Unusual high nuclearity and pseudo-tetrahedral Zn_8O_{13} core found in a self-assembled complex

Jesús Sanmartín,[a] Manuel R. Bermejo,*[a] Ana M. García-Deibe[a] and Antonio L. Llamas-Saiz[b]

[a] *Departamento de Química Inorgánica, Facultade de Química, Campus Sur, Universidade de Santiago de Compostela, E-15706 Santiago de Compostela, Galicia, Spain. E-mail: qimb45@uscmail.usc.es*

[b] *Unidade de Raios X. Vicerrectorado de Investigación, Universidade de Santiago de Compostela, Campus Sur, E-15706 Santiago de Compostela, Galicia, Spain*

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An electrochemical synthesis yielded powdery $[Zn_2(L)(H_2O)]_n$ [H_4L = *N,N′*-bis(3-hydroxysalicylidene)-1,4-diaminobutane] and crystals of $[Zn_8(L)_4(H_2O)_3]\cdot H_2O\cdot 0.25MeCN$, whose X-ray crystal structure shows an unusual pseudo-tetrahedral Zn_8O_{13} core assembled by thirteen μ-phenoxo bridges, where Zn(II) ions are pentaco-ordinated.

A large number of S-bridged polynuclear zinc complexes are described in the literature,[1] but not so many examples of high nuclearity are found containing O- and N-donor ligands. An interesting approach to design these compounds is the assembly of simple units into polynuclear molecules.[2] The ability of compartmental or polynucleating ligands to hold closely metal ions is useful for this.[3,4] Therefore, the behaviour of the hexadentate Schiff base H_4L has been studied here. This ligand was prepared by condensation of 2,3-dihydroxybenzaldehyde and 1,4-diaminobutane in a 2 : 1 molar ratio.

The synthesis of the complexes was performed by using an electrochemical method,[4,5] with the cell summarised as: $Zn_{(+)}|MeCN + H_4L|Pt_{(-)}$. An acetonitrile solution of H_4L (0.10 g) was electrolysed (V = 14.5 V) for a calculated time (195 min) according to: $2Zn_{(s)} + H_4L \rightarrow Zn_2(L)(H_2O)_x + 2H_{2(g)}$. Anodic zinc was dissolved during the reaction (0.065 g), whilst hydrogen was evolved at the Pt cathode. An insoluble product $[Zn_2(L)(H_2O)]_n$,† was easily isolated from solution (yield: 90%). The brown solution obtained was slowly evaporated and small crystals were collected and later crystallographically identified as $Zn_8(L)_4(H_2O)_3\cdot H_2O\cdot 0.25MeCN$.‡

The study of the free ligand and both complexes by IR spectroscopy indicates that the Schiff base is behaving as hexadentate, through its potential oxygen and nitrogen donor atoms.[4–7] Positive ion ES mass spectrometry shows for $[Zn_2(L)(H_2O)]_n$ two peaks related to fragments of the type $Zn_2(L)^{2+}$ and $Zn_3(L)_2{}^{2-}$ at *m/z* (abundance) 453 (4×10^3) and 847 (2×10^3), respectively. This seems to be in accordance with a polymeric nature for the complex.

X-Ray diffraction studies of $Zn_8(L)_4(H_2O)_3\cdot H_2O\cdot 0.25MeCN$ revealed its molecular structure as a neutral octanuclear

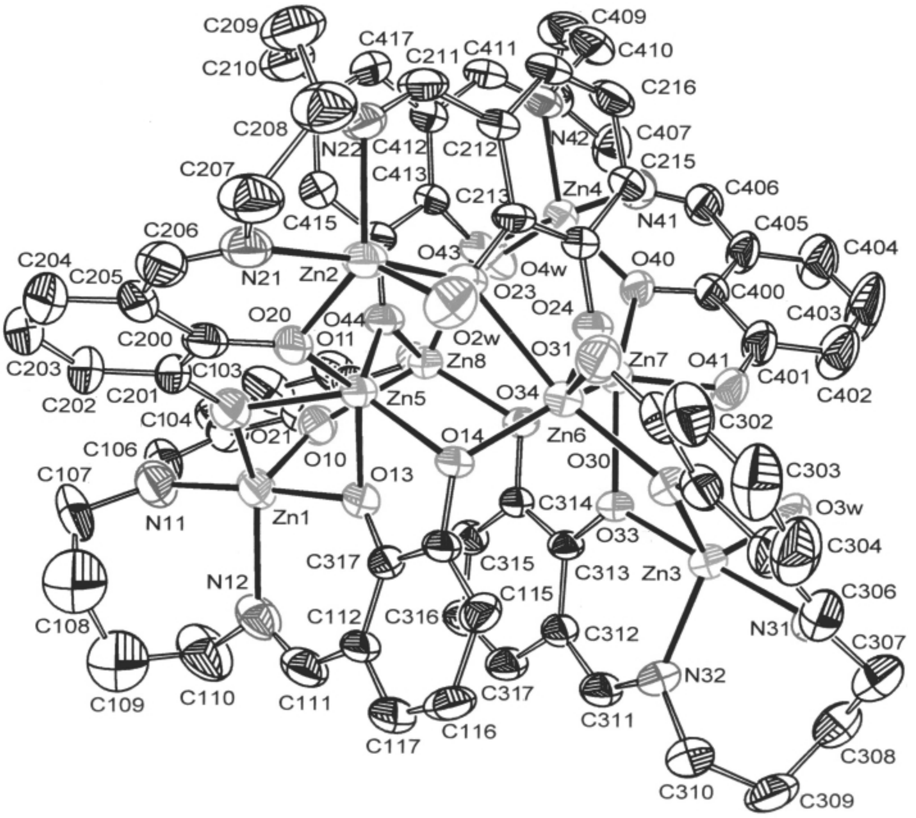

Fig. 1 ORTEP plot of $Zn_8(L)_4(H_2O)_3$. Atoms are represented by their 30% probability ellipsoids. Disordered atoms, H atoms, parentheses and some C atom labels are omitted for clarity. Angle ranges: Zn–O–Zn 126.8(3)–99.5(2)°; around Zn(1) 78.1(2)–176.8(3)°; around Zn(2) 87.5(2)–175.3(3)°; around Zn(3) 88.1(2)–178.3(3)°; around Zn(4) 88.0(2)–176.0(3)°; around Zn(5) 79.1(2)–137.3(2)°; around Zn(6) 76.5(2)–162.3(2)°; around Zn(7) 76.8(2)–155.5(2)°; around Zn(8) 77.5(2)–146.4(3)°.

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complex (Fig. 1), where all the Zn ions are pentacoordinated. Four tetradeprotonated ligand units, L^{4-}, assemble the metal ions in a pseudo-tetrahedral arrangement by means of thirteen μ-phenoxo bridges. This is an interesting example of three-dimensional supramolecular architecture.

Atoms Zn(1), Zn(2), Zn(3) and Zn(4) lie on the pseudo-tetrahedron vertexes, having three water molecules bonded to three of them (Fig. 2). The other four inner Zn atoms [Zn(5)–Zn(8)] lie on four of the tetrahedron edges, and so they almost form a square. Additionally, the crystal contains encapsulated water (one molecule dispersed in five different positions with occupation factors of 20%) and acetonitrile (25% occupation factor) in the asymmetric unit.

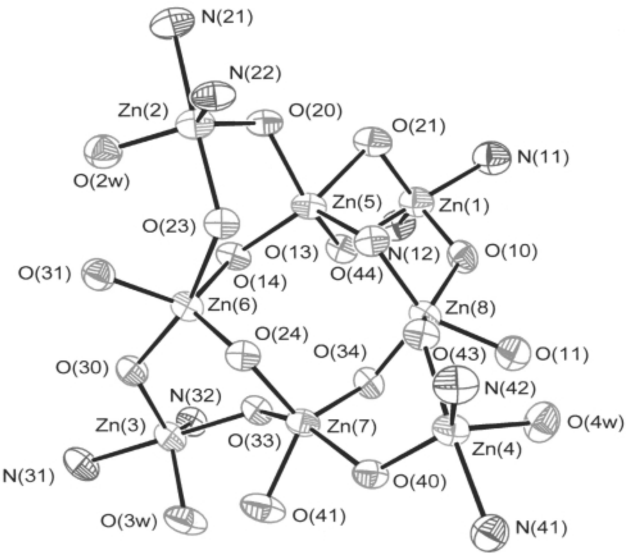

Fig. 2 A drawing of the coordination environments for $Zn_8(L)_4(H_2O)_3$. Dotted lines highlight the pseudo-tetrahedral shape.

Zn(x) (x = 1–4), are in N_2O_3 environments, which are formed by the inner N_2O_2 compartment of each L^{4-} unit and an additional O atom. This corresponds to a coordinated water molecule O(xw) for Zn(x) (x = 2–4), whilst for Zn(1) a μ-phenoxo bridge to Zn(5), through O(21), completes its coordination polyhedron. These environments can be described as slightly distorted trigonal-bipyramidal,[8] where Zn(1) is the most distorted. An imino N atom and its opposite inner phenolic O atom are occupying the axial positions in all cases.

Likewise, each one of these four outer metal centres is bound to two other inner Zn ions by two μ-$O_{phenolate}$ bridges through the inner oxygen atoms of their corresponding ligand units [O(x0) and O(x3)] for Zn(x) (x = 1–4). Additionally, Zn(1) is also bound through the outer O(21). Thus, Zn(1)···Zn(5) [3.182(2) Å] is the shortest Zn···Zn distance, the longest being 3.901(2) Å. These values are in the range found for other polynuclear zinc complexes containing imino or amino ligands with μ-oxo bridges.[2,9–11]

For the other four inner metal centres, Zn(5)–Zn(8), O_5 environments are formed exclusively by the sixteen phenolic donor atoms, with each metal ion simultaneously bound to three different ligand units. The polyhedron around Zn(6) can be also described as trigonal bipyramidal, with two inner O atoms in axial positions, and three outer phenolic O atoms in the equatorial plane. By contrast, the environments of Zn(5), Zn(7) and Zn(8) can be considered as distorted square pyramids.[8]

Zn–N and Zn–O distances [2.021(7)–2.156(9) and 1.910(6)–2.328(5), respectively], lie within the ranges found for other polynuclear complexes with N- and O-donor ligands.[9,12,13]

Some related Schiff bases had been previously designed as potentially compartmental and binucleating, being able to accommodate, two metal ions (d + f or less commonly d + d) in different modes.[6,7] Here, the intricate bridging behaviour of L^{4-} leads to much higher polynucleating ability. Thus, the ligand unit containing Zn(2) in its inner compartment is also coordinated to Zn(1), Zn(5), Zn(6) and Zn(7), whilst the other three ligand units are each bonded to four metal ions.

This structure is very unusual and one of the rare and recent examples of oxygen bridged octanuclear Zn(II) complexes.[9,14] No Schiff base ligands are present in these two cores, which are significantly different and contain additional bridging oxo or hydroxo groups.

Therefore, to our knowledge, this is the first example of an octanuclear μ-phenoxo bridged zinc complex containing Schiff base ligands. The long methylene chain of L^{4-} appears to provide enough flexibility to achieve such high nuclearity. This factor seems to be important. Thus, in the case of an amino octanuclear complex,[9] high nuclearity could not be observed when the more rigid imino ligand derivative was employed.

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Notes and references

† Elemental analyses: found(calc.) for $[Zn_2(L)(H_2O)]_n$: C, 45.4(45.7); H, 4.0(3.8); N, 6.0(5.9); O, 16.5(16.9)%.

‡ *Crystal data* for $Zn_8(L)_4(H_2O)_3\cdot H_2O\cdot 0.25MeCN$: $C_{72.5}H_{72.75}N_{8.25}O_{20}Zn_8$; M_r = 1902.60; monoclinic, space group $P2_1/n$ (no. 14), a = 13.606(2), b = 17.608(3), c = 32.497(4) Å, β = 91.698(6), V = 7782.3(19) $Å^3$, T = 293(2) K, Z = 4; μ(Cu-Kα) = 3.310 mm^{-1}; 33 682 reflections measured, 16 195 reflections unique (R_{int} = 0.12); $R1$ = 0.0895, $wR2$ = 0.2625 ($F > 4\sigma(F)$; for all data $R1$ = 0.2279, $wR2$ = 0.3450.[15] One C atom of a methylene chain was found in two disordered positions [C(408) and C(48′)]. Their occupancy parameters were fixed and refined anisotropically and isotropically, respectively. Disperse electronic density could be found around C108 and C109, but a satisfying disorder model was not established. Both atoms have been isotropically refined due to the high values found for the anisotropic thermal parameters. Hydrogen atoms were included, using a riding model, except for the coordinated water molecules, where H atoms could be located, fixed and given isotropic displacement parameters of 0.1 $Å^2$. Five water molecules were also located with occupancy parameters fixed to 0.2. In addition, a MeCN molecule was found and fixed with an occupancy parameter of 0.25. Disordered atoms and solvent molecules were treated with some restraints.

CCDC 182/1582. See http://www.rsc.org/suppdata/cc/b0/b001368o/ for crystallographic files in .cif format.

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