

Zinc enzyme modelling with zinc complexes of polar pyrazolylborate ligands

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Abstract

The Zn–OH₂ and Zn–OH complexes of the new tris(pyrazolyl)borate ligands with pyridyl and carboxamido substituents were investigated for their reactivity towards hydrolyzeable substrates. Tp^{4-Py,Me}Zn–OH inserted CO₂ and CS₂ in methanol forming the Zn–OCO–OMe and Zn–SCSOMe products. In non-aqueous media, both types of complexes with both types of substituents on the Tp ligands effected stoichiometric cleavage of tris(*p*-nitrophenyl)phosphate and *p*-nitrophenyl acetate. In solutions containing water and the MOPS buffer, up to eight *p*-nitrophenyl groups per equivalent of zinc complex could be cleaved from the esters, and the resulting bis(*p*-nitrophenyl)phosphate was also degraded to mono(*p*-nitrophenyl)phosphate. This is the first time that pyrazolylborate–zinc complexes have shown catalytic activity in hydrolytic reactions.

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1. Introduction

The hydrolysis of esters and phosphates, particularly tris(*p*-nitrophenyl)phosphate, is the most thoroughly studied reaction in the modelling of zinc enzymes with coordination compounds of zinc. The review articles bear witness to this [1–5], the leading researchers in the field have worked on it [6–12], and there is continued activity until today [13–18]. We too have worked in this area [19–24], and we have derived a mechanistic pathway. [25,26].

During these studies, like in other fields of enzyme modelling, it became evident that the more well-defined the model complexes were the lower was their catalytic efficiency. This holds particularly for those cases where four- or five-coordinate Zn–OH₂ or Zn–OH complexes could actually be isolated and used as enzyme models. Thereby the best structural models, typically (tripod) Zn–X species reproducing the tetrahedral environment of zinc in the

enzymes [27], were often useful only for stoichiometric, but rarely for catalytic hydrolyses.

We experienced this with our pyrazolylborate–zinc–hydroxide complexes, which were the first structurally correct and functional models of the active state of hydrolytic zinc enzymes [28]. They could be used in a stoichiometric fashion for all types of hydrolyses [19,20,24,25]. But their application for catalyses was prevented by product inhibition. Typically, both products of the hydrolysis of a triarylphosphate, i.e. the phenolate and the diarylphosphate, ended up in stable TpZn–phenolate and TpZn–phosphate complexes.

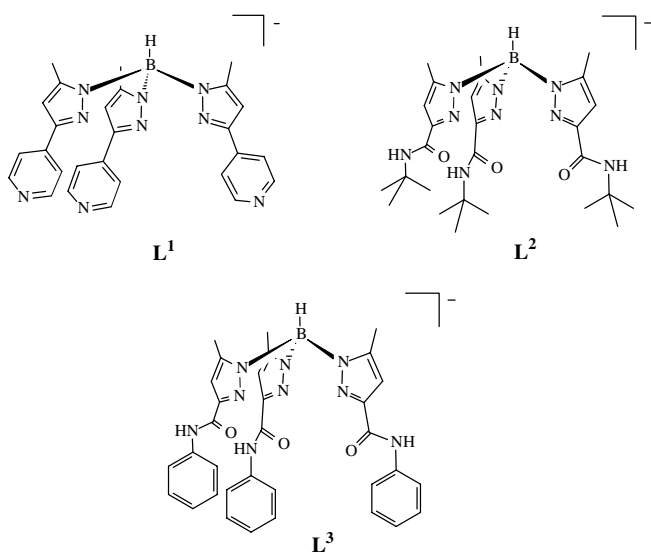
We assume that the major reason for this catalytic inability is the non-polar nature of the hitherto employed pyrazolylborates and their zinc complexes. The synthetic procedure for the Tp ligands, i.e. heating a pyrazole and KBH₄ up to 200 °C, has limited the substituents allowed on the pyrazoles almost entirely to hydrocarbon groups. As a result the ligands and their complexes have been insoluble in water and water-containing solvents. Consequentially, during the hydrolytic reactions very little water was

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available to overcome the product inhibition and to reconstitute the hydrolytically active complexes.

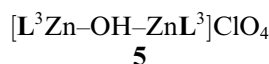
The way out of this dilemma had to be the synthesis of water-soluble pyrazolylborates. We, among others (see Ref. [29]), have recently succeeded in this task [30]. In addition, we could convert the new 4-pyridyl- and carboxamido-substituted Tp ligands to Zn–OH₂ and Zn–OH complexes [31]. Thereby we had available the desired enzyme models which could be employed in the presence of water.

This paper reports our investigations on their stoichiometric and catalytic hydrolyses of esters and organophosphates. The Zn–OH₂ and Zn–OH complexes of L¹–L³ were used.



2. Results and discussion

The aqua- and hydroxo-complexes of ligands L¹–L³ which could be isolated are 1–5 [31]. Of these, the mononuclear hydroxides 2 and 4 are rather labile and cannot be handled in solution for extended periods, for which reason only 2 was used, and for some stoichiometric reactions only. Aqua complexes 1 and 3 and the hydroxide-bridged dinuclear complex 5 persisted in solutions containing water and buffer, and hence were suitable for catalytic reactions.



2.1. Stoichiometric reactions

After introducing the TpZn–OH complexes as enzyme models [28], we had used them extensively for stoichiometric model reactions [26]. It could be expected, therefore,

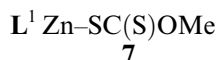
that hydroxides 2 and 4 would react accordingly. This was borne out by the hydrolytic reactions of 2.

When CO₂ was bubbled through a methanolic solution of 2, it could be seen by ¹H NMR that all of 2 was consumed after four hours. The isolation of the expected methylcarbonate complex proved difficult, however, being hampered by slow decomposition of the starting material and the product. Thus only a mediocre yield of impure Tp^{4-Py,Me}Zn–OCOOME could be obtained by speedy isolation, or careful crystallization produced a very small amount of the desired product in the unusual composition 6. We assume that the chloride in 6 originates from traces of HCl often found in dichloromethane.

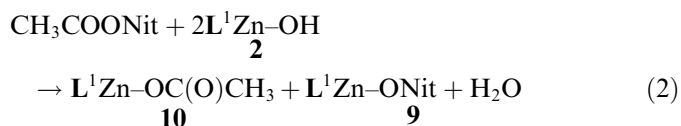
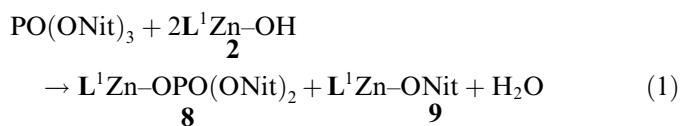


The composition of 6 was determined by a structure determination and by ¹H NMR. Fig. 1 shows the contents of the asymmetric unit in the crystals. 6 is a chain-like coordination polymer with alternating L¹Zn–OCOOME and L¹ZnCl units, each of which uses one of its Tp's pyridyl substituents to coordinate to the next unit in the chain. This way all zinc ions become five-coordinate with a rather distorted trigonal-bipyramidal geometry. The formation of coordination dimers and polymers is very common for zinc complexes of L¹–L³ [30,31], and the related complex Tp^{3-Py,Me}Zn–OCOOME is a pyridyl bridged dimer [32]. The bond lengths at both zinc ions (see Fig. 1) are normal, including the elongations at the axes of the trigonal bipyramids. Thus the main value of the structure determination of 6 consists in the proof that it contains L¹Zn–OCOOME.

The reaction of 2 with CS₂ in the presence of methanol proceeded more smoothly and produced the xanthogenate complex 7 in a good yield. The main indicators for the presence of a Zn–SC(S)OMe unit in 7 are the IR band for C=S at 1208 cm⁻¹ and the OMe resonance in the ¹H NMR spectrum at 3.17 ppm. The NMR spectra of 7 do not point to association by a splitting of the pyridyl resonances. We therefore assume that 7 is monomeric, using the OMe function of the xanthogenate ligand to make zinc five-coordinate, just as was observed in L¹Zn–OC(O)Me [30].



The cleavage of activated esters by 2 could be performed with the *p*-nitrophenolates PO(ONit)₃ and CH₃COONit. As expected, the reactions were stoichiometric, and they consumed two equivalents of 2 per equivalent of substrate according to the following equations:



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