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Tetrahedron 60 (2004) 1895–1902
Tetrahedron

From calixfurans to heterocyclophanes containing isopyrazole units

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Received 17 September 2003; revised 18 November 2003; accepted 11 December 2003

Abstract—Cyclic poly-1,4-diketones **2**, obtained by the oxidation of the furan units present in calix[4]furan **1a** and calix[6]furan **1c** have been converted into the novel heterocyclophanes **4a** and **4c** containing four and six isopyrazole units, respectively. Solution studies have demonstrated the ability of **4a** and **4c** to act as ligands for transition metals. The crystal structures of **4a** and the coordination compound formed by **4c** with 2 equiv. of *cis*-$PtCl_2(DMSO)_2$ have been determined. In the solid state **4c** is shown to bind aromatic substrates within its cavity.

1. Introduction

Macrocycles containing aromatic units have been a topic of active research for many years.[1] The aromatic units, being rigid building blocks, allow the design and synthesis of molecular cavities having defined spatial characteristics,[2] and also serve as binding sites for hosts capable of interacting with their π-electron systems.[3] Benzo rings have been the most frequently used aromatic subunits, as for example in the calixarenes.[1a,b,f] However, heterocyclic rings are also of equal interest for the construction of cyclophane-type molecular receptors because the presence of hetero-atoms provides a means for the incorporation of specific stereoelectronic characteristics within the macrocyclic structure.[4]

As part of our ongoing research on the synthesis of heterocalixarenes, we have developed effective methods for the preparation of calix[*n*]furans (n=4–12)[5] and explored the conversion of their furan units into other aromatic systems such as naphthalene[6] and pyrrole.[7a,b]

The conversion of calix[6]furan **1c** to calix[6]pyrrole **3c** is based on the use of **1c** as the precursor of the cyclic polyketone **2c**,[8] which is subjected to the Paal–Knorr reaction with $AcONH_4$ to give **3c**[7a,b] (Scheme 1). This result encouraged us to investigate the use of polyketones **2a-c** for the synthesis of macrorings containing heterocyclic units other than pyrrole.

With this goal in mind, we reacted polyketones **2a-c** with hydrazine hydrate (Scheme 1). In principle, these reactions can lead to the formation of macrocycles containing either isopyrazole[9] (**4a-c**) or dihydropyridazine[10] units (**5a-c**), since the pair of nucleophilic nitrogen atoms of hydrazine have the potential to react with pairs of carbonyl units placed in either 1,3- or 1,4- relative positions within the polyketonic macroring. Both types of heterocyclic units are interesting components for the construction of hetero-cyclophanes because of their potential ability to bind a number of metal cations and also molecules capable of forming hydrogen bonds with the nitrogen atoms.[11,12]

2. Results and discussion

Treatment of **2a** and **2c** with hydrazine hydrate in either EtOH, or THF gave the isopyrazole-based macrocycles **4a** and **4c**, which were easily isolated (35 and 45% yield, respectively) by column chromatography (SiO_2, DCM/MeOH 95:5). However, decaketone **2b** gave a complex mixture and no evidence for the formation of **4b**. Moreover, none of these reactions produced detectable amounts of **5a-c**.

The ^1H NMR spectrum of **4a** (300 MHz, $CDCl_3$, 20 °C)

Keywords: Macrocycles; N ligands; Isopyrazole; Metal coordination; X-ray structure.
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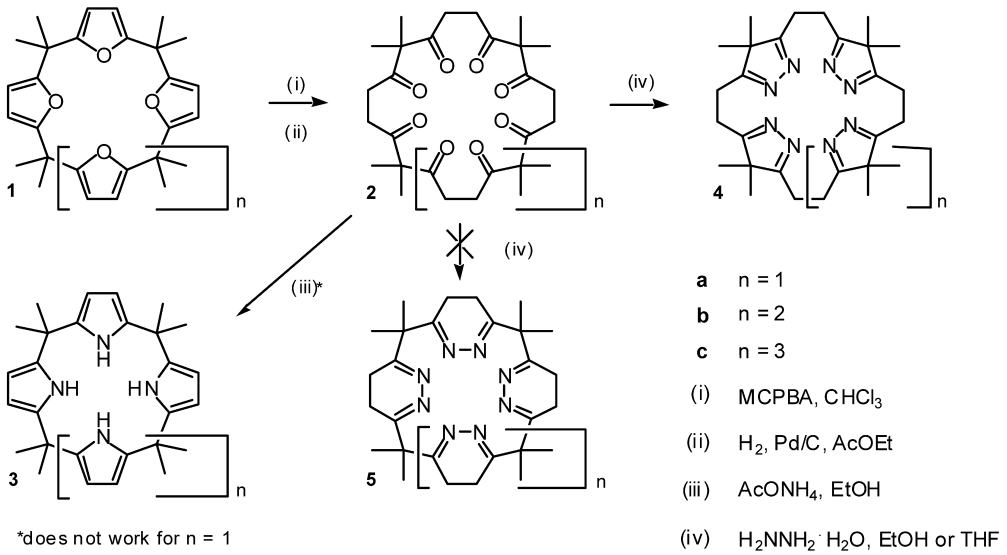
doi:10.1016/j.tet.2003.12.028



Scheme 1.

contains a broad signal (centred at δ 2.93) for the methylene protons which indicates a slow conformational mobility of the macrocycle on the NMR time-scale in this solvent and at this temperature; however, these methylene resonances appear as a sharp singlet at δ 2.84 in CD_3CN. The ^1H NMR spectrum of **4c** in $CDCl_3$ shows a sharp singlet for the methylene protons (δ 2.95) and a spectrum consistent with a time-averaged D_{6h} symmetry in solution. The ^{13}C NMR spectra of **4a** and **4c** are almost identical and each shows four resonances (consistent with D_{4h} and D_{6h} time-averaged symmetries, respectively, in solution).

Macrocycles **4a** and **4c** gave single crystals from toluene. The X-ray structure of **4a** (Fig. 1) shows the molecule to adopt a conformation with an alternating 'up/down' orientation of the isopyrazole units and approximate S_4 symmetry. The plane formed by the centroids of the bridging ethylidene units is planar to within 0.16 Å. Rings A, B, C, and D are inclined by 71, 77, 68, and 58°, respectively, to this plane, with in each case their N–N bonds being canted towards the macroring centre. The

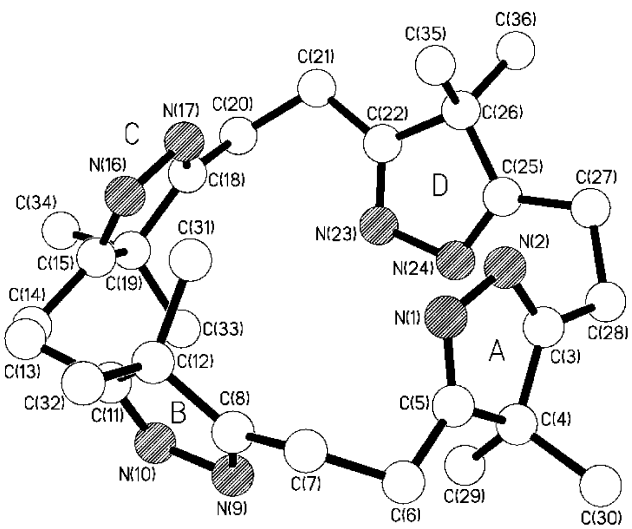


Figure 1. The X-ray structure of **4a**.

ethylidene units adopt *gauche* conformations with torsional twist angles of 68, −70, 65, and −65° about C(6)–C(7), C(13)–C(14), C(20)–C(21), and C(27)–C(28), respectively. The *trans*-annular centroid–centroid separations of the diametrically opposite isopyrazole units are 6.4 and 6.5 Å, respectively.

Within the isopyrazole rings there is a distinct pattern of bond localisation with the C=N and N–N bonds having average lengths of 1.283(2) and 1.459(2) Å, respectively. A comparison of these distances with literature values is not possible as to the best of our knowledge **4a** (and the following related structures) represent the first crystallographically characterised examples of molecules containing the isopyrazole unit (vide infra).

The structure also contains an included molecule of water of solvation and though this molecule is disordered there is evidence that it is involved in H-bonding with N(9) in one molecule and N(17) of another. There is a stacking of centrosymmetrically related N(23)-containing isopyrazole units (centroid–centroid separation of 3.62 Å and mean interplanar separation of 3.31 Å). There is an analogous approach between the N(9)-containing pairs of rings, though here the centroid···centroid separation is much larger at 4.34 Å.

The X-ray structure of **4c** (Fig. 2) shows that this molecule also adopts a conformation having an alternating up/down orientation of the isopyrazole units. The overall molecular geometry is here rectangular, with the long sides containing two isopyrazole units and the shorter ones a single isopyrazole ring. The overall molecular dimensions are ca. 8.0×12.0 Å, corresponding to the separations of C(20) and C(20A) and of the centroids of the two isopyrazole rings (B and B′) occupying the 'short sides', respectively.

The molecule is centrosymmetric and the centres of the six ethylidene linkages are coplanar to within 0.10 Å. Rings A, B, and C are inclined by 76, 66, and 80°, respectively, to this plane with in each case their nitrogen atoms being oriented towards the macroring centre. The ethylidene units adopt

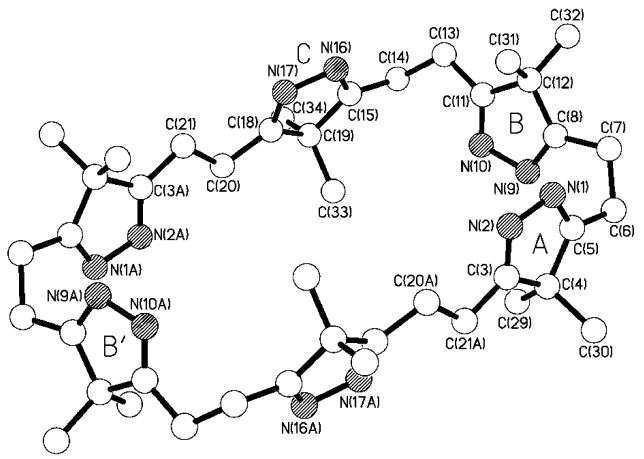


Figure 2. The X-ray structure of **4c**.

conformations with torsional twist angles of −66, 86, −166° about C(6)–C(7), C(13)–C(14), C(20)–C(21), respectively. A toluene molecule is trapped within the macrocycle cavity and exhibits an in-plane *p*-xylene-simulating disorder about the crystallographic centre of symmetry. Adventitious water molecules (two) are sited over the periphery of the macrocycle and are hydrogen-bonded to N(16) and N(16A), geometry: O···N 2.96, H···N 2.08 Å, O–H···N 166°. The other proton of the water molecule forms an intermolecular hydrogen bond to N(1) with geometry: O···N 2.95, H···N 2.05 Å, O–H···N 175°. The stacking of isopyrazole units observed in **4a** is not present in this structure, the separation of the centroids of the N(9)-containing rings of symmetry related molecules being 4.56 Å and too long for any significant interaction.

The observation of the trapping of toluene within the cavity of **4c** led us to expect that this macrocycle would also be able to include *p*-xylene. The X-ray analysis of single crystals of **4c** obtained from *p*-xylene confirmed this hypothesis. The structure (Fig. 3) is isomorphous with that obtained from toluene and the *p*-xylene molecule is ordered about the crystallographic inversion centre. The conformation of the macrocycle is only slightly perturbed, having overall dimensions of ca. 7.9×12.1 Å. The centres of the six linking ethylidene groups are coplanar to within 0.08 Å and rings A, B and C are inclined by 75, 59, and 82°, respectively, to this plane; the torsional twists about the CH_2–CH_2 bonds are −65, 83, and −168°. The bonding within the isopyrazole units in **4c**·*p*-xylene does not differ significantly from that observed in **4a**.

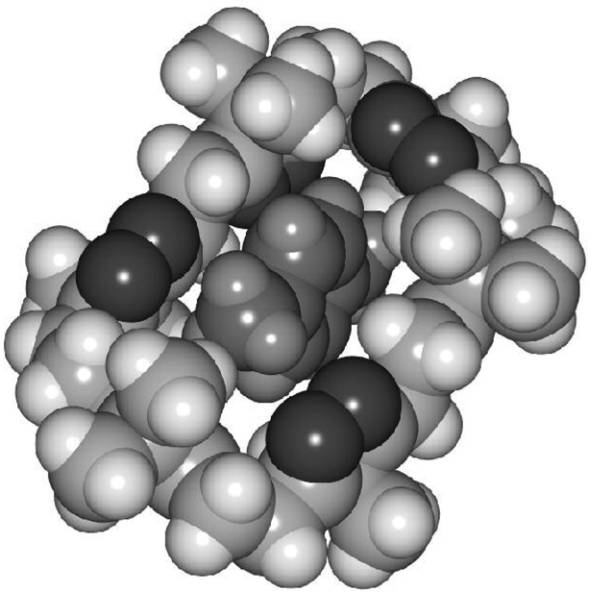


Figure 3. Space-filling representation of the solid-state structure of **4c**·*p*-xylene.

As in **4c**·$2H_2O$·$PhCH_3$ there are two included water molecules that are hydrogen-bonded intramolecularly to N(16) and intermolecularly to N(1); the hydrogen-bonding geometries [O···N, H···N (Å), O–H···N (°)] are 2.96, 2.07, 170 and 2.99, 2.11, 167, respectively. The small contraction in the width of the macrocyclic cavity compared with **4c**·$2H_2O$·$PhCH_3$ is interesting and may reflect an enhanced binding of *p*-xylene relative to toluene. An analysis of host–guest contacts reveals an overlap between the isopyrazole N(17)=C(18) bond and the *p*-xylene π-system; the distance of N(17) from the plane of the *p*-xylyl ring is 3.47 Å. This interaction is consistent with the electron-rich character of the *p*-xylyl unit and the π-electron deficient nature of the diene residue in isopyrazoles.[13] This binding is supplemented by a C–H···π interaction between one of the hydrogen atoms in each *p*-xylene methyl group and one of the C=N bonds in rings B and B′; the H···bond–centroid distance is 2.89 Å and the C–H···π angle is 161°.

We were unable, however, to observe any relevant complexation induced shifts in the ^{1}H NMR spectra of **4c** in $CDCl_3$, CD_2Cl_2 and CD_3CN upon addition of either toluene or *p*-xylene.

Pyrazole-based ligands have been widely studied for their ability to form coordination compounds with transition metals.[11] However, in almost all cases, the pyrazole unit in these ligands is 'aromatic' and in a deprotonated (pyrazolato) form. Indeed, to the best of our knowledge and prior to this study, only very few coordination compounds of isopyrazoles have been reported[14] and none of these have been crystallographically characterised.

Thus we decided to test the ability for **4a** and **4c** to form coordination compounds with selected transition metal ions. We treated methanolic solutions of both **4a** and **4c** with $Cu(ClO_4)_2$ (1:2 and 1:3 molar ratios, respectively). This led to an immediate change in colour (from almost colourless to dark blue), followed by the formation of dark precipitates which were insoluble in common solvents (including water, and DMSO). An attempt to confirm the nature of metal complexation of the ligand by IR spectroscopy was hindered by the fact that the characteristic absorptions associated with the C=N stretch were obscured by the perchlorate counterion. For this reason, we did not pursue the study of these precipitates any further.

Subsequently we treated **4a** and **4c** with *cis*-$PtCl_2(DMSO)_2$ or *cis*-$PtMe_2(DMSO)_2$. These platinum compounds[15] were chosen because their coordinated DMSO molecules are easily replaced by nitrogen-based ligands.[16]

The ^{1}H NMR spectrum of **4a** and $PtCl_2(DMSO)_2$ ($CDCl_3$, 1:1 ratio, 5×10^{-3} M) revealed, within a few minutes of mixing, the almost predominant formation of stoichiometric coordination compounds between $PtCl_2$ and the macrocycle—as confirmed by the appearance of the typical resonance for 'free' DMSO (δ 2.62, compared to δ 3.53 for Pt-coordinated DMSO).[16b] The displacement of DMSO from the Pt centre appears to be the prevailing process until 2 mol of $PtCl_2(DMSO)_2$ are added. Further addition of $PtCl_2(DMSO)_2$ does not produce quantitative displacement of DMSO from the Pt centre. Changes in the spectrum of **4a** upon addition of $PtCl_2(DMSO)_2$ include the appearance of novel and complex sets of resonances for the macrocycle methyl groups, which point to the likely existence of a mixture of coordination compounds having not only various stoichiometries, but also different regio- and stereochemistries. A very similar behaviour is also observed in CD_3CN.

Further evidence for the formation of various coordination compounds was obtained by the positive ESI-MS spectrum[17] of a mixture of **4a** and $PtCl_2(DMSO)_2$ (1:2 in CH_3CN, recorded within minutes after mixing); the significant peaks and the related assignments are listed in Table 1.

Table 1. Data for the positive ESI-MS spectrum of the reaction mixture formed by **4a** with $PtCl_2(DMSO)_2$ (1:2) in CH_3CN

m/z[a]	[Assignment]	Rel. int. (%)
489	$[M+H]^+$	100
511	$[M+Na]^+$	33
516[b]	$[2M+Fe]^{++}$	60
527	$[M+K]^+$	28
797	$[M+H+PtCl(DMSO)]^+$	22
977	$[2M+H]^+$	5
1063	$[M+PtCl_2PtCl(DMSO]^+$	52
1141	$[M+PtCl_2PtCl(DMSO)_2]^+$	7
1485	$[M+PtCl_2PtCl_2(DMSO)PtCl(DMSO)_2]^+$	4

[a] The *m/z* values indicated relate to the most abundant peak within the isotopic pattern calculated for the given composition.
[b] The presence of iron is presumed to be due to interactions with the metal components of the injection device.

When **4a** was treated with 1 equiv. of *cis*-$PtMe_2(DMSO)_2$ in $CDCl_3$, the most significant resonances observed in the ^{1}H NMR spectrum were at δ 0.56 for the Pt coordinated Me units ^2J (PtCH) 86 Hz, at δ 1.11, 1.15, and 1.35 ppm (2:1:1 intensity ratio, respectively) for the macrocycle methyl units, and a set of multiplets centred at 2.91, 3.22, and 3.51 ppm (1:2:1 intensity ratio, respectively) for the methylene groups. There were no resonances for Pt coordinated DMSO molecules, and only those for the free DMSO molecules were present.

These data are consistent with the prevalent formation of a 1:1 complex [(**4a**)$PtMe_2$] in which two nitrogen atoms of two different but adjacent isopyrazole units are coordinated to the metal centre in a way similar to that observed in the solid state for the larger analogue **4c** (vide infra).

The addition of 2 equiv. of *cis*-$PtMe_2(DMSO)_2$ produced changes in the spectra consistent with the dominant formation of a coordination compound with composition [Me_2Pt(**4a**)$PtMe_2$]. Apart from the Pt–Me resonances (δ 0.55, ^2J (PtCH) 86 Hz) there were only two signals for the methyl groups of the macrocycle (δ 1.14 and 1.34, 1:1 ratio) and two multiplets for the methylene protons (centred at δ 3.21 and 3.50 ppm, 1:1 ratio). These data suggest the predominant formation of the coordination compound shown in Fig. 4 (we exclude a *syn*-geometry for the $PtMe_2$ units because of unfavourable steric interactions).

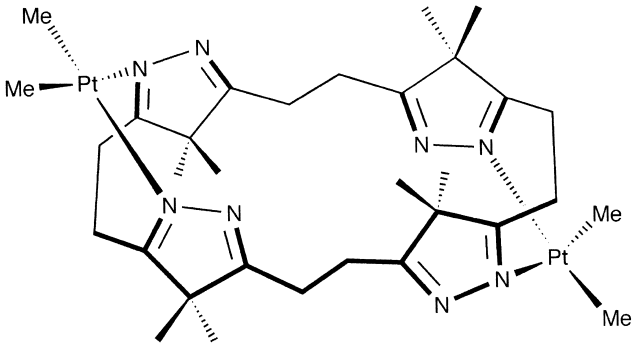


Figure 4. Schematic representation of the 1:2 complex formed between **4a** and $PtMe_2$.

The reaction mixtures of **4c** with either $PtCl_2(DMSO)_2$ or $PtMe_2(DMSO)_2$ (various stoichiometric proportions in $CDCl_3$) gave complex ^{1}H NMR spectra. However, it was evident that the nitrogen units of **4c** are capable of replacing either one or both of the DMSO ligands at the Pt centre (free DMSO molecules are formed) whereas the singlets observed for the methyl and methylene protons in the non-coordinated macrocycle give rise to multiple signals. The positive ESI-MS spectrum of the reaction mixture of **4c** with $PtCl_2(DMSO)_2$ (1:2 in CH_3CN) shows a much more complex set of peaks. Initial attempts to interpret these patterns in terms of simple stoichiometric coordination ratios was not possible. Alternative scenarios invoking the formation of mixed platinum complexes wherein some of the chloride ligands are replaced by acetonitrile gave a better (but not perfect) fit with the observed mass spectrum.

The $CDCl_3$ solution of **4c** with 2 equiv. of $PtCl_2(DMSO)_2$ gave very small colourless crystals suitable for X-ray analysis. The structure revealed that these crystals were the

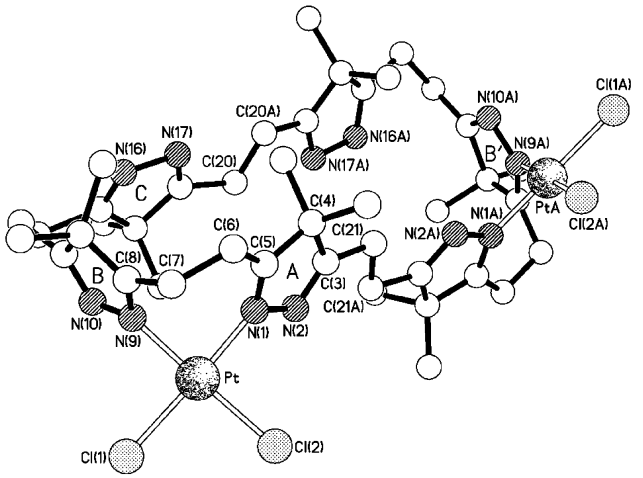


Figure 5. The X-ray structure of the [Cl_2Pt(**4c**)$PtCl_2$].

C_2 symmetric bis-platinum complex [Cl_2Pt(**4c**)$PtCl_2$] illustrated in Figure 5.

As was postulated for **4a**, the platinum atoms are coordinated to nitrogen atoms of adjacent pairs of isopyrazole rings. The platinum atoms are localised on one side of the molecule bridging between the isopyrazole rings positioned at the corners of the rectangular shaped macrocycle and lie one 'above' and one 'below' the mean plane of the macrocycle. This mode of coordination produces a helical twist of the macroring of ca. 45° about the axis joining the centroids of B and B′ isopyrazole units (Fig. 5). The macrocycle has a conformation with a 'down/down/up/down/up/up' pattern for the N–N bonds compared with the regularly alternating up/down arrangement seen in both **4a** and **4c**·toluene/*p*-xylene. The conformation and overall dimensions of the macrocycle (ca. 4.5×9.7 Å) are very different in the complex compared with those in the toluene and xylene adducts, exhibiting a contraction in both the length and breadth but retaining an *anti* geometry for the ethylidene linkages in the two 'long' sides. Most noticeable is the substantial reduction in the breadth, the macrocycle being effectively self-filling. Another feature that emerges from this structure is that once the first two $PtCl_2$ ligands have been coordinated in the geometry observed, the conformation of the macrocycle is constrained such that only one further $PtCl_2$ unit can in principle be coordinated after flipping of one of the remaining pair of non-coordinated isopyrazole rings.

The structure is heavily solvated with chloroform molecules, some of which are ordered, but many that are not and which could not be resolved. The poor quality of the crystals, their instability (two different crystals had to be used for the limited resolution data collection) and their tendency to desolvate spontaneously on removal from solution resulted in relatively large errors in the derived bond lengths and angles. The Pt–Cl and Pt–N distances (av. 2.298(6) and 1.96(2) Å, respectively) are unexceptional and comparable with those seen in for example a dinuclear complex of platinum with 4,4′-dipyrazolylmethane.[18] An analysis of the geometries of the isopyrazole rings is, however, not meaningful because of the large estimated standard deviations in their bond lengths. An analysis of the packing of the molecules revealed no important inter-complex interactions but did show the presence of a network of large channels that extend through the crystal in the *c* direction (Fig. 6).

3. Conclusions

The isopyrazole-containing macrocycles described here are easily obtained in satisfactory yields from the appropriate calixfuran precursors. These macrocycles have been shown to form coordination compounds with platinum complexes and are likely to coordinate other transition metals as well. The larger 'hexameric' macrocycle **4c** is also capable of complexing aromatic substrates by inclusion, though this property has only been proven in the solid state. The diene components of the isopyrazole units are also capable of undergoing cycloadditions, thereby offering a further means to manipulate these macrocyclic systems synthetically. We are currently exploring the use of these compounds for the selective extraction of metal ions from aqueous into organic phases.

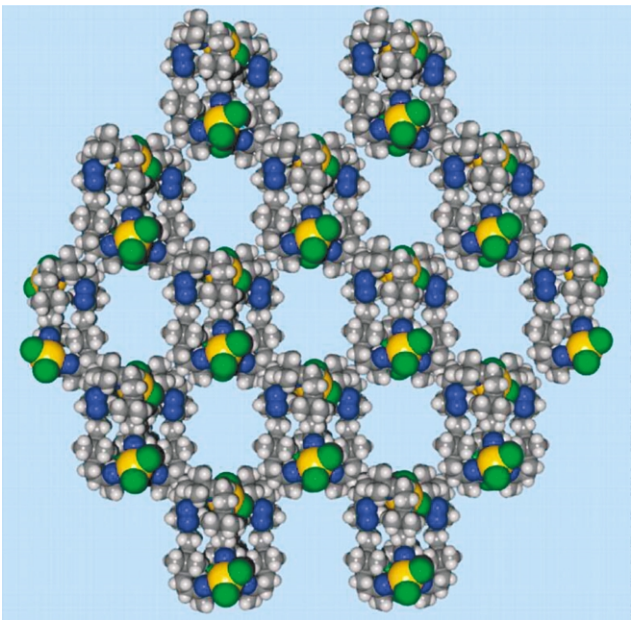


Figure 6. Space-filling representation of the packing in the solid state of molecules of [Cl_2Pt(**4c**)$PtCl_2$] showing the honeycomb pattern of channels that extend in the crystallographic *c* direction.

4. Experimental

4.1. General methods and instrumentation

All chemicals were standard reagent grade and were used without further purification. All air-sensitive and/or moisture sensitive reactions were conducted under a dry argon atmosphere. Thin layer chromatography (TLC) was conducted on Merck SiO_2 60 F254 plastic plates. Compounds were visualised with iodine, vanillin, or by examination under UV light. Column chromatography was conducted on Aldrich Silica gel 230–400 mesh, 60 Å. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-300 at 300 and 75 MHz, respectively, using the residual proton resonances of the solvents ($CDCl_3$, CD_3CN and CD_2Cl_2) as δ reference. Electron impact mass spectra (EI-MS) were measured on a Finnigan Mat 90 spectrometer operated by Dr Marcello Saitta. Electrospray ionisation mass spectra (ESI-MS) were recorded on a Mariner™ (PerSeptive Biosystems) electrospray ionisation-time of flight (ESI-TOF) mass spectrometer using the following conditions: spray tip potential, 4000 V; nozzle potential, 85 V; detector voltage 2200 V; nozzle temperature 140 °C. The samples, dissolved in CH_3CN at a concentration of about 10^{-6} M, were introduced at a flow rate of 7 mL/min. IR spectra were recorded on a Mattson Genesis II FT-IR spectrometer in mineral oil mull using NaCl disks. Melting points were determined on a Kofler hot stage apparatus, and are not corrected.

The syntheses for compounds **1**, **2**, and **3** have been reported elsewhere.[5a,7,8]

Table 2. Crystal data, data collection and refinement parameters[a]

Data	**4a**	**4c**	**4c**	$[Cl_2Pt(\mathbf{4c})PtCl_2]$
Formula	$C_{28}H_{40}N_8$	$C_{42}H_{60}N_{12}$	$C_{42}H_{60}N_{12}$	$C_{42}H_{60}N_{12}Cl_4Pt_2$
Solvent	$C_7H_8{\cdot}H_2O$	$C_7H_8{\cdot}2(H_2O)$	$C_8H_{10}{\cdot}2(H_2O)$	$10(CHCl_3)$
Formula weight	598.8	861.2	875.2	2458.7
Colour, habit	Colourless prisms	Pale yellow rhombs	Pale yellow rhombs	Colourless needles
Crystal size (mm)	0.80×0.40×0.20	0.52×0.48×0.12	0.77×0.67×0.07	0.83×0.03×0.03
Lattice type	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group, number	$P\bar{1}$, 2	$P2_1/c$, 14	$P2_1/c$, 14	$C2/c$, 15
T (K)	193	183	183	183
Cell dimensions				
a (Å)	10.337(1)	14.727(1)	15.070(2)	29.659(4)
b (Å)	10.493(1)	14.816(2)	14.591(2)	23.380(4)
c (Å)	16.871(1)	11.512(2)	11.487(1)	15.940(2)
α (°)	101.15(1)	—	—	—
β (°)	95.87(1)	105.87(1)	105.50(1)	95.11(1)
γ (°)	99.01(1)	—	—	—
V (Å^3)	1751.7(2)	2416.2(5)	2434.0(4)	11009(3)
Z	2	2[b]	2[b]	4[c]
D_c (g cm^{-3})	1.135	1.184	1.194	1.483
$F(000)$	648	932	948	4800
Radiation used	Cu Kα	Cu Kα	Cu Kα	Cu Kα
μ (mm^{-1})	0.56	0.59	0.59	12.56
θ range (°)	2.7–63.0	4.3–64.0	4.3–60.0	3.6–55.0
No. of unique refln.				
Measured	5613	3701	3606	6953
Observed, $\lvert F_o\rvert>4\sigma(\lvert F_o\rvert)$	4731	3033	2933	3409
No. of variables	438	329	299	535
R_1[d]	0.039	0.047	0.061	0.084
wR_2[e]	0.094	0.116	0.154	0.189
Weights a, b[f]	0.040, 0.448	0.056, 0.703	0.083, 0.473	0.075, 12.463
Largest difference peak, hole (e Å^{-3})	0.17, −0.17	0.21, −0.15	0.50, −0.43	1.80, −1.30

[a] Details in common: graphite monochromated radiation, ω-scans, Siemens P4 diffractometer, rotating anode source, refinement based on F^2.
[b] The molecule has crystallographic C_i symmetry.
[c] The molecule has crystallographic C_2 symmetry.
[d] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$.
[e] $wR_2=\sqrt{\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}}$.
[f] $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$.

4.1.1. Macrocycle 4a. $N_2H_4{\cdot}H_2O$ (573 mg, 0.55 mL, 11.40 mmol) was added to a solution of octaketone **2a** (960 mg, 1.90 mmol) in THF (50 mL) and the mixture was refluxed for 4 h. After removal of the solvent at reduced pressure, the crude product was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 95:5) to give a major fraction which was crystallized from toluene: 330 mg, 35%, mp 262–264 °C; ^{1}H NMR (CD_3CN) δ: 1.06 (s, 24H, CH_3), 2.84 (s, 16H, CH_2); ^{13}C NMR ($CDCl_3$) δ: 19.7 (CH_3), 21.9 (CH_2), 60.0 [$C(CH_3)_2$], 181.6 (C═N); EI-MS: 489 $(M+1)^+$; selected IR absorptions: 1637 (w), 1577 (m) cm^{-1}. Anal. Calcd for $C_{28}H_{40}N_8{\cdot}C_7H_8{\cdot}H_2O$: C, 70.20; H, 8.42. Found: C, 70.02; H, 8.39.

4.1.2. Macrocycle 4c. $N_2H_4{\cdot}H_2O$ (90 mg, 1.78 mmol) was added to a suspension of dodecaketone **2c** (150 mg, 0.20 mmol) in THF (10 mL) and the mixture was refluxed for 4 h. After removal of the solvent at reduced pressure, the crude product was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 95:5) to give a major fraction which was crystallized from toluene: 60 mg, 41%; mp>260 °C from *p*-xylene; ^{1}H NMR ($CDCl_3$) δ: 1.12 (s, 36H, CH_3), 2.92 (s, 24H, CH_2); ^{13}C NMR ($CDCl_3$) δ: 20.2 (CH_3), 22.0 (CH_2), 60.1 [$C(CH_3)_2$], 182.0 (C═N); EI-MS: 733 $(M+1)^+$; selected IR absorptions: 1630 (w), 1570 (m) cm^{-1}. Anal. Calcd for $C_{42}H_{60}N_{12}{\cdot}C_7H_8{\cdot}2H_2O$: C, 68.34; H, 8.43. Found: C, 68.38; H, 8.31.

A summary of the crystal data, data collection, and refinement parameters for the structures reported in this paper is given in Table 2. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Cryatallography Data Centre as supplementary publication numbers CCDC 214699-214702. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:+44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

This work was supported by the MURST/MIUR, Messina and Catania Universities in Italy. We thank Professor S. Lanza and Professor L. Monsù Scolaro at Messina University for helpful discussions and for supplying the platinum complexes *cis*-$PtMe_2(DMSO)_2$ and *cis*-$PtCl_2$-$(DMSO)_2$.

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