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Mono- and Dinuclear Zinc Complexes of XDK, H_2XDK = *m*-Xylenediamine Bis(Kemp's triacid imide), and Their Reaction with Phosphate Esters

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The reaction of $Zn(NO_3)_2{\cdot}6H_2O$ with H_2XDK and NaOH afforded the mononuclear zinc complex, $[Zn(XDK)(H_2O)]$ (**1**), in good yield. Treatment with pyridine converted complex **1** to $[Zn(XDK)(py)_2]{\cdot}H_2O$ (**2**$\cdot H_2O$), which was characterized by X-ray crystallography (**2**$\cdot CHCl_3$: monoclinic, $P2_1/c$, a = 12.324(4) Å, b = 14.902(3) Å, c = 24.674(5) Å, β = 102.86(3)°, V = 4418(2) $Å^3$, Z = 4, and R = 0.088 and R_w = 0.089 for 3833 independent reflections having $I > 3\sigma(I)$). Complex **2** has two Zn−O and two Zn−N bonds at average distances of 2.04 and 2.07 Å, respectively, contributed by a distorted XDK and two pyridine ligands. There is also a longer interaction to a third oxygen atom of the XDK ligand, Zn−O = 2.39 Å. Recrystallization of **2**$\cdot H_2O$ from a methanol/pyridine mixed solvent gave $\{Zn(\eta^1\text{-carboxylato})_2(py)_2\}$ (**2′**), which was isolated and structurally characterized (**2′**$\cdot CH_3OH$: monoclinic, $P2_1/n$, a = 12.257(2) Å, b = 16.448(2) Å, c = 20.432(3) Å, β = 103.46(1)°, V = 4006.0(9) $Å^3$, Z = 4, and R = 0.048 and R_w = 0.054 for 4140 independent reflections with $I > 3\sigma(I)$). Complex **1** readily reacted with $Zn(NO_3)_2{\cdot}6H_2O$ to give the dizinc complex, $[Zn_2(XDK)(NO_3)_2(CH_3OH)(H_2O)_2]$ (**3**), and a similar reaction in the presence of pyridine gave $[Zn_2(XDK)(py)_2(NO_3)_2]{\cdot}2H_2O$ (**4**$\cdot 2H_2O$). Complex **4** was characterized by X-ray crystallography (**4**$\cdot CH_2Cl_2{\cdot}Et_2O$: monoclinic, $P2_1/n$, a = 17.938(3) Å, b = 21.232(4) Å, c = 15.436(3) Å, β = 112.48(1)°, V = 5432(2) $Å^3$, Z = 4, and R = 0.072 and R_w = 0.082 for 3590 independent reflections with $I > 3\sigma(I)$). The $Zn\cdots Zn$ separation is 3.739(2) Å, and both zinc atoms adopt a tetrahedral geometry. When complex **1** was treated with $Zn(acac)_2{\cdot}2H_2O$, the asymmetrical dinuclear zinc complex, $[Zn_2(XDK)(acac)_2(CH_3OH)_2]{\cdot}H_2O$ (**5**$\cdot H_2O$), was obtained in good yield. An X-ray crystallographic analysis revealed a dizinc structure bridged by XDK and acac ligands; one zinc atom has trigonal bipyramidal geometry, and the other, octahedral geometry. The $Zn\cdots Zn$ interatomic distance is 3.463(1) Å (**5**: monoclinic, $P2_1/c$, a = 17.629(3) Å, b = 12.373(1) Å, c = 21.731(4) Å, β = 90.11(2)°, V = 4740(1) $Å^3$, Z = 4, and R = 0.049 and R_w = 0.054 for 5137 independent reflections with $I > 3\sigma(I)$). Reaction of complex **3** with phosphate ester salts $Na\{(RO)_2PO_2\}$, R = Ph or *p*-NO_2-Ph, yielded the phosphate-bridged dinuclear zinc complexes, $[Zn_2(XDK)\{\mu\text{-}(RO)_2PO_2\}(CH_3OH)_2](NO_3)$ (**6a**, R = Ph; **6b**, R = *p*-NO_2Ph), which were further transformed into $[Zn_2(XDK)\{\mu\text{-}(RO)_2PO_2\}(py)_2](NO_3)$ (**7a**, R = Ph; **7b**, R = *p*-NO_2Ph) by treatment with pyridine. These phosphate ester-bridged dizinc compounds are structural models for postulated intermediates in the mechanism proposed for phosphate ester hydrolysis by *Escherichia coli* alkaline phosphatase and DNA polymerase I, both of which contain a pair of zinc atoms in their active sites.

Introduction

Metalloproteins with redox-active dinuclear metal sites have attracted much attention in bioinorganic chemistry, and a wide variety of model compounds have been prepared to mimic their physical properties and biological activities.[1] In contrast, biomimetic chemistry for enzymes that contain nonredox active dimetallic centers has been slower to develop.[2] Recent biological structural work has revealed that di- or trinuclear metal centers promote a variety of nonredox enzymatic reactions, including the hydrolysis of amides (peptides),[3,4] inorganic pyrophosphate,[5] or phosphate esters (DNA and RNA),[6−9] as well as the aldose−ketose isomerization of carbohydrates.[10] Divalent alkaline earth or transition metal ions such as Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} are indispensable to these reactions.

Knowledge about the structures of enzymes containing di- and trizinc active sites, in particular, is rapidly expanding through X-ray crystallographic studies.[11] Hydrolyses of single-stranded ribo- and deoxyribonucleotides and of phospholipids are catalyzed by P1 nuclease from *Penicillium citrinum*[6] and phospholipase C from *Bacillus cereus*,[7] respectively. These proteins contain three zinc atoms in close proximity to one another in their active sites, two of which are bridged by an aspartate residue and water at a separation of 3.2−3.3 Å. The phosphate complex of alkaline phosphatase from *Escherichia*

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coli,[8] which catalyzes the hydrolysis of phosphate monoesters, consists of a Zn_2Mg (or Zn_3) active site assembly. Here the two zinc atoms are 3.94 Å apart and bridged by a bidentate phosphate, and the magnesium (or third zinc) atom is linked to one atom of the zinc pair by an aspartate residue at a distance of 4.88 Å. DNA polymerase I from *E. coli* (Klenow fragment)[9] contains a dizinc active site bridged by an aspartate residue, which can house a monodentate bridging dinucleotide with a Zn··Zn separation of 3.9 Å. Although detailed catalytic mechanisms for these enzymes have not been established, it has been proposed[8,9] that, during phosphate ester hydrolysis, the dinuclear metal center binds, orients, and activates the substrate, while stabilizing a pentacoordinate phosphorus transition state.

From these studies, it is apparent that di- and trinuclear zinc complexes containing carboxylate bridges would be of value to synthesize as models for the catalytic centers in the hydrolytic enzymes. Few structurally characterized dizinc compounds in this class are available, however, examples being $[Zn_2(\mu\text{-OH})(\mu\text{-}CH_3CO_2)_2(Me_3tacn)_2](ClO_4)$[12] ($Me_3tacn$ = 1,4,7-trimethyl-1,4,7-triazacyclononane), $[Zn_2(\mu\text{-}CH_3CO_2)_3][Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]_n$,[13] $[Zn_2(\mu\text{-}CH_3CH{=}CHCO_2)_4(C_9H_7N)_2]$,[14] $[Zn_2(\mu\text{-}CH_3CO_2)(CH_3CO_2)_2(\mu\text{-}OCH_3)]_n$,[15] $[Zn_2(BBAP)(H_2O)(\mu\text{-}PhCO_2)](ClO_4)_2$[16] (HBBAP = 2,6-bis[bis(2-benzimidazolylmethyl)aminomethyl]-4-methylphenol), $[Zn_2(\mu\text{-}CO_3)L](ClO_4)$[17] (L = α,α′-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecan-6-yl)-*o*-xylene), and $[Zn_2(\mu\text{-}CH_3CO_2)_3(bpy)_2](ClO_4)$.[18] In the present article we report the synthesis and characterization of mono- and dinuclear zinc complexes with *m*-xylenediamine bis(Kemp's triacid imide) (H_2XDK)[19] and their reaction with organic phosphate esters. The XDK ligand was employed since it is known to be remarkably effective in stabilizing dinuclear transition metal cores.[20,21] Some of these results were previously communicated in preliminary form.[20c]

Experimental Section

All manipulations were carried out in air and all reagents and solvents were used as received. *m*-Xylenediamine bis(Kemp's triacid imide) (H_2XDK) was prepared by a known method.[19]

Physical Measurements. NMR spectra were recorded on a Bruker AC250 or a Varian UNITY300 instrument. ^1H NMR spectra were measured at 250 or 300 MHz; chemical shifts are reported versus tetramethylsilane and were calibrated relative to solvent peaks. $^{31}P\{^1H\}$ NMR spectra were measured at 121 MHz with 85% H_3PO_4 as an external reference. Infrared spectra were recorded on a BIO-RAD SPC 3200 spectrometer. Molar conductivity was measured at 24 °C in methanol, and tetra-*n*-butylammonium hexafluorophosphate was used as a reference. Conductivities (κ) were recorded with a Fisher Scientific Model 9-326 conductivity bridge by using two platinized platinum electrodes fixed at a distance of 5 mm. The concentration (c) range was 0.3–2.5 mM, and a linear relation between κ and c was observed. The reported molar conductivities (Ω^{-1} cm^2 mol^{-1}) were derived from the slopes of a plot of conductivity (Ω^{-1} cm^{-1}) versus concentration (mol cm^{-3}).

Preparation of $[Zn(XDK)(H_2O)]$ (1). A methanolic solution (30 mL) of H_2XDK (406 mg, 0.699 mmol) and NaOH (1.5 mmol, 0.45 M in MeOH) was added to a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (403 mg, 1.36 mmol) in methanol (30 mL). The mixture was stirred at room temperature for 30 min. The solvent was removed by a rotary evaporator, and the residue was washed with water and Et_2O. The resultant white powder was dissolved in 60 mL of methanol, which was filtered and concentrated to a volume of 25 mL. An addition of Et_2O (10 mL) to the solution gave colorless microcrystals of $[Zn(XDK)(H_2O)]$ (1), which were collected, washed with Et_2O, and dried in vacuo (377 mg, 81% vs XDK). Anal. Calcd for $C_{32}H_{40}N_2O_9Zn$: C, 58.05; H, 6.09; N, 4.23. Found: C, 57.81; H, 6.13; N, 4.18. ^1H NMR (CD_3OD): δ 1.28 (s, 6H, Me), 1.31 (s, 12H, Me), 1.96 (s, 6H, *m*-Me), 1.28–1.36 (d, 4H, CH), 2.84 (d, 4H, CH, J = 13 Hz), 1.62 (d, 2H, CH, J = 13 Hz), 2.16 (d, 2H, CH, J = 13 Hz), 7.17 (s, 1H, Ar), 7.34 (s, 1H, Ar). IR (Nujol): 3443, 1735 (m), 1680 (s), 1624 (m), 1595 (s), 1193 (s), 1185 (s), 957, 851, 763 cm^{-1}.

Preparation of $[Zn(XDK)(py)_2]{\cdot}H_2O$ ($2{\cdot}H_2O$). A methanolic solution (30 mL) of $[Zn(XDK)(H_2O)]$ (1) (112 mg, 0.169 mmol) and an excess of pyridine (py) (0.80 mL, 9.9 mmol) were stirred at room temperature for 30 min. The solvent was removed by a rotary evaporator, and the residue was extracted with 20 mL of dichloromethane. The extract was concentrated to 2 mL, and addition of 2 mL of Et_2O gave colorless crystals of $[Zn(XDK)(py)_2]{\cdot}H_2O$ ($2{\cdot}H_2O$), which were collected, washed with Et_2O, and dried in vacuo (57 mg, 41%). Anal. Calcd for $C_{42}H_{50}N_4O_9Zn$: C, 61.50; H, 6.14; N, 6.83. Found: C, 61.19; H, 5.90; N, 6.64. ^1H NMR ($CDCl_3$): δ 1.22 (s, 6H, Me), 1.31 (s, 12H, Me), 1.95 (s, 6H, *m*-Me), 1.26–1.31 (d, 4H, CH), 2.85 (d, 4H, CH, J = 13 Hz), 1.57 (d, 2H, CH, J = 13 Hz), 2.13 (d, 2H, CH, J = 13 Hz), 7.14 (s, 1H, Ar), 7.39 (s, 1H, Ar) 7.48, 7.91, 8.54 (m, 10H, py). IR (Nujol): 3400 (br), 1729 (m), 1689 (s), 1608 (s), 1195 (s), 1185 (s), 957, 760, 722 cm^{-1}. Recrystallization of $2{\cdot}H_2O$ from a $CHCl_3/Et_2O$ solvent mixture at room temperature yielded crystals of $[Zn(XDK)(py)_2]{\cdot}CHCl_3$ ($2{\cdot}CHCl_3$) which were suitable for X-ray crystallography. Good crystals of $[Zn(XDK)(py)_2]{\cdot}CH_3OH$ ($2'{\cdot}CH_3OH$) were also obtained by recrystallization of $2{\cdot}H_2O$ from a concentrated methanol solution containing a small amount of pyridine, although the yield was low. The ^1H NMR spectra in $CDCl_3$ of $2{\cdot}CHCl_3$ and $2'{\cdot}CH_3OH$ were identical to that of $2{\cdot}H_2O$.

Preparation of $[Zn_2(XDK)(NO_3)_2(CH_3OH)(H_2O)_2]$ (3). To a methanolic solution (30 mL) of $[Zn(XDK)(H_2O)]$ (1) (145 mg, 0.221 mmol) was added solid $Zn(NO_3)_2{\cdot}6H_2O$ (78 mg, 0.265 mmol). The solution was stirred at room temperature for 3 h, and the solvent was removed under reduced pressure. The residue was recrystallized from a mixture of MeOH (1 mL), Et_2O (5 mL), and hexane (2 mL) to produce colorless crystals of $[Zn_2(XDK)(NO_3)_2(CH_3OH)(H_2O)_2]$ (3), which were collected, washed with Et_2O, and dried in vacuo (85 mg, 43% based on 1). Anal. Calcd for $C_{33}H_{46}N_4O_{17}Zn_2$: C, 43.97; H, 5.14; N, 6.21. Found: C, 43.62; H, 4.90; N, 5.91. ^1H NMR (CD_3OD): δ 1.32 (s, 18H, Me), 1.97 (s, 6H, *m*-Me), 1.38 (d, 4H, CH, J = 14 Hz), 2.84 (d, 4H, CH, J = 14 Hz), 1.65 (d, 2H, CH, J = 13 Hz), 2.18 (d, 2H, CH, J = 13 Hz), 7.15 (br, 1H, Ar), 7.21 (s, 1H, Ar). IR (Nujol): 3400–

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3200, 1736 (m), 1678 (s), 1597 (s), 1296 (s), 1199 (s), 959, 891, 850, 766, 721 cm^{-1}. Treatment of **3** with H_2O and recrystallization from MeOH regenerated **1**, as judged by IR and ^{1}H NMR spectroscopy.

Preparation of $[Zn_2(XDK)(py)_2(NO_3)_2]\cdot 2H_2O$ (4·2H$_2$O). To a solution of methanol (30 mL) containing $[Zn(XDK)(H_2O)]$ (**1**) (164 mg, 0.248 mmol) was added $Zn(NO_3)_2\cdot 6H_2O$ (88 mg, 0.298 mmol). The solution was stirred at room temperature for 3 h and used without isolating **3**. An excess of pyridine (0.40 mL, 4.9 mmol) was added to the solution, and the mixture was stirred at room temperature for 3 h. The solvent was removed by a rotary evaporator and the residue extracted with dichloromethane. The extract was filtered and concentrated to 5 mL, and an addition of 3 mL of Et_2O gave colorless crystals of $[Zn_2(XDK)(py)_2(NO_3)_2]\cdot 2H_2O$ (**4**·2H$_2$O), which were collected, washed with Et_2O, and dried in vacuo (207 mg, 81% based on **1**). Anal. Calcd for $C_{42}H_{52}N_6O_{16}Zn_2$: C, 49.08; H, 5.10; N, 8.18. Found: C, 48.99; H, 4.85; N, 8.27. ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 6H, Me), 1.30 (s, 12H, Me), 1.89 (s, 6H, *m*-Me), 1.18−1.21 (d, 4H, CH), 2.76 (d, 4H, CH, J = 14 Hz), 1.48 (d, 2H, CH, J = 13 Hz), 2.07 (d, 2H, CH, J = 13 Hz), 7.12 (s, 1H, Ar), 7.15 (s, 1H, Ar) 7.50, 7.91, 8.54 (m, 10H, py). IR (Nujol): 3400 (w), 1735 (m), 1693 (s), 1611 (s), 1270, 1183 (s), 1071, 1050, 956, 848, 760, 722, 699 cm^{-1}. Recrystallization of $[Zn_2(XDK)(py)_2(NO_3)_2]\cdot 2H_2O$ from a CH_2Cl_2/Et_2O solvent system at room temperature produced crystals of $[Zn_2(XDK)(py)_2(NO_3)_2]\cdot CH_2Cl_2\cdot Et_2O$ (**4**·CH$_2$Cl$_2$·Et$_2$O) suitable for X-ray study.

Preparation of $[Zn_2(XDK)(acac)_2(CH_3OH)_2]\cdot H_2O$ (5·H$_2$O, acac = 2,4-Pentanedionate). Portions of $[Zn(XDK)(H_2O)]$ (**1**) (200 mg, 0.302 mmol) and $Zn(acac)_2\cdot 2H_2O$ (91 mg, 0.303 mmol) were refluxed in 25 mL of methanol for 30 min. The resultant clear solution was cooled to room temperature, passed through a glass filter, and concentrated to ca. 5 mL to afford fine colorless crystals of $[Zn_2(XDK)(acac)_2(CH_3OH)_2]\cdot H_2O$ (**5**·H$_2$O), which were collected, washed with a small amount of ethanol and hexane, and dried in vacuo (175 mg, 59%). Anal. Calcd for $C_{44}H_{62}N_2O_{15}Zn_2$: C, 53.40; H, 6.31; N, 2.83. Found: C, 53.62; H, 6.18; N, 2.90. IR (Nujol): 3437 (br), 1730, 1680 (s), 1591 (s), 1519, 1180 (s), 1017 (s), 957, 764 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 6H, Me), 1.29 (s, 12H, Me), 1.92 (s, 6H, *m*-Me), 1.86 (s, 12H, acac CH_3), 1.13 (d, 4H, CH, J = 14 Hz), 2.94 (d, 4H, CH, J = 14 Hz), 1.46 (d, 2H, CH, J = 13 Hz), 2.07 (d, 2H, CH, J = 13 Hz), 3.42 (s, 6H, CH_3OH), 5.22 (s, 2H, acac H), 7.08 (s, 1H, Ar), 7.32 (s, 1H, Ar). Recrystallization of **5**·H$_2$O by slow evaporation of the methanolic solution gave block-shaped crystals of $[Zn_2(XDK)(acac)_2(CH_3OH)_2]$ (**5**), which were suitable for X-ray crystallography.

Preparation of $[Zn_2(XDK)\{(RO)_2PO_2\}(CH_3OH)_2](NO_3)$ (6a, R = Ph; 6b, R = *p*-NO$_2$Ph). To a solution of $[Zn(XDK)(H_2O)]$ (**1**) (224 mg, 0.338 mmol) in methanol (20 mL) was added $Zn(NO_3)_2\cdot 6H_2O$ (110 mg, 0.372 mmol). The mixture was stirred at room temperature for 3 h. A methanolic solution (20 mL) of diphenyl phosphoric acid (HDPP) (102 mg, 0.406 mmol) and NaOH (0.43 mmol, 0.45 M in MeOH) was added to the solution, which was further stirred at room temperature. After 12 h, the solvent was removed under reduced pressure and the residue extracted with 30 mL of dichloromethane, which was filtered and concentrated to 5 mL. Diethyl ether (5 mL) was added to the concentrated solution to produce colorless crystals of $[Zn_2(XDK)(DPP)(CH_3OH)_2](NO_3)\cdot 1.5CH_2Cl_2$ (**6a**·1.5CH$_2$Cl$_2$), which were collected, washed with Et_2O, and dried in vacuo (281 mg, 69%). Anal. Calcd for $C_{47.5}H_{59}N_3O_{17}Zn_2PCl_3$: C, 47.07; H, 4.91; N, 3.47. Found: C, 46.77; H, 4.99; N, 3.47. ^{1}H NMR (CD_3OD): δ 1.25 (s, 6H, Me), 1.32 (s, 12H, Me), 1.97 (s, 6H, *m*-Me), 1.2−1.4 (m, 4H, CH), 2.85 (d, 4H, CH, J = 13 Hz), 1.65 (d, 2H, CH, J = 13 Hz), 2.18 (d, 2H, CH, J = 13 Hz), 5.53 (s, CH_2Cl_2), 7.1−7.4 (m, 12H, Ar). ^{31}P{^{1}H} NMR (CD_3OD): δ −10.7 (s). IR (Nujol): 3443 (br), 1716 (m), 1676 (s), 1599 (s), 1297, 1236, 1197, 1061, 958 (s), 764, 723 cm^{-1}. A similar procedure using bis(*p*-nitrophenyl) phosphoric acid hydrate (HBNPP·H$_2$O) gave $[Zn_2(XDK)(BNPP)(CH_3OH)_2](NO_3)\cdot CH_2Cl_2$ (**6b**·CH$_2$Cl$_2$, 68%). Anal. Calcd for $C_{47}H_{56}N_5O_{21}Zn_2PCl_2$: C, 44.82; H, 4.48; N, 5.56. Found: C, 44.57; H, 4.04; N, 5.76. ^{1}H NMR (CD_3OD): δ 1.26 (s, 6H, Me), 1.32 (s, 12H, Me), 1.97 (s, 6H, *m*-Me), 1.2−1.4 (m, 4H, CH), 2.84 (d, 4H, CH, J = 14 Hz), 1.65 (d, 2H, CH, J = 14 Hz), 2.18 (d, 2H, CH, J = 14 Hz), 5.54 (s, CH_2Cl_2), 7.20 (br, 1H, Ar), 7.22 (s, 1H, Ar), 7.45, 8.27 (2 x d, 2 × 4H, BNPP, J = 9 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2/CD_3OD): δ −6.7 (s). IR (Nujol): 3421 (br), 1723 (m), 1682 (s), 1614 (s), 1592 (s), 1522 (s), 1492, 1295, 1259, 1112, 924 (s), 765, 722 cm^{-1}.

Preparation of $[Zn_2(XDK)\{(RO)_2PO_2\}(py)_2](NO_3)$ (7a, R = Ph; 7b, R = *p*-NO$_2$Ph). An excess amount of pyridine (0.20 mL, 2.5 mmol) was added to a solution of **6a**·1.5CH$_2$Cl$_2$ (40 mg, 0.041 mmol) in methanol (20 mL). The mixture was stirred at room temperature for 3 h. The solvent was removed by a rotary evaporator, and the residue was extracted with 20 mL of $CHCl_3$, which was filtered and concentrated to 2 mL. Diethyl ether (2 mL) was added to the concentrated solution to give colorless crystals of $[Zn_2(XDK)(DPP)(py)_2](NO_3)\cdot CHCl_3$ (**7a**·CHCl$_3$), which were collected, washed with Et_2O, and dried in vacuo (52 mg, 82%). Anal. Calcd for $C_{55}H_{59}N_5O_{15}Zn_2PCl_3$: C, 50.89; H, 4.58; N, 5.39. Found: C, 51.02; H, 4.68; N, 5.48. ^{1}H NMR ($CDCl_3$): δ 1.16 (s, 6H, Me), 1.21 (s, 12H, Me), 1.87 (s, 6H, *m*-Me), 1.1−1.3 (m, 4H, CH), 2.74 (d, 4H, CH, J = 14 Hz), 1.44 (d, 2H, CH, J = 13 Hz), 2.04 (d, 2H, CH, J = 13 Hz), 7.0−7.3 (m, 12H, Ph) 7.44, 7.85, 8.52 (m, 10H, py). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −6.0 (s). IR (Nujol): 1732 (m), 1693 (s), 1606 (s), 1293, 1199, 1111 (s), 935 (s), 761, 700 cm^{-1}. A similar procedure using bis(*p*-nitrophenyl) phosphoric acid hydrate (HBNPP·H$_2$O) gave $[Zn_2(XDK)(BNPP)(py)_2](NO_3)\cdot 1.5CHCl_3$ (**7b**·1.5CHCl$_3$, 66%). Anal. Calcd for $C_{55.5}H_{57.5}N_7O_{19}Zn_2PCl_{4.5}$: C, 46.04; H, 4.00; N, 6.77. Found: C, 45.62; H, 4.26; N, 6.81. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 6H, Me), 1.20 (s, 12H, Me), 1.86 (s, 6H, *m*-Me), 1.1−1.3 (m, 4H, CH), 2.70 (d, 4H, CH, J = 14 Hz), 1.44 (d, 2H, CH, J = 13 Hz), 2.04 (d, 2H, CH, J = 13 Hz), 7.05 (br, 2H, Ar), 7.30, 8.14 (2 x d, 2 × 4H, BNPP, J = 9 Hz), 7.49, 7.90, 8.51 (m, 10H, py). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −8.6 (s). IR (Nujol): 1733 (m), 1693 (s), 1607 (s), 1592 (s), 1520, 1297, 1222, 1111, 933, 851, 760 (s), 694 cm^{-1}.

X-ray Crystallographic Analyses of $[Zn(XDK)(py)_2]\cdot CHCl_3$ (2·CHCl$_3$), $[Zn(XDK)(py)_2]\cdot CH_3OH$ (2′·CH$_3$OH), $[Zn_2(XDK)(py)_2(NO_3)_2]\cdot CH_2Cl_2\cdot Et_2O$ (4·CH$_2$Cl$_2$·Et$_2$O), and $[Zn_2(XDK)(acac)_2(CH_3OH)_2]$ (5). Crystal parameters and experimental conditions are listed in Table 1. All data were collected on an Enraf-Nonius CAD4 diffractometer by using graphite monochromatized Mo Kα (λ = 0.710 69 Å) radiation. Three standard reflections were monitored every ~200 reflections and showed no systematic decrease in intensity. Reflection data were corrected for Lorentz−polarization and absorption effects.

Structure Solution and Refinement. 2·CHCl$_3$. The structure was solved by direct methods with SHELXS-86.[22] The zinc atom was located in the initial E map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The coordinates of all hydrogen atoms were calculated at the ideal positions, taking the C−H distance to be 0.95 Å, and were not varied. The structure was refined by full-matrix least-square techniques minimizing $\Sigma w(|F_o| - |F_c|)^2$. Final refinement with anisotropic thermal parameters for non-hydrogen atoms converged to R = 0.088 and R_w = 0.089, where $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$).

2′·CH$_3$OH. The structure was solved by direct methods with SIR92.[23] The zinc atom and most atoms of XDK and pyridine were located initially, and subsequent difference Fourier syntheses gave the positions of remaining non-hydrogen atoms. The coordinates of all hydrogen atoms except for those of the solvent molecule were determined by difference Fourier syntheses. Final full-matrix least-square refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for hydrogen atoms converged to R = 0.048 and R_w = 0.054.

4·CH$_2$Cl$_2$·Et$_2$O. The structure was solved and refined by procedures similar to those described for **2**·CHCl$_3$. Final refinement with anisotropic thermal parameters for non-hydrogen atoms (the carbon atoms of solvent molecules were refined isotropically) converged at R = 0.072 and R_w = 0.082. The dichloromethane molecules in the lattice were disordered and refined with the following model. The CH_2Cl_2 molecule was oriented in three independent directions related by a pseudo-C_3 symmetry axis and populations of 0.2, 0.2, and 0.6. This model required

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(23) Burla, M. C.; Camalii, M.; Cascarano, C.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

Table 1. Crystallographic and Experimental Data for $[Zn(XDK)(py)_2]{\cdot}CHCl_3$ (**2**$\cdot CHCl_3$), $[Zn(XDK)(py)_2]{\cdot}CH_3OH$ (**2'**$\cdot CH_3OH$), $[Zn_2(XDK)(py)_2(NO_3)_2]{\cdot}CH_2Cl_2{\cdot}Et_2O$ (**4**$\cdot CH_2Cl_2{\cdot}Et_2O$), and $[Zn_2(XDK)(acac)_2(CH_3OH)_2]$ (**5**)

compd	**2**$\cdot CHCl_3$	**2'**$\cdot CH_3OH$	**4**$\cdot CH_2Cl_2{\cdot}Et_2O$	5
formula	$C_{43}H_{49}N_4O_8ZnCl_3$	$C_{43}H_{52}N_4O_9Zn$	$C_{47}H_{60}N_6O_{15}Zn_2Cl_2$	$C_{44}H_{60}N_2O_{14}Zn_2$
fw	921.63	834.29	1150.69	971.72
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	12.324(4)	12.257(2)	17.938(3)	17.629(3)
b, Å	14.902(3)	16.448(2)	21.232(4)	12.373(1)
c, Å	24.674(5)	20.432(3)	15.436(3)	21.731(4)
β, deg	102.86(3)	103.46(1)	112.48(1)	90.11(2)
V, Å^3	4418(2)	4006.0(9)	5432(2)	4740(1)
Z	4	4	4	4
T, °C	−110	−90	−110	−110
D_{calcd}, g cm^{-1}	1.386	1.384	1.407	1.362
abs coeff, cm^{-1}	7.93	6.75	10.50	10.77
trans factor	0.95−1.00	0.91−1.00	0.74−1.00	0.85−1.00
2θ range, deg	$3 < 2\theta < 45$	$3 < 2\theta < 49$	$3 < 2\theta < 46$	$3 < 2\theta < 50$
no. of unique data	6021	6899	7715	8738
no. of obsd data ($I > 3\sigma(I)$)	3383	4140	3590	5137
no. of variables	533	707	633	560
R^a	0.088	0.048	0.072	0.049
$R_w{}^a$	0.089	0.054	0.082	0.054

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$. More details about the weighting scheme and other experimental protocols may be found in: Carnahan, E. M.; Rardin, R. L.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 5193.

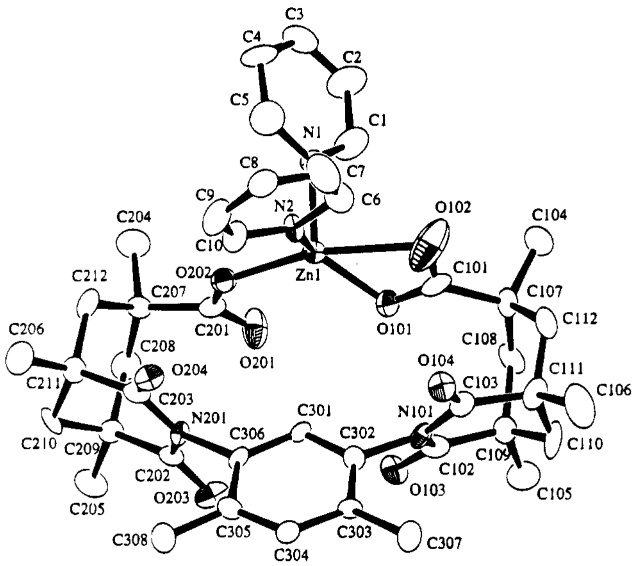

Figure 1. ORTEP view of $[Zn(XDK)(py)_2]$ (**2**). Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

the Cl atoms to be refined with occupancies of 0.8, 0.8 and 0.4, corresponding to sharing of two (0.2 + 0.6) and one (0.2 + 0.2) sets of molecules, respectively.

$[Zn_2(XDK)(acac)_2(CH_3OH)_2]$ (5). The structure was solved by direct methods with SIR92.[23] The coordinates of all hydrogen atoms were determined by difference Fourier synthesis, and were fixed with an appropriate B_{iso} in the refinement. Final refinement with anisotropic thermal parameters for non-hydrogen atoms converged at $R = 0.049$ and $R_w = 0.054$.

For the above structure determinations, atomic scattering factors and values of f' and f'' for Zn, Cl, O, N, and C were taken from the literature.[24] All calculations were carried out on a Digital Equipment VAX Station 3100 or 4000 with the TEXSAN program system.[25] The perspective views were drawn by using the program ORTEP.[26] Final atomic parameters for the coordination spheres of compounds **2**$\cdot CHCl_3$, **2'**$\cdot CH_3OH$, **4**$\cdot CH_2Cl_2{\cdot}Et_2O$, and **5** are listed in Table 2. A complete compilation of final parameters for all atoms is supplied as supporting information.

Results and Discussion

Mononuclear Zinc(II) Complexes of the XDK Ligand. The zinc compounds presented in this report are summarized in Scheme 1 together with their known or postulated structures. Treatment of $Zn(NO_3)_2{\cdot}6H_2O$ with H_2XDK (1 equiv) and NaOH (2 equiv) in methanol and subsequent workup gave colorless microcrystals of $[Zn(XDK)(H_2O)]$ (**1**) in good yield. The IR spectrum indicated the presence of XDK (1735−1595 cm^{-1}) and H_2O (3443 cm^{-1}), and the ^{1}H NMR spectrum in CD_3OD showed two singlets at δ 1.28 and 1.31 with an intensity ratio of 1:2, corresponding to the methyl groups of cyclohexane rings, and one singlet at δ 1.96 for the methyl groups of the xylyl unit. These results are consistent either with a zinc XDK aqua complex of C_{2v} symmetry, as would occur in a pentacoordinate monomer, or with fluxional behavior. Possible structures for **1** include the unsymmetrical model depicted in Scheme 1, an arrangement where the water molecule is pointed downward toward the XDK ligand and hydrogen bonded to the imide moiety, or a square pyramidal complex with a tetradentate XDK and an axial water ligand. The structure in Scheme 1 has a tridentate XDK ligand, similar to that revealed by the crystal structure analysis of $[Zn(XDK)(py)_2]$ (**2**; vide infra), which would have to be fluxional to account for the NMR spectrum. We have thus far not been able to obtain X-ray-quality crystals of this mononuclear zinc complex in order to distinguish between these and other possibilities. Compound **1** is a good precursor for preparing heterodimetallic complexes[20c] as well as the dinuclear zinc compounds described here.

Reaction of $[Zn(XDK)(H_2O)]$ (**1**) with excess pyridine in methanol afforded a colorless complex formulated as $[Zn(XDK)(py)_2]{\cdot}H_2O$ (**2**$\cdot H_2O$). Recrystallization from $CHCl_3/Et_2O$ gave an unhydrated compound $[Zn(XDK)(py)_2]{\cdot}CHCl_3$ (**2**$\cdot CHCl_3$), which was characterized in an X-ray crystallographic analysis. An ORTEP drawing of complex **2** with the atomic numbering scheme is given in Figure 1. Some selected bond lengths and angles are listed in Table 3. The complex consists of one zinc atom coordinated by two nitrogen atoms of pyridine ligands and two oxygen atoms of the carboxylate groups of XDK in a

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(24) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. (b) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(25) *TEXSAN Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

(26) Johnson, C. K. *ORTEP-II*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 2. Atomic Positional and Thermal Parameters for Atoms in the Coordination Spheres of **2**·CHCl$_3$, **2′**·CH$_3$OH, **4**·CH$_2$Cl$_2$·Et$_2$O, and **5**[a,b]

atom	*x*	*y*	*z*	B_{eq}	atom	*x*	*y*	*z*	B_{eq}
[Zn(XDK)(py)$_2$]·CHCl$_3$ (**2**·CHCl$_3$)									
Zn(1)	0.7056(1)	0.04191(8)	0.36319(5)	2.02(5)	N(2)	0.8301(6)	−0.0260(5)	0.4187(3)	1.9(3)
O(101)	0.5846(8)	0.1326(6)	0.3702(4)	5.6(5)	C(101)	0.552(1)	0.1024(9)	0.4089(6)	3.6(6)
O(102)	0.5978(9)	0.0328(8)	0.4325(4)	7.9(6)	C(107)	0.4497(8)	0.1399(7)	0.4275(4)	2.3(5)
O(201)	0.6824(7)	0.1760(6)	0.2719(3)	4.5(4)	C(201)	0.767(1)	0.1304(7)	0.2758(4)	2.5(5)
O(202)	0.8043(6)	0.0777(5)	0.3151(3)	2.8(3)	C(207)	0.8259(8)	0.1330(7)	0.2266(4)	2.2(4)
N(1)	0.6258(6)	−0.0643(5)	0.3171(3)	2.0(4)					
[Zn(XDK)(py)$_2$]·CH$_3$OH (**2′**·CH$_3$OH)									
Zn(1)	0.36223(5)	0.16038(4)	0.55944(3)	1.69(2)	N(2)	0.2171(3)	0.2209(2)	0.5130(2)	1.8(2)
O(101)	0.5027(3)	0.2202(2)	0.5755(2)	2.4(1)	C(101)	0.4972(4)	0.2922(3)	0.5997(2)	2.0(2)
O(102)	0.4229(3)	0.3155(2)	0.6255(2)	3.1(2)	C(107)	0.5887(4)	0.3518(3)	0.5894(2)	1.7(2)
O(201)	0.3015(3)	0.0721(2)	0.6044(2)	2.5(2)	C(201)	0.2472(4)	0.1051(3)	0.6445(2)	2.0(2)
O(202)	0.2641(3)	0.1753(2)	0.6642(2)	2.4(2)	C(207)	0.1525(4)	0.0540(3)	0.6617(2)	1.9(2)
N(1)	0.3939(3)	0.0933(3)	0.4793(2)	1.9(2)					
[Zn$_2$(XDK)(py)$_2$(NO$_3$)$_2$]·CH$_2$Cl$_2$·Et$_2$O (**4**·CH$_2$Cl$_2$·Et$_2$O)									
Zn(1)	0.33292(8)	0.44259(8)	0.0153(1)	2.80(7)	O(42)	0.1242(9)	0.5320(5)	−0.233(1)	11.2(9)
Zn(2)	0.13293(8)	0.44385(7)	−0.1857(1)	2.53(6)	O(43)	0.055(1)	0.6133(6)	−0.222(1)	15(1)
O(101)	0.2504(5)	0.4143(4)	0.0596(6)	3.9(5)	N(1)	0.4265(6)	0.3942(5)	0.1056(7)	2.7(5)
O(102)	0.1370(5)	0.4151(4)	−0.0639(6)	3.4(4)	N(2)	0.0427(6)	0.3926(5)	−0.2708(7)	2.9(5)
O(201)	0.3351(5)	0.4133(4)	−0.1035(6)	3.5(4)	N(3)	0.328(2)	0.5615(8)	−0.009(2)	10(1)
O(202)	0.2199(5)	0.4184(4)	−0.2256(6)	3.2(4)	N(4)	0.0731(9)	0.5574(7)	−0.208(1)	6.2(7)
O(31)	0.391(1)	0.5320(7)	0.019(1)	11(1)	C(101)	0.1764(9)	0.4150(6)	0.021(1)	2.5(6)
O(32)	0.261(1)	0.5295(7)	−0.036(2)	15(1)	C(107)	0.1270(9)	0.4169(6)	0.085(1)	3.1(6)
O(33)	0.326(1)	0.6185(6)	−0.022(1)	11(1)	C(201)	0.2951(8)	0.4137(6)	−0.187(1)	2.4(6)
O(41)	0.0390(8)	0.5236(5)	−0.1774(9)	7.8(7)	C(207)	0.3426(8)	0.4102(6)	−0.253(1)	2.8(6)
[Zn$_2$(XDK)(acac)$_2$(CH$_3$OH)$_2$] (**5**)									
Zn(1)	0.71702(4)	0.19265(5)	0.56993(3)	2.68(3)	C(3)	0.6624(3)	0.1010(4)	0.8618(2)	3.0(3)
Zn(2)	0.70680(4)	0.20770(5)	0.72882(3)	2.84(3)	C(4)	0.6270(3)	0.1968(5)	0.8459(2)	3.0(3)
O(1)	0.7230(2)	0.0608(3)	0.7674(2)	3.5(2)	C(5)	0.5862(3)	0.2605(5)	0.8950(3)	3.9(3)
O(2)	0.6250(2)	0.2390(3)	0.7923(2)	3.3(2)	C(6)	0.5626(4)	0.0245(6)	0.6967(3)	5.6(4)
O(3)	0.6557(2)	0.1273(3)	0.6457(2)	3.1(2)	C(7)	0.6071(3)	0.0521(5)	0.6410(3)	3.6(3)
O(4)	0.6676(2)	0.0891(3)	0.5140(2)	4.1(2)	C(8)	0.5928(4)	−0.0043(5)	0.5864(3)	4.8(4)
O(5)	0.7862(2)	0.2961(3)	0.7882(2)	3.4(2)	C(9)	0.6236(4)	0.0153(5)	0.5282(3)	4.5(3)
O(6)	0.7607(2)	0.2822(3)	0.4950(2)	3.5(2)	C(10)	0.6009(4)	−0.0593(6)	0.4756(3)	6.3(4)
O(101)	0.8135(2)	0.1193(3)	0.5863(2)	3.3(2)	C(21)	0.7668(3)	0.4008(5)	0.8140(3)	4.3(3)
O(102)	0.8065(2)	0.1888(3)	0.6801(2)	2.8(2)	C(22)	0.8224(3)	0.2546(5)	0.4561(3)	4.3(3)
O(201)	0.6629(2)	0.3287(3)	0.5860(2)	2.8(2)	C(101)	0.8357(3)	0.1238(4)	0.6419(2)	2.6(2)
O(202)	0.6790(2)	0.3509(3)	0.6876(2)	3.0(2)	C(107)	0.8932(3)	0.0412(4)	0.6635(2)	2.9(3)
C(1)	0.7324(3)	−0.0710(5)	0.8447(3)	3.7(3)	C(201)	0.6484(3)	0.3735(4)	0.6374(2)	2.6(2)
C(2)	0.7055(3)	0.0364(4)	0.8224(2)	2.9(3)	C(207)	0.5861(3)	0.4588(4)	0.6376(2)	2.7(2)

[a] Estimated standard deviations are given in parentheses. [b] All atoms were refined with anisotropic thermal parameters; reported here is the isotropic equivalent, defined as in the following: Fischer, R. X.; Tillmanns, E. *Acta Crystallogr.* **1988**, *C44*, 775.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for [Zn(XDK)(py)$_2$]·CHCl$_3$ (**2**·CHCl$_3$)[a]

Distances			
Zn(1)−O(101)	2.048(9)	Zn(1)−O(202)	1.953(7)
Zn(1)−O(102)	2.39(1)	Zn(1)···O(201)	2.977(8)
Zn(1)−N(1)	2.066(8)	Zn(1)−N(2)	2.078(7)
O(101)−C(101)	1.20(1)	O(102)−C(101)	1.26(1)
O(201)−C(201)	1.23(1)	O(202)−C(201)	1.25(1)
C(101)−C(107)	1.54(1)	C(201)−C(207)	1.55(1)
Angles			
O(101)−Zn(1)−O(202)	115.7(3)	O(101)−Zn(1)−O(102)	56.4(3)
O(101)−Zn(1)−N(1)	106.6(3)	O(101)−Zn(1)−N(2)	135.3(4)
O(102)−Zn(1)−O(202)	166.0(4)	O(102)−Zn(1)−N(1)	94.5(4)
O(102)−Zn(1)−N(2)	87.0(3)	O(202)−Zn(1)−N(1)	99.2(3)
O(202)−Zn(1)−N(2)	93.8(3)	N(1)−Zn(1)−N(2)	100.4(3)
Zn(1)−O(101)−C(101)	101.3(9)	Zn(1)−O(202)−C(201)	117.9(7)
Zn(1)−O(102)−C(101)	83.4(8)		

[a] Estimated standard deviations are given in parentheses. See Figure 1 for atom labels.

distorted tetrahedral arrangement (Zn(1)−N(1) = 2.066(8) Å, Zn(1)−N(2) = 2.078(7) Å, Zn(1)−O(101) = 2.048(9) Å, and Zn(1)−O(202) = 1.953(7) Å). In addition, O(102) interacts weakly with the zinc atom (Zn(1)−O(102) = 2.39 (1) Å), expanding the O(101)−Zn(1)−N(2) angle to some extent (135.3(4)°), but the O(201) atom is out of bonding range, Zn(1)···O(201) being 2.977(8) Å. The tridentate XDK ligand is fairly distorted. The triacid imide parts are twisted with respect to the xylyl ring from their idealized values of 90°, the dihedral angles between the xylyl ring and the imide planes being 64° [N(101)C(102)C(103)O(103)O(104)] and 74° [N(201)C(202)C(203)O(203)O(204)]. The two carboxylate groups are also twisted with respect to one another, subtending a dihedral angle of 14°. Compound **2** is the first example of a structurally characterized mononuclear zinc XDK complex. Similar coordination of XDK was observed in [Co(XDK)-(neocuproine)] (neocuproine = 2,9-dimethylphenanthroline).[27]

Recrystallization of **2**·H$_2$O from a concentrated methanol/pyridine solution gave the compound [Zn(XDK)(py)$_2$]·CH$_3$OH (**2′**·CH$_3$OH), which was characterized by X-ray crystallography. An ORTEP plot of **2′** showing the atomic numbering scheme is given in Figure 2, and selected bond lengths and angles are listed in Table 4. The structure is clearly mononuclear, the zinc atom in {Zn(η^1-carboxylato)$_2$(py)$_2$} having a distorted tetrahedral geometry with two pyridine nitrogen and two XDK carboxylate oxygen donor ligands (Zn(1)−N(1) = 2.085(4) Å, Zn(1)−N(2) = 2.067(4) Å, Zn(1)−O(101) = 1.943(4) Å, Zn(1)−O(201) = 1.957(3) Å). In **2′**, XDK acts as a bidentate ligand with the carboxyl oxygen atoms, O(102) and O(202), removed from coordination sphere of the metal center (Zn-

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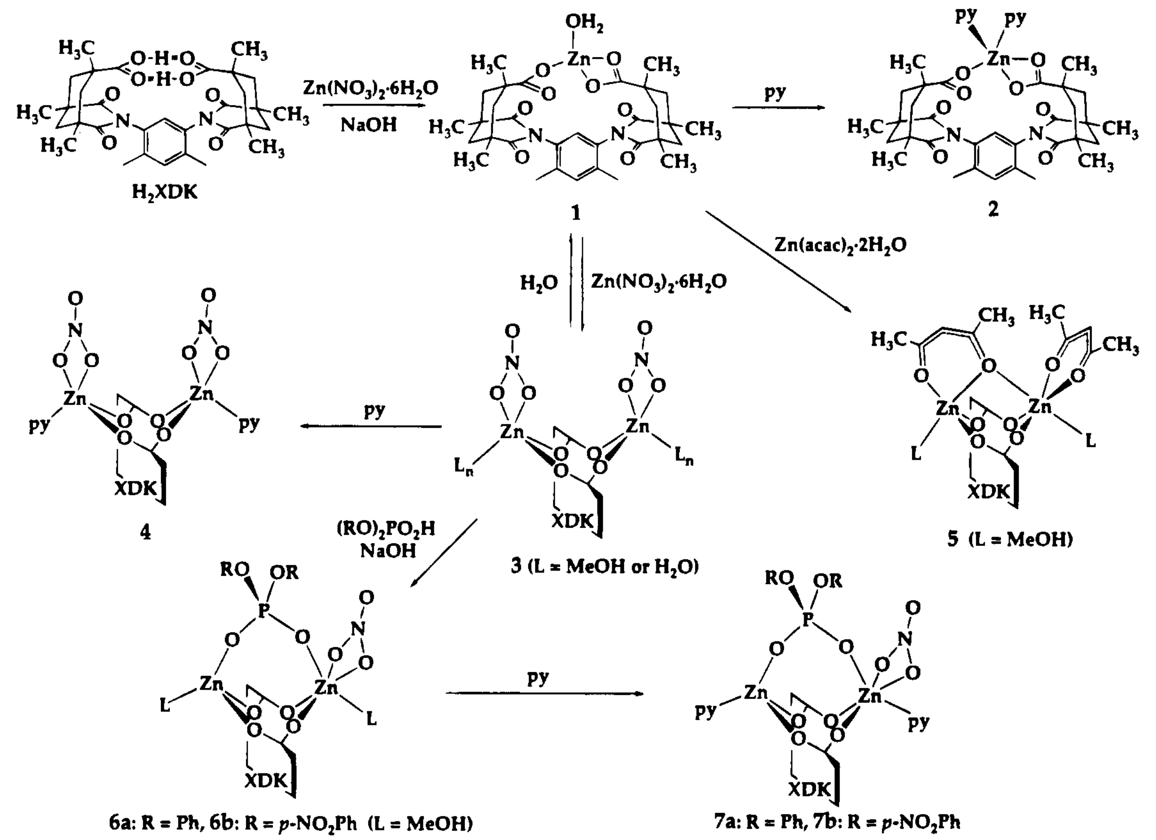
(27) Watton, S. P.; Davis, M. I.; Pence, L. E.; Rebek, J. Jr.; Lippard, S. J. *Inorg. Chim. Acta.* in press.

Scheme 1



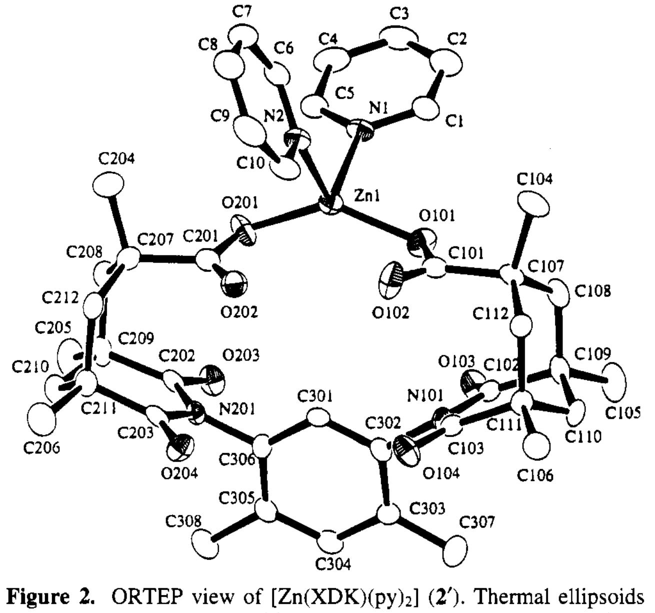


Figure 2. ORTEP view of [Zn(XDK)(py)$_2$] (**2′**). Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

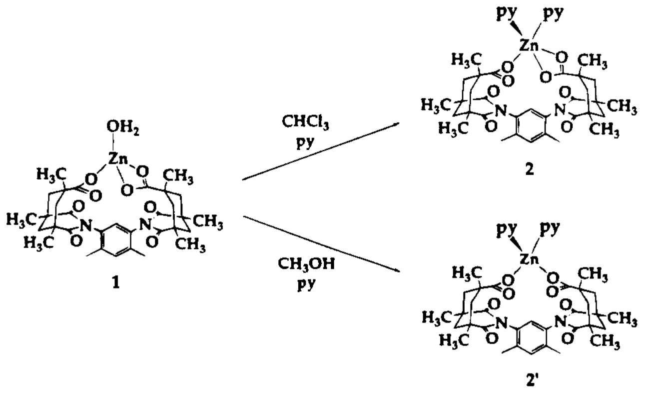
(1)···O(102) = 2.901(4) Å, Zn(1)···O(202) = 2.699(4) Å). The structures of **2** and **2′** are consistent with the observation that solvent polarity can influence the carboxylate chelation modes.[28] Polar solvents with a high dielectric constant favor monodentate carboxylate binding where nonpolar solvents favor chelation. It is therefore reasonable that XDK is a tridentate ligand in solvents such as CHCl$_3$ from which **2**, {Zn(η^1-carboxylato)(η^2-carboxylato)(py)$_2$}, was obtained but a bidentate ligand in **2′**, {Zn(η^1-carboxylato)$_2$(py)$_2$}, which was isolated from methanol (Scheme 2).

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for [Zn(XDK)(py)$_2$]·CH$_3$OH (**2′**·CH$_3$OH)[a]

	Distances		
Zn(1)–O(101)	1.943(4)	Zn(1)–O(201)	1.957(3)
Zn(1)···O(102)	2.901(4)	Zn(1)···O(202)	2.699(4)
Zn(1)–N(1)	2.085(4)	Zn(1)–N(2)	2.067(4)
O(101)–C(101)	1.291(6)	O(102)–C(101)	1.217(6)
O(201)–C(201)	1.289(6)	O(202)–C(201)	1.225(6)
C(101)–C(107)	1.541(7)	C(201)–C(207)	1.538(7)
	Angles		
O(101)–Zn(1)–O(201)	135.7(2)	O(101)–Zn(1)–N(1)	94.6(2)
O(101)–Zn(1)–N(2)	117.9(2)	O(201)–Zn(1)–N(1)	97.9(2)
O(201)–Zn(1)–N(2)	101.1(2)	N(1)–Zn(1)–N(2)	101.1(2)
Zn(1)–O(101)–C(101)	113.9(3)	Zn(1)–O(201)–C(201)	107.1(3)

[a] Estimated standard deviations are given in parentheses. See Figure 2 for atom labels.

Scheme 2



Dinuclear Zinc(II) Complexes of the XDK Ligand. The reaction of [Zn(XDK)(H$_2$O)] (**1**) (1 equiv) with Zn(NO$_3$)$_2$·6H$_2$O (1 equiv) in methanol yielded colorless crystals of [Zn$_2$(XDK)(NO$_3$)$_2$(CH$_3$OH)(H$_2$O)$_2$] (**3**). The IR spectrum showed

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(28) Connolly, J. A.; Kim, J. H.; Banaszcyk, M.; Drouin, M.; Chin, J. *Inorg. Chem.* **1995**, *34*, 1094.

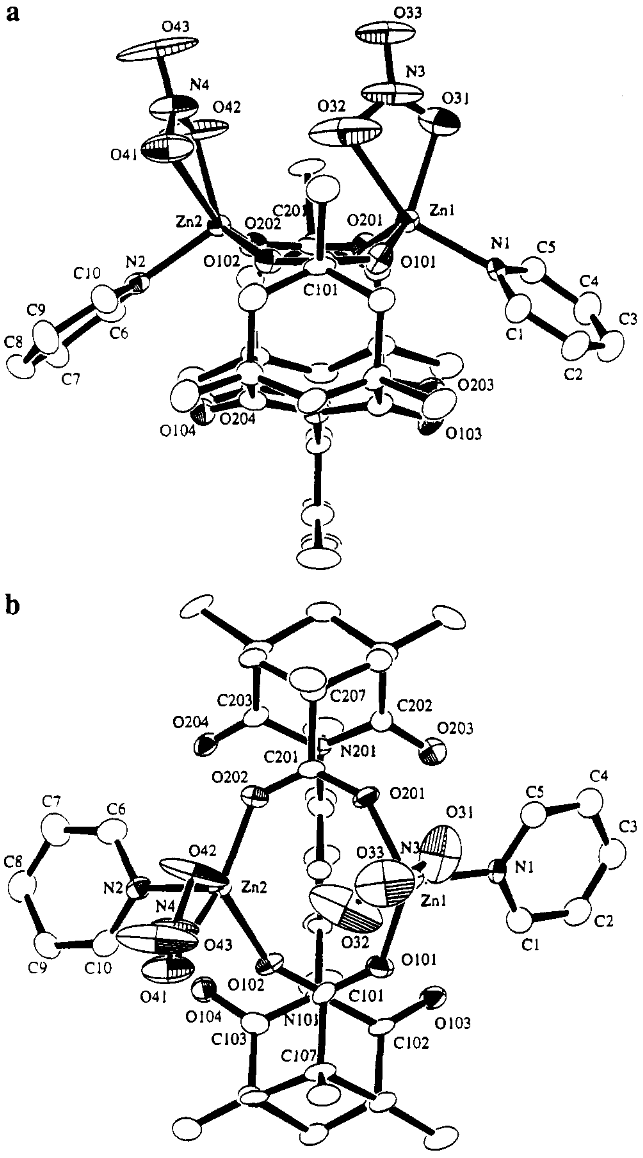

Figure 3. ORTEP plots of $[Zn_2(XDK)(NO_3)_2(py)_2]$ (**4**), viewed (a) along and (b) perpendicular to the dicarboxylate plane. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

the presence of XDK (1736–1597 cm^{-1}), nitrate anions (1296 cm^{-1}), and hydroxyl groups (~3200–3400 cm^{-1}). The ^1H NMR spectrum in $CDCl_3$ revealed one set of symmetrical XDK resonances. By analogy with $[Co_2(XDK)(NO_3)_2(CH_3OH)_2(H_2O)_3]$[29] and $[Mg_2(XDK)(NO_3)(CH_3OH)_4(H_2O)_2](NO_3)$,[30] as well as the crystal structure of **4** (vide infra), complex **3** is inferred to have a dinuclear XDK-bridged structure with coordinated nitrate anions, as depicted in Scheme 1. Details of the geometry at zinc and the nature of the terminal ligands are uncertain. The molar conductivity of 150 Ω^{-1} cm^2 mol^{-1} measured for solutions of **3** in methanol at 24 °C indicated the compound to be a 1:2 electrolyte; the nitrate anions are therefore dissociated from the dinuclear center in this solvent. Treatment of **3** with water quantitatively regenerated the mononuclear complex **1**.

When a methanolic solution of **3**, generated in situ from the reaction of $[Zn(XDK)(H_2O)]$ (**1**) and $Zn(NO_3)_2{\cdot}6H_2O$, was treated with an excess amount of pyridine, colorless crystals of $[Zn_2(XDK)(py)_2(NO_3)_2]{\cdot}2H_2O$ (**4**$\cdot 2H_2O$) were obtained in good yield. The ^1H NMR spectrum showed the presence of XDK and pyridine in a 1:2 ratio. Three singlets for the methyl groups of XDK were observed at δ 1.24, 1.30, and 1.89 with an intensity ratio of 1:2:1, implying a symmetrical structure. In the IR spectrum, characteristic absorptions corresponding to XDK and nitrate anions were observed at 1611–1735 cm^{-1} and at 1270 cm^{-1}, respectively. The molar conductivity of 168 Ω^{-1} cm^2 mol^{-1} in solution corresponds to a 1:2 electrolyte, indicating replacement of the nitrate anions by methanol. Recrystallization of **3** from dichloromethane/diethyl ether afforded crystals of $[Zn_2(XDK)(py)_2(NO_3)_2]{\cdot}CH_2Cl_2{\cdot}Et_2O$ (**4**$\cdot CH_2Cl_2{\cdot}Et_2O$), which were characterized by X-ray crystallography.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $[Zn_2(XDK)(py)_2(NO_3)_2]{\cdot}CH_2Cl_2{\cdot}Et_2O$ (**4**$\cdot CH_2Cl_2{\cdot}Et_2O$)[a]

	Distances		
Zn(1)···Zn(2)	3.739(2)		
Zn(1)–O(101)	1.948(8)	Zn(1)–O(201)	1.950(8)
Zn(1)–O(31)	2.16(2)	Zn(1)–O(32)	2.22(2)
Zn(1)–N(1)	2.01(1)	Zn(2)–O(102)	1.951(8)
Zn(2)–O(202)	1.960(8)	Zn(2)–O(41)	2.43(1)
Zn(2)–O(42)	1.99(1)	Zn(2)–N(2)	1.98(1)
O(31)–N(3)	1.22(2)	O(32)–N(3)	1.30(3)
O(33)–N(3)	1.23(2)	O(41)–N(4)	1.16(1)
O(42)–N(4)	1.24(1)	O(43)–N(4)	1.23(1)
	Angles		
O(101)–Zn(1)–O(201)	121.5(4)	O(101)–Zn(1)–O(31)	133.4(6)
O(101)–Zn(1)–O(32)	88.1(5)	O(101)–Zn(1)–N(1)	98.3(4)
O(201)–Zn(1)–O(31)	97.1(6)	O(201)–Zn(1)–O(32)	98.4(6)
O(201)–Zn(1)–N(1)	100.2(4)	O(31)–Zn(1)–O(32)	59.1(6)
O(31)–Zn(1)–N(1)	99.5(5)	O(32)–Zn(1)–N(1)	153.3(6)
O(102)–Zn(2)–O(202)	118.4(4)	O(102)–Zn(2)–O(41)	86.5(4)
O(102)–Zn(2)–O(42)	128.0(5)	O(102)–Zn(2)–N(2)	100.8(4)
O(202)–Zn(2)–O(41)	149.5(4)	O(202)–Zn(2)–O(42)	96.0(4)
O(202)–Zn(2)–N(2)	100.8(4)	O(41)–Zn(2)–O(42)	53.5(4)
O(41)–Zn(2)–N(2)	90.6(4)	O(42)–Zn(2)–N(2)	110.1(6)
Zn(1)–O(101)–C(101)	130.4(9)	Zn(2)–O(102)–C(101)	145.3(9)
Zn(1)–O(201)–C(201)	141.5(9)	Zn(2)–O(202)–C(201)	135.8(9)
Zn(1)–O(31)–N(3)	94(2)	Zn(1)–O(32)–N(3)	89(1)
Zn(2)–O(41)–N(4)	86(1)	Zn(2)–O(42)–N(4)	105.0(9)
O(31)–N(3)–O(32)	118(2)	O(31)–N(3)–O(33)	122(3)
O(32)–N(3)–O(33)	119(3)	O(41)–N(4)–O(42)	115(1)
O(41)–N(4)–O(43)	121(1)	O(42)–N(4)–O(43)	123(1)

[a] Estimated standard deviations are given in parentheses. See Figure 3 for atom labels.

ORTEP drawings of the complex with the atomic numbering scheme are given in Figure 3a,b. Some selected bond lengths and angles are listed in Table 5. The complex contains a bis(μ-carboxylato)dizinc(II) core coordinated to XDK, which serves as a tetradentate and bridging ligand. The two zinc ions are not linked by any atoms other than the XDK carboxylates. The nonbonding Zn···Zn distance is 3.739(2) Å, which is longer than that in the (μ-hydroxo)bis(μ-acetato)dizinc(II) complex, $[Zn_2(\mu\text{-}OH)(\mu\text{-}CH_3CO_2)_2(Me_3tacn)_2](ClO_4){\cdot}H_2O$ (**8**, 3.311(2) Å),[12] but comparable to the Zn···Zn separations in the active sites of *E. coli* alkaline phosphatase (3.94 Å)[8a] and *E. coli* DNA polymerase I (3.9 Å).[9a] As previously discovered for (μ-oxo)diiron(III) XDK complexes, the two zinc atoms lie substantially out of the plane defined by the two convergent carboxylate groups.[20b] This displacement can be quantified by the metal deviation (d) from this plane and the fold angle (ϕ) across the two carboxylate oxygen atoms (Figure 4). The average d and ϕ values in **4** are 0.59 Å and 18°, respectively, smaller than those found in $[Fe_2(\mu\text{-}O)(XDK)(CH_3OH)_5(H_2O)]^{2+}$ (d = 1.21 Å; ϕ = 37 °).[20b] The less distorted geometry in **4** may reflect the absence of additional bridging ligands. The $Zn{-}O_{CO_2}{-}C_{CO_2}$ angles are significantly expanded as a result of the outofplane binding mode (average $Zn{-}O_{CO_2}{-}C_{CO_2}$, 138.3°; range,

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(29) Watton, S. P.; Lippard, S. J. Unpublished result.

(30) Yun, J. W.; Tanase, T.; Pence, L. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 4407.

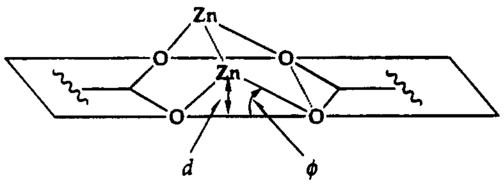


Figure 4. Definition of structural parameters *d* and *φ*, which define deviations of the zinc atoms from the dicarboxylate plane of XDK.

145.3(9)-130.4(9)°). The $Zn-O_{CO_2}$ bonds are not weakened, however, despite the observed distortion (average $Zn-O_{CO_2}$, 1.952 Å; range, 1.948(8)−1.960(8) Å).

Each zinc atom is pentacoordinate, being coordinated by two oxygen atoms of the XDK carboxylate groups, two oxygen atoms of the nitrate anion, and one pyridine nitrogen atom. The Kemp's triacid imide moieties of the XDK ligand are nearly symmetrically disposed with respect to the xylyl ring, the dihedral angles between the imide planes and the xylyl ring being 87 and 86°. The two carboxylate groups are almost coplanar, with a twist angle of 3°. The pyridine molecules are rotated at right angles with respect to the carboxylate plane to avoid steric repulsions. The nitrate anions are coordinated to the metals in an asymmetric, bidentate manner, with O(31)−Zn(1)−O(32) = 59.1(6)° and O(41)−Zn(2)−O(42) = 53.5(4)°. The interaction between the O(41) and the Zn(2) atoms seems to be very weak on the basis of the relatively long distance of 2.43(1) Å. Moreover, the large thermal motions of the nitrate anions imply somewhat weak interactions with the metal centers. The present crystal structure reveals the cleft-shaped XDK ligand to be effective for stabilizing the dinuclear zinc core without additional bridges.

When [Zn(XDK)(H_2O)] (**1**) was treated with $Zn(acac)_2 \cdot 2H_2O$ in refluxing methanol, $[Zn_2(XDK)(acac)_2(CH_3OH)_2] \cdot H_2O$ (**5**·H_2O) was obtained in good yield. The IR spectrum indicated the presence of XDK (∼1586−1728 cm^{-1}) and acac (1520 cm^{-1}). Recrystallization of **5**·H_2O by slow evaporation from methanol gave block-shaped crystals suitable for X-ray crystallography. An ORTEP diagram of the complex with its atomic numbering scheme is provided in Figure 5, and selected bond lengths and angles are summarized in Table 6. The complex is composed of two zinc ions with one XDK, two acac, and two coordinated methanol ligands. The dizinc center is bridged by the two XDK carboxylate groups and is also asymmetrically bridged by the O(3) atom of the acac ligand, Zn(1)−O(3)−Zn(2) = 104.5(1)°. The Zn···Zn separation is 3.463(1) Å, slightly longer than in the (μ-hydroxo)bis(μ-acetato)dizinc(II) complex (**8**, 3.311(2) Å).[12] The distance is comparable to that in the phenoxo-bridged compound, $[Zn_2(BBAP)(\mu\text{-}OBz)(H_2O)](ClO_4)_2 \cdot 4CH_3OH$ (**9**, 3.443(3) Å)[16] (HBBAP = 2,6-bis[bis(2-benzimidazolylmethyl)-aminomethyl]-4-methylphenol), and significantly shorter than in **4**, 3.739(2) Å. The acac bridging reduces the Zn···Zn separation by ∼0.28 Å. The Zn(1) atom has trigonal bipyramidal geometry comprising the two carboxylate oxygen atoms of XDK (Zn(1)−O(101) = 1.960(4) Å, Zn(1)−O(201) = 1.966(3) Å, O(101)−Zn(1)−O(201) = 141.8(2)°), two oxygen atoms of acac (Zn(1)−O(3) = 2.131(3) Å, Zn(1)−O(4) = 1.969(4) Å, O(3)−Zn(1)−O(4) = 90.4(2)°), and the hydroxyl oxygen atom of methanol (Zn(1)−O(6) = 2.117(4) Å). The O(3) and O(6) atoms occupy the axial sites with respect to the triangular plane (O(3)−Zn(1)−O(6) = 168.3(1)°). The six-membered chelate ring containing the acac ligand, [Zn(1)O(3)C(7)C(8)C(9)O(4)], is planar and nearly parallel to the [Zn(1)Zn(2)O(3)] plane, the dihedral angle being 9°. The Zn(2) atom adopts a distorted octahedral geometry, the ligands being two carboxylate oxygen atoms of XDK (Zn(2)−O(102) = 2.067(3) Å, Zn(2)−O(202) = 2.044(3) Å, O(102)−Zn(2)−O(202) = 94.4(1)°), two oxygen atoms of acac (Zn(2)−O(1) = 2.022(4) Å, Zn(2)−O(2) = 2.034(4) Å, O(1)−Zn(2)−O(2) = 89.4(1)°), and the bridging oxygen atom of acac, O(3), in one axial site and the hydroxyl oxygen atom of methanol

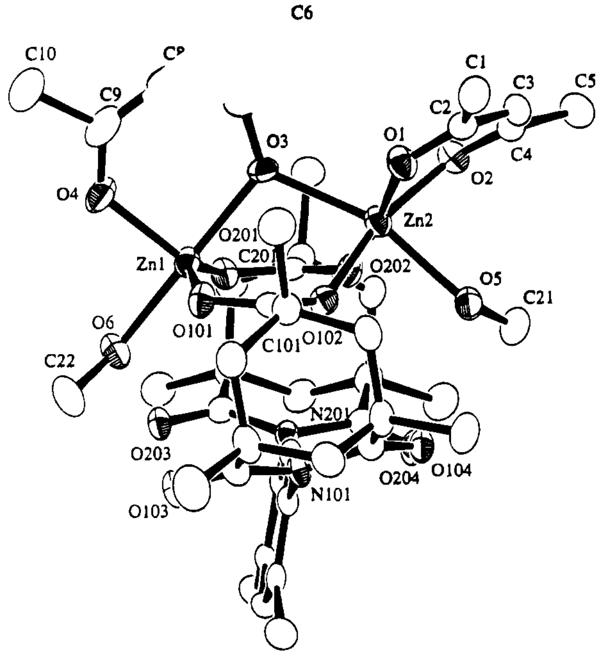


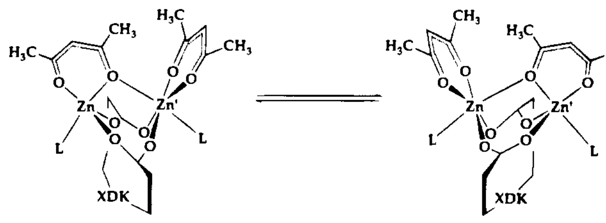
Figure 5. An ORTEP view of $[Zn_2(XDK)(acac)_2(CH_3OH)_2]$ (**5**). Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms are omitted for clarity.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for $[Zn_2(XDK)(acac)_2(CH_3OH)_2]$ (**5**)[a]

	Distances		
Zn(1)···Zn(2)	3.463(1)		
Zn(1)−O(3)	2.131(3)	Zn(1)−O(4)	1.969(4)
Zn(1)−O(6)	2.117(4)	Zn(1)−O(101)	1.960(4)
Zn(1)−O(201)	1.966(3)	Zn(2)−O(1)	2.022(4)
Zn(2)−O(2)	2.034(4)	Zn(2)−O(3)	2.248(3)
Zn(2)−O(5)	2.195(4)	Zn(2)−O(102)	2.067(3)
Zn(2)−O(202)	2.044(3)	O(1)−C(2)	1.272(6)
O(2)−C(4)	1.278(6)	O(3)−C(7)	1.270(6)
O(4)−C(9)	1.238(7)	O(5)−C(21)	1.453(7)
O(6)−C(22)	1.419(6)	C(1)−C(2)	1.492(7)
C(2)−C(3)	1.398(7)	C(3)−C(4)	1.383(7)
C(4)−C(5)	1.510(7)	C(6)−C(7)	1.484(8)
C(7)−C(8)	1.398(8)	C(8)−C(9)	1.399(9)
C(9)−C(10)	1.522(8)		
	Angles		
O(3)−Zn(1)−O(4)	90.4(2)	O(3)−Zn(1)−O(6)	168.3(1)
O(3)−Zn(1)−O(101)	97.2(1)	O(3)−Zn(1)−O(201)	86.6(1)
O(4)−Zn(1)−O(6)	91.5(2)	O(4)−Zn(1)−O(101)	101.1(2)
O(4)−Zn(1)−O(201)	116.9(2)	O(6)−Zn(1)−O(101)	93.7(2)
O(6)−Zn(1)−O(201)	82.3(1)	O(101)−Zn(1)−O(201)	141.8(1)
O(1)−Zn(2)−O(2)	89.4(1)	O(1)−Zn(2)−O(3)	89.5(1)
O(1)−Zn(2)−O(5)	96.6(1)	O(1)−Zn(2)−O(102)	89.5(1)
O(1)−Zn(2)−O(202)	173.9(1)	O(2)−Zn(2)−O(3)	110.2(1)
O(2)−Zn(2)−O(5)	87.6(1)	O(2)−Zn(2)−O(102)	166.8(1)
O(2)−Zn(2)−O(202)	87.8(1)	O(3)−Zn(2)−O(5)	161.3(1)
O(3)−Zn(2)−O(102)	83.0(1)	O(3)−Zn(2)−O(202)	86.3(1)
O(5)−Zn(2)−O(102)	79.4(1)	O(5)−Zn(2)−O(202)	88.7(1)
O(102)−Zn(2)−O(202)	94.4(1)	Zn(2)−O(1)−C(2)	124.7(3)
Zn(2)−O(2)−C(4)	121.5(3)	Zn(1)−O(3)−Zn(2)	104.5(1)
Zn(1)−O(3)−C(7)	124.0(4)	Zn(2)−O(3)−C(7)	131.2(4)
Zn(1)−O(4)−C(9)	127.1(4)	Zn(2)−O(5)−C(21)	121.4(3)
Zn(1)−O(6)−C(22)	127.7(3)	Zn(1)−O(101)−C(101)	114.7(3)
Zn(2)−O(102)−C(101)	139.1(3)	Zn(1)−O(201)−C(201)	128.8(3)
Zn(2)−O(202)−C(201)	132.9(3)		

[a] Estimated standard deviations are given in parentheses. See Figure 5 for atom labels.

Scheme 3[a]



[a] L = MeOH.

(Zn(2)−O(3) = 2.248(3) Å, Zn(2)−O(5) = 2.195(4) Å, O(3)−Zn(2)−O(5) = 161.3(1)°) in the other. The six-membered acac chelate ring assumes an envelope conformation and is nearly perpendicular to the [Zn(1)Zn(2)O(3)] plane, the dihedral angle being 102°.

The metal atoms are substantially displaced from the plane of the bridging dicarboxylate system in **5**, as was the case for **4**. The distances from carboxylate plane (*d*) are 1.18 Å for Zn(2) and 0.46 Å for Zn(1), and the average ϕ being 28°, midway between the values in [Fe$_2$(μ-O)(XDK)(CH$_3$OH)$_5$(H$_2$O)]$^{2+}$ (37°) and [Zn$_2$(XDK)(NO$_3$)$_2$(py)$_2$] (**4**) (18°). The out-of-plane distortion is more significant around the octahedral zinc site (Zn(2)) than the trigonal bipyramidal site (Zn(1)), as also reflected in the bond angles around the carboxylate oxygen atoms (Zn−O$_{\mathrm{CO_2}}$−C$_{\mathrm{CO_2}}$). The XDK ligand is somewhat distorted from the C$_{2v}$ symmetrical form, one of the Kemp's triacid imide moieties twisting toward the Zn(1) atom. The dihedral angles between the xylyl and imide planes, [N(101)C(102)C(103)C(109)C(111)] and [N(201)C(202)C(203)C(209)C(211)], are 70 and 81°, respectively. The two carboxylate groups are almost coplanar, with a dihedral angle of 5°, and are perpendicular to the [Zn(1)Zn(2)O(3)] plane. The O(5)···O(104) and O(6)···O(203) interatomic distances are 2.896(5) and 2.813(5) Å (O(104)···H(1)−O(5) = 167°, O(203)···H(59)−O(6) = 155°, O(104)···H(1) = 1.88 Å, O(203)···H(59) = 1.82 Å), indicating the presence of hydrogen bonding interactions between the hydroxyl groups of the coordinated methanols and the carbonyl groups of the imide moieties. The asymmetric dizinc structure is rare, but a similar structure occurs in complex **9**. Since acac ligands can be easily replaced by other ligands and substrates, the dizinc compound **5** is a good precursor to models for the active sites of zinc-containing enzymes such as phospholipase C and P1 nuclease (vide infra).[6,7]

The ^{1}H NMR spectrum of **5** dissolved in CDCl$_3$ showed only one singlet for the methyl groups of the acac ligands together with two singlets corresponding to the methyl groups of cyclohexane rings in XDK, with an intensity ratio of 1:2, and one singlet for the methyl groups of xylyl unit. These results suggest that rapid exchange might occur between bridging and chelating acac ligands at room temperature, one possibility for which is indicated in Scheme 3. The ^{1}H NMR spectrum in CD$_2$Cl$_2$, however, did not change over the temperature range 25 to −85°C, revealing that, if exchange is taking place, it has a low-energy barrier.

Reactions of Dinuclear Zinc(II)−XDK Complexes with Phosphate Esters. Treatment of dizinc complex **3**, formed by reacting [Zn(XDK)(H$_2$O)] (**1**) and Zn(NO$_3$)$_2$·6H$_2$O, with diphenyl phosphoric acid HDPP and NaOH in situ afforded [Zn$_2$(XDK)(DPP)(CH$_3$OH)$_2$](NO$_3$)·1.5CH$_2$Cl$_2$ (**6a**·1.5CH$_2$Cl$_2$) in good yield. Elemental analysis indicated **6a** to have one XDK, one diphenyl phosphate, one nitrate anion, and two methanol molecules for two zinc atoms, as well as 1.5 dichloromethane molecules of solvation obtained during recrystallization. The IR spectrum also confirmed the presence of XDK, nitrate ion, diphenyl phosphate (1236 cm^{-1}), and hydroxyl groups. In the ^{1}H NMR spectrum in CD$_3$OD, three singlets for the methyl groups of XDK were observed at δ 1.25, 1.32, and 1.97 (intensity ratio = 1:2:1), suggesting a symmetrical structure (C$_{2v}$) as observed in complexes **3** and **4**. Multiplets for the phenyl groups of phosphate ester were also observed at δ 7.1−7.4, together with a singlet for methylene chloride at δ 5.53. The molar conductivity of **6a** at 24 °C in methanol, 93 Ω^{-1} cm^2 mol^{-1}, was slightly greater than that expected for a 1:1 electrolyte, indicating partial dissociation of diphenyl phosphate. The ^{31}P{^{1}H} NMR spectrum of **6a** in CD$_3$OD consisted of a single resonance (δ −10.7) at room temperature, which was resolved into two signals (δ −9.4 and −13.0) at low temperatures. These chemical shift values match those of free and bound phosphate, respectively, further consistent with some phosphate ester dissociation. The analogous complex, [Zn$_2$(XDK)(BNPP)(CH$_3$OH)$_2$](NO$_3$)·CH$_2$Cl$_2$ (**6b**·CH$_2$Cl$_2$), was also obtained in 68% yield by using bis(p-nitrophenyl) phosphoric acid (HBNPP).

Phosphate esters serve as bidentate bridging ligands in many dinuclear transition metal complexes. Structurally characterized examples include [Fe$_2$(μ-O){μ-(PhO)$_2$PO$_2$}(HBpz$_3$)$_2$], [Fe$_2$(μ-OH){μ-(R$_2$PO$_2$)}$_2$(HBpz$_3$)$_2$]$^+$ (R = PhO or Ph), [Fe$_2${μ-(PhO)$_2$PO$_2$}$_3$(HBpz$_3$)$_2$]$^+$,[31] [Cu$_2$(UN−O){μ-(p-NO$_2$PhO)$_2$PO$_2$}] (UN−OH = 2-[bis(2-pyridylethyl)amino]-6-[(bis(2-pyridylethyl)amino)methyl]phenol),[32] [Fe$_2$(μ-O){μ-(PhO)PO$_3$}$_2$(Me$_3$tacn)$_2$],[33] [Co$_2$(en)$_4${μ-(PhO)PO$_3$}$_2$]$^{2+}$,[34] [Zn{μ-(p-NO$_2$PhO)PO$_3$}{HB(^{i}Pr$_2$pz)$_3$}$_2$],[35] [(TPA)Zn{PO(O)(OC$_6$H$_4$NO$_2$)O}Zn(TPA)] (TPA = tris[(2-pyridyl)-methyl]amine),[36] [Fe$_2$(BHPP){μ-(PhO)$_2$PO$_2$}$_2$]$^+$, [Fe$_2$(BHPMP){μ-(PhO)$_2$PO$_2$}$_2$]$^+$ (H$_3$BHPP = 1,3-bis[((2-hydroxybenzyl)(2-pyridylmethyl)amino)methyl]-2-propanol, and H$_3$BHPMP = 2,6-bis[((2-hydroxybenzyl)(2-pyridylmethyl)amino)methyl]-4-methylphenol),[37] [Fe$_2$(μ-O)(TPA)$_2${μ-(PhO)$_2$PO$_2$}]$^{3+}$,[38] and [Fe$_2$(BPMP){μ-(PhO)$_2$PO$_2$}$_2$]$^{2+}$ (HBPMP = 2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenol).[39] On the basis of these structures as well as that of the dimagnesium analog [Mg$_2$(XDK){(RO)$_2$PO$_2$}(NO$_3$)(CH$_3$OH)$_3$(H$_2$O)],[30] compound **6** is tentatively assigned a geometry comprising two zinc atoms bridged by XDK and diphenyl phosphate ligands (Scheme 1).

When **6** was treated with an excess amount of pyridine, colorless crystals of [Zn$_2$(XDK){(RO)$_2$PO$_2$}(py)$_2$](NO$_3$) (**7a**, R = Ph; **7b**, R = p-NO$_2$Ph) were obtained in good yield. The ^{1}H NMR spectra indicated the presence of XDK, diphenyl phosphate, and pyridine with the ratio of 1:1:2. A structure for **7** is postulated in Scheme 1. The Zn$_2$(μ-carboxylate)$_2$(μ-diphenyl phosphate) structure is important as a model for substrate-binding in the active sites of alkaline phosphatase and DNA polymerase I, where the hydrolysis of phosphate esters was

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suggested to proceed by a two-metal-ion-promoted mechanism.[8,9] We are currently evaluating the hydrolysis reactions of phosphate esters promoted by dinuclear zinc and other metal complexes supported by the XDK ligand.

Conclusions

The cleft-shaped dicarboxylate anion XDK is an effective ligand for constructing dinuclear zinc complexes in which the terminal ligands are substitutionally labile. These complexes can form without the need for an additional bridging ligand. The bridged XDK complexes can be synthesized in a stepwise fashion *via* the mononuclear zinc complex. Auxiliary ligands such as 2,4-pentanedionate and organic phosphate esters can be readily introduced into the bridging position of the dizinc center. These complexes are useful structural models for species postulated to occur at the active sites of dizinc- and trizinc-containing metalloenzymes which hydrolyze phosphate esters and related functionalities.

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Supporting Information Available: Tables of crystallographic and experimental data, complete atomic positional and thermal parameters, and bond distances and angles for **2**$\cdot$$CHCl_3$, **2′**$\cdot$$CH_3OH$, **4**$\cdot$$CH_2Cl_2\cdot Et_2O$, and **5** (47 pages). Ordering information is given on any current masthead page.

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