

Novel three-dimensional framework based on Ba₉ cores involving unprecedented $\mu_5\text{-}\eta^3\text{:}\eta^3$ -acetate anions

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A three-dimensional framework based on a body-centered Ba₉ cluster has been assembled, in which the bridging acetate anions show novel $\mu_5\text{-}\eta^3\text{:}\eta^3$ -, $\mu_4\text{-}\eta^2\text{:}\eta^2$ - and $\mu_3\text{-}\eta^2\text{:}\eta^2$ -bridging coordination modes, while the perchlorate anions display an unusual $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ -coordination mode.

Inorganic high-nuclearity clusters continue to attract considerable attention because they represent a bridge between molecular and solid state chemistry and because they are useful tools for understanding the size-dependent physical properties of electronic material.¹ The preparation of such complexes enables their nanoscopic dimensions to be combined with the rich redox and magnetic properties of the constituent metals, and leads to novel materials with promising electronic, magnetic, optical and catalytic properties.²

In general, hydrophilic groups such as hydroxy, oxo, and carboxylate lie within the core and induce core aggregation, while hydrophobic groups form the periphery preventing the core from infinite aggregation.³ The acetate anion acting as a good bridging ligand for the formation of metal clusters has also been studied extensively.⁴ Although the cluster chemistry of the transition metals is now finely established and huge clusters have been isolated—especially clusters of molybdenum, copper, silver,⁵ and alkaline earth metals,^{6,7}—the synthesis of high-nuclearity clusters is still a great challenge, and little work on open-framework coordination polymers based on clusters has been reported.⁸ Alkaline earth metal compounds have been increasingly studied owing to their applications in a variety of research fields, especially in the search for new precursors for superconductors and complex metal oxides. In this context, inorganic polymers of different dimensionality have been structurally characterized.^{9,10} Among them, barium is an important metal in many of the high-temperature superconductors (YBa₂Cu₃O₇, HgBa₂CuO₄, HgBa₂Ca₂Cu₃O₈).⁶

Herein we report the synthesis and structure of a three-dimensional framework based on the largest body-centered Ba₉ core in common aqueous solution. In this compound, acetate ions display a novel $\mu_5\text{-}\eta^3\text{:}\eta^3$ -bridging coordination mode and perchlorate anions display an unusual $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ -coordination mode, respectively, which represent the largest numbers of coordination bonds of the corresponding ions. To the best of our knowledge, no barium cluster over eight atoms has been reported. Evaporating the aqueous solution of the mixture of Ba(CH₃CO₂)₂ and Ba(ClO₄)₂ in a molar ratio of 7 : 1 gave the compound [Ba₉(CH₃CO₂)₁₄(ClO₄)₄]_n,[†] **1**, which was confirmed by elemental analysis and IR spectroscopy.

Single-crystal X-ray analysis[‡] revealed that the compound is a three-dimensional network based on a Ba₉(CH₃CO₂)₁₄(ClO₄)₄ *I*-center tetragonal prism connected by bridging acetate and perchlorate ligands. Fig. 1 shows the coordination geometries of the three kinds of barium atom in the Ba₉ core. The barium atoms Ba(1) and Ba(2) as well as their symmetry-related atoms [Ba(1A), Ba(1B), Ba(1C), Ba(2A), Ba(2B) and Ba(2C)], symmetry code A: 1 - x, y, -z; B: 1 - x, 1 - y, -z; C: x, 1 - y, -z] occupy the vertex positions, while the barium atom Ba(3) occupies the *I*-center of the tetragonal prism with average Ba ··· Ba separations from the central to the vertex barium atom of ca. 4.27 Å.

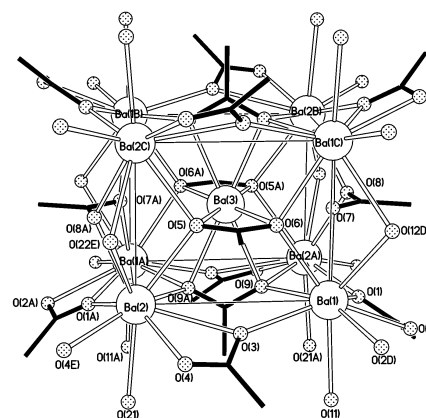


Fig. 1 Structure of the Ba₉ core. Selected bond lengths (Å): Ba(1)–O(1) 2.819(2), Ba(1)–O(2) 2.855(2), Ba(1)–O(3) 2.824(2), Ba(1)–O(6) 2.810(1), Ba(1)–O(7) 2.845(2), Ba(1)–O(9) 2.838(2), Ba(1)–O(11) 2.888(3), Ba(1)–O(2D) 2.657(2), Ba(1)–O(12D) 3.005(2), Ba(2)–O(3) 3.044(2), Ba(2)–O(4) 2.731(2), Ba(2)–O(5) 2.844(1), Ba(2)–O(21) 2.891(2), Ba(2)–O(1A) 2.694(2), Ba(2)–O(8A) 2.726(2), Ba(2)–O(9A) 2.885(2), Ba(2)–O(4E) 2.680(2), Ba(2)–O(22E) 3.045(3), Ba(3)–O(9) 2.750(2), Ba(3)–O(5) 2.762(3), Ba(3)–O(6) 2.888(3). (Symmetry code A: 1 - x, y, -z; B: 1 - x, 1 - y, -z; C: x, 1 - y, -z; D: 1.5 - x, 0.5 - y, 1 - z, E: 0.5 - x, 0.5 - y, -z.)

For this tetragonal prism, the edges of the square face [defined by atoms Ba(1), Ba(2A), Ba(1C) and Ba(2B)] are ca. 4.64 Å on average and the height, the separation between Ba(1) and Ba(2), is about 5.47 Å. The central barium atom [Ba(3)] is coordinated by eight oxygen atoms from four $\mu_5\text{-}\eta^3\text{:}\eta^3$ -CH₃CO₂⁻ with C_{2h} local symmetry. The mirror plane involving the Ba(3) atom is formed by two $\mu_5\text{-}\eta^3\text{:}\eta^3$ -CH₃CO₂⁻ containing oxygen atoms [O(5), O(6), O(5A) and O(6A)], respectively] and two $\mu_4\text{-}\eta^2\text{:}\eta^2$ -CH₃CO₂⁻ containing oxygen atoms [O(7), O(8), O(7A) and O(8A)], and the two-fold rotation axis perpendicular to the plane passes through the Ba(3) atom, the center of oxygen atoms O(9) and O(9A), and carbon atoms of the $\mu_5\text{-}\eta^3\text{:}\eta^3$ -CH₃CO₂⁻ ligand. The corresponding two-fold rotation and mirror plane symmetry operations can generate the other parts of the Ba₉ core. The vertex barium atom [Ba(1)] is nine-coordinated, surrounded by oxygen atoms O(9) and O(6) from two $\mu_5\text{-}\eta^3\text{:}\eta^3$ -CH₃CO₂⁻, O(7) from $\mu_4\text{-}\eta^2\text{:}\eta^2$ -CH₃CO₂⁻, O(1), O(2), O(2D) [symmetry code D: 1.5 - x, 0.5 - y, 1 - z] and O(3) from three $\mu_3\text{-}\eta^2\text{:}\eta^2$ -CH₃CO₂⁻, and O(11) and O(12D) from two $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ -ClO₄⁻, respectively. The vertex barium [Ba(2)] is also nine coordinated similarly to Ba(1) surrounded by oxygen atoms O(3), O(4), O(5), O(9A) O(8A), O(1A) and O(4E) [symmetry code E: 0.5 - x, 0.5 - y, -z] from six different CH₃CO₂⁻ anions and O(21) and O(22E) from two $\mu_4\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2$ -ClO₄⁻, respectively. Each $\mu_5\text{-}\eta^3\text{:}\eta^3$ -CH₃CO₂⁻ [defined by atoms O(5), O(6), C(5) and C(6), or O(9), O(9A), C(9) and C(10)] is placed on one of the rectangle faces of the prism [defined by Ba(1), Ba(2), Ba(1C) and Ba(2C), or Ba(1), Ba(2), Ba(1A) and Ba(2A), respectively] with each oxygen atom being terminally bound to the central barium atom and two vertex

barium atoms, respectively. The $\mu_4\text{-}\eta^2\text{-}\eta^2\text{-CH}_3\text{CO}_2^-$ [defined by atoms O(7), O(8), C(7), and C(8)] occupies the square face with each oxygen atom being terminally bound to two vertex barium atoms. Each $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-CH}_3\text{CO}_2^-$ [defined by atoms O(1), O(2), C(1) and C(2), or O(3), O(4), C(3) and C(4)] is positioned at the edge of the tetragonal prism with one oxygen atom [O(1) or O(3)] bridging the two barium atoms on the edge, and another one [O(2) or O(4)] bridging two other barium atoms, from one vertex and a symmetry-related one [Ba(1D) and Ba(2E)] of a neighboring Ba_9 cluster, respectively. Those $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-CH}_3\text{CO}_2^-$ anions as well as the ClO_4^- anions (Fig. 2) link the Ba_9 clusters

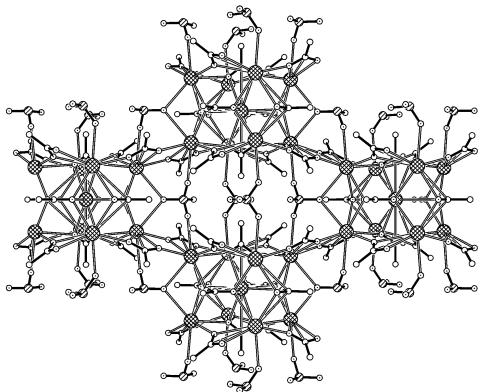
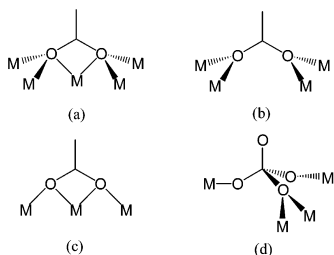


Fig. 2 3-D network of compound **1** showing the bridging mode of the ClO_4^- anion.

together to form a three-dimensional network. It is interesting to find that each ClO_4^- anion bridges four vertex barium atoms in an unusual $\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2$ fashion.

A noteworthy feature is that the acetate ligands adopt three types of bridging pattern: $\mu_5\text{-}\eta^3\text{-}\eta^3$ -, $\mu_4\text{-}\eta^2\text{-}\eta^2$ - and $\mu_3\text{-}\eta^2\text{-}\eta^2$ -bridging coordination modes and the perchlorate anions display an unusual $\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2$ -coordination mode as shown in Scheme 1.



Scheme 1 Coordination modes exhibited for the acetate and perchlorate anions in **1**: (a) $\mu_5\text{-}\eta^3\text{-}\eta^3\text{-O}_2\text{CMe}$, (b) $\mu_4\text{-}\eta^2\text{-}\eta^2\text{-O}_2\text{CMe}$, (c) $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-O}_2\text{CMe}$, (d) $\mu_4\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-O}_3\text{ClO}$.

In general, carboxylate groups display a variety of binding geometries, such as monodentate terminal, chelating, bidentate bridging and monodentate bridging, in coordination chemistry and the active sites of metalloenzymes.¹¹ To the best of our knowledge, no example containing the $\mu_5\text{-}\eta^3\text{-}\eta^3$ -coordination mode of acetate has been reported and the coexistence of $\mu_5\text{-}\eta^3\text{-}\eta^3$ -, $\mu_4\text{-}\eta^2\text{-}\eta^2$ - and $\mu_3\text{-}\eta^2\text{-}\eta^2$ -bridging modes for acetate groups in the same structure is unprecedented. In this novel double salt, the acetate group exhibits an unprecedented μ_5 coordination mode with the highest ligation number (HLN) of five, namely the largest number of coordination bonds that a particular anion can form with neighboring metal centers in its complexes,¹² whereas the perchlorate anion shows the HLN of four. It is of interest to determine the HLN of simple inorganic polyatomic anions, since the possible coordination modes of anionic ligands have to be considered in the design of polynuclear metal complexes¹³ and the crystal engineering of coordination networks.¹⁴

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Notes and references

† Synthesis of compound **1**: $\text{Ba}(\text{CH}_3\text{CO}_2)_2$ (2.55 g, 10 mmol) and $\text{Ba}(\text{ClO}_4)_2$ (0.5 g, 1.5 mmol) were mixed in 25 mL water. Then the mixed solution was filtered and evaporated slowly at room temperature to afford colorless block crystals. Yield: 62%. Anal. calc. for $\text{C}_{28}\text{H}_{42}\text{Ba}_9\text{Cl}_4\text{O}_{44}$: C, 13.7; H, 1.7. Found: C, 13.8; H, 1.8%. IR (KBr, cm^{-1}): 3447s, 1534s, 1424s, 1345m, 1146s, 1114s, 1073s, 1055s, 933m, 657s, 628s, 473w.

‡ Crystal data for **1**: $\text{C}_{28}\text{H}_{42}\text{Ba}_9\text{Cl}_4\text{O}_{44}$, $M_r = 2460.48$, monoclinic, space group $C2/m$, $a = 21.261(2)$, $b = 12.668(1)$, $c = 15.154(1)$ Å, $\beta = 133.276(1)^\circ$, $V = 2971.7(4)$ Å³, $T = 293$ K, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 6.147$ mm^{-1} , 18330 reflections measured, 3519 independent reflections ($R_{\text{int}} = 0.0398$), $R_1 = 0.0305$, $wR_2 = 0.0771$ for 3286 observed reflections [$I > 2\sigma(I)$]. CCDC reference number 189676. See <http://www.rsc.org/suppdata/dt/b2/b207889a/> for crystallographic data in CIF or other electronic format.

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