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Synthesis of complexes with the polydentate ligand N,N′-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide

Yolanda Pérez [a], Andrew L. Johnson [b,*], Paul R. Raithby [b]

[a] Departamento de Química Inorgánica y Analítica, E.S.C.E.T, Universidad Rey Juan Carlos 28933 Móstoles, Madrid, Spain
[b] Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

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ABSTRACT

The pentadentate ligand N,N′-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide ($POPYH_4$) has been used to prepare a variety of new complexes $[HNEt_3]_2[Zn_4Cl(POPYH)_3]$ (**2**), $[HNEt_3][PdCl(POPYH_2)]$ (**3**), $[HNEt_3][Ni(POPYH)]$ (**4**) and K[Ni(POPYH)] (**5**) which show the versatility of this multidentate ligand. The complexes have been characterised spectroscopically and their molecular and crystal structures have been determined by single crystal X-ray diffraction techniques. In these complexes the ligand exhibits different modes of coordination towards different transition metal ions. The structure of triethylammonium salt of the Zn(II) dianion **2** consists of an unusual tetra-zinc core supported by three POPYH ligands each one of which links two adjacent zinc centres through two oxygen and two nitrogen donor atoms. The salt of the square planar Pd(II) anion **3** contains one $POPYH_2$ ligand which coordinates in a tridentate fashion through the two deprotonated amido groups and by the central pyridine nitrogen donor. The two Ni(II) salts **4** and **5** contain the same $[Ni(POPYH)]^-$ anion in which the square planar Ni(II) centre is chelated by a POPYH ligand through the two deprotonated amido nitrogen atoms, the pyridine nitrogen and a deprotonated hydroxyl group.

1. Introduction

The interest in metal complexes of ligands that contain amide moieties stems from their occurrence in metalloproteins and metal complexes of glycopeptide antibiotics such as bleomycin (BLM) [1]. In addition, the use of ligands pyridine-2,6-dicarboxamide to stabilize high formal oxidation states of metal ions due to the good σ-donor properties of the deprotonated nitrogen atom has been well documented [2]. These ligands have been considered as model compounds for the study of the effect of intramolecular and intermolecular hydrogen bonding [3]. In addition, pyridine carboxamide ligands have found use in asymmetric catalysis, [4] dendrimer synthesis [4a] and gold(III) [5] and platinium(II) [6] complexes with antitumour properties.

Structurally characterised Iron(III) complexes with the N,N′-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide ligand ($POPYH_4$), which is based on the pyridine-2,6-dicarboxamide moiety and contains two additional phenolic groups donors, have been reported previously [7]. Two of these iron complexes contain the fully deprotonated pentadentate ligand which lies in the equatorial plane of metal and the coordination environment is completed by two monodentate ligands which sit the two axial sites to give an unusual coordination number of seven for Fe(III). In two other structurally characterised Fe(III) complexes the ligand is only partially deprotonated and is coordinated to the iron centre through the deprotonated phenolate oxygen atoms in a bidentate fashion. Coordination and reactivity of the $POPYH_4$ ligand towards a range of M(II) ions (Co, Ni, Cu, Mn, Zn and Cd) [8] and lanthanide ions (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Y) [9] have also been described, but to date structural elucidation of these structures has not been reported. We have previously reported the structure of the potassium complex $[POPYH_4{\cdot}KOAc{\cdot}2NCMe]$ as part of a wider study into the use of the $POPYH_4$ ligand system in extended molecular arrays [10]. In this paper we report the synthesis, characterisation and crystal structures of a series of new complex anions of zinc, palladium and nickel that contain partially deprotonated forms of the N,N′-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide ligand and which displays a range of coordination modes that are dependant on the electronic requirements of the metal centres.

2. Results and discussion

2.1. Structural analysis of the ligand POPYH

The ligand $POPYH_4$ has been synthesised previously [8] by reacting 2 equiv. of 2-aminophenol with 1 equiv. of 2,6-pyridinedicarbonyl dichloride in THF. However, since the crystal structure of

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* Corresponding author. Fax: +44 1225383183.
E-mail address: a.l.johnson@bath.ac.uk (A.L. Johnson).

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the compound has not been reported yellow needles of the ligand suitable for X-ray analysis were grown by vapour diffusion of ethyl acetate into DMF solution of the ligand and a crystal structure determination carried out.

In the crystal the neutral $POPYH_4$ molecule co-crystallises with a dimethylformamide solvent molecule. The molecular structure of the $POPYH_4$ ligand (**1**) is shown in Fig. 1 which also includes the dimethylformamide molecule, while selected bond lengths and angles are listed in Table 1. The molecular parameters all lie within the expected ranges and are similar to those reported for both [POPYH4·KOAc·2NCMe] [10] and N,N′-bis(2-methoxyphenyl)pyridine-2,6-dicarboxamide [11]. The $C–N_{amide}$ [N(2)–C(6) = 1.349(2), N(3)–C(13) = 1.3417(18) Å] and C═O [O(1)–C(6) = 1.2256(17), O(2)–C(13) = 1.2337(16) Å] distances are in accord with the distances found in derivatives of 2,6-pyridinedicarboxamide [$C–N_{amide}$ = 1.317–1.367 and C═O = 1.226–1.247 Å] [12]. The $POPYH_4$ molecule is not planar and the two phenyl rings make angles of 8.9(1) and 18.3(2)° with the central pyridine ring, respectively, while the dihedral angle between the two phenyl rings is 25.5(2)°. The torsion angles of C(5)–C(6)–N(2)–C(7) 177.1(1)° and O(1)–C(6)–N(2)–C(7) −3.6(3)° and C(1)–C(13)–N(3)–C(14) −173.7(1) and O(2)–C(13)–N(3)–C(14) 3.8(2)° confirm that the carboxamide units are essentially planar. In the dimethylformamide molecule the N(4) atom adopts a planar geometry with a maximum deviation from the N(4)C(20)C(21)C(22) plane of −0.003(1) Å for N(4). Overall, the bond parameters for $POPYH_4$ similar to those reported in the potassium bis-acetonitrile adduct [10].

In the crystal structure of $POPYH_4$.DMF there is a network of hydrogen bonds linking adjacent molecules. The two hydrogen atoms of the hydroxyl groups of $POPYH_4$ act as hydrogen bond donors; one, H(4O), to the carbonyl oxygen atom O(2) in an adjacent $POPYH_4$ molecules and the second, H(3O), to the oxygen of the dimethylformamide solvent O(5). The parameters associated with these hydrogen bonds are presented in Table 1.

Table 1
Selected bond lengths (Å) and angles (°) for $POPYH_4$ 1

Bond lengths (Å)			
O(1)–C(6)	1.2256(17)	O(2)–C(13)	1.2337(16)
N(2)–C(6)	1.349(2)	N(3)–C(13)	1.3417(18)
N(2)–C(7)	1.4102(19)	N(3)–C(14)	1.4056(19)
C(8)–O(3)	1.3618(17)	O(4)–C(15)	1.3591(17)
Bond angles (°)			
O(1)–C(6)–C(5)	120.87 (14)	O(2)–C(13)–C(1)	121.46(13)
O(1)–C(6)–N(2)	124.99(14)	O(2)–C(13)–N(3)	123.93(14)
N(2)–C(6)–C(5)	114.13(13)	N(3)–C(13)–C(1)	114.57(12)
C(6)–N(2)–C(7)	129.17(14)	C(13)–N(3)–C(14)	128.95(12)
Hydrogen-bonds (Å)			
D–H···A	d(D–H)	d(H···A)	d(D···A)
N(2)–H(2N)···N(1)	0.903(17)	2.226(16)	2.6783(17)
N(3)–H(3N)···N(1)	0.882(16)	22.49(16)	2.6992(18)
O(3)–H(3O)···O(5)	0.94(2)	1.70(2)	2.6340(17)
O(4)–H(4O)···O(2A)	0.92(2)	1.74(2)	2.6584(14)

Symmetry codes used to generate equivalent atoms (A): *x + 1, y, z.*

3. Syntheses of complexes

In order to explore the versatility of $POPYH_4$ (**1**) with a range of transition metal halides and to establish the factors that influence the level of deprotonation of the ligand in the complexes obtained, reactions between **1** and the metal salts, $ZnCl_2$, $PdCl_2$ and $NiCl_2$, in the presence of a base (Scheme 1) have been explored. In each reaction a solution of the ligand **1** in hot CH_3CN was treated with an excess of NEt_3 to facilitate the removal of the protons that could be dissociated and 1 equiv. of the $ZnCl_2$, $PdCl_2$ or $NiCl_2·6H_2O$ were added to obtain the complexes **2**, **3** and **4**, respectively. The complex **5** was synthesised by reaction of ligand **1** dissolved in hot methanol with 2 equiv. of $NiCl_2·6H_2O$ and KOH as the base.

The ^1H NMR spectrum of **3** shows only one set of the signals indicating that the two phenolic rings are magnetically equivalent in solution. Nevertheless the spectra ^1H NMR spectra of the complexes **2**, **4** and **5** display a more complex pattern for the signals for the phenolic rings suggesting the different coordination of the ligand to metal. In the ^1H NMR spectra of **3**, **4** and **5** the absence of the amide protons confirms that the ligand coordinates in a deprotonated form. In the ^1H NMR spectrum of **2** the disappearance of the OH signal indicates that the coordination of the ligand is *via* the deprotonated phenolic oxygen donors. In the case of complexes **4** and **5**, ^1H NMR studies showed no indication of exchange between the coordinated (de-protonated) and uncoordinated

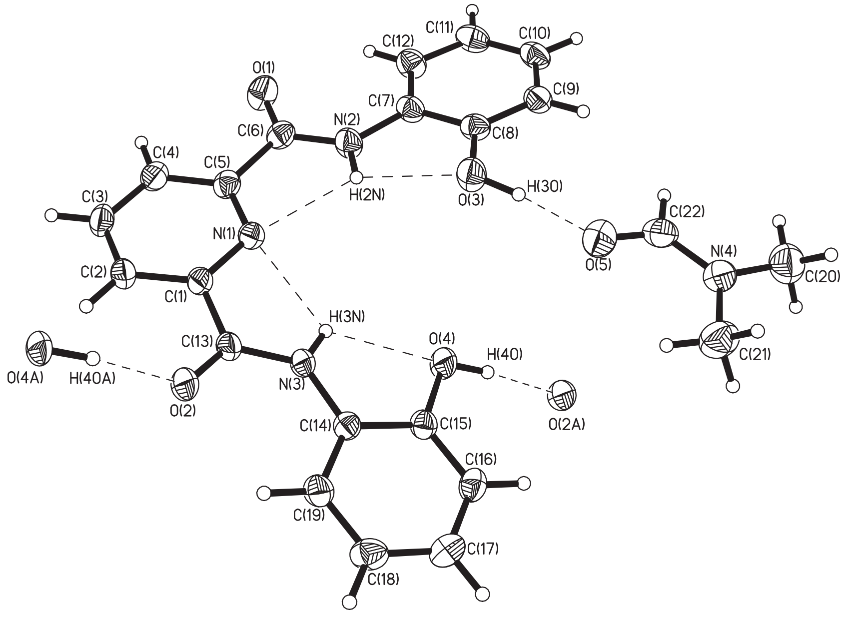
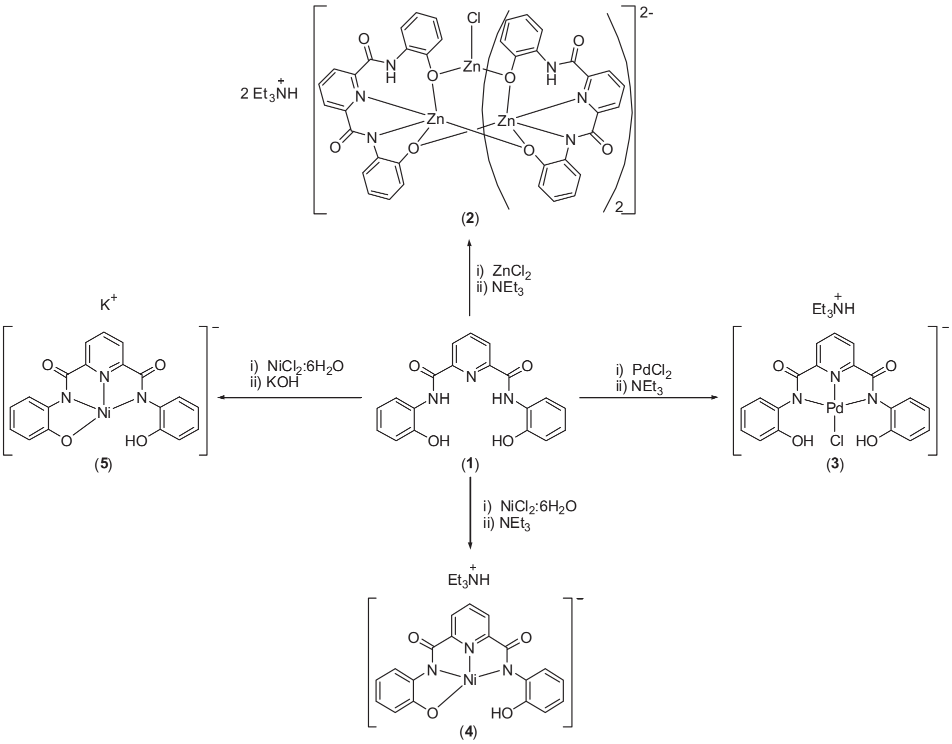


Fig. 1. The structure of $POPYH_4·DMF$ showing the atom numbering scheme and the H-bonding netwok. The O(2A), H(4OA), O(4A) atoms are generated by the symmetry operator *x* + 1, *y*, *z*, and are included to show the H-bonding environment around the $POPYH_4$ molecule. The anisotropic displacement parameters have been drawn at the 50% probability level.



Scheme 1.

(protonated) phenolic groups, a feature which has been observed in related *bis*-aminopropane-pyridine-2,6-dicarboxamide complexes [13].

3.1. Molecular structure of $[HNEt_3]_2[Zn_4Cl(POPYH)_3]$ (2)

Reaction of $ZnCl_2$ with 1 in a 1:1 stoichiometric ratio, in the presence of NEt_3, resulted in an immediate colour change to the reaction mixture. After workup and cooling at −10°C a crop of yellow/orange crystals **2** where isolated and characterised. Crystallographic analysis of a suitable crystal of **2** shows that the complex is composed of an unusual tetranuclear $[Zn_4Cl(POPYH)_3]^{2-}$ anion with two triethylammonium cations. In the structure one of the triethylammonium cations was so severely disordered that no chemically sensible model for it could be refined so that, as a last resort, it and several part occupancy water molecules were removed from the model and the electron density compensated for using the SQUEEZE [14] routine in PLATON [15]. Satisfactory refinement was then achieved and the structural parameters did not alter significantly between the refinements using the unSQUEEZEd and the SQUEEZEd data. Full confidence can be given to the charge balance in the structure as the remaining amine hydrogen atom was clearly located in the electron density difference map (but was refined with an AFIX constraint).

The unusual $[Zn_4Cl(POPYH)_3]^{2-}$ unit consist of four zinc centres linked by three $[POPYH]^{3-}$ ligands with one zinc atom additionally coordinated to a chlorine ligand (Fig. 2). Selected bond lengths and angles are collected in Table 2. If viewed down the Cl1–Zn1 bond direction the dianion has *pseudo*-three-fold symmetry. Each zinc centre is tetra-coordinate adopting the expected tetrahedral geometry. The metals are linked by two deprotonated phenolic oxygen atoms from two different ligands. Zn(2), Zn(3), Zn(4) are also coordinated by one deprotonated carboxamido nitrogen donor and one pyridine nitrogen donor from the same ligand, while the coordination environment of Zn(1) is completed by a third phenolic oxygen atom and a terminal chloride atom. The bonds length of Zn(3)–O(4), Zn(4)–O(8) and Zn(2)–O(12) are notably longer than the other due to the coordination of adjacent carboxamido nitrogen to the metal. The Zn–N_{py} distances [Zn(3)–N(1) = 2.213(5), Zn(4)–N(4) = 2.266(5) and Zn(2)–N(7) = 2.223(5) Å] are longer than those found in related zinc pyridine complexes [16].

A search of the Cambridge Structural Database [17] reveals that the structure of the anion is quite unique. While there are over 100

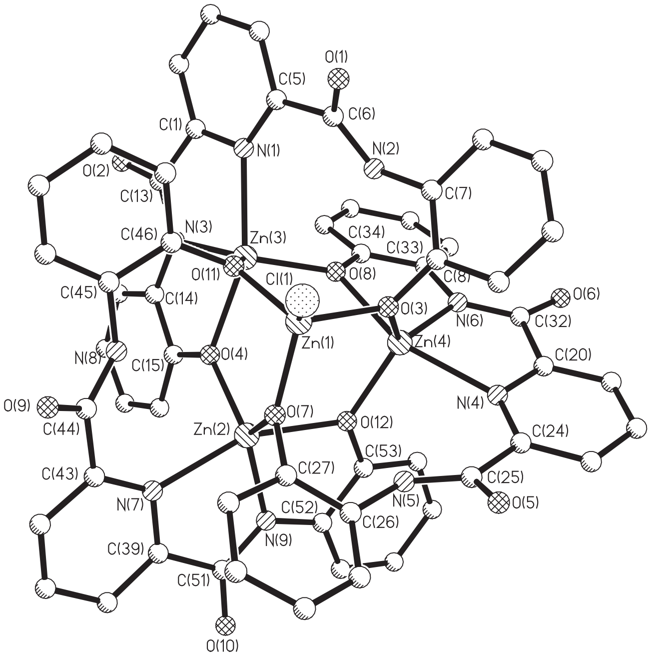


Fig. 2. The structure of the $[Zn(POPYH)_3Cl]^{2-}$ dianion in **2** showing the atom numbering scheme. Hydrogen atoms have been omitted for clarity.

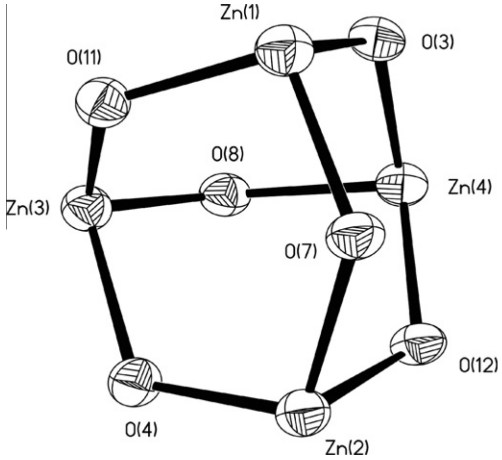


Fig. 3. The “Zn_4O_6” core in the structure of the $[Zn(POPYH)_3Cl]^{2-}$ dianion.

examples of Zn_4O_4 cubic core structures this appears to be the first example of a Zn_4O_6 core that can best be described as an adamantane-like structure, as shown in Fig. 3. This structure reflects the versatility of the $[POPYH_{4-n}]^{n-}$ ligand and the ability to stabilise polynuclear metal complexes. This is an aspect of its chemistry which has not been established previously since, in all the structurally characterised examples of complexes that contain this ligand, the ligand only coordinates to one metal centre [7].

3.2. Molecular structure of $[HNEt_3][Pd(POPYH_2)Cl]$ (3)

The X-ray crystallographic study reveals that the salt **3** is composed of $[Pd(POPYH_2)Cl]^-$ anion with a triethylammonium cation. Selected bond lengths and angles are collected in Table 3. The palladium atom adopts the distorted squared-planar geometry expected for four-coordinate Pd(II). The $POPYH_2^{2-}$ ligand employs three nitrogen donor atoms (two deprotonated carboxamido nitrogen atoms and one pyridine nitrogen atom) to coordinate the palladium centre, as illustrated in Fig. 4. The fourth coordination site is occupied by chlorine atom with Pd(1)–Cl(1) distance 2.303(2) Å, similar to the normal value found for Cl^- *trans* to a pyridine ligand [18]. The Pd(1)–N(3) and Pd(1)–N(1) bond lengths are in the expected region for Pd(1)–N_{amide} and Pd(1)–N_{py} interactions, respectively [19]. The bite angles N(1)–Pd(1)–N(3) and N(1)–Pd(1)–N(2) of the ligand are 79.9(3)° and 80.1(3)°, respectively, while the N(2)–Pd(1)–N(3) angle of 160.0(3)° angle is *ca.* 20° from the ideal angle of 180°.

Nevertheless, the N(1)–Pd(1)–Cl(1) angle of 177.88(19)° is close to linear. The chelate rings show subtle differences upon complexation (ligand **1**: C(13)–N(3)–C(14) = 128.94(12)°, C(6)–N(2)–C(7) = 129.16 (13)° while the equivalent angles in complex **3** are C(7)–N(3)–C(21) = 117.1(7)°, C(6)–N(2)–C(7) = 118.1(7)°).

In the crystal the salt crystallises in the monoclinic space group *P2₁/c* and the cation and anion are linked by an intermolecular hydrogen bond [N(4)–H(4)···O(1): 0.84 Å longer than those found in related zinc, 1.89 Å, 2.786(9) Å, 162.6°]. There is also an intramolecular hydrogen bond involving the hydroxyl hydrogen atom on O(2) [O(2)–H(2A)···O(1): 0.94 Å, 1.95 Å, 2.691(7) Å, 146.9°] and an intermolecular hydrogen bond involving the other hydroxyl hydrogen bond [O(4)–H(4A)···O3 {*1−x, −y, 1−z*} 0.84 Å, 1.93 Å, 2.733(8) Å, 160.8°].

3.3. Molecular structure of $[HNEt_3][Ni(POPYH)]\ 1.5H_2O$ (4)

The crystal structure of complex **4** reveals that the asymmetric unit contains a $[Ni(POPYH_2)]^-$ anion with a triethylammonium cation and one and a half molecules of water. Selected bond lengths

Table 3
Selected bond lengths (Å) and angles (°) for the complex **3**

Bond lengths (Å)			
Pd(1)–N(1)	1.940(6)	Pd(1)–Cl(1)	2.303(2)
Pd(1)–N(3)	2.028(6)	Pd(1)–N(2)	2.060(7)
O(2)–C(16)	1.387(11)	O(1)–C(1)	1.270(10)
N(2)–C(1)	1.333(10)	N(3)–C(7)	1.347(10)
N(2)–C(11)	1.434(10)	N(3)–C(21)	1.435(10)
C(7)–O(3)	1.246(9)	O(4)–C(26)	1.372(10)
Bond angles (°)			
N(2)–Pd(1)–N(3)	160.0(3)	N(1)–Pd(1)–Cl(1)	177.88(19)
N(1)–Pd(1)–N(2)	80.1(3)	N(1)–Pd(1)–N(3)	79.9(3)
O(1)–C(1)–C(2)	118.2(8)	O(3)–C(7)–C(6)	119.0(7)
O(1)–C(1)–N(2)	127.3(8)	O(3)–C(7)–N(3)	128.1(8)
N(2)–C(1)–C(2)	114.5(8)	N(3)–C(7)–C(6)	112.8(8)
C(1)–N(2)–C(11)	118.1(7)	C(7)–N(3)–C(21)	117.1(7)

Table 2
Selected bond lengths (Å) and angles (°) for the complex **2**

Bond lengths (Å)					
Zn(1)–O(3)	1.963(4)	Zn(1)–O(7)	1.964(4)	Zn(1)–O(11)	1.957(4)
Zn(4)–O(3)	1.990(4)	Zn(2)–O(7)	2.031(4)	Zn(3)–O(11)	2.001(4)
Zn(2)–O(4)	1.972(4)	Zn(3)–O(8)	1.955(4)	Zn(2)–O(12)	2.126(4)
Zn(3)–O(4)	2.155(4)	Zn(4)–O(8)	2.132(4)	Zn(4)–O(12)	1.973(4)
Zn(3)–N(1)	2.213(5)	Zn(4)–N(4)	2.266(5)	Zn(2)–N(7)	2.223(5)
Zn(3)–N(3)	1.975(5)	Zn(4)–N(6)	1.957(5)	Zn(2)–N(9)	1.988(5)
O(1)–C(6)	1.230(8)	O(5)–C(25)	1.238(8)	O(9)–C(44)	1.246(8)
O(2)–C(13)	1.235(9)	O(6)–C(32)	1.256(8)	O(10)–C(51)	1.235(8)
O(3)–C(8)	1.378(7)	O(7)–C(27)	1.392(7)	O(11)–C(46)	1.357(8)
O(4)–C(15)	1.359(7)	O(8)–C(34)	1.370(8)	O(12)–C(53)	1.354(7)
Zn(1)–Cl(1)	2.189(2)				
Bond angles (°)					
Zn(1)–O(3)–Zn(4)	120.1(2)	Zn(1)–O(7)–Zn(2)	125.9(2)	Zn(1)–O(11)–Zn(3)	122.3(2)
Zn(2)–O(4)–Zn(3)	122.8(2)	Zn(3)–O(8)–Zn(4)	122.9(2)	Zn(4)–O(12)–Zn(2)	123.1(2)
O(4)–Zn(3)–N(1)	158.8(2)	O(8)–Zn(4)–N(4)	159.1(2)	O(12)–Zn(2)–N(7)	158.3(2)
N(3)–Zn(3)–N(1)	80.2(2)	N(6)–Zn(4)–N(4)	79.7(2)	N(9)–Zn(2)–N(7)	81.0(2)
O(1)–C(6)–C(5)	118.1(7)	O(5)–C(25)–C(24)	116.8(6)	O(9)–C(44)–C(43)	118.1(6)
O(2)–C(13)–C(1)	117.9(6)	O(6)–C(32)–C(20)	116.7(6)	O(10)–C(51)–C(39)	117.3(6)
O(1)–C(6)–N(2)	124.6(7)	O(5)–C(25)–N(5)	124.4(7)	O(9)–C(44)–N(8)	122.2(6)
O(2)–C(13)–N(3)	128.9(7)	O(6)–C(32)–N(6)	128.8(7)	O(10)–C(51)–N(9)	128.5(6)
N(2)–C(6)–C(5)	117.4(6)	N(5)–C(25)–C(24)	118.8(6)	N(8)–C(44)–C(43)	119.7(6)
N(3)–C(13)–C(1)	113.2(6)	N(6)–C(32)–C(20)	114.6(6)	N(9)–C(51)–C(39)	113.2(5)
C(6)–N(2)–C(7)	122.1(6)	C(25)–N(5)–C(26)	123.6(6)	C(44)–N(8)–C(45)	122.7(6)
C(13)–N(3)–C(14)	125.1(6)	C(32)–N(6)–C(33)	125.0(6)	C(51)–N(9)–C(52)	124.4(5)

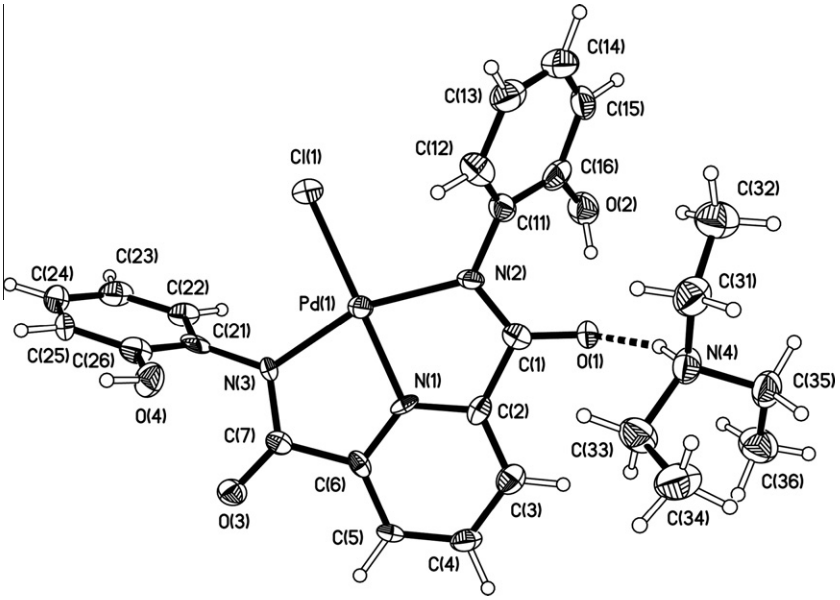


Fig. 4. The structure of the salt $[HNEt_3][Pd(POPYH_2)Cl]$ **3** showing the intermolecular hydrogen bond between the cation and the anion. The anisotropic displacement parameters have been drawn at the 50% probability level.

Table 4
Selected bond lengths (Å) and angles (°) for the complex **4**.

Bond lengths (Å)			
Ni(1)–N(1)	1.806(2)	Ni(1)–O(3)	1.862(2)
Ni(1)–N(2)	1.842(2)	Ni(1)–N(3)	1.907(2)
C(13)–O(2)	1.247(3)	O(1)–C(6)	1.249(2)
N(3)–C(13)	1.340(3)	N(2)–C(6)	1.333(3)
C(14)–N(3)	1.422(3)	N(2)–C(7)	1.408(3)
O(4)–C(15)	1.359(3)	O(3)–C(8)	1.353(3)
Bond angle (°)			
N(2)–Ni(1)–N(3)	167.08(8)	N(1)–Ni(1)–O(3)	171.44(7)
N(1)–Ni(1)–N(2)	83.68(8)	N(1)–Ni(1)–N(3)	83.42(8)
O(1)–C(6)–C(5)	122.58(19)	O(2)–C(13)–C(1)	119.95(19)
O(1)–C(6)–N(2)	128.3(2)	O(2)–C(13)–N(3)	128.9(2)
N(2)–C(6)–C(5)	109.11(17)	N(3)–C(13)–C(1)	111.11(17)
C(6)–N(2)–C(7)	129.24(17)	C(13)–N(3)–C(14)	120.17(17)

and angles are collected in Table 4. The geometry around the central nickel atom is close to square planar, with the four donor atoms consisting of two deprotonated carboxamido nitrogen atoms, one deprotonated phenolate oxygen atom and one pyridine nitrogen atom as displayed in Fig. 5. The Ni(1)–N_{amide} distances [1.8415(17) and 1.9066(17) Å] are similar to those found in other square-planar Ni complexes with pyridine amide ligands (1.835–1.932 Å) [20]. Nevertheless, the Ni(1)–N_{amide} distances are shorter, compared to those in Ni complexes where the pyridine amide ligands are coordinated in a tridentate mode (2.109–2.135 Å) [2a,21]. The demands of the ligand bite angles are reflected in the relatively narrow N(1)–Ni(1)–N(2) = 83.68(8)° and N(1)–Ni(1)–N(3) = 83.42(8)° angles. The *trans* N(2)–Ni(1)–N(3) = 167.08(8)° and N(1)–Ni(1)–O(3) = 171.44(7)° angles also show deviations from the ideal value of 180°.

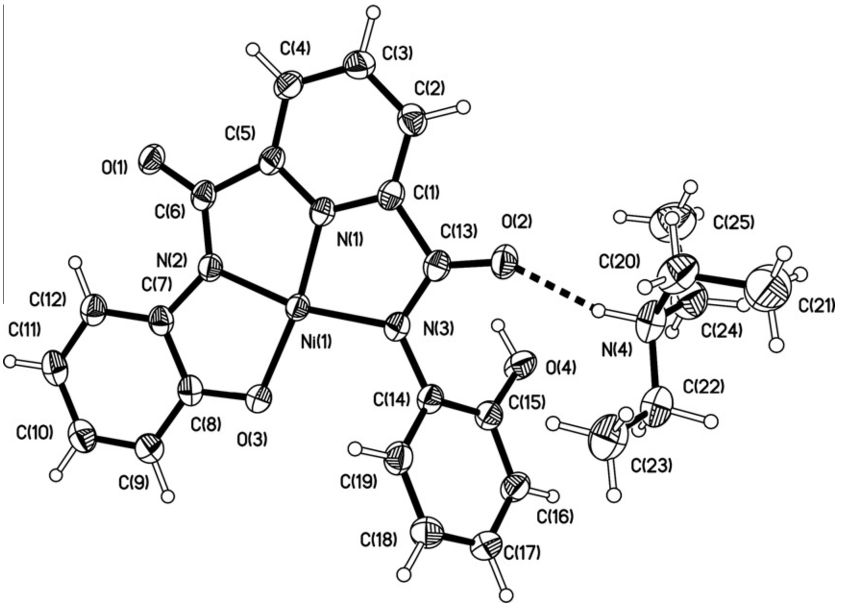


Fig. 5. The structure of $[HNEt_3][Ni(POPYH)]$ **4** showing the atom numbering scheme. The solvent water molecules have been omitted for clarity. The anisotropic displacement parameters have been drawn at the 50% probability level.

In the crystal structure the cation and anion are linked through an intermolecular hydrogen bond from the triethylammonium proton to a carbonyl oxygen atom on the anion [N(4)–H(4)···O(2) 0.931 Å, 1.85 Å, 2.737(2) Å, 159.8°]. There is also a hydrogen bond from the hydroxyl group on the anion with a carbonyl oxygen atom on an adjacent molecule [O(4)–H(4)···O(1) {*−x, 1 − y, −z*} 0.87(4) Å, 1.83(4) Å, 2.672(2) Å, 161(3)°] and a hydrogen bond involving one of the solvent water molecules and the coordinated hydroxyl oxygen atom on the anion, O(3) [O(1S)–H(1S)···O(3) {*−x, 1 − y, −z*} 0.827(10) Å, 2.002(15) Å, 2.797(3) Å, 161(4)°].

3.4. Molecular structure of K[Ni(POPYH)].2MeOH (5)

In the crystal structure of K[Ni(POPYH)]·2MeOH each asymmetric unit contains one cation, one anion and two molecules of methanol solvent. The [Ni(POPYH)]$^-$ anion is essentially identical to that found in **4**. The molecular structure of the anion **5** is illustrated in Fig. 6 while selected bond lengths and angles are collected in Table 5. The coordination to nickel is close to square planar, similar to that for Ni in the complex **4**. The hydroxyl hydrogen on the uncoordinated oxygen atom, O(4), forms an intermolecular hydrogen bond to the carbonyl oxygen atom, O(1), on an adjacent anion [O(4)–H(4O)···O(1) {*−x, 1 − y, −z*} 0.830(10) Å, 1.92(2) Å, 2.649(3) Å, 147(4)°], a feature that is also observed in the packing of **4**. However, the presence of the potassium ion and the two methanol molecules are responsible for major differences in the crystal packing compared to **4**. The two methanol solvent molecules hydrogen bond to the coordinated hydroxyl oxygen atom, O(3), on the [Ni(POPYH)]$^-$ anion [O(1S)–H(1O)···O3 0.827(10) Å, 1.900(12) Å, 2.716(3) Å, 169(3)°, and O(2S)–H(2O)···O3 0.830(10) Å, 1.965 (15) Å, 2.778(3) Å, 166(4)°. The K$^+$ ion interacts with one of the carbonyl oxygen atoms, O(1), on one [Ni(POPYH)]$^-$ anion (K(1)···O(1) 2.731(1) Å), and with the other carbonyl oxygen atom, O(2), on an adjacent anion related by the symmetry operation *1 − x, 1 − y, -z* at a distance of 2.570(2) Å. The cation also interacts with the methanol oxygen atoms O(1S) and O(2S) from two different symmetry related methanol molecules [K(1)···O(1S) {*x, −y − 1.5, z − 0.5*} 2.603(2) Å and K(1)···O(2S) {*1 − x, 1 − y, −z*} 2.570(2) Å], and the uncoordinated hydroxyl oxygen atom O(4) related by the symmetry operation *−x, 1 − y, −z* at a distance of 2.933(3) Å. The potassium coordination environment is completed by an interaction with the π cloud of the C(17)–C(18) bond of the free aromatic ring [K(1)···C(17) {*x, −y-1.5, z − 0.5*} 3.424(4) and K(1)···C(18) {*x, −y − 1.5, z − 0.5*}3.317(4) Å]. This gives the potassium ion a distorted octahedral coordination environment as illustrated in Fig. 7.

Table 5
Selected bond lengths and angles for the complex (**5**)

Bond lengths (Å)			
Ni(1)–N(1)	1.801(3)	Ni(1)–O(3)	1.865(2)
Ni(1)–N(2)	1.835(2)	Ni(1)–N(3)	1.909(2)
C(13)–O(2)	1.239(4)	O(1)–C(6)	1.252(4)
N(3)–C(13)	1.358(4)	N(2)–C(6)	1.334(4)
C(14)–N(3)	1.432(4)	N(2)–C(7)	1.404(4)
O(4)–C(15)	1.372(4)	O(3)–C(8)	1.372(4)
Bond angles (°)			
N(2)–Ni(1)–N(3)	167.29(12)	N(1)–Ni(1)–O(3)	170.73(10)
N(1)–Ni(1)–N(2)	83.68(11)	N(1)–Ni(1)–N(3)	83.60(11)
O(1)–C(6)–C(5)	122.0(3)	O(2)–C(13)–C(1)	120.5(3)
O(1)–C(6)–N(2)	128.2(3)	O(2)–C(13)–N(3)	128.2(3)
N(2)–C(6)–C(5)	109.8(3)	N(3)–C(13)–C(1)	111.3(3)
C(6)–N(2)–C(7)	127.9(3)	C(13)–N(3)–C(14)	117.3(2)

4. Conclusion

The series of investigations in this work show that the N,N′-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide ligand (POPYH$_4$), under basic conditions, displays a versatile coordination chemistry in its interactions with a range of transition metal ions. Previously, only the chemistry with Fe(III) had been explored [9]. In a partially deprotonated form the ligand forms mononuclear monoanionic salt complexes with nickel(II) and palladium(II), in complexes **3**, **4** and **5**, satisfying the requirement of the square planar coordination geometry for these d^8 ions. In the reaction with Zn(II) salts a unique tetranuclear dianion **2** with an unusual

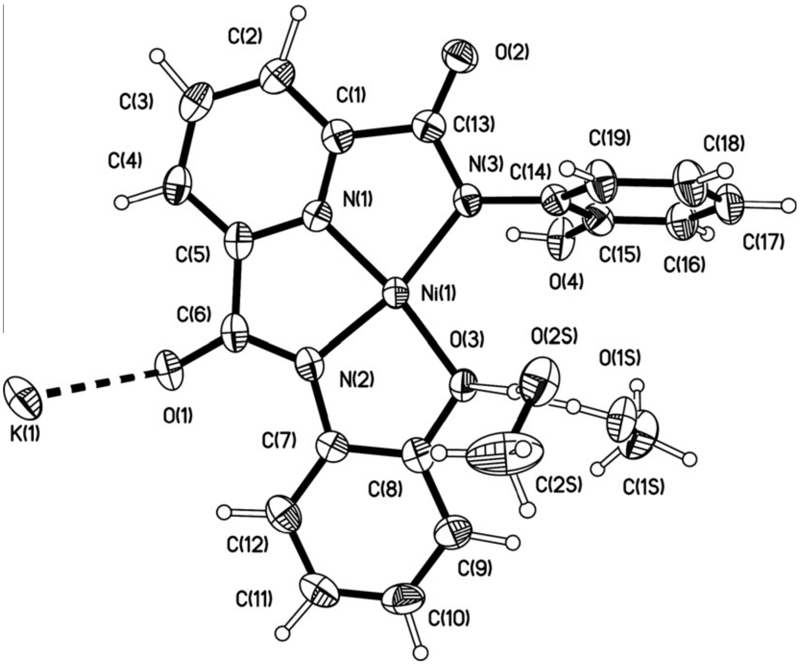


Fig. 6. The structure of K[Ni(POPYH)].2MeOH **5** showing the interaction of the [Ni(POPYH)]$^-$ anion with the K$^+$ cation and the two methanol solvent molecules. The anisotropic displacement parameters have been drawn at the 50% probability level.

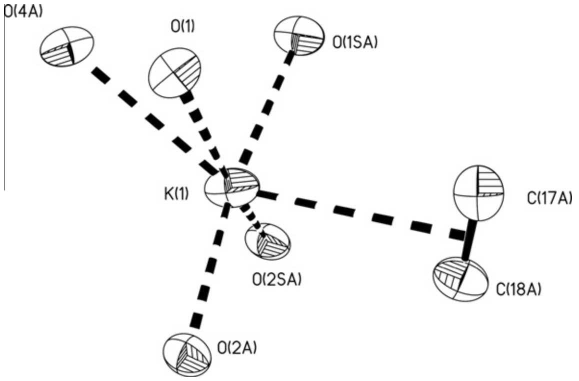


Fig. 7. The coordination environment of the potassium cation in K[Ni(POPYH)].2-MeOH **5** showing the distorted octahedral environment.

Zn_4O_6 adamantane core is formed. This represents the first polynuclear complex of the $[POPYH_{4-n}]^{n-}$ ligand and provides and impetus for studies of this ligand with early first row transition metals and the heavier transition metals from the second and third row of the *d* block.

5. Experimental section

Ligand synthesis was performed using standard Schlenk tube technique under an atmosphere of dry nitrogen. Complexation reactions were conducted under aerobic conditions. All commercial materials and solvents were used as received; Triethylamine and pyridine were distiled from appropriate drying agents.

6. Preparation of compounds

6.1. Synthesis of N,N′-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide ($POPYH_4$) (1)

The ligand was prepared following a reported procedure for 2,6-pyridinedicarbonyldichloride compound [8]. Pale yellow needles of the ligand suitable for X-ray analysis were grown by vapour diffusion of ethyl acetate into DMF solution of the ligand. Yield: 5.78 g, 92%.

6.2. Synthesis of $[HNEt_3]_2[Zn_4Cl(POPYH)_3]$ (2)

To a stirring solution of $POPYH_4$ (0.33 g, 1 mmol) in CH_3CN (50 mL) at 70 °C was added NEt_3 (0.3 mL, 2.15 mmol). The bright yellow solution was allowed to stir for 15 min and a solution of $ZnCl_2$ (0.14 g, 1 mmol) in hot CH_3CN (10 mL) was then added. The mixture was heated under reflux for 3 h and cooled to 25 °C. The solution was filtered and the solvent was removed under vacuum. The yellow solid was dissolved in ethanol and pale yellow/orange crystals were obtained. Yield: 0.74 g, 56%. ^1H NMR (300 MHz, DMSO-d^6, 25 °C): $\delta = 1.19$ (t, 3H, $-HNCH_2CH_3$), 3.01 (q, 2H $-HNCH_2CH_3$), 6.06 (d, 1H, $J = 8.1$ Hz, C_6H_4), 6.23 (m, 2H, C_6H_4), 6.38 (m, 2H, C_6H_4), 6.62 (t, 1H, $J = 7.8$ Hz, C_6H_4), 7.86 (d, 1H, $J = 8.1$ Hz, C_6H_4), 8.30 (t, 1H, $J = 7.8$ Hz, C_6H_4), 8.39 (d, 1H, $J = 7.8$ Hz, C_5H_3N), 8.49 (d, 1H, $J = 7.5$ Hz, C_5H_3N), 8.66 (d, 1H, $J = 8.1$ Hz, C_5H_3N), 11.43 (s, 1H, N–H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d^6, 25 °C): $\delta = 113.6$ (C10), 114.1 (C17), 116.4 (C11), 117.5 (C18), 118.6 (C19), 119.9 (C12), 120.7 (C9), 120.9 (C16), 124.9 (C7), 128.1 (C14), 135.7 (C–OH), 140.1 (C–OH), 150.0 (C5), 151.7 (C1), 152.8 (C3), 152.9 (C2, C4), 160.5 (C=O), 161.4 (C=O). Selected IR bands (KBr–Nujol, cm^{-1}): 3352 (w, NH), 1654 (s, C=O), 1608 (m), 1575 (s), 1526 (s), 1465 (s), 1316 (w), 1271 (m), 1239 (w). UV–Vis spectrum in EtOH, λ_{max} nm (ε, $M^{-1}\,cm^{-1}$): 311 (11560). Found (calc. for $C_{57}H_{33}N_9O_{12}ClZn_4$): C 51.39 (51.36), H 2.47 (2.50), N 9.30 (9.46).

6.3. Synthesis of $[HNEt_3][PdCl(POPYH_2)]$ (3)

To a stirring solution of $POPYH_4$ (0.66 g, 2 mmol) in CH_3CN (50 mL) at 70 °C was added NEt_3 (0.6 mL, 4.3 mmol). The solution was allowed to stir for 15 min and a solution of $PdCl_2$ (0.36 g, 2 mmol) in hot CH_3CN (10 mL) was then added. The mixture was refluxed for 3 h and then cooled to 25 °C. The brown solution was filtered and the solvent was removed under vacuum. The brown solid was dissolved in THF and yellow/orange crystals were obtained. Yield: 0.59 g, 66%. ^1H NMR (300 MHz, DMSO-d^6, 25 °C): $\delta = 1.17$ (t, 3H, $-HNCH_2CH_3$), 3.06 (q, 2H $-HNCH_2CH_3$), 6.62 (m, 2H, C_6H_4), 6.69 (m, 2H, C_6H_4), 6.89 (m, 2H, C_6H_4), 7.03 (m, 2H, C_6H_4), 7.78 (d, 1H, $J = 7.8$ Hz, C_5H_3N), 8.17 (m, 1H, C_5H_3N), 8.25 (t, 1H, $J = 7.8$ Hz, C_5H_3N), 9.52 (s, 1H, $-HNCH_2CH_3$) 10.41 (s, 2H, O–H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d^6, 25 °C): $\delta = 115.3$ (C10, C17), 116.9 (C11, C18), 123.8 (C19, C12), 128.2 (C9, C16), 133.7 (C7, C14), 139.4 (C–OH), 150.1 (C2, C4), 150.2 (C3), 163.1 (C5, C1), 167.3 (C=O). Selected IR bands (KBr–Nujol, cm^{-1}): 3210 (w, O–H), 1604 (s, C=O), 1582 (s), 1541 (s) 1457 (vs), 1377 (s), 1229 (w), 1172 (m), 1100 (w), 1035 (m), 761 (m). Found (calc. for $C_{19}H_{13}N_3O_4Pd{\cdot}HNEt_3$): C 54.32 (54.11), H 5.17 (5.09), N 9.92 (10.10).

6.4. Synthesis of $[HNEt_3][Ni(POPYH)]$ (4)

Complex **4** was made using an identical method to that used to synthesis **3**, using $NiCl_2{\cdot}6H_2O$ (0.48 g, 2 mmol). Complex **4** was isolated by filtration following recrystallization from hot acetonitrile to give complex **4** as yellow/orange crystals. Yield: 0.66 g, 66%. ^1H NMR (300 MHz, DMSO-d^6, 25 °C): $\delta = 1.12$ (t, 3H, $-HNCH_2CH_3$), 3.08 (q, 2H $-HNCH_2CH = 3$), 6.05 (m, 1H, C_6H_4), 6.18 (m, 1H, C_6H_4), 6.45 (m, 1H, $C_6H = 4$), 6.76 (m, 2H, C_6H_4), 6.94 (m, 1H, C_6H_4), 7.20 (m, 1H, C_6H_4) 7.35 (d, 1H, $J = 7.8$ Hz, C_6H_4), 7.52 (d, 1H, $J = 7.2$ Hz, C_5H_3N), 7.73 (m, 1H, C_5H_3N), 8.1 (t, 1H, $J = 7.8$ Hz, C_5H_3N), 10.44 (s, 1H, O–H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d^6, 25 °C): $\delta = 112.9$ (C10), 114.4 (C17), 117.6 (C11), 117.9 (C18), 118.6 (C19), 121.1 (C12), 122.3 (C9), 124.3 (C16), 128.0 (C7), 134.3 (C14), 139.4 (C–OH), 140.1 (C–OH), 150.4 (C5), 150.7 (C1), 153.6 (C3), 161.5 (C2, C4), 165.2 (C=O), 166.2 (C=O). Selected IR bands (KBr–Nujol, cm^{-1}): 3281 (w, O–H), 1617 (s, C=O), 1585 (s), 1464 (vs), 1377 (m), 1290 (m), 1180 (w), 1095 (w), 1031 (w), 731 (m). UV-Vis spectrum in EtOH, λ_{max} nm (ε, $M^{-1}\,cm^{-1}$): 311 (11300). Found (calc. for $C_{19}H_{13}N_3O_4Ni{\cdot}HNEt_3$): C 59.46 (59.32), H 5.29 (5.38), N 11.66 (11.07).

6.5. Synthesis of K[Ni(POPYH)] (5)

Complex **5** was made using an identical method to that used to synthesis **3**, using $NiCl_2{\cdot}6H_2O$ (0.48 g, 2 mmol) and KOH (0.25 g, 4.5 mmol) in place of triethylamine. Complex **5** was isolated by filtration following recrystallization from hot methanol to give complex **5** as yellow/orange crystals. Yield: 0.29 g, 72%. ^1H NMR (300 MHz, DMSO-d^6, 25 °C): $\delta = 6.06$ (m, 1H, C_6H_4), 6.14 (m, 1H, C_6H_4), 6.43 (m, 1H, C_6H_4), 6.72 (m, 2H, C_6H_4), 6.93 (m, 1H, C_6H_4), 7.20 (m, 1H, C_6H_4) 7.34 (d, 1H, $J = 7.8$ Hz, C_6H_4), 7.51 (d, 1H, $J = 7.2$ Hz, C_5H_3N), 7.71 (m, 1H, C_5H_3N), 7.99 (t, 1H, $J = 7.8$ Hz, C_5H_3N), 10.44 (s, 1H, O–H). 13C ^1H NMR (75 MHz, DMSO-d^6, 25 °C): $\delta = 111.8$ (C10), 113.4 (C17), 116.7 (C11), 117.4 (C18), 120.0 (C19), 121.2 (C12), 121.3 (C9), 123.2 (C16), 127.0 (C7), 133.2 (C14), 138.2 (C–OH), 139.0 (C–OH), 149.3 (C5), 149.7 (C1), 152.6 (C3), 161.5 (C2, C4), 164.2 (C=O), 165.2 (C=O). Selected IR bands (KBr–Nujol, cm^{-1}): 3321 (w, O–H), 1614 (s, C=O), 1573

Table 6
Crystal data for compounds **1–5**

	1	**2**	**3**	**4**	**5**
Chemical formula	$C_{19}H_{15}N_3O_4.(C_3H_7NO)$	$C_{69}H_{92}ClN_{11}O_{14}Zn_4$	$C_{25}H_{29}ClN_4O_4Pd$	$C_{25}H_{31}N_4NiO_{5.5}$	$C_{21}H_{20}KN_3NiO_6$
Formula weight	422.44	1596.47	591.37	534.25	508.21
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	7.4020(1)	16.5860(5)	10.0390(2)	12.1690(2)	7.6550(2)
b (Å)	10.8050(2)	15.4580(5)	20.0330(6)	10.8170(2)	13.5910(5)
c (Å)	26.6320(7)	29.9250(11)	12.9080(4)	18.5920(3)	20.7350(8)
α (°)	90	90	90	90.00	90.00
β (°)	97.487(1)	99.877(2)	112.598(1)	92.693(1)	90.876(1)
γ (°)	90	90	90	90	90
V (Å^3)	2111.83(7)	7558.6(4)	2396.64(11)	2444.60(7)	2157.00(13)
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Z	4	4	4	4	4
D_c (g cm^{-3})	1.329	1.403	1.639	1.452	1.565
μ (mm^{-1})	0.096	1.357	0.927	0.840	1.136
$F(0\,0\,0)$	888	3328	1208	1124	1048
Crystal size (mm)	0.30 × 0.15 × 0.15	0.15 × 0.10 × 0.08	0.20 × 0.13 × 0.01	0.20 × 0.13 × 0.10	0.15 × 0.15 × 0.10
T_{max}/T_{min}	0.994/0.908	1.000/0.892	1.000/0.844	1.000/0.910	1.000/0.898
θ limits (°)	3.36–25.02	2.91–23.35	3.57–20.86	3.62–30.50	3.15–27.49
Measured reflection	11760	10719 (after SQUEEZE)	14537	46658	14015
Unique reflections	3651	10719	2489	7280	4691
Independent reflections R_{int}	0.0424	0.000	0.1713	0.0736	0.0685
Observed reflections ($I > 2\sigma(I)$)	2770	7603	1842	4982	3237
R_1, wR_2 (obs data)	0.0364, 0.0850	0.0573, 0.1748	0.0558, 0.0860	0.0445, 0.1129	0.0463, 0.1085
R_1, wR_2 (all data)	0.0569, 0.0947	0.0845, 0.1913	0.0907, 0.0952	0.0820, 0.1323	0.0828, 0.1238
Max residual electron density (e Å^{-3})	0.162	0.513	0.535	0.702	0.406

(s), 1489 (s), 1463 (vs), 1377 (m), 1273 (m), 1144 (w), 1093 (w), 1029 (w), 732 (m). UV–Vis spectrum in EtOH, λ_{max} nm (ε, $M^{-1}\cdot cm^{-1}$): 371 (12030). Found (calc. for $C_{19}H_{12}N_3O_4Ni\cdot K$: C 51.48 (51.38), H 2.71 (2.72), N 9.23 (9.46).

7. Crystallography

X-ray data collection and structure determination: All data collections for **1**–**5** were carried out on a Bruker KappaCCD diffractometer, equipped with an Oxford Cryosystems Cryostream crystal cooling apparatus, using graphite monochromated Mo K radiation. Structure solution and refinements were performed using SHELX86 [22] and SHELX97 [23] software, respectively. Full matrix anisotropic refinement on F^2 was implemented and refinement continued until convergence was reached. In the final least-squares cycles a weighting scheme was introduced that minimised the variance. For **1**, all the hydrogen atoms were located from the Fourier difference map and were freely. For the other structures the hydrogen atoms were included at calculated positions and allowed to ride on the bonded carbon or oxygen atom with the H-atom assigned a displacement parameter 1.2 times that of the adjacent atom (1.5 times for methyl H-atoms), except in **4** and **5** where the hydroxyl H-atom was allowed to refine freely (**4**) or DFIXed (**5**) and the water H-atoms were dFIXed to the oxygen atom position Crystals of **2** small and weakly diffracting, hence the low resolution level. In the structure of **2** one of the $[HNEt_3]^+$ and several low occupancy water molecules were so severely disordered that no chemically sensible, stable refinement model could be found and, as a last resort, these atoms were removed and the structure was SQUEEZEd using the SQUEEZE [12] routine in PLATON [13]. This procedure gave a stable refinement for the rest of the structure (details of the SQUEEZE results are included in the cif file for **2**). In the case of complex **3**, a poor resolution to the data was obtained because of weakly diffracting crystals, and no observed data beyond 0.8 Å resolution was collected. A summary of crystal data, data collection and refinement parameters for the structural analysis is given in Table 6.

Acknowledgements

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Appendix A. Supplementary data

CCDC 747981-747985; contains the supplementary crystallographic data for compounds **1**–**5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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