Synthesis and Molecular Structure of Novel Zinc(II) Complexes: $[\{Zn(HL)Cl_2\}_n]$, $[Zn_2L_2Cl_2]$ and $[Zn_2(\mu\text{-}OH)LCl_2]$ [HL = 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol]†

Chun-Tong Chen, Wen-Kuen Chang, Shiann-Cherng Sheu, Gene-Hsiang Lee, Tong-Ing Ho,* Yuan-Chuan Lin* and Yu Wang*

Department of Chemistry, National Taiwan University, Taipei, Taiwan

The synthesis of a new bifunctional ligand, 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol (HL), and the structures of its complexes with zinc(II) are described. The ligand reacts with zinc chloride to form a macromolecular complex, $[\{Zn(HL)Cl_2\}_n]$ **1**. In basic solution two binuclear zinc(II) complexes, $[Zn_2L_2Cl_2]$ **2** and $[Zn_2(\mu\text{-}OH)LCl_2]$ **3**, are formed under different reaction conditions. The molecular structures of complexes **1** and **2** have been characterized by X-ray diffraction: **1**, monoclinic, space group = $P2_1/c$, $Z = 4$, $a = 12.357(2)$, $b = 12.400(2)$, $c = 14.957(4)$ Å, $\beta = 100.18(2)°$; **2**, triclinic, space group = $P\bar{1}$, $Z = 1$, $a = 9.194(1)$, $b = 10.040(1)$, $c = 10.316(2)$ Å, $\alpha = 114.40(2)$, $\beta = 115.93(2)$, $\gamma = 89.16(1)°$. The co-ordination sphere of zinc(II) in complex **1** is tetrahedral, in **2** it is distorted square pyramidal.

Many binuclear metal complexes with two oxygen bridges have long been of considerable interest in chelate systems.[1-11a,12,13e,14,15] Recently, such complexes have been intensively studied in the field of dioxygen transfer.[12-14,16,17] Some containing pyrazolyl as ligand were prepared as models for copper proteins in the hopes that they would mimic the active site of biological systems.[11]

In a binuclear zinc(II) complex bis(μ-hydroxy)bis[tris(dimethylphenylsilyl)methylzinc] with two hydroxy bridges the co-ordination sphere of zinc is in trigonal planar.[8] A five-co-ordinated zinc(II) complex, a dimer of *N*-methylsalicylideneiminate, was found in 1966.[2] Its structure is of C_i symmetry, and the configuration around the metal atom can be described as a distorted trigonal bipyramid. Combining the skeleton of this complex with pyrazole after the model of a copper protein,[11] we have prepared the ligand, 4-methyl-2,6-bis(pyrazol-1-ylmethyl)-phenol which reacts with metal ions to give binuclear complexes (see Scheme 1). In this paper we report a series of novel zinc(II) complexes.

Results and Discussion

Synthesis.—The ligand 4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenol (HL), which possesses two potential nitrogen and one oxygen donor site, was prepared. Its synthesis (Scheme 1) is similar to those of Hpeac[11d] and Hbpeac,[11c] (Hpeac = 2,6-bis[2-(pyrazol-1-ylethyl)methylamino]-*p*-cresol Hbpeac = 2,6-bis{bis[2-(pyrazol-1-ylethyl)amino]}-*p*-cresol) which have two and four side-arm pyrazolyl groups respectively. Chloromethylation[18] of *p*-cresol gives 2,6-bis(chloromethyl)-*p*-cresol, which is then treated with pyrazole in chloroform and triethylamine to produce the ligand, an air-stable white substance.

Mixing the ligand with 1 equivalent of $ZnCl_2 \cdot 2H_2O$ in tetrahydrofuran (thf) for 1 d produces complex **1**. However slow addition of 1 equivalent of $ZnCl_2 \cdot 2H_2O$ in methanol to the ligand in basic methanol solution at 50–60 °C for 2 d and then standing for 1 week gave pale yellow crystals of complex **2**. Complex **2** is also formed when the ligand is treated with 2 equivalents of $ZnCl_2 \cdot 2H_2O$ using the same procedure. However, a different reaction occurs when 2 equivalents of $ZnCl_2 \cdot 2H_2O$ are immediately added to 1 equivalent of ligand in basic aqueous methanol solution. After refluxing for 0.5 h, complex **3** was obtained as a white fine powder.

The two 2:1 reactions of zinc(II) ion and the sodium salt of the ligand give different complexes *via* different pathways. In the first case, it is proposed that 1 equivalent of zinc(II) ion reacts with 1 equivalent of ligand to form the intermediate **A**. Because of the low concentration of zinc(II) this dimerizes to form complex **2**. In the second case, 2 equivalents of zinc(II) react with 1 equivalent of ligand to form complex **3** *via* intermediates **A** and **B** (see Scheme 2).

Molecular Structure of $[Zn(HL)Cl_2] \cdot 0.5C_6H_6 \cdot 0.5C_6H_{14}$ **1**.—Crystals of complex **1** were grown from thf–hexane as colourless needles. Crystal data are given in Table 1, final atomic parameters in Table 2, and selected bond distances and angles in Table 3. The repeating unit is shown in Fig. 1.

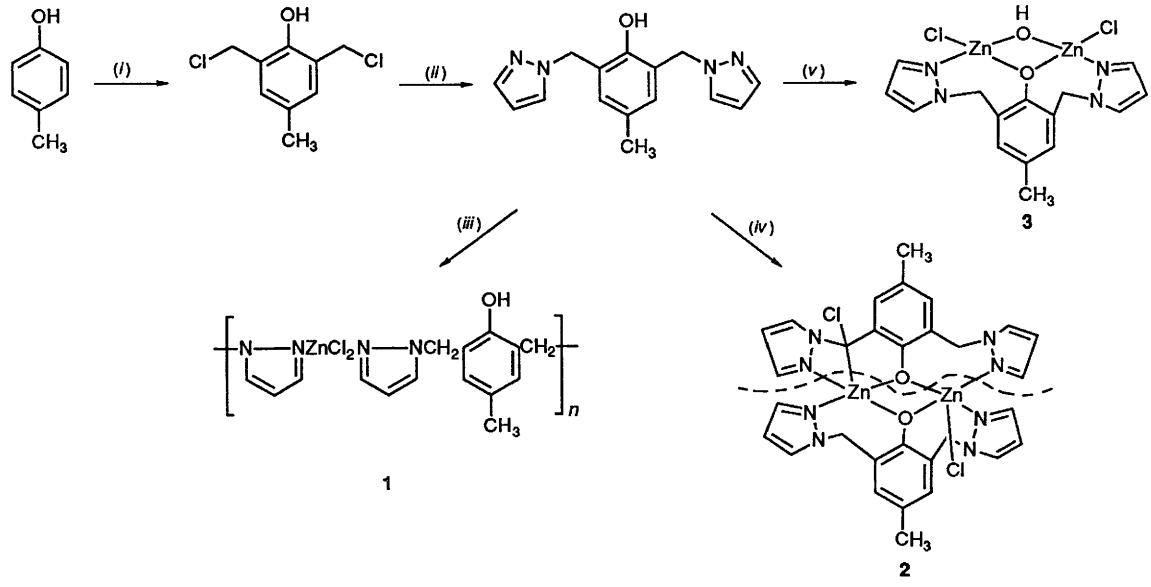
The co-ordination sphere of zinc(II) in this polymeric structure is distorted tetrahedral involving two chloride ions and two nitrogen atoms, N(1) and N(3), of the pyrazolyl rings of the ligands. The bond angle Cl(1)–Zn–Cl(2) 119.68(17)° is larger than the normal tetrahedral angle, and the Cl(1)–Zn–N(1) 107.1(4)° and Cl(2)–Zn–N(3) 102.1(3)° are smaller. The Zn–Cl bond distances are 2.191(4) and 2.246(4) Å for Cl(1) and Cl(2) respectively.

Since the ligand has two pyrazolyl rings at *meta* positions, it serves as a bridging ligand between neighbouring metal centres through two nitrogen atoms, N(1) and N(3); thus the complex becomes an infinite zigzag chain in the solid. Scattered throughout the polymeric crystal are C_6H_6 and C_6H_{14} solvent molecules and the repeat unit is $Zn(HL)Cl_2 \cdot 0.5C_6H_6 \cdot 0.5C_6H_{14}$. The complex is stable in air and in solution.

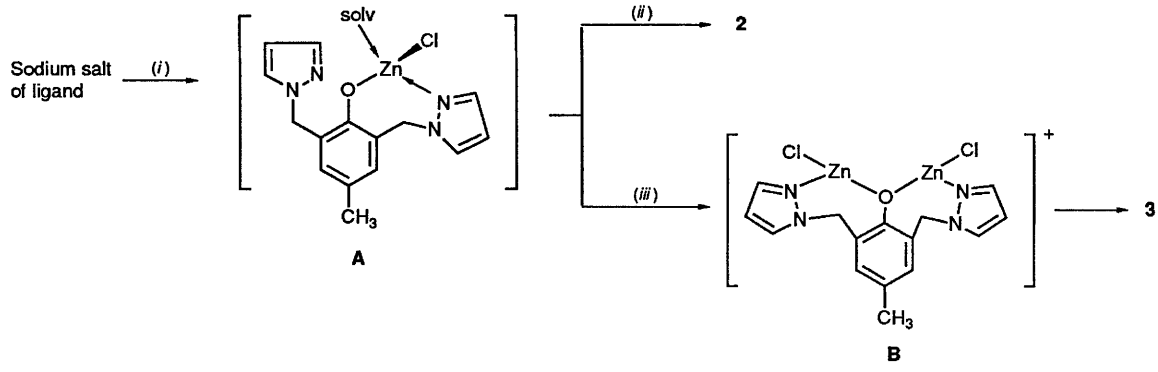
Molecular Structure of $[Zn_2L_2Cl_2]$ **2**.—The molecular structure is shown in Fig. 2, crystal data are given in Table 1, non-hydrogen atomic coordinates in Table 4, and selected bond distances and angles in Table 3.

† *catena*-Poly[dichlorozinc-μ-4-methyl-2,6-bis(pyrazol-1-ylmethyl)-phenol-$\kappa N^2:\kappa N^{2'}$]bis[μ-4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenolato-$\kappa N^2O:\kappa N^{2'}O$]-bis[chlorozinc(II)], and μ-hydroxo-[4-methyl-2,6-bis(pyrazol-1-ylmethyl)phenolato-$\kappa N^2O:\kappa N^{2'}O$]-bis[chlorozinc(II)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 1 (*i*) $(CH_2O)_x$, HCl; (*ii*) pyrazole, NEt_3, $CHCl_3$; (*iii*) 1 equivalent $ZnCl_2$, thf; (*iv*) 1 equivalent $ZnCl_2$, NaOH, MeOH; (*v*) 2 equivalents $ZnCl_2$, NaOH(aq), MeOH



Scheme 2 solv = Solvent. (*i*) $ZnCl_2$; (*ii*) dimerization; (*iii*) $ZnCl_2$, OH^-

Table 1 Crystallographic data for complexes **1** and **2**

Complex	**1**	**2**
Formula	$[Zn(HL)Cl_2]\cdot 0.5C_6H_6\cdot 0.5C_6H_{14}$	$[Zn_2L_2Cl_2]$
M	492.6	736.3
Crystal size/mm	0.08 × 0.10 × 0.45	0.3 × 0.4 × 0.5
Crystal form	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	12.357(2)	9.194(1)
b/Å	12.400(2)	10.040(1)
c/Å	14.957(4)	10.316(2)
α/°		114.40(2)
β/°	100.18(2)	115.93(2)
γ/°		89.16(1)
U/Å^3	2255.6(8)	763.7(2)
Z	4	1
$F(000)$	1004	368
μ/mm^{-1}	1.37	1.83
2θ range/°	2–45	2–50
Scan parameters:	1.7 + 0.7 tan θ	1.3 + 0.7 tan θ
Total number of reflections:	2939 (1482 > 2σ)	2678 (2354 > 2σ)
$\Delta\rho_{max}$	0.46	0.83
R, R'	0.066, 0.10	0.030, 0.028
S	2.87	2.84

The dimer structure has $\bar{1}$ symmetry at the centre of the molecule. The co-ordination sphere of Zn is roughly square pyramidal with two oxygen bridges and two nitrogen atoms of pyrazole as the base and a chloride ion at the apex. Two Zn–O distances are significantly different, similar to those in bis[bis-(*N*-methylsalicylideneiminato)zinc].[2] Two Zn–N distances are larger than those of complex **1**. The two chloride ions are in a *trans* arrangement, the Zn–Cl distances being the same as the longer one of complex **1**. The zinc centre is displaced from the co-ordinated N_2O_2 plane by 0.5943(13) Å toward the chloride ion. The Zn···Zn′ distance is 3.2453(10) Å, and the phenolate oxygen bridge angle, Zn–O–Zn′, is 104.62(8)°. The phenolate oxygen atom is three-co-ordinated in a planar fashion. Structurally, complex **2** is similar to that of a Robson-type of macrocyclic binuclear copper(II) complex $[Cu_2(C_{24}H_{26}N_4O_2)Br_2]$[15] and is different from those models studied by Sorrell *et al.*[11c]

Spectroscopy.—In the IR spectrum the C–H and C=N stretching vibration of the pyrazolyl groups in complex **1** shift to higher frequencies (3132, 3112 and 1514 cm^{-1} respectively) relative to those of the ligand and the unco-ordinated phenol group shows a sharp peak at 3406 cm^{-1}. For complexes **2** and **3** there is a new peak near 1570 cm^{-1} as the phenolate group is co-ordinated to two zinc(II) ions. Complex **3** shows a broad absorption at 3432 cm^{-1} for the bridging hydroxide group (see Experimental section).

In the UV spectrum the pyrazolyl group absorption of complex **1** shifts to 215 from the 212 nm of the ligand. Complexes **2** and **3** show two pyrazolyl group absorptions[19] as the phenolate group is also co-ordinated (see Experimental section).

In general, the ^{1}H NMR signals of complex **1** showed only a

Table 2 Final atomic positional parameters of non-hydrogen atoms for complex **1**

Atom	*x*	*y*	*z*
Zn	0.223 87(14)	0.742 16(13)	0.235 97(11)
Cl(1)	0.350 0(3)	0.777 1(3)	0.153 9(3)
Cl(2)	0.170 3(3)	0.872 2(3)	0.323 2(3)
O	−0.084 7(7)	0.894 8(7)	0.261 9(6)
N(1)	0.090 7(9)	0.687 3(9)	0.150 8(8)
N(2)	−0.009 9(11)	0.667 3(8)	0.168 0(8)
N(3)	0.279 6(9)	0.626 4(9)	0.328 7(8)
N(4)	0.305 1(9)	0.521 9(9)	0.314 7(8)
C(1)	0.084 8(13)	0.670 8(12)	0.062 4(12)
C(2)	−0.018 9(16)	0.639 6(13)	0.020 0(11)
C(3)	−0.079 6(13)	0.639 5(12)	0.090 9(12)
C(4)	−0.034 2(12)	0.662 6(10)	0.260 0(10)
C(5)	−0.142 7(12)	0.708 7(11)	0.267 1(9)
C(6)	−0.227 3(13)	0.640 0(10)	0.275 9(11)
C(7)	−0.330 3(12)	0.674 3(11)	0.282 2(10)
C(8)	−0.426 0(13)	0.597 8(12)	0.291 2(11)
C(9)	0.351 9(11)	0.287 5(11)	0.218 7(10)
C(10)	0.266 0(12)	0.355 5(10)	0.224 0(9)
C(11)	−0.162 6(12)	0.820 1(11)	0.267 5(9)
C(12)	0.288 2(11)	0.476 2(10)	0.223 1(9)
C(13)	0.354 7(13)	0.478 1(11)	0.390 4(11)
C(14)	0.359 5(13)	0.552 6(13)	0.460 1(10)
C(15)	0.313 2(12)	0.640 0(11)	0.415 5(10)
C(16)	0.086 0(16)	0.956 1(17)	0.022 6(13)
C(17)	0.077 5(17)	1.047 4(18)	−0.021 0(15)
C(18)	−0.000 3(20)	0.949 1(19)	0.083 1(14)
C(19)	0.478(3)	0.545 7(20)	−0.015 1(22)
C(20)	0.608 8(19)	0.569 9(19)	0.007 5(16)
C(21)	0.614 1(21)	0.706 7(23)	0.019 6(17)

Table 3 Selected bond distances (Å) angles (°) of complexes **1** and **2***

Complex **1**			
Zn–Cl(1)	2.191(4)	Zn–N(1)	2.013(12)
Zn–Cl(2)	2.246(4)	Zn–N(3)	2.030(11)
Cl(1)–Zn–Cl(2)	119.68(17)	Cl(2)–Zn–N(1)	108.6(3)
Cl(1)–Zn–N(1)	107.1(4)	Cl(2)–Zn–N(3)	102.1(3)
Cl(1)–Zn–N(3)	109.5(3)	N(1)–Zn–N(3)	109.6(5)
Complex **2**			
Zn ··· Zn′	3.2453(10)	Zn–O′	2.0720(19)
Zn–Cl	2.2403(11)	Zn–N(1)	2.125(3)
Zn–O	2.0291(19)	Zn–N(3)	2.1832(25)
Cl–Zn–O	107.33(7)	O–Zn–N(3)	92.53(8)
Cl–Zn–O′	111.99(7)	O′–Zn–N(1)	89.40(9)
Cl–Zn–N(1)	101.57(8)	O′–Zn–N(3)	144.77(9)
Cl–Zn–N(3)	103.18(7)	N(1)–Zn–N(3)	85.60(9)
O–Zn–O′	75.38(8)	Zn–O–Zn′	104.62(8)
O–Zn–N(1)	150.66(9)		

* Primed atoms related to unprimed equivalents by symmetry element at 0, ½, 0.

small chemical shift relative to those of the ligand. This is also found with other zinc(II) complexes containing Schiff bases.[20] However, complexes **2** and **3** showed a large downfield chemical shift of pyrazolyl C^3H at δ 7.91 relative to that of the ligand at δ 7.72. Most resonances of the pyrazolyl rings in the three complexes became singlets and broad upon co-ordination (see Experimental section).

Structure of $[Zn_2(\mu\text{-OH})LCl_2]$ **3**.—Comparing the IR, UV and ^1H NMR spectra for the ligand and complexes **1–3** and bearing in mind the pseudo-noble gas configuration of zinc(II) ion, we propose that complex **3** contains a bridging hydroxide group as shown in Scheme 1.

Table 4 Final atomic positional parameters of non-hydrogen atoms for complex **2**

Atom	*x*	*y*	*z*
Zn	0.051 31(4)	0.457 89(4)	0.148 10(4)
Cl	0.066 94(11)	0.640 64(10)	0.374 60(10)
O	0.149 34(23)	0.553 32(22)	0.057 17(23)
N(1)	−0.081 6(3)	0.271 0(3)	0.125 1(3)
N(2)	−0.143 3(3)	0.137 1(3)	0.008 2(3)
N(3)	0.269 5(3)	0.365 6(3)	0.237 6(3)
N(4)	0.401 7(3)	0.352 7(3)	0.210 2(3)
C(1)	−0.096 5(4)	0.248 3(4)	0.236 9(4)
C(2)	−0.168 7(5)	0.102 3(5)	0.176 7(5)
C(3)	−0.199 0(4)	0.035 0(4)	0.019 6(5)
C(4)	−0.183 5(4)	0.133 0(4)	0.164 1(4)
C(5)	0.331 8(4)	0.790 0(3)	0.207 2(4)
C(6)	0.492 7(4)	0.874 8(3)	0.299 3(4)
C(7)	0.627 7(4)	0.808 5(4)	0.327 1(3)
C(8)	0.801 3(4)	0.901 0(4)	0.428 1(4)
C(9)	0.599 0(4)	0.654 0(4)	0.257 5(3)
C(10)	0.440 5(4)	0.567 8(3)	0.166 7(3)
C(11)	0.303 4(4)	0.636 2(3)	0.142 2(3)
C(12)	0.411 9(4)	0.400 9(3)	0.097 8(4)
C(13)	0.521 2(4)	0.313 2(3)	0.312 8(4)
C(14)	0.467 0(4)	0.297 1(3)	0.409 9(4)
C(15)	0.312 1(4)	0.331 0(4)	0.360 3(4)

Experimental

Chemicals.—All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. 2,6-Bis(chloromethyl)-*p*-cresol was prepared according to the literature.[18]

Physical Methods.—Melting points were obtained with a Thomas Hoover capillary apparatus. Proton NMR spectra were recorded on a Bruker AM-200WB instrument at 200 MHz using $(CD_3)_2SO$ and $CDCl_3$ as solvents. Chemical shifts are reported in ppm relative to $SiMe_4$ as internal standard. Mass spectra were recorded on a Finnigan MAT TSQ-46C instrument, infrared spectra on a Perkin-Elmer 983G spectrometer using KBr as support, and ultraviolet-visible spectra on a Perkin-Elmer 555 spectrometer. Elemental analysis were obtained using a Perkin-Elmer 240C instrument.

Syntheses.—4-*Methyl*-2,6-*Bis*(*pyrazol*-1-*ylmethyl*)*phenol.* Pyrazole (1.4 g, 20.5 mmol) was dissolved in chloroform (5 cm^3) and triethylamine (3 cm^3) then 2,6-bis(chloromethyl)-*p*-cresol (2.05 g, 10 mmol) in chloroform (5 cm^3) was added to the solution for 2 min. After refluxing for 3 h, the solvents were removed under reduced pressure and the residue was washed with acetone. The product was crystallized from a mixture of ethyl acetate and hexane. The crude pale yellow crystals (2.3 g, 85%) which were dissolved in ethyl acetate were purified by column chromatography (silica gel 60) using ethyl acetate–hexane (1:9) (R_f = 0.4) as eluent. The eluent was then removed to obtain a white solid (2.2 g, 82%), m.p. 135–136 °C (Found: C, 67.25; H, 6.00; N, 21.70. $C_{15}H_{16}N_4O$ requires C, 67.15; H, 6.00; N, 20.90%); ν_{max} 3122m, 3104s, 1602m, 1508s, and 1480s cm^{-1}; λ_{max}(MeOH) 212 (ε 13 950) and 283 (4200 dm^3 mol^{-1} cm^{-1}). NMR: δ_H 2.13 (3 H, s, aryl CH_3), 5.3 (4 H, s, aryl CH_2N), 6.23 (2 H, t, *J* 2.05, pyrazolyl C^4H), 6.78 (2 H, s, aryl H), 7.46 (2 H, d, *J* 2.05, pyrazolyl C^5H), 7.72 (2 H, d, *J* 2.05 Hz, pyrazolyl C^3-H) and 9.97 (1 H, s, phenol OH). *m/z* 268 (M^+, 60.74), 269 ($[M + 1]^+$, 16.27), and 270 ($[M + 2]^+$, 2.17%).

catena-*Poly*[*dichlorozinc*-μ-4-*methyl*-2,6-*bis*(*pyrazol*-1-*ylmethyl*)*phenol*-κN^2:κ$N^{2'}$], $[\{Zn(HL)Cl_2\}_n]$ **1**. 4-Methyl-2,6-bis(pyrazol-1-ylmethyl)phenol (0.268 g, 1 mmol) was first dissolved in thf (50 cm^3); $ZnCl_2 \cdot 2H_2O$ (0.171 g, 1 mmol) in thf (50 cm^3) was then added and stirred at room temperature for 1 d. Hexane (600 cm^3) was added to the solution as precipitator. The white powder formed was dried over silica gel (0.36 g, 90%)

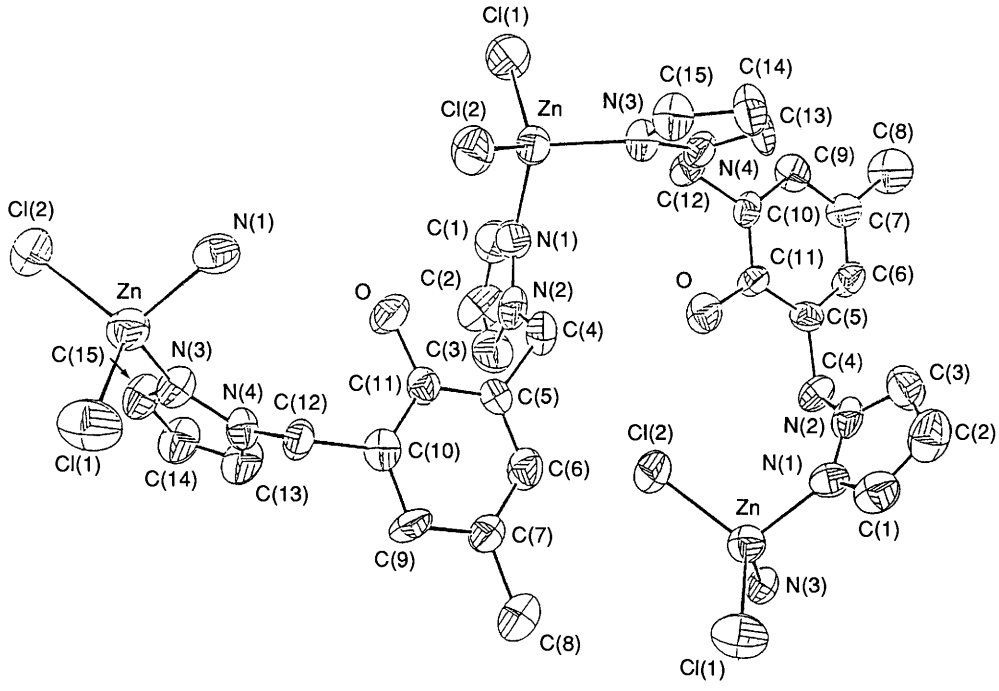


Fig. 1 The repeat unit of complex **1**

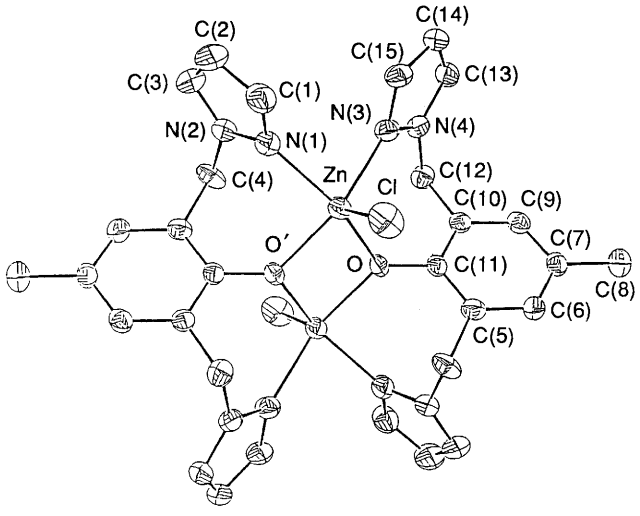


Fig. 2 Molecular structure of complex **2**

(Found: C, 44.50; H, 3.70; N, 13.60%. $C_{15}H_{16}Cl_2N_4OZn$ requires C, 44.55; H, 4.00; N, 13.85%); ν_{max} 3406vs, 3132m, 3112s, 1603w, 1514m and 1490s cm^{-1}; λ_{max}(thf) 215 (ε 46.88) and 283 [9.87 dm^3 $(g\ l^{-1})^{-1}$ cm^{-1}]. NMR: δ_H 2.16 (3 H, s), 5.3 (4 H, s), 6.23 [2 H, t, *J* 2.0 Hz], 6.83 (2 H, s), 7.46 (2 H, s), 7.7 (2 H, s), and 10.1 (1 H, br).

Bis[μ-4-*methyl*-2,6-*bis*(*pyrazol*-1-*ylmethyl*)*phenolato*-$\kappa N^2O:\kappa N^{2'}O$]-*bis*[*chlorozinc*(II)], $[Zn_2L_2Cl_2]$ **2**. The phenol ligand (0.268 g, 1 mmol) and sodium hydroxide (0.2 g, 5 mmol) were dissolved in methanol (40 cm^3) and kept at 50–60 °C. The salt $ZnCl_2 \cdot 2H_2O$ (0.171 g, 1 mmol) in methanol (40 cm^3) was then slowly added over 2 d. The solution was allowed to stand for another week at 50–60 °C. Half of the solvent was evaporated under an open condenser during this period. Pale yellow crystals of complex **2** (0.3 g, 81.5%) were obtained (Found: C, 49.05; H, 4.05; N, 15.20. $C_{30}H_{30}Cl_2N_8O_2Zn_2$ requires C, 48.95; H, 4.10; N, 15.20%); ν_{max} 3125m, 3106m, 1609m, 1572w, 1507s and 1470s cm^{-1}; λ_{max}(MeOH) 203 (ε 59 600), 218 (sh, 36 750) and 288 (7100 dm^3 mol^{-1} cm^{-1}). NMR: δ_H 2.12 (3 H, s), 5.36 (4 H, s), 6.25 (2 H, s), 6.87 (2 H, s), 7.4 (2 H, s), and 7.91 (2 H, br).

μ-*Hydroxo*-[4-*methyl*-2,6-*bis*(*pyrazol*-1-*ylmethyl*)*phenolato*-$\kappa N^2O:\kappa N^{2'}O$]-*bischlorozinc*(II)], $[Zn_2(\mu\text{-}OH)LCl_2]$ **3**. The phenol ligand (0.268 g, 1 mmol) was dissolved in methanol (40 cm^3) and mixed with sodium hydroxide (0.2 g, 5 mmol) in water (2 cm^3) to form a homogeneous solution. The salt $ZnCl_2 \cdot 2H_2O$ (0.35 g, 2.05 mmol) in methanol (20 cm^3) was then added. After refluxing for 0.5 h, the solvents were removed under reduced pressure and the residue washed with water (150 cm^3). The suspension was allowed to stand until a solid precipitated. The product **3** (0.432 g, 92%) was obtained as a white powder and dried over silica gel (Found: C, 36.85; H, 3.30; N, 11.10. $C_{15}H_{16}Cl_2N_4OZn_2$ requires C, 37.05; H, 3.30; N, 11.55%); ν_{max} 3432br, 3125m, 3106m, 1610w, 1573w, 1507m and 1471s cm^{-1}; λ_{max}(MeOH) 202 (ε 51 100), 216 (sh, 36 000) and 290 (5880 dm^3 mol^{-1} cm^{-1}). NMR: δ_H 2.08 (3 H, s), 5.3 (4 H, s), 6.26 (2 H, s), 6.78 (2 H, s), 7.45 (2 H, s) and 7.91 (2 H, br).

Structure Determination.—Suitable crystals of complexes **1** and **2** were chosen. Intensity data were collected at room temperature on a CAD-4 diffractometer using monochromated Mo-Kα radiation (λ 0.7107 Å). The unit-cell constants were derived from a least-squares refinement of 25 setting reflections. The θ–2θ scan technique and a variable scan speed were used to obtain the integrated intensities. Three reference reflections were monitored throughout the measurement; the variation of the absorption intensities was less than 2% in both cases. No absorption correction was applied. Other details of the crystal data are given in Table 1.

The structures were solved by the heavy-atom method; subsequent Fourier syntheses based on the heavy atom revealed the positions of all the non-hydrogen atoms. Least-squares refinement including anisotropic thermal parameters for all non-hydrogen atoms was performed and the final results are given in Tables 2 and 4. For both crystals a unit weighting scheme of the form $1/\sigma^2(F_o)$ was used. All the hydrogen-atom parameters were calculated according to the ideal geometry and were not refined. The structural analyses were carried out on Microvax III using NRCVAX programs.[21] Atomic scattering factors were taken from ref. 22.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

This work was supported by the National Science Council, Taiwan.

References

1 S. Yamada, *Coord. Chem. Rev.*, 1966, **1**, 415.
2 P. L. Orioli, M. D. Vaira and L. Sacconi, *Inorg. Chem.*, 1966, **5**, 400.
3 S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.
4 P. W. Ball, *Coord. Chem. Rev.*, 1969, **4**, 361.
5 W. P. Griffith, *Coord. Chem. Rev.*, 1970, **5**, 459.
6 M. Calligaris, G. Nardin and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385.
7 V. McKee, J. V. Dagdigian, R. Bau and C. A. Reed, *J. Am. Chem. Soc.*, 1981, **103**, 7000.
8 S. S. Al-Juaid, N. H. Buttrus, C. Eaborn, P. B. Hitchcock, A. T. L. Roberts, J. D. Smith and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1986, 908.
9 B. P. Murch, F. C. Bradley, P. D. Boyle, V. Papaefthymiou and L. Que, jun., *J. Am. Chem. Soc.*, 1987, **109**, 7993.
10 B. S. Snyder, G. S. Patterson, A. J. Abrahamson and R. H. Holm, *J. Am. Chem. Soc.*, 1989, **111**, 5214.
11 (*a*) T. N. Sorrell, D. L. Jameson and C. J. O'Connor, *Inorg. Chem.*, 1984, **23**, 190; (*b*) T. N. Sorrell and A. S. Borovik, *J. Chem. Soc., Chem. Commun.*, 1984, 1489; (*c*) T. N. Sorrell, C. J. O'Connor, O. P. Anderson and J. H. Reibenspies, *J. Am. Chem. Soc.*, 1985, **107**, 4199; (*d*) T. N. Sorrell, C. C. Shen and C. J. O'Connor, *Inorg. Chem.*, 1987, **26**, 1755.
12 S. J. Lippard, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 344.
13 (*a*) J. E. Pate, R. W. Cruse, K. D. Karlin and E. I. Solomon, *J. Am. Chem. Soc.*, 1987, **109**, 2624; (*b*) K. D. Karlin, R. W. Cruse, Y. Gultneh, A. Farooq, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, p. 2268; (*c*) K. D. Karlin, M. S. Haka, R. W. Cruse, G. J. Meyer, A. Farooq, Y. Gultneh, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1988, **110**, 1196; (*d*) R. R. Jacobson, Z. Tyeklar, A. Farooq, K. D. Karlin, S. Liu and J. Zubieta, *J. Am. Chem. Soc.*, p. 3690; (*e*) K. D. Karlin, P. Ghosh, R. W. Cruse, A. Farooq, Y. Gultneh, R. R. Jacobson, N. J. Blackburn, R. W. Strange and J. Zubieta, *J. Am. Chem. Soc.*, p. 6769.
14 N. Kitajima, K. Fujisawa and Y. Moro-oka, *J. Am. Chem. Soc.*, 1989, **111**, 8975.
15 S. K. Mandal, L. K. Thompson, M. J. Newlands, E. J. Gabe and K. Nag, *Inorg. Chem.*, 1990, **29**, 1324.
16 S. M. Wang, J. R. Tzou, M. N. Chen and N. C. Li, *Inorg. Chim. Acta*, 1986, **125**, 229; N. C. Li, J. R. Tzou, S. W. Chen, S. M. Wang, Y. C. Chou, N. T. Liang and H. J. Lin, *Inorg. Chim. Acta*, 1987, **138**, 121.
17 *Oxygen Complexes and Oxygen Activation by Transition Metals*, eds. A. E. Martell and D. T. Sawyer, Plenum, New York and London, 1988.
18 I. G. Farbenindustrie, *Br. Pat.*, 1931, 347 887.
19 E. Bernarducci, W. F. Schwinding, J. L. Hughey, K. Krogh-Jespersen and H. J. Schugar, *J. Am. Chem. Soc.*, 1981, **103**, 1686.
20 R. Bertani and G. Facchin, *Inorg. Chim. Acta*, 1989, **165**, 73.
21 E. J. Gabe, Y. Le Page, P. S. White and F. L. Lee, *Acta Crystallogr., Sect. A*, 1987, **43**, S294.
22 *International Tables for* X-*Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 15*th October* 1990; *Paper* 0/04639F