A water reduction process performed by zinc metal under very mild conditions[†]

María J. Romero,^a Rosa Pedrido,^{*a} Ana M. González-Noya,^b Miguel Martínez-Calvo,^a Guillermo Zaragoza^c and Manuel R. Bermejo^{*a}

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Water reduction can be electrochemically promoted by zinc under very mild conditions, as demonstrated by the formation of the complex $[Zn(H_2O)_6][Zn_3(L)_3(\mu_3-O)]$, whose anion consists of a Zn_3O_4 cluster incorporating a μ_3 -oxo anion.

The study of polynuclear coordination compounds with novel metal cores¹ has experienced increased interest in the last two decades due to their potential applications as functional materials,² catalysts³ or models for active sites in metalloenzymes.⁴ In particular, numerous zinc cluster complexes have been assembled in order to reproduce some enzymatic behaviours.⁵ For example, it is well known that zinc(II) ions can promote hydrolytic reactions by coordinating a nucleophilic water to lower its p*K*_a without the complication of radical reactions.⁶ Additionally, the ability of zinc(II) to adopt a variety of coordination numbers and geometries, combined with its rapid ligand exchange capacity, allows it to accommodate the structural rearrangements that must occur during the course of many chemical reactions.^{2,4}

Numerous examples of polynuclear zinc complexes featuring oxo anions coordinated to the metal centres have been reported to date. Most of these compounds were synthesized by employing chemical methods that involve the introduction of dioxygen,⁷ water⁸ or carbon dioxide⁹ into the reaction media or/and by using different basic agents.^{7,10} In these cases, zinc metal or zinc coordination compounds themselves are able to carry out electron transfer or hydrolysis processes, releasing into the media oxo or hydroxo anions that could act as potential ligands.

On the other hand, the efficient catalytic reduction of water by zinc metal for the generation of hydrogen is one of the most challenging chemical transformations in industry at present, since hydrogen could be considered as a clean energy source if it is produced using renewable electricity. This reaction is carried out by employing special conditions, which involve the careful control of factors such as pressure and temperature¹¹ or the presence of suitable catalysts (Pd, Pt, Ni, Rh, Mn).¹²

During the last few decades our group and others have employed Schiff base ligands derived from salicylaldehyde to assemble polynuclear complexes.¹³ It is also well known that zinc(II) ions have a strong affinity for aromatic sulfonamides. With the aim of preparing new polynuclear zinc complexes that potentially could bind oxo anions and may have catalytic activity, we have designed the new ligand 5-(dimethylamino)-N-(2-(2-hydroxybenzylideneamino)phenyl)naphthalene-1-sulfonamide, named H₂L (Scheme 1).

Herein we report a zinc cluster complex assembled after a water reduction process carried out under mild conditions by coordinated Zn^{2+} ions in an electrochemical cell.

Equimolecular condensation of salicylaldehyde and *N*-(2-aminophenyl)-5-(dimethylamino)-1-naphthalenesulfonamide gave rise to the [N₂O] tridentate ligand H₂L.† Electrochemical oxidation of a zinc plate¹⁴ in the presence of a degassed commercial acetonitrile solution of H₂L yielded the neutral solid complex [Zn(H₂O)₆][Zn₃(L)₃(μ ₃-O)] (1), which was readily characterised by analytical and spectroscopic techniques. The MALDI-TOF mass spectrum of 1 exhibits peaks corresponding to the [Zn(H₂O)₆][Zn₃(L)₃(μ ₃-O)] fragmentation, thus confirming the proposed molecular formula in solution.† The stoichiometry of this compound was further confirmed by its molar conductivity value, which is compatible with a 1:1 electrolyte compound.¹⁵

Slow evaporation of the mother liquors yielded green crystals corresponding to the complex $[Zn(H_2O)_6][Zn_3(L)_3(\mu_3-O)]$ · $3CH_3CN\cdot H_2O$ (1·3CH₃CN·H₂O), which was completely characterised, including by X-ray diffraction.‡ It should be noted that this process is totally reproducible and all attempts to obtain the solid complex 1 or the crystalline 1·3CH₃CN·H₂O under the same experimental conditions gave identical results.

The structure of $1.3CH_3CN \cdot H_2O$ consists of a trinuclear anionic complex $[Zn_3(L)_3(\mu_3-O)]^{2-}$ and a hexaaquo cation $[Zn(H_2O)_6]^{2+}$, solvated by three acetonitrile and one water molecules (Fig. 1 and 2). The anionic entity $[Zn_3(L)_3(\mu_3-O)]^{2-}$ is



Scheme 1 Ligand H₂L

^a Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela, Santiago de Compostela, Galicia, E-15782, Spain. E-mail: rosa.pedrido@usc.es,

manuel.bermejo@usc.es; Fax: +34 981597525; Tel: +34 981563100 ^b Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela, Lugo, Galicia, E-27002, Spain

^c Unidade de Difracción de Raios X, Edificio CACTUS, Universidade de Santiago de Compostela, Campus Sur, Santiago de Compostela, Galicia, E-15782, Spain

[†] Electronic supplementary information (ESI) available: Synthesis and experimental data for H₂L and complexes 1, 1·3CH₃CN·H₂O and 2. ORTEP diagram, selected bond distances and angles for 1·3CH₃CN·H₂O. 1 and 2 characterization figures. CCDC 766560. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc00256a



Fig. 1 Ball and stick representation of the anionic cluster $[Zn_3(L)_3(\mu_3-O)]^{2-}$ in 1·3CH₃CN·H₂O. The $[Zn(H_2O)_6]^{2+}$ counterion, solvate acetonitrile and water molecules are omitted for clarity.



Fig. 2 Hydrogen bonding interactions between two $[Zn_3(L)_3(\mu_3-O)]^{2-}$ molecules and the $[Zn(H_2O)_6]^{2+}$ cation.

built by three molecules of dianionic ligand $[L]^{2-}$ bound to three zinc(II) ions through a [N₂O] donor system, together with an oxo anion coordinated in a μ_3 -bridging mode. Each phenol oxygen establishes a μ_2 -oxo bridge between two zinc centres. This coordination mode allows the assembly of a Zn₃O₄ central core, which could be described as a pseudo-cube with a vacant position at the opposite vertex to the oxygen atom O1. The metal and the phenol oxygen atoms in the Zn₃O₄ core describe one six-membered metallacycle with a chair-type conformation (Fig. S2, ESI†), while the coordination of the μ_3 -oxo anion gives rise to three four-membered metallacycles, which correspond to the three faces of the distorted pseudo-cube.

The zinc(1) ions are located in $[N_2O_3]$ pentacoordinated environments in the trinuclear cluster, with distorted square-pyramidal geometries, according to their calculated τ parameters ($\tau_1 = 0.28$, $\tau_2 = 0.04$, $\tau_3 = 0.15$).¹⁶ A weak intramolecular interaction between the Zn2 atom and one oxygen atom from the dansyl group [Zn2···O52, 2.681(3) Å] is also observed (Fig. 1).

The Zn–N and Zn–O bond distances are similar to those found in other salen polynuclear Zn(II) complexes.^{5d,17–19} The Zn···Zn bond distances in this anionic cluster (close to 3.1 Å) are slightly longer than the sum of the van der Waals radii for two zinc atoms (2.8 Å).^{20,21} These distances are in the order of The hexaaquo counterion appears between two cluster molecules of $[Zn_3(L)_3(\mu_3\text{-}O)]^{2-}$ (Fig. 2) due to the establishment of numerous hydrogen bond contacts (Table S2, ESI†).

At this point the origin of the μ_3 -oxo anion in compound **1** must be analysed. Considering all the literature reports concerning the catalytic activity of Zn^{2+} ,²⁴ we propose that this anion was generated *in situ* by means of a water reduction process catalysed by zinc(II) ions during the electrochemical synthesis of the zinc(II) complex. To confirm our proposal, the electrochemical synthesis was repeated under an inert atmosphere, but employing completely dry acetonitrile. Under these conditions a complex with a $Zn_2(L)_2$ stoichiometry (**2**) was isolated[†] but this rapidly evolved in solution to form complex **1**.²⁵ It is clear from these findings that the absence of water in the medium avoided the catalytic conversion of the dimer into the trinuclear cluster and therefore that the presence of water is essential to generate complex **1**.

A possible mechanism for the formation of complex 1 would involve two different redox processes (Scheme 2). In the first stage, the zinc anode undergoes an oxidation to generate Zn^{2+} ions, while the sulfonamide N-H and phenoxo O-H bonds from the ligand H₂L are reduced to give the bideprotonated $[L]^{2-}$. The coordination of two bideprotonated ligands to two Zn(II) ions would result in a dimeric compound with μ_2 -phenoxo bridges between the two metal centres (I).²⁶ The particular preferences of Zn(II) in terms of coordination number would provide a suitable kernel for coordination of one additional water molecule from the medium to one of the metal centres, thus one of the zinc(II) ions achieves a pentacoordinated environment (II).²⁴ Since the electrochemical oxidation of the Zn plate would continue in the cell once the $Zn_2(L)_2$ dimer is formed, aqueous Zn(II) ions { $[Zn(H_2O)_6]^{2+}$ } and two electrons are released into the solution. One of these electrons would perform a metal-water bond reduction, generating a coordinated hydroxo anion (III).²⁷ This hydroxo anion, which acts as a μ_2 -oxo bridge, would be able to incorporate a new zinc(II) ion and a third anionic ligand unit into the complex (IV). In the final step, the trinuclear complex would experience a second reduction on the zinc-OH bond,



Scheme 2 Proposed mechanism for the formation of 1.

creating an O^{2-} anion that would complete the pentacoordinated environment of the third metal centre $([Zn_3(L)_3(\mu_3-O)]^{2-})$.

The coexistence of Zn^{2+} , e⁻, H₂O, Zn_2L_2 and L^{2-} in solution makes the formation of compound 1 possible, with the oxo anion being the key piece in the assembly of the trinuclear cluster. We must stress that all the catalytic reduction stages yield hydrogen gas, which is liberated from the cathode throughout the process.

An electrochemical water reduction process catalysed by Zn^{2+} ions in the presence of the ligand H_2L leads to the formation of a μ_3 -oxo anion, which acts as the key component in the assembly of the trinuclear zinc cluster $[Zn_3(L)_3(\mu_3-O)]^{2-}$.

The main advantages of the electrochemical method to achieve the water reduction in the presence of zinc metal are (i) its reproducibility and (ii) the use of very mild conditions, since the reaction occurs in the absence of reducing agents, basic reagents or external catalysts.

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Notes and references

‡ Crystal data for 1·3CH₃CN·H₂O: (C₈₁H₈₀N₁₂O₁₄S₃Zn_{3.50}), M_w = 1770.65, crystal dimensions: 0.25 × 0.24 × 0.24 mm, triclinic, space group: *P*-1, *a* = 15.344(5), *b* = 16.139(5), *c* = 18.408(6) Å, *α* = 75.772(5)°, *β* = 81.362(5)°, *γ* = 70.021(4)°, *V* = 4142(2) Å³, *Z* = 1, *μ* = 1.148 mm⁻¹, *F*(000) = 1830. Radiation λ (Mo-K α) = 0.71073 Å, *T* = 293(2) K, reflections collected/unique 34313/15033 (*R*_{int} = 0.0540), *R* (all data) = 0.0953, w*R* (all data) = 0.146, GOF = 0.994, max./min. residual density 0.859/-0.648 e Å⁻³. CCDC 766560.

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