

Oligonuclear zinc complexes of 2-pyridylmethanol

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The title ligand HL leads to the zinc complexes [(HL)₂Zn(μ-Cl)₂Zn(HL)₂]ZnCl₄ **1 and [Zn(ZnL₂)₆]Cl₂ **2**; the ligand arrangement and core structure of **2** make the self-assembly of this complex understandable and show its topological relation to the cadmium iodide structure.**

Metal alkoxides, specifically those of zinc, are oligomeric or polymeric,¹ and it is actually difficult to obtain simple mononuclear zinc alkoxide complexes like [Zn(OR)₂L₂] or [Zn(OR)L₃].² Such complexes seem attractive either as precursors of new ZnO-containing materials³ or as models of the enzyme-substrate combination in horse-liver alcohol dehydrogenase (ADH).⁴ We therefore tried to obtain such species in a more stable form by making use of the chelate effect, combining the L and OR functions in one ligand molecule. Our ligand of choice was 2-pyridylmethanol whose alkoxide anion can form a five-membered chelate ring. We found that chelation takes place when the ligand is combined with zinc and chloride. The resulting complexes, however, had the unexpected compositions Zn₃(HL)₄Cl₆ and Zn₇L₁₂Cl₂,[†] which were found by X-ray analysis to belong to compounds **1** and **2**.[‡]

Compound **1** resulted from ZnCl₂ and HL in diethyl ether. Its strong tendency of formation under these circumstances is obvious from the fact that the reactions were quantitative with respect to HL for stoichiometric ratios ranging from 3 : 4 to 3 : 2. Complex **1** is soluble only in strong donor solvents, and crystals were obtained by diffusion of hexane into a thf solution. Their structure determination (see Fig. 1) revealed the ionic nature of **1** containing the centrosymmetrical dinuclear dication comprised of two (HL)₂ZnCl units. Being a five-membered chelate ring ligand, HL favours octahedral coordination of zinc, as it does for copper in the only other structurally characterized HL complex of a transition metal, [Cu(HL)₂(salicylate)₂].⁵

As ZnCl₂-HL combinations, either with or without additional base, did not lead to pyridylmethanolato complexes, a non-polar approach to them was attempted by reacting Zn[N(SiMe₃)₂]₂

with HL. In hydrocarbon solvents this produced a precipitate of approximate composition ZnL₂. Attempts to purify this by crystallization from strong donor solvents failed, and surprisingly it reacted with CHCl₃ or CH₂Cl₂ incorporating chlorine with formation of **2** which is soluble in these solvents from which it crystallizes upon diffusion of hexane into the solution. Subsequently it was found that **2** results directly from Zn[N(SiMe₃)₂]₂ and HL in CH₂Cl₂. At the moment we can only speculate on the course of this reaction which seems to take part of its driving force from the ideal geometry of the resulting Zn₇L₁₂ cation (see below).

The formula drawing of **2** in which the chelate ligands are indicated only symbolically indicates the highly symmetrical nature of the complex dication comprised of a central ZnO₆ unit surrounded in a disk-like fashion by six ZnO₄N₂ units. This is the first such heptametal arrangement for zinc, and it bears no relation to the double cubane arrangement in [Zn₇Me₆(OMe)₈].⁶ Its stability and preferred formation become understandable when viewing a space filling model of it, Fig. 2. The six aromatic rings on each side of the Zn₇O₁₂N₁₂ scaffold are stacked in triples of pairs such that they perfectly encapsulate the polar inner structure of the cation. The hydrophobic exterior of the cation offers no point of attachment for the chloride anions or the solvating dichloromethane molecules, and it is the reason for the good solubility of **2**. We can think of no other chelate ligand arrangement or core structure of a Zn_xL_y complex derived from 2-pyridylmethanol that would lead to such a perfect match. Thus the cations of **2** are an illustrative example of self-assembly.

When looking at the inorganic core of **2** alone (Fig. 3), another general feature of this complex becomes visible. To a good approximation the O and N atoms form two layers of a close packed array, and of the octahedral interstices in this array one half are filled with zinc ions. Thus the cations of **2** represent fragments of the cadmium iodide or brucite structure inside an organic ligand environment. In this respect **2** is a topological equivalent of the Fe₁₇ and Fe₁₉ complexes of the tetradentate

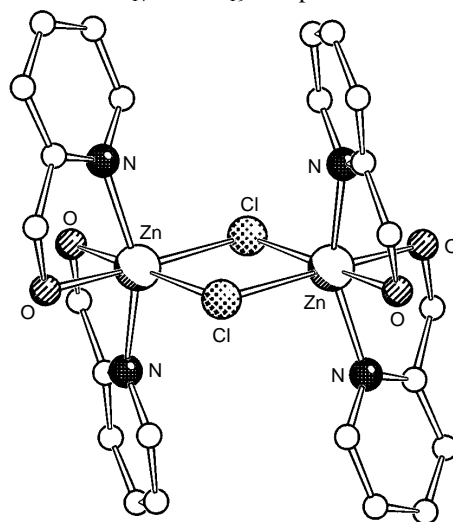
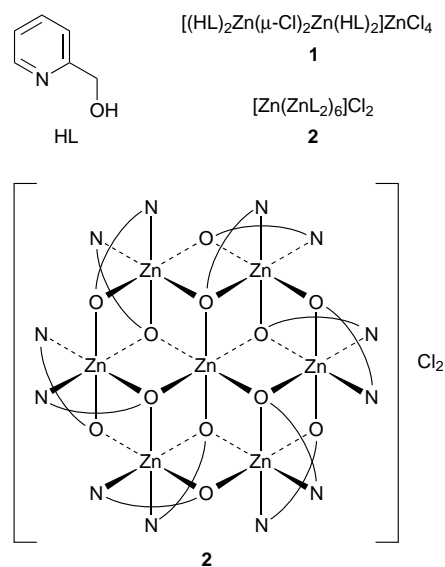


Fig. 1 Atomic arrangements (bond lengths in Å) in the dication of **1**: Zn-O 2.214(3), 2.217(3); Zn-N 2.075(4), 2.083(3); Zn-Cl 2.409(2), 2.459(2) Å

HEIDI ligand.⁸ In both cases the same assembly principle, *i.e.* matching of the ligands' and the core's spatial requirements, is operative.

One would assume that complexes like **2** should exist for pyridylmethanolato complexes of other transition metals. But while the oligonucleating ability of this ligand is well documented,[§] we found no other complex like **2** and no other complex with a M_7X_{24} core like in **2** in the literature.

While Fig. 3 points to the materials aspect of these complexes, the aspect of modelling zinc-coordinated intermediates of ADH-catalysed alcohol oxidation lies in the bonding type of the 2-pyridylmethyl-derived ligands. Complex **1**

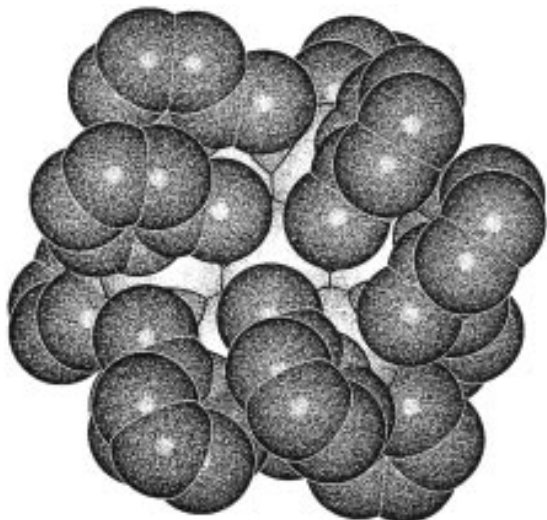


Fig. 2 SCHAKAL plot⁷ of the $[Zn(ZnL_2)_6]$ cation of **2**

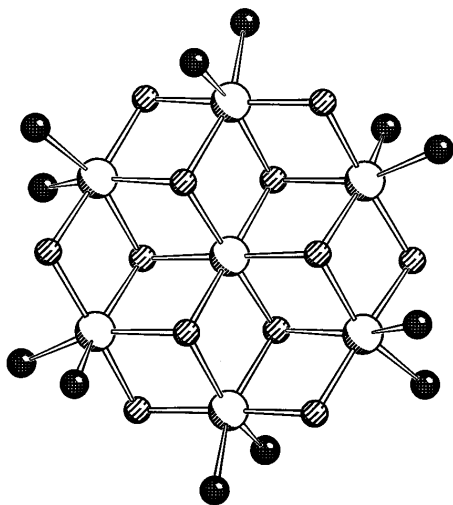


Fig. 3 The $Zn_7O_{12}N_{12}$ arrangement (bond lengths in Å) in the $[Zn(ZnL_2)_6]$ unit of **2** (Zn colourless, O striped, N dark): for the central zinc $Zn-(\mu_3-O)$ 2.089(3)–2.127(3); for the peripheral zinc ions $Zn-(\mu_3-O)$ 2.110(3)–2.186(3), $Zn-(\mu-O)$ 2.012(3)–2.066(3), $Zn-N$ 2.132(3)–2.182(3)

corresponds to the zinc-bound alcohol, **2** to the zinc-bound alkoxide, and the complex $[Zn_2Cl_4(2\text{-pyridylcarbaldehyde})_2]\cdot H_2O$ previously reported by us⁹ represents aldehyde coordination by the same type of chelating ligand. Although all three species are zinc chloride compounds as well, their compositions and structures differ so much that a comparative discussion must await the further development of the zinc complex chemistry of these ligands.

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Footnotes

† Both compounds yielded satisfactory analytical data. *Selected spectroscopic data:* **1:** IR (KBr) 3732w, 3421s, br (OH), 1611m, 1572w (ring), ¹H NMR $\{[^2H_8]thf-(CD_3)_2SO, 20:1\}$ 4.62 (s, br, 2 H, CH₂), 5.26 (s, br, 1 H, OH). **2:** IR (KBr) 1603s, 1571m (ring), ¹H NMR (CDCl₃) 4.44–4.77 (m, 2 H, CH₂), 5.29 (d, ²J 6.8 Hz, 1 H, CH₂), 5.39 (d, ²J 6.9 Hz, 1 H, CH₂).

‡ *Crystal data:* **1:** C₁₂H₁₄Cl₃N₂O₂Zn_{1.5}, $M = 422.68$, monoclinic, space group $C2/c$, $a = 19.144(2)$, $b = 8.546(5)$, $c = 20.654(4)$ Å, $\beta = 103.00(4)^\circ$, $U = 3293(3)$ Å³, $Z = 8$, $D_c = 1.71$ g cm⁻³, $R = 0.054$, $wR_2 = 0.197$ for 3212 reflections. **2:** C₃₆H₃₆ClN₆O₆Zn_{3.5}·2CH₂Cl₂, $M = 1082.85$, triclinic, space group $P\bar{1}$, $a = 12.380(6)$, $b = 14.286(4)$, $c = 14.671(5)$ Å, $\alpha = 61.40(2)$, $\beta = 72.95(3)$, $\gamma = 74.91(3)^\circ$, $Z = 2$, $D_c = 1.67$ g cm⁻³, $R = 0.037$, $wR_2 = 0.087$ for 6741 reflections.

Common data: data were taken at 183(2) K with Mo-K α radiation on a Nonius CAD4 diffractometer. The structures were solved by direct methods and refinement against F^2 using the SHELX program suite.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/379.

§ The Cambridge Crystallographic Data File contains 6 dinuclear, 1 trinuclear, 4 tetranuclear, and 1 hexanuclear pyridylmethanolato complexes.

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