A new type of mixed-metal precursor is found by combining ionic substructures with bulky *tert*-butoxy groups. Volatility is introduced by inserting sterically important O(Bu) groups, rendering the external sphere of the cluster mainly hydrophobic, and thus minimizing the intermolecular interactions. The

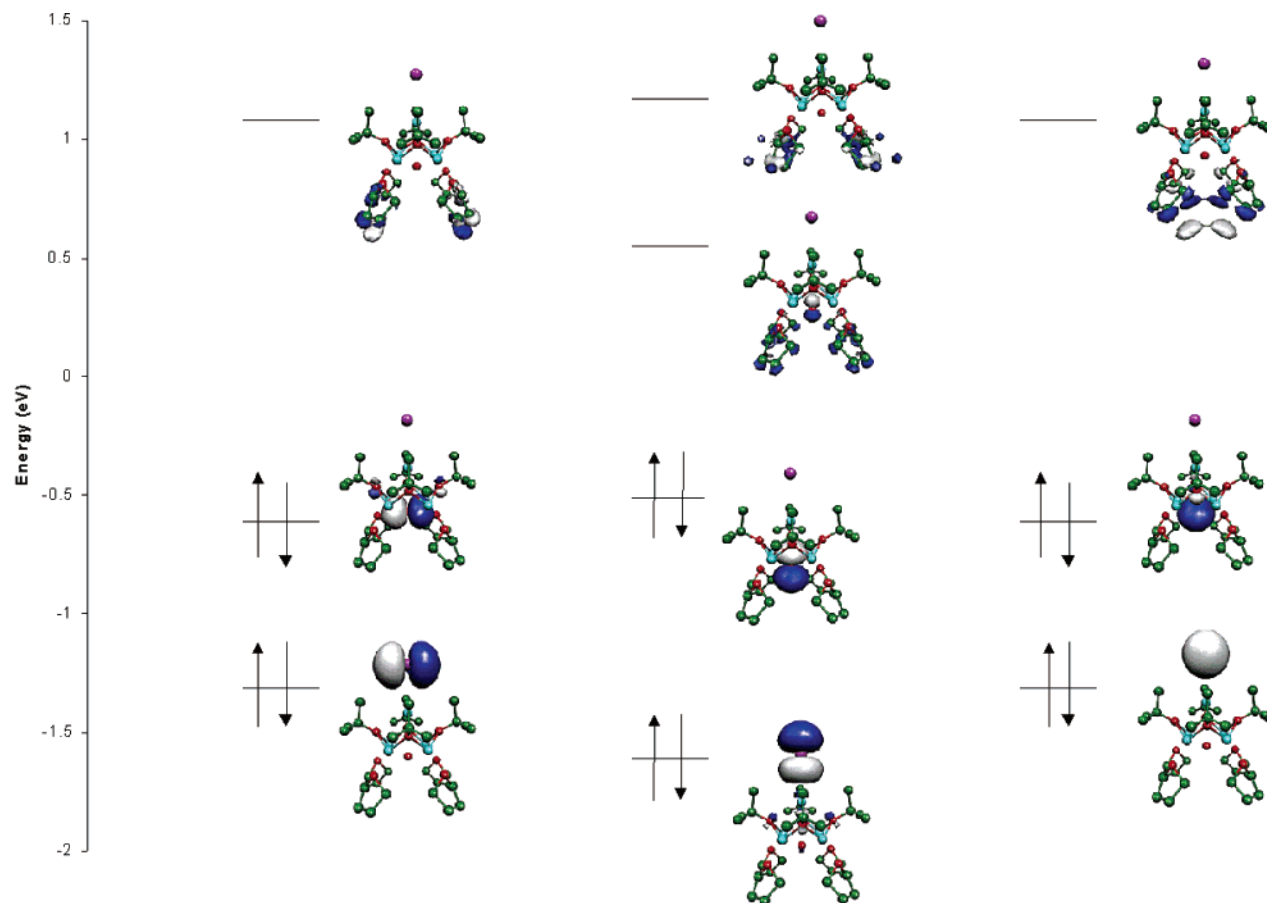


Figure 10. Molecular orbitals of structure 6.

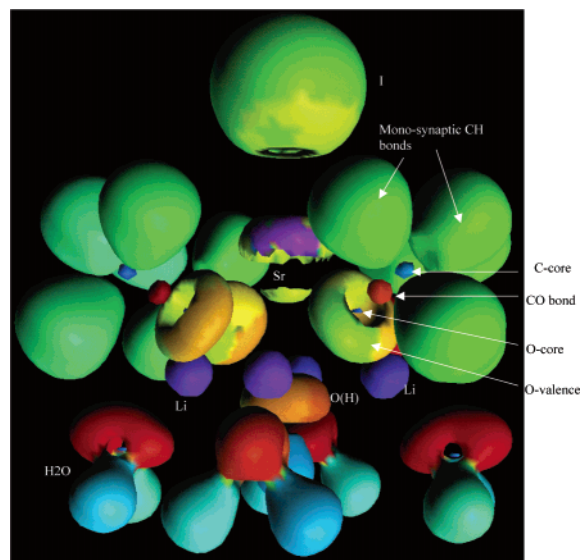


Figure 11. ELF of structure $\text{SrLi}_4(\text{OH})(\text{OCH}_3)(\text{H}_2\text{O})_4$ (contour plot 0.8).

theoretical calculations using the program *elf* allow some conclusions to be drawn about the bonding situation in the purely alkaline earth metal clusters as well as in the mixed-metal ones. It can be concluded that the cluster cores in all cases are held together through ionic bonds, i.e., mainly electrostatic interactions. Charge distributions from DFT methods are revealed to be partially basis set dependent and are ambiguous. It can also be shown that the mixed-metal cluster 7 can be potentially used as a sol-gel precursor, and possibly as a volatile CVD

precursor, for generating oxide materials such as high T_c superconductors. Further investigations in this direction are currently under way.

Experimental Section

The alkaline earth metal iodides were purchased from Aldrich (CaI_2), Fluka (SrI_2), and Merck (BaI_2), and all were dried at 200 °C under vacuum before use. ${}^n\text{BuLi}$ was obtained from Fluka and Aldrich (1.6 M in hexane, but usually already contaminated with 0.1–0.4 M LiOH when freshly opened); ${}^n\text{BuOLi}$ was synthesized from ${}^n\text{BuOH}$ and ${}^n\text{BuLi}$ or purchased 1 M/THF from Fluka. The solvent THF was stored under nitrogen, dried over Na/benzophenone, and freshly distilled prior to use. All reactions were carried out under an inert atmosphere of nitrogen.

The NMR spectra were recorded on a Varian Gemini 300 spectrometer, and the chemical shifts are relative to TMS as an internal standard.

The IR spectra were registered on a Perkin-Elmer Spectrum One FT-IR spectrometer on CsI plates in Nujol.

4. The solution of $({}^n\text{BuLi})_m(\text{LiOH})_n$ in hexane can be typically obtained by partial hydrolysis, i.e., by adding a solution of hexane to which a known amount of water has been added of a commercially available solution of 1.6 M BuLi, leading to a ratio of ${}^n\text{BuLi}$ to LiOH of 1:1, followed by evaporation of hexane in order to obtain a solution of approximately 2 M in Li^+ . A Gilman's titration³⁸ of the so prepared solutions reproducibly revealed concentrations of 1.1 M in ${}^n\text{BuLi}$ and 1 M in LiOH.

CaI_2 (0.45 g, 1.53 mmol) was dissolved in 20 mL of freshly dried and distilled THF in order to yield a light yellow solution. At room

(38) Gilman, H.; Haubein, A. H. *J. Am. Chem. Soc.* **1944**, *66*, 1515–1516.

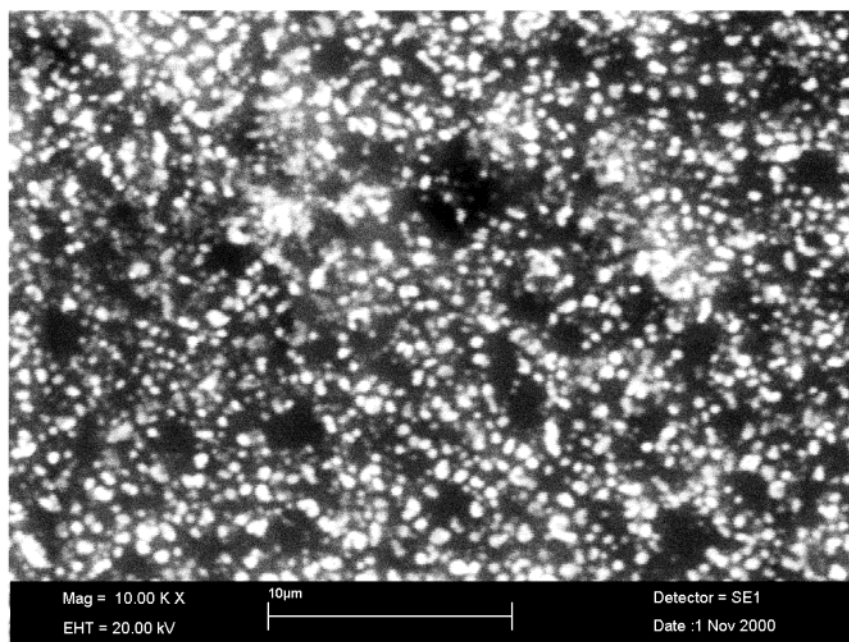


Figure 12. SEM image of the BaO depot on SrTiO₃

temperature, 1.4 mL of a hexane solution containing 1.1 M ⁿBuLi (1.54 mmol) and 1 M LiOH (1.4 mmol) was added dropwise to the stirred solution. After 2 days at room temperature, the colorless solution was cooled to $-25\text{ }^{\circ}\text{C}$ to give colorless crystals of **4** within 24 h. Yield: 87% (for CaI₂). Satisfactory analysis for Ca, I, C, and H. The presence of Li in **4** was determined by ICP-MS⁹ and ⁷Li NMR, giving a signal at 1.83 ppm in *d*₈-THF (LiCl in D₂O as standard). IR (CsI, Nujol) (cm⁻¹): 3640(m), 3550(s), 3300(s), 3200(s), 2900(vs, Nujol), 1500-(vs, Nujol), 1370(s, Nujol), 1340(s, Nujol), 1290(s), 1240(s), 1180-(vs), 1050(vs), 910(vs), 665(vs), 575(s), 360(s), 280(m), 240(m).

5. SrI₂ (0.43 g, 1.26 mmol) was dissolved in 30 mL of freshly dried and distilled THF by heating to reflux. Not all the solid dissolves, and the mixture is treated with 3 equiv of ⁿBuLi/LiOH solution as for **4**. The reaction solution is allowed to stand at room temperature for three weeks, after which colorless distorted octahedral crystals of **5** form together with a white precipitate of starting material. The yield was estimated to be 25% referring to SrI₂, and single crystals were separated from the solid under the microscope for analysis. IR (CsI, Nujol) (cm⁻¹): 3652(m), 3548(s), 3302(s), 3200(s), 2900(vs, Nujol), 1500(vs, Nujol), 1370(s, Nujol), 1340(s, Nujol), 1295(s), 1246(s), 1233(m), 1177(vs), 1050(vs), 912(vs), 667(vs), 582(s), 288(m), 255(m). Anal. Found (Calcd): C 29.21 (29.75), H 4.99 (5.13), O 11.97 (12.10), I 35.5 (34.92).

6. A 1 M (5 mmol, 5 mL) solution of LiO^tBu containing traces of LiOH (1%) in THF was added to 25 mL of a white suspension of SrI₂ in THF (0.39 g, 1.1 mmol), to yield a yellow turbid solution after 2 h of stirring at room temperature. After filtration of the precipitate, the yellow solution was allowed to stand at room temperature. Colorless single crystals of **6** (in a yield of 50% referred to SrI₂) suitable for X-ray analysis grew from the solution in a few days. ¹H NMR (300 MHz, C₆D₆, 293 K): δ 1.05 (s, CH₃), 1.41 (m, CH₂ thf), 3.57 (m, CH₂O thf) ppm. ⁷Li NMR (116 MHz, C₆D₆, 293 K): δ 3.22 (s) ppm. ¹H NMR (300 MHz, *d*₈-THF, 293 K): δ 1.14 (s, CH₃), 1.78 (m, CH₂ thf), 3.62 (m, CH₂O thf). ⁷Li NMR (116 MHz, *d*₈-THF, LiCl 1 M/D₂O, 293 K): δ 0.29 ppm. MS/EI (low-res mass data (centroid)): 45(9), 55(54), 56(13), 57(100), 59(38) ((CH₃)₂COH⁺), 67(14), 69(35), 70(6), 71(24), 81(20), 83(22), 85(11), 95(20), 97(17), 109(11), 111(7), 128-(5). IR: (cm⁻¹) 3676(w), 3545(m), 2993(s), 2923(Nujol), 2818(s), 1769-(w), 1595(m), 1476(s), 1459(Nujol), 1427(s), 1376(Nujol), 1360(m), 1083(w), 857(s), 722(Nujol), 502(s).

7. A 0.2 M (4 mmol, 20 mL) solution of LiO^tBu in THF was added to 0.391 g (1 mmol) of BaI₂ and 0.024 g (1 mmol) of LiOH dissolved

in 20 mL of freshly dried and distilled THF in order to yield a milky white solution after 30 min of stirring. The solution was cooled to $-20\text{ }^{\circ}\text{C}$ to give colorless crystals of **7**. Yield: 50% (for BaI₂). ¹H NMR (300 MHz, *d*₈-THF, 20 $^{\circ}\text{C}$): δ 1.147 ppm (s, CH₃), 1.78 ppm (m, CH₂ thf), 3.62 ppm (m, CH₂O thf), 4.5 ppm (s, OH). ¹³C NMR (*d*₈-THF, 20 $^{\circ}\text{C}$): δ 31.78 ppm (CH₃). ⁷Li NMR (116 MHz, *d*₈-THF, 20 $^{\circ}\text{C}$, LiCl 1 M/D₂O): δ 0.84 ppm, T1 = 1.8 s. IR (CsI, Nujol) (cm⁻¹): 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-res): (M⁺) = 889 (6%), (M⁺ - ^tBuOH) = 815 (8%), (M⁺ - 2^tBuOH) = 741 (7%), plus degradation compounds at 355 (10%), 281 (56%), 207 (100%), 133 (16%), 73 (38%), and 59 (3%).

Crystallographic Part. Single-crystal data for 4: see ref 18. Crystallographic data for **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-116066. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Single-crystal data for 5: C₃₆H₇₄O₁₁Sr₃I₄, *M* = 1453.41 g mol⁻¹, rhombohedral, space group *R*(-3) (No. 148), *a* = 19.136(3) Å, *c* = 25.373(5) Å, *V* = 8046(2) Å³, *Z* = 6, ρ_{calc} = 1.800 Mg m³, *F*(000) = 4224, *T* = 223 K, λ = 0.71073 Å, μ (Mo K α) = 5.319 mm⁻¹, 4.04 $^{\circ}$ < 2 θ < 59.8 $^{\circ}$, 5186 reflections of which 5186 unique and 4008 observed, 169 parameters refined, GOOF(on *F*²) = 1.026, R1 = $\sum|F_o - F_c|/\sum F_o$ = 0.1631, wR2 = 0.4797 for *I* > 2 σ and R1 = 0.2060, wR2 = 0.5294 for all data.

Crystals of **5** were measured on an ENRAF-NONIUS four-circle diffractometer at 223 K. The data collection was best for a crystal of 0.22 × 0.11 × 0.10 mm and 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.³⁹ Strong disorder was observed for the THF molecules bound to Sr. All the heavy atoms of the cluster could be refined anisotropically. Due to the presence of heavy atoms such as iodine, the positions of the hydrogen atoms could not be determined and were thus calculated, except for the OH groups, where the H atoms could be found in the Fourier map. Strong absorption problems occur for the iodide anions despite the absorption correction, giving high remaining electron density of up to four electrons close to these anions at distances of about 0.8 Å,

(39) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, 1997.

accounting for a rather bad overall R value. Crystallographic data for **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168439. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Single-crystal data for 6: $C_{32}H_{68}O_8ILi_4Sr$, $M = 839.15 \text{ g mol}^{-1}$, tetragonal, space group $P4/n$ (No. 85), $a = 15.5078(10) \text{ \AA}$, $c = 10.1836(7) \text{ \AA}$, $V = 2449.1(3) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 4.552 \text{ Mg m}^{-3}$, $F(000) = 3480$, $T = 200 \text{ K}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(\text{Mo K}\alpha) = 7.069 \text{ mm}^{-1}$, $4.78^\circ < 2\theta < 52^\circ$, 28 356 reflections of which 2409 unique and observed, 146 parameters refined, $\text{GOOF}(\text{on } F^2) = 0.816$, $R1 = \sum |F_o - F_c| / \sum F_o = 0.0679$, $wR2 = 0.1884$ for $I > 2\sigma$ and $R1 = 0.1008$, $wR2 = 0.2130$ for all data.

Crystals of **6** were measured on a STOE IPDS diffractometer at 200 K. The data collection was best for a crystal of $0.18 \times 0.09 \times 0.07 \text{ mm}$ and 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.³⁹ Slight disorder was observed for the THF molecules bound to Li and the *tert*-butyl groups. All the heavy atoms of the cluster could be refined anisotropically. Due to the presence of heavy atoms such as iodine, the positions of the hydrogen atoms could not be determined and were thus calculated. Crystallographic data for **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-168440. Copies of the data can be obtained free of charge on application to CCDC, 12

Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Single-crystal data for 7: see ref 23. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1821803. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. K.M.F. and E.D.G. thank Profs. A. F. Williams and C. Piguet and the University of Geneva for their generous support. Furthermore, K.M.F. and E.D.G. thank the Swiss National Foundation for financial support with research grants. K.M.F. and P.B. thank Prof. A. Daul of the University of Fribourg, Switzerland, for kindly providing us with the ELF program and Mrs. C. Lepetit, CNRS-Toulouse, France, and Prof. B. Silvi, Paris, France, for helpful discussions. Prof. J.-M. Triscone, Prof. R. Flükiger, Dr. T. Tybell, and J.-Y. Genoud of the Physics Department, University Geneva, are thanked for the substrate and the SEM pictures of the thin films.

Supporting Information Available: CIF-files for **5** and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0205737