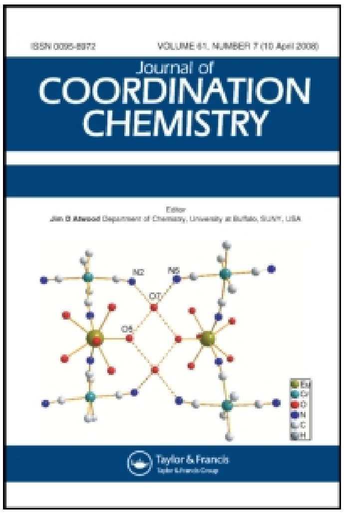

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Syntheses and characterization of nickel(II), zinc(II) and palladium(II) complexes derived from three pyrazole-based polydentate ligands

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Syntheses and characterization of nickel(II), zinc(II) and palladium(II) complexes derived from three pyrazole-based polydentate ligands

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Two pyrazole-based polydentate ligands, 1,3-*bis*(5-methyl-3-phenylpyrazol-1-yl)-propan-2-ol (Hmppzpo) and 1,3-*bis*(5-methyl-3-*p*-isopropylphenylpyrazol-1-yl)-propan-2-ol (Hmcpzpo), have been synthesized. A third ligand, 1,3-*bis*(3,5-dimethylpyrazol-1-yl)-propan-2-ol (Hdmpzpo), has been synthetically modified. Seven new M(II) coordination compounds of general formula $M_2L_2X_2$ (M = Zn, Ni; X = NO_3 or ClO_4; L = dmpzpo, mppzpo or mcpzpo) or MLX (M = Pd; L = dmpzpo; X = Cl) were synthesized and structurally characterized by elemental analysis and FT-IR analysis. The crystal structures of $[Zn_2(\mu\text{-dmpzpo-O,N,N}')_2(NO_3)_2]\cdot 2H_2O$ (**1** $\cdot 2H_2O$), $[Ni_2(\mu\text{-dmpzpo-O,N,N}')_2(CH_3CN)_2](ClO_4)_2$ (**2**) and $Pd(\mu\text{-dmpzpo-N,N}')Cl_2$ (**4**) were determined by single-crystal X-ray crystallography. The crystal structures show that complexes **1** $\cdot 2H_2O$ and **2** are center-symmetric dinuclear compounds, with two metal ions bridged by two alkoxo groups and each metal ion with a distorted square-pyramidal environment. The palladium complex, **4**, displayed square-planar coordination geometry around the Pd(II) ion with *trans* arrangement.

Keywords: Zinc(II), nickel(II) and palladium(II) complexes; Polydentate ligands; Pyrazole; Crystal structure

1. Introduction

Coordination environments of metal ions in biomolecules often consist of nitrogen and oxygen donor atoms, provided by histidines, aspartates or glutamates. Since pyrazoles resemble imidazoles [1–3], polypyrazole borates, the so-called scorpionates, have been used to obtain ligand systems for mimicking structures and functions of certain metalloenzymes, metal ion recovery or in catalysis. Derivatives of polypyrazole borates have also been documented without boron and with N and O(S) donors [4–6]. To design appropriate polydentate ligands, besides the coordination sites, spacer groups play a very important role. These spacers regulate the steric factors and the polynucleating abilities of ligands by altering their length and substituents. Moreover, a certain flexibility, whereby the coordination geometries may adapt

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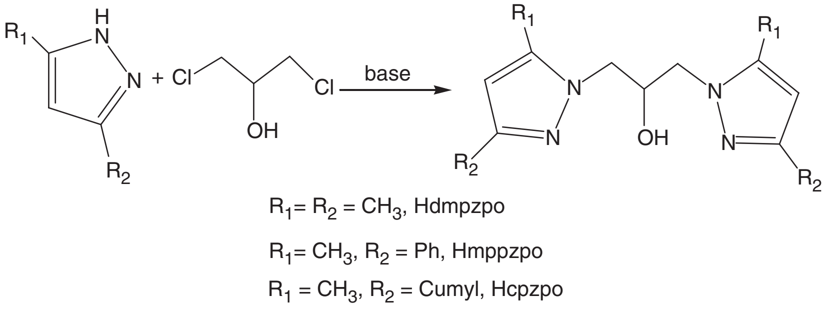
to oxidation state changes, and to one or two 'open' positions at the metal ion site [7], may be beneficial for catalytic reactions. For example, the bidentate ligand 1,3-*bis*(3,5-dimethylpyrazol-1-yl)propane only formed mononuclear metal species [8]; when a carboxyl group was introduced on the central carbon of the bridge, the ligand 1,3-*bis*(3,5-dimethylpyrazol-1-yl)-2-butanoic acid was obtained, for which only one oxygen of the carboxyl group binds to Cu(II), forming a mononuclear metal compound without coordination of the pyrazole rings [9]. When a hydroxyl group was incorporated on the central carbon atom of the propyl spacer, the ligand 1,3-*bis*(3,5-dimethylpyrazol-1-yl)propan-2-ol gave dinuclear Cu(II) complexes and catalytic activities for polymerization of 2,6-dimethylphenol (DMP) were investigated [10].

Since the substituents on the pyrazole ring can be easily altered to regulate the steric and electronic factors of the pyrazole, we designed and synthesized (modified) three pyrazole-based flexible ligands with different substituents at the 3-position of the pyrazole ring, as shown in scheme 1, similar to the ligands reported by Reedijk's group [9]. Here we report the synthesis and characterization of three ligands, 1,3-*bis*(3,5-dimethyl-pyrazol-1-yl)propan-2-ol (Hdmpzpo), 1,3-*bis*(5-methyl-3-phenylpyrazol-1-yl)propan-2-ol (Hmppzpo) and 1,3-*bis*(5-methyl-3-*p*-cumylpyrazol-1-yl)propan-2-ol (Hmcpzpo) (scheme 1), and their complexes, $[Zn_2(\mu\text{-dmpzpo-O,N,N}')_2(NO_3)_2]\cdot 2H_2O$ (**1** $\cdot 2H_2O$), $[Ni_2(\mu\text{-dmpzpo-O,N,N}')_2(CH_3CN)_2]\cdot(ClO_4)$ (**2**), $[Ni_2(\mu\text{-dmpzpo-O,N,N}')_2(NO_3)_2]$ (**3**), $[Pd(\mu\text{-dmpzpo-N,N}')Cl_2]$ (**4**), $[Zn_2(\mu\text{-mppzpo-O,N,N}')_2(NO_3)_2]$ (**5**), $[Zn_2(\mu\text{-mcpzpo-O,N,N}')_2(NO_3)_2]$ (**6**) and $[Ni_2(\mu\text{-mcpzpo-O,N,N}')_2(ClO_2)]$ (**7**). Complexes **1** $\cdot 2H_2O$, **2**, **4** were structurally characterized by single crystal X-ray crystallographic analyses.

2. Experimental

2.1. *Ligand syntheses*

1,3-*bis*(3,5-dimethylpyrazol-1-yl)propan-2-ol (Hdmpzpo) was synthesized as described by the literature with modification [9]. 3,5-Dimethylpyrazole (4.00 g, 0.042 mol) was added slowly to a suspension of sodium hydroxide (1.75 g, 0.042 mol) in 60 mL of dry THF. The suspension was refluxed for 3 h. Then 2 mL (0.021 mol) of



Scheme 1. The synthetic route to three pyrazole-based polydentate ligands.

1,3-dichloropropan-2-ol was added in portions to the resulting grey suspension. The mixture was refluxed for 3 h, cooled to room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure and the residue extracted with 25 mL of ethanol-water. Crystallization occurred upon cooling to 4°C. The white crystals (3.0 g, 75% yield, higher than the yield reported [9]) were separated by filtration over a glass filter. $F_w = 248.32\,\mathrm{g\,mol^{-1}}$, m.p. = 105–106°C (lit. 104°C [9]). ^{1}H NMR ($CDCl_3$, ppm): $\delta = 2.08$ (6H, s), 2.12 (6H, s), 3.8–4.0 (4H, m), 4.2 (1H, m), 5.4 (1H, m), 5.7 (2H, s). Anal. Calcd for $C_{13}H_{20}N_4O$: C, 62.88; H, 8.12; N, 22.56. Found: C, 62.76; H, 8.10; N, 22.10%.

For 1,3-*bis*(5-methyl-3-phenylpyrazol-1-yl)propan-2-ol (Hmppzpo), 5-methyl-3-phenylpyrazole (5.00 g, 0.0316 mol) was added slowly to a suspension of sodium hydride (1.32 g, 0.033 mol) (60% dispersion in mineral oil) in 90 mL of dry THF. The reaction mixture was refluxed for 5 h under nitrogen. Then 1.5 mL (0.0158 mol) of 1,3-dichloropropan-2-ol was added in portions to the resulting grey suspension. The solution was refluxed for 2 days, cooled to room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure and the residue was extracted with 15 mL of ethanol–water. Crystallization occurred upon cooling to 4°C. White crystals (3.6 g, 61.2% yield) were separated by filtration over a glass filter. $F_w = 372.46\,\mathrm{g\,mol^{-1}}$, m.p. = 145–147°C. ^{1}H NMR ($CDCl_3$): $\delta = 2.18$ (6H, pyz-3, s), 4.0–4.2 (4H, m), 4.4 (1H, m), 5.4 (1H, brs), 6.2 (2H, pyz-4, s), 7.2 (2H, Ph-4, m), 7.3 (4H, Ph-3, 5, m), 7.6 (4H, Ph-2, 6, m) ppm. Anal. Calcd for $C_{23}H_{24}N_4O$: C, 74.17; H, 6.49; N, 15.04. Found: C, 73.91; H, 6.08; N, 14.84%.

The synthesis of Hmcpzpo was similar to that of Hmppzpo. White crystals (3.20 g, 56% yield) were obtained. $F_w = 456.62\,\mathrm{g\,mol^{-1}}$, m.p. = 138-140°C. ^{1}H NMR ($CDCl_3$): $\delta = 1.2$ (12H, d), 2.1 (6H, pyz-3, s), 2.85 (2H, m), 4.1 (4H, m), 4.2 (1H, m), 5.4 (1H, s), 6.2 (2H, pyz-4, s), 7.1 (4H, Ph-3, 5, dd), 7.6 (4H, Ph-2, 6, dd) ppm. Anal. Calcd for $C_{29}H_{36}N_4O$: C, 76.28; H, 7.95; N, 12.27. Found: C, 76.11; H, 7.88; N, 11.95%.

2.2. *Complex syntheses*

$[Zn_2(\mu\text{-dmpzpo-O,N,N'})_2(NO_3)_2]\cdot 2H_2O$ (1 · 2H$_2$O). A solution of Hdmpzpo 0.0500 g (0.20 mmol) in 10 mL of THF was combined with 0.0083 g (0.20 mmol) sodium hydroxide dissolved in 10 mL of methanol, and stirred for 30 min. Then, a solution of 0.0298 g (0.10 mmol) of $Zn(NO_3)_2\,6H_2O$ in 10 mL of methanol was added dropwise and stirred for 30 min at room temperature to form a white precipitate, which was filtered and washed several times with water and THF, to afford 0.0632 g (yield: 80%) of **1** · 2H$_2$O. Single block-like crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of a methanol solution of the product for two weeks. $F_w = 785.44\,\mathrm{g\,mol^{-1}}$. Anal. Calcd for $C_{26}H_{38}N_{10}O_8Zn_2$: C, 45.84; H, 4.88; N, 18.88%. Found: C, 45.79; H, 4.11; N, 18.79%. IR(KBr): 3437, 3216, 2915, 1632, 1554, 1462, 1419, 1097, 804, 767, 707 cm^{-1}.

$[Ni_2(\mu\text{-dmpzpo-O,N,N'})_2(CH_3CN)_2](ClO_4)_2$ (2). To a solution of Hdmpzpo 0.1000 g (0.403 mmol) in 10 mL of methanol was added 0.0096 g (0.400 mmol) LiOH and stirred for 30 min, followed by a solution of 0.0735 g (0.20 mmol) of $Ni(ClO_4)_2\cdot 6H_2O$ in 10 mL of methanol dropwise and stirred for 3 h at 50°C.

The resulting solution was filtered and the solvent was removed by evaporation. The residue was extracted with CH_2Cl_2 to remove the remaining reactants. The resulting extract was evaporated and then extracted with MeCN. Dark green powder, obtained after evaporation of the solvent, was washed with cold methanol to afford 0.0653 g (yield: 37%) of **2**. Single crystals of **2** suitable for X-ray crystallographic analysis were obtained from slow diffusion of ether into CH_3CN solution of **2**. $F_w = 891.06\,g\,mol^{-1}$. Anal. Calcd for $C_{30}H_{42}Cl_2Ni_2N_{10}O_{10}$: C, 40.44; H, 4.75; N, 15.72%. Found: C, 38.14; H, 4.869; N, 14.13%. IR(KBr): 2980, 2932, 2868, 1632, 1555, 1461, 1431, 1091, 623 cm^{-1}.

[Ni_2(μ-dmpzpo-O,N,N′)$_2$(NO_3)$_2$] (3). A similar procedure as that described for **2** was followed using $Ni(NO_3)_2 \cdot 6H_2O$ instead of $Ni(ClO_4)_2 \cdot 6H_2O$. The green precipitate obtained was washed with cold methanol to afford 0.0521 g (yield: 32%) of **3**. $F_w = 736.03\,g\,mol^{-1}$. Anal. Calcd for $C_{26}H_{38}N_{10}O_8Ni_2$: C, 42.43; H, 5.206; N, 19.03%. Found: C, 41.69; H, 5.194; N, 18.53%. IR(KBr): 2923, 2819, 1628, 1553, 1465, 1431, 1332 cm^{-1}.

[Pd(Hdmpzpo-N,N′)Cl_2] (4). To a solution of Hdmpzpo 0.0496 g (0.20 mmol) in 10 mL of acetonitrile was added dropwise 0.0359 g (0.20 mmol) $PdCl_2$ in 10 mL of acetonitrile and stirred at 50°C for 3 h. The resulting solution was concentrated to *ca.* 5 mL and ether added to afforded brown crystalline powder 0.0653 g (yield: 78%) of **4**. Single crystals of **4** suitable for X-ray crystallographic analysis were obtained from slow diffusion of ether into CH_3CN solution of **4** for two weeks. $F_w = 425.63\,g\,mol^{-1}$. Anal. Calcd for $C_{13}N_4OH_{20}PdCl_2$: C, 36.68; H, 4.74; N, 13.16%. Found: C, 36.34; H, 4.88; N, 13.13%. IR(KBr): 3444, 2925, 2849, 1640, 1555, 1499, 1428 cm^{-1}.

[Zn_2(μ-mppzpo-O,N,N′)(ClO_4)$_2$] (5). Complex **5** was synthesized in a similar manner to that used for complex **1** $\cdot 2H_2O$, using Hmppzpo and $Zn(ClO_4)_2 \cdot 6H_2O$ instead of Hdmpzpo and $Zn(NO_3)_2 \cdot 6H_2O$. Yield: 0.0852 g (79%). $F_w = 1072.59\,g\,mol^{-1}$. Anal. Calcd for $C_{46}H_{46}Cl_2N_8O_{10}Zn_2$: C, 51.51; H, 4.32; N, 10.45%. Found: C, 51.47; H, 4.29; N, 10.48%. IR(KBr): 3200, 2980, 2955, 2860, 1597, 1557, 1519, 1458, 1430, 1097, 763, 637 cm^{-1}.

[Zn_2(μ-mcpzpo-O,N,N′)$_2$(ClO_4)$_2$] (6). Complex **6** was synthesized in a similar manner to that used for complex **1** $\cdot 2H_2O$, Hmcpzpo being employed instead of Hdmpzpo. Yield: 0.0927 g (94.2%). $F_w = 1240.91\,g\,mol^{-1}$. Anal. Calcd for $C_{58}H_{70}Cl_2N_8O_{10}Zn_2$: C, 56.14; H, 5.69; N, 9.03%. Found: C, 55.81; H, 5.74; N, 9.06%. IR(KBr): 3199, 2981, 2950, 2922, 2868, 1605, 1551, 1515, 1450, 1367, 1091, 760, 686, 635 cm^{-1}.

[Ni_2(μ-mcpzpo-O,N,N′)$_2$(ClO_4)] (7). A similar procedure to that described for **2** was followed using Hmcpzpo instead of Hdmpzpo and in THF. The resulting product is yellow crystalline powder. Yield: 0.0681 g (37%). $F_w = 1227.52\,g\,mol^{-1}$. Anal. Calcd for $C_{58}H_{70}N_8O_{10}Ni_2Cl_2$: C, 56.75; H, 5.75; N, 9.13%. Found: C, 56.53;

H, 5.41; N, 9.71%. IR(KBr): 3146, 2930, 1617, 1560, 1490, 1459, 1119, 1089, 841, 630 cm^{-1}.

2.3. *Physical measurements*

All reagents and solvents were purchased from commercial sources and used as received, unless stated otherwise. THF was dried by sodium. The syntheses of all organic compounds were performed under an atmosphere of nitrogen, but their purification was commonly performed in air. Elemental analysis (C, H, N) was determined with a German Vario EL III instrument. ^{1}H NMR spectra were recorded using a Bruker AVANCE 300MHZ spectrometer. IR spectrum was recorded from KBr pellets in the range 4000–400 cm^{-1} on an American Thermo Nicolet AVATAR 360FT-IR spectrophotometer.

2.4. *Single crystal X-ray diffraction analysis*

Determination of the unit cell and data collection for complexes **1** $\cdot$ 2H$_2$O, **2** and **4** were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω-2θ scan technique. The structures were solved by direct methods using SHELXS-97 [11] and refined against F2 by full matrix least-squares using SHELXL-97 [11]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated using a riding model. The crystals used for diffraction study showed no decomposition during data collection. A summary of the crystal data, experimental details and refinement

Table 1. Crystallographic data for **1** $\cdot$ 2H$_2$O, **2** and **4**.

Compound	**1** $\cdot$ 2H$_2$O	**2**	**4**
Chemical formula	$C_{26}H_{42}N_{10}O_{10}Zn_2$	$C_{30}H_{42}Cl_2Ni_2N_{10}O_{10}$	$C_{13}H_{19}Cl_2N_4OPd$
Formula weight	785.44	891.06	425.63
Temperature (K)	291(2)	293(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$	C2/c
Crystal color	Colorless	Green	Brown
Crystal description	Block	Parallelepiped	Prism
a (Å)	8.663(9)	11.709(2)	23.861(3)
b (Å)	10.766(11)	12.527(3)	8.9216(10)
c (Å)	10.774(11)	14.259(3)	16.4322(18)
β (°)	79.144(12)	110.66(3)	105.505(2)
V (Å^3)	910.4(16)	1957.0(7)	3370.8(6)
Z	2	2	8
$D_{\text{Calc.}}$(g cm^{-3})	1.433	1.680	1.677
μ (Mo-Kα)	1.380	1.164	1.421
F(000)	408	924	1712
Reflection measured	5350	13048	10296
Unique reflections (R_{int})	2426	4419	4006
Final R indices	$R_1 = 0.0955$, $wR_2 = 0.2355$	$R_1 = 0.0739$, $wR_2 = 0.2119$	$R_1 = 0.0271$, $wR_2 = 0.0649$
R indices (all data)	$R_1 = 0.0767$, $wR_2 = 0.2174$	$R_1 = 0.1198$, $wR_2 = 0.2422$	$R_1 = 0.0385$, $wR_2 = 0.0672$
Goodness-of-fit on F^2	1.079	1.056	1.010

Table 2. Selected bond lengths () and angles (°) for **1** · $2H_2O$, **2** and **4**.

1 · $2H_2O$		**2**		**4**	
Zn(1) · · · Zn(1)A	3.043(3)	Ni(1) · · · Ni(1)A	3.066(4)	Pd(1)–N(1)	2.008(2)
Zn(1)–O(1)	2.042(6)	Ni(1)–O(1)	1.931(4)	Pd(1)–N(3)	2.018(2
Zn(1)–O(1)A	1.994(6)	Ni(1)–N(1)	2.046(4)	Pd(1)–Cl(1)	2.2822(7)
Zn(1)–N(1)A	2.110(7)	Ni(1)–O(1)A	1.994(4)	Pd(1)–Cl(2)	2.2869(7)
Zn(1)–N(4)	2.097(7)	Ni(1)–N(4)	2.040(5)	N(1)–Pd(1)–N(3)	98.93(8)
Zn(1)–O(2)	2.166(7)	Ni(1)–N(5)	2.052(5)	N(1)–Pd(1)–Cl(1)	89.73(6)
Zn(1)–O(1)–Zn(1)A	97.9(2)	O(1)–Ni(1)–O(1)A	77.31(17)	N(1)–Pd(1)–Cl(2)	178.46(6)
O(1)–Zn(1)–O(1)A	82.1(2)	O(1)A–Ni(1)–N(5)	96.63(19)	N(3)–Pd(1)–Cl(1)	177.82(6)
O(2)–Zn(1)–O(1)A	151.2(3)	O(1)–Ni(1)–N(4)	151.33(18)	N(3)–Pd(1)–Cl(2)	88.56(6)
N(4)–Zn(1)–N(1)A	102.9(3)	N(2)–N(1)–Ni(1)	123.1(3)	Cl(1)–Pd(1)–Cl(2)	91.78(6)
O(1)–Zn(1)–N(4)	86.5(3)	O(1)A–Ni(1)–N(4)	85.89(17)	N(4)–N(3)–Pd(1)	122.89(1)
N(4)–Zn(1)–O(1)A	103.2(2)	N(1)–Ni(1)–N(5)	94.91(19)	N(2)–N(1)–Pd(1)	123.26(1)
O(2)–Zn(1)–N(4)	103.9(3)	O(1)–Ni(1)–N(1)	90.16(16)	O(1) · · · Cl(2)^i	3.217(5)
O(1)–Zn(1)–N(1)A	169.5(2)	N(3)–N(4)–Ni(1)	119.9(3)	O(1)–H(1)–Cl(2)	156.97(6)
O(2)–Zn(1)–N(1)A	92.3(3)	O(1)A–Ni(1)–N(1)	164.59(16)		
O(2)–Zn(1)–O(1)	90.0(2)	N(4)–Ni(1)–N(5)	101.8(2)		
O(1)A–Zn(1)–N(1)A	91.0(3)	Ni(1)–O(1)–Ni(1)A	102.69(17)		
		N(4)–Ni(1)–N(1)	101.71(18)		
		O(1)–Ni(1)–N(5)	103.1(2)		

Symmetry positions for **1** · $2H_2O$: A at $1-x$, $1-y$, $-z$; for **2**: A at $-x$, $-y+1$, $-z$; for **4**: i at x, $2-y$, $1/2+z$.

results are listed in table 1. Selected bond lengths and angles of **1** · $2H_2O$, **2** and **4** are listed in table 2.

3. Results and discussion

3.1. *Description of crystal structures of the complexes*

A perspective view of the metal coordination environments of [Zn_2(dmpzpo-O,N,N′)$_2$(NO_3)$_2$] · $2H_2O$ with the atomic numbering scheme is shown in figure 1 and selected bond lengths and angles are listed in table 2. Structurally, **1** · $2H_2O$ is similar to *bis* [μ-4-methyl-2,6-*bis*(pyrazol-1-ylmethyl)phenolato-κN^2O : κN^2O′]-*bis*[chloridozinc (II)] ($Zn_2L_2Cl_2$) [12]. The dinuclear species **1** · $2H_2O$ has $\bar{1}$ symmetry with two zinc ions bridged by two alkoxo groups with a Zn $\cdots$ Zn distance of 3.043 Å, shorter by ~0.2 Å than that in ($Zn_2L_2Cl_2$) [12]. Each zinc is coordinated by nitrogen donors of two pyrazole rings from one ligand and two oxygen atoms of two alkoxo groups and one oxygen of a nitrate. As a five-coordinate system, its structure is intermediate between the idealized square-pyramidal and trigonal-bipyramidal extremes with a geometric parameter $\tau = 0.30$ according to the definition of Addison [13]. The distortion away from the square-pyramidal geometry is the consequence of inter- and intra-ligand steric interference in the equatorial plane. The Zn–O1, Zn–O1A and Zn–O2 bond distances are 2.042(6), 1.994(6) and 2.166(7) Å, respectively. The distances of Zn–N1A and Zn–N4 are 2.110(7) and 2.097(7) Å, respectively, with average bond distance of 2.099(7) Å. The Zn1, O1, Zn1A, O1A atoms form a parallelogram, with Zn–O–Zn and

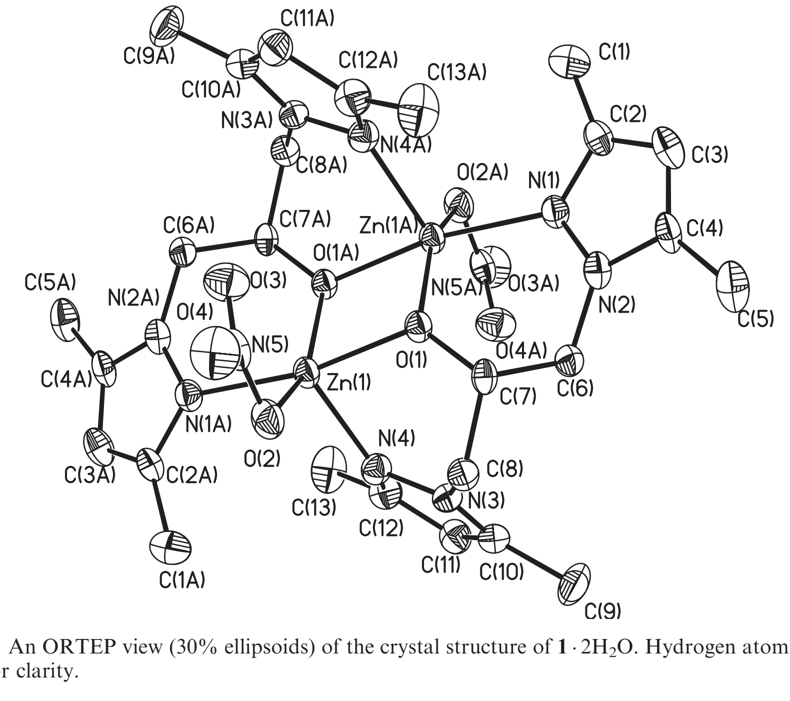


Figure 1. An ORTEP view (30% ellipsoids) of the crystal structure of **1** · $2H_2O$. Hydrogen atoms have been omitted for clarity.

O–Zn–O angles of 97.9(2) and 82.1(2) Å, respectively. The two nitrate counter ions are *trans*.

The structure of $[Ni_2(dmpzpo\text{-}O,N,N')_2(CH_3CN)_2]^{2+}$, **2**, is shown in figure 2, and selected bond lengths and angles are listed in table 2. The crystal structure of **2** is similar to that of $\mathbf{1}\cdot 2H_2O$. The ClO_4^- counterion is not coordinated with the metal due to its weak binding ability. As a five-coordinate system, **2** is more square-pyramidal in structure than $\mathbf{1}\cdot 2H_2O$ with the geometric parameter $\tau = 0.22$. The apical position of the square pyramid is occupied by acetonitrile, with a Ni–N5 bond distance of 2.052(5) Å, which is comparable to those of $Ni\text{–}N_{pz}$ bond distances (Ni–N1 = 2.046(4) and Ni–N4 = 2.040(5) Å), indicative of a strong interaction between acetonitrile and nickel(II) ion. In **2**, similar to $\mathbf{1}\cdot 2H_2O$, Ni1, O1, Ni1A, O1A atoms form a parallelogram with Ni–O–Ni and O–Ni–O angles of 102.7(2) and 77.3(2) Å, respectively, and Ni1–O1 and Ni1–O1A bond distances of 1.931(4) and 1.994(4) Å, respectively. Two pyrazole rings of each ligand fold toward one nickel, unlike the coordination mode of pyrazole rings in $\mathbf{1}\cdot 2H_2O$.

A perspective view of the metal coordination environment of **4** with the atomic numbering is shown in figure 3; selected bond lengths and angles are listed in table 2. The palladium is in a slightly distorted square-planar coordination geometry; the basal plane consists of two nitrogens of the pyrazole rings and two chlorides. The angles between *trans* coordinating atoms slightly deviate from linearity (177.82–178.46°). The average Pd–N and Pd–Cl bond lengths are 2.013(2) and 2.2846(7) Å, respectively. The Cl1–Pd–Cl2 angle is 91.78(3)°. One chloride ion is hydrogen bonded to the hydroxyl group of the adjacent molecule, forming a one-dimensional chain

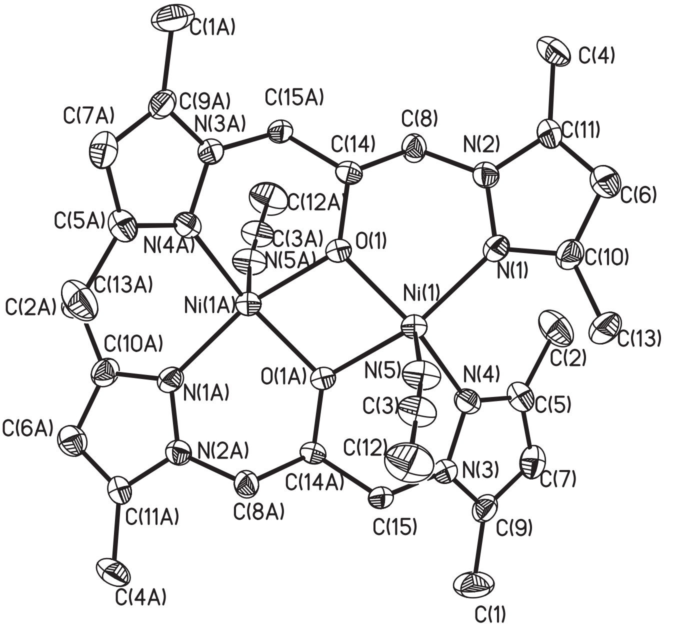


Figure 2. An ORTEP view (30% ellipsoids) of the crystal structure of the cationic part in the crystal of **2**. Hydrogen atoms have been omitted for clarity.

along the c axis depicted in figure 4, with O $\cdots$ Cl contacts of 3.217(5) Å and O–H $\cdots$ Cl angle of 156.97(6)°.

3.2. *Infrared spectra*

IR spectra in the range 4000–400 cm^{-1} show all the expected bands corresponding to the ligand and the counter ions. In the ligands an intense band at 3200 cm^{-1} indicates the presence of a hydroxyl group. For all Zn(II) and Ni(II) complexes the disappearance of the characteristic stretching vibration of the hydroxyl indicates deprotonation and coordination of alkoxo groups with metal ions. Complexes **2**, **5**, **6**, and **7** display ionic perchlorate bands at *ca.* 1100 and 630 cm^{-1}. Complexes $\mathbf{1} \cdot 2H_2O$ and **3** show the characteristic band of ionic nitrate at 1310 cm^{-1}. The stretching vibrations of the coordinated pyrazole rings shift to higher frequency in comparison with free pyrazole rings (from 1611 (C=C) and 1551 cm^{-1} (C=N) to 1632 (C=C) and 1555 cm^{-1} (C=N), respectively, for complex **2**, for example) indicative

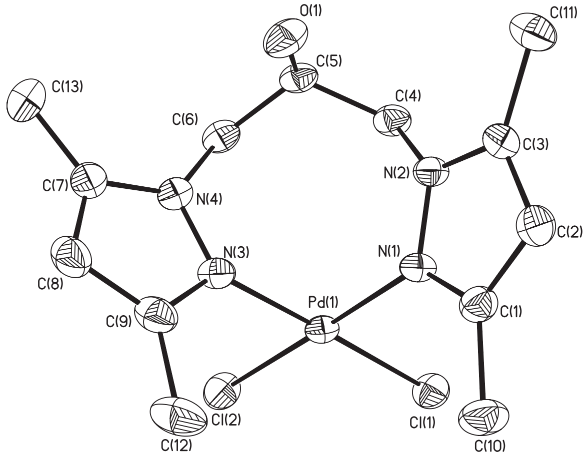


Figure 3. An ORTEP view (30% ellipsoids) of the crystal structure of **4**. Hydrogen atoms have been omitted for clarity.

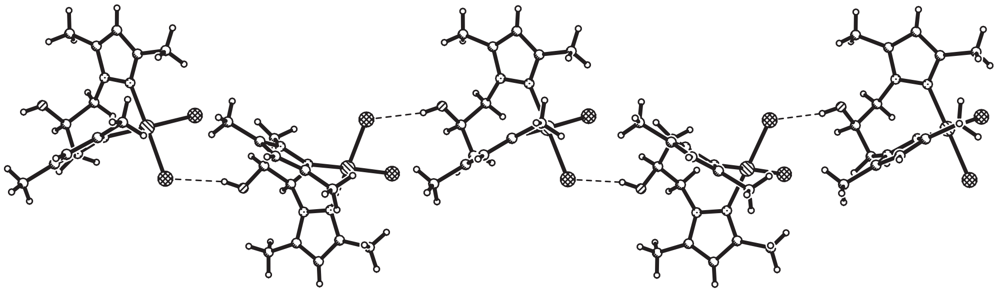


Figure 4. A view (omitting hydrogen atoms for clarity) of a fragment of the H-bonded one-dimensional array of **4** down the b axis.

of coordination of metal with the pyrazole rings [14a, 14b]. A sharp adsorption at 3444 cm^{-1} for the palladium(II) complex **4** can be ascribed to the free hydroxyl group of the ligand, showing that there was no interaction between the hydroxyl group with the Pd(II) although we tried to deprotonate using NaH, indicative of the strong tendency of Pd(II) ion toward square-planar environment. There was a medium band at 1163 cm^{-1} in the spectrum of **4** assigned to the ν(C–Cl) vibration [14c].

4. Conclusions

Two new pyrazole-based N, O, N ligands have been synthesized, and another was synthetically modified. Divalent zinc, nickel and palladium complexes derived from these pyrazole-based ligands were prepared. The crystal structures of $\mathbf{1} \cdot 2H_2O$ and **2** revealed binuclear Zn(II) and Ni(II) compounds, with distorted square-pyramid coordination geometry around each metal ion and a center of symmetry in each complex. The palladium(II) complex **4** showed a slightly distorted square-planar coordination environment around the Pd(II) and the molecules formed a one-dimensional chain through intermolecular $O\text{–}H \cdots Cl$ hydrogen bonding. Unfortunately, since we failed to grow single crystals suitable for X-ray diffraction analysis of Zn(II) and Ni(II) complexes derived from Hmppzpo and Hcpzpo, studying the steric effects of phenyl and cumyl groups on the coordination geometry was unfeasible.

Supplymentary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 626296, 640629 and 640630 for $\mathbf{1} \cdot 2H_2O$, **2** and **4**. Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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