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Structure determination of di-μ-hydroxo-bis[(2-(2-pyridyl)phenyl-κ^2N,C^1)palladium(II)] by X-ray powder diffractometry

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The title compound was synthesized in the form of a powder, and was studied by elemental analysis, IR spectroscopy, thermogravimetry and mass spectroscopy. Its crystal structure was then determined by X-ray powder diffractometry, using X-ray diffraction data collected in the reflection Bragg–Brentano geometry. The methodology followed in the present study to resolve the crystal structure consisted of peak indexing, then the use of the Monte-Carlo/parallel tempering search algorithm, and finally Rietveld refinement coupled with difference-Fourier synthesis. We found that the crystals are composed of monoclinic unit cells, with 1.5 molecules in the asymmetric unit and therefore six molecules per unit cell. In addition, we concluded that the complexes adopt a planar conformation, forming trimers created by groups of parallel molecules.

1. Introduction

There is growing interest in the synthesis and characterization of $\mathrm{Pd^{II}}$ di-μ-hydroxo complexes, in particular due to their potential utility in catalytic processes (Kannan *et al.*, 2003). For example, they have been employed (Anandhi *et al.*, 2003; Sharp, 2000) as precursors in the preparation of unusual oxo and imido derivatives that are also relevant to C—O and C—N bond-forming reactions in catalytic processes. In addition, the reactivity towards protic substrates of $[\mathrm{Pd}(\mu\text{-OH})L^n]_2$ (L^n = orthometalated imine-based ligands) dinuclear compounds provides a general route to obtain dinuclear complexes with double and mixed bridges that have shown liquid crystal behaviour (Díez *et al.*, 2001). In this context, previous studies have shown the utility of the binuclear hydroxo complexes containing Pd in the preparation of an extensive selection of new compounds by simple acid–base reactions (Ruiz *et al.*, 2001; Sánchez *et al.*, 1999). In particular, among hydroxo-bridged precursors, we have previously synthesized and investigated some precursors with C^N cyclometallated backbones [C^N = phenylazophenyl, 2-(2-pyridyl)phenyl, 7,8-benzoquinolyl or 2-(2-oxazolinyl)phenyl; Ruiz *et al.*, 1999; Sánchez *et al.*, 2003, 2004]. Unfortunately, these precursors are extremely insoluble in most common solvents and, in general, the size of crystal resulting from the synthesis is too small for their study by conventional single-crystal diffractometry. Given these circumstances, the determination of the crystal structure is very difficult since it has to be performed by X-ray powder diffractometry.

The determination of crystal structures by X-ray powder diffractometry is far from being routine and therefore it is used only when single-crystal diffractometry is not viable. This scenario occurs if the single crystals are of insufficient quality and size, as is the case with many organometallic substances

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and coordination compounds. Several studies have demonstrated that X-ray powder diffractometry is effective in the determination of highly complex, organic and inorganic crystal structures (Altomare *et al.*, 2003; Brodski *et al.*, 2003; David *et al.*, 2002; García-Cuesta *et al.*, 2004; Harris, 2002; Rukiah *et al.*, 2004). With this in mind, in the present study we investigated the molecular structure and thermal stability of the [Pd(μ-OH)(phpy)]$_2$ [phpy = 2-(2-pyridyl)phenyl] compound by a variety of instrumental procedures, and then determined its crystal structure by X-ray powder diffractometry.

2. Experimental

2.1. Synthesis

The complex was obtained by treating a solution of [{Pd(μ-OOCMe)(phpy)}$_2$] (0.500 mmol) in acetone (10 ml) with a 20% solution of NBu_4OH (aqueous, 1.100 mmol). After 1 h stirring at ambient temperature a yellow solid was obtained and the resulting suspension was then concentrated to one-fifth of the initial volume. Water addition completed the precipitation of the complex, which was subsequently filtered off, washed with water and hexane, and finally air-dried (yield, 90%).

2.2. Instrumental procedures

The elemental analysis of carbon (C), hydrogen (H) and nitrogen (N) was performed using a Carlo Erba EA 1108 microanalyzer. Calculated for $C_{22}H_{18}N_2O_2Pd_2$ (wt %): C 47.6, H 3.2, N 5.0; found experimentally: C 47.8, H 3.5, N 4.9. IR spectra were recorded on a Perkin–Elmer FT-IR 16F PC spectrophotometer, using Nujol mulls between polyethylene sheets. IR (cm^{-1}): ν(OH) 3503vs, ν(phpy) 1604s, 1576s. The thermogravimetric curve was measured on a Shimadzu TGA-50 thermobalance, using air flow (50 ml min^{-1}), a heating rate of 5 K min^{-1}, an alumina crucible and a sample mass of 5.43 mg. Mass spectrometric analyses were performed with a Fisons VG Autospec double-focusing spectrometer, operated in the positive mode at an accelerating voltage of 8 kV and resolution of at least 1000; ions were produced by fast-atom bombardment (FAB) with a beam of 25 keV Cs atoms. FAB-MS *m*/*z*: 538 [{Pd(phpy)}$_2$(OH)]$^+$, 521 [{Pd(phpy)}$_2$]$^+$, 415 [Pd(phpy)$_2$]$^+$, 277 [Pd(phpy)(OH)]$^+$, 260 [Pd(phpy)]$^+$.

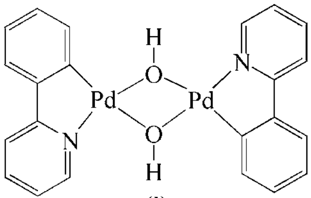
2.3. X-ray diffraction

The X-ray powder diffraction pattern of the title complex was measured with a computer-controlled Bruker D8 laboratory diffractometer, operated in the reflection Bragg–Brentano geometry and configured in the θ/θ mode to maintain a horizontal sample position at all times. This instrument is equipped with a secondary graphite monochromator and has divergence and scattering slits of 2 mm. The data were collected at ambient temperature, using Cu $K\alpha$ radiation (λ = 1.54178 Å), over the 2θ range 5–100°, with a step width of 0.02° and a counting time of 30 s per step. To have a baseline for the rapid correction of the instrumental shifts, the powder sample was also mixed with silicon powder (Standard Reference Material® 640*c*) and a second pattern was then collected under similar experimental conditions. The refined values for the lattice parameters were obtained by Rietveld refinement using the *FULLPROF* program (Rodriguez-Carvajal, 2001). The e.s.d.s for the lattice parameters are indeed the precision of the refined lattice parameters determined by the non-linear fitting procedure and are not therefore a measurement of the accuracy of the lattice parameters. The *FULLPROF* software reports standard uncertainties that describe the precision of the parameters; these deviations represent the accuracy only if there is no systematic error. A better estimate of the accuracy of the structural parameters is obtained by multiplying the sigmas by the parameter SCOR (sigma corrected ratio).

3. Results

3.1. Spectroscopic and thermogravimetric studies

In the present work, the neutral cyclopalladated complex [{Pd(μ-OH)(phpy)}$_2$] [see (I)] was prepared by simple metathesis from the soluble, easily accessible [{Pd(μ-OOCMe)(phpy)}$_2$] compound by the addition of 2 equivalents of NBu_4OH (Aiello *et al.*, 2000).



(I)

The synthesis reaction takes place in acetone at ambient temperature and the precipitation is completed by water addition. Although it is also possible to synthesize this compound starting from the di-μ-Cl complex, this latter route is much more laborious and is not recommended because of serious insolubility problems (Constable *et al.*, 1991). In addition, the synthesis reaction starting from [{Pd(μ-OOCMe)(phpy)}$_2$], as used in this study, can be more easily monitored by IR spectroscopy. Thus, the disappearance of a very strong carbonyl absorption band and the observation of a new stretching vibration at 3505 cm^{-1} (see Fig. 1) lend support to the formation of the desired [{Pd(μ-OH)(phpy)}$_2$] complex. Relevant bands for the 2-(2-pyridyl)phenyl ligand also appeared at 1604 and 1576 cm^{-1}, and a band at 524 cm^{-1} may be tentatively assigned to the Pd—O vibration.

The thermal stability of the title complex was investigated by thermogravimetry in air. As seen in Fig. 2, this compound decomposes between 421 and 623 K, with a 58.9% mass loss that is slightly greater than the mass of the orthometalated ligands. Between 623 and 923 K, a slow mass gain is observed to occur; similar behaviour has previously been found for other dinuclear orthometalated Pd complexes (Ananias *et al.*, 2004). Decomposition of PdO occurs in the interval 1101–1128 K, with a final residue of 38.56%, in excellent accordance with the chemical formula $C_{22}H_{18}N_2O_2Pd_2$.

Further evidence for the dinuclearity of the [{Pd(μ-OH)(phpy)}$_2$] complex was obtained by FAB mass spectrometry, using the m/z values for the observed fragments (538 [{Pd(phpy)}$_2$(OH)]$^+$, 521 [{Pd(phpy)}$_2$]$^+$, 415 [Pd(phpy)$_2$]$^+$, 277 [Pd(phpy)(OH)]$^+$, 260 [Pd(phpy)]$^+$). This technique is very useful for the characterization of mono- and multinuclear transition metal complexes, since it provides information about molecular weights, fragmentation patterns and structural elucidation (Cooks & Pachuta, 1987). It is also of special relevance for compounds that cannot be studied in solution. The spectra of the OH-bridged compound synthesized here showed a similar fragmentation pattern to those of analogue compounds, which includes the peaks corresponding to [{Pd(phpy)}$_2$(OH)]$^+$, [{Pd(phpy)}$_2$]$^+$ and [Pd(phpy)$_2$]$^+$. The abundances of the signals around the pattern ion are consistent with the natural isotopic abundances.

3.2. Structure determination by X-ray diffractometry

3.2.1. Data reduction and indexing. The peak positions were identified using a derivative-based algorithm that is implemented in the peak search utility of the *WINPLOTR* software package (Roisnel & Rodriguez-Carvajal, 2001). The indexing was carried out using the *CRYSFIRE* (Shirley, 1999) software package, which is designed to launch the commonest indexing programs: *ITO*, *TREOR*90, *DICVOL*91, *KOHL*, *TAUP*, *FJZN* and *LZON*. The best solution, obtained with *ITO*, yielded a monoclinic cell with a = 15.956 (1), b = 16.164 (1), c = 10.983 (1) Å, β = 92.075 (4)°, V = 2831 (3) Å^3 and M(20) = 22.7. By examining the data with *CHECKCELL* (Laugier & Bochu, 2000), the space group was unambiguously found to be $P2_1/n$. From the cell volume, we deduced the presence within the asymmetric unit of more than one molecule (Kempster & Lipson, 1972).

To assess the choices of the cell and space group, and to estimate the shape and width of the Bragg reflections as well as the instrumental shifts, we also performed a Le Bail fit (Le Bail *et al.*, 1988; profile refinement) implemented as the profile-matching option in the *FULLPROF* program (Rodriguez-Carvajal, 2001). This fitting procedure, which makes no reference to any structure model, was conducted by describing the peak shape with a pseudo-Voigt function, with the asymmetry correction being the Berar–Baldinozzi function (Bérar & Baldinozzi, 1993). In addition, the background was corrected by a linear interpolation between 68 points regularly distributed along the pattern. The final residuals were R_p = 0.0769, $R_{\rm wp}$ = 0.132, $R_{\rm exp}$ = 0.0976 and χ^2 = 2.21. The low values of these residuals confirm the validity of the space group and cell found by *ITO*.

3.2.2. Monte Carlo methods. A first approximation to the crystal structure was obtained by Monte Carlo methods, using the parallel tempering algorithm implemented in the *FOX* software package (Favre-Nicolin & Cerný, 2000). This package allows one to work in the Z-matrix formalism, which is especially useful for molecules of relative complexity (Barros-García *et al.*, 2005; García-Cuesta *et al.*, 2004; González-Méndez *et al.*, 2004). In this formalism the geometry of the molecules is described by the bond distances, the bond angles and the dihedral angles. The utility of the Monte Carlo methods is that they are capable of establishing the position of the Pd atoms (which are the heaviest atoms) and 2-(2-pyridyl)phenyl ligands (which have known structure) within the cell. To that end, the metal atoms and aromatic ligands were treated as independent blocks and the ligands were treated as rigid bodies (bond lengths and angles fixed). Therefore, this step performs only the translations and rotations of the rigid molecules inside the cell. After 5 000 000 movements, the weighted residual was $R_{\rm wp}$ = 0.142. We observed that the ligands and Pd atoms converged to nearly coplanar positions, with distances Pd—C and Pd—N close to the bond distance (*ca* 2 Å).

3.2.3. Rietveld refinement. The atomic coordinates of the Pd atoms and orthometalated ligands obtained by Monte Carlo methods were used to initialize the Rietveld refinements, which were performed using the *FULLPROF* program (Rodriguez-Carvajal, 2001). In a first step we refined the scale factor, the instrumental shifts (zero-point 2θ shift, and systematic shifts depending on the transparency and off-centering of the sample), the background, the Debye–Waller

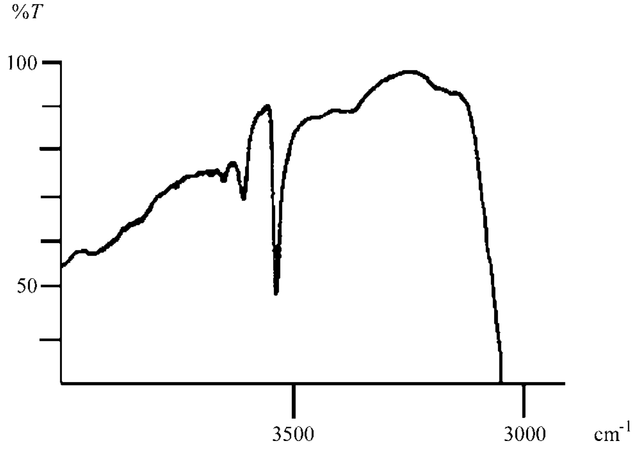


Figure 1
Detail of the IR spectrum of the [{Pd(μ-OH)(phpy)}$_2$] complex in the OH region.

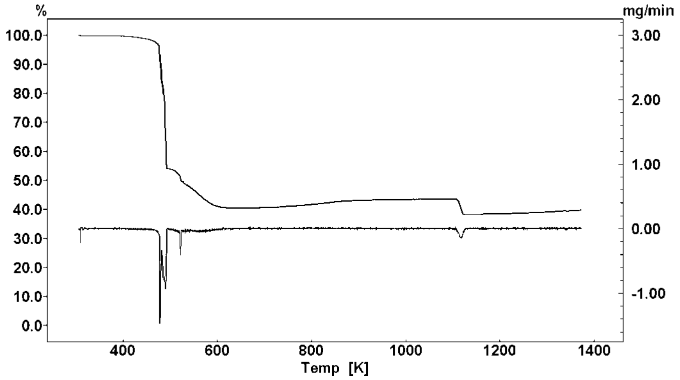


Figure 2
Thermogravimetric curve of the [{Pd(μ-OH)(phpy)}$_2$] complex.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{18}N_2O_2Pd_2$
M_r	555.2
Cell setting, space group	Monoclinic, $P2_1/n$
Temperature (K)	298 (2)
a, b, c (Å)	15.9574 (10), 16.1807 (10), 10.9808 (7)
β (°)	92.115 (4)
V (Å^3)	2833.2 (3)
Z	6
D_x (Mg m^{-3})	1.953
Radiation type	Cu $K\alpha$
Specimen form, colour	Powder, brown
Specimen size (mm)	Micrometric powder
Specimen preparation pressure (kPa)	101.3 (2)
Specimen preparation temperature (K)	298 (2)
Data collection	
Diffractometer	Bruker D8
Data collection method	Specimen mounting: drifted powder on off-cut Si; mode: reflection; scan method: step
2θ (°)	$2\theta_{\min} = 4.9752$, $2\theta_{\max} = 99.9752$, increment = 0.02
Refinement	
Refinement on	Intensity
R factors and goodness of fit	$R_p = 0.09834$, $R_{wp} = 0.12852$, $R_{exp} = 0.06098$, $R_B = 0.10283$, $S = 2.11$
Wavelength of incident radiation (Å)	1.54183
Excluded region(s)	None
Profile function	Pseudo-Voigt
No. of parameters	76
H-atom treatment	Constrained to parent site
Weighting scheme	1
$(\Delta/\sigma)_{\max}$	<0.0001

Computer programs used: *FOX* (Favre-Nicolin & Cerný, 2000), *FULLPROF* (Rodriguez-Carvajal, 2001).

Table 2
Selected bond lengths (Å) and angles (°), and torsion angles (°) for the[{Pd(μ-OH)(phpy)}$_2$] complex.

Pd1—C1	2.08 (1)	Pd2—O1	2.06 (3)
Pd1—N1	2.10 (1)	Pd2—O2	2.07 (3)
Pd1—O1	2.06 (3)	Pd3—C23	2.07 (1)
Pd1—O2	2.13 (3)	Pd3—N3	2.08 (2)
Pd2—C12	2.07 (2)	Pd3—O3	2.14 (3)
Pd2—N2	2.09 (1)	Pd3—O3^{i}	2.10(3)
O1—Pd1—O2	75 (2)	N2—Pd2—C12	77 (1)
O1—Pd1—N1	88 (2)	N2—Pd2—O1	163 (2)
O1—Pd1—C1	161 (2)	O3—Pd3—O3^{i}	75 (2)
O2—Pd1—C1	117 (2)	N3—Pd3—O3	96 (2)
N1—Pd1—C1	77 (1)	O3—Pd3—C23	164 (2)
N1—Pd1—O2	158 (2)	O3^{i}—Pd3—C23	112 (2)
O1—Pd2—O2	76 (2)	N3—Pd3—C23	77 (9)
O2—Pd2—N2	98 (2)	N3—Pd3—O3^{i}	171 (2)
O2—Pd2—C12	172 (2)	Pd3···Pd3^{i}	3.37 (1)
O1—Pd2—C12	106 (2)	Pd1···Pd2	3.28 (1)
Pd1—O1—Pd2—O2	−7.93	Pd3—O3—Pd3^{i}—O3^{i}	0

Symmetry code: (i) $-x, 2-y, -z$.

global parameter and the cell parameters, as well as the shape, width and asymmetry of the Bragg reflections assumed to have pseudo-Voigtian form, while fixing all the atomic coordinates (excluding the H atoms). After this refinement, we found the positions of the O atoms by the Fourier difference utility implemented in the *GFOURIER* program. The H atoms were then added at the theoretical positions calculated using the *SXGRAPH* program (Farrugia, 1999), except the hydroxyl H atoms that could not be positioned properly; this complete crystal structure model was then Rietveld refined again. In this second Rietveld refinement, soft constraints were imposed on the atom–atom distances for the Pd and O atoms, whereas the orthometalated ligands were refined as rigid groups. Refinements of individual $B_{\rm iso}$ values were tried but the values became negative, so a global $B_{\rm iso}$ was mantained. The final residuals were $R_{\rm I} = 0.0984$, $R_p = 0.0954$, $R_{wp} = 0.1246$, $R_{exp} = 0.0610$ and $\chi^2 = 4.17$; the refined cell parameters were $a = 15.9574\,(10)$, $b = 16.1807\,(10)$, $c = 10.9808\,(7)$ Å, $\beta = 92.115\,(3)$°, and $V = 2833.2\,(3)$ Å^3. We also tried to refine texture, but no favoured directions were found and the refinement did not improve. Comparison of this R_{wp} with that obtained from the Le Bail fit showed that the error associated with the structural model was small, thereby supporting the validity of the crystal structure. The plotted output from the Rietveld analysis is shown in Fig. 3. Table 1 gives the most representative crystallographic parameters.[1] Fig. 4 shows a representation of the refined crystal structure.

4. Description of the crystal structure of [{Pd(μ-OH)(phpy)}$_2$]

We discuss next the crystal structure of the [{Pd(μ-OH)(phpy)}$_2$] complex and how it compares with other Pd complexes of known crystal structure. The X-ray powder diffraction study of this compound showed that the crystals are composed of monoclinic unit cells, with six molecules per unit cell. Two of these six molecules are located at special positions, more specifically at inversion centers. The asymmetric unit is formed by 1.5 molecules and 69 atoms (see Fig. 5).

Palladium atoms exhibit a square-planar coordination and complexes adopt a planar conformation with a mean Pd—Pd distance of 3.33 (5) Å. Selected bond lengths and angles are given in Table 2.

A survey using the Cambridge Structural Database (CSD; Allen, 2002), Version 5.27, updated May 2006, revealed the existence of 14 dinuclear Pd complexes bridged by two OH groups. Their reference codes and selected geometrical parameters are listed in Table 3. The average value of the Pd—O distance calculated for these 14 complexes is 2.05 (1) Å. The O—Pd—O and Pd—O—Pd angles in these complexes vary in narrow ranges and have average values of 79.66 (9) and 91.1 (3)°, respectively. A relevant conformational parameter in these complexes is the Pd···Pd distance, which is seen to vary between 2.971 and 3.179 Å with a mean value of 3.07 (7) Å. In the structure reported in this article the Pd···Pd

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: RY5007). Services for accessing these data are described at the back of the journal.

Table 3
Relevant geometrical parameters in complexes containing a $\{Pd(\mu\text{-OH})\}_2$ core.

Refcode	Mean Pd—O (Å)	Mean O—Pd—O (°)	Mean Pd—O—Pd (°)	Pd···Pd (Å)	Pd—O—Pd—O (°)
FACHEX	2.06 (4)	80.39 (10)	99.59 (10)	3.141 (1)	0.00
IXOMOX	2.072 (1)	80.85 (4)	98.77 (5)	3.145 (1)	−6.60 (10)
JIHJIT	2.08 (1)	77.04 (8)	96.3 (1)	3.095 (2)	−27.1 (3)
KEFLIQ	2.09 (3)	79.8 (2)	99 (2)	3.170 (2)	−11.9 (4)
LANBOR	2.09 (2)	76.8 (2)	90.8 (6)	2.981 (15)	35.8 (2)
MALDAE	2.015 (9)	76.58 (9)	95.5 (6)	2.984 (1)	−29.74 (12)
MARCUD	2.005 (1)	82.34 (10)	97.66 (10)	3.018 (1)	0.00 (8)
NACVAP	2.08 (2)	78.5 (5)	92.9 (7)	3.016 (1)	31.3 (3)
QIYWOK	2.017 (2)	81.7 (3)	98.3 (3)	3.051 (1)	0.00
SOGHOL	2.073 (6)	81.2 (3)	98.8 (4)	3.147 (1)	−0.03 (15)
ULINAE	2.023 (1)	81.95 (2)	94.45 (1)	2.971 (1)	20.14 (10)
YUNBOY	2.079 (3)	80.19 (10)	99.81 (10)	3.179 (1)	0.03 (15)
DEGKUW	2.023 (2)	80.38 (7)	99.30 (5)	3.083 (1)	5.92 (9)
XAYGOU	2.034 (6)	80.4 (2)	99.62 (10)	3.108 (1)	0.00

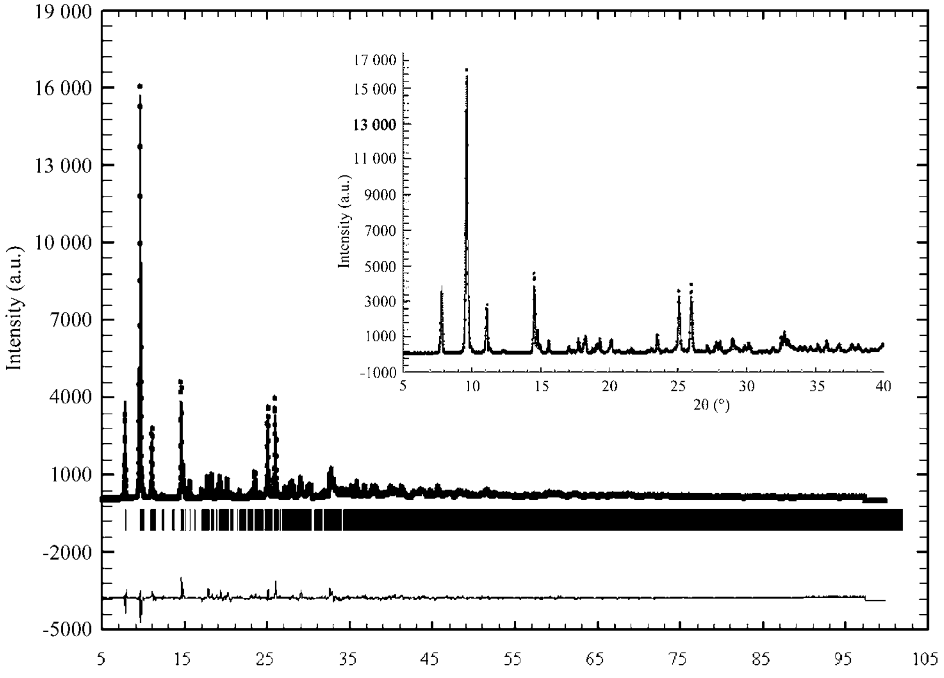

Figure 3
Plot output from the Rietveld analysis of the X-ray diffraction pattern corresponding to the $[\{Pd(\mu\text{-OH})(phpy)\}_2]$ complex. Points are the experimental X-ray diffraction data; the solid line is the calculated pattern; the residuals are plotted as the line at the bottom.

intramolecular distance is clearly longer than those in the CSD (Table 2); it is worth noting that the Pd···Pd intermolecular distance is significantly smaller, *ca* 3.17 (9) Å. It is possible to characterize the conformation of the $\{Pd(\mu\text{-OH})\}_2$ core by the Pd—O—Pd—O torsion angle, which should be close to zero for a planar conformation and significantly different from zero for a bent conformation. From Table 3 it is evident that both types of conformation (planar and bent) are possible for the complexes containing $\{Pd(\mu\text{-OH})\}_2$ cores. In the reported structure one molecule lies on a centre of inversion, so it is strictly planar; in the other molecule (Table 2) the Pd—O—Pd—O torsion angle is close to zero, thereby indicating a planar conformation. The bending angle between the coordination planes of the two metal atoms in binuclear complexes of d^8 transition metal ions has been studied in detail (Aullón, 1998, 1999), although the trends reported there do not clearly apply to the 14 complexes under study. The planar conformation found correlates with the high Pd···Pd distance. It should be noted that no metal–metal interaction has been reported (López *et al.*, 1991) for distances higher than 3 Å.

Comparison between the data in Tables 2 and 3 shows that the other geometrical parameters in the complex studied are similar to those that have been reported for previously characterized analogous compounds. The O—Pd—O angle shows a mean value of 75.3 (4)°, close to the low value of the range presented for this parameter in Table 3.

Finally, as can be seen in Fig. 4, in the reported crystal structure there are 'trimers' formed by groups of parallel molecules, with the distance between mean planes being 3.16 (9) Å. In these 'trimers' the shortest O···O distance is 2.911 Å, suggesting that a hydrogen-bond interaction is possible, although the H atoms being introduced at calculated positions prevents a conclusive assertion.

5. Conclusion

X-ray powder diffractometry was used in conjunction with IR spectroscopy, thermogravimetry and mass spectrometry to establish the crystal structure of the $[\{Pd(\mu\text{-OH})(phpy)\}_2]$ [phpy = 2-(2-pyridyl)phenyl] complex. It has been proved that it is possible to use heavy atoms (palladium in this case) and ligands as independent and rigid blocks to obtain a first approximation to the crystal structure Monte Carlo methods. This can be applied in the structural elucidation of organometallic and coordination compounds when it is not possible to obtain single crystals. We found that crystals are monoclinic with six molecules per unit cell. Complexes adopt a planar conformation; data in the Cambridge Structural Database reveal that both conformations, planar and bent, are frequent in dinuclear Pd complexes bridged by two OH groups.

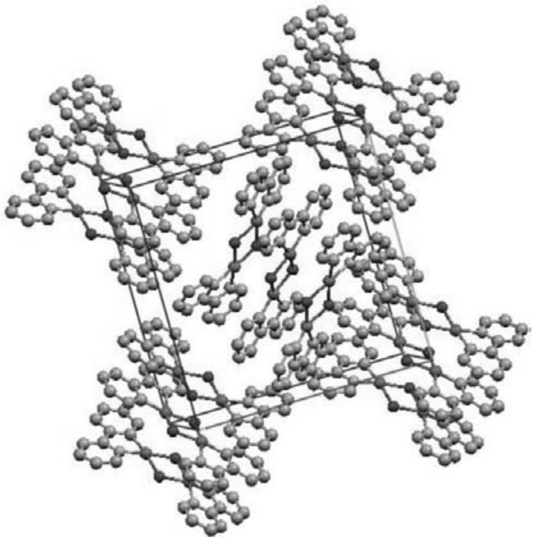

Figure 4
Crystal packing of the [{Pd(μ-OH)(phpy)}$_2$] complex.

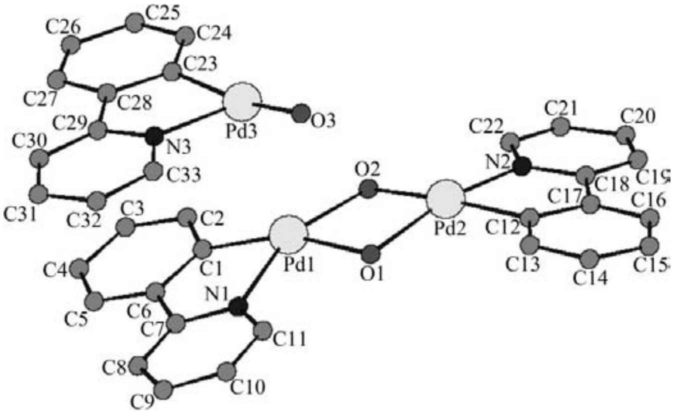

Figure 5
Asymmetric unit with labelling scheme. H atoms are omitted for clarity.

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