

Dinuclear Zinc Complexes of Phenol-Based “End-off” Compartmental Ligands: Synthesis, Structures and Phosphatase-Like Activity

Ko-ji Abe, Jun Izumi, Masaaki Ohba, Takusi Yokoyama, and Hisashi Ōkawa*

Department of Chemistry, Faculty of Sciences, Kyushu University,
Hakozaki 6-10-1, Higashiku, Fukuoka 812-8581

(Received August 21, 2000)

The phenol-based compartmental ligands of the “end-off” type, 2,6-bis{*N*-[2-(dimethylamino)ethyl]iminomethyl}-4-methylphenol (L^1), 2-{*N*-[2-(dimethylamino)ethyl]iminomethyl}-6-{*N*-methyl-*N*-[2-(dimethylamino)ethyl]aminomethyl}-4-bromophenol (L^2), 2,6-bis{2-[(2-pyridyl)ethyl]iminomethyl}-4-methylphenol (L^3) and 2-[*N,N*-di(2-pyridylmethyl)aminomethyl]-6-{*N*-[2-(dimethylamino)ethyl]iminomethyl}-4-methylphenol (L^4), have formed dinuclear zinc complexes: $[Zn_2(L^1)(AcO)_2]PF_6$ (**1**), $[Zn_2(L^1)(NCS)_3]$ (**2**), $[Zn_2(L^2)(AcO)_2]PF_6$ (**3**), $[Zn_2(L^2)(NCS)_3]$ (**4**), $[Zn_2(L^3)(AcO)_2]PF_6$ (**5**), $[Zn_2(L^3)(NCS)_3]$ (**6**), $[Zn_2(L^4)(AcO)_2]ClO_4$ (**7**), $[Zn_2(L^4)(AcO)(NCS)_2]$ (**8**) and $[Zn_2(L^4)(NCS)_3]$ (**9**). The crystal structures of **1**, **5**·(DMF)_{0.5}(2-PrOH)_{0.5}, **7**·CHCl₃, **8**·(2-PrOH) and **9**·3CHCl₃ have been determined. Complexes **1** and **5**·(DMF)_{0.5}(2-PrOH)_{0.5} have a di- μ -acetato- μ -phenolato-dizinc(II) core comprised of two square-pyramidal Zn centers. **7**·CHCl₃ has a similar dinuclear core, but it is comprised of one square-pyramidal Zn and one pseudo-octahedral Zn. **8**·(2-PrOH) has a μ -acetato- μ -phenolato-dizinc(II) core with a unidentate thiocyanato-*N* group on each Zn. **9**·3CHCl₃ exists in two different crystals: one has a μ -thiocyanato-*N*- μ -phenolato-dizinc(II) core, whereas the other has a μ -phenolato-dizinc(II) core. The diacetato complexes, **1**, **3**, **5** and **7**, are stable in solution. Hydrolytic activities of the complexes toward tris(*p*-nitrophenyl) phosphate (TNP) have been studied in aqueous DMF by means of UV-visible spectroscopic and ³¹P NMR methods. Complexes **1**, **3** and **5** have an activity to hydrolyze TNP into bis(*p*-nitrophenyl) hydrogenphosphate (HBNP) in aqueous DMF. In contrast, **7** showed little hydrolytic activity toward TNP in aqueous DMF.

Bimetallic cores exist at the active sites of many metalloenzymes¹ and play essential roles required in biological systems. Dinuclear Zn cores are found in hydroxylases such as alkaline phosphatase,² phospho-lipase C,³ P1 nuclease,⁴ and leucine aminopeptidase.⁵ Recent X-ray crystallographic studies have indicated that the active sites of most hydroxylases are asymmetric with respect to the two Zn centers. It is thought that hydroxylases employ such an asymmetric dinuclear core to facilitate the concerted binding of a substrate on one Zn center and the nucleophilic attack of hydroxide or activated water at the adjacent Zn center.⁶ Some model studies have been carried out to mimic the hydroxylase functions using dinuclear Zn complexes.⁷

Phenol-based “end-off” compartmental ligands, having pendant arms attached to the 2 and 6 positions of the phenolic ring, have often been used to model bimetallic biosites.^{8–11} Di- μ -carboxylato- μ -phenolato-dimanganese(II) complexes derived from such ligands show Mn catalase-like activity to disproportionate hydrogen peroxide into dioxygen and water.⁸ Urea adducts of dinuclear nickel(II) complexes were derived as structural models of urease,⁹ and chemical conversion of urea into cyanate ion was achieved on dinuclear nickel(II) complexes.¹⁰ Dioxygen adducts of dinuclear cobalt(II), iron(II) and copper(I) complexes of such “end-off” compartmental ligands were extensively studied as models for oxygen-carriers and oxygenases.¹¹

In this work, the “end-off” compartmental ligands (L^1)–(L^4) (Chart 1) were used to synthesize dinuclear zinc(II) complexes, with the hope of providing functional models of phosphatases. The ligands (L^1)–(L^3) have two bidentate

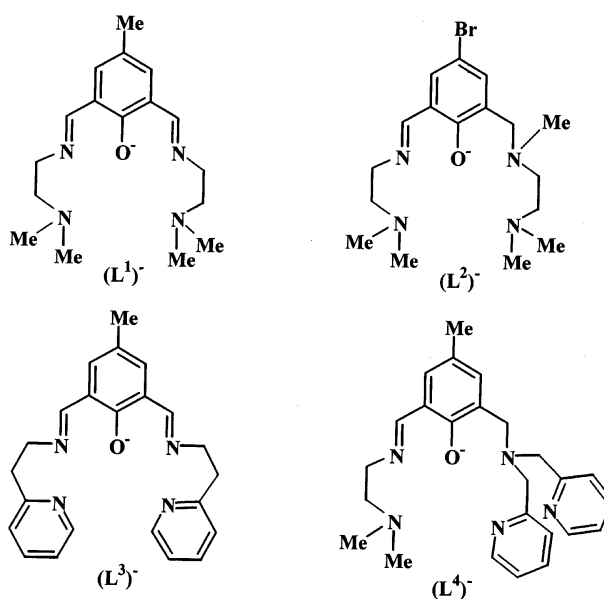


Chart 1. Chemical structures of phenol-based “end-off” compartmental ligands (L^1)–(L^4)[–].

chelating arms. The ligands (L^1)[−] and (L^3)[−] are symmetric with respect to the two chelating arms, whereas (L^2)[−] is asymmetric with respect to the amidic and imidic nature of the articular nitrogens of the bidentate arms. The ligand (L^4)[−] has bidentate and tridentate chelating arms and can provide a dinuclear core in a coordination number asymmetry. The following dinuclear Zn complexes have been obtained: $[Zn_2(L^1)(AcO)_2]PF_6$ (**1**), $[Zn_2(L^1)(NCS)_3]$ (**2**), $[Zn_2(L^2)(AcO)_2]PF_6$ (**3**), $[Zn_2(L^2)(NCS)_3]$ (**4**), $[Zn_2(L^3)(AcO)_2]PF_6$ (**5**), $[Zn_2(L^3)(NCS)_3]$ (**6**), $[Zn_2(L^4)(AcO)_2]ClO_4$ (**7**), $[Zn_2(L^4)(AcO)(NCS)_2]$ (**8**) and $[Zn_2(L^4)(NCS)_3]$ (**9**). The crystal structures of **1**, **5**·(DMF)_{0.5}(2-PrOH)_{0.5} (**5'**), **7**·CHCl₃ (**7'**), **8**·(2-PrOH) (**8'**) and **9**·3CHCl₃ (**9'**) have been determined by X-ray crystallography, and the solution structures of **1–9** in DMF have been examined by ¹H NMR and visible spectra. A focus is placed on phosphatase-like activity of the diacetato complexes **1**, **3**, **5** and **7** toward tris(*p*-nitrophenyl) phosphate (TNP) in aqueous DMF.

Experimental

Physical Measurements. Elemental analyses of C, H, and N were obtained at the Elemental Analysis Service Center of Kyushu University. Analyses of Zn were obtained using a Shimadzu AA-660 atomic absorption/flame emission spectrometer. Infrared spectra were recorded on a Perkin Elmer BX FT-IR system using KBr disks. Molar conductances in DMF were measured with a DKK AOL-10 conductivity meter at room temperature. Electronic spectra were recorded using a Shimadzu UV-3100PC spectrometer. ¹H-NMR spectra (270 MHz) were recorded on a JEOL JNM-GX 400 using tetramethylsilane as the internal standard. ³¹P-NMR spectra were recorded on the same spectrometer using H₃PO₄ (85%) as the external reference. Positive ion fast atom bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX 102A BE/BE four-sector type tandem mass spectrometer using *m*-nitrobenzyl alcohol as the matrix.

Preparation. 2,6-Diformyl-4-methylphenol was prepared by the method of Denton and Suschitzky.¹² The proligands, 5-bromo-3-*N*-[2-(dimethylamino)ethyl]-*N*-methylaminomethylsalicylaldehyde¹³ and 3-*N,N*-di(2-pyridylmethyl)aminomethyl-5-methylsalicylaldehyde,^{8d,8e} were prepared by the methods in our previous papers. Other chemicals were of reagent grade and were used as purchased.

$[Zn_2(L^1)(AcO)_2]PF_6$ (1**).** The ligand HL^1 was prepared in situ by reacting 2,6-diformyl-4-methylphenol (164 mg, 0.5 mmol) and *N,N*-dimethylethylenediamine (88 mg, 1.0 mmol) in methanol (10 cm³) at the boiling temperature. To the ligand solution was added zinc(II) acetate tetrahydrate (220 mg, 1.0 mmol), and the mixture was stirred at 60 °C for 20 min. A methanol solution (10 cm³) of ammonium hexafluorophosphate (82 mg, 1.0 mmol) was then added, and the solution was concentrated to ca. 10 cm³ to form yellow crystals. The yield was 523 mg (75%). Found: C, 35.64; H, 4.89; N, 8.05; Zn, 18.3%. Calcd. for C₂₁H₃₃F₆N₄O₅PZn₂: C, 36.17; H, 4.77; N, 8.07; Zn, 18.8%. Molar conductance [Λ_M/S cm² mol^{−1}]: 61 in DMF. UV-vis [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 390 (10400) in DMF. Selected IR data (KBr) 1655, 1640, 1598, 1549, 1449, 842, 557 cm^{−1}.

$[Zn_2(L^1)(NCS)_3]$ (2**).** This was obtained as yellow microcrystals by the reaction of HL^1 and Zn(NCS)₂ in methanol. Yield: 23%. Found: C, 39.60; H, 4.50; N, 15.87; Zn, 21.0%. Calcd. for C₂₀H₂₇N₇O₃S₃Zn₂: C, 39.48; H, 4.47; N, 16.11; Zn, 21.5%. Molar conductance [Λ_M/S cm² mol^{−1}]: 47 in DMF. UV-vis [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 391 (10700) in DMF. Selected IR (KBr) data: 2090,

1992, 1650, 819, 488, 462, 410 cm^{−1}.

$[Zn_2(L^2)(AcO)_2]PF_6$ (3**).** The ligand HL^2 was prepared in situ by reacting 5-bromo-3-*N*-[2-(dimethylamino)ethyl]-*N*-methylaminomethylsalicylaldehyde (157 mg, 0.5 mmol) and *N,N*-dimethylethylenediamine (44 mg, 0.5 mmol) in methanol (10 cm³) at the boiling temperature. To this solution was added zinc(II) acetate tetrahydrate (220 mg, 1.0 mmol), and the mixture was stirred at 60 °C for 20 min. A methanol solution (10 cm³) of ammonium hexafluorophosphate (82 mg, 1 mmol) was then added, and the mixture was concentrated to ca. 10 cm³ to give yellow microcrystals. The yield was 300 mg (77%). Found: C, 32.41; H, 4.40; N, 7.20; Zn, 16.8%. Calcd. for BrC₂₁F₆H₃₄N₄O₅PZn₂: C, 32.54; H, 4.46; N, 7.18; Zn, 16.6%. FAB MS *m/z* 633 for $\{Zn_2(L^2)(AcO)_2\}^+$. Molar conductance [Λ_M/S cm² mol^{−1}]: 61 in DMF. UV-vis [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 365 (6200) in DMF. Selected IR (KBr) data: 1648, 1600, 1446, 844, 558 cm^{−1}.

$[Zn_2(L^2)(NCS)_3]$ (4**).** This was obtained as yellow microcrystals by the reaction of HL^2 and Zn(NCS)₂ in methanol. Yield: 86%. Found: C, 35.12; H, 4.17; N, 14.20; Zn, 18.9%. Calcd. for BrC₂₀H₂₈N₇O₃S₃Zn₂: C, 34.85; H, 4.09; N, 14.22; Zn, 19.0%. Molar conductance [Λ_M/S cm² mol^{−1}]: 48 in DMF. UV-vis [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 374 (6700) in DMF. Selected IR (KBr) data: 2078, 2024, 1644, 826, 752, 482, 461, 412 cm^{−1}.

$[Zn_2(L^3)(AcO)_2]PF_6$ (5**).** The ligand HL^3 was prepared in situ by reacting 2,6-diformyl-4-methylphenol (164 mg, 0.5 mmol) and 2-(2-pyridyl)ethylamine (122 mg, 1.0 mmol) in methanol (20 cm³). To this solution was added zinc(II) acetate tetrahydrate (220 mg, 1.0 mmol), and the mixture was stirred at 60 °C for 20 min. A solution of ammonium hexafluorophosphate (82 mg, 1.0 mmol) in methanol (10 cm³) was then added, and the mixture was concentrated to ca. 10 cm³ to result in the precipitation of yellow microcrystals. Yield: 335 mg (86%). Found: C, 43.31; H, 4.41; N, 7.99; Zn, 17.4%. Calcd. for C₂₇F₆H₂₉N₄O₅PZn₂: C, 43.31; H, 4.42; N, 7.61; Zn, 17.0%. FAB MS *m/z* 621.1 for $\{Zn_2(L^3)(AcO)_2\}^+$. Molar conductance [Λ_M/S cm² mol^{−1}]: 61 in DMF. UV-vis [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 390 (10800) in DMF. Selected IR (KBr) data: 1649, 1633, 1596, 1571, 1552, 1490, 1444, 1414, 843, 558 cm^{−1}.

Single crystals of $[Zn_2(L^3)(AcO)_2]PF_6 \cdot (DMF)_{0.5} \cdot (2-PrOH)_{0.5}$ (**5'**) suitable for X-ray crystallography were grown when a DMF solution of **5** was diffused with 2-propanol (2-PrOH).

$[Zn_2(L^3)(NCS)_3]$ (6**).** This was obtained as yellow microcrystals by the reaction of HL^3 and Zn(NCS)₂ in methanol. Yield: 32%. Found: C, 46.35; H, 3.40; N, 14.45; Zn, 16.8%. Calcd. for C₂₆H₂₃N₇O₃S₃Zn₂: C, 46.16; H, 3.43; N, 14.49; Zn, 19.3%. Molar conductance [Λ_M/S cm² mol^{−1}]: 58 in DMF. UV-vis [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 397 (9300) in DMF. Selected IR (KBr) data: 2077, 2030, 1649, 1630, 1608, 1554, 816, 712, 701, 478, 466, 418 cm^{−1}.

$[Zn_2(L^4)(AcO)_2]ClO_4$ (7**).** A solution of HL^4 was prepared in situ by reacting 3-*N,N*-di(2-pyridylmethyl)aminomethyl-5-methylsalicylaldehyde (157 mg, 0.5 mmol) with *N,N*-dimethylethylenediamine (44 mg, 0.5 mmol) in methanol (5 cm³) at the boiling temperature. To this solution was added zinc(II) acetate tetrahydrate (210 mg, 1.0 mmol), and the mixture was stirred at 60 °C for 30 min. A methanol solution (10 cm³) of sodium perchlorate (120 mg, 1.0 mmol) was then added, and the mixture was diffused with ether to give yellow microcrystals. The yield was 222 mg (58%). Found: C, 45.56; H, 4.73; N, 9.12; Zn, 17.1%. Calcd. for C₂₉ClH₃₆N₅O₉Zn₂: C, 45.58; H, 4.87; N, 9.14; Zn, 17.0%. FAB MS: *m/z* 664 for $\{Zn_2(L^4)(AcO)_2\}^+$. Molar conductance [Λ_M/S cm² mol^{−1}]: 49 in DMF, 32 in DMSO. UV-vis [λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)]: 367 (6100) in DMF. Selected IR (KBr) data: 3436,

2926, 1637, 1604, 1464, 1431, 1311, 1092, 1022, 775, 624 cm⁻¹.

Single crystals of [Zn₂(L⁴)(AcO)₂]ClO₄·CHCl₃ (**7'**) suitable for X-ray crystallography were grown by recrystallization from a chloroform/hexane mixture.

[Zn₂(L⁴)(AcO)(NCS)₂] (**8**). A methanol solution HL⁴ (0.5 mmol) was prepared as described for **7**. To this was added zinc(II) acetate tetrahydrate (210 mg, 1.0 mmol), and the mixture was stirred for 30 min. Sodium thiocyanate (81 mg, 1.0 mmol) was then added, and the mixture was stirred for 30 min and allowed to stand at room temperature to provide yellow crystals. The yield was 234 mg (64%). Found: C, 48.16; H, 4.59; N, 13.57; Zn, 18.1%. Calcd. for C₂₉H₃₅N₇O₃S₂Zn₂: C, 48.07; H, 4.87; N, 13.53; Zn, 18.0%. FAB MS: *m/z* 655 for {Zn₂(L⁴)(AcO)(NCS)}⁺. Molar conductance [*A*_M/S cm² mol⁻¹]: 71 in DMF, 50 in DMSO. UV-vis [*λ*_{max}/nm (ε/M⁻¹ cm⁻¹)]: 370 (5700) in DMF. Selected IR (KBr) data: 3469, 2915, 2081, 1641, 1577, 1463, 1434, 1303, 1017, 765 cm⁻¹.

Single crystals of [Zn₂(L⁴)(AcO)(NCS)₂]·2(2-PrOH) (**8'**) suitable for X-ray crystallography were grown when a DMF solution of **8** was diffused with 2-propanol.

[Zn₂(L⁴)(NCS)₃] (**9**). To a methanol solution HL⁴ (0.5 mmol) was added zinc(II) thiocyanate (182 mg, 1.0 mmol), and the mixture was stirred for 30 min. Sodium thiocyanate (42 mg, 0.5 mmol) was then added, and the mixture was allowed to stand at room temperature to give yellow crystals. The yield was 202 mg (64%). Found: C, 46.57; H, 4.11; N, 15.50; Zn, 18.0%. Calcd. for C₂₈H₃₀N₈OS₃Zn₂: C, 46.61; H, 4.19; N, 15.53; Zn, 18.1%. Molar conductance [*A*_M/S cm² mol⁻¹]: 73 in DMF. UV-vis [*λ*_{max}/nm (ε/M⁻¹ cm⁻¹)]: 379 (5300) in DMF. Selected IR (KBr) data: 3469, 2908, 2072, 1984, 1639, 1608, 1563, 1463, 1441, 1023, 762 cm⁻¹.

Single crystals of [Zn₂(L⁴)(NCS)₃]·3CHCl₃ (**9'**) suitable for X-ray crystallography were grown when a chloroform solution of **9** was diffused with *n*-hexane.

Studies of Phosphatase-Like Activity. The hydrolytic activity of the di-acetato complexes (**1**, **3**, **5** and **7**) toward tris(*p*-nitrophenyl) phosphate (TNP) was studied in aqueous DMF (H₂O:DMF = 0.3:99.7 in volume) at 25 °C by means of UV-visible and ³¹P NMR methods. A solution of a complex and TNP in aqueous DMF (H₂O:DMF = 0.3:99.7 in volume; [complex] = 5.0 × 10⁻⁴ M and [TNP] = 5.0 × 10⁻⁴ M) was prepared and subjected to visible spectral measurements (1 M = 1 mol dm⁻³). A complex solution of 5.0 × 10⁻⁴ M was used as the reference, and the hydrolysis of TNP was followed by measuring the difference spectra. For ³¹P-NMR spectroscopic studies, a solution of a complex and TNP in aqueous DMF (H₂O:DMF = 0.3:99.7; [complex] = 2.5 × 10⁻³ M and [TNP] = 2.5 × 10⁻² M) was prepared, and the hydrolysis of TNP was followed by a decrease in the TNP signal near -16 ppm and by observing a ³¹P signal arising from the hydrolysis of TNP.

For comparative studies, the following bnp (bnp = bis(*p*-nitrophenyl) phosphate) complexes, [Zn₂(L)(bnp)₂]ClO₄ (L = L¹, L² and L³), were prepared.

[Zn₂(L¹)(bnp)₂]ClO₄ (**10**). To a methanol solution of HL¹ (0.5 mmol) (prepared as described for complex **1**) was added zinc(II) perchlorate hexahydrate (372 mg, 1.0 mmol), and the mixture was stirred at 60 °C for 20 min. A solution of di(*p*-nitrophenyl) sodium phosphate (NaBNP) (362 mg, 1.0 mmol) in methanol (120 cm³) was then added, and the mixture was concentrated to ca. 100 cm³ to give yellow microcrystals. Yield: 428 mg (70%). Found: C, 40.77; H, 3.57; N, 9.28; Zn, 10.8%. Calcd. for C₄₁ClH₄₃N₈O₂₁P₂Zn₂: C, 40.63; H, 3.58; N, 9.25; Zn, 10.8%. Molar conductance [*A*_M/S cm² mol⁻¹]: 85 in DMF. UV-vis [*λ*_{max}/nm (ε/M⁻¹ cm⁻¹)]: 360 (7100) in DMF. Selected IR (KBr) data: 1661,

1519, 1345, 1243, 1207, 1108 cm⁻¹.

[Zn₂(L²)(bnp)₂]ClO₄ (**11**). This was obtained as yellow crystals in a way similar to that for **10**. Yield: 60%. Found: C, 38.35; H, 3.46; N, 8.67; Zn, 9.7%. Calcd. for BrC₄₁ClH₄₄N₈O₂₁P₂Zn₂: C, 38.09; H, 3.43; N, 8.67; Zn, 10.1%. Molar conductance [*A*_M/S cm² mol⁻¹]: 86 in DMF. UV-vis [*λ*_{max}/nm (ε/M⁻¹ cm⁻¹)]: 384 (9100) in DMF. Selected IR (KBr) data: 1648, 1521, 1348, 1297, 1250, 1220, 1108 cm⁻¹.

[Zn₂(L³)(bnp)₂]ClO₄ (**12**). This was obtained as yellow crystals in a way similar to that for **10**. Yield: 50%. Found: C, 44.17; H, 3.03; N, 8.81; Zn, 10.2%. Calcd. for C₄₁ClH₃₉N₈O₂₁P₂Zn₂: C, 44.10; H, 3.07; N, 8.75; Zn, 10.2%. Molar conductance [*A*_M/S cm² mol⁻¹]: 85 in DMF. UV-vis [*λ*_{max}/nm (ε/M⁻¹ cm⁻¹)]: 387 (8800) in DMF. Selected IR (KBr) data: 1650, 1520, 1347, 1238, 1227, 1207, 1108 cm⁻¹.

Crystal Structure Analyses. Crystal structures of [Cu₂(L¹)(AcO)₂]PF₆ (**1**), [Zn₂(L³)(AcO)₂]PF₆·(DMF)_{0.5}(2-PrOH)_{0.5} (**5'**), [Zn₂(L⁴)(AcO)₂]ClO₄·CHCl₃ (**7'**), [Zn₂(L⁴)(AcO)(NCS)₂]·(2-PrOH) (**8'**) and [Zn₂(L⁴)(NCS)₃]·3CHCl₃ (**9'**) were determined by X-ray crystallography. Each single crystal was mounted on a glass fiber and used for X-ray structural measurements. Intensities and lattice parameters were obtained on a Rigaku AFC-7R automated four-circle diffractometer, using graphite-monochromated Mo-*Kα* radiation (*λ* = 0.71069 Å) and a 12 kW rotating anode generator at 23 ± 1 °C. The cell parameters were determined by 25 reflections in the 2θ range of 29.8° < 2θ < 30.0°. For the intensity data collections, the ω - 2θ scan mode was used to a maximum 2θ value of 55.0° at the scan rate of 16° min⁻¹. The weak reflections (*I* < 10.0σ(*I*)) were rescanned (maximum of 4 scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal-to-detector distance was 235 mm, and the computer-controlled detector aperture was set to 9.0 × 13.0 mm (horizontal × vertical). Three standard reflections were monitored every 150 reflections. Over the course of the data collection, the standards decreased by 5.0% for **1**, -4.6% for **7'**, -1.14% for **8'** and 15.2% for **9'**. A linear correction factor was applied to the data to account for the phenomena. The linear absorption coefficient, *μ*, for Mo-*Kα* radiation was 17.8 cm⁻¹ for **1**, 14.0 cm⁻¹ for **5'**, 15.6 cm⁻¹ for **7'**, 14.4 cm⁻¹ for **8'** and 16.4 cm⁻¹ for **9'**. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.81 to 1.00 for **1**, from 0.95 to 1.00 for **5'**, from 0.42 to 1.00 for **7'**, from 0.92 to 1.00 for **8'** and from 0.68 to 1.00 for **9'**. The intensity data were corrected for Lorentz and polarization factors. Pertinent crystallographic parameters are summarized in Table 1.

The structures were solved by direct methods and expanded using Fourier techniques. Refinements were carried out by the full-matrix least-squares method, where the function minimized is Σ_w(|*F*_o - *F*_c|)² with *w* = 1/σ²(*F*_o). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at the calculated positions and were not refined.

Neutral atom scattering factors were taken from Cromer and Waber.¹⁴ Anomalous dispersion effects were included in *F*_{calc}; the values for Δ*f*' and Δ*f*'' were those of Creagh and McAuley.¹⁵ The values for the mass attenuation coefficients were those of Creagh and Hubbel.¹⁶ All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.¹⁷

Crystallographic data have been deposited at the CCDC, 12

Table 1. Crystallographic Parameters for $[\text{Zn}_2(\text{L}^1)(\text{AcO})_2]\text{PF}_6$ (**1**), $[\text{Zn}_2(\text{L}^3)(\text{AcO})_2]\text{ClO}_4 \cdot (\text{DMF})_{0.5} \cdot (2\text{-PrOH})_{0.5}$ (**5'**), $[\text{Zn}_2(\text{L}^4)(\text{AcO})_2]\text{ClO}_4 \cdot \text{CHCl}_3$ (**7'**), $[\text{Zn}_2(\text{L}^4)(\text{AcO})(\text{NCS})_2] \cdot 2\text{-PrOH}$ (**8'**), $[\text{Zn}_2(\text{L}^4)(\text{NCS})_3] \cdot 3\text{CHCl}_3$ (**9'**)

Complex	1	5'	7'	8'	9'
Formula	$\text{C}_{21}\text{H}_{33}\text{N}_4\text{O}_5\text{PF}_6\text{Zn}_2$	$\text{C}_{30}\text{H}_{39}\text{N}_5\text{O}_{6.50}\text{PF}_6\text{Zn}_2$	$\text{C}_{30}\text{H}_{37}\text{N}_5\text{O}_9\text{Cl}_4\text{Zn}_2$	$\text{C}_{32}\text{H}_{41}\text{N}_7\text{O}_4\text{S}_2\text{Zn}_2$	$\text{C}_{59}\text{H}_{63}\text{N}_{16}\text{S}_6\text{O}_2\text{Zn}_4\text{Cl}_9$
Crystal color	yellow	yellow	colorless	colorless	colorless
F.W.	697.24	849.39	766.87	782.60	1801.21
Cryst. dims/mm	$0.20 \times 0.30 \times 0.40$	$0.30 \times 0.20 \times 0.20$	$0.20 \times 0.30 \times 0.20$	$0.20 \times 0.20 \times 0.08$	$0.20 \times 0.15 \times 0.20$
Crystal system	triclinic	orthorhombic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}(\#2)$	$\text{Pbca}(\#61)$	$P\bar{1}(\#2)$	$P2_1/c(\#14)$	$P\bar{1}(\#2)$
<i>a</i> /Å	11.446(2)	20.171(5)	12.782(10)	14.501(2)	13.90(3)
<i>b</i> /Å	15.054(2)	22.603(4)	14.406(4)	15.516(2)	23.2(1)
<i>c</i> /Å	8.802(1)	16.470(5)	11.343(2)	16.957(2)	12.97(2)
α /deg	93.33(1)	90.00	107.42(2)		97.5(3)
β /deg	102.14(1)	90.00	93.23(3)	100.94(1)	93.7(1)
γ /deg	100.24(1)	90.00	77.99(4)		85.6(4)
<i>V</i> /Å ³	1452.0(4)	7508(2)	1949(1)	3745.9(8)	4121(22)
<i>Z</i>	2	8	2	4	2
<i>D_c</i> /g cm ⁻³	1.595	1.503	1.506	1.388	1.451
<i>R</i> ^{a)}	0.047	0.055	0.064	0.049	0.064
<i>R_w</i> ^{b),c)}	0.049	0.064	0.076	0.042	0.083

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $R_w = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma[wF_o^2]\}^{1/2}$. c) $w = 1/\Sigma^2(F_o)$.

Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 151667–151671. The data are also deposited as Document No. 74009 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussions

Syntheses and General Properties. The “end-off” compartmental ligands, $(L^1)^-(L^4)^-$, combine two Zn ions to provide two types of dinuclear zinc complexes. One type is the di- μ -acetato- μ -phenolato-dizinc(II) core complexes, $[Zn_2(L)(AcO)_2]X$ ($X^- = PF_6^-$ or ClO_4^-) (**1**, **3**, **5** and **7**), that were obtained by the reaction of HL^1 – HL^4 with zinc(II) acetate tetrahydrate in the presence of PF_6^- or ClO_4^- ion. They show the $\nu_{as}(COO)$ and $\nu_s(COO)$ vibrations of the acetate group at 1610–1600 and 1450–1440 cm^{-1} , respectively. The small separation between the two vibrations ($< 200\text{ cm}^{-1}$) is in accord with a bridging function of the acetate group,¹⁸ as demonstrated by X-ray crystallography for **1**, **5'** and **7** (see below). The complexes show an intense band at 365–390 nm that is attributed to the π – π^* transition associated with the azomethine linkage.^{19,20}

The other type is $[Zn_2(L)(NCS)_3]$ (**2**, **4**, **6** and **9**) that was prepared by the reaction of HL^1 – HL^4 and $Zn(NCS)_2$. Complex **2** shows two $\nu(CN)$ vibrations at 2080 and 1995 cm^{-1} . Similarly, **4**, **6** and **9** each show two $\nu(CN)$ vibrations. Evidently, there are two bonding modes of NCS^- group in these complexes. X-ray structural studies for analogous $[Ni_2(L^2)(NCS)_3(MeOH)]^9$ have indicated a μ -thiocyanato- N - μ -phenolato-dinickel(II) core with a terminal thiocyanato nitrogen on each Ni. A similar dinuclear core structure is supposed for the present thiocyanato complexes. Molar conductances for the complexes at $1 \times 10^{-3}\text{ M}$ in DMF (Λ_M : 47–73 $S\text{ cm}^2\text{ mol}^{-1}$) indicate that they behave as 1:1 electrolytes in DMF. Electronic spectra of the complexes show the π – π^* transition band in the region of 374–397 nm.

The asymmetric ligand $(L^4)^-$ exhibits versatility in complexation to form another type of complex, $[Zn_2(L^4)(AcO)(NCS)_2]$ (**8**). It shows the $\nu_{as}(COO)$ and $\nu_s(COO)$ modes of the acetate group at 1577 and 1434 cm^{-1} , respectively, and one $\nu(CN)$ vibration at 2081 cm^{-1} .

Crystal Structures. $[Zn_2(L^1)(AcO)_2]PF_6$ (**1**). An ORTEP²¹ view of the cationic part of **1** is shown in Fig. 1, together with the numbering scheme. The selected bond distances and angles are given in Table 2.

It has a di- μ -acetato- μ -phenolato-dizinc(II) core with a Zn1–Zn2 interatomic separation of 3.237(4) Å. The environments about Zn1 and Zn2 are similar but not equivalent. The geometry about Zn1 and Zn2 can be regarded as trigonal-bipyramid (the parameter τ^{22} is 0.461 for Zn1 and 0.503 for Zn2), with the phenolic oxygen O1 and the terminal nitrogen N2 (N4) at the axial sites and with the imino nitrogen N1 (N3) and the two acetate oxygens O2 and O4 (O3 and O5) on the trigonal plane. The O1–Zn1–N2 angle is 163.8° and the O1–Zn2–N4 angle is 168.1°. The sum of the angles of N1–Zn1–O2, O2–Zn1–O4 and O4–Zn1–N1 is 359.1°, and the sum of the angles of N3–Zn2–O3, O3–Zn2–O5 and

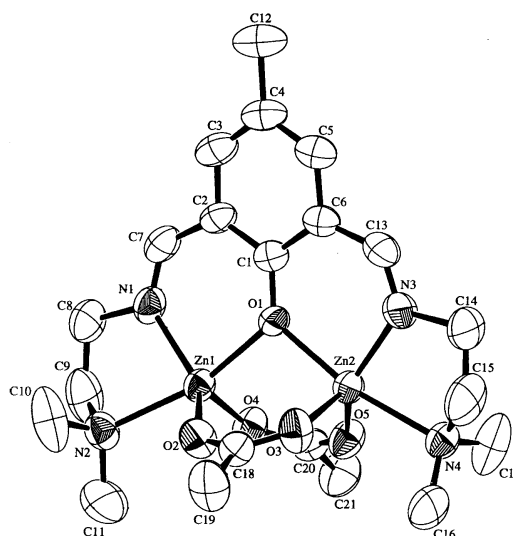


Fig. 1. An ORTEP view of the cationic part of **1** with the atom numbering scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Zn_2(L^1)(AcO)_2]ClO_4$ (**1**)

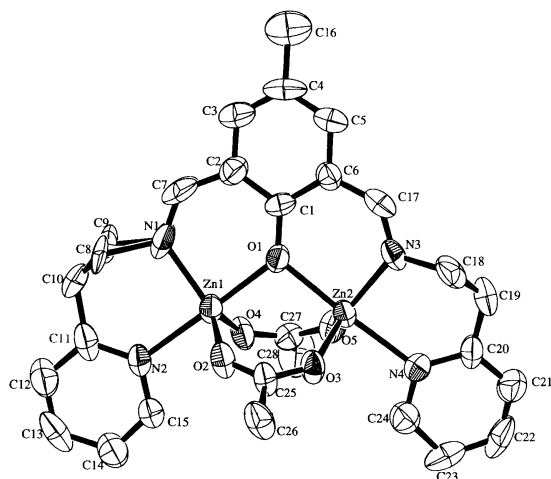
Zn(1)–O(1)	2.093(3)	Zn(1)–O(2)	1.971(3)
Zn(1)–O(4)	1.975(3)	Zn(1)–N(1)	2.035(4)
Zn(1)–N(2)	2.192(4)	Zn(2)–O(1)	2.098(3)
Zn(2)–O(3)	1.983(3)	Zn(2)–O(5)	1.967(3)
Zn(2)–N(3)	2.017(4)	Zn(2)–N(4)	2.218(4)
O(1)–Zn(1)–O(2)	95.2(1)	O(1)–Zn(1)–O(4)	97.3(1)
O(1)–Zn(1)–N(1)	87.2(1)	O(1)–Zn(1)–N(2)	163.8(2)
O(2)–Zn(1)–O(4)	114.1(2)	O(2)–Zn(1)–N(1)	136.1(2)
O(2)–Zn(1)–N(2)	86.9(2)	O(4)–Zn(1)–N(1)	108.9(2)
O(4)–Zn(1)–N(2)	96.5(2)	N(1)–Zn(1)–N(2)	80.2(2)
O(1)–Zn(2)–O(3)	96.4(1)	O(1)–Zn(2)–O(5)	94.8(1)
O(1)–Zn(2)–N(3)	88.5(2)	O(1)–Zn(2)–N(4)	168.1(1)
O(3)–Zn(2)–O(5)	111.7(2)	O(3)–Zn(2)–N(3)	109.6(2)
O(3)–Zn(2)–N(4)	92.7(2)	O(5)–Zn(2)–N(3)	137.9(2)
O(5)–Zn(2)–N(4)	88.9(2)	O(3)–Zn(2)–N(4)	81.3(2)

O5–Zn2–N3 is 359.2°.

$[Zn_2(L^3)(AcO)_2]PF_6 \cdot (DMF)_{0.5} \cdot (2-PrOH)_{0.5}$ (**5'**). An ORTEP view is shown in Fig. 2 together with the numbering scheme. The selected bond distances and angles are summarized in Table 3.

The dinuclear core of **5'** is essentially the same as that of **1**. The two Zn ions are bridged by the phenolic oxygen of $(L^3)^-$ and two acetate groups in the syn-syn mode, in the Zn1–Zn2 interatomic separation of 3.297(2) Å. The two Zn ions have a similar trigonal-bipyramidal geometry with the phenolic oxygen O1 and the terminal nitrogen N2 (N4) at the axial sites and with the imino nitrogen N1 (N3) and the two acetate oxygens O2 and O4 (O3 and O5) on the trigonal base. The O1–Zn1–N2 angle is 179.1°. The sum of the N1–Zn1–O2, O2–Zn1–O4 and O4–Zn1–N1 angles are 359.8°. The O1–Zn2–N4 angle is 174.6° and the sum of the N3–Zn2–O3, O3–Zn2–O5 and O5–Zn2–N3 angles is 359.7°.

$[Zn_2(L^4)(AcO)_2]ClO_4 \cdot CHCl_3$ (**7'**). An ORTEP view of **7'**

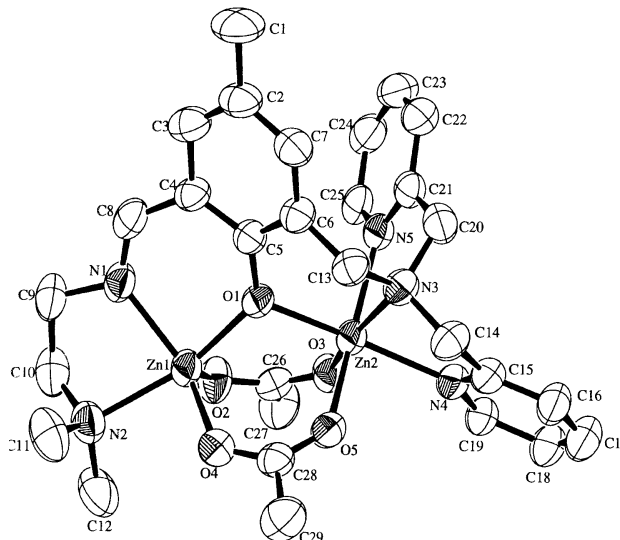
Fig. 2. An ORTEP view of **5'** with the atom numbering scheme.Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{Zn}_2(\text{L}^3)(\text{AcO})_2]\text{ClO}_4 \cdot (\text{DMF})_{0.5} \cdot (2\text{-PrOH})_{0.5}$ (**5'**)

Zn(1)—O(1)	2.120(5)	Zn(1)—O(2)	1.988(5)
Zn(1)—O(4)	1.978(5)	Zn(1)—N(1)	2.018(8)
Zn(1)—N(2)	2.197(6)	Zn(2)—O(1)	2.115(5)
Zn(2)—O(3)	1.970(5)	Zn(2)—O(5)	1.983(5)
Zn(2)—N(3)	2.011(6)	Zn(2)—N(4)	2.202(6)
O(1)—Zn(1)—O(2)	92.8(2)	O(2)—Zn(1)—O(4)	95.0(2)
O(1)—Zn(1)—N(1)	88.0(3)	O(1)—Zn(1)—N(2)	179.1(2)
O(2)—Zn(1)—O(4)	114.9(2)	O(2)—Zn(1)—N(1)	123.4(4)
O(2)—Zn(1)—N(2)	87.5(2)	O(4)—Zn(1)—N(1)	121.4(4)
O(4)—Zn(1)—N(2)	85.6(2)	N(1)—Zn(1)—N(2)	91.1(3)
O(1)—Zn(2)—O(3)	94.7(2)	O(1)—Zn(2)—O(5)	92.3(2)
O(1)—Zn(2)—N(3)	88.5(2)	O(1)—Zn(2)—N(4)	174.6(2)
O(3)—Zn(2)—O(5)	118.4(2)	O(3)—Zn(2)—N(3)	117.7(3)
O(3)—Zn(2)—N(4)	90.4(2)	O(5)—Zn(2)—N(3)	123.6(2)
O(5)—Zn(2)—N(4)	83.8(2)	N(3)—Zn(2)—N(4)	90.5(3)

is given in Fig. 3, together with the atom numbering scheme. The selected bond distances and bond angles are summarized in Table 4.

The two Zn ions are bridged by the phenolic oxygen and two acetate groups in the syn-syn mode. The Zn1–Zn2 interatomic separation is 3.29(1) Å. The geometry about Zn1 bound to the bidentate arm can be regarded as a distorted square-pyramid ($\tau = 0.325$) with the phenolic oxygen O1, the nitrogens N1 and N2 of the bidentate arm and one acetate oxygen O4 on the equatorial base and another acetate oxygen (O2) at the apex. The Zn1-to-donor bond distances range from 1.976(6) to 2.177(7) Å. The Zn2 bound to the tridentate arm has a six-coordinate geometry with larger Zn2-to-donor distances ranging from 2.019(5) to 2.215(6) Å. One of the pyridyl nitrogens (N4) is situated trans to the phenolic oxygen, and the other pyridyl nitrogen (N5) is cis to the phenolic oxygen.

$[\text{Zn}_2(\text{L}^4)(\text{AcO})(\text{NCS})_2] \cdot (2\text{-PrOH})$ (8'**).** An ORTEP view for **8'** is given in Fig. 4, together with the atom numbering scheme. The selected bond distances and bond angles are summarized in Table 5.

Fig. 3. An ORTEP view of **7'** with the atom numbering scheme.Table 4. Selected Bond Distances (Å) and Angles (deg) $[\text{Zn}_2(\text{L}^4)(\text{AcO})_2]\text{ClO}_4 \cdot \text{CHCl}_3$ (**7'**)

Zn(1)—O(1)	2.026(5)	Zn(1)—O(2)	1.986(5)
Zn(1)—O(4)	1.976(6)	Zn(1)—N(1)	2.078(7)
Zn(1)—N(2)	2.177(7)	Zn(2)—O(1)	2.080(5)
Zn(2)—O(3)	2.019(5)	Zn(2)—O(5)	2.116(5)
Zn(2)—N(3)	2.194(6)	Zn(2)—N(4)	2.151(6)
Zn(2)—N(5)	2.215(6)		
O(1)—Zn(1)—O(2)	103.0(2)	O(2)—Zn(1)—O(4)	93.0(2)
O(1)—Zn(1)—N(1)	86.9(2)	O(1)—Zn(1)—N(2)	161.6(2)
O(2)—Zn(1)—O(4)	113.1(2)	O(2)—Zn(1)—N(1)	103.8(2)
O(2)—Zn(1)—N(2)	92.4(2)	O(4)—Zn(1)—N(1)	142.1(2)
O(4)—Zn(1)—N(2)	90.1(3)	N(1)—Zn(1)—N(2)	79.6(3)
O(1)—Zn(2)—O(3)	101.7(2)	O(1)—Zn(2)—O(5)	84.9(2)
O(1)—Zn(2)—N(3)	89.9(2)	O(1)—Zn(2)—N(4)	162.8(2)
O(1)—Zn(2)—N(5)	91.8(2)	O(3)—Zn(2)—O(5)	99.5(2)
O(3)—Zn(2)—N(3)	164.3(2)	O(3)—Zn(2)—N(4)	93.1(2)
O(3)—Zn(2)—N(5)	90.9(2)	O(5)—Zn(2)—N(3)	92.0(2)
O(5)—Zn(2)—N(4)	84.1(2)	O(5)—Zn(2)—N(5)	169.6(2)
N(3)—Zn(2)—N(4)	77.4(2)	N(3)—Zn(2)—N(5)	78.1(2)
N(4)—Zn(2)—N(5)	96.7(2)		

The complex has a μ -acetato- μ -phenolato-dizinc(II) dinuclear core in a Zn1–Zn2 interatomic separation of 3.524(1) Å. The Zn1 bound to the bidentate arm has a square-pyramidal geometry with O1, N1 and N2 of (L^4)[−] and O2 of the bridging acetate group on the base and an isothiocyanate nitrogen at the apex. The discrimination parameter (τ) is 0.045. The Zn1-to-donor bond distances range from 1.998(5) to 2.177(6) Å. The Zn2 bound to the tridentate arm has a six-coordinate geometry together with O3 of the bridging acetate group and a thiocyanate nitrogen. The Zn2-to-donor bond distances range from 2.048(7) to 2.231(6) Å. One of the pyridyl nitrogens (N5) is situated trans to the bridging phenolic oxygen, and the other pyridyl nitrogen (N4) is situated cis to the phenolic oxygen. The terminal thiocyanate group on Zn1 and that on Zn2 are sit-

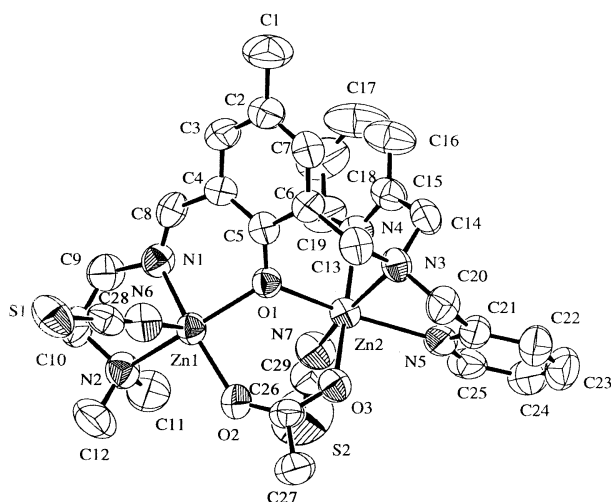


Fig. 4. An ORTEP view of **8'** with the atom numbering scheme.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[\text{Zn}_2(\text{L}^4)(\text{AcO})(\text{NCS})_2] \cdot 2\text{-PrOH}$ (**8'**)

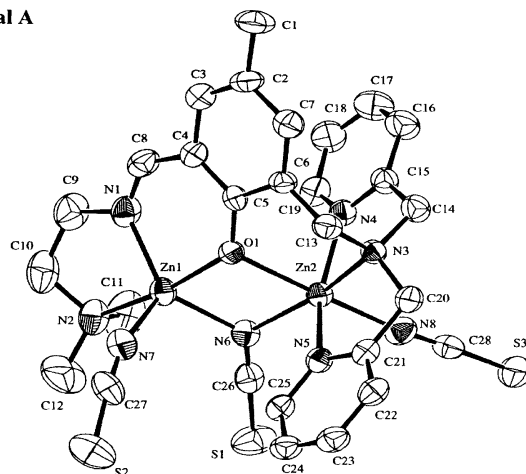
Zn(1)–O(1)	2.016(5)	Zn(1)–O(2)	1.998(5)
Zn(1)–N(1)	2.087(6)	Zn(1)–N(2)	2.177(6)
Zn(1)–N(6)	2.011(7)	Zn(2)–O(1)	2.107(5)
Zn(2)–O(3)	2.108(5)	Zn(2)–N(3)	2.231(6)
Zn(2)–N(4)	2.168(6)	Zn(2)–N(5)	2.213(6)
Zn(2)–N(7)	2.048(7)		
O(1)–Zn(1)–O(2)	93.1(2)	O(1)–Zn(1)–N(1)	84.7(2)
O(1)–Zn(1)–N(2)	151.3(2)	O(1)–Zn(1)–N(6)	108.7(2)
O(2)–Zn(1)–N(1)	154.0(2)	O(2)–Zn(1)–N(2)	90.6(2)
O(2)–Zn(1)–N(6)	103.8(3)	N(1)–Zn(1)–N(2)	79.8(3)
N(1)–Zn(1)–N(6)	101.5(3)	N(2)–Zn(1)–N(6)	97.9(3)
O(1)–Zn(2)–O(3)	86.7(2)	O(1)–Zn(2)–N(3)	86.9(2)
O(1)–Zn(2)–N(4)	88.7(2)	O(1)–Zn(2)–N(5)	159.6(2)
O(1)–Zn(2)–N(7)	104.2(2)	O(3)–Zn(2)–N(3)	94.8(2)
O(3)–Zn(2)–N(4)	171.6(2)	O(3)–Zn(2)–N(5)	85.4(2)
O(3)–Zn(2)–N(7)	94.9(2)	N(3)–Zn(2)–N(4)	78.0(2)
N(3)–Zn(2)–N(5)	75.0(5)	N(3)–Zn(2)–N(7)	165.7(2)
N(4)–Zn(2)–N(5)	96.6(2)	N(4)–Zn(2)–N(7)	93.0(3)
N(5)–Zn(2)–N(7)	95.3(3)		

uated trans to each other with respect to the mean molecular plane formed by Zn1, O1, Zn2 and the acetate bridge.

$[\text{Zn}_2(\text{L}^4)(\text{NCS})_3] \cdot 3\text{CHCl}_3$ (9'**).** ORTEP views for **9'** are given in Fig. 5, together with the atom numbering scheme. The selected bond distances and bond angles are summarized in Table 6.

There are two crystallographically-independent molecules (A and B) in the crystal. In molecule A, the two Zn ions are doubly bridged by the endogenous phenolic oxygen and an exogenous thiocyanate nitrogen, in the Zn–Zn separation of 3.245(9) Å. The Zn1 bound to the bidentate arm has a square-pyramidal geometry with O1, N1 and N2 of $(\text{L}^4)^-$ and the bridging thiocyanate nitrogen N6 on the base and a terminal thiocyanate nitrogen N7 at the axial site. The Zn2 bound to the tridentate arm has a six-coordinate environment with further

Crystal A



Crystal B

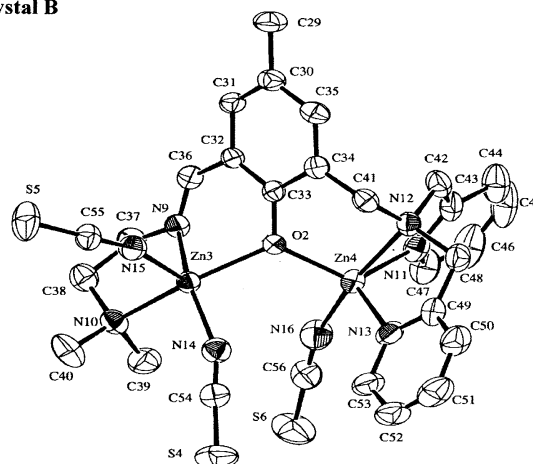


Fig. 5. An ORTEP view of **9'** with the atom numbering scheme.

coordination of a terminal thiocyanate nitrogen N8. The N8 is situated trans to the bridging phenolic oxygen, and the two pyridyl nitrogens are situated cis to the phenolic oxygen.

In molecule B, the two Zn ions are singly bridged by the endogenous phenolic oxygen in a Zn–Zn intermetallic separation of 3.543(5) Å. The Zn3 bound to the bidentate arm has a five-coordinate environment together with two terminal thiocyanate nitrogens. The geometry about the metal is regarded as a square-pyramid with O2, N9 and N10 of $(\text{L}^4)^-$ and a thiocyanate nitrogen N14 on the base and another thiocyanate nitrogen N15 at the apex. The discrimination parameter (*t*) is 0.068. The Zn4 bound to the tridentate arm has a distorted five-coordinate environment with further coordination of a thiocyanate nitrogen N16. The geometry about the metal is regarded as a trigonal-bipyramid, with the articular nitrogen N12 and a thiocyanate nitrogen N16 at the axial sites and with the phenolic oxygen O2 and the pyridyl nitrogens N11 and N13 on the trigonal base.

Solution Structures. All the diacetato complexes (**1**, **3**, **5** and **7**) are stable in DMF, judged from the low dependence of their conductances and absorption spectra upon complex con-

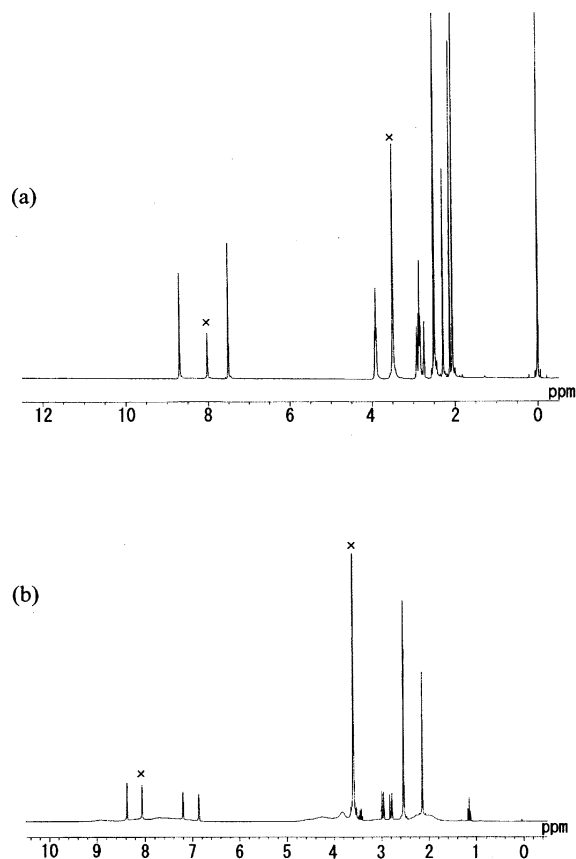
Table 6. Selected Bond Distances (Å) and Angles (deg) for $[\text{Zn}_2(\text{L}^4)(\text{NCS})_3] \cdot 3\text{CHCl}_3$ (**9'**)

Zn(1)–O(1)	2.052(5)	Zn(1)–N(1)	2.019(8)
Zn(1)–N(2)	2.253(8)	Zn(1)–N(6)	2.116(7)
Zn(1)–N(7)	1.994(8)	Zn(2)–O(1)	2.185(5)
Zn(2)–N(3)	2.196(6)	Zn(2)–N(4)	2.127(7)
Zn(2)–N(5)	2.136(7)	Zn(2)–N(6)	2.182(7)
Zn(2)–N(8)	2.077(8)	Zn(3)–O(2)	2.084(5)
Zn(3)–N(9)	2.111(7)	Zn(3)–N(10)	2.211(6)
Zn(3)–N(14)	1.977(8)	Zn(3)–N(15)	1.999(7)
Zn(4)–O(2)	1.982(5)	Zn(4)–N(11)	2.127(7)
Zn(4)–N(12)	2.230(7)	Zn(4)–N(13)	2.094(7)
Zn(4)–N(16)	2.004(9)		

O(1)–Zn(1)–N(1)	87.9(3)	O(1)–Zn(1)–N(2)	165.8(3)
O(1)–Zn(1)–N(6)	83.3(2)	O(1)–Zn(1)–N(7)	98.7(3)
N(1)–Zn(1)–N(2)	82.5(3)	N(1)–Zn(1)–N(6)	128.9(3)
N(1)–Zn(1)–N(7)	121.9(3)	N(2)–Zn(1)–N(6)	94.7(3)
N(2)–Zn(1)–N(7)	95.2(3)	N(6)–Zn(1)–N(7)	109.2(3)
O(1)–Zn(2)–N(3)	87.9(2)	O(1)–Zn(2)–N(4)	86.3(2)
O(1)–Zn(2)–N(5)	93.6(2)	O(1)–Zn(2)–N(6)	78.7(2)
O(1)–Zn(2)–N(8)	172.9(2)	N(3)–Zn(2)–N(4)	78.8(3)
N(3)–Zn(2)–N(5)	77.6(3)	N(3)–Zn(2)–N(6)	165.6(2)
N(3)–Zn(2)–N(8)	96.7(3)	N(4)–Zn(2)–N(5)	156.3(3)
N(4)–Zn(2)–N(6)	105.5(3)	N(4)–Zn(2)–N(8)	89.3(3)
N(5)–Zn(2)–N(6)	97.7(3)	N(5)–Zn(2)–N(8)	92.6(3)
N(6)–Zn(2)–N(8)	97.2(3)	O(2)–Zn(3)–N(9)	81.9(2)
O(2)–Zn(3)–N(10)	151.3(2)	O(2)–Zn(3)–N(14)	94.8(3)
O(2)–Zn(3)–N(15)	106.0(2)	N(9)–Zn(3)–N(10)	79.5(3)
N(9)–Zn(3)–N(14)	155.4(3)	N(9)–Zn(3)–N(15)	99.2(3)
N(10)–Zn(3)–N(14)	93.2(3)	N(10)–Zn(3)–N(15)	98.4(3)
N(14)–Zn(3)–N(15)	105.1(3)	O(2)–Zn(4)–N(11)	121.9(3)
O(2)–Zn(4)–N(12)	90.3(2)	O(2)–Zn(4)–N(13)	114.7(2)
O(2)–Zn(4)–N(16)	98.4(3)	N(11)–Zn(4)–N(12)	77.0(3)
N(11)–Zn(4)–N(13)	117.9(3)	N(11)–Zn(4)–N(16)	95.2(3)
N(12)–Zn(4)–N(13)	79.2(3)	N(12)–Zn(4)–N(16)	170.5(3)
N(13)–Zn(4)–N(16)	100.2(4)		

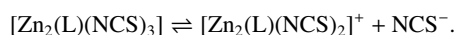
centration. Furthermore, the FAB mass spectra of the diacetato complexes clearly showed a parent ion peak corresponding to $\{\text{Zn}_2(\text{L})(\text{AcO})_2\}^+$ (see Experimental Section). ^1H NMR (400 MHz) spectra for **1** and **7** were measured in d_7 -DMF to examine their solution structures (Fig. 6). The NMR spectrum of **1** shows three singlets at 2.01, 2.24 and 2.49 ppm in a relative intensity of 2:1:4, which are assigned to the acetate methyl, the ring methyl and the *N*-methyl protons, respectively. The ring proton and the azomethine proton appear as singlets at 7.51 and 8.67 ppm, respectively. The ethylene protons at 2.85 and 3.91 ppm show an A_2B_2 pattern. The results clearly indicate that **1** retains the di- μ -acetato- μ -phenolato-dizinc(II) core (Fig. 1), if one assumes D_2 symmetry in solution.

Based on X-ray crystallography, **7** is asymmetric with respect to the two acetate bridges and the coordination modes of the two pyridyl residues (Fig. 3). Furthermore, the two methyl groups on the terminal amino nitrogens are not equivalent in the crystal. In its ^1H NMR spectrum (Fig. 6(b)), the methyl groups on the terminal amino nitrogens appear as a singlet at 2.65 ppm. Notably, the acetate methyl groups are not resolved. The pyridyl protons are also unresolved owing to broadening,

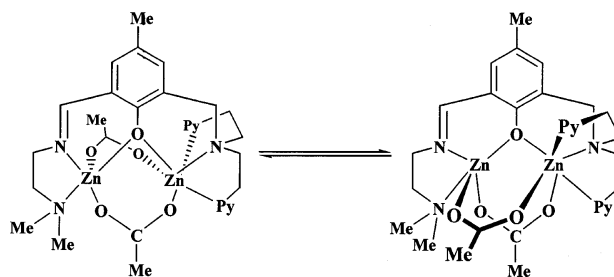
Fig. 6. ^1H NMR spectra of (a) $[\text{Zn}_2(\text{L}^1)(\text{AcO})_2]\text{PF}_6$ (**1**) and (b) $[\text{Zn}_2(\text{L}^4)(\text{AcO})_2]\text{ClO}_4$ (**7**) in d_7 -DMF.

though the phenol ring protons (6.87 and 8.06 ppm) and the azomethine proton (8.38 ppm) are clearly resolved. The ethylene protons of the bidentate chain at 4.4–3.6 ppm are also broadened. Such NMR spectral features suggest a slow molecular inversion with respect to the mean molecular plane (see Chart 2).

As discussed above, the tri(thiocyanato) complexes (**2**, **4**, **6** and **9**) act as 1:1 electrolytes in DMF, indicating that one NCS-group is dissociated:



This is supported by a concentration-dependence of the electronic spectra. In general, the π - π^* transition band shifted to a shorter wavelength with a concomitant increase in intensity

Chart 2. Molecular inversion of **7** in solution.

when the complex concentration was lowered. For example, **2** shows the band maximum at 402 nm (ϵ : 9100 M⁻¹ cm⁻¹) at the concentration of 1×10^{-3} M but at 394 nm (ϵ : 10500 M⁻¹ cm⁻¹) at the concentration of 1×10^{-4} M.

The ¹H NMR spectrum for **2** also supports the dissociation of the complex in DMF. The spectrum at ca. 1×10^{-2} M has two pairs of signals due to the ring and the azomethine protons, a pair of sharp singlets at 7.48 and 7.31 ppm and another pair of broad bands at 8.76 and 8.50 ppm. In addition to these, some weaker singlets exist in the region of 8.5–7.2 ppm. The methylene protons next to the imine nitrogen appear as a sharp triplet at 3.74 ppm and a broad band at 3.92 ppm. The *N*-methyl protons appear at 2.45 and 2.40 ppm as dominant peaks. The result indicates that **2** exists in two or more different structures in solution. The ¹H NMR spectrum of **9** is much more complicated. It has two singlets due to the methyl group on the phenolic ring (2.05 and 2.10 ppm in an approximate ratio of 1:4) and three or more signals due to the *N*-methyl group. Furthermore, it showed many signals in the region 9.0–6.6 ppm. The NMR spectral feature of **9** means that the molecules A and B (see Fig. 5) and their dissociated species exist in solution.

Phosphatase-Like Activity. From the above discussion, we conclude that the diacetato complexes (**1**, **3**, **5** and **7**) retain the di- μ -acetato- μ -phenolato-dizinc(II) core in DMF, whereas the tri(thiocyanato) complexes (**2**, **4**, **6** and **9**) are dissociated into [Zn₂(L)(NCS)₂]⁺ of unknown structure in DMF. For such reasons, our studies on phosphatase-like activity are restricted to the diacetato complexes **1**, **3**, **5** and **7**. We have confirmed that the ¹H-NMR spectra of **1** and **7** in D₂O-*d*₆-DMF (0.3:99.7) are essentially the same as those in *d*₆-DMF. This fact means the diacetato complexes to be stable in an aqueous DMF solution for the study of phosphatase-like activity discussed below.

In Fig. 7(a) are shown the difference-spectral changes with time for a solution of **1** and TNP ([**1**] = 5×10^{-4} M and [TNP] = 5×10^{-4} M) in aqueous DMF (H₂O:DMF = 0.3:99.7). The band at 270 nm due to TNP diminished with time, with a concomitant increase at 315 nm (due to BNP) and 420 nm (*p*-nitrophenolate). This result clearly demonstrates the hydrolysis of TNP by **1**. Similarly, **3** and **5** hydrolyzed TNP (Fig. 7(b), (c)). In these cases, the resulting *p*-nitrophenol predominantly exists in the protonated form: *p*-nitrophenol itself has an absorption at 330 nm. In contrast, **7** showed little hydrolytic activity toward TNP (Fig. 7(d)).

In order to examine the hydrolytic reaction in more detail, a solution of **1** and TNP ([**1**] : [TNP] = 1 : 10) in aqueous DMF (H₂O : DMF = 0.3 : 99.7) was subjected to ³¹P-NMR spectroscopic measurements (Fig. 8(a)). The solution showed two signals at -9.8 and -16.0 ppm after 12 hours. The signal at -16.0 ppm is ascribed to intact TNP and the signal at -9.8 ppm to a BNP species arising from the hydrolysis of TNP. The intensity ratio of the signal at -9.8 ppm to the signal at -16.0 ppm was approximately 2:3, indicating that four molecules of TNP were hydrolyzed by one complex after 12 hours. Similarly, **3** and **5** showed a hydrolytic activity toward TNP (Fig. 8(b) and (c)). Based on the ³¹P spectra, 3.3 and 2.8 molecules of TNP were hydrolyzed by **3** and **5**, respectively, after 12 hours. For

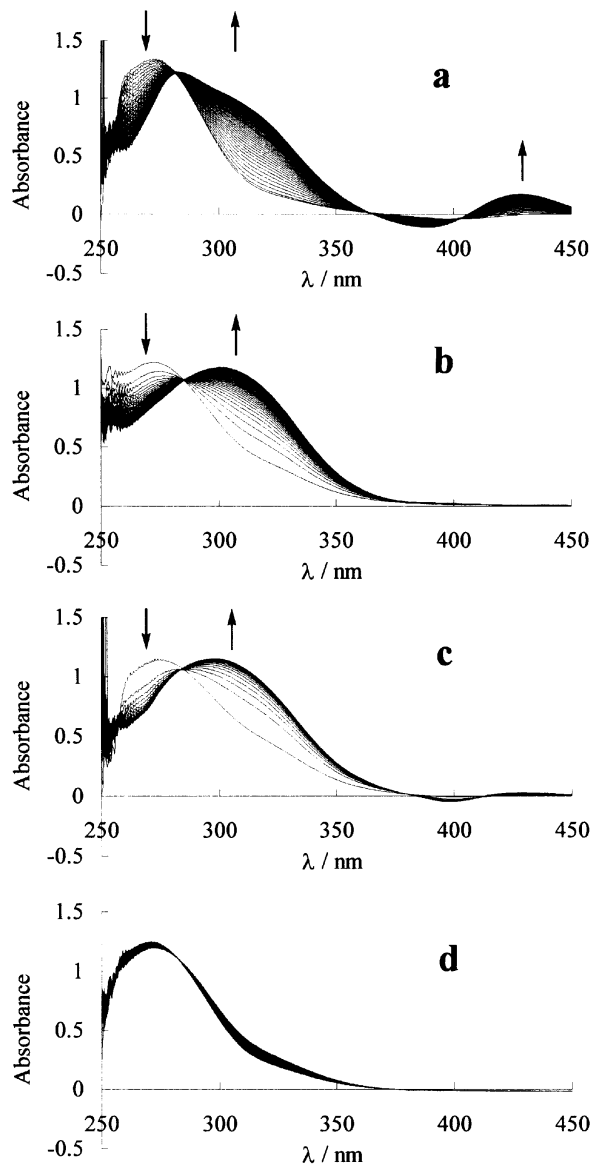


Fig. 7. Difference spectral changes with time for a solution of a complex and TNP in aqueous DMF at 25 °C (H₂O : DMF = 0.3 : 99.7 in volume, [complex] = 5×10^{-4} M and [TNP] = 5×10^{-4} M): (a) for complex **1**, (b) for **3**, (c) for **5**, and (d) for **7**.

the solution of TNP and **7**, no appreciable ³¹P resonance due to BNP was recognized after 12 hours.

In our recent study using a dinuclear Zn^{II}(OH)Pb^{II} complex,²³ the hydrolysis of TNP into BNP proceeds by the concerted binding of TNP on the Pb center and the nucleophilic attack of the hydroxide at adjacent Zn center. This reaction was essentially stoichiometric owing to the formation of a stable bnp intermediate. Such a stable bnp intermediate can be a cause for the slow hydrolysis by **1**, **3** and **5**. As a promising candidate for the intermediate, [Zn₂(L)(bnp)₂]ClO₄ (L = L¹ (**10**), L² (**11**), L³ (**12**)) were derived; a corresponding bnp complex of (L⁴)⁻ could not be obtained in spite of our many efforts. Complexes **10**–**12** may have a di- μ -bnp- μ -phenolato-dizinc(II)

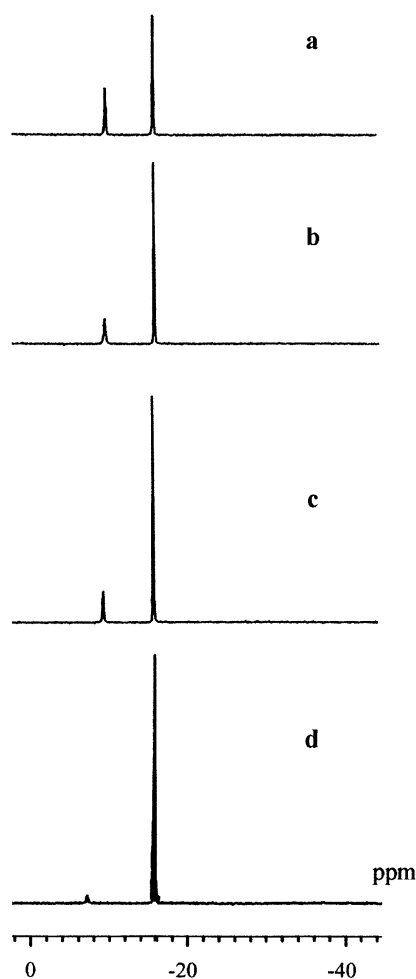
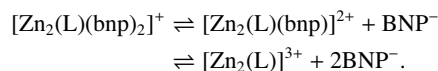


Fig. 8. ^{31}P NMR spectra for a solution of TNP and a complex ($[\text{TNP}]/[\text{complex}] = 10/1$): (a) for complex **1**, (b) for **3**, (c) for **5**, and (d) for **7**.

core similar to the di- μ -acetato- μ -phenolato-dizinc(II) core of **1**, **3** and **5**. In contrast to our expectation, the di-bnp complexes, **10–12**, were readily dissociated in DMF:



This was evidenced by their molar conductances ($85\text{--}86 \text{ S cm}^2 \text{ mol}^{-1}$ at $1 \times 10^{-3} \text{ M}$ in DMF) that are large for 1:1 electrolytes¹⁸ and increased to $120\text{--}130 \text{ S cm}^2 \text{ mol}^{-1}$ at lowered concentration of $1 \times 10^{-4} \text{ M}$. Electronic spectra of the complexes were also dependent upon the complex concentration. In general, the $\pi\text{--}\pi^*$ band of the azomethine linkage shifted to a longer wavelength with a concomitant increase in intensity when the complex concentration was lowered. The ^{31}P NMR spectra of **10**, **11** and **12** showed a resonance at -8.3 , -9.0 and -8.7 ppm , respectively. The different ^{31}P resonances for **10–12** may reflect the degree in the dissociation of the complexes. It must be mentioned that bis(*p*-nitrophenyl) hydrogenphosphate (HBNP) and bis(*p*-nitrophenyl) sodium phosphate (NaBNP) show the ^{31}P resonance at -11.2 and -7.8 ppm , respectively. In the hydrolytic reaction of TNP by **1**, **5** and **7**, the resulting BNP is moderately protonated, judged from the ^{31}P resonance appearing at $-9.8\text{--}9.5 \text{ ppm}$ (see Fig. 8).

Thus, **1**, **3** and **5** have a C_2 symmetric di- μ -acetato- μ -phenolato-dizinc(II) core consisting of two trigonal-bipyramidal Zn ions and show a hydrolytic activity toward TNP. Complex **7** has no such activity because one of the Zn centers is coordinatively saturated. A likely mechanism of the TNP hydrolysis by **1**, **3** and **5** is shown in Chart 3. The addition of water or TNP to one Zn center of **I** affords $[\text{Zn}(\text{L})(\text{AcO})_2(\text{H}_2\text{O})]^+$ (**IIa**) or $[\text{Zn}(\text{L})(\text{AcO})_2(\text{TNP})]^+$ (**IIb**). We have shown that $[\text{Mn}_2(\text{L})(\text{AcO})_2(\text{NCS})]$ ($\text{L} = \text{L}^1$ or L^2), analogous to **IIa** and **IIb**, has a C_s symmetric core with the cis arrangement of the thiocyanate-N group on one Mn and the sixth vacant site of the adjacent Mn

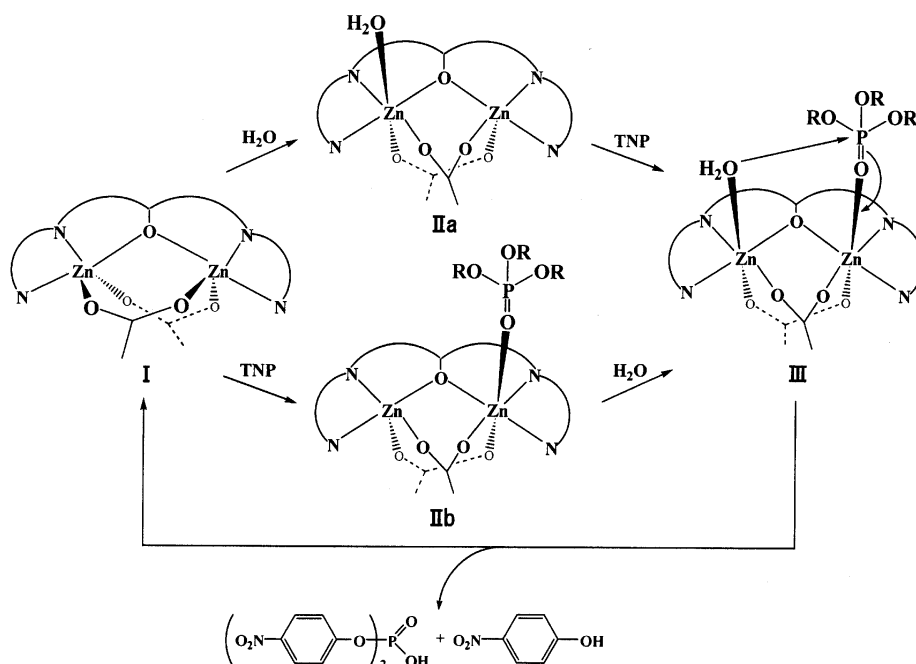


Chart 3. Proposed mechanism of TNP hydrolysis by **1**, **3** and **5** ($\text{R} = p\text{-nitrophenyl}$).

with respect to the mean molecular plane.^{8–10} Such a C_s symmetric core results from the steric requirement of the ligands when one metal center adopts a six-coordinate geometry. The further addition of TNP to **IIa** or the addition of water to **IIb** leads to the intermediate $[\text{Zn}(\text{L})(\text{AcO})_2(\text{H}_2\text{O})(\text{TNP})]^+$ (**III**), that allows a nucleophilic attack of the water (or hydroxide) to the phosphorus nucleus of the adjacent TNP. The low hydrolytic activity of **1**, **3** and **5** may relate to their D_2 symmetric core (**I**) that is distorted with difficulty into the C_s symmetric core (**II**).

This work was supported by a Grant-in-Aid for Scientific Research (No. 09440231) from the Ministry of Education, Science, Sports and Culture. Thanks are also due to the Daiwa Anglo-Japanese Foundation and the British Council for the support.

References

- 1 D. E. Fenton and H. Ōkawa, "Perspectives on Bioinorganic Chemistry," JAI Press, London (1993), Vol. 2, 81; K. D. Karlin, *Science*, **261**, 701 (1993).
- 2 E. E. Kim and H. W. Wyckoff, *J. Mol. Biol.*, **218**, 449 (1991).
- 3 E. Hough, L. K. Hansen, B. Birknes, K. Jynge, S. Hansen, A. Hordvik, C. Little, E. J. Dodson, and Z. Derewenda, *Nature (London)*, **338**, 357 (1989).
- 4 A. Lahm, S. Volbeda, F. Sakijama, and D. Suck, *J. Mol. Biol.*, **215**, 207 (1990).
- 5 S. K. Burley, R. R. David, R. M. Sweet, A. Taylor, and W. N. Lipscomb, *J. Mol. Biol.*, **224**, 113 (1992).
- 6 E. Kimura, *Prog. Inorg. Chem.*, **41**, 443 (1994).
- 7 J. S. Seo, N. Sung, R. C. Hynes, and J. Chin, *Inorg. Chem.*, **35**, 7472 (1996); D. H. Vance, and A. W. Czarnik, *J. Am. Chem. Soc.*, **115**, 12165 (1993); W. H. Jr. Chapman and R. Breslow, *J. Am. Chem. Soc.*, **117**, 5462 (1995); M. Yashiro, A. Ishikubo, and M. Komiyama, *J. Chem. Soc., Chem. Commun.*, **1995**, 1793; M. Irisawa, N. Takeda, and M. Komiyama, *J. Chem. Soc., Chem. Commun.*, **1995**, 1221; T. Koike, M. Inoue, E. Kimura, and M. Shiro, *J. Am. Chem. Soc.*, **118**, 3091 (1996); P. Hurst, B. K. Takasaki, and J. Chin, *J. Am. Chem. Soc.*, **118**, 9982 (1996); A. Tsubouchi and T. C. Bruice, *J. Am. Chem. Soc.*, **116**, 11614 (1994); K. G. Ragunathan and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **35**, 1219 (1996); P. Molenveld, S. Kapsabeils, J. F. J. Engbersen, and D. N. Reinhoudt, *J. Am. Chem. Soc.*, **119**, 2948 (1997); S. T. Frey, N. N. Murthy, S. T. Weintraub, L. K. Thompson, and K. D. Karlin, *Inorg. Chem.*, **36**, 956 (1997); P. Hendry and A. M. Sageson, *Prog. Inorg. Chem.*, **38**, 201 (1990); S. Hikichi, M. Tanaka, Y. Morooka, and N. Kitajima, *J. Chem. Soc., Chem. Commun.*, **1992**, 814; C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fusi, C. Giorgi, P. Paoletti, B. Valtancoli, and D. Zanchi, *Inorg. Chem.*, **36**, 2784 (1997).
- 8 H. Sakiyama, H. Ōkawa, and R. Isobe, *J. Chem. Soc., Chem. Commun.*, **1993**, 882; H. Sakiyama, H. Tamaki, M. Kodera, N. Matsumoto, and H. Ōkawa, *J. Chem. Soc., Dalton Trans.*, 591 (1993); H. Sakiyama, H. Ōkawa, and M. Suzuki, *J. Chem. Soc., Dalton Trans.*, 3832 (1993); C. Higuchi, H. Sakiyama, H. Ōkawa, R. Isobe, and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 1097 (1994); C. Higuchi, H. Sakiyama, H. Ōkawa, and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 4015 (1995).
- 9 T. Koga, H. Furutachi, H. Nakamura, N. Fukita, M. Ohba, K. Takahashi, and H. Ōkawa, *Inorg. Chem.*, **37**, 989 (1998).
- 10 S. Uozumi, H. Furutachi, M. Ohba, H. Ōkawa, D. E. Fenton, K. Shindo, S. Murata, and D. J. Kitko, *Inorg. Chem.*, **37**, 6281 (1998).
- 11 M. Suzuki, H. Furutachi, and H. Ōkawa, *H. Coord. Chem. Rev.*, in press.
- 12 D. A. Denton and H. Suschitzky, *J. Chem. Soc.*, 4741 (1963).
- 13 S. Uozumi, M. Ohba, H. Ōkawa, and D. E. Fenton, *Chem. Lett.*, 673 (1997).
- 14 D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.
- 15 D. C. Creagh and W. J. McAuley, "International Tables for X-ray Crystallography," ed by A. J. C. Wilson et al., Kluwer Acad., Boston (1992), pp. 219–222.
- 16 D. C. Creagh and J. H. Hubbell, "International Tables for X-ray Crystallography" ed by A. J. C. Wilson et al., Kluwer Acad., Boston (1992), pp. 200–206.
- 17 TEXSAN, Molecular Structure Corporation, Houston, TX, 1985.
- 18 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980).
- 19 B. Bosnich, *J. Am. Chem. Soc.*, **90**, 627 (1968).
- 20 R. S. Downing and F. L. Urbach, *J. Am. Chem. Soc.*, **91**, 5977 (1969).
- 21 C. K. Johnson, Report 3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
- 22 A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.
- 23 M. Yamami, H. Furutachi, T. Yokoyama, and H. Ōkawa, *Chem. Lett.*, **1988**, 211; M. Yamami, H. Furutachi, T. Yokoyama, and H. Ōkawa, *Inorg. Chem.*, **37**, 6823 (1998).