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Solution-stable trinuclear zinc(II) cluster from 4-methyl-2-*N*-(2-pyridylmethylene)aminophenol (HPyrimol)†

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The reaction of zinc^{II} acetate with 4-methyl-2-*N*-(2-pyridylmethyl)aminophenol (HPyramol) in methanol leads to a solution stable linear trinuclear zinc cluster with intramolecular ligand oxidation.

Hydroxo- and carboxylate-bridged Zn complexes are attractive because of their potential relevance as models of sugar-metabolizing enzymes.[1–6] A number of hydrolases are known to contain two or more zinc ions in close proximity at their respective active sites.[7,8] Furthermore, zinc carboxylates have been extensively and successfully used in the field of supramolecular self-assembly.[9,10] The preparation of metal–organic materials is of current interest due to the large variety of possible applications such as catalysis, magnetism or host–guest chemistry.[11] The present paper describes the preparation and characterisation of a trinuclear zinc(II) complex, namely $[Zn_3(Pyrimol)_2(CH_3CO_2)_4]$ obtained in acetonitrile from 4-methyl-2-*N*-(2-pyridylmethyl)aminophenol (HPyramol)[12] which appeared to be oxidized to 4-methyl-2-*N*-(2-pyridylmethylene)aminophenol (HPyrimol) upon coordination with the metal salt (Fig. 1).

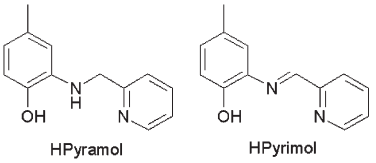

Fig. 1 4-methyl-2-*N*-(2-pyridylmethyl)aminophenol (HPyramol) and 4-methyl-2-*N*-(2-pyridylmethylene)aminophenol (HPyrimol).

A methanol solution (20 mL) of HPyramol (100 mg, 0.47 mmol) was added to a methanol solution of $Zn(OAc)_2·2H_2O$ (140 mg, 0.66 mmol). The reaction mixture was left at room temperature in air. After a few days, the initial light yellow solution turned red and after a few weeks, dark red crystals suitable for X-ray diffraction study were obtained, which were collected by filtration (45% yield based on the ligand). The crystals were formulated by elemental microanalysis (Found: C, 47.34; H, 4.22; N, 6.79. Calc. for $C_{34}H_{34}N_4O_{10}Zn_3$: C, 47.77; H, 4.01; N, 6.55) and structurally characterized by X-ray diffraction analysis.‡ The molecular structure is centrosymmetric with Zn(2) on an inversion center. As shown in Fig. 2, the three zinc(II) centres [Zn(1), Zn(2) and $Zn(1)^{[-x,-y,1-z]}$] are bridged by a total of four carboxylates and two Pyrimol ligands. All carboxylate oxygens are coordinated to one Zn atom, respectively. Zn(1) is further coordinated by the two nitrogens from a Pyrimol ligand and its phenolate moiety. This phenolic oxygen atom bridges the external zinc(II) ions to the central one. This arrangement results in an almost perfect octahedral geometry for Zn(2) [O(1)–Zn(2)–O(22) 92.02(5), O(22)–Zn(2)–O(32) 94.40(5) and O(1)–Zn(2)–O(22)a 87.98(5)°]. Zn(1) is in a distorted trigonal bipyramidal [O(1)–Zn(1)–N(12) 154.48(5), O(23)–Zn(1)–N(9) 117.37(5), O(33)–Zn(1)–N(9) 129.16(5), and O(23)–Zn(1)–O(33) 112.63(6)°] environment. In the crystal, the oxidized ligand HPyrimol is found, as a result of a metal-assisted oxidation of HPyramol (Fig. 1). This phenomenon has not yet been reported for a non-redox metal like zinc, but a mechanism was given for the iron-catalysed oxidation of a related ligand proposed by Morgenstern-Badarau *et al.*[13,14] The presence of the HPyrimol form in the crystal structure was proven by the N(9)–C(10) bond length (1.285(2) Å), the N(9)–C(10)–C(11) bond angle (117.79(15)°), and the N(9)–C(10)–C(11)–C(16) torsion angle (−178.07(16)°). The difference Fourier map reveals that only one hydrogen atom is bound to C(10). Close examination of the structure revealed that the Zn–O (range 1.9486(12)–2.1403(12) Å) and Zn–N (range 2.0772(14)–2.1940(13) Å) bond lengths can be considered as normal by comparison with the similar few examples reported in the literature.[15–20] The intramolecular Zn(1)···Zn(2) distance is 3.3553(2) Å, which is in the expected range for a carboxylate bridged metal–metal entity.

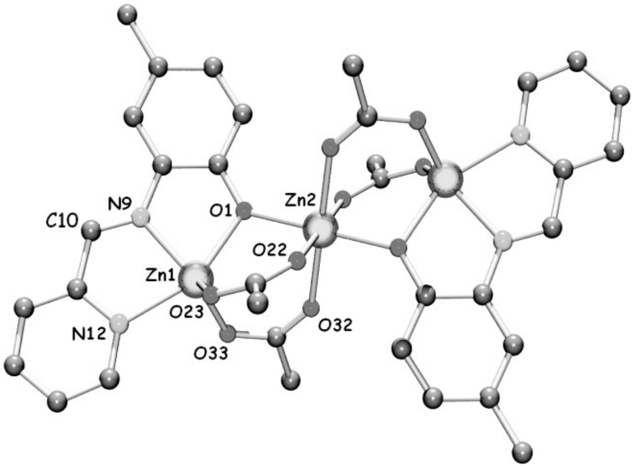

Fig. 2 Crystal structure of $[Zn_3(Pyrimol)_2(OAc)_4]$. Hydrogen atoms are omitted for clarity. Selected bond distances: Zn(1)–O(1) 2.0791(11); Zn(1)–O(23) 1.9674(12); Zn(1)–O(33) 1.9486(12); Zn(1)–N(9) 2.0772(14); Zn(1)–N(12) 2.1940(13); Zn(2)–O(1); 2.0496(11); Zn(2)–O(22); 2.1403(12); Zn(2)–O(32) 2.1383(12) Å.

The trinuclear zinc complex was studied by ^1H NMR in CD_3OD and its spectrum was compared with the one of the initial HPyramol ligand in CD_3OD (Fig. 3).§ Firstly, the chemical shift at 4.43 ppm (Fig. 3**A**, b) corresponding to the CH_2 of the ligand is not present for the complex. Instead, a singlet appears at 8.81 ppm which corresponds to the imino C_{sp^2}–H of the oxidised ligand (Fig. 3**B**, k). In addition, the IR spectrum of the free HPyramol ligand shows one sharp band at 3391 cm^{-1} corresponding to the N–H stretching. No absorption band is observed in this range for the trinuclear zinc complex. The rest of the NMR signals can easily be assigned

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† Electronic supplementary information (ESI) available: ^1H NMR spectra of the free ligand and of the complex; stability of the ligand Hypramol in MeOH, ^1H NMR studies; X-ray powder diffraction pattern of the bulk material. See http://www.rsc.org/suppdata/dt/b4/b407637k/

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to the coordinated ligand (all the signals being down-shifted). An extra signal is located at 1.99 ppm which is ascribed to the methyl groups of the bridging acetates (Fig. 3**B**, j). This NMR spectrum agrees with the existence of the zinc cluster $[Zn_3(Pyrimol)_2(OAc)_4]$ in solution which is confirmed by the ESI-MS peak at *m*/*z* 872 corresponding to $[M + H_2O]^+$. In addition, the X-ray powder diffraction pattern was recorded for the solid bulk material and was compared to the calculated one from the crystal structure data. It is evidential of the homogeneity of the isolated material (see ESI†).

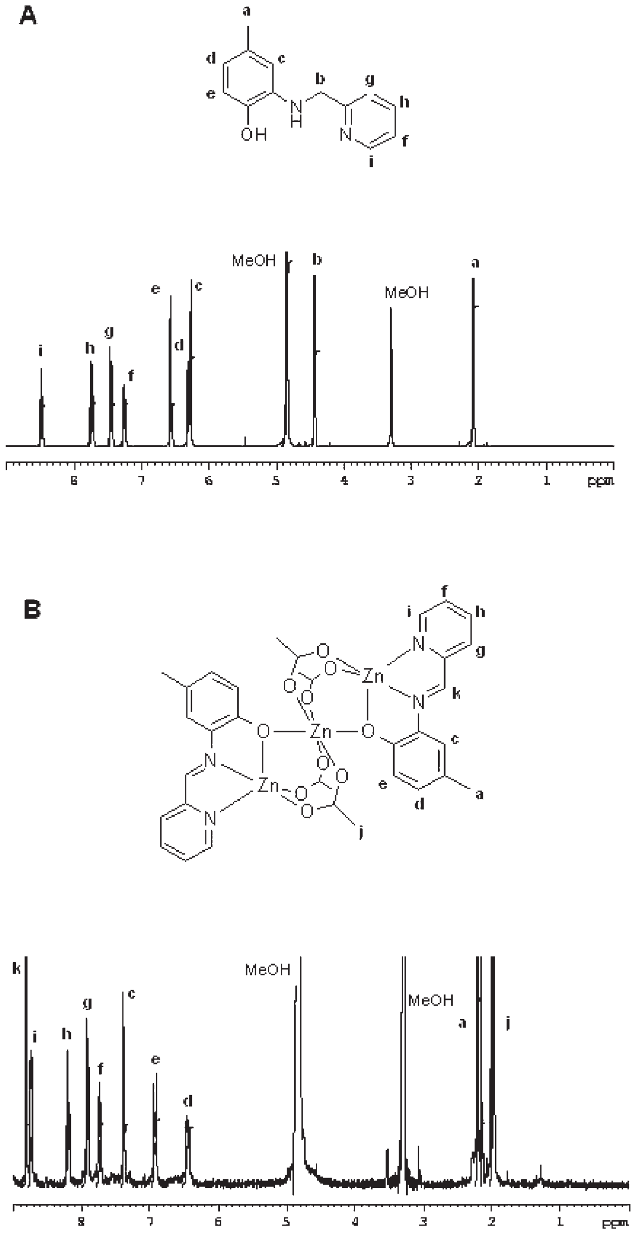

Fig. 3 ^{1}H NMR. A: initial HPyramol ligand; B: trinuclear zinc complex.

Metalloenzymes with zinc-containing polymetallic centers are the subject of much current attention. A new trinuclear zinc complex has been prepared which contains a rarely reported linear array of zinc ions which may mimic the active site of *E. coli* alkaline phosphatase.[21] The zinc^{II} coordination compound is stable in chloroform solution and its ^{1}H NMR spectrum has been recorded. Taking advantage of this stability, the intramolecular oxidation of the ligand is currently under investigation as the kinetics of the reaction can be followed by ^{1}H or ^{13}C NMR.

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Notes and references

‡ A single crystal of $Zn_3[(Pyrimol)(C_2H_3O_2)_2]_2$ was analyzed at 150 K: $C_{34}H_{34}N_4O_{10}Zn_3$ + disordered solvent, $M = 854.82$, dark red block, $0.51 \times 0.42 \times 0.24$ mm^3, monoclinic, space group $P2_1/c$ (No. 14) with $a = 8.9553(1)$, $b = 20.0267(2)$, $c = 11.6205(1)$ Å, $\beta = 122.3754(6)°$, $V = 1760.13(3)$ Å^3, $Z = 2$, $Dc = 1.613$ g cm^{-3}; μ(Mo–Kα) = 2.090 mm^{-1}, $F(000) = 872$. X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å). 18677 reflections were collected up to a resolution of $(\sin \theta/\lambda) = 0.65$ Å^{-1}, 3997 reflections were unique ($R_{int} = 0.0401$). An absorption correction based on multiple measured reflections was applied (correction range 0.45–0.61). The structure was solved with Direct Methods (SHELXS-86[22]) and refined with SHELXL-97[23] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined as rigid groups. 235 parameters were refined with no restraints, resulting in $R1/wR2 = 0.0254/0.0684$ for $I > 2\sigma(I)$ and $R1/wR2 = 0.0293/0.0705$ for all reflections. The residual electron density ranged from −0.53 to 0.52 e Å^{-3}. The crystal structure contains voids (113 Å^3 unit cell^{-1}) filled with disordered methanol molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON,[24] routine CALC SQUEEZE) resulting in 29 e$^-$ unit cell^{-1}. CCDC reference number 239236. See http://www.rsc.org/suppdata/dt/b4/b407637k/ for crystallographic data in CIF or other electronic format.

§ The stability of free HPyramol in methanol was verified by ^{1}H NMR and no oxidation to HPyrimol was observed (see ESI†).

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