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Anion-templated synthesis and structural characterisation of Ni/Pd-containing metalla-macrocycles

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Abstract

The crystal structure of the precursor $[Pd(PPh_3)_2(Hatu)][CF_3SO_3]_2$ (**1**) and the anion-templated syntheses of the nickel/palladium metalla-macrocycles $[Pd_2Ni_2(atu)_4(PPh_2R)_4X]^{3+}$ (R = Ph, X = I, **2**; R = Py, X = Cl, **3**; atu = deprotonated amidinothiourea) are herein reported. The three new compounds have been structurally characterised and, for **1** and **3**, interesting intermolecular interactions leading to dimers and extended structures in the solid state, respectively, have been observed.

Keywords: Metalla-macrocycles; Templating agents; Palladium and nickel complexes; Triphenylphosphine; Anion template; Hydrogen bonding

1. Introduction

Metal-containing polygons have received increasing attention over the past few years (for reviews see [1]) due to their potential applications in areas, such as catalysis [2], nanomaterials [3] and molecular sensing [4]. For such potential applications to be realised, rational and high-yielding synthetic routes to the metalla-assemblies are needed. One approach utilises templated self-assembly processes. Templating agents make use of non-covalent interactions (such as electrostatic forces, H-bonding, π–π interactions and hydrophobic effects) to pre-arrange specific building blocks in a suitable geometry for the superstructures to be formed [5]. Whilst cationic and neutral species have been widely employed as templating agents [6,7], anions have only fairly recently been successfully utilised in this role [8]. This relatively limited application has been attributed to their more diffuse nature, pH sensitivity and their relatively high solvation free energies [9]. The first examples of anion-templated syntheses were reported by Hawthorne and coworkers [10] and Müller and coworkers [11] in the early 1990s. Since then, the use of anions as templating agents has started to emerge as a useful synthetic alternative for the controlled synthesis of complex assemblies, such as cages [12], macrocycles [13], helicates [14], rotaxanes [15] and pseudorotaxanes [16].

During the past few years we have studied the role of anions as templating agents for the synthesis of several metalla-cages [17,18] and metalla-macrocycles [19]. In the course of these studies, the complex $Ni(atu)_2$ (Hatu = amidinothiourea; atu = deprotonated form of Hatu) has proven to be a particularly good building block for the anion-directed syntheses (see Scheme 1). This we believe is due to the presence within this complex of several potential donor atoms (i.e., sulfur and nitrogen), and to the various NH groups for potential H-bonding or further coordination.

In this paper, we report the synthesis and structural characterisation of the monometallic precursor $[Pd(PPh_3)_2(Hatu)][CF_3SO_3]_2$ (**1**) and of the metalla-macrocycles $[Pd_2Ni_2(atu)_4(PPh_3)_4I][ClO_4]_3$ (**2**) and $[Pd_2Ni_2(atu)_4(PPh_2Py)_4Cl][ClO_4]_2Cl$ (**3**). These investigations provide new insights into the solid-state structures of these metalla-macrocycles.

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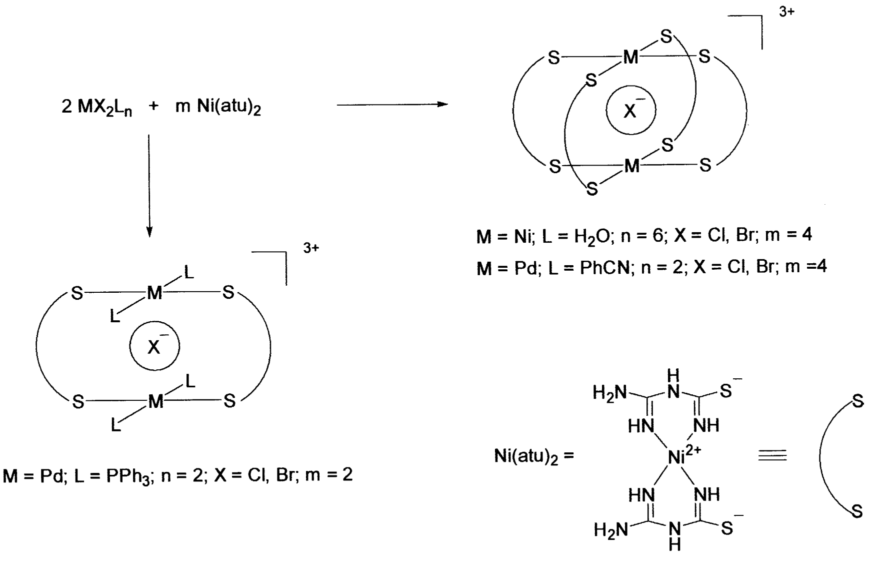
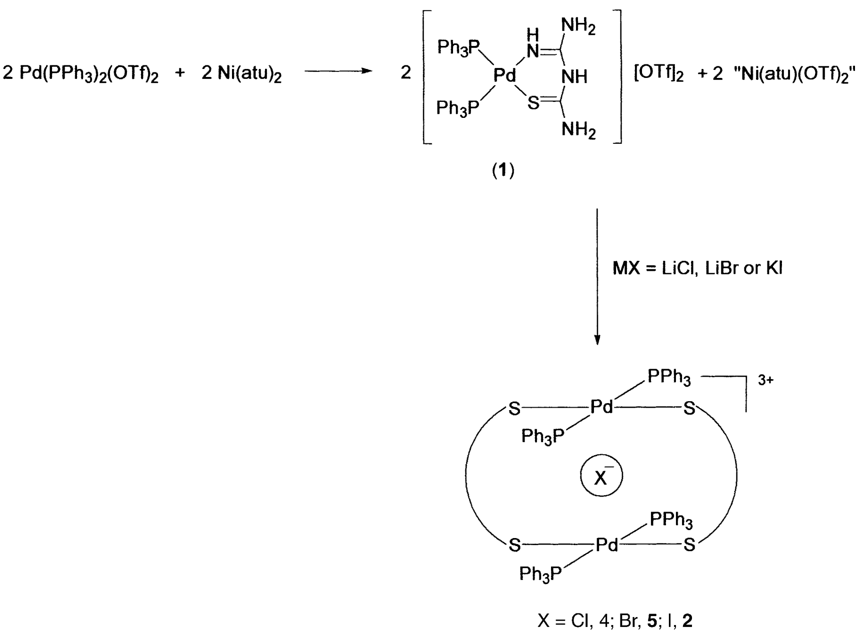


Scheme 1.

2. Results and discussion

2.1. Synthesis and structural characterisation of $[Pd(PPh_3)_2(Hatu)][CF_3SO_3]_2$ *(**1**)*

We have reported previously [19] the reaction between the palladium complexes $Pd(PPh_3)_2X_2$ (where X = Cl, Br, CF_3SO_3 and NO_3) and $Ni(atu)_2$ (prepared in situ from $Ni(ClO_4)_2$ and two equivalents of Hatu). When X = Cl or Br, the formation in high yields of the metalla-macrocycles $[Pd_2Ni_2(atu)_4(PPh_3)_4X]^{3+}$ (X = Cl, **4**; Br, **5**) is observed. In contrast, the reactions in the presence of bulkier and non-spherical anions, such as $CF_3SO_3^-$ and NO_3^- do not lead to the synthesis of the macrocycles but to a simpler rearrangement of the palladium and nickel complexes' coordination spheres. Specifically, the new complex $[Pd(PPh_3)_2(Hatu)][CF_3SO_3]_2$ and an unidentified nickel compound (which does not contain phosphine) are formed. The further addition of the appropriate halide to this reaction mixture leads to the formation of the metalla-macrocycles (see Scheme 2). Thus, it is possible to prepare not only the chloride and bromide-containing metalla-macrocycles but also the iodide analogue $[Pd_2Ni_2(atu)_4(PPh_3)_4I][ClO_4]_3$ (**2**).



Scheme 2.

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

Bond lengths			
Pd–S(1)	2.3148(14)	Pd–N(3)	2.059(4)
Pd–P(1)	2.3200(13)	Pd–P(2)	2.2717(13)
Bond angles			
N(3)–Pd–P(2)	177.27(13)	N(3)–Pd–S(1)	88.11(13)
P(2)–Pd–S(1)	89.43(5)	N(3)–Pd–P(1)	86.97(13)
P(2)–Pd–P(1)	95.40(5)	S(1)–Pd–P(1)	173.45(5)

Although the intermediate complex **1** had previously been isolated and spectroscopically characterised [19], the exact binding mode of the Hatu ligand in this complex was not established. Amidinothiourea has several potential-coordinating modes since it can act as an *N*,*N* or *S*,*N*-ligand and can be either neutral or negatively charged (by deprotonation). Hence, it was of interest to determine the structure of **1** and so establish the exact coordination of the Hatu ligand (which in turn might prove important in understanding the detailed mechanism of the subsequent templating process).

Complex **1** can be prepared either by reacting $[Pd(PPh_3)_2(CF_3SO_3)_2]$ with $Ni(atu)_2$ (which is the first step in the reaction that later leads to the formation of the metalla-macrocycles) or by reacting $[Pd(PPh_3)_2(CF_3SO_3)_2]$ directly with one equivalent of Hatu. The $^{31}P\{^1H\}$ NMR spectrum of this complex showed two doublets at 32.4 and 30.5 indicating the non-equivalence of the phosphorous atoms (which is due to the phosphorous atoms having a different environment as a consequence of the asymmetric *S*,*N* coordination of the atu ligand). Crystals of **1** suitable for an X-ray structural analysis were obtained by layering a solution of **1** in methanol with diethyl ether. The molecular structure of the complex is shown in Fig. 1.

The geometry at palladium is slightly distorted square planar with *cis* angles in the range 86.97(13)°–95.40(5)°. There are noticeable departures from planarity within the coordination sphere with the palladium and the four coordinated atoms being planar to within only 0.04 Å whereas Pd/N(3)/S(1)/P(2) are coplanar to within 0.01 Å with P(1) lying 0.15 Å out of this plane. The two Pd–P distances differ significantly with that *trans* to nitrogen being ca. 0.05 Å shorter than that *trans* to sulfur (Table 1). This is consistent with a stronger *trans* influence from the sulfur than from the nitrogen donor group. An analogous behaviour has been previously observed in the complex $[Pd(S_2N_2H)(PMe_2Ph)_2][BF_4]$ [20] (which, as far as we know, is the only other structurally characterised compound with a $PdP_2(S,N)$ coordination environment). An interesting feature of complex **1** is a substantial folding of the six-membered chelate ring [ca. 36° out of plane about the S(1)···N(3) vector]. This geometry contrasts with that observed previously in both *N*,*N* and *N*,*S*-bonded metal–atu complexes where the folding distortions are less than or equal to 10° [17,19,21].

Because of the "all-donor" nature of the complex there are no inter-complex hydrogen-bonding interactions. However, there are significant cation··· anion N–H···O interactions which lead to the formation of discrete hydrogen-bonded dimer pairs that utilise all six of the donor N–H groups (Fig. 2). It is possible that the distinctly folded geometry of the six-membered chelate ring that we observe in **1** is a consequence of these intermolecular cation···anion interactions.

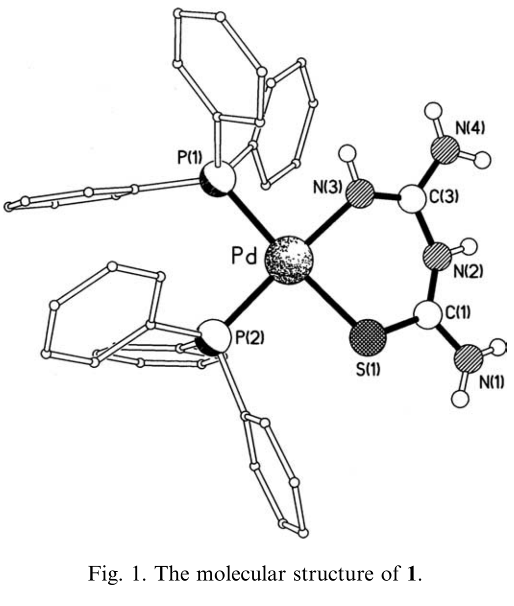


Fig. 1. The molecular structure of **1**.

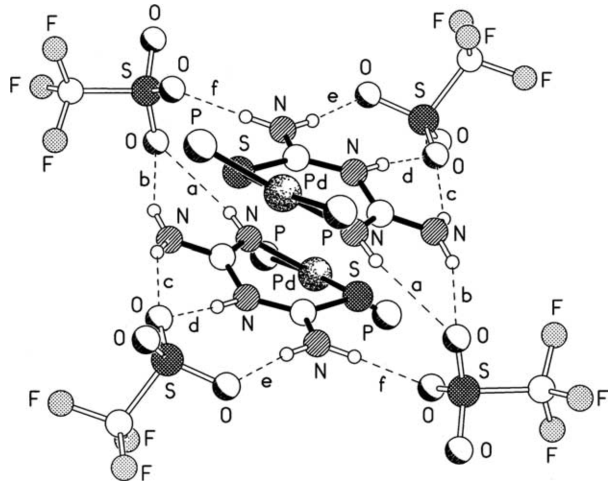


Fig. 2. The formation of discrete dimer pairs in the crystals of **1** via cation···anion N–H···O hydrogen bonding (the phenyl rings have been omitted for clarity). Hydrogen bonding geometries [N···O], [H···O] distances (Å), [N–H···O] angle (°); (a) 3.23, 2.43, 147; (b) 3.08, 2.24, 156; (c) 3.04, 2.22, 151; (d) 2.80, 1.91, 172; (e) 2.87, 1.97, 172; (f) 2.80, 1.91, 172.

2.2. Structural characterisation of [$Pd_2Ni_2(atu)_4(PPh_3)_4I$][$ClO_4$]$_3$ (**2**)

As has already been described the metalla-cages [$Pd_2Ni_2(atu)_4(PPh_3)_4X$]$^{3+}$ (X = Cl, Br, I) can be prepared by reacting $Pd(PPh_3)_2(CF_3SO_3)_2$ with $Ni(atu)_2$ (formed in situ from $Ni(ClO_4)_2$ and Hatu) in the presence of stoichiometric amounts of the corresponding halide anion. Whilst the chloride- and bromide-containing macrocycles **4** and **5** were previously structurally characterised [19] the iodide analogue demonstrated to be more difficult to crystallise and hence its solid-state structure was not established. However, since the size and geometry of the anion are essential for determining the geometry of the final product, it was of interest to determine the solid-state structure of the iodide-containing metalla-macrocycle. This complex was prepared by reacting $Pd(PPh_3)_2(CF_3SO_3)_2$ in THF with $Ni(atu)_2$ in methanol for 2 h and then adding stoichiometric amounts of iodide. Minutes after this anion was added, the $^{31}P\{^1H\}$ NMR spectrum of the mixture showed the disappearance of the two doublets (corresponding to the precursor [$Pd(PPh_3)_2(atu)$][CF_3SO_3]$_2$) and the appearance of a singlet at 18.5 ppm (corresponding to the metalla-macrocycle **2**). The reaction mixture was left stirring for 2 h after which time full conversion was observed. An orange solid was obtained after removal of the solvent under reduced pressure. This solid was washed with diethyl ether and recrystallised from a methanol/diethyl ether mixture. On the basis of $^{31}P\{^1H\}$ NMR, IR and elemental analyses, this product was characterised as the previously reported metalla-macrocycle [$Pd_2Ni_2(atu)_4(PPh_3)_4I$][$ClO_4$]$_3$ (**2**). After several crystallisation attempts, crystals of **2** suitable for X-ray crystallography were eventually obtained by slow diffusion of diethyl ether into a solution of **2** in methanol. The X-ray structure of this complex reveals as expected that the templating iodide anion is positioned centrally within the macrocyclic cavity (Fig. 3 and Table 2).

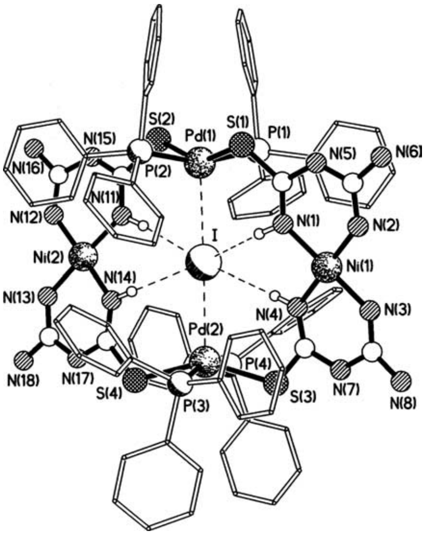


Fig. 3. The molecular structure of **2** [X = I] showing the N–H···I hydrogen bonding to the encapsulated iodide anion. Hydrogen bonding geometries [N···I], [H···I] distances (Å), [N–H···I] angle (°); (a) 3.56, 2.69, 165; (b) 3.55, 2.65, 172; (c) 3.55, 2.65, 175; (d) 3.55, 2.67, 166.

The Pd···I distances in this compound are 3.093(1) and 3.096(1) Å. This is consistent with the increasing interaction between the anion and the palladium centres on going from chloride → bromide → iodide, the Pd···X distances when X = I being the shortest that we have observed in this series of complexes [19]; in the chloride analogue **4** the distance is 3.267(1) and in the bromide (**5**) it is 3.140(1) Å. In addition the deviations of the palladium atoms from their P_2S_2 coordination planes are larger at 0.50 Å in each case, cf. 0.43 Å [Cl] and 0.48 Å [Br]. The twisting of the "upper" PdS_2P_2 unit with respect to its "lower" counterpart about the Pd···Pd vector is ca. 36°, cf. 44° and 46° for the chloride and bromide species, respectively. The overall dimensions of the macrocycle [Pd···Pd × Ni··· Ni] are 6.19 × 9.22 Å, cf. 6.53 × 8.69 [Cl] and 6.22 × 9.05 [Br], reflecting the flexibility of the metallacycle and the influence of the N–

Table 2
Comparative selected bond lengths (Å) and angles (°) for **4** [X = Cl], **5** [X = Br], **2** [X = I] and **3**

	4 [X = Cl]	**5** [X = Br]	**2** [X = I]	**3**
Pd–S	2.320(2)	2.336(2)	2.349(2)	2.317(3)
	2.332(3)	2.338(3)	2.350(2)	2.324(3)
		2.340(3)	2.356(2)	2.330(3)
		2.345(3)	2.360(2)	2.332(3)
Pd–P	2.341(2)	2.335(3)	2.344(2)	2.327(3)
	2.351(2)	2.342(3)	2.347(2)	2.329(3)
		2.347(3)	2.349(2)	2.337(3)
		2.358(3)	2.352(2)	2.345(3)
Ni–N(inside)	1.867(9)	1.865(8)	1.875(8)	1.864(9)
	1.885(8)	1.868(8)	1.879(8)	1.873(8)
		1.879(8)	1.886(8)	1.873(9)
		1.884(8)	1.897(8)	1.877(10)
Ni–N(outside)	1.846(13)	1.832(9)	1.847(10)	1.842(9)
	1.851(10)	1.847(9)	1.849(10)	1.846(11)
		1.855(9)	1.861(10)	1.851(12)
		1.870(8)	1.868(10)	1.865(10)
S–Pd–P	86.15(8)	83.42(9)	83.55(8)	84.70(10)
	86.22(9)	85.18(10)	83.82(9)	85.31(10)
	88.02(9)	85.32(10)	84.60(9)	86.13(11)
	91.97(9)	86.55(10)	84.61(9)	86.77(11)
		88.82(11)	90.26(9)	88.20(10)
		90.92(9)	90.35(10)	89.79(11)
		90.74(10)	91.34(9)	90.93(11)
		90.94(10)	92.00(8)	91.64(11)
S–Pd–S	157.14(10)	149.93(9)	148.63(8)	153.10(12)
		150.91(10)	149.44(8)	153.75(12)
P–Pd–P	160.48(9)	161.54(9)	161.17(9)	161.04(11)
		162.86(10)	162.23(8)	162.67(11)

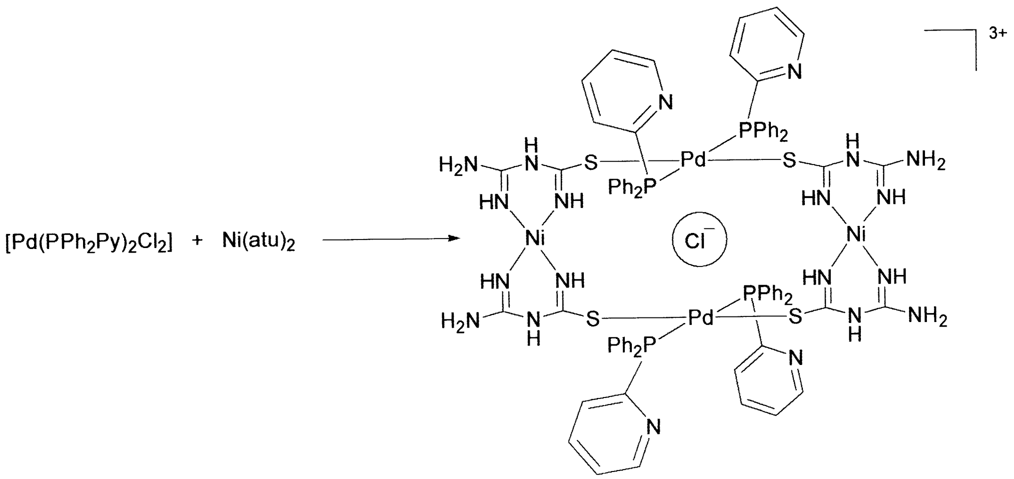


Fig. 4. Schematic representation of **3** showing the potential coordinating pyridyl groups.

H···X hydrogen bonds which become progressively longer as one goes from chloride → iodide. The two Ni(atu)$_2$ moieties have near-planar conformations with folds in their chelate rings ranging between only 0° and 8°. Other gross structural features are very similar to those of the bromide complex, there being an intramolecular π–π stacking interaction between an "upper" and "lower" pair of phenyl rings thereby restricting approach to the central anion (the mean interplanar separation is 3.61 Å). An analysis of inter-metallacycle interactions was not considered realistic as both the perchlorate anions and the included solvent molecules are disordered.

2.3. Anion-directed synthesis of $[Pd_2Ni_2(atu)_4(PPh_2Py)_4Cl][ClO_4]Cl$ (3)

Having clearly established the templating role of the anions, it was of interest to prepare metalla-macrocycles with different phosphines. Specifically, the anion-templated synthesis of a metalla-macrocycle with coordinated PPh$_2$Py (where Py = 2-pyridyl) instead of PPh$_3$ was studied. Such species could potentially lead to the formation of extended structures by coordination of the pyridine nitrogen to a second metal centre (see Fig. 4).

Macrocycle **3** was prepared by reacting a suspension of [Pd(PPh$_2$Py)$_2$Cl$_2$] in CH$_2$Cl$_2$ with Ni(atu)$_2$ in methanol (formed in situ) for 2 h. The reaction mixture was monitored by $^{31}P\{^1H\}$ NMR until full conversion of the starting material ($\delta = 22.6$ ppm) to **3** ($\delta = 19.9$ ppm) had been achieved (after approximately 2 h). An orange solid was isolated from the reaction mixture by addition of diethyl ether. On the basis of IR, $^{31}P\{^1H\}$ NMR, FAB-MS and elemental analyses, this solid was formulated as [Pd$_2$Ni$_2$(atu)$_4$(PPh$_2$Py)$_4$Cl][ClO$_4$]$_2$Cl (**3**).

Crystals suitable for X-ray structural analysis were obtained by slow diffusion of diethyl ether into a methanol solution of **3**. The metalla-macrocycle was found to have an overall structure virtually identical to that of its triphenylphosphine analogue **4**. The chloride anion is positioned essentially centrally between the two independent palladium centres at distances of 3.108(3) and 3.171(3) Å. The palladium atoms are displaced from their P$_2$S$_2$ planes by 0.46 and 0.44 Å for Pd(1) and Pd(2), respectively. The twist of the "upper" and "lower" coordination planes with respect to each other is here 52°, cf. 44° in the triphenylphosphine species **4**. The transannular Pd···Pd and Ni···Ni distances are 6.28 and 8.82 Å, values that are smaller and greater,

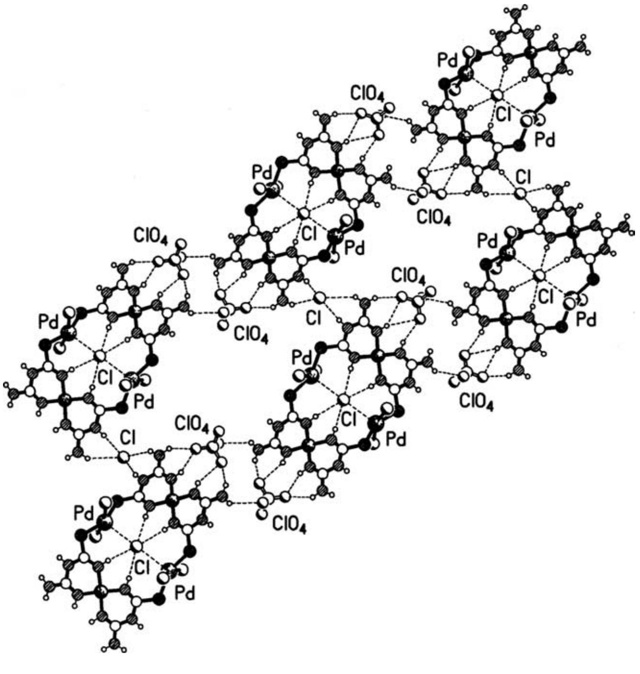


Fig. 5. Part of one of the extended two-dimensional sheets of N–H···O and N–H···Cl linked metallacycles present in the crystals of **3**.

respectively, than those in the triphenylphosphine complex [6.53, 8.69 Å] reflecting the increased twist between the two palladium coordination planes (vide supra). There are no intramolecular aromatic···aromatic interactions of note. Unfortunately, it was not possible to determine unambiguously the positions of the pyridyl rings within the phosphines. This failure may be a consequence of randomisation of their relative positions throughout the crystal.

In contrast to **2**, here the perchlorate anions are moderately well ordered, though the "external" chloride anion does exhibit some disorder (80:20). Ignoring the solvent molecules one can see that regular two-dimensional hydrogen-bonded sheets are produced by a combination of N–H···O and N–H···Cl hydrogen bonds to the non-encapsulated ClO_4 and Cl anions (Fig. 5).

The thermal vibration parameters of the perchlorate oxygen atoms are, however, somewhat larger than those of the atoms of the metallacycle probably reflecting an attempt to satisfy the hydrogen bonding potential of the many N–H donor sites on the periphery of the macrocycle.

3. Conclusions

The structural determination of $[Pd_2Ni_2(atu)_4(PPh_3)_4I][ClO_4]_3$ (**2**) presented in this work has provided the opportunity to compare important structural features with those of the previously reported analogues **4** and **5**. The three halides act as good templating agents for the assembly of $Ni(atu)_2$ and $Pd(PPh_3)_2$ units, in spite of their differences in size. The structural features discussed in this paper indicate the reasons for this *templating flexibility*: the Pd···X interactions increase on going from chloride → bromide → iodide which in turn make the Pd···Pd distances shorter in the same order. Consequently the dimensions of the macrocycle along the Pd···Pd axis are reduced. On the other hand, due to the relative twist of the "upper" PdS_2P_2 unit with respect to its "lower" counterpart about the Pd···Pd vector, the N–H···X hydrogen bonds become longer on going from chloride to iodide, i.e., the macrocycle becomes larger along the Ni···Ni axis from chloride to iodide. As a consequence of this structural flexibility, the three different halides can all act as templating agents for the formation of the metalla-macrocycles.

The possibility of forming extended structures in the solid state has also been demonstrated. The external H-bonding donor groups in one of the macrocycles (**3**) have been successfully used to interact with perchlorate and chloride anions to form two-dimensional extended networks. We are currently studying the possibility of forming other networks by using H-bonding and pyridine–ligand interactions.

4. Experimental

4.1. General

Reactions were carried out routinely using Schlenk-line techniques under an atmosphere of pure nitrogen. The solvents were used dry and free of oxygen. Infrared spectra were recorded on a Perkin–Elmer 1720 Fourier-transform spectrometer between 4000 and 250 cm^{-1} as KBr pellets. $^{31}P\{^1H\}$ NMR spectra were measured on a JEOL JNM-EX270 Fourier-transform spectrometer operating at a frequency of 109.4 MHz with chemical shifts reported relative to H_3PO_4, and mass spectra were recorded by J. Barton at Imperial College on a VG AutoApec-Q as FAB using 3-nitrobenzyl alcohol as matrix. The compounds $Ni(atu)_2$ and $Pd(PPh_3)(CF_3SO_3)_2$ were prepared according to reported procedures [17,22].

4.2. Preparations

4.2.1. Synthesis of $[Pd(PPh_3)_2(atu)][CF_3SO_3]_2$ (1) from Hatu and $Pd(PPh_3)_2(CF_3SO_3)_2$

A solution of Hatu (0.05 g, 0.46 mmol) in methanol (25 ml) was added to a solution of $Pd(PPh_3)_2(CF_3SO_3)_2$ (0.43 g, 0.46 mmol) in THF (20 ml). The reaction mixture was left stirring at room temperature for 2 h. Most of the solvent was evaporated under reduced pressure and a yellow solid precipitated upon addition of diethyl ether. Yield: 0.29 g (60%). Found: C, 45.76; H, 3.37; N, 5.24%. $C_{40}H_{36}N_4P_2S_3O_6F_6Pd$ requires C, 45.89; H, 3.44; N, 5.35. ν_{max}/cm^{-1} (KBr) 3330s, 3200s (NH) 3061m (CH), 1686m, 1585m (CN), 1481m (Ph), 1260s ($CF_3SO_3^-$). δ^P(Methanol) 32.4 (d, $J = 25$ Hz, 1P), 30.5 (d, $J = 25$ Hz, 1P). FAB-MS$^+$: m/z 747 $\{[Pd(PPh_3)_2(atu)]^+\}$, 630 $\{[Pd(PPh_3)_2]^+\}$, 485 $\{[Pd(PPh_3)(atu)]^+\}$.

4.2.2. Synthesis of $[Pd(PPh_3)_2(atu)][CF_3SO_3]_2$ (1) from $Ni(atu)_2$ and $Pd(PPh_3)_2(CF_3SO_3)_2$

To a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.05 g, 0.14 mmol) in methanol (15 ml), Hatu (0.03 g, 0.28 mmol) in methanol (25 ml) was added. An immediate colour change to dark orange (due to the formation of $Ni(atu)_2$) was observed. The resulting mixture was added to a solution of $Pd(PPh_3)_2(CF_3SO_3)_2$ (0.10 g, 0.13 mmol) in THF (25 ml). The reaction mixture was left stirring at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and a yellow-orange solid precipitated upon addition of diethyl ether. This solid was analysed by $^{31}P\{^1H\}$ NMR and FAB-MS demonstrating to be the same complex **1** than the one obtained by reacting $Pd(PPh_3)_2(CF_3SO_3)_2$ directly with Hatu. No further purification was carried out. δ^P(Methanol) 32.4 (d, $J = 25$ Hz, 1P), 30.5 (d, $J = 25$ Hz, 1P). FAB-MS$^+$: m/z 747 $\{[Pd(PPh_3)_2(atu)]^+\}$, 630 $\{[Pd(PPh_3)_2]^+\}$, 485 $\{[Pd(PPh_3)(atu)]^+\}$.

4.2.3. Synthesis of [$Pd_2(PPh_3)_4Ni_2(atu)_4I][ClO_4]_3$ (**2**)

To a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.08 g, 0.22 mmol) in methanol (15 ml), Hatu (0.05 g, 0.44 mmol) in methanol (25 ml) was added. An immediate colour change to dark orange (due to the formation of $Ni(atu)_2$) was observed. The resulting mixture was added to a solution of $Pd(PPh_3)_2(CF_3SO_3)_2$ (0.20 g, 0.22 mmol) in THF (30 ml). Few minutes later KI (0.02 g, 0.11 mmol) was added as a solid to the reaction mixture which was left stirring at room temperature for 2 h. The solvent was evaporated under reduced pressure and the resulting dark orange solid was recrystallised from a methanol/diethyl ether mixture. Yield: 0.20 g (80%). Found: C, 42.21; H, 3.43; N, 9.92. $C_{80}H_{80}N_{16}P_4S_4O_{12}ICl_3Ni_2Pd_2$ requires C, 42.29; H, 3.52; N, 9.87. ν_{max}/cm^{-1} (KBr) 3343s, 3214s (NH) 3053m (C–H), 1663s, 1599s (CN), 1481m (Ph), 1092s (ClO_4^-). δ^P(Methanol) 18.5 (s).

4.2.4. Synthesis of [$Pd_2(PPh_2Py)_4Ni_2(atu)_4Cl][ClO_4]_2Cl$ (**3**)

To a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.14 g, 0.40 mmol) in methanol (25 ml), Hatu (0.10 g, 0.81 mmol) in methanol (25 ml) was added. An immediate colour change to dark orange-red (due to the formation of $Ni(atu)_2$) was observed. The resulting mixture was added to $PdCl_2(PPh_2Py)_2$ (0.29 g, 0.41 mmol) suspended in CH_2Cl_2 (25 ml). The reaction mixture was left stirring at room temperature for 2 h. The solvent was evaporated under reduced pressure and the resulting orange solid was recrystallised from a methanol/diethyl ether mixture. Yield 0.27 g (61%). Found: C, 41.28; H, 3.63; N, 12.77. $[C_{76}H_{76}N_{20}P_4S_4Ni_2Pd_2{\cdot}Cl](Cl)(ClO_4)_2{\cdot}MeOH{\cdot}H_2O{\cdot}CH_2Cl_2$ requires C, 41.53; H, 3.73; N, 12.42. ν_{max}/cm^{-1} (KBr) 3338s, 3201s (NH) 3049m (CH), 1654s, 1597s (CN), 1478m (Ph), 1094s (ClO_4^-). δ^P(Methanol) 19.9 (s). FAB-MS$^+$: m/z 1557 {$[Pd_2(PPh_2Py)_4Ni(atu)_2]^+$}, 1360 {$[Pd_2(PPh_2Py)_2Ni_2(atu)_4Cl]^+$}, 1324 {$[Pd_2(PPh_2Py)_2Ni_2(atu)_4]^+$}, 1061, {$[Pd_2(PPh_2Py)Ni_2(atu)_4]^+$}.

4.3. Crystallography

4.3.1. Crystal data for **1**

$[C_{38}H_{36}N_4P_2SPd](SO_3CF_3)_2 \cdot CH_2Cl_2$, $M = 1217.1$, monoclinic, $P2_1/n$ (no. 14), $a = 12.360(1)$, $b = 24.145(3)$, $c = 17.218(2)$ Å, $\beta = 92.94(1)°$, $V = 5132(1)$ Å^3, $Z = 4$, $D_c = 1.575$ g cm^{-3}, μ(Cu Kα) $= 7.18$ mm^{-1}, $T = 183$ K, yellow prisms; 7609 independent measured reflections, F^2 refinement, $R_1 = 0.052$, $wR_2 = 0.117$, 5937 independent observed absorption corrected reflections $[|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°]$, 590 parameters. CCDC 183543.

4.3.2. Crystal data for **2**

$[C_{80}H_{80}N_{16}P_4S_4Ni_2Pd_2 \cdot I](ClO_4)_3 \cdot 4.5EtOH \cdot 5MeO\text{-}5MeOH \cdot 0.25H_2O$, $M = 2645.2$, triclinic, $P\bar{1}$ (no. 2), $a = 19.122(3)$, $b = 19.487(2)$, $c = 21.178(1)$ Å, $\alpha = 86.56(1)°$, $\beta = 76.08(1)°$, $\gamma = 61.08(1)°$, $V = 6690(1)$ Å^3, $Z = 2$, $D_c = 1.313$ g cm^{-3}, μ(Cu Kα) $= 6.36$ mm^{-1}, $T = 203$ K, orange platy prisms; 19,831 independent measured reflections, F^2 refinement, $R_1 = 0.077$, $wR_2 = 0.204$, 13,515 independent observed absorption corrected reflections $[|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°]$, 1311 parameters. CCDC 183454.

4.3.3. Crystal data for **3**

$[C_{76}H_{76}N_{20}P_4S_4Ni_2Pd_2 \cdot Cl](Cl)(ClO_4)_2 \cdot 3.5MeOH \cdot Et_2O \cdot 0.5H_2O \cdot 0.5CH_2Cl_2$, $M = 2359.5$, monoclinic, $P2/c$ (no. 13), $a = 30.023(3)$, $b = 15.237(1)$, $c = 25.184(2)$ Å, $\beta = 101.95(1)°$, $V = 11271(2)$ Å^3, $Z = 4$, $D_c = 1.390$ g cm^{-3}, μ(Cu Kα) $= 5.73$ mm^{-1}, $T = 183$ K, yellow platy needles; 16,712 independent measured reflections, F^2 refinement, $R_1 = 0.090$, $wR_2 = 0.235$, 10,416 independent observed absorption corrected reflections $[|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 120°]$, 1173 parameters. CCDC 183455.

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