Supplementary Material (ESI) for Dalton Transactions

Structural characterization of a dizinc(II) complex with η^2-phosphate diesters and internal N-H···O-P hydrogen bonding

Juan C. Mareque Rivas*, Rafael Torres Martín de Rosales and Simon Parsons

School of Chemistry, The University of Edinburgh,

Joseph Black Building, King's Buildings,

West Mains Road, Edinburgh, EH9 3JJ, UK

Tel:44-(0)131-650-4761

Fax:44-(0)131-650-4743

*To whom correspondence should be addressed. Email:juan.mareque@ed.ac.uk.

Experimental Section

General. Reagents were obtained from commercial sources and used as received unless otherwise noted. Solvents were dried and purified under N_2 by using standard methods[1] and were distilled immediately before use. Buffer solutions of HEPES (2-(4-(2-hydroxyethyl)-1-piperazinyl)ethanesulfonic acid, (50mM in D_2O) pD 7.4 (20 ºC) were used for the phosphate binding studies and the ionic strength was adjusted to 0.1 N with $NaNO_3$. The pD values in D_2O were corrected for a deuterium isotope effect using the expression pD = pH-meter reading + 0.4. All compounds were prepared under N_2 unless otherwise mentioned. Bpapa was synthesized according to a recently reported procedure.[2] The NMR spectra were obtained using a Bruker DPX 360 at 20 °C in CD_3CN unless otherwise noted. ^{13}C and ^{1}H chemical shifts are referenced with respect to the carbon (δ_C 1.32 and 118.26 ppm) and residual proton (δ_H 1.94 ppm) solvent peaks. ^{31}P resonances were referenced to external 85% H_3PO_4 (δ_P 0 ppm). Mass spectra were performed on a micromass Platform II system operating in Flow Injection Analysis mode with the electrospray method. Elemental analyses were carried out by the microanalyses service provided by the School of Chemistry at the University of Edinburgh.

Synthesis.

$[((bpapa)Zn(\mu\text{-}\eta^2\text{-}DBP)_2Zn(bpapa)](PF_6)_2$ 1. $ZnCl_2$ (55 mg, 0.4 mmol) and $AgPF_6$ (202 mg, 0.8 mmol) were dissolved in dry acetronitrile (20 mL) and the solution was stirred for 1 h resulting in the appearance of a white precipitate, AgCl, which was removed by filtration. Dibenzyl phosphate (110 mg, 0.4 mmol) was then added to the

solution. After stirring at room temperature overnight, bpapa (122 mg, 0.4 mmol) was added and the reaction mixture was kept stirring at room temperature for 4 h after which time a grey precipitate was removed by centrifuge. The solution was evaporated under vacuum to give a yellow solid (203 mg). Re-crystallization of the solid from CH_3OH at room temperature yielded crystals suitable for X-ray diffraction studies with the following spectroscopic and analytical data (Found: C, 48.27; H, 4.16; N, 8.78. Calc. for $C_{64}H_{66}N_{10}O_8P_4F_{12}Zn_2$: C, 48.47; H, 4.19; N, 8.83).

^{1}H NMR (CD_3CN, 360.1 MHz, 293 K) δ_H (ppm) 9.10 (d, J = 4.9 Hz, 2H, py-*H6*), 7.99 (td, J = 7.8, 1.7 Hz, 2H py-*H4*), 7.50 (m, 4H, py-*H5* and py-H3), 7.46 (t, J = 8.6 Hz, 1H, py'-*H4*), 7.36-7.31 (m,10H, P-O-($CH_2C_6H_5$)$_2$), 6.59 (br, py'-NH_2), 6.56 (t, J = 8.8 Hz, 2H, py'-*H3* and py'-*H5*), 5.04 (d, J = 7.6 Hz, 4H, P-O-($CH_2C_6H_5$)$_2$), 4.09 (s, 4H, NCH_2-py), 3.83 (s, 2H, NCH_2-py'). ^{13}C NMR (CD_3CN, 90.5 MHz, 293 K) δ_C (ppm); 161.7, 155.9 (py'-*C2* and py'-*C6*), 152.1 and 159.1 (py-*C2* and py-*C6*), 142.0 (py-*C3*), 141.8 (py'-*C3*), 129.4, 128.8 and 128.5 (P-O-CH_2-C_6H_5)$_2$, 125.8 and 125.5 (py-*C4* and py-*C5*), 112.6 and 112.3 (py'-*C4* and py'-*C5*), 68.6 (d, $^2J_{P-C}$ = 5 Hz, P-O-*C*H_2-C_6H_5), 57.4 (N*C*H_2-py'), 56.8 (N*C*H_2-py). ^{31}P NMR (CD_3CN, 145.8 MHz, 293 K) δ_P(ppm) 1.059. ESI-MS (+ ion) Found 646.2, Calcd. 646.16 (100%).

X-ray Crystallography.

Crystals suitable for X-ray diffraction studies were grown by slow evaporation of methanol solutions at room temperature.

Intensity data for [(bpapa)Zn(μ-η^2-DBP)$_2$Zn(bpapa)](PF$_6$)$_2$ **1**·0.3CH_3OH were collected at 150 K using a Bruker-AXS SMART APEX area detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined to convergence against F^2 data using the SHELXTL suite of programs.[3] Data were corrected for absorption applying empirical

methods using the program SADABS,[4] and the structures were checked for higher symmetry using the program PLATON.[5] All non-hydrogen atoms were refined anisotropically unless otherwise noted. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic displacement parameters. The N-H hydrogens were located in the difference map and refined isotropically. One of the phenyl groups of DBP (C12C13C14C15C16C17) was disordered and modeled over two positions with 60% and 40% occupancy. Chemically equivalent bonds and angles in the disordered fragment were restrained to be similar. The PF_6^- anion was also disordered and modeled over two positions with 60% and 40% occupancy.

References

1. W. L. F.Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, 4th Ed., Oxford: Butterworth-Heinemann, 1997.
2. J. C. Mareque Rivas, E. Salvagni, R. Torres Martín de Rosales and S. Parsons, *Dalton Trans*., 2003, 3339.
3. SHELXS and SHELXL 97, G. M. Sheldrick, University of Göttingen, 1997.
4. (a) G.M. Sheldrick, *SADABS*, Empirical absorption correction program, University of Göttingen, 1995, based upon the method of Blessing;[4b] (b) R. H. Blessing, *Acta Crystallogr., Sect. A,* 1995, **51**, 33.
5. A. L. Spek, *PLATON*, *Acta Crystallogr., Sect. A*. 1990, **46**, C-34.

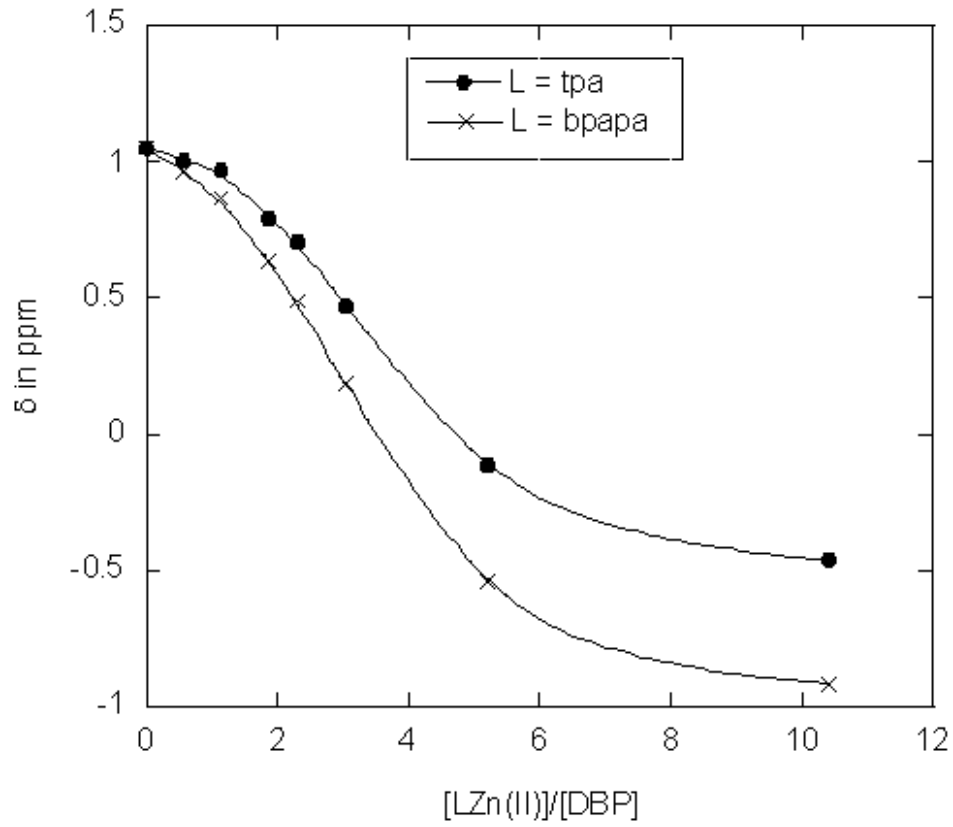

Fig. S1 Changes of the ^{31}P chemical shift of DBP at 20 ºC (5 mM in D_2O, pD 7.4 with I = 1 ($NaNO_3$)) upon addition of increasing amounts of $[(tpa)Zn(S)](PF_6)_2$ and $[(bpapa)Zn(S)](PF_6)_2$ (50 mM in S = CD_3CN).

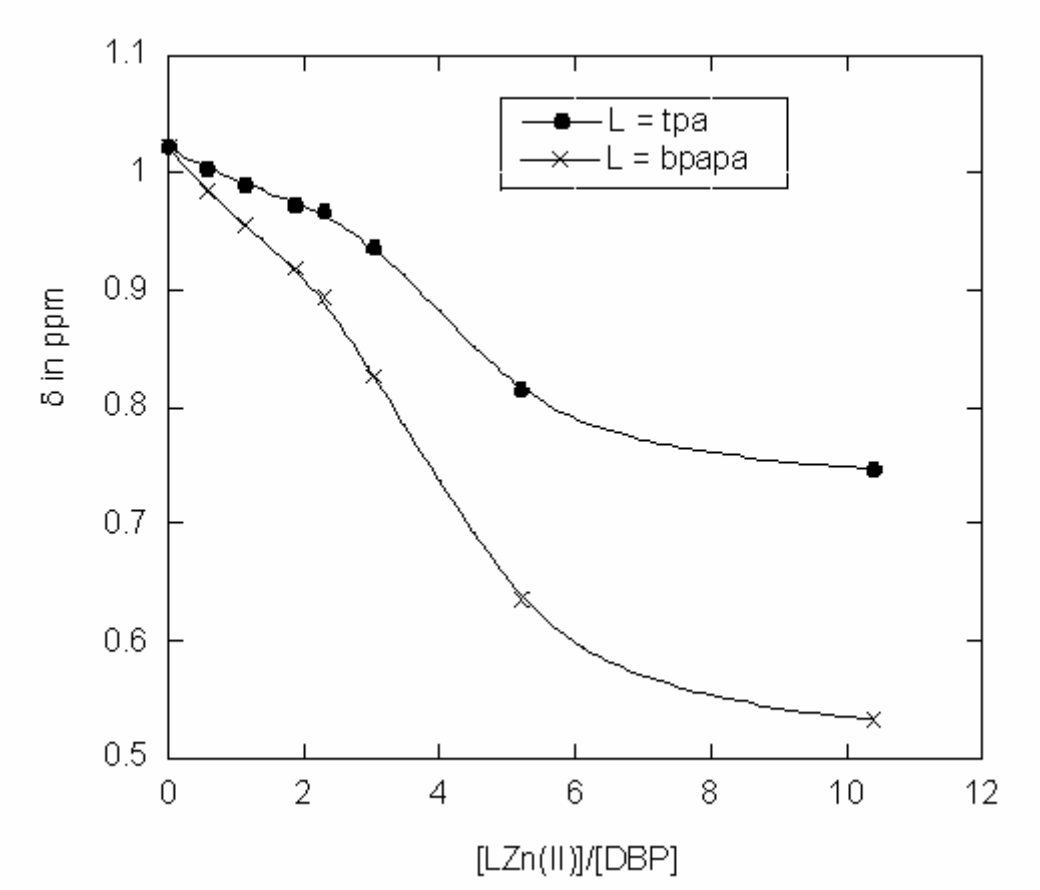

Fig. S2 Changes of the ^{31}P chemical shift of DBP at 20 ºC (5 mM in D_2O, pD 7.4 with I = 0.1 (NaCl)) upon addition of increasing amounts of $[(tpa)Zn(S)](PF_6)_2$ and $[(bpapa)Zn(S)](PF_6)_2$ (50 mM in S = CD_3CN)

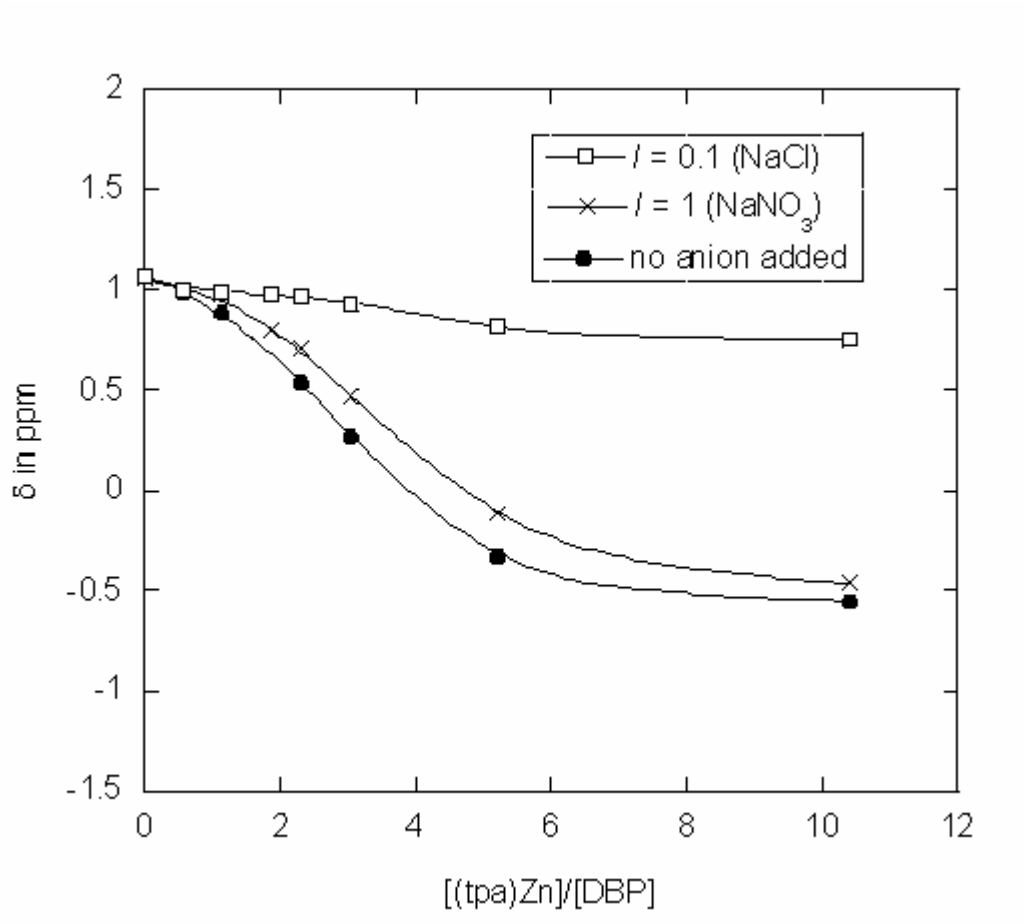

Fig. S3 Changes of the ^{31}P chemical shift of DBP at 20 ºC (5 mM in D_2O, pD 7.4 with upon addition of increasing amounts of $[(tpa)Zn(S)](PF_6)_2$ (50 mM in S = CD_3CN) in the absence and presence of different anions.

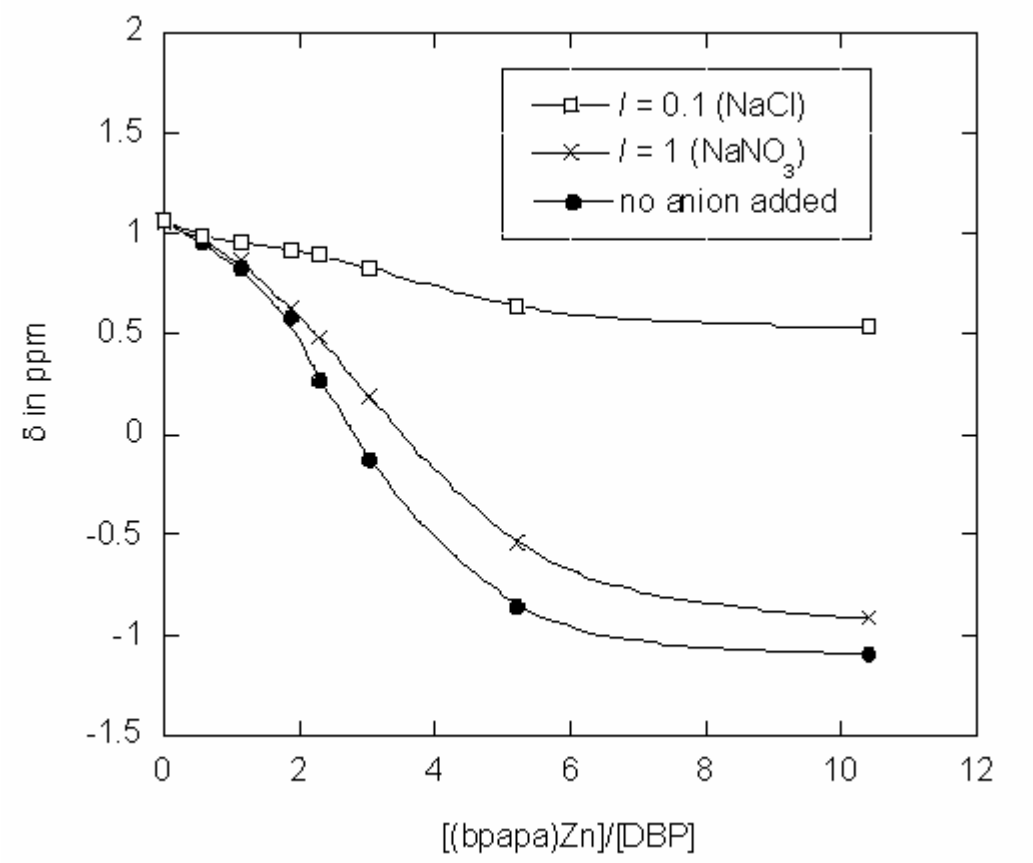

Fig. S4 Changes of the ^{31}P chemical shift of DBP at 20 ºC (5 mM in D_2O, pD 7.4 with upon addition of increasing amounts of $[(bpapa)Zn(S)](PF_6)_2$ (50 mM in S = CD_3CN) in the absence and presence of different anions.