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Synthesis, structure and characterisation of amido derivatives of [9]aneN_3 (1,4,7-triazacyclononane)‡

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The amido species OHC[9]aneN_3 (1-formyl-1,4,7-triazacyclononane), [OHC[9]aneN_3H]BPh_4, $(OHC)_3$[9]aneN_3 (1,4,7-triformyl-1,4,7-triazacyclononane) and $(PhOC)_3$[9]aneN_3 (1,4,7-tribenzoyl-1,4,7-triazacyclononane) have been synthesised, characterised and their crystal structures determined. The conformations of these compounds are discussed in terms of their solid-state structures and of their ^1H and ^{13}C NMR spectra in solution. Symmetric isomers derived from hindered rotation about the N–C (amide) bond are generally preferred to asymmetric ones, with the N–C(O)R (R = H or Ph) forming a planar unit *exo* to the triazamacrocycle. Complexation of Pd^{II} with OHC[9]aneN_3 confirms the bidentate binding of this ligand and affords $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2{\cdot}2H_2O$, the single-crystal structure of which shows the Pd atom at an inversion centre with Pd–N 2.057(13) and 2.065(10) Å. The amide functions lie above and below the square-planar metal centre with Pd ··· N (amide) 3.021(12) Å. The retention of planarity within the amide function upon complexation [torsion angle for C(2)–N(1)–C(10)–O(11) −6(2)°] suggests that there is no interaction between the amide group and the metal centre.

Interest in cyclic orthoamides and related compounds stems in part from the unusual reactivity that such compounds show in comparison to their non-macrocyclic analogues.[1–7] In 1974 Richman and Simmons[1] reported the reaction between [12]aneN_4 (1,4,7,10-tetraazacyclododecane) and $C(OEt)_4$ to yield the corresponding tetracyclic amine. Protonation of this species with HCl afforded an intramolecular guanidinium ion in which all the ring CH_2 groups are equivalent. This contrasts with non-macrocyclic analogues such as $C(NMe_2)_4$ which dissociate readily and irreversibly to give $NHMe_2$ and the hexamethylguanidinium ion $[C(NMe_2)_3]^+$ in water.[8] The insertion of PR groups into [12]aneN_4 *via* reaction of RPF_4 (R = Ph or Me) with *N,N′,N″,N‴*-tetrakis(trimethylsilyl)-1,4,7,10-tetraazacyclododecane has also been achieved.[2] This method has been developed further by Atkins[3,4] to incorporate phosphorus atoms into triazamacrocycles by reaction of $P(NMe_2)_3$. Interestingly, the tricyclic phosphorus triamide derived from [9]aneN_3 (1,4,7-triazacyclononane) could not be isolated, the failure being attributed to ring strain caused by the expected long P–N bond length.[3] The insertion of CH groups into triazamacrocycles has been reported by several workers.[5–7,9] The crystal structures of orthoamide derivatives of [9]aneN_3[10] and of [12]aneN_3 (1,5,9-triazacyclododecane)[11] have been determined, the latter as both the trihydrate and also in the anhydrous form. The structure of the trihydrate confirms an all-*trans* configuration, although the anhydrous material is a 1 : 1 mixture of the all-*trans* configuration and the *cis,cis,trans* configuration, where two of the lone pairs are *syn* periplanar. The structure of the complex $[MoL(CO)_3]$ (L = orthoamide of [12]aneN_3) has also been reported[12] and shows L acting as a tridentate donor to the metal centre in the expected all-*trans* conformation. It is important to note the strain in the N–Mo–N bond angles which have values of 57.7(1) and 58.0(1)°.

The suitability of orthoamides as potential precursors to functionalised macrocycles was first reported by Weisman *et al.*,[13] and can be used for the synthesis of linked macrocycles. Thus reaction of the orthoamide of [9]aneN_3 with a terminal diiodoalkane affords a dicationic intermediate which can be hydrolysed to yield a product containing two [9]aneN_3 macrocycles linked by an alkyl chain. Such 'ear-muff' compounds have been reported previously *via* much lower-yielding syntheses: the original synthesis by Takamoto and co-workers[14] achieved a yield of 1%. This was increased to 40% by Wieghardt *et al.*,[15] through a synthesis involving statistical ditosylation of [9]aneN_3, followed by alkylation with 1,2-dibromoethane and then detosylation; a similar synthesis has been reported by Sessler *et al.*[16] The orthoamide approach is more straightforward and results in a higher yield.[17]

We were interested in developing the chemistry of asymmetrically functionalised [9]aneN_3 compounds, particularly amido derivatives such as OHC[9]aneN_3 (1-formyl-1,4,7-triazacyclononane). Amides are basic *via* the O-donors rather than the N; we reasoned that monofunctionalised compounds such as OHC[9]aneN_3 would therefore act as bi- rather than tri-dentate ligands, thus affording complexes in which two N-donors would bind to the metal centre, leaving the amide function *exo* to the ring available for hydrogen bonding. We have recently reported the preparation of asymmetrically functionalised pendant-arm compounds from the orthoamide of [9]aneN_3.[18]

Results and Discussion

Monoamide derivatives of [9]aneN_3

The compound [9]aneN_3 was synthesised following the method reported by Richman and Atkins[19] for the synthesis of azamacrocycles. The conversion of [9]aneN_3 into its orthoamide derivative, 1,4,7-triazatricyclo[5.2.1.$0^{4,10}$]decane **I**, was achieved in high yield by reaction of [9]aneN_3 with neat $(MeO)_2CHNMe_2$,[7] and was purified by bulb-to-bulb distillation. Hydrolysis of the orthoamide in dilute hydrochloric acid for 8 h afforded OHC[9]aneN_3 in yields ranging from 50 to 70% (Scheme 1). The ^{13}C NMR spectrum of OHC[9]aneN_3 is presented in Fig. 1. Six methylene resonances are observed consistent with the expected restricted rotation around the

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‡ *Non-SI unit employed:* D ≈ 3.33 × 10^{-30} C m.

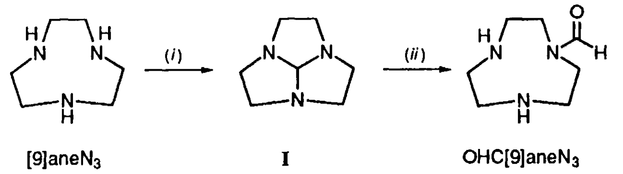
Table 1 Selected bond lengths (Å), angles and torsion angles (°) for OHC[9]aneN$_3$

N(1)–C(1)	1.335(2)	N(1)–C(2)	1.461(2)
N(1)–C(9)	1.465(2)	C(2)–C(3)	1.527(2)
C(3)–N(4)	1.454(2)	N(4)–C(5)	1.457(2)
C(5)–C(6)	1.518(3)	C(6)–N(7)	1.469(2)
N(7)–C(8)	1.458(2)	C(8)–C(9)	1.520(2)
C(1)–O	1.233(2)		
C(1)–N(1)–C(2)	119.23(13)	C(1)–N(1)–C(9)	120.25(13)
C(2)–N(1)–C(9)	120.22(12)	N(1)–C(2)–C(3)	113.75(13)
C(2)–C(3)–N(4)	112.45(14)	C(3)–N(4)–C(5)	118.21(14)
N(4)–C(5)–C(6)	113.32(15)	C(5)–C(6)–N(7)	112.90(14)
C(6)–N(7)–C(8)	115.31(13)	N(7)–C(8)–C(9)	112.43(13)
N(1)–C(9)–C(8)	114.13(13)	O–C(1)–N(1)	124.50(14)
C(3)–C(2)–N(1)–C(9)	109.01(16)	C(3)–C(2)–N(1)–C(1)	−77.21(18)
C(8)–C(9)–N(1)–C(2)	−69.59(18)	C(8)–C(9)–N(1)–C(1)	116.70(16)
C(2)–N(1)–C(1)–O	1.1(2)	C(9)–N(1)–C(1)–O	174.85(14)
N(1)–C(2)–C(3)–N(4)	−65.44(18)	C(2)–C(3)–N(4)–C(5)	103.00(17)
C(3)–N(4)–C(5)–C(6)	−128.22(16)	N(4)–C(5)–C(6)–N(7)	71.71(18)
C(5)–C(6)–N(7)–C(8)	−77.39(17)	C(6)–N(7)–C(8)–C(9)	126.40(14)
N(7)–C(8)–C(9)–N(1)	−61.97(17)		

Table 2 Hydrogen-bonding interactions (Å) in OHC[9]aneN$_3$

Contact	d/Å	Symmetry operation*
O(1) ··· H(7′)	2.24(3)	$(1 + x, y, z)$
H(7) ··· O(1″)	2.24(3)	$(x - 1, y, z)$
N(7) ··· H(4‴)	2.44(3)	$(-x, \frac{1}{2} + y, \frac{1}{2} - z)$
H(4) ··· N(7⁗)	2.44(3)	$(-x, y - \frac{1}{2}, \frac{1}{2} - z)$

* Of primed atom.



[9]aneN$_3$ I OHC[9]aneN$_3$

Scheme 1 (i) $(MeO)_2CHNMe_2$; (ii) water, H^+

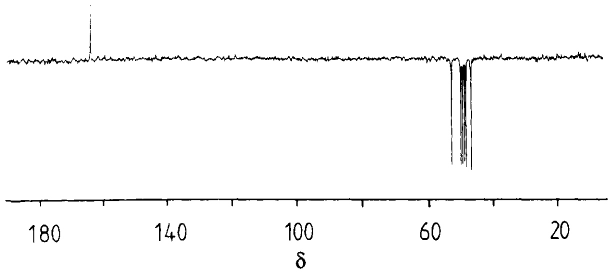


Fig. 1 The ^{13}C DEPT (distortionless enhancements by polarisation transfer) NMR spectrum of OHC[9]aneN$_3$

C–N bond of the amide moiety. This leads to inequivalence of each C atom of the ring. The structures of OHC[9]aneN$_3$ and its monoprotonated salt [OHC[9]aneN$_3$H]BPh$_4$ were determined by single-crystal X-ray diffraction in order to ascertain the extent of any intermolecular interactions.

Crystals suitable for X-ray analysis were obtained by evaporation of a CHCl$_3$ solution of OHC[9]aneN$_3$. Selected bond lengths, angles and torsions are given in Table 1 and a view of the molecule is shown in Fig. 2. The macrocycle adopts a [333] conformation according to Dale's notation;[20] the C(2)C(9)N(1)–C(1)O(1)H(1) amide moiety is essentially planar [C(2)–N(1)–C(1)–O(1) torsion = 1.1(2)°], with the short N(1)–C(1) bond length [1.335(2) Å] being consistent with the double-bond character of C–N bonds in typical amide groups.[21]

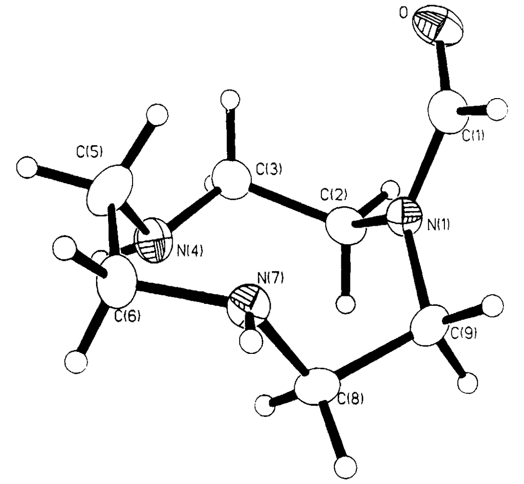


Fig. 2 Structure of OHC[9]aneN$_3$ with the numbering scheme adopted

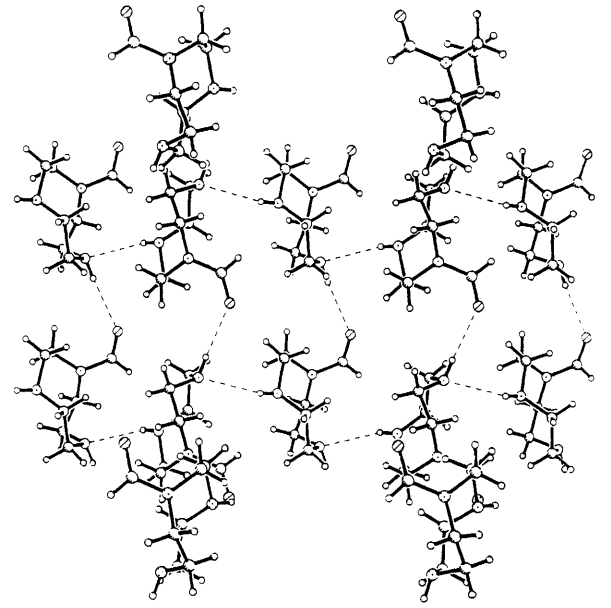


Fig. 3 Packing diagram of OHC[9]aneN$_3$

The main point of interest regarding this structure is the strained conformation adopted by the macrocyclic ring. This is reflected in the torsion angles H(7)–N(7)–C(8)–H(8A) and

Table 3 Selected bond lengths (Å), angles and torsion angles (°) for $[OHC[9]aneN_3H]BPh_4$

N(1)–C(10)	1.338(7)	N(1)–C(2)	1.454(7)
N(1)–C(9)	1.479(7)	C(2)–C(3)	1.517(8)
C(3)–N(4)	1.511(7)	N(4)–C(5)	1.486(7)
C(5)–C(6)	1.522(8)	C(6)–N(7)	1.457(8)
N(7)–C(8)	1.470(7)	C(8)–C(9)	1.501(8)
C(10)–O(11)	1.226(7)		
C(10)–N(1)–C(2)	120.3(5)	C(10)–N(1)–C(9)	119.0(5)
C(2)–N(1)–C(9)	120.6(5)	N(1)–C(2)–C(3)	116.0(5)
N(4)–C(3)–C(2)	113.8(5)	C(5)–N(4)–C(3)	119.2(4)
N(4)–C(5)–C(6)	115.6(5)	N(7)–C(6)–C(5)	113.5(5)
C(6)–N(7)–C(8)	115.0(5)	N(7)–C(8)–C(9)	114.2(5)
N(1)–C(9)–C(8)	114.7(5)	O(11)–C(10)–N(1)	125.1(6)
C(9)–N(1)–C(2)–C(3)	−59.8(8)	C(10)–N(1)–C(2)–C(3)	124.4(6)
C(2)–N(1)–C(9)–C(8)	100.8(6)	C(10)–N(1)–C(9)–C(8)	83.4(7)
C(2)–N(1)–C(10)–H(10)	176.6(7)	C(2)–N(1)–C(10)–O(11)	−3.4(10)
C(9)–N(1)–C(10)–H(10)	0.8(10)	C(9)–N(1)–C(10)–O(11)	−179.2(6)
N(1)–C(2)–C(3)–N(4)	−67.6(7)	C(2)–C(3)–N(4)–C(5)	67.5(7)
C(3)–N(4)–C(5)–C(6)	62.0(7)	N(4)–C(5)–C(6)–N(7)	−62.6(7)
C(5)–C(6)–N(7)–C(8)	−67.9(7)	C(6)–N(7)–C(8)–C(9)	112.8(6)
N(7)–C(8)–C(9)–N(1)	−71.7(1)		

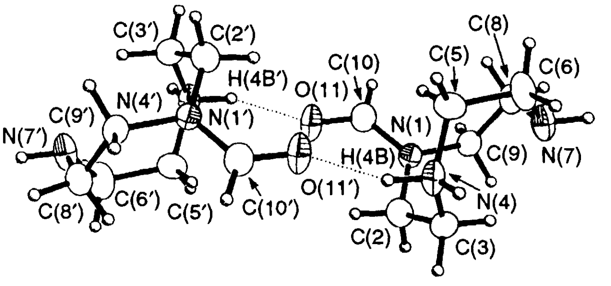
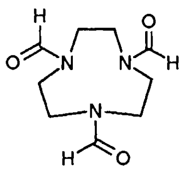


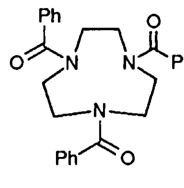
Fig. 4 Structure of the cation of $[OHC[9]aneN_3H]BPh_4$ with the numbering scheme adopted

$H(4)–N(4)–C(5)–H(5B)$ of 5.8(18) and −18.4(18)° respectively. Molecular models show the ring to be sufficiently flexible that this conformation need not be adopted. The ring strain is counterbalanced by long-range intermolecular hydrogen bonding between the amide and amine functions of adjacent molecules. This can be seen in the packing diagram (Fig. 3). Each molecule makes four long-range contacts to adjacent molecules *via* CO · · · HN and NH · · · N interactions of 2.24(3) and 2.44(3) Å respectively. These contacts are listed in Table 2. Consideration of the relative energies involved in hydrogen bonds (12–25 kJ mol^{-1}) and of the energy difference between eclipsed and staggered conformations (10–20 kJ mol^{-1}) leads to the conclusion that the ring strain is compensated for by the hydrogen bonding. However, it must be borne in mind that these hydrogen bonds are long relative to those observed in amino acids (1.8–1.9 Å),[22] and hence the energy gain will not be very large. Crystal-packing forces may also have an effect upon the macrocyclic conformation.

Whilst attempting to prepare a nickel(II) complex of $OHC[9]aneN_3$ colourless crystals were obtained analysis of which suggested the composition $[OHC[9]aneN_3H]BPh_4$. The FAB mass spectrum did not show a molecular-ion peak for the cation $OHC[9]aneN_3H^+$ (*m*/*z* 158), although there was a strong peak at *m*/*z* 315 corresponding to a dimer $[(OHC[9]aneN_3)_2H]^+$. A single-crystal structure determination was undertaken in order to confirm the nature of this product and for comparison with that of the unprotonated amide. The assignment as the monoprotonated ligand was confirmed. Selected bond lengths, angles and torsions are given in Table 3 and a view of the cation is shown in Fig. 4. As in $OHC[9]aneN_3$, the amide moiety is planar with a C(9)–N(1)–C(10)–H(10) torsion angle of 0.8(10)°. The bond lengths are very similar to those observed for $OHC[9]aneN_3$ with the ring adopting a [2223] conformation and with H–C–X–H torsions (X = C or N) in the range 48.5–68.6°. The protons on N(4) and N(7) were located and these N atoms can therefore be assigned as NH_2^+ and NH respectively. The cations form a dimeric structure linked together *via* equivalent NH · · · OC contacts of 1.822(7) Å between the amide O-donor [O(11)] of one cation and one H atom [H(4B)] of the protonated N-donor [N(4)] of the other cation, with the two molecules related by an inversion centre at ($\frac{1}{2}$, 0, 1) (Fig. 4). This explains the presence of the peak at *m*/*z* 315 (for the dimer) in the FAB mass spectrum and the absence of a molecular-ion peak for the $OHC[9]aneN_3$ monomer.



$(OHC)_3[9]aneN_3$

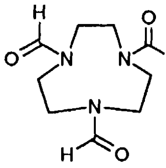


$(PhOC)_3[9]aneN_3$

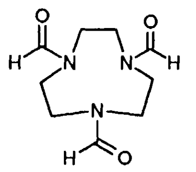
Triamide derivatives of $[9]aneN_3$

We argued that the incorporation of three amide functions into $[9]aneN_3$ will give a potential tridentate donor ligand, which could co-ordinate to a metal centre *via* the three amide O atoms. Reaction of $[9]aneN_3$ with formic acid and acetic anhydride affords 1,4,7-triformyl-1,4,7-triazacyclononane $(OHC)_3[9]aneN_3$ in high yield, while treatment of $[9]aneN_3$ with PhCOCl yielded the tribenzoyl species $(PhCO)_3[9]aneN_3$. The IR spectra of these compounds showed the presence of ν_{CO} amide stretches at 1664 and 1636 cm^{-1} respectively. The incorporation of three amide groups into $[9]aneN_3$ also introduces the possibility of two isomers, due to the planarity of the amide group and its period of rotation of approximately 0.1 s.[21,22] This has been observed in the ^1H and ^{13}C NMR spectra of $OHC[9]aneN_3$ (Fig. 1). The two possible isomers for the triamide are the symmetric isomer **A** with all amide functions equivalent (a tristellane conformation) and the asymmetric isomer **B**.

The slow rotation about the amide C–N bond allows different isomers to be observed.[21] The symmetric isomer of the triamide should exhibit two ring signals in the ^{13}C NMR spectrum, whilst the asymmetric isomer should exhibit six.



A
Symmetric isomer



B
Asymmetric isomer

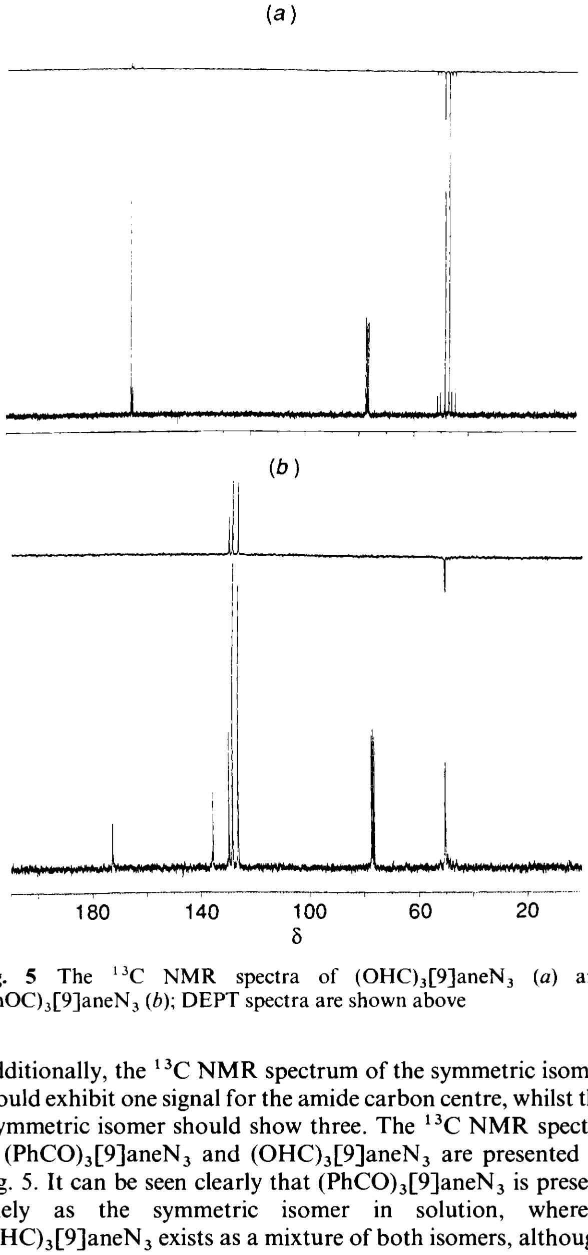


Fig. 5 The ^{13}C NMR spectra of $(OHC)_3[9]aneN_3$ (*a*) and $(PhOC)_3[9]aneN_3$ (*b*); DEPT spectra are shown above

Additionally, the ^{13}C NMR spectrum of the symmetric isomer should exhibit one signal for the amide carbon centre, whilst the asymmetric isomer should show three. The ^{13}C NMR spectra of $(PhCO)_3[9]aneN_3$ and $(OHC)_3[9]aneN_3$ are presented in Fig. 5. It can be seen clearly that $(PhCO)_3[9]aneN_3$ is present solely as the symmetric isomer in solution, whereas $(OHC)_3[9]aneN_3$ exists as a mixture of both isomers, although the symmetric isomer is present in about four-fold excess. The ^1H NMR spectrum of $(OHC)_3[9]aneN_3$ (Fig. 6) shows the three amide CH resonances of the asymmetric isomer at δ 7.96, 8.08 and 8.22, and the more intense amide CH signal for the symmetric isomer at δ 8.03. The prevalence of the symmetric isomers in solution can be rationalised in terms of dipole–dipole interactions within the molecules, the dipole moments of amides being of the order 3.75 ± 0.1 D,[21,23] particularly large in comparison to polar molecules such as HF (1.75 D) or H_2O (1.84 D). It would appear that the symmetric isomers of $(OHC)_3[9]aneN_3$ and $(PhCO)_3[9]aneN_3$ allow more favourable dipole alignment than do the asymmetric isomers. Steric arguments may also be relevant to these systems.

As stated previously, amides are generally poor donors to metal centres, although anchoring them within a chelate ring would be expected to increase the stability of the resultant complexes. The compounds $(OHC)_3[9]aneN_3$ and $(PhCO)_3[9]aneN_3$ may both be potential donors to metal centres *via* the three amide O atoms. Preliminary studies confirm that complexes of type $[M(OHC[9]aneN_3)_2]^{x+}$ (M = Ni, Co or Cu) can be prepared. The IR spectra of these species exhibit a lowering of the ν_{CO} amide stretching vibration by 30 cm^{-1} consistent with binding of the O atoms of the amide group to the metal centre.[24] In order to study their potential ligating ability and to shed light on their conformational properties, single-crystal structure determinations of $(OHC)_3[9]aneN_3$ and $(PhCO)_3[9]aneN_3$ were undertaken.

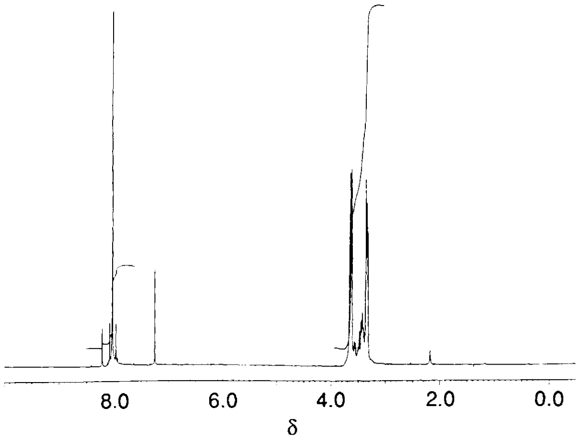


Fig. 6 Proton NMR spectrum of $(OHC)_3[9]aneN_3$

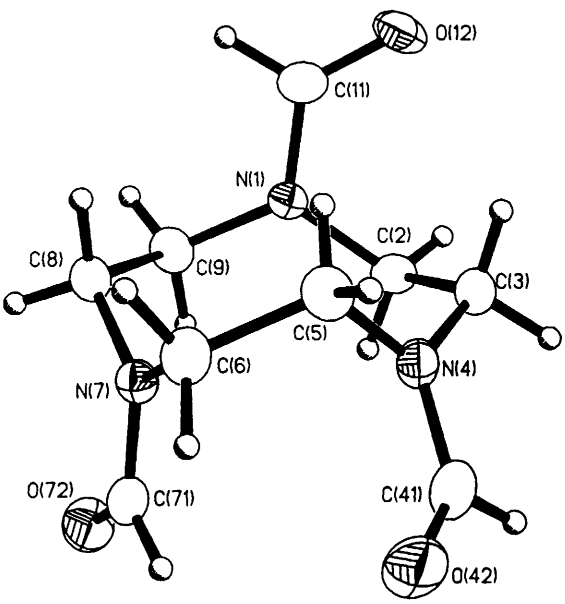


Fig. 7 Structure of $(OHC)_3[9]aneN_3$ with the numbering scheme adopted

Colourless plates suitable for X-ray diffraction purposes were obtained by cooling a concentrated solution of $(OHC)_3[9]aneN_3$ in ethanol. Selected bond lengths, angles and torsions are given in Table 4. A view of the molecule is shown in Fig. 7. The molecule possesses no crystallographically imposed symmetry, thus each atom is unique. All three amide functions are essentially planar and are oriented in the same direction around the ring to afford the symmetric isomer (as in the NMR spectra).

Selected bond lengths, angles and torsions for $(PhCO)_3[9]aneN_3$ are given in Table 5, and a view of the molecule is shown in Fig. 8. The molecule possesses no crystallographically imposed symmetry, thus each atom is unique. All three amide functions are essentially planar and are oriented in the same direction around the ring to give the symmetric isomer, as in the structure of $(OHC)_3[9]aneN_3$.

Table 4 Selected bond lengths (Å), angles and torsion angles (°) for (OHC)$_3$[9]aneN$_3$

N(1)–C(11)	1.338(2)	N(1)–C(9)	1.459(3)
N(1)–C(2)	1.464(3)	C(11)–O(12)	1.225(2)
C(2)–C(3)	1.514(3)	C(3)–N(4)	1.462(3)
N(4)–C(41)	1.338(3)	N(4)–C(5)	1.460(3)
C(41)–O(42)	1.228(3)	C(5)–C(6)	1.522(3)
C(6)–N(7)	1.456(3)	N(7)–C(71)	1.337(3)
N(7)–C(8)	1.461(3)	C(71)–O(72)	1.228(3)
C(8)–C(9)	1.521(3)		
C(11)–N(1)–C(9)	119.8(2)	C(11)–N(1)–C(2)	117.9(2)
C(9)–N(1)–C(2)	121.1(2)	O(12)–C(11)–N(1)	124.2(2)
N(1)–C(2)–C(3)	115.5(2)	N(4)–C(3)–C(2)	115.5(2)
C(41)–N(4)–C(5)	120.3(2)	C(41)–N(4)–C(3)	120.5(2)
C(5)–N(4)–C(3)	118.7(2)	O(42)–C(41)–N(4)	124.7(2)
N(4)–C(5)–C(6)	114.3(2)	N(7)–C(6)–C(5)	113.6(2)
C(71)–N(7)–C(6)	120.2(2)	C(71)–N(7)–C(8)	119.5(2)
C(6)–N(7)–C(8)	120.0(2)	O(72)–C(71)–N(7)	125.3(2)
N(7)–C(8)–C(9)	114.5(2)	N(1)–C(9)–C(8)	114.7(2)
C(9)–N(1)–C(11)–O(12)	−174.4(2)	C(2)–N(1)–C(11)–O(12)	−6.5(3)
C(11)–N(1)–C(2)–C(3)	75.0(2)	C(9)–N(1)–C(2)–C(3)	−117.4(2)
N(1)–C(2)–C(3)–N(4)	64.0(3)	C(2)–C(3)–N(4)–C(41)	106.6(2)
C(2)–C(3)–N(4)–C(5)	−81.1(2)	C(5)–N(4)–C(41)–O(42)	1.5(3)
C(3)–N(4)–C(41)–O(42)	173.7(2)	C(41)–N(4)–C(5)–C(6)	−62.2(2)
C(3)–N(4)–C(5)–C(6)	125.5(2)	N(4)–C(5)–C(6)–N(7)	−49.5(3)
C(5)–C(6)–N(7)–C(71)	108.8(2)	C(5)–C(6)–N(7)–C(8)	−77.4(2)
C(6)–N(7)–C(71)–O(72)	176.8(2)	C(8)–N(7)–C(71)–O(72)	3.0(3)
C(71)–N(7)–C(8)–C(9)	−75.4(2)	C(6)–N(7)–C(8)–C(9)	110.7(2)
C(11)–N(1)–C(9)–C(8)	−89.4(2)	C(2)–N(1)–C(9)–C(8)	103.1(2)
N(7)–C(8)–C(9)–N(1)	−65.7(2)		

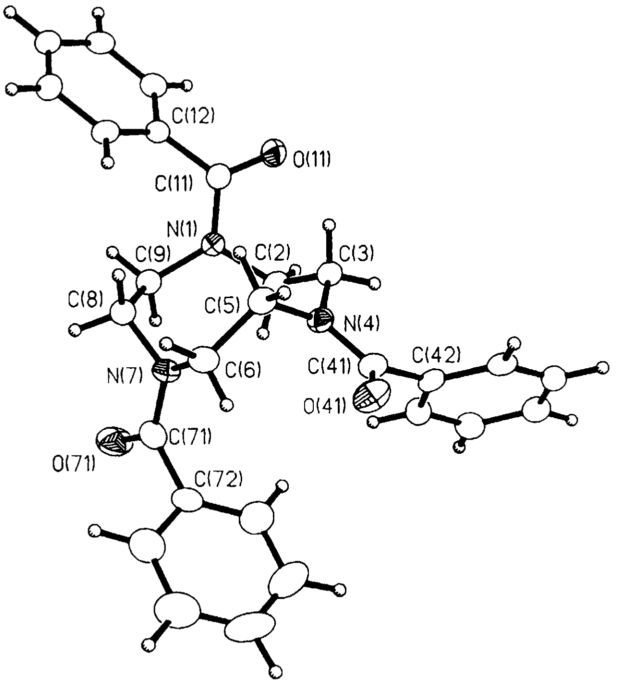


Fig. 8 Structure of (PhOC)$_3$[9]aneN$_3$ with the numbering scheme adopted

Ring conformations of (OHC)$_3$[9]aneN$_3$ and (PhCO)$_3$[9]aneN$_3$

Table 6 presents the equivalent ring torsion angles for (OHC)$_3$[9]aneN$_3$ and (PhOC)$_3$[9]aneN$_3$. The conformations of the rings are very similar although formally they show [333] and [234] conformations respectively (a corner being defined as a torsion angle of less than 90°).[20] This conformational similarity cannot be attributed to crystal-packing forces, since these molecules adopt very different packing motifs. One might expect the rings to adopt C_3 or pseudo-C_3 symmetry, with the amide groups oriented outwards from the ring. However, the observed conformations lead to two amide groups being directed above the ring and one group being directed below. This is illustrated in Figs. 7 and 8, which show both compounds viewed from the same perspective. Molecular models of these molecules show that the conformations adopted in the solid state minimise C–H bond eclipsing in the ring, and that a ring of C_3 symmetry would adopt an unfavourable conformation where all of the ring protons are eclipsed.

The crystal structures of (OHC)$_3$[9]aneN$_3$ and (PhCO)$_3$[9]aneN$_3$ show that neither species is preorganised to co-ordinate to a metal centre *via* the three O atoms. However, they do confirm the presence of the symmetric isomer in the solid state, which has also been observed in the solution state. Molecular models of theoretical complexes show that the symmetric isomer is more likely to act as a facially co-ordinating ligand to a metal centre than is the asymmetric isomer. Interestingly, Lattermann[25] has reported a functionalised triamide derivative of [9]aneN$_3$ which exhibits columnar mesophase (liquid crystalline) behaviour. The mesophase behaviour of this substance is lost upon reduction of the amide groups, and may be related to the consequent loss of rigidity in the central ring. Although the structure of (PhCO)$_3$[9]aneN$_3$ thus represents the core of Lattermann's liquid-crystal derivative, it is of limited significance in explaining the mesophase behaviour since such behaviour necessarily occurs at temperatures where the molecules have sufficient energy to change conformation.

[Pd(OHC[9]aneN$_3$)$_2$]X$_2$ [X = PF$_6^-$ or B(C$_6$F$_5$)$_4^-$]

We undertook a series of metal-complexation reactions to determine the modes of co-ordination of these amides. Since OHC[9]aneN$_3$ would be expected to act primarily as a bidentate ligand, its binding to d^8 Pd^{II} was investigated. Reaction of Pd(O$_2$CMe)$_2$ with 2 molar equivalents of OHC[9]aneN$_3$ in CH$_2$Cl$_2$ affords a pale yellow solid after work-up and addition of NH$_4$PF$_6$. The IR spectrum confirmed the presence of ligand (1651 cm^{-1}) and counter ion (837 cm^{-1}) and FAB mass spectrometry gave peaks at *m*/*z* 561 [PdL$_2$(PF$_6$)], 418 (PdL$_2$) and 261 (PdL) (L = OHC[9]aneN$_3$).

Table 5 Selected bond lengths (Å), angles and torsion angles (°) for $(PhOC)_3[9]aneN_3$

N(7)–C(71)	1.357(2)	N(7)–C(6)	1.464(2)
N(7)–C(8)	1.474(2)	C(6)–C(5)	1.520(3)
C(5)–N(4)	1.461(2)	N(4)–C(41)	1.360(2)
N(4)–C(3)	1.466(2)	C(3)–C(2)	1.520(3)
C(2)–N(1)	1.472(2)	N(1)–C(11)	1.369(2)
N(1)–C(9)	1.469(2)	C(9)–C(8)	1.523(3)
C(71)–O(71)	1.227(2)	C(71)–C(72)	1.500(3)
C(41)–O(41)	1.230(2)	C(41)–C(42)	1.496(3)
C(11)–O(11)	1.230(2)	C(11)–C(12)	1.497(2)
C(71)–N(7)–C(6)	122.5(2)	C(71)–N(7)–C(8)	116.9(2)
C(6)–N(7)–C(8)	117.3(2)	N(7)–C(6)–C(5)	113.2(2)
N(4)–C(5)–C(6)	114.4(2)	C(41)–N(4)–C(5)	117.6(2)
C(41)–N(4)–C(3)	122.5(2)	C(5)–N(4)–C(3)	117.3(2)
N(4)–C(3)–C(2)	114.1(2)	N(1)–C(2)–C(3)	114.0(2)
C(11)–N(1)–C(9)	124.4(2)	C(11)–N(1)–C(2)	115.4(2)
C(9)–N(1)–C(2)	117.2(2)	N(1)–C(9)–C(8)	116.0(2)
N(7)–C(8)–C(9)	115.3(2)	O(71)–C(71)–N(7)	121.0(2)
O(71)–C(71)–C(72)	120.6(2)	N(7)–C(71)–C(72)	118.4(2)
C(73)–C(72)–C(71)	121.9(2)	C(77)–C(72)–C(71)	119.1(2)
O(41)–C(41)–N(4)	121.4(2)	O(41)–C(41)–C(42)	120.1(2)
N(4)–C(41)–C(42)	118.5(2)	C(47)–C(42)–C(41)	121.6(2)
C(43)–C(42)–C(41)	119.7(2)	O(11)–C(11)–N(1)	120.4(2)
O(11)–C(11)–C(12)	119.5(2)	N(1)–C(11)–C(12)	120.2(2)
C(17)–C(12)–C(11)	123.8(2)	C(13)–C(12)–C(11)	117.4(2)
C(71)–N(7)–C(6)–C(5)	135.0(2)	C(8)–N(7)–C(6)–C(5)	−66.2(2)
N(7)–C(6)–C(5)–N(4)	−64.9(2)	C(6)–C(5)–N(4)–C(41)	−78.6(2)
C(6)–C(5)–N(4)–C(3)	119.5(2)	C(41)–N(4)–C(3)–C(2)	124.3(2)
C(5)–N(4)–C(3)–C(2)	−74.8(2)	N(4)–C(3)–C(2)–N(1)	84.2(2)
C(3)–C(2)–N(1)–C(11)	74.5(2)	C(3)–C(2)–N(1)–C(9)	−123.8(2)
C(11)–N(1)–C(9)–C(8)	−113.5(2)	C(2)–N(1)–C(9)–C(8)	86.6(2)
C(71)–N(7)–C(8)–C(9)	−83.9(2)	C(6)–N(7)–C(8)–C(9)	116.1(2)
N(1)–C(9)–C(8)–N(7)	−68.3(2)	C(6)–N(7)–C(71)–O(71)	168.3(2)
C(8)–N(7)–C(71)–O(71)	9.4(3)	C(6)–N(7)–C(71)–C(72)	−10.7(3)
C(8)–N(7)–C(71)–C(72)	−169.6(2)	O(71)–C(71)–C(72)–C(73)	100.6(2)
N(7)–C(71)–C(72)–C(73)	−80.4(3)	O(71)–C(71)–C(72)–C(77)	−77.9(3)
N(7)–C(71)–C(72)–C(77)	101.0(2)	C(5)–N(4)–C(41)–O(41)	4.2(3)
C(3)–N(4)–C(41)–O(41)	165.1(2)	C(5)–N(4)–C(41)–C(42)	−176.6(2)
C(3)–N(4)–C(41)–C(42)	−15.7(2)	O(41)–C(41)–C(42)–C(47)	116.2(2)
N(4)–C(41)–C(42)–C(47)	−63.1(2)	O(41)–C(41)–C(42)–C(43)	−61.0(2)
N(4)–C(41)–C(42)–C(43)	119.8(2)	C(9)–N(1)–C(11)–O(11)	−163.5(2)
C(2)–N(1)–C(11)–O(11)	−3.3(2)	C(9)–N(1)–C(11)–C(12)	16.0(3)
C(2)–N(1)–C(11)–C(12)	176.2(2)	O(11)–C(11)–C(12)–C(17)	−137.4(2)
N(1)–C(11)–C(12)–C(17)	43.1(3)	O(11)–C(11)–C(12)–C(13)	39.2(2)
N(1)–C(11)–C(12)–C(13)	−140.3(2)		

Table 6 Comparison of torsion angles (°) for $(OHC)_3[9]aneN_3$ and $(PhOC)_3[9]aneN_3$

	$(OHC)_3[9]aneN_3$	$(PhCO)_3[9]aneN_3$
N(1)–C(2)–C(3)–N(4)	64.0(3)	84.2(2)
C(2)–C(3)–N(4)–C(5)	−81.1(2)	−74.8(2)
C(3)–N(4)–C(5)–C(6)	125.5(2)	119.5(2)
N(4)–C(5)–C(6)–N(7)	−49.5(3)	−64.9(2)
C(5)–C(6)–N(7)–C(8)	−77.4(2)	−66.2(2)
C(6)–N(7)–C(8)–C(9)	110.7(2)	116.1(2)
N(7)–C(8)–C(9)–N(1)	−65.7(2)	−68.3(2)
C(8)–C(9)–N(1)–C(2)	103.1(2)	86.6(2)
C(9)–N(1)–C(2)–C(3)	−117.4(2)	−123.8(2)

Microanalytical data confirmed the assignment of this material as $[Pd(OHC[9]aneN_3)_2][PF_6]_2$. However, the product was only soluble in dmf (dimethylformamide) or dmso (dimethyl sulfoxide), which hindered further characterisation and crystal growth. The ion $[B(C_6F_5)_4]^-$ was therefore used in preference to $[PF_6]^-$, as counter ion in order to prepare a more soluble analogue. A pale yellow solid was isolated, the IR spectrum of which indicated the presence of ligand and counter ion. Mass spectrometry and analytical data confirmed further the assignment of this material as $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2$. A single-crystal structure determination of $[Pd(OHC[9]aneN_3)_2]^{2+}$ was therefore undertaken to compare with the structure reported for $[Pd([9]aneN_3)_2]^{2+}$.[26–28]

Single-crystal structure of $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2 \cdot 2H_2O$

Pale yellow columns of diffraction quality were grown by the diffusion of hexane into a CH_2Cl_2 solution of the complex at −20 °C. Selected bond lengths, angles and torsions are given in Table 7. A view of the $[Pd(OHC[9]aneN_3)_2]^{2+}$ cation is shown in Fig. 9(*a*). The Pd atom lies on an inversion centre and the ligands are bound to the metal centre *via* the two amine donors N(4) and N(7) at distances of 2.057(13) and 2.065(10) Å respectively. The macrocycle adopts a [333] conformation, with the amide functions lying above and below the square-planar metal centre, giving a Pd ··· N(1) distance of 3.021(12) Å. The retention of planarity of the amide function upon complexation [C(2)–N(1)–C(10)–O(11) torsion angle – 6(2)°] suggests that there is no interaction of the amide group with the metal centre. This is also consistent with the spectral evidence which shows only a very slight shift in $\nu_{C=O}$. The structure of the $[Pd(OHC[9]aneN_3)_2]^{2+}$ cation is thus similar to that of $[Pd([9]aneN_3)_2]^{2+}$ in that the Pd^{II} is co-ordinated in a square-planar fashion, with no apical interactions to the rest of the ligand.[27,28]

In $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2 \cdot 2H_2O$ the water molecules are interchelated and bridge the cationic units to form an overall chain structure as illustrated in Fig. 9(*b*). Each water molecule [O(1s)] lies in a bridging position between the amide

Table 7 Selected bond lengths (Å), angles and torsion angles (°) for $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2\cdot 2H_2O$

Pd–N(4)	2.057(13)	Pd–N(7)	2.065(10)
N(1)–C(10)	1.35(2)	N(1)–C(2)	1.43(2)
N(1)–C(9)	1.46(2)	C(2)–C(3)	1.53(2)
C(3)–N(4)	1.51(2)	N(4)–C(5)	1.51(2)
C(5)–C(6)	1.51(2)	C(6)–N(7)	1.51(2)
N(7)–C(8)	1.50(2)	C(8)–C(9)	1.52(2)
C(10)–O(11)	1.268(14)		
N(4)–Pd–N(7)	82.9(4)	C(10)–N(1)–C(2)	115.3(13)
C(10)–N(1)–C(9)	118.9(13)	C(2)–N(1)–C(9)	124.7(12)
N(1)–C(2)–C(3)	118.5(13)	N(4)–C(3)–C(2)	111.8(13)
C(5)–N(4)–C(3)	111.4(10)	C(5)–N(4)–Pd	101.1(9)
C(3)–N(4)–Pd	121.0(9)	N(4)–C(5)–C(6)	110.1(13)
N(7)–C(6)–C(5)	110.7(10)	C(8)–N(7)–C(6)	112.6(10)
C(8)–N(7)–Pd	111.9(8)	C(6)–N(7)–Pd	109.3(8)
N(7)–C(8)–C(9)	118.6(13)	N(1)–C(9)–C(8)	112.7(11)
O(11)–C(10)–N(1)	126(2)		
C(9)–N(1)–C(2)–C(3)	−35(2)	C(10)–N(1)–C(2)–C(3)	157.0(14)
C(2)–N(1)–C(9)–C(8)	109.8(16)	C(10)–N(1)–C(9)–C(8)	−82.7(16)
C(2)–N(1)–C(10)–H(10)	174.2(17)	C(2)–N(1)–C(10)–O(11)	−6(2)
C(9)–N(1)–C(10)–H(10)	6(2)	C(9)–N(1)–C(10)–O(11)	−174.5(14)
N(1)–C(2)–C(3)–N(4)	−65.1(18)	C(2)–C(3)–N(4)–C(5)	134.9(13)
C(3)–N(4)–C(5)–C(6)	−75.9(14)	N(4)–C(5)–C(6)–N(7)	−39.0(15)
C(5)–C(6)–N(7)–C(8)	128.2(12)	C(6)–N(7)–C(8)–C(9)	−60.1(16)
N(7)–C(8)–C(9)–N(1)	−60.0(16)		
Hydrogen-bonding interactions			
O(1s) ··· H(4N)	2.388(16)	O(1s) ··· H(7N′)	2.274(15)
O(1s) ··· O(11″)	2.815(15)	O(11″) ··· (7N′)	2.417(14)

Primed atoms are related by the symmetry operation −x, −y, −z; doubly primed ones by −1 − x, −y, −z.

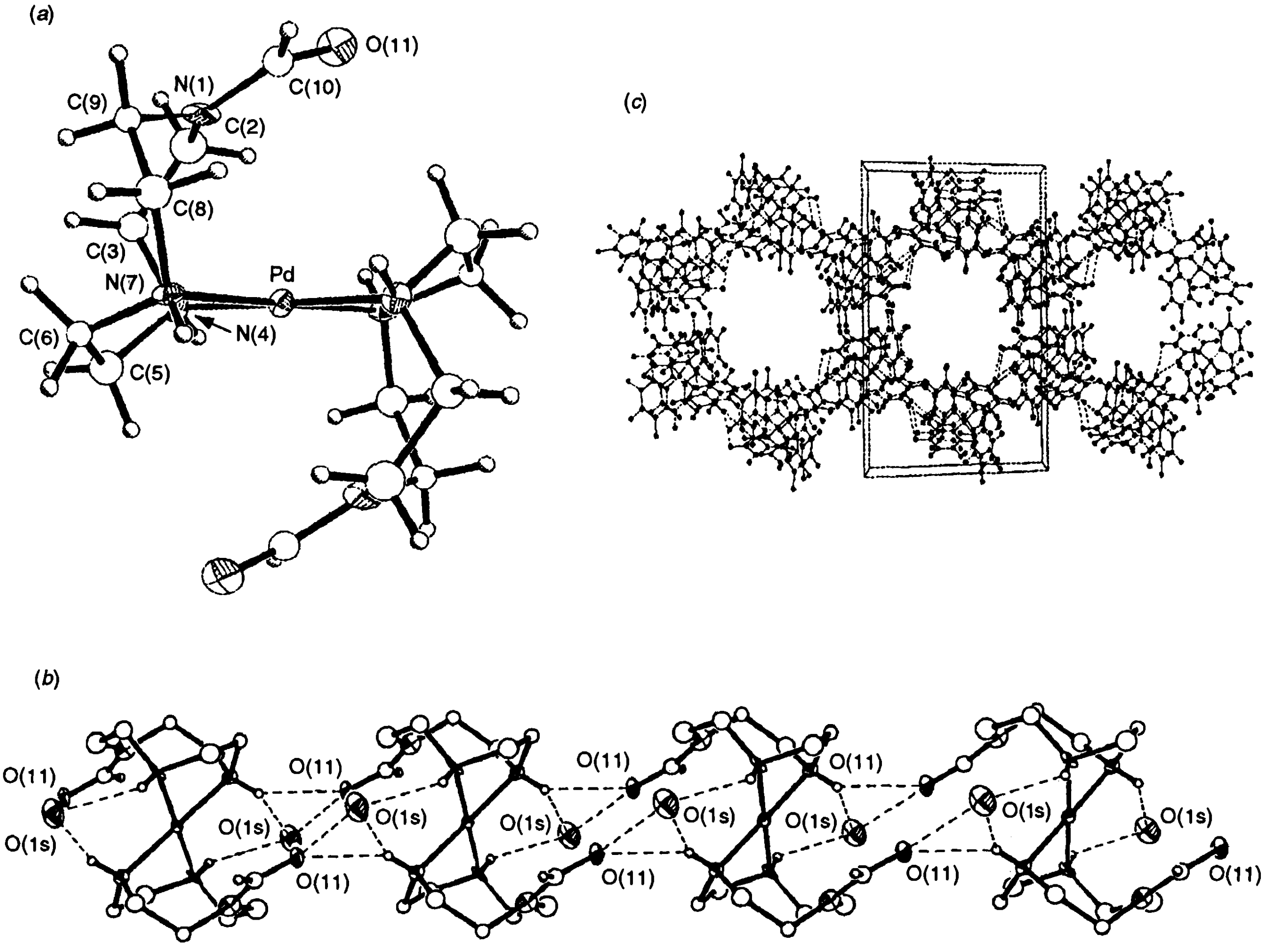


Fig. 9 Structure of $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2\cdot 2H_2O$: (*a*) view of the cation $[Pd(OHC[9]aneN_3)_2]^{2+}$, (*b*) view of the cation chain $\{[Pd(OHC[9]aneN_3)_2]^{2+}\cdot 2H_2O\}_n$ and (*c*) packing diagram for $[BPh_4]^-$ anions

function of one cation and two amine hydrogen atoms of the adjacent cation. There is also a long-range contact between the amide group of one cation and an amine of the next. These interactions are represented by the dashed lines in Fig. 9(*b*). Table 7 lists the hydrogen-bonding distances between the bridging water molecule and the amide and amine functions. Unfortunately, the hydrogen atoms on the water molecule were not located, therefore only distances to the O(1s) atom can be quoted: the O(1s) ··· O(11′) distance of 2.815(15) Å is typical for an OH ··· O hydrogen bond.

A view of the arrangement of the $B(C_6F_5)_4^-$ counter ions which form the rest of the structure is shown in Fig. 9(*c*). The anions form an unusual array which can be described as a hexagonal 'honeycomb' structure. This leads to channels of approximate diameter 8.2 Å which accommodate the cationic $\{[Pd(OHC[9]aneN_3)_2{\cdot}2H_2O]^{2+}\}_n$ chains.

Electrochemistry of $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2{\cdot}2H_2O$

One important property of macrocycles is their ability to stabilise unusual metal oxidation states. For example, $[9]aneN_3$ has been shown to facilitate the oxidation of palladium(II)[26–28] and platinum(II)[29] metal centres. Thus, $[Pt([9]aneN_3)_2]^{2+}$ can be oxidised to $[Pt([9]aneN_3)_2]^{4+}$ by bubbling O_2 through a solution of the complex at 90 °C. The complex $[Pt([9]aneN_3)_2]^{2+}$ has been shown to be square planar, whereas $[Pt([9]aneN_3)_2]^{4+}$ would be expected to be octahedral.[29] The facile nature of this oxidation has been attributed to the ready availability of the extra amine donors to bind to the metal and stabilise any higher oxidation states. The compound $[9]aneN_3$ has also been shown to stabilise the oxidation of Pd^{II} to Pd^{III} and Pd^{IV} in the complex $[Pd([9]aneN_3)_2][PF_6]_2$. The Pd^{II}–Pd^{III} couple of +0.070 V and Pd^{III}–Pd^{IV} couple of +0.450 V (*vs.* ferrocene–ferrocenium) are particularly accessible and the stability of the palladium(III) species has allowed structural characterisation.[26]

Cyclic voltammetry was performed upon $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2$ in MeCN–$NBu^n_4PF_6$ at 298 K, in the range −2.4 to +1.1 V (*vs.* ferrocene–ferrocenium). No oxidative or reductive processes were observed, which contrasts with the behaviour of $[Pd([9]aneN_3)_2][PF_6]_2$ described above. It is concluded that the presence of the amide group in $OHC[9]aneN_3$ precludes stabilisation of palladium-(III) or -(IV) species. Thus, co-ordination of the amide N or O atoms to give octahedral metal species is not possible in this system.

$[Pd(OHC[9]aneN_3)Cl_2]$

Reaction of $PdCl_2$ with 1 molar equivalent of $OHC[9]aneN_3$ in refluxing acetonitrile for 16 h affords a peach-coloured precipitate. The IR spectrum indicated the presence of an amide group (ν_{CO} 1658 cm^{-1}) and analytical data confirmed the stoichiometry as $[Pd(OHC[9]aneN_3)Cl_2]$. However, the product was insoluble in all common solvents except dmso, and attempts to grow crystals by evaporation of a warm dmso solution were unsuccessful. This complex was prepared in order to compare the structure with that of $[Pd(OHC[9]aneN_3)_2]^{2+}$, which exhibits intermolecular hydrogen bonding. The insolubility of $[Pd(OHC[9]aneN_3)Cl_2]$ may in fact be due to such hydrogen-bonding interactions. Alternatively, an oligo- or poly-meric structure (possibly with bridging Cl^- ions) may be present in the solid state.

Reactions of Ni^{II} with $OHC[9]aneN_3$

Reaction of Pd^{II} with $OHC[9]aneN_3$ has been shown to give a product where the amide functions of the ligand do not interact with the metal centre. Nickel(II) amine complexes such as $[Ni([9]aneN_3)_2]^{2+}$[30,31] are six-co-ordinate and octahedral. Thus, the reaction of Ni^{II} with $OHC[9]aneN_3$ is of interest to monitor potential nickel–amide interactions. Reaction of nickel(II) salts with $OHC[9]aneN_3$ was investigated under different conditions but no amide complexes were characterised crystallographically.

$[Ni(OHC[9]aneN_3)_2(OH_2)_2][NO_3]_2$

Reaction of $[Ni(H_2O)_6][NO_3]_2$ with 2 molar equivalents of $OHC[9]aneN_3$ in ethanol affords an orange precipitate. Upon standing in air, this changed to yellow over a period of 6 h. Microanalysis of the yellow solid suggested an overall stoichiometry $[Ni(OHC[9]aneN_3)_2(OH_2)_2][NO_3]_2$. The IR spectrum indicated the presence of amide (ν_{CO} 1681 cm^{-1}) and nitrate (ν_{NO} 1381 cm^{-1}) functions. Assuming that the nickel(II) centre is co-ordinated to four amines in a square-planar fashion, then the co-ordination sphere could be completed by interactions with water, nitrate or perhaps the amide function of the ligand. Such structures are of course speculative.

Hydrolysis of $OHC[9]aneN_3$

Reaction of $[Ni(MeCN)_6][BF_4]_2$ with 2 molar equivalents of $OHC[9]aneN_3$ in refluxing MeCN for 72 h affords a pink solid after chromatography on Sephadex LH-20. The IR spectrum indicates the presence of BF_4^- and exhibits ν_{CH}/ν_{NH} stretches, but no evidence of a ν_{CO} stretch for the amide group. The FAB mass spectrum shows peaks corresponding to $[Ni([9]aneN_3)_2]^+$ and $[Ni([9]aneN_3)_2][BF_4]^+$ at m/z = 316 and 403 respectively. The assignment of this material as $[Ni([9]aneN_3)_2][BF_4]_2$ was confirmed by electronic absorption spectroscopy. The data for the material matched those reported for $[Ni([9]aneN_3)_2]^{2+}$ by Yang and Zompa[30] [$\tilde{\nu}_{max}/cm^{-1}$ ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$) = 11 500 (8), 12 500 (8), 19 800 (6) and 30 200 (23)]. It appears therefore that the nickel(II) ion has catalysed the hydrolysis of the amide function. Literature reports of analogous hydrolyses with ligands such as dmf, dma (dimethylacetamide) and simple peptides have shown that the mechanism involves co-ordination of the amide O atom to the metal centre.[32] It is assumed that a small quantity of water present in the reaction effects hydrolysis of the amide. It is unclear whether the mechanism involves the amine donors of $OHC[9]aneN_3$ being co-ordinated to a nickel(II) centre whilst the amide group is being hydrolysed.

In an attempt to isolate reaction intermediate(s) in the hydrolysis of $OHC[9]aneN_3$ by Ni^{II}, $OHC[9]aneN_3$ and $[Ni(MeCN)_6][BF_4]_2$ were refluxed in MeCN for 2 h. A purple solid was isolated in approximately 25% yield after chromatography on Sephadex LH-20. The absorption spectrum showed the material was not $[Ni([9]aneN_3)_2]^{2+}$, and the IR spectrum showed a ν_{CO} amide stretch at 1700 cm^{-1}, shifted from the value of 1656 cm^{-1} for the free amide. The FAB mass spectrum showed peaks at m/z = 431 and 342, which can be assigned to $[Ni([9]aneN_3)(OHC[9]aneN_3)][BF_4]^+$ and $[Ni([9]aneN_3)(OHC[9]aneN_3)]^+$ respectively. Clearly, this product is a potential intermediate in the hydrolysis of $OHC[9]aneN_3$ by the nickel(II) centre.

Experimental

Infrared spectra were recorded as KBr discs or thin films (between CsI plates) on a Perkin-Elmer 1600 Series FT-IR spectrometer, fast atom bombardment (FAB) and electron ionisation (EI) mass spectra on a Kratos MS 50TC spectrometer, with the FAB spectra in a 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by the University of Edinburgh Chemistry Department microanalytical service. The UV/VIS spectra were recorded on a Perkin-Elmer Lambda-9 spectrometer. Cyclic voltammetry was performed using a conventional three-electrode cell with platinum counter and micro working electrodes and an Ag–AgCl reference. Data were recorded and manipulated using a General Purpose Electrochemical System

(GPES) Version 3 software connected to an Autolab PSTAT10 potentiostat. Proton NMR spectra were recorded on Brüker WP80, WP200 and AC250 spectrometers, operating at 80.13, 200.13 and 250.13 MHz respectively, ^{13}C NMR spectra on WP200 and AC250 spectrometers, operating at 50.32 and 62.89 MHz respectively.

Syntheses

1-Formyl-1,4,7-triazacyclononane (OHC[9]aneN$_3$). This compound was prepared according to the method of Weisman *et al.*[13] 1,4,7-triazatricyclo[5.2.1.0^{4,10}]decane (**I**) (5 g, 0.036 mol) was stirred in hydrochloric acid (20 cm^3, 2.8 mol dm^{-3}) at room temperature for 8 h. The solution was then cooled to 0 °C and adjusted to pH 12 with NaOH solution (5 mol dm^{-3}). The product was extracted immediately with CHCl$_3$ (5 × 50 cm^3), the combined extracts were dried (MgSO$_4$) and the solvent removed under reduced pressure to give a clear, viscous oil which crystallised upon standing. Recrystallisation from CHCl$_3$–hexane gave white needles (yield 2.61 g, 44.6%). NMR (CDCl$_3$): ^{1}H (200.13 MHz), δ 2.01 (2 H, s, NH), 2.65–2.77 (4 H, m, CH$_2$), 2.98–3.10 (4 H, m, CH$_2$), 3.31–3.44 (4 H, m, CH$_2$) and 8.11 (1 H, s, NCHO); ^{13}C (50.32 MHz), δ 46.58, 48.14, 48.62, 49.20, 49.73, 52.59 (CH$_2$) and 163.79 (NCHO) (Found: C, 54.4; H, 10.1; N, 26.4. $C_7H_{15}N_3O$ requires C, 53.5; H, 9.60; N, 26.7%). IR (KBr disc): 3321s (NH), 2879s (CH), 1656vs (CO), 1450s, 1161s, 971m and 762s cm^{-1}. EI mass spectrum: m/z = 157 OHC[9]aneN$_3$$^+$.

[OHC[9]aneN$_3$H]BPh$_4$. The salt Ni(NO$_3$)$_2$·6H$_2$O (0.040 g, 0.14 mmol) and OHC[9]aneN$_3$ (0.064 g, 0.42 mmol) were added to water (10 cm^3) and left for 24 h. The initial green colour changed to yellow, accompanied by the formation of a green suspension. The solution was centrifuged and the pale yellow solution was decanted. A solution of NaBPh$_4$ (0.102 g, 0.3 mmol) in water (2 cm^3) was then added to yield a white precipitate. This was isolated by centrifugation, washed with water, dissolved in acetone and filtered. The acetone solution was then concentrated *in vacuo* and the residue triturated with diethyl ether to yield a white solid. Yield 0.121 g, 61% (Found: C, 77.7; H, 7.70; H, 8.65. $C_{31}H_{36}BN_3O$ requires C, 78.00; H, 7.55; N, 8.80%) IR (KBr disc): 3341m (NH), 3167w, 3056w, 2983w, 1660s, 1578m, 1479m, 1423m, 1382m and 737m cm^{-1}. EI mass spectrum: m/z = 315 [(OHC[9]aneN$_3$H)(OHC[9]aneN$_3$)]$^+$.

(OHC)$_3$[9]aneN$_3$. The method used was based upon that reported by Sheehan and Wang[33] for the preparation of formamides. The compound [9]aneN$_3$ (0.60 g, 4.65 mmol) was dissolved in formic acid (40 cm^3) and acetic anhydride (15 cm^3) was added dropwise with stirring over 20 min. This mixture was stirred at room temperature for 60 min, then water (20 cm^3) was added and the solution was concentrated *in vacuo*. The residue was triturated with ether and recrystallised from hot ethanol to give the product as white needles (yield 0.41 g, 41.4%). Analysis showed there to be two isomers in solution: the major product (80%) is the symmetric isomer with all formyl groups equivalent, whilst the minor product (20%) is the asymmetric isomer with each formyl group inequivalent. NMR (CDCl$_3$): ^{1}H (250.13 MHz), δ 3.31–3.65 (12 H, m, ring CH$_2$, both isomers), 8.03 (3 H, s, NCHO, symmetric isomer), 7.96, 8.08, 8.22 (1 H, s, NCHO, unsymmetric isomer); ^{13}C (62.89 MHz), δ 46.93, 48.46 (CH$_2$, symmetric isomer), 163.90 (NCHO, symmetric isomer), 44.65, 45.84, 46.04, 46.93, 50.13, 51.28 (CH$_2$, unsymmetric isomer), 163.22, 163.30 and 163.73 (NCHO, unsymmetric isomer) (Found: C, 50.7; H, 7.05; N, 19.7. $C_9H_{15}N_3O_3$ requires C, 50.3; H, 7.90; N, 19.4%).

(PhCO)$_3$[9]aneN$_3$. The method used was based upon that reported by White[34] for the preparation of benzoylamides. Benzoyl chloride (1.80 g, 13.00 mmol) was added dropwise with stirring to a solution of [9]aneN$_3$ (0.50 g, 3.88 mmol) in pyridine (10 cm^3) at 0 °C over 10 min. The solution was allowed to warm to room temperature and then added to 1 mol dm^{-3} HCl solution (100 cm^3) to give a yellow precipitate. This was filtered off, washed with water and recrystallised from hot methanol–water (2:1). Recrystallisation was also possible by evaporation of an acetone–water mixture. Yield 1.398 g, 81.7%. NMR (CDCl$_3$): ^{1}H (250.13 MHz), δ 3.70, 3.78 (12 H, br s, CH$_2$, ring) and 7.36 (15 H, br s, aryl H); ^{13}C (62.89 MHz), δ 50.36, 50.52 (CH$_2$, ring), 126.49, 128.44, 129.82 (aromatic CH), 135.62 (aromatic quaternary) and 172.69 (NCOPh) (Found: C, 73.1; H, 6.30; N, 9.60. $C_{27}H_{27}N_3O_3$ requires C, 73.4; H, 6.10; N, 9.50%). IR (KBr disc): 3062m, 2975m, 2923m, 1636s (CO), 1443m and 1265m cm^{-1}.

[Pd(OHC[9]aneN$_3$)$_2$][PF$_6$]$_2$. The compound [Pd(O$_2$CMe)$_2$] (0.050 g, 0.23 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm^3) to give an orange solution; OHC[9]aneN$_3$ (0.070 g, 0.46 mmol) was added as a solution in CH$_2$Cl$_2$ (5 cm^3), which gave a change to pale yellow and afforded a small amount of white precipitate. The solution was left to stand for 24 h, after which the solvent was removed *in vacuo* and the residue taken up in the minimum volume of water. The salt NH$_4$PF$_6$ (0.072 g, 0.44 mmol) was then added as a solution in water (1 cm^3) and the mixture refrigerated for 24 h to afford a very pale yellow precipitate. This was collected, washed with water, ethanol and ether and dried *in vacuo* (yield 0.049 g, 31.5%) (Found: C, 22.5; H, 4.65; N, 11.15. $C_{14}H_{30}F_{12}N_6O_2P_2Pd$ requires C, 23.8; H, 3.70; N, 11.9%). IR (KBr disc): 3302m, 3073w, 2901m, 1651vs, 1458m, 1426m, 1377m and 837 cm^{-1}. FAB mass spectrum: m/z = 561 [PdL$_2$(PF$_6$)]$^+$, 418 [PdL$_2$]$^+$ and 261 [PdL]$^+$ (L = OHC[9]aneN$_3$).

[Pd(OHC[9]aneN$_3$)$_2$][B(C$_6$F$_5$)$_4$]$_2$. The compound [Pd(O$_2$CMe)$_2$] (0.050 g, 0.23 mmol) was dissolved in CH$_2$Cl$_2$ (10 cm^3) to give an orange solution; OHC[9]aneN$_3$ (0.070 g, 0.46 mmol) was added as a solution in CH$_2$Cl$_2$ (5 cm^3), which gave a change to pale yellow and afforded a small amount of white precipitate. The solution was left to stand for 24 h, then the solvent was removed *in vacuo* and the residue taken up in the minimum volume of water. The salt Li[B(C$_6$F$_5$)$_4$] (0.306 g, 0.23 mmol) was then added as a solution in water (5 cm^3). A white precipitate formed immediately which was very fine and difficult to filter, therefore acetone was added until the solution cleared and the mixture was allowed to evaporate. A pale yellow precipitate formed after several days was collected and dried *in vacuo*. Yield 0.260 g, 65.5% (Found: C, 41.6; H, 1.80; N, 4.00. $C_{62}H_{30}B_2F_{40}N_6O_2Pd$ requires C, 41.9; H, 1.70; N, 4.75%). IR (KBr disc): 2928m, 1696m, 1669s, 1516s, 1464s, 1374m, 1274m, 1089m and 1669m cm^{-1}. FAB mass spectrum: m/z = 1098 [Pd(OHC[9]aneN$_3$)$_2${B(C$_6$F$_5$)$_4$}]$^+$

[Pd(OHC[9]aneN$_3$)Cl$_2$]. The compounds PdCl$_2$ (0.155 g, 0.88 mmol) and OHC[9]aneN$_3$ (0.138 g, 0.88 mmol) were dissolved in acetonitrile (25 cm^3) and the solution was refluxed for 16 h under N$_2$. This gave rise to a peach-coloured precipitate which was collected, washed with MeCN, and then Et$_2$O and dried *in vacuo*. Yield 0.220 g, 75.2% (Found: C, 25.2; H, 5.10; N, 12.6. $C_7H_{15}Cl_2N_3OPd$ requires C, 25.1; H, 4.50; N, 12.6%). IR (KBr disc): 3485w, 3217w, 3141m, 1658s, 1378m and 1127m cm^{-1}.

[Ni(OHC[9]aneN$_3$)$_2$(OH$_2$)$_2$][NO$_3$]$_2$. The salt Ni(NO$_3$)$_2$·6H$_2$O (0.060 g, 0.21 mmol) and OHC[9]aneN$_3$ (0.064 g, 0.42 mmol) were dissolved separately in ethanol (10 cm^3) and the two solutions mixed to yield an orange precipitate. This was collected by centrifugation, washed with ethanol, then ether and dried *in vacuo*. Upon standing in air the orange colour faded to yellow over a period of 6 h. Yield 0.085 g, 77.2%

Table 8 Crystallographic data

	OHC[9]aneN_3	[OHC[9]aneN_3H]BPh_4	$(OHC)_3$[9]aneN_3	$(PhOC)_3$[9]aneN_3	[Pd(OHC[9]ane$N_3)_2$][$B(C_6F_5)_2]_2\cdot 2H_2O$
Formula	$C_7H_{15}N_3O$	$C_{31}H_{36}BN_3O$	$C_9H_{15}N_3O_3$	$C_{27}H_{27}N_3O_3$	$C_{62}H_{34}B_2F_{40}N_6O_4Pd$
M	157.21	477.4	213.24	441.52	1814.5
Crystal symmetry	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$Pbca$	$P2_1/a$	$P2_1/c$
a/Å	7.157(4)	10.405(10)	11.618(7)	15.015(3)	8.002(6)
b/Å	9.355(8)	10.396(10)	12.195(7)	10.807(2)	24.36(3)
c/Å	12.357(12)	14.199(12)	14.454(8)	15.334(4)	16.41(2)
α/°		93.76(7)			
β/°		101.87(7)		115.887(19)	103.36(8)
γ/°		119.57(7)			
U/Å^3	827	1282	2048	2238.5	3112
No. of reflections measured at ± ω	12	9	51	32	9
2θ range/°	28–32	18–26	24–28	30–32	16–24
Z	4	2	8	4	2
D_c/g cm^{-3}	1.262	1.237	1.383	1.310	1.936
Crystal dimensions/mm	0.55 × 0.30 × 0.25	0.20 × 0.15 × 0.07	0.54 × 0.54 × 0.11	0.27 × 0.51 × 0.73	0.18 × 0.07 × 0.07
μ(Mo-Kα)/mm^{-1}	0.082	0.074	0.105	0.086	0.465
F(000)	344	512	912	936	1792
Data collected	1334	3356	1575	3118	5180
$2\theta_{max}$/°	50	45	45	45	45
h,k,l ranges	−2 to 8, −11 to 11, 0–14	−11 to 10, −11 to 11, 0–15	0–12, 0–13, 0–15	−16 to 14, 0–11, 0–16	−8 to 8, 0–26, 0–17
Unique data	862		1337	2925	3022
R_{int}	0.015		0.0037	—	0.037
Data with $F > 4\sigma(F)$	832	3323	1331	2915	3020
Crystal decay	5%	None	None	None	6%
Absorption correction	None	None	None	None	DIFABS
R	0.0228	0.0682	0.0319	0.0342	0.0772
wR_2	0.0292[a]	0.2138	0.0755	0.0883	0.1253
$S(F^2)$	2.636[b]	1.065	1.064	1.096	0.896
No. parameters	161	278	197	406	360
x,y In weighting scheme, $w^{-1} = \sigma^2(F_o^2) + (xP)^2 + yP$[d]	0.000 05[c]	0.0719, 3.46	0.0425, 0.003 8	0.0386, 0.9207	0.0412, 0
Final ΔF residuals/e Å^{-3}	+0.14, −0.13	+0.57, −0.48	+0.12, −0.16	+0.14, −0.16	+0.56, −0.73

[a] Residual is $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [b] $S(F)$. [c] x In weighting scheme, $w^{-1} = \sigma^2(F) + xF$. [d] $P = \frac{1}{3}[\max(F_o^2,0) + 2F_c]^2$.

Table 9 Atomic coordinates for OHC[9]aneN_3

Atom	*x*	*y*	*z*
C(2)	0.301 8(3)	−0.104 43(16)	0.392 41(12)
C(3)	0.294 0(3)	−0.105 65(18)	0.268 91(12)
N(4)	0.106 91(21)	−0.133 18(14)	0.228 08(11)
C(5)	−0.001 0(3)	−0.012 91(20)	0.186 78(13)
C(6)	−0.194 40(25)	−0.001 60(18)	0.236 35(12)
N(7)	−0.190 64(21)	0.045 62(13)	0.349 68(10)
C(8)	−0.138 22(24)	−0.063 68(17)	0.428 09(13)
C(9)	0.022 66(23)	−0.016 76(18)	0.500 10(11)
N(1)	0.196 50(19)	0.012 54(13)	0.441 64(9)
C(1)	0.269 12(23)	0.143 96(16)	0.441 50(12)
O	0.420 74(17)	0.175 87(11)	0.400 80(9)

Table 10 Atomic coordinates for [OHC[9]aneN_3H]BPh_4

Atom	*x*	*y*	*z*
N(1)	7 980(5)	1 942(5)	11 325(3)
C(2)	7 060(7)	2 634(7)	11 325(4)
C(3)	6 291(6)	2 425(6)	12 149(4)
N(4)	5 042(5)	816(5)	12 085(3)
C(5)	5 466(6)	−343(6)	12 235(4)
C(6)	6 513(7)	−82(7)	13 240(4)
N(7)	8 013(5)	1 297(6)	13 458(3)
C(8)	9 008(6)	1 293(7)	12 859(4)
C(9)	9 310(6)	2 379(6)	12 170(4)
C(10)	7 692(7)	970(7)	10 532(4)
O(11)	6 637(5)	536(5)	9 785(3)
B	10 548(7)	−2 209(7)	12 673(4)
C(11)	9 730(4)	−2 768(3)	13 585(2)
C(12)	9 327(4)	−4 166(3)	13 831(2)
C(13)	8 503(4)	−4 652(3)	14 520(3)
C(14)	8 082(4)	−3 740(4)	14 964(2)
C(15)	8 485(4)	−2 343(3)	14 719(2)
C(16)	9 309(4)	−1 857(3)	14 030(2)
C(21)	9 181(3)	−2 430(4)	11 671(2)
C(22)	7 647(3)	−3 141(4)	11 675(2)
C(23)	6 541(3)	−3 309(4)	10 856(2)
C(24)	6 968(3)	−2 765(4)	10 034(2)
C(25)	8 501(4)	−2 054(4)	10 030(2)
C(26)	9 608(3)	−1 887(4)	10 849(2)
C(31)	11 956(3)	−342(3)	13 081(2)
C(32)	11 953(3)	775(3)	12 594(2)
C(33)	13 103(4)	2 276(3)	12 961(2)
C(34)	14 256(3)	2 660(3)	13 814(3)
C(35)	14 259(3)	1 543(4)	14 301(2)
C(36)	13 108(4)	43(3)	13 934(2)
C(41)	11 406(4)	−3 179(4)	12 395(2)
C(42)	11 249(4)	−3 707(4)	11 428(2)
C(43)	12 076(4)	−4 358(4)	11 226(2)
C(44)	13 060(4)	−4 481(4)	11 989(3)
C(45)	13 218(4)	−3 953(4)	12 956(2)
C(46)	12 391(4)	−3 302(4)	13 159(2)

Table 11 Atomic coordinates for $(OHC)_3$[9]aneN_3

Atom	*x*	*y*	*z*
N(1)	3237(1)	7248(1)	2933(1)
C(11)	2098(2)	7392(2)	2995(1)
O(12)	1619(1)	8284(1)	2942(1)
C(2)	3946(2)	8199(2)	2693(2)
C(3)	4120(2)	9030(2)	3458(2)
N(4)	4749(1)	8633(1)	4268(1)
C(41)	5835(2)	8949(2)	4422(2)
O(42)	6391(1)	8729(1)	5120(1)
C(5)	4126(2)	8000(2)	4965(2)
C(6)	4657(2)	6888(2)	5180(1)
N(7)	4917(1)	6241(1)	4359(1)
C(71)	6010(2)	6083(2)	4101(2)
O(72)	6323(1)	5517(1)	3445(1)
C(8)	3994(2)	5672(2)	3869(2)
C(9)	3714(2)	6141(2)	2920(1)

Table 12 Atomic coordinates for $(PhOC)_3$[9]aneN_3

Atom	*x*	*y*	*z*
N(1)	4008(1)	−1403(1)	6445(1)
C(2)	4612(2)	−2427(2)	7032(1)
C(3)	5367(1)	−2026(2)	8034(1)
N(4)	6131(1)	−1192(1)	8031(1)
C(5)	6199(1)	36(2)	8462(1)
C(6)	5385(1)	923(2)	7836(2)
N(7)	4462(1)	796(1)	7945(1)
C(8)	3549(1)	552(2)	7063(1)
C(9)	3328(2)	−802(2)	6774(2)
C(11)	3815(1)	−1246(2)	5501(1)
O(11)	3185(1)	−506(2)	4985(1)
C(12)	4378(2)	−2015(2)	5096(1)
C(13)	5328(2)	−1714(2)	5246(2)
C(14)	5826(2)	−2436(3)	4852(2)
C(15)	5368(2)	−3452(3)	4302(2)
C(16)	4415(2)	−3752(3)	4139(2)
C(17)	3926(2)	−3039(3)	4538(2)
C(41)	6888(1)	−1699(2)	7892(1)
O(41)	6901(1)	−2808(1)	7718(1)
C(42)	7709(1)	−873(2)	7943(1)
C(43)	8677(1)	−1099(2)	8634(1)
C(44)	9440(2)	−341(2)	8679(1)
C(45)	9264(2)	603(2)	8017(2)
C(46)	8314(2)	810(2)	7319(2)
C(47)	7541(2)	92(2)	7287(1)
C(71)	4489(1)	1265(2)	8786(1)
O(71)	5261(1)	1703(1)	9410(1)
C(72)	3576(1)	1259(2)	8948(1)
C(73)	3398(2)	2297(2)	9390(1)
C(74)	2586(1)	2340(2)	9585(1)
C(75)	1938(1)	1354(2)	9345(1)
C(76)	2113(1)	317(2)	8921(1)
C(77)	2934(1)	265(2)	8732(1)

(Found: C, 31.2; H, 6.40; N, 20.8. $C_{14}H_{34}N_8NiO_{10}$ requires C, 31.5; H, 6.35; N, 21.0%). IR (KBr disc): 3432w, 3109m, 2927w, 1681s, 1381s, 1407s, 1295m and 1040w cm^{-1}.

[Ni([9]aneN_3)$_2$][BF_4]$_2$. The complex [Ni(MeCN)$_6$][BF_4]$_2$ was prepared according to a standard literature procedure.[35,36] The compounds OHC[9]aneN_3 (0.352 g, 2.2 mmol) and Ni(BF_4)$_2$·6.5MeCN (0.10 g, 0.21 mmol) were stirred in freshly distilled acetonitrile (10 cm^3) for 2 h under N_2 to give a yellow solution. The reaction mixture was then refluxed for 72 h. The solvent was removed *in vacuo* and the residue chromatographed on Sephadex LH-20 (with acetonitrile as eluent). A peach-coloured band was collected which gave a pink precipitate upon addition of ether. The solid was collected, washed with ether and dried *in vacuo*. Yield 0.025 g, 23.9%. IR (KBr disc): 3329m, 2937w, 2877w, 1472m and 1054 cm^{-1}; FAB mass spectrum: *m*/*z* = 316 [NiL_2]$^+$, 403 [$NiL_2(BF_4)$]$^+$ (L = [9]aneN_3). Electronic spectrum: $\tilde{\nu}_{max}/cm^{-1}$ ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$) = 11 500 (8), 12 500 (8), 19 800 (6) and 30 200 (23).

[Ni([9]aneN_3)(OHC[9]aneN_3)][BF_4]$_2$. The compounds OHC[9]aneN_3 (0.130 g, 0.83 mmol) and Ni(BF_4)$_2$·6.5MeCN (0.197 g, 0.41 mmol) were dissolved in freshly distilled acetonitrile (10 cm^3) to give a yellow solution. This was refluxed for 2 h, the solvent removed *in vacuo* and the residue chromatographed on Sephadex LH-20 (with acetone as eluent). A purple band was collected, which upon addition of ether afforded a purple solid. This was recrystallised from acetonitrile–ether. Yield 0.055 g. IR (KBr disc): 3324m, 3166m, 2938w, 1700s, 1463m, 1055s and 821w cm^{-1}; FAB mass spectrum; *m*/*z* 342 [Ni([9]aneN_3)(OHC[9]aneN_3)]$^+$, 431 [Ni([9]aneN_3)(OHC[9]aneN_3)(BF_4)]$^+$. Electronic spectrum: $\tilde{\nu}_{max}/cm^{-1}$ ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$) = 11 726 (3), 21 080 (4) and 28 050 (18).

Table 13 Atomic coordinates for $[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2 \cdot 2H_2O$

Atom	*x*	*y*	*z*
Pd	0	0	0
N(1)	−1 444(16)	182(5)	1 525(7)
C(2)	−2 024(21)	−372(7)	1 367(11)
C(3)	−695(18)	−819(7)	1 341(9)
N(4)	154(13)	−739(5)	619(7)
C(5)	2 073(18)	−814(7)	891(9)
C(6)	2 887(17)	−315(6)	1 371(9)
N(7)	2 023(14)	203(5)	984(6)
C(8)	1 462(17)	566(7)	1 611(9)
C(9)	188(16)	341(6)	2 081(8)
C(10)	−2 639(18)	571(7)	1 249(9)
O(11)	−4 152(11)	491(5)	817(6)
B	11 110(21)	1 652(8)	4 595(10)
C(11)	12 776(14)	1 319(6)	5 195(6)
C(12)	13 287(15)	1 321(6)	6 052(7)
C(13)	14 726(15)	1 036(6)	6 504(7)
C(14)	15 642(17)	711(6)	6 082(7)
C(15)	15 262(15)	720(6)	5 217(6)
C(16)	13 799(17)	1 002(6)	4 817(8)
F(12)	12 499(9)	1 621(4)	6 542(5)
F(13)	15 057(10)	1 033(4)	7 343(5)
F(14)	17 041(9)	435(4)	6 511(5)
F(15)	16 165(10)	403(4)	4 801(5)
F(16)	13 436(10)	948(3)	3 968(4)
C(21)	9 649(15)	1 223(5)	4 054(8)
C(22)	8 188(16)	1 446(5)	3 551(9)
C(23)	6 819(14)	1 140(4)	3 079(7)
C(24)	6 882(16)	585(5)	3 152(8)
C(25)	8 352(18)	336(6)	3 622(11)
C(26)	9 639(16)	664(5)	4 060(8)
F(22)	7 999(10)	1 990(3)	3 461(5)
F(23)	5 427(9)	1 384(3)	2 595(5)
F(24)	5 596(10)	273(3)	2 709(5)
F(25)	8 426(11)	−220(3)	3 658(6)
F(26)	10 965(9)	371(3)	4 549(4)
C(31)	10 004(19)	2 015(5)	5 146(8)
C(32)	9 272(19)	1 750(5)	5 719(9)
C(33)	8 413(18)	2 010(5)	6 255(8)
C(34)	8 161(17)	2 569(5)	6 167(8)
C(35)	8 874(18)	2 852(5)	5 610(8)
C(36)	9 747(17)	2 578(5)	5 128(8)
F(32)	9 413(10)	1 203(3)	5 810(5)
F(33)	7 800(11)	1 732(4)	6 820(5)
F(34)	7 320(11)	2 844(4)	6 656(5)
F(35)	8 700(10)	3 407(3)	5 559(5)
F(36)	10 315(10)	2 903(3)	4 561(5)
C(41)	12 049(17)	2 029(6)	3 984(7)
C(42)	13 333(17)	2 395(6)	4 365(7)
C(43)	14 358(16)	2 667(6)	3 925(7)
C(44)	14 177(17)	2 577(6)	3 090(7)
C(45)	12 887(15)	2 236(6)	2 681(7)
C(46)	11 881(16)	1 984(6)	3 138(7)
F(42)	13 634(10)	2 495(4)	5 190(4)
F(43)	15 568(10)	3 033(4)	4 338(5)
F(44)	15 234(10)	2 840(4)	2 690(5)
F(45)	12 720(10)	2 142(4)	1 853(4)
F(46)	10 742(9)	1 612(3)	2 661(4)
O(1s)	−3 193(13)	−1 265(5)	−324(7)

Single-crystal structural determinations

Table 8 summarises the crystallographic data, and Tables 9–13 give atomic coordinates for the compounds investigated.

$OHC[9]aneN_3$. Crystals of diffraction quality were obtained directly from the reaction. Evaporation of a $CHCl_3$ solution of $OHC[9]aneN_3$ gave a clear, viscous oil which crystallised upon standing overnight. Data were acquired at 150 K on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,[37] using Mo-Kα X radiation (λ 0.710 73 Å), ω–2θ scans and a learnt-profile method.[38] The structure was solved by direct methods using SHELXS 86[39] and refined on *F* using SHELX 76.[40] All non-H atoms were refined with anisotropic thermal parameters and the positional and isotropic thermal parameters of H atoms were refined freely.

$[OHC[9]aneN_3H]BPh_4$. Slow diffusion of diethyl ether vapour into an acetonitrile solution yielded colourless blocks of suitable diffraction quality. Data were collected as described above. The structure was solved by direct methods using SHELXS 86[39] and refined against F^2 using SHELXL 93.[41] All non-H atoms were refined with anisotropic thermal parameters and phenyl rings were refined as hexagons. The H atoms on N(4) and N(7) were initially located from the difference map, but all H atoms were allowed to ride on their parent C or N atoms during refinement.

$(OHC)_3[9]aneN_3$. Colourless plates suitable for X-ray diffraction were obtained by cooling of a concentrated solution of $(OHC)_3[9]aneN_3$ in ethanol. Data were collected as described above. The structure was solved by direct methods using SHELXS 86[39] and refined on F^2 using SHELXL 93.[41] All non-H atoms were refined with anisotropic thermal parameters and H atoms were allowed to ride on their parent atoms.

$(PhCO)_3[9]aneN_3$. Crystals suitable for X-ray diffraction studies were obtained by the cooling of a hot solution of $(PhCO)_3[9]aneN_3$ in a mixture of methanol–water (2:1). Data were collected as described above. The structure was solved by direct methods using SHELXS 86[39] and refined on F^2 using SHELXL 93.[41] All non-H atoms were refined with anisotropic thermal parameters and H atoms were refined freely with isotropic thermal parameters.

$[Pd(OHC[9]aneN_3)_2][B(C_6F_5)_4]_2 \cdot 2H_2O$. Pale yellow columns of X-ray quality were grown by diffusion of hexane into a CH_2Cl_2 solution of the complex at −20 °C. Data were collected as described above. A decay correction (6%) was applied, but no absorption correction. The structure was solved by a combination of heavy-atom and direct methods (DIRDIF[42]) and refined on F^2 using SHELXL 93.[41] At isotropic convergence, corrections (maximum 1.102, minimum 0.852) for absorption were applied empirically using DIFABS.[43] The Pd, F, O and N atoms were refined with anisotropic thermal parameters and H atoms were placed in calculated positions and allowed to ride on their parent atoms. The C_6F_5 rings of the counter ion were restrained to have similar geometries.

Other crystallographic programs used in this work were SHELXTL PC,[44] CAMERON[45] and CALC.[46]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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