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Rapid phosphorus triester hydrolysis catalyzed by bimetallic tetrabenzimidazole complexes†

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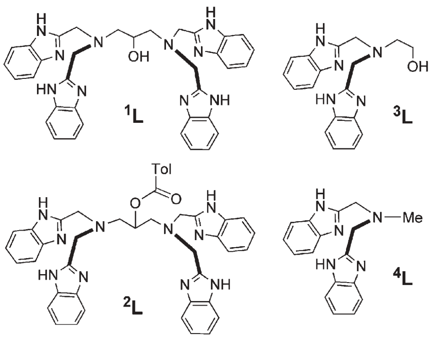
Bimetallic complexes based on the binucleating ligand *N*,*N*,*N*′,*N*′-tetrakis[(2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (^{1}L) and its new toluoyl ester derivative (^{2}L) catalyze the hydrolysis of phosphorus triesters at ambient temperature with activities rivalling the fastest known systems.

The development of new methods for accelerating the hydrolysis of organophosphorus esters under mild conditions is an important area of industrial and academic research. Phosphorus triester compounds, which include several common pesticides (*e.g.*, Paraoxon), are accepted as suitable mimics of G-type nerve agents (*e.g.*, sarin, soman).[1] These compounds are not only highly toxic, but they are also highly persistent in the environment.[1] Consequently, the development of methods that rapidly mitigate or degrade these substances are important from environmental and national security perspectives.

There are basically three common types of catalysts for the hydrolysis of phosphorus esters. These are (1) enzymes (metal-containing and metal-free),[2] (2) iodosobenzoic acid-based nucleophilic catalysts,[3] and (3) coordination complexes.[4] Enzymes that catalyze the hydrolysis of phosphorus esters frequently feature two or more metal centers in their active sites. This paradigm suggests that cooperative bimetallic mechanisms likely play an important role in substrate and/or nucleophile activation. Indeed, this observation has inspired the widespread development and use of synthetic bimetallic complexes in this context.[5] Members of this class of complexes are exceptionally effective catalysts for the hydrolysis of phosphorus diesters. The development of transition-metal-based catalysts for the hydrolysis of phosphorus triesters, however, remains relatively poorly developed. Indeed, the use of bimetallic complexes as catalysts in this context remains essentially unexplored.[6] Herein, we report that bimetallic complexes based on the binucleating ligand *N*,*N*,*N*′,*N*′-tetrakis[(2-benzimidazolyl) methyl]-2-hydroxy-1,3-diaminopropane (^{1}**L**) and its new toluoyl ester derivative (^{2}**L**) are able to rapidly accelerate the hydrolysis of phosphorus triesters at ambient temperature. It was found that homobimetallic and heterobimetallic Cu(II), Zn(II), and Co(II) complexes of ligands ^{1}**L** and ^{2}**L** catalyze the hydrolysis of *p*-nitrophenyl diphenylphosphate (PNPDPP) in aqueous ethanol solution (pH 8.7) with relative rates, in many cases, that exceed those achieved by the most effective known transition-metal-based systems.[7]



Scheme 1 Ligands used in catalytic studies.

The tetrabenzimidazole ligand ^{1}**L** (Scheme 1) was prepared by condensation of 1,2-diaminobenzene with 2-hydroxy-1,2-diaminopropanetetraacetic acid, as described by Reed and co-workers.[8] Reaction of ^{1}**L** with one equivalent of toluoyl chloride in the presence of K_2CO_3 afforded the new ester-modified ligand ^{2}**L** in good yield.‡ ^{1}**L** is a versatile ligand that is known to form well-defined homo- and heterobimetallic complexes with a wide range of 3d metals. These complexes have been explored for a variety of uses including the modeling of metalloproteins and enzymes that perform diverse functions,[9] including phosphorus diester binding/

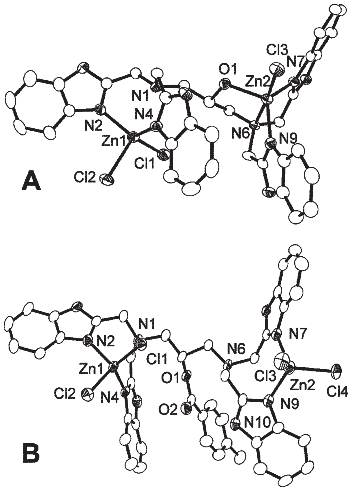


Fig. 1 **(A)** Structure of ^{1}L·Zn$_2$·2EtOH·2H$_2$O drawn with 50% thermal ellipsoids. An outer-sphere chloride ion, hydrogens, and co-crystallized solvent (EtOH, H$_2$O) are omitted. **(B)** Structure of ^{2}L·Zn$_2$·2EtOH drawn with 50% thermal ellipsoids. Hydrogens and co-crystallized ethanol are omitted.

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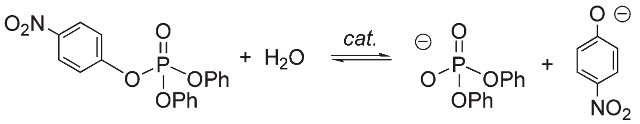
activation.[10] Consequently, we were interested in exploring the use of $^{1}\mathbf{L}$ and $^{2}\mathbf{L}$ for the formation of metal-containing complexes in the context of hydrolyzing organophosphorus triesters. The dizinc complex $^{1}\mathbf{L}Zn_2Cl_4$ ($^{1}\mathbf{L{\cdot}Zn_2}$) was conveniently prepared by reaction of $^{1}\mathbf{L}$ with two equivalents of $ZnCl_2$ in EtOH solution. Cooling the solution to −15 °C yielded the product as colorless crystals in 86% isolated yield. The analogous procedure using $^{2}\mathbf{L}$ in place of $^{1}\mathbf{L}$ gave $^{2}\mathbf{L}Zn_2Cl_4$ ($^{2}\mathbf{L{\cdot}Zn_2}$) in 55% isolated yield. The two dizinc complexes have been characterized by single-crystal X-ray diffraction§ to confirm their bimetallic nature.[11] As shown in Fig. 1A, the solid-state structure of $^{1}\mathbf{L{\cdot}Zn_2}$ indicates that the hydroxyl donor is coordinated to only one of the two Zn centers. Thus, one Zn center (Zn1) has a coordination number (CN) of four and distorted tetrahedral geometry, but the second (Zn2) has a CN of five and approximate trigonal bipyramidal geometry. In contrast, the structure of $^{2}\mathbf{L{\cdot}Zn_2}$ (Fig. 1B) features a pair of four-coordinate, distorted tetrahedral Zn centers. The toluoyl ester is not coordinated to a Zn center, instead the carbonyl oxygen (O2) is involved in H-bonding with a benzimidazole (N10) group.

In order to test their catalytic activities under mild conditions, the bimetallic complexes of $^{1}\mathbf{L}$ and $^{2}\mathbf{L}$ were tested with PNPDPP as a model phosphorus triester substrate in 50 mM *N*-ethylmorpholine buffer (pH 8.70) at ambient temperature. PNPDPP has become the unofficial standard simulant for phosphorus triester hydrolysis reactions.[12,13] Its extensive use allows for straightforward comparison of kinetic data obtained with many different catalysts under widely varying reaction conditions. The kinetic studies were conducted by monitoring the formation of the *p*-nitrophenolate anion (at 401 nm) using UV-visible spectrometry for greater than 4 half-lives. For each of the reactions, the kinetics for the formation of *p*-nitrophenolate were consistent with a pseudo-first-order reaction coming to equilibrium. All kinetic studies were run in at least triplicate, so the interpolated constants are listed as average values with error bars of ±1 standard deviation. As can be seen in Table 1 (entries 1–4, 6, 13), the non-complexed ligands ($^{1}\mathbf{L}$ and $^{2}\mathbf{L}$) and the simple metal salts ($ZnCl_2$, $CoCl_2$, $CuCl_2$) do not have any discernible effect on the hydrolysis rate of PNPDPP compared to the reaction in the absence of added catalyst. In contrast, the presence of 0.125 mM $^{1}\mathbf{L{\cdot}Zn_2}$ accelerated the rate of PNPDPP hydrolysis by a factor of 13 (entry 7). Identical results were obtained using crystallized samples of $^{1}\mathbf{L{\cdot}Zn_2}$ and samples prepared *in situ*. The use of $^{1}\mathbf{L{\cdot}Co_2}$ and $^{1}\mathbf{L{\cdot}Cu_2}$ in place of $^{1}\mathbf{L{\cdot}Zn_2}$ afforded similar results (entries 8 and 9). Interestingly, the use of some heterobimetallic species yielded superior results. For example, $^{1}\mathbf{L{\cdot}Zn{\cdot}Cu}$ yielded a rate enhancement of 23 times. This rate enhancement is comparable to that observed for (TMEDA)$CuCl_2$[4,14] (entry 5), which is generally viewed as the benchmark catalyst for PNPDPP hydrolysis. Making the assumption that $^{1}\mathbf{L{\cdot}Zn{\cdot}Cu}$ is a statistical mixture of the possible homo- and heterobimetallic species, then the

Table 1 Catalyzed hydrolysis of PNPDPP.[a]



PNPDPP

Entry	Catalyst[b]	$t_{1/2}$/h	$10^5\ k_{obs}/s^{-1}$	$k_{obs}/M^{-1}s^{-1}$[c]	Relative rate[d]
1	None	30 ± 6	0.66 ± 0.13	NA	1
2	$ZnCl_2$	31 ± 5	0.6 ± 0.1	NA	0.9
3	$CoCl_2$	30 ± 4	0.67 ± 0.08	NA	1.0
4	$CuCl_2$	28 ± 3	0.70 ± 0.09	NA	1.0
5	(TMEDA)$CuCl_2$	1.3 ± 0.1	14.4 ± 0.7	1.15 ± 0.05	22
6	$^{1}\mathbf{L}$	31 ± 5	0.6 ± 0.1	NA	0.9
7	$^{1}\mathbf{L{\cdot}Zn_2}$	2.4 ± 0.9	9 ± 3	0.7± 0.2	14
8	$^{1}\mathbf{L{\cdot}Co_2}$	3.1 ± 0.5	6 ± 1	0.50 ± 0.08	9.1
9	$^{1}\mathbf{L{\cdot}Cu_2}$	2.3 ± 0.7	9 ± 4	0.7 ± 0.3	14
10	$^{1}\mathbf{L{\cdot}Zn{\cdot}Co}$	1.6 ± 0.4	12 ± 2	1.0 ± 0.2	18
11	$^{1}\mathbf{L{\cdot}Zn{\cdot}Cu}$	1.3 ± 0.3	15 ± 4	1.2 ± 0.3	23
12	$^{1}\mathbf{L{\cdot}Co{\cdot}Cu}$	3.0 ± 0.4	6.4 ± 0.9	0.52 ± 0.07	9.7
13	$^{2}\mathbf{L}$	24 ± 4	0.8 ± 0.2	NA	1.2
14	$^{2}\mathbf{L{\cdot}Zn_2}$	0.18 ± 0.05	110 ± 40	9 ± 3	170
15	$^{2}\mathbf{L{\cdot}Co_2}$	0.5 ± 0.1	40 ± 10	3 ± 1	61
16	$^{2}\mathbf{L{\cdot}Cu_2}$	0.19 ± 0.07	100 ± 60	8 ± 5	150
17	$^{2}\mathbf{L{\cdot}Zn{\cdot}Co}$	0.24 ± 0.04	80 ± 10	6 ± 1	120
18	$^{2}\mathbf{L{\cdot}Zn{\cdot}Cu}$	0.14 ± 0.04	140 ± 60	11 ± 5	210
19	$^{2}\mathbf{L{\cdot}Co{\cdot}Cu}$	0.4 ± 0.1	50 ± 20	4 ± 2	76
20	$^{3}\mathbf{L{\cdot}Zn}$	1.63 ± 0.09	11.8 ± 0.7	0.47 ± 0.03	18
21	$^{3}\mathbf{L{\cdot}Co}$	3.3 ± 0.9	5.8 ± 0.9	0.23 ± 0.04	8.8
22	$^{3}\mathbf{L{\cdot}Cu}$	2.7 ± 0.1	7.2 ± 0.3	0.29 ± 0.01	11
23	$^{4}\mathbf{L{\cdot}Zn}$	1.30 ± 0.06	14.8 ± 0.7	0.59 ± 0.03	22
24	$^{4}\mathbf{L{\cdot}Co}$	0.98 ± 0.05	20.0 ± 1.0	0.80 ± 0.04	30
25	$^{4}\mathbf{L{\cdot}Cu}$	3.7 ± 0.4	5.2 ± 0.6	0.21 ± 0.02	7.9

[a] *Conditions:* 35% EtOH, 50 mM 4-ethylmorpholine buffer, pH 8.7, 21 ± 1 °C, [PNPDPP] = 1.25×10^{-4} M. For entries 2–5 [metal] = 0.125 mM. For entries 7–12 and 14–25 [metal] = 0.25 mM. [b] Abbreviated catalysts are mixtures of ligands and metal chlorides (*e.g.*, $^{1}\mathbf{L{\cdot}Zn_2}$ is formed from $^{1}\mathbf{L}$ and two equivalents of $ZnCl_2$). Catalysts prepared with two metal salts (*e.g.*, $^{1}\mathbf{L{\cdot}Zn{\cdot}Co}$) are expected to form mixtures of homo- and heterobimetallic complexes. [c] Second-order rate constants are calculated with [catalyst] = 0.125 mM for entries 5, 7–19 while [catalyst] = 0.25 mM for entries 20–25. [d] Based on the observed pseudo-first-order rate constants.

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heterobimetallic species is calculated to perform the PNPDPP hydrolysis at 35 times the uncatalyzed reaction. These bimetallic complexes of $^{1}\mathbf{L}$ are comparable to the fastest known metal-based catalysts for PNPDPP hydrolysis. Complexes of the ester ligand $^{2}\mathbf{L}$, however, are significantly faster and have catalytic activities between 4 to 10 times greater than that of (TMEDA)CuCl$_2$ under identical conditions. The best results were obtained for the Zn- and Cu-containing complexes $^{2}\mathbf{L{\cdot}Zn_2}$, $^{2}\mathbf{L{\cdot}Cu_2}$, **and** $^{2}\mathbf{L{\cdot}Zn{\cdot}Cu}$ (entries 14, 16, and 18), which catalyze the hydrolysis of PNPDPP at a rate *ca.* 200 times faster than the uncatalyzed reaction.

As described above, the rate of PNPDPP hydrolysis catalyzed by the bimetallic complexes occurs with pseudo-first-order dependence on PNPDPP concentration. The reaction order in catalyst was also of interest. This was determined for $^{1}\mathbf{L{\cdot}Zn_2}$ by analysis of the hydrolysis rate as a function of catalyst concentration. Reaction rates were determined using nine different catalyst concentrations between 0.0125 mM and 0.125 mM. A plot of $-\log(k_{\text{obs}})$ *versus* $-\log([^{1}\mathbf{L{\cdot}Zn_2}])$ was found to be linear with a slope of 1.3. Thus, the reaction is approximately first-order in catalyst concentration. Repeating the experiment with $^{2}\mathbf{L{\cdot}Zn_2}$ indicated a reaction order of 1.1 for the more active, toluoyl-ester-modified catalyst.

For comparison, the mononucleating ligands $^{3}\mathbf{L}$ and $^{4}\mathbf{L}$ (Scheme 1) were prepared and used to support catalysts for PNPDPP hydrolyses. As shown in entries 20–25, complexes prepared with MCl$_2$ (M = Zn, Co, Cu) were effective catalysts for PNPDPP hydrolysis. These displayed activities similar (at equal metal concentrations) to those of bimetallic derivatives of $^{1}\mathbf{L}$, but far less than those of derivatives of $^{2}\mathbf{L}$.

In summary, homo- and heterobimetallic Cu(II), Zn(II), and Co(II) complexes of *N*,*N*,*N*′,*N*′-tetrakis[(2-benzimidazoyl)-methyl]-2-hydroxy-1,3-diaminopropane ($^{1}\mathbf{L}$) and its toluoyl ester derivative ($^{2}\mathbf{L}$) were found to be excellent catalysts for the hydrolysis of PNPDPP under mild conditions. The hydrolysis rates of these complexes were found to approach and/or surpass the best reported metal-based catalysts, with the $^{2}\mathbf{L}$-based bimetallic complexes being more active than the analogous $^{1}\mathbf{L}$ complexes. We are currently exploring the effects of modifying these and related ligands to maximize reactivity and gain more detailed mechanistic insight. Additionally, these and related catalysts are being incorporated onto solid nanostructured supports to aid in catalyst recovery and to potentially amplify reactivity.

Notes and references

‡ See ESI† for details of syntheses and catalytic studies.

§ Crystal data for $^{1}\mathbf{L{\cdot}Zn_2}{\cdot}2EtOH{\cdot}2H_2O$: $C_{39}H_{50}Cl_4N_{10}O_5Zn_2$, M = 1011.43, space group $P\bar{1}$ (No. 2), triclinic, a = 12.3747(4), b = 13.7692(5), c = 14.0177(5) Å, α = 93.140(1), β = 111.015(1), γ = 93.478(1)°, V = 2218.0(1) Å^3, Z = 2, T = 152 K, μ = 1.376 mm^{-1}, 17620 reflections measured, 10150 independent reflections (R_{int} = 0.0527), R_1 (for $F_o > 4\sigma F_o$) = 0.0799, wR_2 (all data) = 0.2252, GOF = 1.021 for 541 parameters. Crystal data for $^{2}\mathbf{L{\cdot}Zn_2}{\cdot}2EtOH$: $C_{47}H_{52}Cl_4N_{10}O_4Zn_2$, M = 1093.53, space group $P2(1)/c$ (No. 14), monoclinic, a = 17.5457(4), b = 12.8691(4), c = 23.3783(8) Å, β = 104.362(1)°, V = 5113.9(3) Å^3, Z = 4, T = 147 K, μ = 1.199 mm^{-1}, 40729 reflections measured, 12192 independent reflections (R_{int} = 0.1076), R_1 (for $F_o > 4\sigma F_o$) = 0.0676, wR_2 (all data) = 0.1766, GOF = 1.020 for 606 parameters. CCDC 290488 and 290489. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602769e

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