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FULL PAPER

Synthesis and characterisation of thioether crown hydrazones, and palladium(II) and platinum(II) complexes of 6-(2,4-dinitrophenylhydrazono)-1,4,8,11-tetrathiacyclotetradecane

Liam R. Sutton, Alexander J. Blake, Wan-Sheung Li and Martin Schröder *

Department of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD

Reaction of the functionalised thioether crowns [14]aneS$_4$-6-one (1,4,8,11-tetrathiacyclotetradecan-6-one, L^1) and [10]aneS$_3$-9-one (1,4,7-trithiacyclodecan-9-one, L^2) with 2,4-dinitrophenylhydrazine in a protic solvent under acidic catalysis afforded the corresponding hydrazones L^3 and L^4, respectively, in high yield. Reaction of [14]aneS$_4$-6-one with *p*-nitrophenylhydrazine under similar conditions affords the hydrazone L^5. Reaction of L^3 with [Pd(MeCN)$_4$][BF$_4$]$_2$ in MeCN yielded the complex [Pd(L^3)][BF$_4$]$_2$, while reaction of this ligand with [Pt(EtCN)$_4$][CF$_3$SO$_3$]$_2$ in MeCN afforded [Pt(L^3)][CF$_3$SO$_3$]$_2$. The single-crystal structures of L^3–L^5 and of [Pd(L^3)][BF$_4$]$_2$ have been determined. In all cases, π–π stacking is observed, the free macrocycles crystallising as polymeric arrays of face-sharing hydrazone moieties. In [Pd(L^3)]$^{2+}$, π–π interactions alternate with face sharing between planar [PdS$_4$]$^{2+}$ units constructing a one-dimensional polymeric array. The hydrazone function forces distortions of the respective macrocyclic rings and imparts chirality to the [Pd(L^3)]$^{2+}$ cation. The potential of these molecules as building blocks for macrocyclic liquid crystals and extended supramolecular arrays is discussed, as is the need to consider steric factors in rationalising the reactivity of keto-functionalised thioether crowns.

Homoleptic sulfur-donor macrocycles bearing extended functionality are still rare and have only recently been applied to the synthesis of mesogenic materials, both as free macrocycles and as binding agents for the late transition-metal ions.[1] The common feature of such materials is that the macrocycle bears a number of lengthy organic substituents which generate the anisotropy necessary to induce liquid-crystalline behaviour.[2] Since derivatisation of a thioether crown must necessarily occur on the carbon backbone, work has been undertaken to build in precursor functionality which can be used subsequently for extended derivatisation. Macrocyclic thioether crowns have now been synthesized with hydroxyl,[3] methine,[4] hydroxymethyl[5] and ketone[6] functionalities. Most examples of further derivatisation have focused on hydroxyl derivatives.[1,5,7] To date our own work in this area has concentrated on esterification of [14]- and [16]-aneS$_4$-diols.[1]

Keto-functionalised thioether crowns, first synthesized independently by Setzer and Kellogg and their co-workers,[6a,b] have been treated with hydrazine by Kellogg and co-workers[8] to yield both inter- and intra-molecular azines, demonstrating that these carbonyl groups readily undergo sterically innocuous condensations. However, attempted Wittig and Grignard additions to these ketones were unsuccessful, the reason proposed being that they have a high tendency to enolise due to the sulfur atoms situated β to the carbonyl group.[8]

The tetradentate thioether crown [14]aneS$_4$ (1,4,8,11-tetrathiacyclotetradecane) co-ordinates to an extensive range of metal atoms, most commonly as a platform for a square-planar S$_4$ donor set.[9] The d^8 palladium(II) cation usually adopts square-planar co-ordination and this is observed in its complexes with both the parent ligand[10] and with several functionalised derivatives[11] where the hydrocarbon links form the sides of a shallow bowl with the PdS$_4$ square as its base. We report herein the synthesis of phenylhydrazono derivatives of [14]-aneS$_4$-6-one (1,4,8,11-tetrathiacyclotetradecan-6-one, L^1) and [10]aneS$_3$-9-one (1,4,7-trithiacyclodecan-9-one, L^2) and complexes with Pd^{II} and Pt^{II}.

Results and Discussion

The ligands were synthesized from the appropriate ketonic starting material *via* condensation with aryl-substituted hydrazines to generate resonance-stabilised functionalised macrocycles incorporating an sp^2-hybridised carbon atom. Interdependence of the conformation of each macrocycle and the nature of its substituent is evident by comparison of the single-crystal structures of the parent ketones, L^1 and L^2, their hydrazones L^3–L^5, and [Pd(L^3)]$^{2+}$.

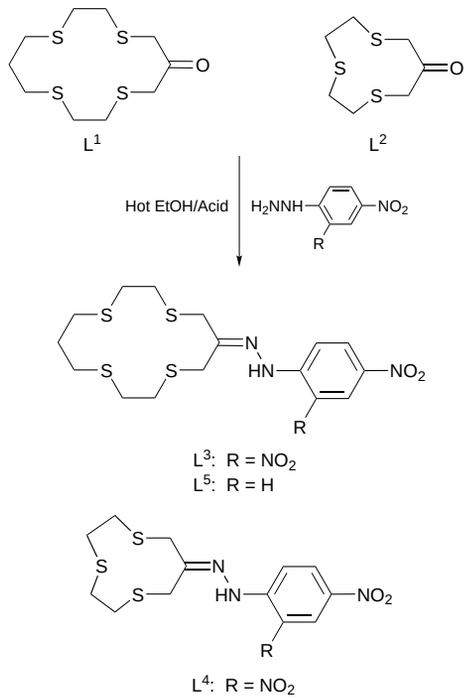
Synthesis of L^1 and L^2

The ketones used for further derivatisation, L^1 and L^2, were prepared by literature methods developed primarily by Kellogg and co-workers[6a] and by Setzer *et al.*[6b] Crystal structure determinations[6c,12] reveal that L^1 and L^2 adopt exodentate conformations similar to those exhibited by their unsubstituted parent macrocycles with little distortion due to the presence of the carbonyl oxygen.

Synthesis and structural description of L^3–L^5

Compounds L^3 and L^4 were synthesized by the condensation[13] of 2,4-dinitrophenylhydrazine with L^1 and L^2 respectively (Scheme 1). The hydrazine was suspended in EtOH, then protonated by the careful addition of concentrated H$_2$SO$_4$, to yield a bright yellow solution. This was then added to a colourless solution of the ketone in boiling EtOH, generating instant orange cloudiness in the mixture. Cooling to room temperature afforded almost quantitative yields of hydrazone. Analogously, L^5 was synthesized from L^1 and *p*-nitrophenylhydrazine using glacial acetic acid to dissolve the hydrazine in EtOH. Crystallisation at −18 °C yielded a mixture of product and excess of hydrazinium salt. Recrystallisation from EtOH afforded a 63% yield of yellow hydrazone L^5.

Selected bond lengths and angles are listed in Table 1. Features of note are the hydrogen bonds in compounds L^3 and L^4 between the hydrazone protons and an oxygen atom of the nitro groups in the *ortho* positions of the phenyl groups. Furthermore, the solid-state conformations of the macrocyclic core change significantly on condensation with the hydrazones. The crystal structure of L^3 [Fig. 1(*a*)] reveals a marked distortion of the macrocycle by comparison with the structure of L^1, which displays a quite regular [3434] conformation.[6a] The



Scheme 1 Synthesis of hydrazones

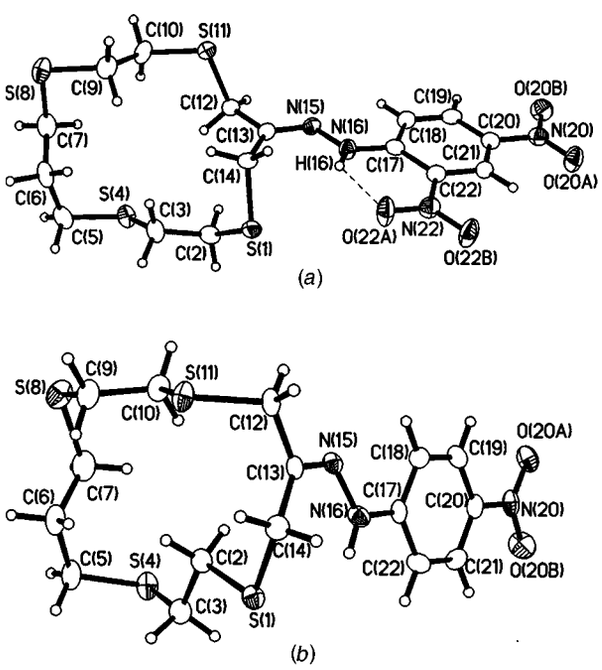


Fig. 1 Structures of compounds L^3 (*a*) and L^5 (*b*)

irregular [2435] conformation adopted by the macrocycle in L^3 is, we propose, the result of a minimisation of steric interaction between the hydrazone proton H(16) and S(1) (Table 2). The packing diagram (Fig. 2) illustrates the π–π stacking in the structure.[15] Interplanar separations are 3.383 and 3.407 Å (*cf.* 3.354 Å in graphite),[16] offset such that the centroid–centroid separations between phenyl rings are both 3.905 Å (Table 3).

Fig. 3 shows the structure of a single molecule of compound L^4. The hydrazone proton again induces a solid-state conformational change in the macrocycle relative to its parent ketone which has a [2323] conformation.[12] Significantly, the structure of L^4 shows 8 out of 10 torsion angles less than 90° (Table 2) thus reducing direct contact between H(12) and S(1) and reflecting severe distortions within the ring. Interaction between the π systems of the molecules allows them to stack as arrays of interlocking L shapes (Fig. 4), with interplanar distances of 3.270 and 3.359 Å.

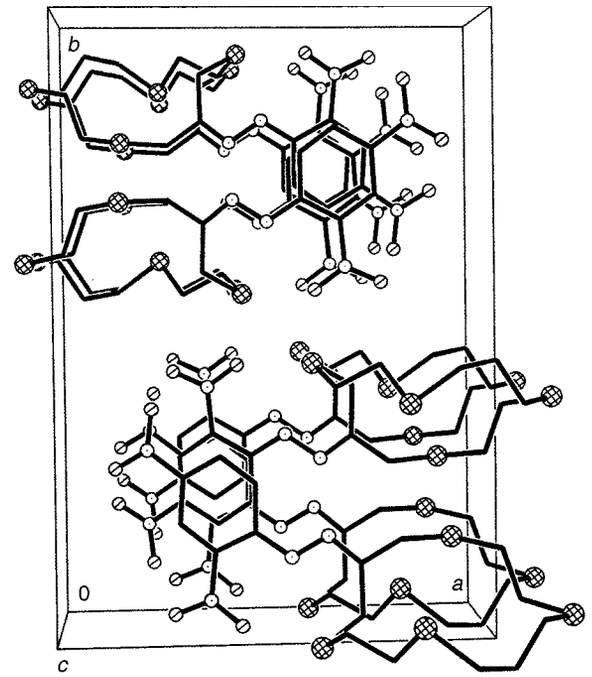


Fig. 2 Packing of compound L^3. Hydrogen atoms omitted for clarity

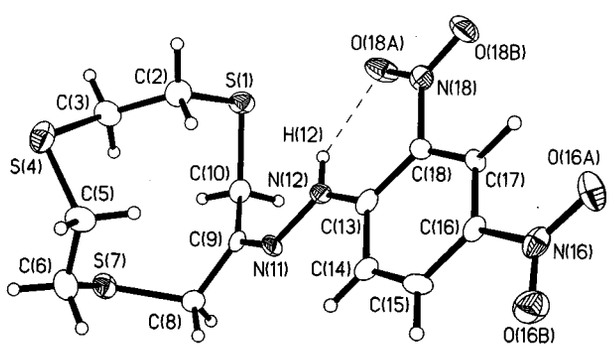


Fig. 3 Structure of compound L^4

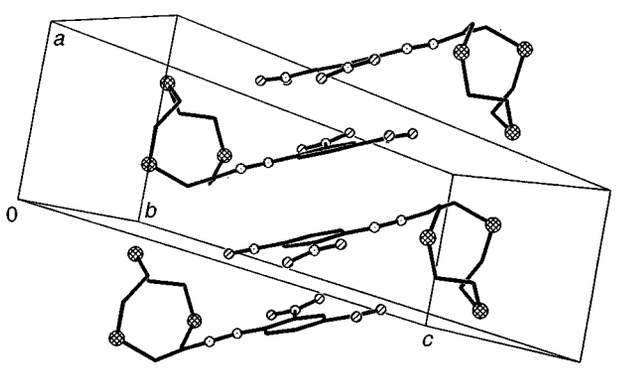


Fig. 4 Packing of compound L^4. Hydrogen atoms omitted for clarity

A similar disruption of the ring conformation occurs in compound L^5, which shows a [23225] conformation [Fig. 1(*b*)], showing that the NH···O_2N hydrogen bond present in L^3 and L^4 is not the key factor in determining the conformation of the macrocycle. Rather, conjugation in the hydrazone forces the NH hydrogen to occupy the position occupied by S(1) in the ketonic macrocycles. By comparison, the structure of an azine-bridged (=N–N=) dimer of [13]aneS_2O_2 (1,4-dioxa-7,11-dithiacyclotridecane) obtained by Kellogg and co-workers[8] displays little distortion of the rings from the expected structure of [13]aneS_2O_2-6-one, highlighting the importance of the hydrazone proton. The π–π stacking motif observed in L^4 is repeated in L^5, with interplanar separations of 3.360 and 3.507 Å.

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

L^3			
C(13)–N(15)	1.289(6)	N(16)–C(17)	1.347(7)
N(15)–N(16)	1.380(6)	O(22A)···H(16)	1.98
C(12)–C(13)–C(14)	118.4(5)	C(17)–N(16)–N(15)	120.0(4)
N(15)–C(13)–C(12)	115.6(3)	N(16)–C(17)–C(18)	120.3(5)
N(15)–C(13)–C(14)	126.0(5)	N(16)–C(17)–C(22)	123.6(5)
C(13)–N(15)–N(16)	116.3(4)		
L^4			
C(9)–N(11)	1.266(7)	N(12)–C(13)	1.351(7)
N(11)–N(12)	1.392(5)	O(18A)···H(12)	2.01
C(8)–C(9)–C(10)	115.1(5)	C(13)–N(12)–N(11)	117.8(5)
N(11)–C(9)–C(8)	114.2(5)	N(12)–C(13)–C(14)	120.0(5)
N(11)–C(9)–C(10)	130.3(5)	N(12)–C(13)–C(18)	124.6(6)
C(9)–N(11)–N(12)	119.3(5)		
L^5			
C(13)–N(15)	1.298(7)	N(16)–C(17)	1.382(7)
N(15)–N(16)	1.375(6)		
C(14)–C(13)–C(12)	117.8(4)	N(15)–N(16)–C(17)	118.4(5)
N(15)–C(13)–C(12)	114.1(5)	N(16)–C(17)–C(18)	121.8(5)
N(15)–C(13)–C(14)	127.6(5)	N(16)–C(17)–C(22)	118.3(5)
C(13)–N(15)–N(16)	117.2(4)		
$[Pd(L^3)][BF_4]_2\cdot 1.5MeCN$			
Pd–S(1)	2.295(4)	C(13)–N(15)	1.29(2)
Pd–S(4)	2.301(3)	N(15)–N(16)	1.27(2)
Pd–S(8)	2.294(4)	N(16)–C(17)	1.41(3)
Pd–S(11)	2.308(4)	O(22A)···H(16)	1.96
S(1)–Pd–S(4)	87.9(2)	N(15)–C(13)–C(12)	116.7(14)
S(8)–Pd–S(4)	87.7(2)	N(15)–C(13)–C(14)	123(2)
S(8)–Pd–S(11)	87.8(2)	N(15)–N(16)–C(17)	119(2)
S(1)–Pd–S(11)	96.6(2)	C(18)–C(17)–N(16)	119(2)
C(14)–C(13)–C(12)	120.8(13)	C(22)–C(17)–N(16)	122(2)

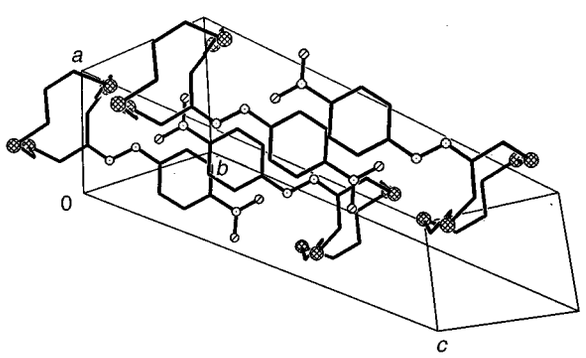


Fig. 5 Packing of compound L^5. Hydrogen atoms omitted for clarity

In the stacking of compounds L^3–L^5, large lateral offsets of neighbouring phenyl rings occur. This is due in part to the extended π systems of the phenyl ring, nitro groups and the hydrazone function. The view of the packing in L^5 in Fig. 5, perpendicular to the aromatic plane, shows the close aligning of phenyl rings in adjacent hydrazones.

Synthesis of complexes of Pd^{II} and Pt^{II}

The complex $[Pd(L^3)][BF_4]_2$ was synthesized by the addition of a solution of $[Pd(MeCN)_4][BF_4]_2$ in MeCN to an orange mixture of MeCN and the partially soluble L^3. The mixture immediately cleared and darkened slightly, the yellow product being crystallised by layering with Et_2O.

Crystals of composition $[Pd(L^3)][BF_4]_2\cdot 1.5MeCN$ were analysed by X-ray crystallography and the structure of the cation is shown in Fig. 6. Disorder modelling of the cation, both anions and both solvate molecules was required to refine the structure, an important factor in the cation being rotation of 180° about the C(13)–N(15) bond. The minor parts of the disorder are omitted for clarity. The Pd–S distances are similar to those in $[Pd([14]aneS_4)][PF_6]_2$,[10] with the sp^2 hybridisation of C(13) leading to an increase in the S(11)–Pd–S(1) angle to 96.6(2)° but with the other three angles lying in the narrow range 87.7(2)–87.9(2)°.

Table 2 Diagnostic torsion angles for compounds L^1–L^5

Compound	S–C–C–X Angles[a]/°	
L^1	−11.2(3)[b]	−5.8(3)[b]
L^3	−73.7(6)	−104.5(5)
L^5	−50.7(7)	133.7(4)
L^2	−20.7, −19.5[c]	137.9, 136.2[c]
L^4	−46.6(8)	123.1(5)
	L^3	L^5
S(1)–C(2)–C(3)–S(4)	160.9(3)	−167.3(3)
C(2)–C(3)–S(4)–C(5)	176.0(4)	−85.5(5)
C(3)–S(4)–C(5)–C(6)	70.4(5)	74.7(5)
S(4)–C(5)–C(6)–C(7)	69.0(6)	50.7(6)
C(5)–C(6)–C(7)–S(8)	−164.2(4)	172.4(4)
C(6)–C(7)–S(8)–C(9)	77.3(4)	65.1(5)
C(7)–S(8)–C(9)–C(10)	72.8(5)	72.6(5)
S(8)–C(9)–C(10)–S(11)	−179.4(3)	−174(3)
C(9)–C(10)–S(11)–C(12)	102.7(4)	170.4(4)
C(10)–S(11)–C(12)–C(13)	−140.4(4)	−79.8(5)
S(11)–C(12)–C(13)–C(14)	75.7(5)	−53.8(6)
C(12)–C(13)–C(14)–S(1)	106.2(5)	137.9(4)
C(13)–C(14)–S(1)–C(2)	−64.1(4)	−45.3(5)
C(14)–S(1)–C(2)–C(3)	−73.4(4)	−178.7(4)
	L^4	
S(1)–C(2)–C(3)–S(4)	158.6(3)	
C(2)–C(3)–S(4)–C(5)	−66.1(5)	
C(3)–S(4)–C(5)–C(6)	−83.5(5)	
S(4)–C(5)–C(6)–S(7)	67.3(6)	
C(5)–C(6)–S(7)–C(8)	72.6(6)	
C(6)–S(7)–C(8)–C(9)	−82.2(5)	
S(7)–C(8)–C(9)–C(10)	−63.9(6)	
C(8)–C(9)–C(10)–S(1)	141.7(4)	
C(9)–C(10)–S(1)–C(2)	−42.1(5)	
C(10)–S(1)–C(2)–C(3)	−63.5(5)	

[a] X = O or N. [b] Ref. 6(*c*). [c] Taken from the Cambridge Structural Database.[12,14]

Table 3 Phenyl ring separations in compounds L^3–L^5 and $[Pd(L^3)][BF_4]_2\cdot 1.5MeCN$

	Centroid–centroid distance[a]/Å	Interplanar separation[b]/Å
L^3	3.905, 3.905	3.383, 3.407
L^4	3.602, 3.700	3.270, 3.359
L^5	4.262, 4.519	3.360, 3.507
$[Pd(L^3)]^{2+}$	3.683, —	3.270, —

[a] Distance between dummy atoms placed at geometric centroids of adjacent phenyl ring carbon atoms. [b] Perpendicular distance from dummy atom to mean plane of adjacent phenyl ring carbon atoms.

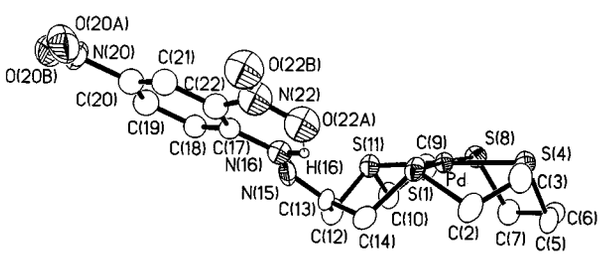


Fig. 6 Structure of the cation in $[Pd(L^3)][BF_4]_2\cdot 1.5MeCN$. Minor parts of disorder and most hydrogens omitted for clarity

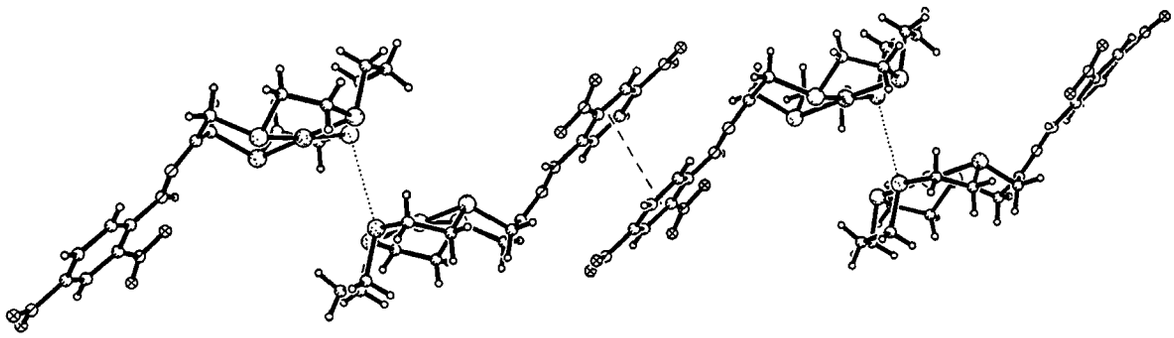


Fig. 7 Linear polymeric array of cations in $[Pd(L^3)][BF_4]_2 \cdot 1.5MeCN$. Minor parts of disorder omitted for clarity. Phenyl centroid separation (– – – –) = 3.683 Å; S(4) · · · S(4) 3.341 Å

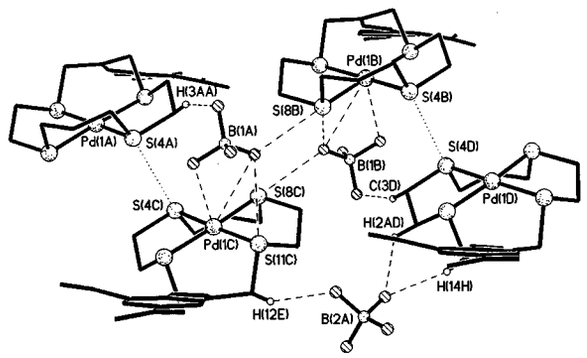


Fig. 8 Influence of BF_4^- on cation packing in $[Pd(L^3)][BF_4]_2 \cdot 1.5MeCN$

Compound L^3 co-ordinates to Pd^{II} to produce a flattened cup-like structure, resulting in chirality since the hydrazone at the rim of the cup can point either clockwise or anticlockwise, generating distinct enantiomers. The sp^2 linkage is rigid and the macrocycle is denied flexibility by the co-ordinated metal atom. In constructing linear polymers of cations (Fig. 7), the dicationic heads are held in close proximity with a shortest contact between neighbouring S(4) atoms of 3.341 Å. The tetrafluoroborate anions appear to exert considerable influence on the arrangement of the cations, with F atoms in close proximity to Pd, S(8) and S(11) and certain H atoms (Fig. 8). The aromatic groups show an interplanar separation of 3.270 Å. The linear polymers, formed from predominantly identical enantiomers, lie side by side to form sheets, with alternate sheets constructed from the alternate enantiomer to produce a racemic crystal.

The complex $[Pt(L^3)][CF_3SO_3]_2$ was synthesized using a similar method to that for $[Pd(L^3)][BF_4]_2$ but using $[Pt(EtCN)_4][CF_3SO_3]_2$ as starting material. The yellow suspension of L^3 in MeCN cleared only slightly on addition of the $[Pt(EtCN)_4][CF_3SO_3]_2$ but no colour change was observed in this case. The cloudiness is presumably due to some hydrolysed platinum(II) starting material, which is relatively moisture-sensitive. The reaction mixture was filtered and the filtrate evaporated, then taken up in a small amount of MeCN and precipitated by layering with Et_2O. Satisfactory characterisation data were obtained for all compounds using NMR, IR and mass spectrometry and elemental analysis.

Conclusion

Thioether crown ketones may be condensed with nitrophenylhydrazines to give new amphiphilic ligands for late transition metals. These ligands may be used in complex-forming reactions with Pd^{II} and Pt^{II}. The crystal structures highlight extensive π–π interaction while in the new palladium(II) complex sheets of parallel chains of chiral amphiphiles are formed. Furthermore, the crystal structures suggest an additional explanation for the failure of many reactions involving keto-functionalised thioether crowns. The marked distortion of the macrocycles due to a remote hydrogen atom implies that the steric interaction between the ring and the added substituent is critical. In our hands, attempted acid-catalysed imine formation using anilines in benzene under azeotropic distillation conditions resulted in C–S bond cleavage and decomposition, presumably *via* β-proton elimination.[17a] Comba *et al.*[17b] have recently investigated thermal C–S bond cleavage and ring contraction in 6-chloro- and 6,13-dichloro-[14]aneS_4. We speculate that the thioether crown hydrazones exhibit intermediate stability compared with crown thioethers bearing small substituents like oxygen and CH_2 and hypothetical examples bearing sterically demanding aromatic imines. The forcing conditions required to synthesize the imines thus cause decomposition. We also conclude that the failure of certain functionalisations of thioether crown ketones has a steric basis.

We are currently attempting to extend the chains attached to the macrocycles using both covalent and non-covalent bonding so increasing the anisotropy of the products. Of particular interest is the nitro–iodo interaction between nitro- and iodobenzenes recently reviewed by Desiraju.[18] These approaches should in due course lead to both thermotropic and lyotropic liquid crystals and extended arrays.

Experimental

Spectra were recorded on a Bruker DPX 300 (^1H and ^{13}C NMR) and a Perkin-Elmer 1600 spectrometer (FTIR, samples in KBr discs). Melting points were measured using a Gallenkamp apparatus and are uncorrected. Elemental analytical data were obtained by the Microanalytical Service (Perkin-Elmer 240B analyser) at the University of Nottingham and EI (electron impact) mass spectra were measured using a VG Autospec VG7070E spectrometer. Electrospray mass spectra were obtained by the EPSRC National Mass Spectrometry Service at the University of Swansea. The compounds [14]aneS_4-6-one (L^1), [10]aneS_3-9-one (L^2), $[Pd(MeCN)_4][BF_4]_2$ and $[Pt(EtCN)_4][CF_3SO_3]_2$ were prepared according to literature methods.[6,19] All starting materials, including anhydrous dimethylformamide, were obtained from Aldrich or Lancaster Synthesis and used without further purification.

Syntheses

1,4,8,11-Tetrathiacyclotetradecane-6-one 2,4-dinitrophenylhydrazone (L^3) and 1,4,7-trithiacyclodecane-9-one 2,4-dinitrophenylhydrazone (L^4). 2,4-Dinitrophenylhydrazine (50 mg, 0.25 mmol) was suspended in EtOH (5 cm^3) in an Erlenmeyer flask (25 cm^3). To the stirred solution were added five drops of concentrated H_2SO_4 yielding a yellow solution. In another Erlenmeyer flask (25 cm^3) compound L^1 (42 mg, 0.15 mmol) or L^2 (31 mg, 0.15 mmol) was dissolved in boiling EtOH (5 cm^3) and stirred; the hydrazine solution was added to this colourless solution giving an orange suspension which on cooling to 4 °C yielded a yellow microcrystalline solid and an orange super-

Table 4 Crystallographic data summary[a]

	L^3	L^4	L^5	$[Pd(L^3)][BF_4]_2 \cdot 1.5MeCN$
Empirical formula	$C_{16}H_{22}N_4O_4S_4$	$C_{13}H_{16}N_4O_4S_3$	$C_{16}H_{23}N_3O_2S_4$	$C_{19}H_{26.5}B_2F_8N_{5.5}O_4PdS_4$
M	462.62	388.48	417.6	804.22
Colour, habit	Yellow plate	Yellow needle	Yellow plate	Yellow column
Crystal size/mm	0.65 × 0.37 × 0.04	0.35 × 0.10 × 0.06	0.47 × 0.22 × 0.12	0.33 × 0.20 × 0.19
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	7.7711(19)	7.249(4)	5.6363(11)	10.181(2)
b/Å	19.458(9)	10.786(4)	8.7733(15)	12.569(3)
c/Å	13.480(4)	21.330(9)	19.833(4)	13.985(3)
α/°	—	—	93.28(2)	96.16(2)
β/°	93.63(3)	96.66(4)	93.55(2)	107.81(2)
γ/°	—	—	105.54(2)	96.02(2)
U/Å^3	2034.3(10)	1656.5(10)	940.3(3)	1676.1(4)
Z	4	4	2	2
D_c/g cm^{-3}	1.511	1.558	1.475	1.594
T/K	150	150	150	210
μ/mm^{-1}	0.498	0.474	0.521	0.881
F(000)	968	808	440	806
2θ Range/°	5–50	5–45	5–45	5–45
Independent reflections	4402	2148	2462	4402
Observed reflections [$\|F_o\| > 4\sigma(\|F_o\|)$]	2463	1265	1866	3257
Absorption correction method	ψ Scans	None	None	Numerical
Maximum, minimum transmission	0.880, 0.803	—	—	0.898, 0.838
Decay correction (%)	Random ±2	Random ±8.5	10	38.6
Number of parameters	253	218	227	381
Weighting scheme a, b[b]	0, 6.41	0.22, 0	0.064, 2.54	0.13, 39.0
Final $R1$ ($wR2$)[c]	0.0688 (0.1171)	0.0556 (0.1213)	0.0557 (0.0842)	0.1071 (0.1439)
Maximum Δ/σ	0.001	0.001	<0.001	0.009
Largest difference peak, hole/e Å^{-3}	0.38, −0.40	0.30, −0.31	0.34, −0.52	1.68, −1.83

[a] Details in common: Stoë Stadi-4 four-circle diffractometer, Oxford Cryosystems open-flow cryostat,[21] graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); ω–θ scans; refinement based on F^2. [b] In $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$. [c] Defined in ref. 20.

natant. The solid was separated by suction filtration, washed with cold EtOH (2 × 5 cm^3) and dried *in vacuo*. Crystals of L^3 suitable for X-ray diffraction were grown by diffusion of Et_2O vapour into a CH_2Cl_2 solution at 4 °C. Compound L^4 was crystallised by slow evaporation of a CH_2Cl_2 solution at room temperature.

Compound L^3: yield 64 mg (93%) (Found: C, 41.9; H, 4.8; N, 11.7. $C_{16}H_{22}N_4O_4S_4$ requires C, 41.5; H, 4.8; N, 12.1%); m.p. 130 °C (decomp.); $\tilde{\nu}_{max}$/cm^{-1} 3311m, 1615vs, 1590s, and 1510s; $\delta_H(CDCl_3)$ 9.16 [1 H, s, $C(NO_2)CHC(NO_2)$], 8.35 (1 H, m, aryl), 7.97 (1 H, m, aryl), 3.75 (2 H, s, *Z*-CH_2C=NNH), 3.63 (2 H, s, *E*-CH_2C=NNH), 3.05–2.90 (8 H, m, SCH_2CH_2S), 2.75 (4 H, m, $CH_2CH_2CH_2$) and 1.95 (2 H, qnt, $CH_2CH_2CH_2$); δ_C[$CDCl_3$, H connectivity confirmed by DEPT (distortionless enhancement of polarisation transfer) 90 and DEPT 135] 151.72 (C=N), 144.80, 138.71 and 130.24 (aryl CN), 129.95, 123.30 and 116.63 (aryl CH), 39.79 (*Z*-CH_2C=NNH) and 33.86, 33.65, 32.59, 32.24, 31.03, 30.70, 29.93 and 29.27 (other CH_2); *m*/*z* (EI) 460 ($M^+ - 2$ H) and 391 ($M^+ - 71$).

Compound L^4: yield 50 mg (87%) (Found: C, 39.7; H, 4.3; N, 14.0. $C_{13}H_{16}N_4O_4S_3$ requires C, 40.2; H, 4.15; N, 14.4%); m.p. 168 °C (decomp.); $\tilde{\nu}_{max}$/cm^{-1} 3157m, 3087w, 2914w, 2852w, 1613vs, 1590s, 1530m, 1513s and 1499s; $\delta_H(CDCl_3)$ 9.15 [1 H, s, $C(NO_2)CHC(NO_2)$], 8.33 (1 H, m, aryl), 7.95 (1H, m, aryl), 3.75 (2 H, s, *Z*-CH_2C=NNH), 3.50 (2 H, s, *E*-CH_2C=NNH) and 3.24–2.83 (8 H, m, SCH_2CH_2S); δ_C($CDCl_3$, H connectivity confirmed by DEPT 90 and DEPT 135) 151.38 (C=N), 144.86, 138.59 and 130.42 (aryl CN), 129.77, 123.34 and 116.55 (aryl CH), 41.68, 35.12, 35.00, 34.16, 33.43 and 31.02 (CH_2); *m*/*z* (EI) 327 ($M^+ - 71$).

1,4,8,11-Tetrathiacyclotetradecane-6-one 4-nitrophenylhydrazone (L^5). In a round-bottomed flask (25 cm^3) equipped with a magnetic stirrer bar and a reflux condenser, compound L^1 (50 mg, 0.18 mmol) was suspended in EtOH (5 cm^3) and refluxed to give a colourless solution. In a second flask (25 cm^3), *p*-nitrophenylhydrazine (50 mg, 0.33 mmol) was suspended in EtOH (5 cm^3) and treated with glacial acetic acid (four drops). On heating, a dark brown solution formed which was mixed with the refluxing ketone solution. The mixture was refluxed for 1 h, then stoppered and stored at −18 °C for 18 h. The resulting precipitate was isolated by suction filtration and recrystallised from EtOH to yield a yellow powder. Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of L^5 in $CHCl_3$.

Compound L^5: yield 47 mg, 0.11 mmol (63%) (Found: C, 46.1; H, 5.7; N, 10.3. $C_{16}H_{23}N_3O_2S_4$ requires C, 46.0; H, 5.6; N, 10.1%); m.p. 141–143 °C (decomp.); $\tilde{\nu}_{max}$/cm^{-1} 3273m, 2920m, 1595vs, 1523s, 1498s, 1481s, 1425w, 1324vs, 1264vs, 1110vs and 1080s; $\delta_H(CDCl_3)$ 9.37 (1 H, s, NH), 8.18 (2 H, m) and 7.10 (2 H, m, aryl), 3.69 (2 H, s) and 3.50 (2 H, s, CH_2C=N), 2.98–2.86 (8 H, m, SCH_2CH_2S), 2.75–2.67 (4 H, m, $CH_2CH_2CH_2$) and 1.90 (2 H, m, $CH_2CH_2CH_2$); $\delta_C(CDCl_3)$ 149.64 (C=N), 142.83 and 140.68 (aryl CN), 125.99 and 112.11 (aryl CH), 40.39, 33.32, 32.69, 32.38, 32.06, 30.72, 30.38, 29.64 and 29.40 (CH_2); *m*/*z* (EI) 417 (M^+).

$[Pd(L^3)][BF_4]_2$. A Schlenk tube (50 cm^3) was charged with compound L^3 (20 mg, 0.04 mmol) and a magnetic stirrer bar and pump-filled with N_2. A solution of $[Pd(MeCN)_4][BF_4]_2$ (19 mg, 0.04 mmol) in degassed MeCN (10 cm^3) was added *via* cannula, which was washed through with degassed MeCN (5 cm^3). The yellow solution became orange as all of the hydrazone dissolved. The solution was stirred for 1 h but no further change was observed. The MeCN solution was then layered with diethyl ether (30 cm^3) and left to stand for 24 h. Orange crystals formed which immediately became powder on suction filtration.

$[Pd(L^3)][BF_4]_2 \cdot 0.5MeCN$: yield 28 mg, 0.038 mmol (94%) (Found: C, 26.5; H, 3.3; N, 7.9. $C_{16}H_{22}B_2F_8N_4O_4PdS_4 \cdot 0.5MeCN$ requires C, 26.8; H, 3.1; N, 8.25%); $\tilde{\nu}_{max}$/cm^{-1} 3432m, 2923w, 2211vs, 1615s, 1596s, 1503m, 1427w, 1340s and 1084s; $\delta_H(CD_3CN)$ 11.12 (1 H, s, NH), 8.99 (1 H, m, CNCHCN), 8.44 (1 H, m) and 7.95 (1 H, m, CNC*HCH*CN), 4.43–4.37 (4 H, m,

$CH_2C{=}N$) and 3.93–2.90 (16 H, m, other SCH_2) ($CH_2CH_2CH_2$ coincident with solvent peaks at 2.20–1.90); $\delta_C(CD_3CN)$ 144.99, 141.33 and 132.78 (aryl CN), 131.35, 123.74 and 118.20 (aryl CH), 43.26, 42.61, 42.35, 39.18, 38.78, 36.14 (2 C), 32.25, 26.26 (CH_2) (CH at 118.20 coincident with CD_3CN, detected using DEPT 90 and 135; C=N not detected but possibly coincident with one of the aryl CN peaks; H connectivity confirmed using DEPT); *m/z* (positive-ion electrospray, MeOH, 80 V) 567 ($M^+ - 2\ BF_4$, 100%).

Crystals suitable for X-ray analysis were grown by diffusion of Et_2O vapour into an MeCN solution of the complex. They were found to be of composition $[Pd(L^3)][BF_4]_2 \cdot 1.5MeCN$.

$[Pt(L^3)][CF_3SO_3]_2$. To a stirred suspension of L^3 (11 mg, 0.024 mmol) in MeCN (5 cm^3) in a round-bottomed flask (25 cm^3) was added a solution of $[Pt(EtCN)_4][CF_3SO_3]_2$ (17 mg, 0.024 mmol) in MeCN (5 cm^3). The flask was stoppered and the mixture stirred for 24 h at room temperature. After this time a faintly cloudy yellow solution had formed which was filtered by gravity. The filtrate was evaporated, the residue taken up in MeCN (2 cm^3) and precipitated by layering with Et_2O and storing at 4 °C for 16 h. A yellow powder was isolated by suction filtration, washed with Et_2O (2 × 5 cm^3) and dried in air.

$[Pt(L^3)][CF_3SO_3]_2$: yield 17 mg, 0.018 mmol (75%) (Found: C, 25.3; H, 2.9; N, 6.0; Pt, 19.0. $C_{18}H_{22}F_6N_4O_{10}PtS_6 \cdot Et_2O$ requires C, 25.7; H, 3.1; N, 5.4; Pt, 18.9%); m.p. 155–160 °C (decomp.); $\tilde{\nu}_{max}/cm^{-1}$ 3454m, 3295w, 2983w, 2926w, 1519s, 1596m, 1502s, 1421w, 1343vs, 1316m, 1261vs, 1165s, 1097w, 1030s, 638s and 518w; $\delta_H(CD_3CN)$ 11.16 (1 H, s, NH), 9.00, 8.44, 7.97 (each 1 H, m, aryl), 4.63–4.40 (3 H, m), 3.96–2.85 (m, 13 H, SCH_2) and 2.12 (H_2O, conceals $CH_2CH_2CH_2$); $\delta_C(CD_3CN)$ 144.99, 141.39, 140.53, 132.60 (C=N and aryl CN), 131.40, 123.80, 120.01 (aryl CH), 43.42, 43.17, 42.27, 41.23, 38.95, 38.47, 36.61, 32.75, 26.12 (other CH); *m/z* (positive-ion electrospray, MeCN) 958 ($M^+ + 2$ H) and 657 ($M^+ - 2\ CF_3SO_3^- - H$) (both peak sets agree closely with theoretical distributions).

Crystallography

Table 4 summarises the crystal data, data collection, structure-solution and refinement parameters for ligands L^3–L^5 and the complex $[Pd(L^3)][BF_4]_2 \cdot 1.5MeCN$. All structures were solved using direct methods and all non-hydrogen atoms except for those in disordered groups were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model.

The asymmetric unit of the complex was found to contain two MeCN sites, one of which was half-occupied: disorder of the full-occupancy MeCN was successfully modelled by an approximately equal distribution of two orientations. Disorder in one BF_4^- was modelled using two-fold rotation about the B(1)–F(1) vector, whilst the other was modelled as two tetrahedra with a common centre at B(2). Disorder in the cation was modelled by a 180° rotation about the C(13)–N(15) vector with a 65:35 random distribution. The symmetry of the unit cell imparts the racemic nature of the crystal. The phenyl ring was restrained to be flat to within 0.02 Å with C–C distances of 1.40(2) Å.

Structure solution and least-squares refinement for all crystals was carried out using Dell Dimension 133 MHz Pentium personal computers running SHELXTL PC software[20] except for the structure solution for L^4 which was performed using SHELXS 86.[22]

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