

Coordination modes of 3-hydroxypicolinic acid: synthesis and crystal structures of palladium(II), platinum(II) and rhenium(V) complexes†

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The new palladium and platinum complexes with 3-hydroxypicolinic acid (HpicOH) $[M(PPh_3)_2Cl(picOH)] \cdot CHCl_3$, $[M(bipy)(picOH)]Cl$ [$M = Pd(II)$ or $Pt(II)$], $K[PdCl(picOH)_2]$ and $[Pt(picOH)_2]$ and the new rhenium complexes $[ReOI_2(PPh_3)(picOH)]$ and $[ReO(PPh_3)(picOH)_2]I$ have been prepared. The crystal structures of $[M(PPh_3)_2Cl(picOH)] \cdot CHCl_3$ [$M = Pd(II)$ **1** or $Pt(II)$ **2**] and $[ReOI_2(PPh_3)(picOH)]$ **3** were determined by X-ray diffraction. Complex **3** exhibits a distorted octahedral geometry with the $picOH^-$ ligand showing *N,O*-chelation with a small bite angle $O-Re-N$ of $74.8(3)^\circ$. In complexes **1** and **2** the metal centre is surrounded by a NP_2Cl donor set in a distorted square planar arrangement. Therefore, the $picOH^-$ ligand is bound through the nitrogen atom, but the distances found between the metal and the carboxylate oxygen $[Pd \cdots O(71) 2.773(5) \text{ \AA}$ or $Pt \cdots O(71) 2.734(4) \text{ \AA}]$ suggest a $[4 + 1]$ coordination consistent with *N,O*-chelation for palladium and platinum centres. Infrared, Raman, 1H and $^{13}C\{^1H\}$ NMR spectroscopic data for the complexes are consistent with the crystallographic results. In the solid state the complex units of **1** and **3** are aggregated in centrosymmetric dimers based on $C-H \cdots Cl$ or $C-H \cdots O$ hydrogen bonding interactions between the chlorine of the $Pd-Cl$ bond (in **1**) or the phenolic oxygen of the $picOH^-$ anion (in **3**) and a hydrogen atom of a phenyl group of a PPh_3 ligand.

Introduction

Complexes of 3-hydroxypicolinic acid (HpicOH) are of bio-inorganic interest¹ and also pose structural ambiguities since they display a number of possible bonding modes.^{2,3} The 3-hydroxypicolinate ligand is a potential chelate with interesting possibilities, either having *N,O*-chelation (through the pyridine nitrogen and the carboxylate group, forming a five-membered chelate ring) or *O,O*-chelation (through the carboxylate group and the deprotonated hydroxyl group, forming a six-membered chelate ring) as shown in Chart 1. The *O,O*-chelation is identical to the salicylate coordination mode reported for related ambidentate ligands.^{4,5} In addition, the 3-hydroxypicolinate ion can also act as a monodentate or bridging ligand.²

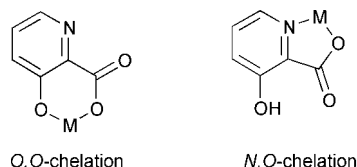


Chart 1

Few complexes of HpicOH have been isolated, those containing transition metals which have been characterized include $K_2[VO(O_2)_2(picOH)] \cdot 3H_2O$,¹ $(^tBu_4N)[ReOCl_3(picOH)]$,³ $[ReOCl(picOH)_2]$,³ $[Ru(bipy)_2(picOH)]Cl \cdot 2H_2O$,² $\{(\mu-picO)[Ru(bipy)_2]\}_2(PF_6)_2 \cdot 3H_2O$ ² and $[AuX_2(picOH)]$ ⁶ ($X = Cl, Br$). Structures of the vanadium, rhenium and gold complexes were determined by X-ray diffraction. Solution studies were reported on gallium complexes such as

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‡ The IUPAC recommended name for 3-hydroxypicolinic acid is 3-hydroxy-2-pyridinecarboxylic acid.

$[Ga(picOH)_n]^{(3-n)+}$ ($n = 1, 2$ or 3),⁷ and on iron⁸ and copper⁹ complexes.

Here we report a number of new palladium, platinum and rhenium complexes with $picOH^-$. The single crystal structures of $[M(PPh_3)_2Cl(picOH)] \cdot CHCl_3$ [$M = Pd(II)$ **1** or $Pt(II)$ **2**] and $[ReOI_2(PPh_3)(picOH)]$ **3** were determined. The molecular structures of these three complexes together with the spectroscopic data suggest that coordination of $picOH^-$ through the ring nitrogen is preferred in these species. Simultaneous bonding to the carboxylate oxygen of $picOH^-$, originating *N,O*-chelation, is clearly shown in the crystal structure of the rhenium complex **3**. Crystal structures of complexes **1** and **2** show instead a weak bonding interaction between the metal and the carboxylate oxygen, consistent with a $[4 + 1]$ coordination of palladium and platinum in these complexes.

Results and discussion

Preparations

Suspensions of *trans*- $[Pd(PPh_3)_2Cl_2]$ or *cis*- $[Pt(PPh_3)_2Cl_2]$ and HpicOH in an ethanol-methanol mixture were stirred for several days in the presence of triethylamine to give complexes **1** and **2** respectively. When $K_2[MCl_4]$ [$M = Pd(II)$ or $Pt(II)$] was used as starting reagent instead of the triphenylphosphine complexes, the compounds obtained were $K[PdCl(picOH)_2] \cdot 2H_2O$ **4** and $[Pt(picOH)_2]$ **5**. The reaction of 2,2'-bipyridine (*bipy*) complexes $[M(bipy)Cl_2]$ [$M = Pd(II)$ or $Pt(II)$] with HpicOH gave the complexes $[Pd(bipy)(picOH)]Cl$ **6** and $[Pt(bipy)(picOH)]Cl \cdot 0.5CH_2Cl_2$ **7**. Complex **3** was obtained by reaction of HpicOH with $[ReOI_2(PPh_3)_2(EtO)]$ in refluxing acetone. The reaction of HpicOH with $[ReO_2I(PPh_3)_2]$ in refluxing methanol gave the

complex $[\text{ReO}(\text{PPh}_3)(\text{picOH})_2]\text{I}$ **8**. Suitable crystals of **1**, **2** and **3** for X-ray diffraction studies were obtained by vapour diffusion of diethyl ether into chloroform solutions of the compounds.

Crystal structures

The crystal structures of complexes *trans*- $[\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{picOH})]\cdot\text{CHCl}_3$ **1**, *cis*- $[\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{picOH})]\cdot\text{CHCl}_3$ **2** and $[\text{ReOI}_2(\text{PPh}_3)(\text{picOH})]$ **3** were determined by single crystal X-ray diffraction.

ORTEP views of the molecular structures of complex entities $[\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{picOH})]$ **1** and $[\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{picOH})]$ **2** including the corresponding atomic notation schemes are shown in Fig. 1 and 2 respectively. Table 1 lists the bond lengths and angles subtended at the metal centre for these two complexes. The coordination geometry around the Pt and Pd centres, comprising the nitrogen atom of the picOH^- anion, two phosphorus atoms of two PPh_3 ligands and one chlorine atom can be described as approximately square planar. However these two complexes display different geometric arrangements. In complex **1** the nitrogen donor of the picOH^- ligand is *trans* to the chlorine atom leading to an angle $\text{N}(1)\text{--Pd--Cl}$ of $170.3(1)^\circ$ while in complex **2** the nitrogen

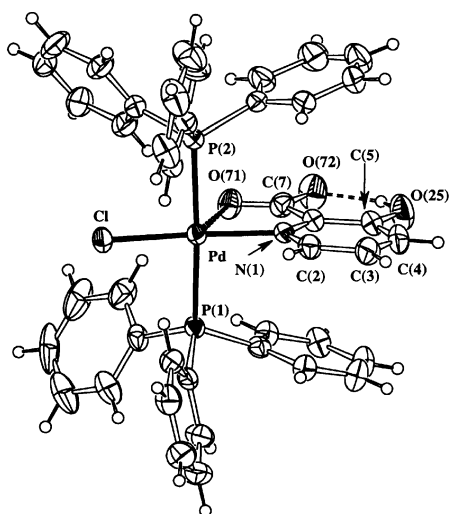


Fig. 1 An ORTEP view of $[\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{picOH})]$ **1** showing the molecular geometry. Thermal ellipsoids are drawn at the 40% probability level. The labelling scheme used for the phenyl rings is omitted for clarity.

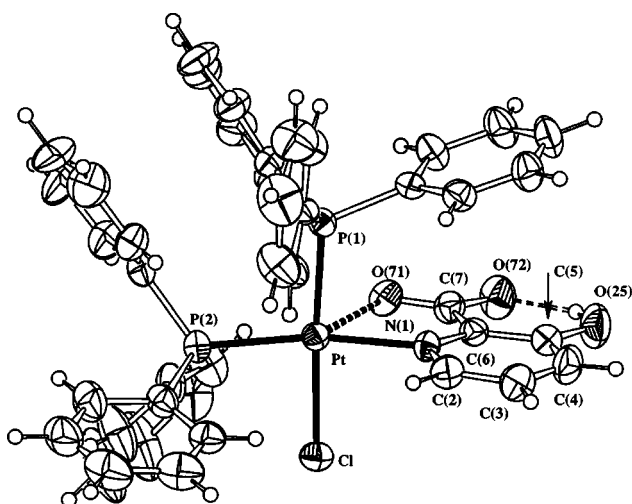


Fig. 2 An ORTEP view of $[\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{picOH})]$ **2** showing the molecular geometry. Thermal ellipsoids are drawn at the 40% probability level. The labelling scheme used for the phenyl rings is omitted for clarity.

Table 1 Selected bond lengths (Å) and angles ($^\circ$) for complexes **1** and **2**

	1	2
	M = Pd(II)	M = Pt(II)
M–N(1)	2.081(4)	2.137(5)
M–P(1)	2.336(1)	2.264(3)
M–P(2)	2.328(1)	2.262(3)
M–Cl(1)	2.306(1)	2.353(3)
N(1)–M–P(1)	91.0(1)	90.2(2)
N(1)–M–P(2)	91.8(1)	169.4(2)
P(2)–M–P(1)	174.4(1)	98.1(1)
N(1)–M–Cl	170.3(1)	86.0(2)
P(2)–M–Cl	88.7(1)	85.5(1)
P(1)–M–Cl	89.4(1)	176.1(1)
O(71)···M–P(1)	89.2(1)	87.7(1)
O(71)···M–P(2)	87.2(1)	118.7(1)
O(71)···M–N(1)	69.3(2)	67.9(2)
O(71)···M–Cl	120.4(1)	92.0(1)

atom is *trans* to the phosphorus atom P(2) of a PPh_3 ligand and the corresponding angle $\text{P}(2)\text{--Pt--N}(1)$ is $169.4(2)^\circ$. The picOH^- ligand is almost perpendicular to the NP_2Cl coordination plane giving a dihedral angle between this plane and the plane defined by the carbon atoms of the aromatic ring of $88.2(1)$ and $85.2(2)^\circ$ for complexes **1** and **2** respectively. In both cases, the relative orientation of the picOH^- ligand may be determined by the minimisation of the steric interactions between the bulky PPh_3 ligands and the picOH^- anion. A more pronounced effect will be expected for complex **1**, where the picOH^- ligand is sandwiched between two phenyl rings of *trans* PPh_3 ligands. In fact the best least squares plane through the NP_2Cl donor atoms set shows a tetrahedral distortion of $\pm 0.145(1)$ Å in *trans* complex **1** while this distortion is reduced to $\pm 0.04(2)$ Å in the *cis* complex **2**. In complex **1** the Pd(II) centre is constrained within the NP_2Cl coordination plane with a slight deviation of $0.040(1)$ Å while in complex **2** the Pt(II) is $0.076(2)$ Å out of this plane.

The coordination of the picOH^- ligand by the nitrogen atom in complexes **1** and **2** forces its carboxylate group to be directed towards the metal centre leading to distances $\text{Pd}\cdots\text{O}(71)$ of $2.773(5)$ Å and $\text{Pt}\cdots\text{O}(71)$ of $2.734(4)$ Å, which suggests a weak bonding interaction consistent with a $[4 + 1]$ coordination geometry. In addition, in both complexes the angle $\text{M}\cdots\text{O}(71)\text{--C}(7)$ [$106.1(4)^\circ$ in **1** and $106.9(4)$ in **2**] is close to 104.5° (the ideal H–O–H angle for the water molecule) indicating that one of the electron lone pairs of the oxygen O(71) displays a suitable orientation to interact with the metal centre.

In order to compare the coordination environment of these two complexes with related ones we carried out a search on the Cambridge Structural Data Base (CSD)¹⁰ of Pd(II) and Pt(II) mononuclear complexes potentially five-co-ordinated, containing the NP_2ClO donor set with the oxygen atom located inside the coordination sphere or outside but at a short distance from the metal centre. No structures of five-co-ordinated complexes with an oxygen atom occupying the fifth position in the coordination sphere were found. By contrast several examples were found of the metal complexes containing an oxygen atom clearly outside the coordination sphere, but located at a short distance from the metal centre (range $\text{Pd}\cdots\text{O}$ $2.863\text{--}3.435$ Å and $\text{Pt}\cdots\text{O}$ $2.951\text{--}3.275$ Å) suggesting a weak bonding interaction between the metal centre and the oxygen atom, consistent with a $[4 + 1]$ coordination. However in most of the cases the angles involving the oxygen atom centred at the metal centre are far from the ideal angles of square-pyramidal or trigonal bipyramidal geometric arrangements and therefore the coordination environment of these complexes cannot be described as $[4 + 1]$. Only one

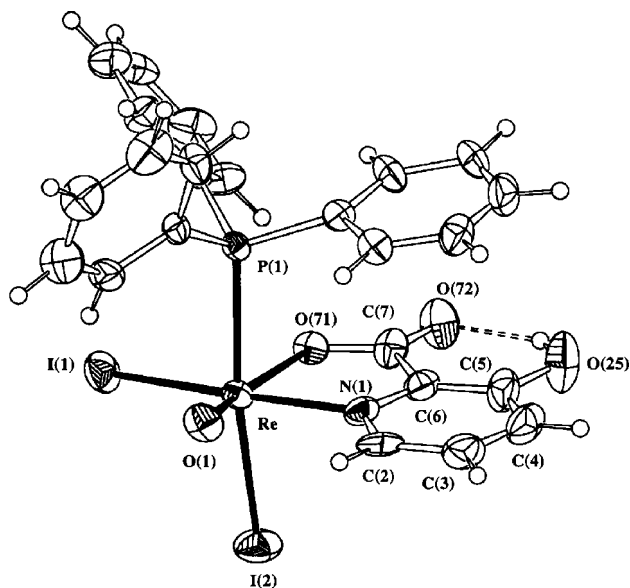


Fig. 3 An ORTEP view of $[\text{ReO}_2(\text{PPh}_3)_2(\text{picOH})]$ **3** showing the molecular geometry. Thermal ellipsoids are drawn at the 40% probability level. The labelling scheme used for the phenyl rings is omitted for clarity.

case of this type of geometry has been reported, the complex $\text{trans}[\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{L})]$ ¹¹ [HL = 8-(methylthio)theophylline = 3,7-dihydro-1,3-dimethyl-8-methylsulfanyl-1H-purine-2,6-dione] which displays, as observed for complex **1**, two *trans* PPh_3 ligands bound to palladium together with a chlorine *trans* to a nitrogen atom from the L^- ligand.

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Re–O(1)	1.669(6)	Re–O(71)	2.074(6)
Re–N(1)	2.159(7)	Re–P(1)	2.502(2)
Re–I(1)	2.668(8)	Re–I(2)	2.736(1)
O(1)–Re–O(71)	161.6(3)	O(71)–Re–N(1)	74.8(3)
O(1)–Re–N(1)	89.0(3)	O(71)–Re–P(1)	80.3(2)
O(1)–Re–P(1)	91.9(2)	I(1)–Re–I(2)	90.04(3)
N(1)–Re–P(1)	92.4(2)	O(71)–Re–I(1)	91.9(2)
O(1)–Re–I(1)	104.8(2)	O(71)–Re–I(2)	88.0(2)
O(1)–Re–I(2)	99.5(2)	N(1)–Re–I(2)	85.0(2)
N(1)–Re–I(1)	165.9(2)	P(1)–Re–I(2)	168.3(1)
P(1)–Re–I(1)	89.8(1)		

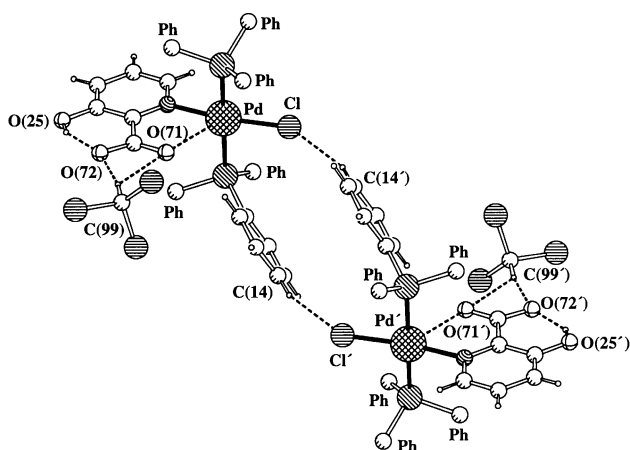


Fig. 4 Hydrogen bonded dimer of $[\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{picOH})] \cdot \text{CHCl}_3$ **1** with a centrosymmetric structure. Intermolecular hydrogen-bond distances (Å) and angles (°) are: H(14)···Cl' [−*x*, 2 − *y*, −*z*] 2.81, C(14)···Cl' 3.70, C(14)–H(14)···Cl' 161.4; H(99)···O(71) [1/2 − *x*, −1/2 + *y*, 1/2 − *z*] 2.57, C(99)···O(71) 3.32, C(99)–H(99)···O(71) 133.6; H(99)···O(72) [1/2 − *x*, −1/2 + *y*, 1/2 − *z*] 2.13, C(99)···O(72) 3.09, C(99)–H(99)···O(72) 168.6.

The oxygen atom of L^- is also directed towards the Pd(II) centre, but with a larger Pd···O distance of 3.435 Å than that found for complex **1**. Another example of this type of geometric arrangement is the Pd(II) complex $\text{trans}[\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{phen})]$ ¹² (phen = 1,10-phenanthroline), in which the phen ligand is bound to the Pd(II) metal centre by one nitrogen and the second nitrogen is also pointing towards the metal with a shorter distance of 2.68(4) Å. From this comparison it is again evident that the *trans* orientation of two PPh_3 ligands forces the sandwiched ligand (phen or L^-) to be perpendicular to the NP_2Cl plane and consequently the second donor atom (N or O) of this ligand is forced to point towards the metal centre.

In addition, several examples of Pd(II) or Pt(II) complexes exhibiting [4 + 1] coordination spheres but with a different donor atom set from **1** and **2** were found in the CSD.¹⁰ For example the complexes¹³ $[\text{Pd}(\text{hfac})_2\{\text{P}(o\text{-tol})_3\}]$ and $[\text{Pt}(\text{hfac})_2\{\text{P}(\text{Cy})_3\}]$ (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate anion, *o*-tol = *o*-tolyl, Cy = cyclohexyl) also have an oxygen atom occupying the fifth coordination position with M···O distances of 2.796(6) (M = Pd) and 2.773(9) Å (M = Pt), slightly longer than those found for **1** and **2**, respectively.

The bond lengths in the metal coordination sphere found for complexes **1** and **2** are within the expected values (see Table 1).

Fig. 3 shows an ORTEP view of the molecular structure of complex **3** with the atomic notation scheme used. Selected bond lengths and angles are given in Table 2. The rhenium centre exhibits a distorted octahedral geometry with the equatorial coordination plane defined by the nitrogen atom and one oxygen atom of the carboxylate group from the picOH[−] ligand, one iodine atom and one oxo ligand. Six-coordination is completed by a phosphorus atom of one PPh_3 ligand and one iodine atom in axial positions. In complex **3** the picOH[−] anion acts unequivocally as a bidentate ligand leading to a O(71)–Re–N(1) bite angle of 74.8(3)°. The corresponding Re–N(1) and Re–O(71) bond lengths are 2.159(7) Å and 2.074(6) Å respectively. These bond lengths are slightly longer than those found for the octahedral complex $[\text{ReOCl}_3(\text{picOH})]^-$ [Re–N 2.11(1) Å and Re–O 2.049(9) Å]. However this oxo complex displays an identical N–Re–O bite angle of 75.0(4)°. Another related oxo complex is $[\text{ReOCl}(\text{picOH})_2]$,³ containing two picOH[−] bidentate units bound to the Re centre in an octahedral geometric arrangement; one of them has comparable Re–N [2.15(2) Å] and Re–O [2.04(1) Å] bond lengths and a N–Re–O bite angle of 75.3(5)°, while the remaining unit exhibits slightly shorter Re–N [2.10(2) Å] and Re–O [2.00(1) Å] bond lengths and consequently the corresponding N–Re–O bite angle of 80.5(6)° is slightly greater. The equatorial Re–I bond length [2.668(8) Å] is shorter than the axial Re–I bond length [2.736(1) Å], but these two distances are within the large range of 2.628–2.952 Å found for Re–I distances in 28 structures of six-coordinated mononuclear rhenium complexes retrieved from the CSD. The Re=O bond length in **3** of 1.669(6) Å is similar to the value of 1.65 Å found in $[\text{ReOCl}_3(\text{picOH})]^-$ and $[\text{ReOCl}(\text{picOH})_2]$.

The charge balances of the molecular formulae for the three complexes require that only one oxygen of HpicOH acid is protonated. The final difference Fourier maps calculated for each complex showed the unambiguous location of a hydrogen atom bonded to the phenolic oxygen atom [O(25), see Fig. 1, 2 and 3]. Therefore intramolecular OH···O hydrogen bonds involving the phenolic OH and the non-bonded carboxylate oxygen atom were found for these three complexes with O···H distances of 1.73 [O(25)···O(72) 2.47 Å, O(25)–H(1)···O(72) 148.5°], 1.74 [O(25)···O(72) 2.47 Å, O(25)–H(1)···O(72) 148.0°] and 2.00 Å [O(25)···O(72) 2.64 Å, O(25)–H(1)···O(72) 139.6°] for **1**, **2** and **3** respectively. These results are consistent with the spectroscopic data (see below).

The crystal structures of complexes **1** and **2** contain $[M(PPh_3)_2Cl(picOH)]$ [$M = Pd(II)$ or $Pt(II)$] and $CHCl_3$ solvent molecules. Complexes **1** and **2** display charge-assisted $C-H \cdots Cl$ interactions involving one hydrogen atom of a phenyl group of a PPh_3 ligand and one chlorine atom from the complex in **1** or from the $CHCl_3$ solvent in **2**. Two molecules of **1** are connected directly *via* $C-H \cdots Cl$ hydrogen bonds leading to a centrosymmetric supramolecular structure with two $Cl \cdots H$ distances of 2.81 Å. Furthermore each carboxylate group of this dimeric species is involved in bifurcated hydrogen bonding interactions with the hydrogen atom of one $CHCl_3$ solvent molecule ($H \cdots O$ distances of 2.57 and 2.13 Å). The structure of this hydrogen bonded dimer is presented in Fig. 4. In complex **2** there is an interaction between one hydrogen of a PPh_3 ligand and one Cl of $CHCl_3$ with a $H \cdots Cl$ distance of 2.66 Å { $C(44) \cdots Cl[x, -1 + y, z]$ 3.57 Å, $C(44)-H \cdots Cl$ 167.1°}. No other significant intermolecular interactions with distances less than the sum of van der Waals radius were found for complex **2**.

The solid-state structure of complex **3** contains no $CHCl_3$ solvent molecules. In the crystal, two molecules are linked directly through short charged assisted $C^{\delta+}-H \cdots O^{\delta-}$ intermolecular contacts involving the oxygen atom of the phenol group and one hydrogen atom of a phenyl ring of the PPh_3 ligand. This supramolecular dimer, shown in Fig. 5, also has a centrosymmetric structure with two $H \cdots O$ distances of 2.56

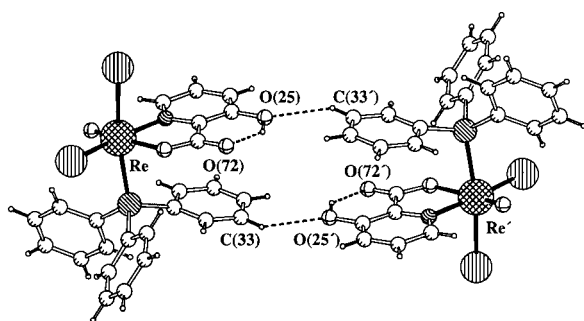


Fig. 5 Hydrogen bonded dimer of $[ReOI_2(PPh_3)(picOH)]$ **3** with a centrosymmetric structure. Intermolecular hydrogen-bond distances (Å) and angles (°) are: $H(33) \cdots O(25)[-x, -y, -z]$ 2.56, $C(33) \cdots O(25)$ 3.38, $C(33)-H(33) \cdots O(25)$ 147.5.

Å. This study shows that the PPh_3 ligands play an important role in the crystal assembly of these three compounds.

Vibrational spectra

Infrared and Raman spectroscopic data for 3-hydroxypicolinic acid (HpicOH) and its complexes are shown in Table 3, tentative assignments are based on those found in the literature for HpicOH complexes^{1,3,6} and for picolinic^{14,15} and salicylic acids.^{5,16} The selected bands of the free ligand, namely the carboxylate asymmetric and symmetric stretches, $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$, and the $C-O$ stretch of the hydroxyl group, $\nu(C-O)_h$, are sensitive to metal coordination as reported for complexes of hydroxybenzoic acids.^{4,5}

The symmetric mode $\nu_s(CO_2)$ shows shifts (up to 60 cm^{-1}) to higher wavenumber on coordination when compared to the free ligand (at 1322 cm^{-1}), suggesting that the ligand is bound to the metal through a carboxylate oxygen; similar shifts were reported for salicylic acid complexes.⁵ Since there is a weak interaction of the carboxylate group with the metal for complexes **1** and **2**, as shown in the crystal structures, shifts in $\nu_s(CO_2)$ for these complexes are possibly also due to hydrogen bonding from the adjacent hydroxyl group. The asymmetric mode $\nu_{as}(CO_2)$ shows small shifts (up to 6 cm^{-1}) on coordination when compared to the free ligand (at 1654 cm^{-1}), generally to a lower wavenumber.

The $\nu(C-O)_h$ stretch at 1283 cm^{-1} for the hydroxyl group of the free ligand shifts to lower wavenumbers on coordination. Though the crystal structures of complexes **1**, **2** and **3** show that this group is not bound to the metals, shifts of $\nu(C-O)_h$ may be due to hydrogen bonding to the adjacent carboxylate group.

The infrared spectrum of complex **1** shows a medium intensity band at 3057 cm^{-1} assigned¹⁶ to the stretching $\nu(C-H)$ vibration of the aromatic rings. A second band with similar intensity is also shown at 2969 cm^{-1} which was not found in the spectrum of the compound before recrystallization in chloroform–diethyl ether. The latter band may be assigned to $\nu(C-H)$ of $CHCl_3$ molecules; this band is shifted to lower wavenumbers when compared with the corresponding band for liquid chloroform (3020 cm^{-1}) possibly due to hydrogen bonding to the complex molecules as shown in the crystal structure of **1**. In the infrared spectrum of complex **3** two very weak bands are found at 3054 and 3082 cm^{-1} , which may be

Table 3 Analytical and spectroscopic data for complexes of 3-hydroxypicolinic acid and the free ligand

Compound	Analysis ^a (%)			Vibrational spectra ^b /cm ⁻¹					
	C	H	N	$\nu_{as}(CO_2)$	$\nu(C-N)$	$\nu_s(CO_2)$	$\nu(C-O)_h$	$\nu(Re=O)$	$\nu(M-N)$
HpicOH				1654 vs 1679(3)	1608 vs 1612(5)	1322 s 1323(5)	1283 s 1286(2)		
1	55.6 (55.9)	3.7 (3.8)	1.5 (1.5)	1648 s	1588 s 1584(10)	1367 s 1374(1)	1272 s		388 s 389(1)
2	51.0 (51.0)	3.5 (3.5)	1.3 (1.4)	1647 s 1642(1)	1592 s 1581(8)	1365 s 1366(1)	1270 s		387 m 364(1)
3	33.8 (33.7)	2.1 (2.1)	1.6 (1.6)	1651 vs 1652(1)	1611 s 1609(1)	1374 w	1252 s 1252(1)	993 s 990(10)	457 m 452(1)
4	28.5 (29.2)	2.5 (2.9)	5.7 (5.7)	1649 vs	1608 sh 1581(1)	1356 s 1368(10)	1234 vs 1241(1)		376 m 333(1)
5	29.2 (30.6)	1.6 (1.7)	5.6 (5.9)	1651 vs	1604 s	1384 m	1237 vs		350 s
6	37.0 (37.1)	2.1 (2.4)	7.3 (7.3)	1649 vs 1657(4)	1601 vs 1603(7)	1372 s 1390(10)	1235 vs 1266(1)		364 s 378(1)
7	34.0 (34.9)	2.7 (2.3)	7.4 (7.4)	1654 vs	1608 vs	1373 m	1248 s		358 m
8	39.1 (41.5)	2.6 (2.6)	2.9 (3.2)	1656 vs	1608 s	1383 m	1248 vs	987 m	454 s

^a Calculated values in parentheses. ^b Raman data in italics.

assigned to $\nu(\text{C-H})$ of PPh_3 . The two bands may possibly correspond to unbound C-H and to the C-H involved in C-H...O hydrogen bonding (shown in the crystal structure of complex **3**), respectively.

In the spectra of the two rhenium complexes the Re=O stretch is seen as a strong band at 987 and 993 cm^{-1} , respectively. Bands assignable to the M-N stretching vibrations were found in the region from 350 to 450 cm^{-1} . M-Cl stretching vibrations were also clearly seen in the spectra of the corresponding Pd and Pt complexes. In addition to the above, PPh_3 and bipy bands were observed in all the applicable spectra.

The proposed formula for complexes **4** to **8** are based on elemental analysis and spectroscopic data, considering analogous complexes that have been reported^{5,17-19} for other bidentate ligands. In complexes **4** and **5** two picOH^- ligands are coordinated to palladium and platinum, respectively, but in **4** a chlorine ligand is also bound to palladium as shown in the infrared spectrum. Complex **4** has possibly either a [4 + 1] geometry or a square planar geometry involving a monodentate picOH^- ligand. For the palladium and platinum complexes **6** and **7** containing 2,2'-bipyridine, cationic species are proposed with a Cl^- counter-anion, since no bands were found in the infrared or Raman spectra for the M-Cl stretching vibration, clearly seen in the spectra of complexes **1**, **2** and **4** with a coordinated chlorine ion. Complexes **6** and **7** are analogous to the reported 6,7-dihydroxycoumarin species.¹⁷ Complex **8** is analogous to the rhenium complexes with maltol, tropolone or hydroxypyridinone ligands that have been reported.^{18,19}

^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra

Proton and carbon NMR data and tentative assignments for HpicOH and complexes **1**, **2** and **3** are given in Table 4 (see Fig. 1-3 for labelling). Protonation of the phenolic oxygen atom (H_{OH}) of the picOH^- ligand is shown in the ^1H NMR spectra by signals at δ 16.5 and 16.9, respectively for complexes **1** and **2**, and at δ 10.6 for complex **3**. Solution $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra are of poor quality for most of the complexes; CPMAS solid state NMR data were used to determine the peak positions for C_5 and C_7 . In comparison with HpicOH , the resonances of C_6 and C_7 are significantly shifted in the spectra of the complexes, while the position of the phenolic carbon atom C_5 is little altered. This is consistent with the N,O-chelation shown in the crystal structures of these complexes.

Experimental

Preparation of complexes

The starting materials, $\text{trans-}[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$,²⁰ $\text{cis-}[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$,²¹ $[\text{M}(\text{bipy})\text{Cl}_2]$ ¹⁷ ($\text{M} = \text{Pd}$ or Pt),

$[\text{ReO}_2\text{I}(\text{PPh}_3)_2]$ ²² and $[\text{ReOI}_2(\text{PPh}_3)_2(\text{EtO})]$ ²² were prepared by the respective literature procedures. All chemicals were of at least reagent grade and used as supplied.

trans-}[\text{Pd}(\text{PPh}_3)_2\text{Cl}(\text{picOH})] \cdot \text{CHCl}_3 (**1**). To a stirred suspension of $\text{trans-}[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ (0.35 g, 0.5 mmol) in ethanol (10 cm^3) was added a methanolic suspension (4 cm^3) of 3-hydroxypicolinic acid (0.14 g, 1 mmol) and triethylamine (0.28 cm^3 , 2 mmol). The resulting yellow suspension was stirred for three weeks. It was centrifuged and a yellow solid isolated, washed with ethanol and dried over silica gel (yield of yellow solid: 0.35 g, 0.44 mmol, 87%). Yellow crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into a solution of the compound in CHCl_3 .

cis-}[\text{Pt}(\text{PPh}_3)_2\text{Cl}(\text{picOH})] \cdot \text{CHCl}_3 (**2**). To a stirred suspension of $\text{cis-}[\text{Pt}(\text{PPh}_3)_2\text{Cl}_2]$ (0.39 g, 0.5 mmol) in ethanol (10 cm^3) was added a methanolic suspension (4 cm^3) of 3-hydroxypicolinic acid (0.14 g, 1 mmol) and triethylamine (0.28 cm^3 , 2 mmol). The resulting white suspension was stirred for six days. It was centrifuged and an off-white solid isolated, washed with ethanol and dried over silica gel (yield of off-white solid: 0.41 g, 0.46 mmol, 92%). Off-white crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into a solution of the compound in CHCl_3 .

$[\text{ReOI}_2(\text{PPh}_3)_2\text{picOH}]$ (3**).** A suspension of $[\text{ReOI}_2(\text{PPh}_3)_2(\text{EtO})]$ (0.31 g, 0.3 mmol) and 3-hydroxypicolinic acid (0.04 g, 0.3 mmol) in acetone (10 cm^3) was refluxed for 30 min. The dark solution was placed in the fridge. After three weeks dark green crystals were isolated, washed with acetone and dried over silica gel. Dark green crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into a solution of the compound in CHCl_3 . Yield: 0.12 g, 0.14 mmol, 46.7%.

$\text{K}[\text{PdCl}(\text{picOH})_2] \cdot 2\text{H}_2\text{O}$ (4**).** A methanolic suspension (4 cm^3) of 3-hydroxypicolinic acid (0.14 g, 1 mmol) was added to an aqueous solution (10 cm^3) of $\text{K}_2[\text{PdCl}_4]$ (0.14 g, 0.5 mmol) and triethylamine (0.28 cm^3 , 2 mmol). The resulting yellow suspension was stirred for one day. It was centrifuged and a yellow solid isolated, washed with ethanol and dried over silica gel. Yield: 0.18 g, 0.37 mmol, 73%.

$[\text{Pt}(\text{picOH})_2]$ (5**).** A methanolic suspension (5 cm^3) of 3-hydroxypicolinic acid (0.06 g, 0.4 mmol) was added to a methanolic suspension (5 cm^3) of $\text{K}_2[\text{PtCl}_4]$ (0.08 g, 0.2 mmol). The resulting suspension was stirred for five days. It was centrifuged and a yellow solution obtained. A yellow solid was isolated from the solution after three days, washed with ethanol and dried over silica gel. Yield 0.04 g, 0.08 mmol, 42.5%.

Table 4 ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectroscopic data for 3-hydroxypicolinic acid and its complexes^a

Compound	Chemical shift (δ)									
	H_2	H_3	H_4	H_{OH}	C_2	C_3	C_4	C_5^c	C_6	C_7^c
HpicOH^b	8.1	7.8	7.9	—	132.1	129.7	129.4	159.4	133.4	164.5
1	8.4	^d	6.7	16.5	135.0	128.1	128.0	161.5	138.3	169.6
2	8.3	^d	7.0	16.9	135.9	127.3	127.1	163.4	138.4	169.4
3	8.0	7.4	7.1	10.6	130.7	128.1	127.2	156.7	140.1	172.3

^a Spectra in CDCl_3 solution unless otherwise stated. ^b In $(\text{CD}_3)_2\text{SO}$ solution. ^c CPMAS solid state NMR data. ^d Peak obscured.

[Pd(bipy)(picOH)]Cl (6). To a stirred suspension of [Pd(bipy)Cl₂] (0.05 g, 0.15 mmol) in ethanol (5 cm³) was added a methanolic suspension (5 cm³) of 3-hydroxypicolinic acid (0.04 g, 0.3 mmol) and triethylamine (0.08 cm³, 0.6 mmol). The resulting yellow suspension was stirred for one day. It was centrifuged and a yellow solid isolated, washed with ethanol and dried over silica gel. Yield: 0.05 g, 0.11 mmol, 76.6%.

[Pt(bipy)(picOH)]Cl·0.5CH₂Cl₂ (7). To a stirred suspension of [Pt(bipy)Cl₂] (0.08 g, 0.2 mmol) in ethanol (5 cm³) was added a methanolic suspension (5 cm³) of 3-hydroxypicolinic acid (0.05 g, 0.4 mmol) and triethylamine (0.11 cm³, 0.8 mmol). The resulting yellow suspension was refluxed for six hours and then stirred for two days. The resulting orange suspension was centrifuged and an orange solution obtained. An orange solid was obtained after addition of 10 cm³ of CH₂Cl₂ to the solution; it was washed with CH₂Cl₂ and dried over silica gel. Yield: 0.02 g, 0.03 mmol, 17.5%.

[ReO(PPh₃)(picOH)₂]I (8). A suspension of [ReO₂-(PPh₃)₂] (0.17 g, 0.2 mmol) and 3-hydroxypicolinic acid (0.05 g, 0.4 mmol) in methanol (30 cm³) was refluxed for 30 min. The reddish brown solution was placed in the refrigerator for two weeks. After evaporation of part of the solvent a dark solid was obtained. It was filtered and washed with diethyl ether. Yield: 0.07 g, 0.08 mmol, 40.4%.

Crystallography

Table 5 lists the pertinent crystallographic data together with refinement details for complexes **1**, **2** and **3**, respectively. Crystal data for all complexes were collected using graphite-monochromated Mo-K α radiation on a MAR research image plate system ($\lambda = 0.71073$ Å) at Reading University. The crystals were positioned at 70 mm from the image plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was performed with the XDS program.²³

An empirical absorption correction was applied to the intensities of complexes **2** and **3** but not **1** using a version of the DIFABS program,²⁴ modified for image plate systems. The positions of the heavy atoms were determined by direct

methods while the positions of the remaining non-hydrogen atoms were subsequently found by difference Fourier methods. The structures were refined by full matrix least squares method on F^2 until convergence. The hydrogen atoms bonded to the carbon atoms were introduced in the refinement at the idealised positions while the hydrogen atoms bonded to the oxygen phenol groups were discernible from Fourier difference maps and were included in the refinement without restraints. All non-hydrogen atoms were refined with anisotropic temperature factors but the values of these parameters for the chlorine atoms of CHCl₃ in **1** indicated that these atoms were affected by some thermal disorder, however no suitably disordered model could be found.

All calculations required to solve and refine the structures were performed with SHELXS and SHELXL within the SHELX97 software package.²⁵ All molecular diagrams were drawn with the PLATON graphical package.²⁶

CCDC reference number 440/185. See <http://www.rsc.org/suppdata/nj/a9/a908560b/> for crystallographic files in .cif format.

Instrumentation

Infrared spectra were measured as KBr disks on a Mattson 7000 FT instrument. Raman spectra were obtained on a Jobin-Yvon T64000 instrument using excitation at 514 nm from a Spectra Physics 2020 argon laser or on a Renishaw Ramascope instrument using excitation at 632 nm from a Spectra Physics 127/25R helium–neon laser or on a Perkin-Elmer Series 1700X FT Raman spectrometer. ¹H and ¹³C NMR spectra were recorded on a Brüker AMX300 spectrometer (¹H, 300 MHz; ¹³C, 75.4 MHz) referenced to SiMe₄ or the solvent. CPMAS ¹³C NMR spectra were recorded on a Brüker MSL 400P spectrometer at 100.6 MHz with a 4.5 μ s 90° pulse, contact time of 2 ms. Microanalyses (C, H and N) were measured by the Department of Chemistry, University of Aveiro.

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Table 5 Crystal data and refinement details for metal complexes **1**, **2** and **3**

	1	2	3
Empirical formula	C ₄₃ H ₃₅ Cl ₄ NO ₃ P ₂ Pd	C ₄₃ H ₃₅ Cl ₄ NO ₃ P ₂ Pt	C ₂₄ H ₁₉ I ₂ NO ₄ PRe
<i>M</i>	923.86	1012.55	856.37
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	18.628(19)	11.002(14)	8.116(9)
<i>b</i> /Å	11.548(13)	12.641(14)	15.241(17)
<i>c</i> /Å	19.432(23)	16.825(18)	21.061(24)
α /°		112.24(1)	
β /°	93.10(1)	93.52(1)	100.17(1)
γ /°		104.51(1)	
<i>V</i> /Å ³	4174(8)	2065(4)	2564(5)
<i>Z</i>	4	2	4
<i>D_c</i> /g cm ⁻³	1.470	1.629	2.218
μ /mm ⁻¹	0.817	3.774	7.239
<i>F</i> (000)	1872	1000	1592
Reflections measured	11 573	7297	7366
Unique reflections	7263 (<i>R</i> _{int} = 0.0237)	7297	4188 (<i>R</i> _{int} = 0.0287)
Absorption correction	No	Yes	Yes
Refined parameters	491	490	301
<i>R</i> and <i>R_w</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0588, 0.1553	0.0438, 0.0986	0.0431, 0.1139
(all unique data)	0.0887, 0.1833	0.0631, 0.1060	0.0625, 0.1250

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