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Dimetallic Activation of Dihydrogen Phosphate by Zn(salphen) Chromophores

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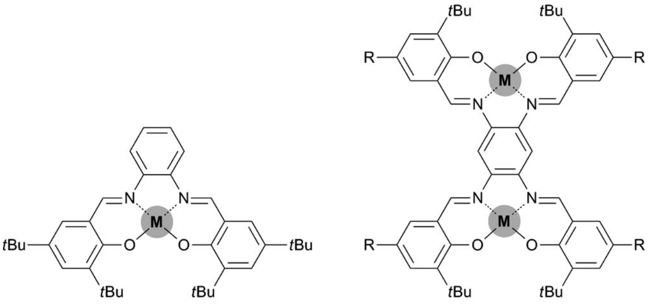
Among a large series of monoanions, dihydrogen phosphate gives an anion-specific reaction with Zn^{II}–salphen complexes based on a proton transfer to the chromophore. Detailed NMR and UV/Vis spectroscopic studies and mass spectrometric analyses point to initial activation of the phosphate anion upon coordination, followed by protonation of the phenolic positions of a second Zn^{II}–salphen structure as supported by kinetic investigations. For a bis(Zn^{II}–salphen) chromophore this process is accompanied by a considerable colour change.

Introduction

Anions are ubiquitous in nature and participate in many essential biological processes.[1] Inorganic phosphate and its derivatives are among the most relevant anions in physiology, spanning a wide range of functions such as the creation of genes, energy storage and signal transduction.[2] A high concentration of phosphate in natural waters is regarded as the main pollutant in cases of eutrophication.[3] This has encouraged chemists to put considerable efforts into the development of recognition and detection methods for phosphate anions. These methods are primarily based on the affinity of the anion for a chemosensor that undergoes photophysical changes upon binding.[4] Most of the reported strategies involve a metal complex (most commonly containing Zn), which binds to the oxo anion,[5] or an organic receptor that can interact through charge-charge or hydrogen-bond interactions.[6] More recently, a promising new anion detection approach was communicated, which is based on a very selective reaction of the anion with the chromophore resulting in a product with altered photophysical properties.[7]

(Multinuclear) Zn^{II}–salphen complexes (see Scheme 1) [salphen = *N*,*N′*-phenylenebis(salicylideneimine)] are relatively cheap building blocks, which are easily fine-tuned. It has been demonstrated that the metal centre in these complexes is highly Lewis-acidic, which allows for strong axial binding of N-donor ligands.[8] This feature has been used progressively in the construction of supramolecular systems[9] and in discrimination and detection methods for alkaloid nuclei[10] and nitroaromatics.[11] In addition, our group recently found that these Zn(salphen) complexes have a high binding affinity for a variety of anions, and this was applied in the construction of multinuclear Zn assemblies.[12] The dihydrogen phosphate monoanion ($H_2PO_4^-$), however, showed very different behaviour in the presence of Zn(salphen) complexes compared to a wide range of other anions, and this prompted us to further explore its behaviour.



Scheme 1. Schematic representation of Zn^{II}-centred and free-base mono- and bis(salphen) complexes **1**–**4**.

Herein, we describe an anion-selective reaction between Zn^{II}–salphen complexes and $H_2PO_4^-$. In the case of a bis(Zn^{II}–salphen) complex this reaction is accompanied by a significant colour change. Kinetic studies support an intermediate state that involves two Zn(salphen) complexes bridged by one molecule of dihydrogen phosphate.

Results and Discussion

Spectroscopic Studies of Phosphate Addition

We analysed solutions of the mono-Zn complex **1** in the presence of different amounts of tetrabutylammonium dihy-

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drogen phosphate ($[Bu_4N]^+[H_2PO_4]^-$) with UV/Vis and NMR spectroscopy and mass spectrometry (MS). In the UV/Vis spectrum (Figure 1), the decrease in the absorption maximum of **1** (λ = 418 nm) is proportional to the $[Bu_4N]^+[H_2PO_4]^-$ concentration, and a new absorption band appears at a lower wavelength (λ = 338 nm). Disappearance of this characteristic metal-to-ligand charge-transfer (MLCT) band was also observed previously for the demetalation of Zn(salphen) complexes induced by axially ligated H_2O,[10b] and it is most likely that a related process occurs here.

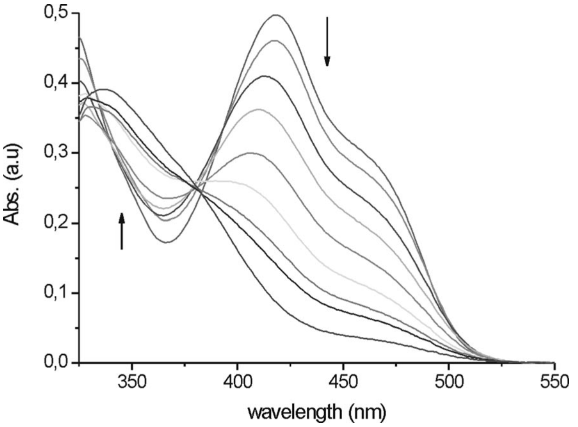


Figure 1. UV/Vis absorption spectra of **1** (2.0×10^{-4} M) in acetone in the presence of 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and 10.0 equiv. of $[Bu_4N]^+[H_2PO_4]^-$. Each spectrum was recorded 30 min after preparation of the sample.

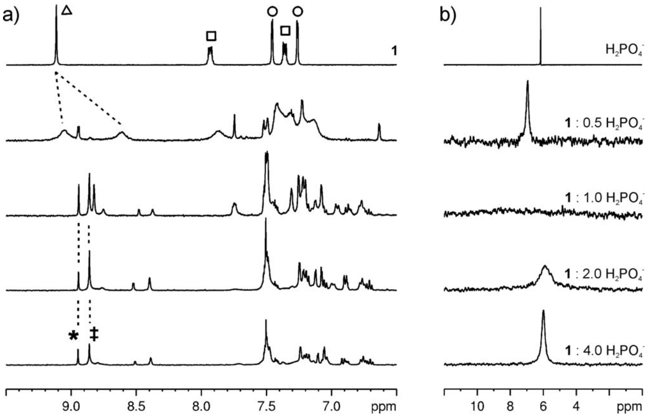
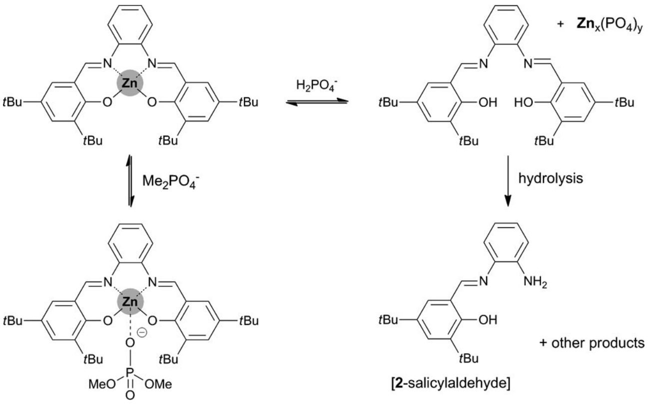


Figure 2. Selected regions of (a) ^1H NMR and (b) $^{31}P\{^1H\}$ NMR spectra obtained after addition of 0–4 equiv. of $[Bu_4N]^+[H_2PO_4]^-$ to **1** ([Zn] = 0.01 M). Labelling scheme Δ = imine H of **1**, □ and ○ = aromatic protons of **1**, * = imine H of free-base salphen, ‡ = imine signal of monoimine (based on 1,2-phenylenediamine and 3,5-di-*tert*-butylsalicylaldehyde).



Scheme 2. Reaction scheme for the addition of $H_2PO_4^-$ and $Me_2PO_4^-$ to Zn(salphen) **1**.

The ^1H NMR spectrum of **1** ([D$_6$]acetone) in the presence of 0.5 equiv. of $H_2PO_4^-$ showed a signal upfield shift for the imine protons (see Figure 2a), which indicates a binding event with the anion.[12] The signals that correspond to the aromatic protons broadened significantly, and this may be due to slow exchange between multiple species or electronic shielding of adjacent Zn(salphen) complexes. Increasing the amount of $H_2PO_4^-$ (up to 4 equiv.) led to sharper signals and the appearance of two new imine resonances. These could be readily assigned to the free-base salphen **2** and a monoimine derivative ([**2**-salicylaldehyde]; Scheme 2), respectively, by comparison with authentic samples.[13] Interestingly, the addition of dimethyl phosphate ($Me_2PO_4^-$) to **1** did not provoke any changes related to decomposition (Supporting Information). Instead the anion appears to simply bind to the Zn centre, and thus the protic nature of $H_2PO_4^-$ must be a key feature in the observed demetalation process (Scheme 2).

The related $^{31}P\{^1H\}$ NMR measurements (Figure 2b) show a small downfield shift for $H_2PO_4^-$ at 0.5 equiv. Addition of larger amounts of phosphate first led to a broadening of the phosphate resonance, followed by signal sharpening and a shift to its original position.

Additional ^1H NMR analyses ([D$_6$]acetone; Supporting Information) of **1** in the presence of another protic anion (i.e. hydrogen sulfate, HSO_4^-) showed that only partial demetalation of **1** occurs. This process is, as in the case of demetalation by H_2O, (benz)imidazoles and purines,[10b,14] completely reversible upon addition of [D$_5$]pyridine. Here, the phenolic positions of the Zn(salphen) structure become protonated after activation of the protic fragments of the coordinating ligands. However, the colorimetric reaction in the presence of $H_2PO_4^-$ cannot simply be attributed to a completely identical process as the spectroscopic changes induced by dihydrogen phosphate do not reverse upon addition of excess [D$_5$]pyridine (Supporting Information). In this respect, it should also be noted that the protons of $H_2PO_4^-$ are less acidic than the proton of HSO_4^-.[15] This fact further points to a more complicated reaction pathway for dihydrogen phosphate.

Mass analyses (ESI-MS, positive and negative mode) of the NMR samples having 0.5, 1.0 and 2.0 equiv. of $H_2PO_4^-$ were carried out (Supporting Information). At the start of the $H_2PO_4^-$ addition (0.5 equiv.), the presence of **1**, its related phosphate coordination complex and the free-base derivative (**2**) could be identified. When the samples contained larger amounts of $H_2PO_4^-$, no Zn-containing species could be identified. Instead, the main products proved to be, as was also observed by ^1H NMR spectroscopy, **2**, the monoimine derivative ([**2**-salicylaldehyde]; Scheme 2) and other unidentified degradation products. Formation of **2** was further supported by X-ray analysis: slow cooling of a solution of **1** in the presence of $[\mathrm{Bu_4N}]^+[\mathrm{H_2PO_4}]^-$ in acetonitrile gave single crystals of the free-base ligand.

From these results it is evident that $\mathrm{H_2PO_4^-}$ addition to Zn(salphen) complexes provokes a demetalation reaction. Upon coordination to the metal centre, the dihydrogen phosphate anion can protonate the inner phenolic positions to give **2**. Although no Zn-containing products could be identified and no precipitation was noted, the Zn atom is tentatively suggested to be expelled from the ligand in the form of a zinc phosphate species with formula $\mathrm{Zn}_x(\mathrm{PO_4})_y$ (Scheme 2).

In contrast to related processes with other protic ligands, the reaction with dihydrogen phosphate is not reversible. This is due to the eventual hydrolysis of the ligand leading to the formation of a number of products, and this feature was exclusively observed for $\mathrm{H_2PO_4^-}$.

Kinetics and Mechanistic Aspects

The reaction order with respect to both $\mathrm{H_2PO_4^-}$ and Zn(salphen) (**1**) was derived by monitoring the reaction progress using UV/Vis spectroscopy. The absorption spectra of a 2.0×10^{-5} M solution of **1** containing 10 equiv. of $\mathrm{H_2PO_4^-}$ (Figure 3a), show a clear isosbestic point at λ = 385 nm indicating the involvement of two different species (i.e., conversion of **1** → **2**). The absorption decrease at λ = 418 nm was used to determine the decrease in concentration of **1** ([ZnL]) and this is equal to (see Supporting Information for more details):

$$-\frac{d[\mathrm{ZnL}]}{dt} = k\cdot[\mathrm{H_2PO_4^-}]^n\cdot[\mathrm{ZnL}]^m$$

The initial reaction rates at four different phosphate concentrations were calculated from the tangent at $t = 0$ in the conversion plots shown in Figure 3b. The resulting logarithmic plot (Figure 3c) reveals a first-order dependence on the concentration of $\mathrm{H_2PO_4^-}$ ($n = 1$). As shown in Figure 3a, the reaction at the highest phosphate concentration (10 equiv. with respect to **1**) was nearly complete within 15 min, and here the integrated rate law was used to determine m. The concentration profile ($d[\mathrm{ZnL}]/dt$) could be best fitted to a pseudo-second-order kinetics equation (Figure 3d). This suggests that two Zn(salphen) complexes are involved in the transition state.

From these results, we can assume that the phosphate anion initially coordinates to the Zn centre (see Scheme 3). This corroborates with the MS studies in which the presence of such a dimetallic species comprising a phosphate fragment was observed. However, upon coordination, the hydrogen atoms of the phosphate anion become acidic enough to protonate the phenolic positions of a second Zn(salphen) complex. The second-order dependence on [Zn] for **1** is in line with the view that two Zn centres take part in this step by an intermolecular pathway. The process is very similar to the mechanism that we reported previously for the demetalation of Zn(salphen) complexes by

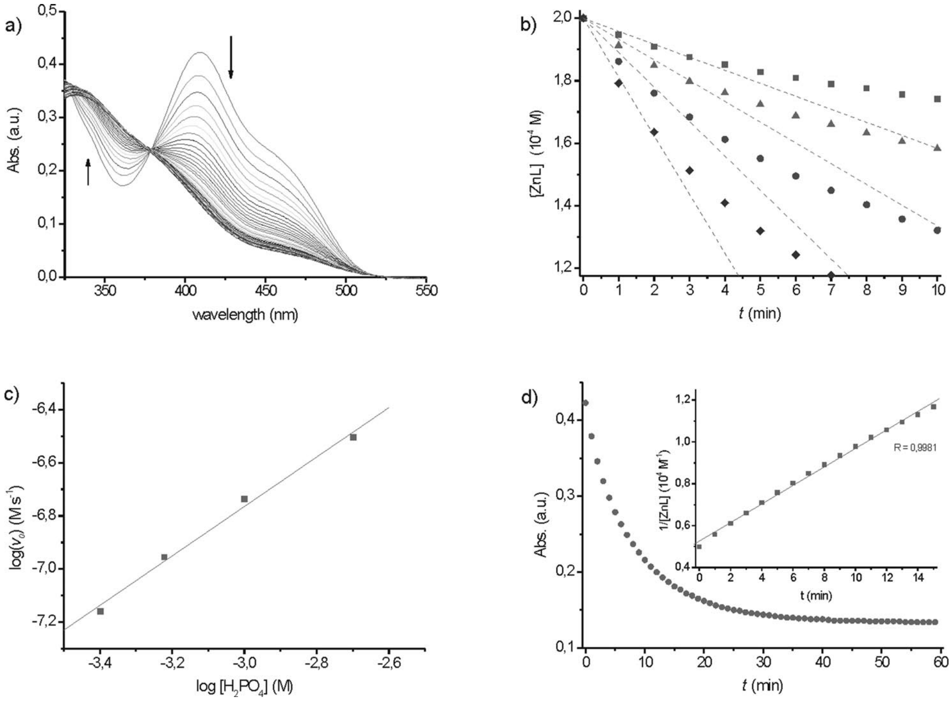
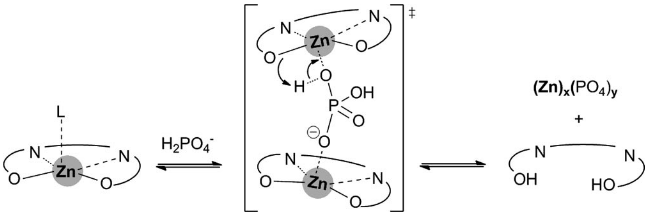


Figure 3. (a) UV/Vis absorption spectra of a 2.0×10^{-4} M solution of **1** containing 10 equiv. (2.0×10^{-3} M) of $[\mathrm{Bu_4N}]^+[\mathrm{H_2PO_4}]^-$ in acetone recorded at 1 min intervals. (b) Rate plots for the demetalation of **1** (2.0×10^{-4} M) with $[\mathrm{H_2PO_4^-}] = 4.0\times10^{-4}$ (■), 6.0×10^{-4} (▲), 1.0×10^{-3} (●), 2.0×10^{-3} M (♦) in acetone and (c) the corresponding initial rate plot with slope = 1. (d) Kinetic study under pseudo-second-order conditions by using the absorption decrease at 418 nm.

axially ligated H_2O, (benz)imidazoles and purines,[10,14] except for the irreversibility upon pyridine addition and the observation of a second-order dependence on the concentration of Zn.



Scheme 3. Proposed transition state in the rate-determining step of the reaction of $H_2PO_4^-$ with Zn^{II}–salphen complexes. L denotes a solvent molecule.

Colorimetric Discrimination between Monoanions

We anticipated that the selective reaction with dihydrogen phosphate would allow us to discriminate between this anion and others upon mixing with Zn(salphen) complexes. The dimetallic complex **3** was used as it provokes a much larger colour change upon demetalation than observed for **1** as the two Zn ions in the former complex are electronically coupled.[16] We tested the ability of **3** to discriminate between $H_2PO_4^-$ and other anions by combining a large series of tetrabutylammonium salts (10 equiv., with respect to Zn) with a solution of the chromophore (0.1 mM) in acetone. Only the addition of the phosphate anion provoked an instantaneous and clear colour change of the solution from red to yellow (Figure 4a). This colorimetric response relates to a large decrease in intensity of the absorption bands at around 502 nm, which are believed to result from MLCT and metal-to-metal charge transfer.[16] At the same time, the absorption in the region around 383 nm, where the free-base analogue has its maximum absorption,[10b] increased. Quantification of these spectral changes for all solutions by calculation of the absorbance ratio ($R = A_{383}/A_{502}$) gives the highest response factor for $H_2PO_4^-$ and is a direct consequence of the demetalation of **3**.

In the case of all the other anions, except for hydrogen sulfate (HSO_4^-), no significant effect was noted on the UV/Vis spectrum and on the colour of the solutions. Conversely, anions that are believed to bind strongly to Zn (i.e. F^-, Cl^-, Br^-, I^-, OAc^-, NO_2^-, CN^-)[12] provoked a darkening of the solution that corresponds to a small redshift in the absorption spectrum.

As a representative example of oxo-anion coordination, we analysed single crystals of a combination of tetrabutylammonium acetate (Bu_4NOAc) with **4** by X-ray diffraction (Figure 5).[17] Suitable crystals were grown from a dichloromethane/acetonitrile solution. The structure comprises a 1:2 assembly with both Zn ions ligated by monodentate OAc anions, which are positioned in an *anti* fashion with respect to the salphen framework. The Zn–O(OAc) bond length [Zn(1)–O(1P) 1.9874(16) Å] is similar to the Zn–O distances Zn(1)–O(1) and Zn(1)–O(2) found within

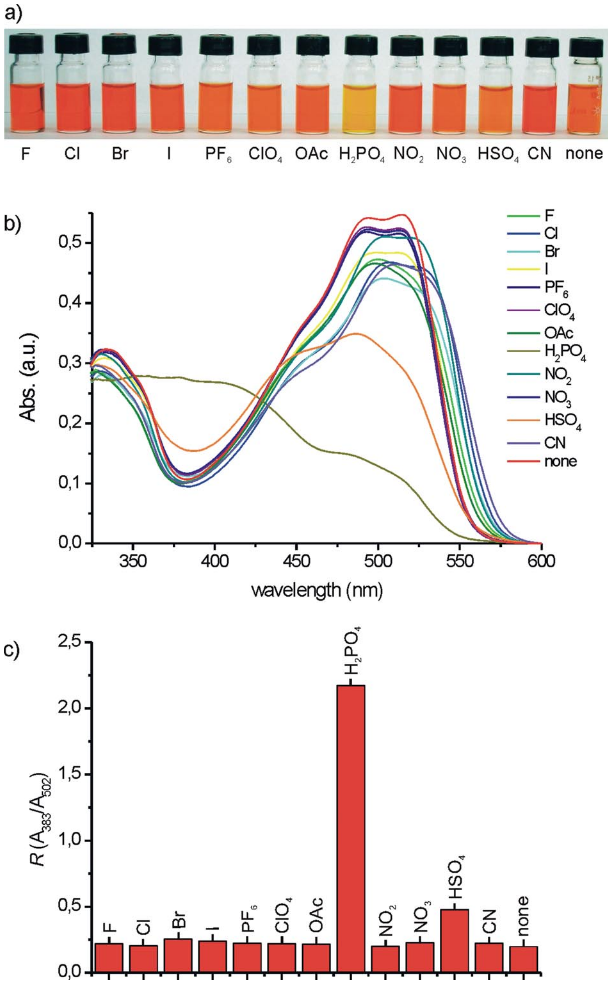


Figure 4. (a) Photograph directly taken after addition of the respective tetrabutylammonium salt (100 µL of a 0.01 M solution in acetone) to **3** (1 mL of a 0.1 mM solution in acetone). To the last vial only acetone was added. (b) UV/Vis traces of the solutions shown in (a) in a 1 mm quartz cuvet and (c) calculated absorbance ratios ($R = A_{383}/A_{502}$).

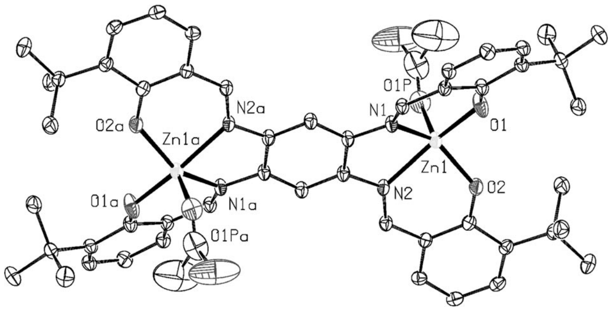


Figure 5. X-ray structure of [**4**·$(OAc)_2$][NBu_4]$_2$. Hydrogen atoms and tetrabutylammonium cations are omitted for clarity, and only a partial numbering scheme is supplied. Complex **4** is shown as it has better crystallization properties than **3**. Selected bond lengths [Å] and angles [°] of [Bu_4N]$_2$[**4**·$(OAc)_2$]: Zn(1)–O(1) 1.9834(15), Zn(1)–O(2) 1.9693(12), Zn(1)–O(1P) 1.9873(16), Zn(1)–N(1) 2.1074(12), Zn(1)–N(2) 2.1267(12); O(1)–Zn(1)–O(2) 96.12(6), O(1)–Zn(1)–N(1) 86.67(5), O(1)–Zn(1)–N(2) 156.19(6), O(2)–Zn(1)–N(1) 142.76(5), O(2)–Zn(1)–N(2) 87.37(5), N(1)–Zn(1)–N(2) 76.70(5).[17]

the salphen complex [1.9834(13) and 1.9693(12) Å, respectively]. The structure presented in Figure 5 is illustrative for the oxophilic nature of the Zn^{II} centres, and a similar type of binding is proposed for $H_2PO_4^-$ to the Zn^{II} centre by its oxo anion (vide supra). Therefore, the structure determined for $[Bu_4N]_2[\mathbf{4}\cdot(OAc)_2]$ may be seen as a good model for the initial stage of dihydrogen phosphate activation, since the coordination of phosphate to Zn is considered a prerequisite to increase the acidity of the phosphate and thus induce the observed hydrolysis reaction.

Conclusions

We have described an anion-mediated colorimetric reaction between dihydrogen phosphate and a bis(Zn–salphen) chromophore. In-depth spectroscopic, spectrometric and kinetic studies support a reaction mechanism in which first the phosphate anion is activated upon coordination to the Zn centre, after which the inner phenolic position of a second Zn(salphen) structure becomes protonated. Although complexes **1** and **3** are demetalated in the presence of protic phosphates through their activation, these cheap and accessible materials may find practical use once full reversibility of this demetalation reaction is addressed and solubility in more polar media (cf., water) is achieved. Our future efforts focus on these issues in order to provide attractive new systems able to sense or discriminate between various phosphates under physiological conditions.

Experimental Section

General Methods and Materials: Compounds **1**–**4** were prepared according to procedures described previously.[8a,10a,16] All other chemicals were commercial products and were used as received. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker Avance 400 Ultrashield instrument at 297 K. Chemical shifts are reported in ppm relative to tetramethylsilane. UV/Vis spectra were measured with a Shimadzu UV2401PC spectrophotometer. Mass analyses and X-ray diffraction studies were carried out by the High Resolution Mass Spectrometry Unit and X-ray Department at the ICIQ (Institute of Chemical Research of Catalonia), Spain.

Stability and Kinetic Studies with UV/Vis Spectroscopy: In a 1 mm quartz cuvet, a solution of **1** (100 µL, 4×10^{-4} M) in acetone was combined with a solution of tetrabutylammonium phosphate (4×10^{-3} M) to give the desired stoichiometry, and then the volume was increased to 200 µL with acetone. After 30 min, a UV/Vis spectrum was acquired of the solutions obtained (i.e. 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0 and 10.0 equiv.). The spectral changes of mixtures containing 2.0, 3.0, 5.0 and 10.0 equiv. of $[Bu_4N]^+[H_2PO_4]^-$ were monitored in real time by recording a spectrum every minute.

Stability Experiments with NMR Spectroscopy and Mass Spectrometry: The desired number of equivalents (0.5–4.0) of the tetrabutylammonium anion ($H_2PO_4^-$, $Me_2PO_4^-$ or HSO_4^-) was added to a solution of **1** (0.5 mL, 0.01 M) in [D6]acetone. After 24 h of equilibration, the ^1H and $^{31}P\{^1H\}$ NMR spectra were measured. The samples containing 0.5, 1.0 and 2.0 equiv. of $[Bu_4N]^+[H_2PO_4]^-$ were concentrated and analysed by ESI-MS (positive and negative mode).

Colorimetric Experiments: To a solution of **3** (1 mL, 0.1 mM) in acetone was added a solution of the respective tetrabutylammonium anion (100 µL, 0.01 M) in acetone. A photograph was taken directly after mixing the solutions. Of the same solutions, a UV/Vis spectrum was recorded instantly (1 mm quartz cuvet).

CCDC-749157 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Experimental data, copies of relevant mass and NMR spectra and further crystallographic details.

Acknowledgments

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[15] $pK_a = 7.20$ for $H_2PO_4^- = H^+ + HPO_4^{2-}$, and $pK_a = 1.99$ for $HSO_4^- = H^+ + SO_4^{2-}$, see: R. N. Goldberg, N. Kishore, R. M. Lennen, *J. Phys. Chem. Ref. Data* **2002**, *31*, 231–370.

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[17] Crystal data for $[Bu_4N]_2[\mathbf{4}\cdot(OAc)_2]$: Formula $2(C_{54}H_{60}N_4O_8Zn_2)\cdot4(C_{16}H_{36}N)\cdot3(C_2H_3N)\cdot2(H_2O)$, $M = 3176.71$, monoclinic, $C2/c$ (no. 15), $a = 39.6952(13)$ Å, $b = 10.8648(4)$ Å, $c = 20.3069(7)$ Å, $\beta = 91.972(1)°$, $V = 8752.8(5)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.205$ g/cm^3, $\mu = 0.606$ mm^{-1}, $\lambda = 0.71073$ Å, $F(000) = 3428$, crystal size $0.15 \times 0.25 \times 0.25$ mm, $T = 100(2)$ K, $\theta_{min-max} = 2.7–37.3°$, total/uniqe data = 39432/20404, $R(int) = 0.032$, data $[I > 2\sigma(I)] = 14370$, $N_{ref}/N_{par} = 20404/513$, GOF = 1.020, $R_1 = 0.0869$ and $wR_2 = 0.1674$ $[I > 2\sigma(I)]$, $R_1 = 0.0581$ and $wR_2 = 0.1525$ (all data), min./max. resd. dens. = –0.802/1.323 e/Å^3.

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