Hydrolytic Cleavage of Diphosphates, Sulfonatophosphates, and Disulfonates by (Pyrazolylborate)zinc Hydroxide Complexes☆

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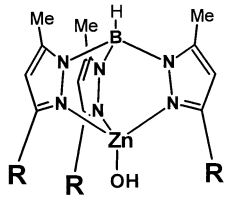
Three (pyrazolylborate)zinc hydroxide complexes Tp*Zn−OH were used as hydrolytic reagents to cleave the P−O−P, P−O−S, and S−O−S linkages of organic diphosphates, sulfonatophosphates, and disulfonates. The resulting complexes of the types Tp*Zn−OPO(OR)$_2$ and Tp*Zn−O-SO$_2$R could also be obtained by condensation reactions between Tp*Zn−OH and HO−PO(OR)$_2$ or HO−SO$_2$R. Two of them were characterized by structure determinations.

Among the many phosphate transferring enzymes, an important class are those which cleave the P−O−P linkages of oligophosphates, e.g. ADP, ATP, or inorganic pyrophosphate[1][2][3]. As a rule these are metalloenzymes, quite often containing two or three metal ions in the active center, typically magnesium, manganese or zinc[4]. In all cases the labile coordination positions on the metal ions are occupied by water molecules in the resting enzymes and by the reacting phosphate entities in the working enzymes. Here like in other hydrolytic metalloenzymes the essential nucleophile is likely to be a M−OH unit[5].

While the modelling of enzymes cleaving phosphate esters by metal coordination compounds is very well established (see preceding paper[6] and references cited therein), we are not aware of related studies concerning the cleavage of P−O−P or related systems[7]. We therefore started such a study using our established "enzyme model" in the form of the highly nucleophilic pyrazolylborate zinc hydroxide complexes Tp*Zn−OH[8][9][10][11][12][13]. Following our preliminary communication on a P−O−P system, i.e. an anhydride of a phosphoric acid[14], we extended the studies to a S−O−S system, i.e. an anhydride of a sulfonic acid, and a P−O−S system, i.e. a mixed anhydride. The latter bears relevance in relation to adenosine-3′-phosphate-5′-phosphosulfate (PAPS), a sulfate resource of various organisms[15]. Our main interest was to find out how efficient our Tp*Zn−OH complexes would be for the cleavage of these anhydride systems.

As the "enzyme models" we used the three Tp*Zn complexes **1a**−**c**. Their "substrates" were chosen to be molecular rather than ionic species, i.e. containing fully esterified phosphate units [(RO)$_2$P(O)O] or sulfate units (RSO$_2$O). The purpose of this was to locate the reactivity in the anhydride linkages rather than the acidic P−OH or S−OH functions and to ease reaction with the Tp*Zn−OH complexes which are not water-soluble. As a result the reactions were predetermined to be stoichiometric rather than catalytic.



1a (Tp^{tBu,Me}Zn-OH) : R = t-butyl

1b (Tp^{Cum,Me}Zn-OH): R = p-cumenyl

1c (Tp^{Pic,Me}Zn-OH) : R = 5′-picolyl

Reactions and Products

It was found that of the three Tp*Zn−OH complexes **1a** does not react with diphosphates. The steric bulk of the *tert*-butyl groups seems to be too high. The other attempts at diphosphate cleavage went smoothly and produced the cleavage products in high yields. Tetraethyl diphosphate and **1b** yielded **2b**, tetraphenyl diphosphate upon reaction with **1b** and **1c** yielded **3b** and **3c** of which **3b** was obtained before by cleavage of PO(OPh)$_3$ with **1b**[6]. Upon recrystallization from acetonitrile which was not fully dried both **3b** and **3c** were converted to adducts, as found out by the subsequent structure determinations. Of these **3b′** results from partial hydrolytic destruction of the Tp^{Cum,Me} ligand while **3c′** simply involves addition of a water molecule.

Tp^{Cum,Me}Zn−OPO(OEt)$_2$ **2b**

Tp^{R,Me}Zn−OPO(OPh)$_2$
3a: R = *t*Bu
3b: R = Cum
3c: R = Pic

(Tp^{Cum,Me})(3-methyl-5-cumenyl-pyrazole)Zn−OPO(OPh)$_2$ **3b′**

(Tp^{Pic,Me})(H$_2$O)Zn−OPO(OPh)$_2$ **3c′**

The S−O−S system employed was the anhydride of *p*-toluenesulfonic acid (SOS). It reacted easily with **1c**, forming **4c** in good yields which was crystallized as a hydrate again. As the mixed anhydride we used that of diphenylphosphate and *p*-toluenesulfonic acid (POS). Its reaction with **1c** at room temperature was complete within about half a day. The product mixture consisted of an equimolar

  1434−1948/98/0202−0271 $ 17.50+.50/0

mixture of **3c** and **4c** as evidenced by IR and ^{1}H- as well as ^{13}C-NMR spectroscopy. The separation of this mixture proved to be too cumbersome, however.

$Tol-SO_2-O-SO_2-Tol$ (SOS) $(PhO)_2PO-O-SO-Tol$ (POS)

$Tp^{R,Me}Zn-OSO_2-Tol$

4a: R = *t*Bu
4b: R = Cum
4c: R = Pic

The first step of the hydrolytic cleavages of the anhydrides by Tp*Zn−OH must result in the liberation of one equivalent of the corresponding acid while the other half of the anhydride becomes attached to zinc as in complexes **2**−**4**. Following the reactions spectroscopically gave no evidence, however, for the free acids $(RO)_2POOH$ or TosOH. Instead only the complexes **2**, **3**, or **4** were observed. This means that the free acids react quickly with excessive Tp*Zn−OH by means of a condensation reaction. Accordingly, employing a 1:1 stoichiometry for Tp*Zn−OH and anhydride resulted in only half-consumption of the anhydride. Therefore a 2:1 stoichiometry was applied for the preparations.

It could then be shown that the formation of the zinc phosphate and sulfonate complexes by condensation is indeed a fast reaction. It worked for the diorganophosphates yielding **3a** and **c** (see preceding paper[6]). It worked for all three Tp*Zn−OH complexes with *p*-toluenesulfonic acid, resulting in complexes **4a**−**c** of which **4a** has already been described by us[16]. For preparative purposes this condensation reaction is the method of choice to obtain complexes like **3** and **4**.

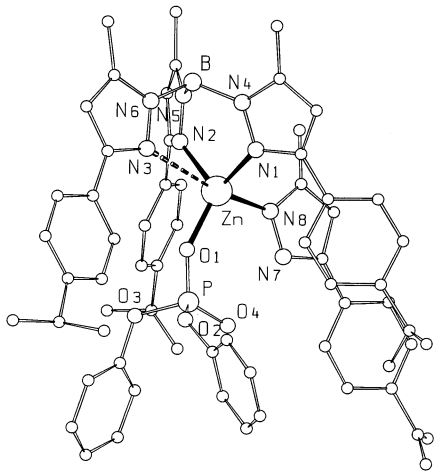
The identification of the Tp*Zn phosphate and sulfonate complexes consisted mainly in the structure determinations described here and in previous papers. The spectral data (see Experimental Section) are in agreement. Specifically the IR bands of the BH, P=O, and S=O functions, the ^{1}H-NMR resonances of the Tp* ligands, and the ^{31}P-NMR resonances are of diagnostic value.

Structure Determinations

The basic structural information on the complex types **2**, **3**, and **4** was already available due to the structure determinations of **4a** and various $Tp^*Zn-OPOX_2$ compounds[6][16][17]. In addition to this, the X-ray analyses of **3b′** and **3c′** were worthwhile because they yielded coordination patterns of zinc which differ from the usual tetrahedral Tp*Zn−X arrangement. In both cases, despite the steric bulk of the pyrazoles′ 3-substituents (Cum, Pic) and despite the presence of the voluminous phosphate ligand, a further ligand (the pyrazole in **3b′** and the water molecule in **3c′**) can exist in the ligand sphere of zinc. This finally breaks the rule that the sterically demanding Tp* ligands are "tetrahedral enforcers". In a later paper we will discuss the mechanistic implications arising from a comparison of the very variable geometry at the five-coordinated zinc ion in Tp*Zn(X)(Y) complexes.

Complex **3b′** (see Figure 1) contains the two coligands (phosphate and pyrazole) close to each other [angle O1−Zn−N8 103.1(2)°] and connected by a hydrogen bond between O4 and N7 (2.78 Å). The coordination of the Tp* ligand to zinc is very unusual. While the pyrazole nitrogen atoms N1 and N2 are attached at normal distances, N3 is practically nonbonding. Thus the geometry of **3b′** is intermediate between a flattened tetrahedron with N8 at the apex and an elongated trigonal bipyramid with N8 at the "short" and N3 at the "long" apex. In terms of a S_N2 substitution at a tetrahedral center this represents a situation close to the final state, i.e. with the entering group (N8) almost firmly bound and the leaving group (N3) almost completely removed. Complex **3b′** is, after $Tp^{Ph,Me}$(3-methyl-5-phenylpyrazole)Zn−OPO(OEt)(OC_6H_4−*p*-NO_2)[6], the second example of this kind of Tp*Zn complexes with a coordination intermediate between four- and fivefold.

Figure 1. Molecular structure of **3b′**[a]

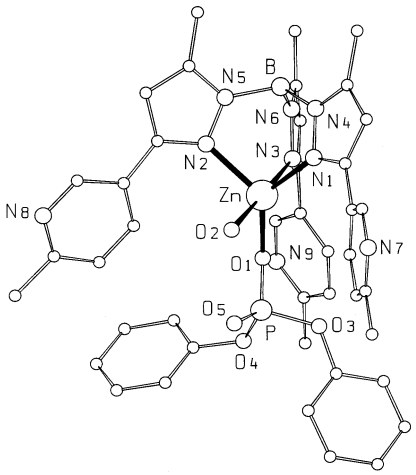


[a] Selected bond lengths [Å] and angles [°]: Zn−O1 1.905(4), Zn−N1 1.983(5), Zn−N2 2.004(5), Zn−N3 3.090(5), Zn−N8 2.080(5), P−O1 1.486(4), P−O4 1.467(4), N8−Zn−N3 171.9(2), Zn−O1−P 147.3(3).

The pyrazole ligand and the phosphate ligand in **3b′** display no unusual features. The Zn−O bond is relatively short, but typical for Tp*Zn−O compounds[6][8][9][10][11][12][13][14]. The phosphate ligand shows the typical equalization of the "single" and "double" P−O bonds P−O1 and P−O4 that we have observed previously[6][18]. Together with the rather large P−O−Zn angle it must reflect a partly ionic nature of the Zn−O bond. Similar observations hold for the Zn−O, P−O, and P−O−Zn interactions in complex **3c′** (see Figure 2). Zinc phosphate complexes not bearing Tp* ligands normally have longer Zn−O bonds, as evidenced by the two examples bearing diphenylphosphate ligands[19][20].

Like in **3b′**, the two coligands in **3c′** (water and phosphate) are linked by a hydrogen bond (O2−O5 2.77 Å). Otherwise there is no similarity between **3b′** and **3c′**. However, **3c′** is a close analogue of the complex $Tp^{Pic,Me}(H_2O)$-Zn−OPO(OC_6H_4−*p*-NO_2)$_2$ which was obtained by phosphate ester hydrolysis[6]. The Tp* ligand in **3c′** is bound in a symmetrical fashion, and the coordination geometry about the zinc ion is strictly trigonal-bipyramidal with one pyrazole nitrogen and the water oxygen on the apical posi-

Figure 2. Molecular structure of **3c′**[a]



[a] Selected bond lengths [Å] and angles [°]: Zn−O1 1.947(3), Zn−N1 2.065(4), Zn−N2 2.069(4), Zn−N3 2.200(4), Zn−O2 2.102(3), P−O1 1.496(3), P−O5 1.464(4), N3−Zn−O2 178.9(1), Zn−O1−P 138.6(2).

tions. The bond lengths at zinc are larger than in tetrahedral Tp*Zn−O complexes[6][8][9][10][11][12][13][14], reflecting the increase in coordination number, and typically the bonds holding the two apical atoms are elongated. A comparison of **3b′** and **3c′** in terms of bond lengths shows that all comparable ligand donor atoms except N3 are closer to zinc in **3b′**, thus qualifying **3b′** as tetrahedral rather than trigonal-bipyramidal.

Conclusions

The work in this paper has shown that the hydrolytic prowess of the Tp*Zn−OH "enzyme models" extends to the cleavage of the E−O−E links in inorganic polyacids. Part of the driving force of the hydrolytic cleavages seems to be the capturing of the resulting anionic fragments as O-bound ligands. These are not replaceable by water or other donor ligands. Instead these can be bound as additional ligands in five-coordinate Tp*(L)Zn−OPO(OR)$_2$ complexes.

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Experimental Section

General experimental methods and measuring techniques see ref.[21]. The Tp*Zn−OH complexes[8][10][22], the diphosphate[23] and the sulfonatophosphate[24] were prepared according to the published procedures. All other reagents were obtained commercially. Solvents were degassed but not dried. IR data (cm^{-1}) were recorded from KBr pellets, ^{1}H- and ^{31}P-NMR data (δ in ppm, int. TMS, ext. H_3PO_4) were recorded from $CDCl_3$ solutions.

Hydrolytic Cleavages: *Tetraethyl Diphosphate and* **1b**: 138 mg (0.200 mmol) of **1b** and 29.0 mg (0.100 mmol) of tetraethyl diphosphate in 20 ml of dichloromethane were stirred at room temp. for 16 h. The solvent was removed in vacuo. Recrystallization from acetonitrile at −25°C yielded 110 mg (66%) of **2b**, m. p. 184°C. − $C_{43}H_{56}BN_6O_4PZn$ (828.1): calcd. C 62.36, H 6.82, N 10.15; found C 61.55, H 6.68, N 9.96. − IR: 2550m (BH), 1252s (P=O). − ^{1}H NMR: 0.85 [t, J = 7.0 Hz, 6 H, Me(OEt)], 1.24 [d, J = 6.9 Hz, 18 H, Me(*i*Pr)], 2.52 [s, 9 H, Me(pz)], 2.92 [sept, J = 6.9 Hz, 3 H, CH(*i*Pr)], 3.44 [dt, J = 7.0 Hz, 7.0 Hz, 4 H, CH_2(OEt)], 6.22 [s, 3 H, CH(pz)], 7.35 [d, J = 8.2 Hz, 6 H, Ph(3,5)], 7.66 [d, J = 8.2 Hz, 6 H, Ph(2,6)]. − ^{31}P NMR: −2.0.

Tetraphenyl Diphosphate and **1b**: As before with 500 mg (0.722 mmol) of **1b** and 174 mg (0.361 mmol) of tetraphenyl diphosphate in 40 ml of CH_2Cl_2. When the reaction and workup were performed under strictly anhydrous conditions, they resulted in 620 mg (93%) of **3b**[6].

Recrystallization of 300 mg (0.325 mmol) of **3b** from hot undried acetonitrile resulted in the formation of 237 mg (86%) **3b′**, m. p. 191°C. − $C_{64}H_{72}BN_8O_4PZn$ (1124.5). calcd. C 68.36, H 6.45, N 9.97; found C 68.11, H 6.43, N 9.95. − IR: 2545 (BH), 1242s (P=O). − ^{1}H NMR: 0.97 [d, ^3J = 6.9 Hz, 18 H, Me(*i*Pr)], 1.24 [d, ^3J = 6.9 Hz, 6 H, Me(*i*Pr(a))], 2.49 [s, 9 H, Me(pz)], 2.49 [s, 3 H, Me(pz(a))], 2.62 [sept, ^3J = 6.9 Hz, 3 H, H(*i*Pr)], 2.89 [sept, ^3J = 6.9 Hz, 1 H, H(*i*Pr(a))], 5.98 [s, 1 H, H(pz(a))], 6.21 [s, 3 H, H(pz)], 6.91 [d, ^3J = 8.2 Hz, 2 H, Ph(3,5(a))], 7.02 [d, ^3J = 8.1 Hz, 6 H, Ph(3,5)], 7.07 [m, 10 H, Ph(phos(2,3,4,5,6))], 7.45 [d, ^3J = 8.2 Hz, 2 H, Ph(2,6(a))], 7.54 [d, ^3J = 8.1 Hz, 6 H, Ph(2,6)]. − ^{31}P NMR: −13.9.

Tetraphenyl Diphosphate and **1c**: As before with 500 mg (0.818 mmol) of **1c** and 200 mg (0.415 mmol) of tetraphenyl diphosphate in 40 ml of CH_2Cl_2 Recrystallization from undried acetonitrile yielded 645 mg (92%) of **3c′**, m. p. 148°C. − $C_{42}H_{43}BN_9O_5PZn$ (861.0): calcd. C 58.54, H 5.03, N 14.64; found C 58.43, H 5.01, N 14.71. − IR: 3300m,br (H_2O), 2557m (BH), 1231s (P=O). − ^{1}H NMR: 2.30 [s, 9 H, Me(py)], 2.56 [s, 9 H, Me(pz)], 6.30 [s, 3 H, H(pz)], 6.76 [d, ^3J = 8.1 Hz, 4 H, Ph(phos(2,6))], 7.06 [m, ^3J = 8.1 Hz, 6 H, Ph(phos(3,4,5))], 7.06 [d, ^3J = 8.0 Hz, 3 H, Py(5)], 8.04 [dd, ^3J = 8.0 Hz, ^4J = 2.1 Hz, 3 H, Py(6)], 8.57 [d, ^4J = 2.1 Hz, 3 H, Py(2)]. − ^{31}P NMR: −15.0.

p-Toluenesulfonic Acid Anhydride (SOS) and **1c**: As before with 500 mg (0.818 mmol) of **1c** and 136 mg (0.413 mmol) of SOS in 40 ml of CH_2Cl_2. Recrystallization from undried acetonitrile/dichloromethane (5:1) yielded 506 mg (79%) of **4c**·H_2O·1/2 CH_2Cl_2, m. p. 132°C. − $C_{37}H_{40}BN_9O_4SZn$·1/2 CH_2Cl_2 (783.0 + 42.5): calcd. C 54.56, H 5.01, N 15.27; found C 54.37, H 4.80, N 15.26. − IR: 3400m,br (H_2O), 2544m (BH), 1378s (S=O). − ^{1}H NMR: 2.21 [s, 9 H, Me(py)], 2.36 [s, 3 H, Me(Tos)], 2.55 [s, 9 H, Me(pz)], 3.25 [s, 2 H, H_2O, (broad)], 6.24 [s, 3 H, H(pz)], 7.00 [d, ^3J = 8.1 Hz, 3 H, Py(5)], 7.06 [d, ^3J = 8.2 Hz, 2 H, Tos(3,5)], 7.24 [d, ^3J = 8.2 Hz, 2 H, Tos(2,6)], 7.98 [dd, ^3J = 8.1 Hz, ^4J = 2.3 Hz, 3 H, Py(6)], 8.51 [d, ^4J = 2.3 Hz, 3 H, Py(2)].

Diphenylphosphato-p-toluenesulfonate (POS) and **1c**: 500 mg (0.818 mmol) of **1c** and 167 mg of POS in 40 ml of CH_2Cl_2 were stirred under anhydrous conditions for 16 h at room temp. The solvent was removed in vacuo and the residue picked up in $CDCl_3$. ^{1}H- and ^{31}P-NMR spectra showed that the starting materials had disappeared and the solution contained an equimolar mixture of **3c** and **4c**.

Condensation Reactions (for **3a** and **c** see preceding paper[6]): **4b**: 276 mg (0.400 mmol) of **1b** and 76.0 mg (0.400 mmol) of *p*-toluenesulfonic acid hydrate in 20 ml of dichloromethane were stirred at room temp. for 8 h under strictly anhydrous conditions. Removal of the solvent in vacuo and recrystallization from carefully dried acetonitrile yielded 265 mg (78%) of **4b**, m. p. 158°C. − $C_{46}H_{53}BN_6O_3SZn$ (846.2): calcd. C 65.29, H 6.31, N 9.93; found

C 64.42, H 6.07, N 9.46. – IR: 2552m (BH), 1292s (S=O). – ^{1}H NMR: 1.12 [d, J = 6.9 Hz, 18 H, Me(*i*Pr)], 2.53 [s, 9 H, Me(pz)], 2.78 [sept, J = 6.9 Hz, 3 H, CH(*i*Pr)], 6.21 [s, 3 H, CH(pz)], 6.86 [d, J = 7.9 Hz, 2 H, CH(Tos)], 7.02 [d, J = 7.9 Hz, 2 H, CH(Tos)], 7.12 [d, J = 8.1 Hz, 6 H, Ph(3,5)], 7.56 [d, J = 8.1 Hz, 6 H, Ph(2,6)].

4c: 500 mg (0.818 mmol) of **1c** and 141 mg (0.819 mmol) of *p*-toluenesulfonic acid hydrate in 40 ml of CH_2Cl_2 were stirred at room temp. for 16 h. Removal of the solvent and recrystallization from acetonitrile/dichloromethane (5:1) under non-anhydrous conditions yielded 583 mg (91%) of **4c**·H_2O·1/2 CH_2Cl_2.

Structure Determinations[25]: Crystals of **3b′** and **3c′** were obtained from undried acetonitrile. Diffraction data were recorded at room temperature with the ω/2θ technique on a Nonius CAD4 diffractometer fitted with a molybdenum tube (K_α, λ = 0.7107 Å) and a graphite monochromator. Semiempirical absorption corrections based on ψ scans were applied. The structures were solved with direct methods and refined anisotropically with the SHELX program suite.[26] Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2. The R values are defined as $R_1 = \Sigma F_o - F_c / \Sigma F_o$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2 / \Sigma[w(F_o^2)^2]\}^{1/2}$. Drawings were produced with SCHAKAL.[27] Table 1 lists the crystallographic data.

Table 1. Crystallographic data for complexes **3b′** and **3c′**

	3b′	**3c′**
formula	$C_{64}H_{72}BN_8O_4PZn$	$C_{42}H_{43}BN_9O_5PZn$
mol. mass	1124.5	861.0
cryst. size [mm]	0.5 × 0.5 × 0.4	0.6 × 0.5 × 0.4
space group	*P*2(1)/*c*	*P*2(1)/*n*
Z	4	4
a [Å]	18.240(2)	12.9610(11)
b [Å]	13.618(4)	16.832(2)
c [Å]	25.104(4)	19.708(4)
β [°]	102.590(15)	105.79(1)
V [Å^3]	6085.7(21)	4137.2(10)
^{d}calcd.[g·cm^{-3}]	1.23	1.38
^{d}obsd. [g·cm^{-3}]	1.19	1.31
μ (Mo-K_α) [mm^{-1}]	0.483	0.689
Θ-range [°]	2.2–23.7	2.4–26.0
hkl range	$-20 \le h \le 20$	$-15 \le h \le 15$
	$0 \le k \le 15$	$-20 \le k \le 0$
	$0 \le l \le 28$	$-24 \le l \le 0$
refl. measd.	9491	8332
indep. refl.	9246	8093
obs. refl. [$I > 2\sigma(I)$]	4006	4396
parameters	732	532
R (obs.. refl.)	$R1$ = 0.058, $wR2$ = 0.105	$R1$ = 0.054, $wR2$ = 0.113
R (all refl.)	$R1$ = 0.241, $wR2$ = 0.166	$R1$ = 0.168, $wR2$ = 0.160
res. el. dens. [e/A^{-3}]	+0.5 / −0.5	+0.5 / −0.4

☆ Dedicated to Professor *Manfred Weidenbruch* on the occasion of his 60th birthday.

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