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Mesogenic Transition Metal Complexes Liquid Crystal Phase Behaviour and Crystal and Molecular Structure of Some Nitrile Complexes of the Platinum Metals

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Mesogenic transition metal complexes

Liquid crystal phase behaviour and crystal and molecular structure of some nitrile complexes of the platinum metals†

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A new range of transition metal-containing liquid crystals is formed by complexing classical organic mesogens directly to a metal. Thus, reaction of $[PdCl_2(PhCN)_2]$ with 4-*n*-pentyl-4′-cyanobiphenyl (5CB) leads to $[PdCl_2(5CB)_2]$ which exhibits a monotropic nematic phase. Complexes of long chain 4-alkyloxy-4′-cyanobiphenyls show enantiotropic mesophases. Analogously, reaction of $[PtCl_2(PhCN)_2]$ or $[Rh_2Cl_2(CO)_4]$ with 4-alkyl-4′-cyanobiphenyls (L) yields mesogenic $[PtCl_2L_2]$ or cis-$[RhCl(CO)_2L]$ respectively. The crystal and molecular structure of $[PdCl_2(5CB)_2]$ and $[PtCl_2(8CB)_2]$ are also reported and show different packing in the solid state.

1. Introduction

Probably the first-known thermotropic metal-containing liquid crystals were the alkali metal salts of the carboxylic acids [1], which form classical lamellar (neat) phases characteristic of soaps, and the diarylmercury derivatives (I) [2], which form smectic phases. Since then, a variety of metal-based materials have been made [3–7] some of which are of particular note. The metal dithiolate complexes described by Giroud [4, 5] are of interest as only the nickel and platinum complexes exhibit mesophases (nematic and smectic). The palladium complexes of the azobenzene esters (II) [6] represent the first systematic attempt to coordinate mesogenic ligands to metals with the aim of obtaining mesogenic complexes. The dinuclear copper(II) carboxylates, also described by Giroud-Godquin *et al.* [7], were the first examples of discotic materials requiring only four peripheral chains. The rhodium and molybdenum analogues of these materials have recently been synthesized [8]. Some mesogenic rhodium carboxylates have also been prepared by Godquin-Giroud *et al.* [9]. A feature of the synthesis of these substances is the need to lose a proton from the ligand and an anionic ligand, X^-, from the metal in order to form the complex.

We have used the coordination of mesogenic organic nitrile ligands to synthesize the first examples of a new range of metal-containing liquid crystal materials [10]. Unlike the complexes just described, these materials require no modification of the ligand prior to complexation. Here we describe our further studies of these new mesogens.

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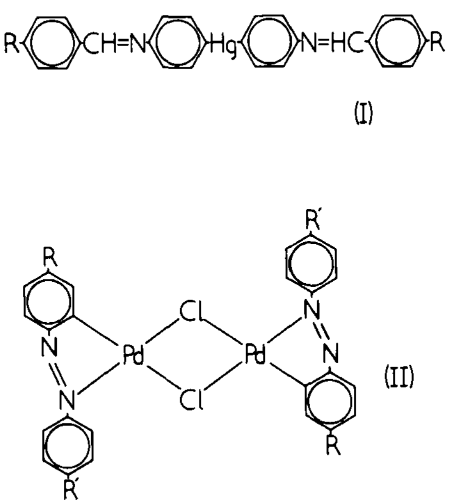

(I)

(II)

Figure 1. Structures of some known metal-containing liquid crystals.

2. Complexes of aryl and alicyclic nitriles

2.1. *Synthesis*

Mesogenic complexes are formed by reaction of $[MCl_2(PhCN)_2]$ (M = Pd, Pt) with a mesogenic nitrile in an organic solvent. The resulting complexes of the formula $[MCl_2L_2]$ (L = mesogenic nitrile) have a trans-square planar geometry and are yellow/orange in colour. The nitrile stretch of the coordinated ligand is about 60–70 cm^{-1} higher than that of the free ligand and this is consistent with a sigma-bonded nitrile (e.g. ν(CN) {5CB, free, Nujol} at 2228 cm^{-1}; ν(CN) {5CB in $[PdCl_2(5CB)_2]$, Nujol} at 2296 cm^{-1}). (The following abbreviations will be used throughout this text. 4-*n*-alkyl-4′-cyanobiphenyls will be represented as *n*CB, where *n* represents the number of carbon atoms in the alkyl chain, e.g. 4-*n*-pentyl-4′-cyanobiphenyl becomes 5CB. Similarly, the 4-*n*-alkyloxy-4′-cyanobiphenyls will be *n*OCB. For the 4-*n*-alkyl-4′-cyanobicyclohexyl compounds, the abbreviations CCHX will be used, so that trans, trans-4′-propyl-bicyclohexyl-4-carbonitrile is represented as CCH3.)

These complexes of platinum and palladium contain two mesogenic ligands, but the appropriate choice of metal allowed the synthesis of mesogenic complexes containing only one. Thus, mesogenic nitriles (L) reacted with $[Rh_2Cl_2(CO)_4]$, cleave the chloride bridges to give the bright orange complexes cis-$[RhCl(CO)_2L]$ (cf. figure 2) which are mesogenic. However, these complexes decompose at their clearing temperature to give a so far uncharacterized green solid. The smectic phase obtained on cooling the complex of 10OCB is probably associated with the ligand.

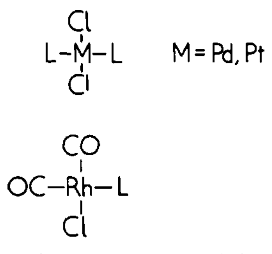

Figure 2. Molecular structures of complexes containing one and two mesogenic ligands.

Complexes of a wide range of mesogenic nitriles have been synthesized and information about their thermal behaviour is collected in table 1. This approach to the synthesis of mesogenic complexes has the advantage that the range of ligands available, plus others which are currently being synthesized, will allow the development of a very wide range of materials indeed.

Table 1. Thermal behaviour of the mesogenic metal complexes.

Compound	Transition	T/°C	ΔH/J g^{-1}	$\Delta S_m/R$
[PdCl$_2$(L)$_2$]				
L = 5CB	K → K′	85·6	2·81	0·64
	K′ → I	125	56·03	11·63
	(I → N)	(92)	−4·24	−0·95
L = 8CB	K → I	120	38·26	9·19
	(I → N)	(89)	−3·49	−0·89
L = 9CB	K → I	110	53·42	13·35
	(I → N)	(98)	−2·52	−0·65
L = 9OCB	K → S_C	119	55·27	13·96
	S_C → S_A	122†		
	S_A → I	146†		
L = CCH3	K → I	181·4	80·43	13·77
	(I → N)	(178·3)†		
L = CCH5	K → I	164·4	77·66	15·02
	(I → N)	(161·8)	−3·40	−1·35
[PtCl$_2$(L)$_2$]				
L = 5CB	K → N	189	48·17	9·55
	N → I	204	7·80	1·46
L = 9OCB	K → K′	161		
	K′ → S_A	167	36·80‡	10·15‡
	S_A → N	187	6·80	1·63
	N → I	209‖	1·68	0·39
L = 8CB	K → N	166	22·19	5·16
	N → I	176†		
[RhCl(CO)$_2$(9OCB)]	K → N	78		
	N → I§	79	99·7‡	17·5‡
[RhCl(CO)$_2$(10OCB)]	K → I§	72	77·49	14·33
	I → S	58	−2·81	−0·52

† Not detected by D.S.C.
‡ Denotes combined transition enthalpies (entropies).
§ Accompanied by a colour change.
‖ With some decomposition.

2.2. *Phase behaviour*

The complexes seem to reflect the mesogenic properties of the parent ligand, so that 5CB has a nematic phase (T_{KN} 24°C; T_{NI} 35°C) as do its complexes with Pd (T_{KI} 125°C; T_{IN} 92°C (monotropic)) and Pt (T_{KN} 189°C; T_{NI} 204°C). Similarly, 9OCB has a smectic and a nematic phase (T_{KS} 64°C; T_{SN} 77·5°C; T_{NI} 80°C) as does its complex with Pt (T_{KS} 167°C; T_{SN} 187°C; T_{NI} 209°C): in the palladium complex, two smectic phases are observed and the nematic phase is suppressed. The palladium complex of 10OCB shows a S_A phase on heating. Curiously, the smectic phases of 8CB and 9CB are suppressed on complexation.

As each ligand is modified in the same way (i.e. by the insertion of a MCl_2 unit), uniform increases in the transition temperatures could have been expected. Indeed, from molecular mean field theory, the T_{NI} is proportional to the average anisotropic interaction energy, so that equal increments in this might (in simple terms) be expected to lead to similar increments in T_{NI}. This is however not found to be the case. For example, the clearing temperature of 5CB increases from 35·5°C in the free ligand to 204°C in its complex with platinum, a difference of 170°C, whilst the clearing temperature of 8CB is raised from 40·5°C in the free ligand to 176°C in *its* platinum complex, an increase this time of only 130°C. Similarly for complexation to palladium, the increases in clearing temperature (free ligand compared to metal complex) are 5CB, 90°C and 8CB, 99°C.

The palladium complex of 5CB exhibits a monotropic nematic phase whilst the platinum complex of the same nitrile shows an enantiotropic nematic phase; this is unexpected. Similar observations have been reported by other authors. Giroud [5] observed that only the nickel and platinum complexes of dithiolate ligands showed mesomorphism. Its absence in the palladium complex was attributed to Pd–Pd interactions in the solid state. Manotti Lanfredi *et al.* [11] showed that palladium stacks with a Pd–Pd distance of 3·4 Å were present in the solid state structure of the non-mesogenic (8-hydroxyquinolinato)-[2-(4′-methoxyphenylazo-N^2)-5-methoxyphenyl] palladium(II) which was derived from a mesogenic precursor complex (complex II in figure 1). Bulkin *et al.* [12] also suggested that the lack of mesomorphism in the palladium complex of 1-4′-*n*-octyloxyphenyl-1,3-butanedione was due to possible intermetallic interactions. However, other explanations for such effects are possible.

3. Crystal and molecular structure of [$PdCl_2(5CB)_2$] and [$PtCl_2(8CB)_2$]

To see if intermolecular interactions were of potential importance in determining the phase behaviour of our materials, we undertook the structure determination of two complexes, [$PdCl_2(5CB)_2$] and [$PtCl_2(8CB)_2$].

3.1. [$PtCl_2(8CB)_2$]

The molecular structure is illustrated in figure 3 and selected bond lengths and angles are listed in table 2. The molecule has crystallographically imposed inversion symmetry and therefore like ligands are strictly *trans*. The coordination geometry around the platinum is close to square (cis angle 87·0°) and necessarily planar (Pt(1)–Cl(1) 2·284(4) Å, Pt(1)–N(1) 1·928(12) Å). The bond angles at N(1) and C(1) differ significantly from 180° (170·5(15)° and 175·1(15)° respectively) and the deviations from collinearity are essentially cumulative (N(1)–C(1) 1·123(18) Å with torsion angle 5·9°). The two six-membered rings are each planar (r.m.s. deviation 0·004 and 0·013 Å) but are non-coplanar (essentially twisted about C(5)–C(8)) to the extent of 30·0°. The *n*-octyl chain adopts an antiperiplanar conformation, all torsion angles are within 3° of 180° (not constrained), after an initial torsional deviation of 33° away from the mean plane of the outer six-membered ring.

The molecules are very elongated; the distance between terminal carbon atoms is 41·9 Å compared to a maximum skeletal breadth of approximately 4·6 Å. Although

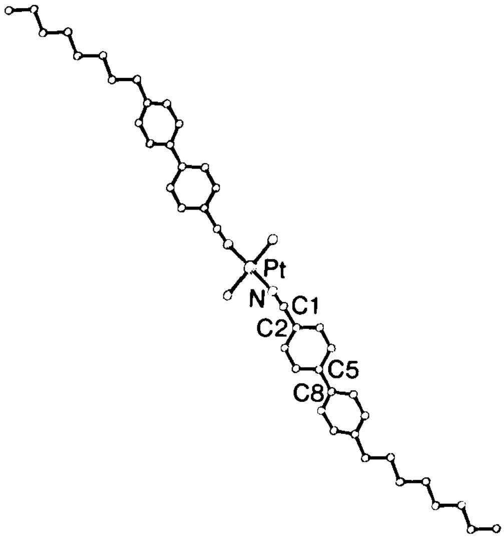

Figure 3. Molecular structure of $[PtCl_2(8CB)_2]$.

Table 2. Selected bond lengths and bond angles with estimated standard deviations for $[PtCl_2(8CB)_2]$.

Pt(1)–Cl(1)	2·284(4) Å
Pt(1)–N(1)	1·928(12) Å
N(1)–C(1)	1·123(18) Å
C(1)–C(2)	1·440(20) Å
C(5)–C(8)	1·488(20) Å
Cl(1)–Pt(1)–N(1)	87·0(4)°
Pt(1)–N(1)–C(1)	170·4(12)°
N(1)–C(1)–C(2)	175·1(15)°

the long axis of the molecule is inclined to all three unit cell axes, the molecules pack in broad sheets which lie parallel to the *C* face of the unit cell, with the long axes of alternate molecules mutually inclined at approximately 55°. Between each broad sheet and its neighbour at a unit cell displacement along the *c* axis there is a gap of 1·62 Å which contains no skeletal atoms, but only some methyl hydrogens. This gap forms a sheet, also parallel to the *C* face, which extends throughout the lattice (cf. figure 4).

3.2. $[PdCl_2(5CB)_2]$

The molecular structure is illustrated in figure 5 and selected bond lengths and angles are listed in table 3. Like the platinum compound, the molecule is situated about a crystallographic inversion centre and is necessarily *trans*. The non-linearity about the CN moiety is only just significant with deviations from 180° of 2·2(6)° N(1) and 3·1(8)° C(1). The rings C(2)–C(7) and C(8)–C(13) are each closely planar with r.m.s. deviations of 0·010 and 0·006 Å respectively. The various planes of the molecule are twisted alternately, the dihedral angles from the Pd/Cl/N plane being: ring 1 (−5·0°), ring 2 (+20·3°), C(14)–C(16) (−37·5°) and C(16)–C(18) (+73·5°). Compared with the platinum compound the angle between the ring planes is smaller (25°, cf. 30°), there is a larger initial torsional step for the aliphatic chain (61°, cf. 33°) and there is a torsion angle of 106° about the C(15)–C(16) bond. The other torsion angles in the

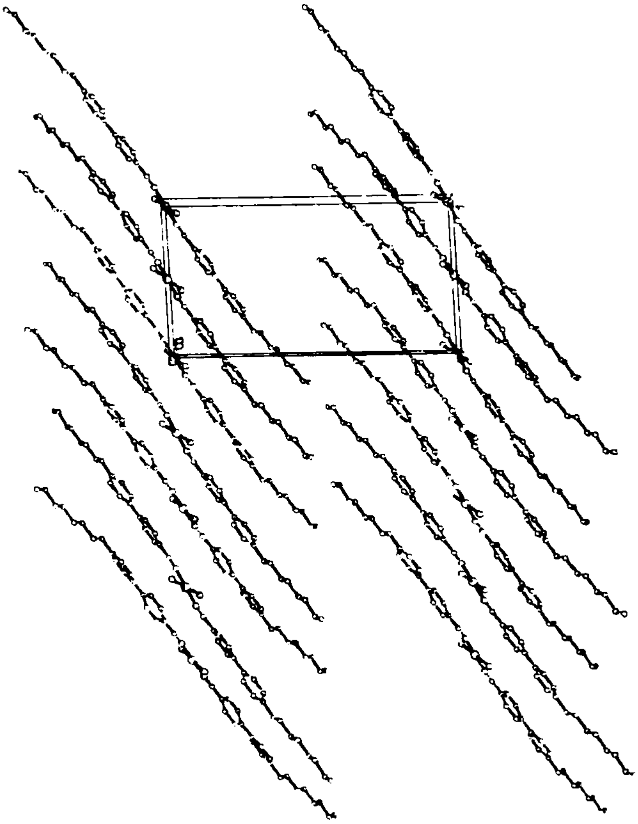

Figure 4. Illustration of the molecular packing in [$PtCl_2(8CB)_2$], viewed along the *b* axis.

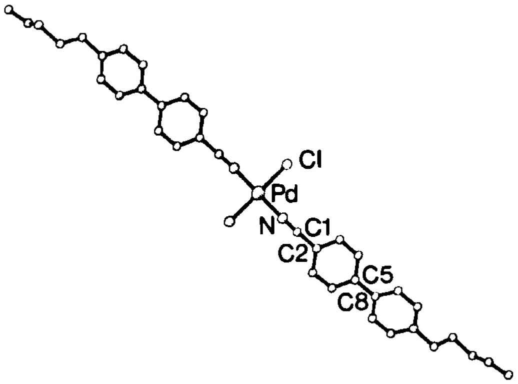

Figure 5. Molecular structure of [$PdCl_2(5CB)_2$].

chain are between 172° and 180°. The space group symmetry requires that all the molecules are strictly parallel, as may be seen in figure 6. Again, the molecules form 'rafts' parallel to the *ab* face with a significant gap between them.

The shortest intermetallic separation in the two materials is quite different and is given in each case by the shortest side of the unit cell. In the platinum material, this is the **b** axis and the distance is 6·56 Å, whilst in the palladium material it is the **a** axis

Table 3. Selected bond lengths and bond angles with estimated standard deviations for $[PdCl_2(5CB)_2]$.

Pd(1)–Cl(1)	2·273(2) Å
Pd(1)–N(1)	1·954(7) Å
N(1)–C(1)	1·131(12) Å
C(1)–C(2)	1·420(12) Å
C(5)–C(8)	1·473(10) Å
Cl(1)–Pd(1)–N(1)	89·4(2)°
Pd(1)–N(1)–C(1)	177·8(6)°
N(1)–C(1)–C(2)	176·9(8)°

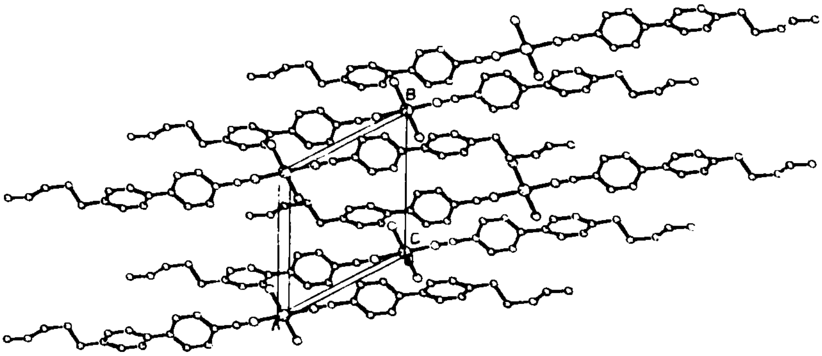

Figure 6. Illustration of the molecular packing in $[PdCl_2(5CB)_2]$, viewed along the *c* axis.

and the distance is 8·31 Å. Both of these separations are well outside accepted limits for interaction and so in the palladium complex, the monotropic phase behaviour is not a consequence of short intermetallic interactions. Obviously then, other effects are important in determining the phase behaviour and work is continuing in an attempt to ascertain what they might be.

4. Physical properties

The palladium complexes of CCH3 and CCH5 each exhibited a monotropic nematic phase (cf. table 1) and it was of interest to see whether mixtures of these two materials would allow the stabilization of a nematic phase. The composition diagram (cf. figure 7) shows that it is indeed possible to stabilize the nematic phase to a range of about 5°C. It is not however clear if a genuine eutectic mixture has been formed, since the phase behaviour of the system is probably affected by disproportionation of the two components such as

$$[PdCl_2(CCH3)_2] + [PdCl_2(CCH5)_2] \rightleftharpoons 2[PdCl_2(CCH3)(CCH5)].$$

One potential use of these complexes is as additives to conventional room temperature liquid crystal materials. As a first step towards determining the physical properties of these metal-containing liquid crystals, we have measured the refractive indices of nematic solutions of $[PdCl_2(5CB)_2]$ in 5CB. Measurements were made on homeotropically aligned films using an Abbé refractometer with a He–Ne laser light source (λ = 633 nm). The results (cf. figure 8) for solutions of three compositions show that the metal complex causes a slight increase in transition temperature and an enhancement of the birefringence. It would appear that the proportionate increase in birefringence is greatest in the region of the transition, and this can be

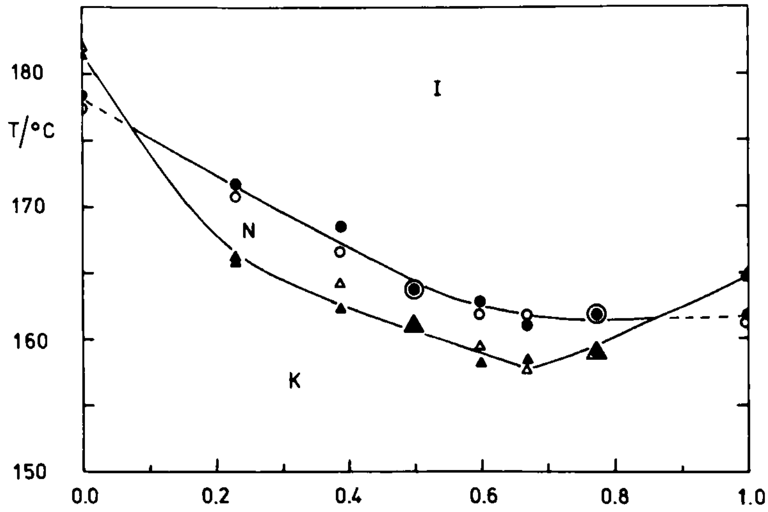

Figure 7. Plot of temperature versus composition for mixtures of [$PdCl_2(CCH_3)_2$] and [$PdCl_2(CCH5)_2$], x axis represents the weight fraction of the CCH5 complex. Data are derived from: ●, ▲ optical measurements; ○, △ D.S.C. measurements.

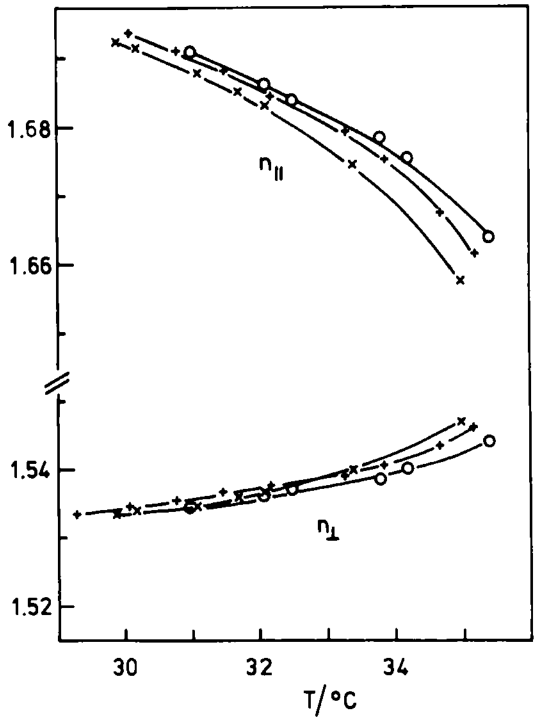

Figure 8. Plot of refractive indices versus temperature for a solution of [$PdCl_2(5CB)_2$] in 5CB at the following compositions: ○ 1·27 wt per cent Pd complex; + 0·77 wt per cent Pd complex; x pure 5CB.

attributed to the increased order of the solute molecules rather than to any significant increase in polarizability anisotropy. Further work is in progress to complete the physical characterization of these new materials.

5. Experimental

Microanalyses were carried out by the University of Sheffield microanalytical service. All solvents were distilled prior to use and mesogenic nitriles were used as supplied. The complexes $[PdCl_2(PhCN)_2]$ [13], $[PtCl_2(PhCN)_2]$ [14] and $[Rh_2Cl_2(CO)_4]$ [15] were prepared according to the literature methods. Yields and microanalytical data for the new compounds are collected in table 4. Typical preparation were as follows; all analogous complexes were prepared in the same way.

5.1. *Preparation of* $[PdCl_2(5CB)_2]$

$[PdCl_2(PhCN)_2]$ (220 mg, 0·56 mmol) was dissolved in dry acetone (5 cm^3) and added to a solution of 5CB (280 mg, 1·22 mmol) in dry acetone (5 cm^3). The resulting mixture was stirred at room temperature for 3 hours. The solvent was removed under vacuum and the residue triturated with ethanol (3 × 10 cm^3), filtered and dried overnight under vacuum to give the complex as an analytically pure material (240 mg, 64 per cent).

5.2. *Preparation of* $[PtCl_2(5CB)_2]$

$[PtCl_2(PhCN)_2]$ (200 mg, 0·42 mmol) was refluxed in toluene (30 cm^3) with a slight excess of 5CB (0·22 cm^3, 0·90 mmol) for 20 hours. On cooling, the solution was evaporated to dryness and the residue was triturated with ethanol (3 × 10 cm^3) and filtered to give the desired compound as a pale yellow solid (102 mg, 32 per cent).

5.3. *Preparation of* $[RhCl(CO)_2L]$

10OCB (172 mg, 0·52 mmol) was added to a solution of $[Rh_2Cl_2(CO)_4]$ (100 mg, 0·26 mmol) in hexane (10 cm^3) and the mixture was stirred under an atmosphere of dinitrogen for 3 hours. During this time, the product precipitated and was finally recovered by filtration. After washing with hexane and air-drying, the compound was analytically pure (yield 200 mg, 74 per cent).

5.4. *Crystal structure determinations*

5.4.1. $[PtCl_2(8CB)_2]$

$C_{42}H_{50}N_2Cl_2Pt$, $M = 848{\cdot}78$, crystallized from dichloromethane/hexane as pale yellow elongated plates; dimensions 0·75 × 0·25 × 0·05 mm. Monoclinic $a = 12{\cdot}508(7)$, $b = 6{\cdot}561(3)$, $c = 23{\cdot}792(14)$ Å, $\beta = 92{\cdot}26(5)°$, $U = 1951{\cdot}0(19)$ Å^3; $D_c = 1{\cdot}445$ g cm^{-3}, $Z = 2$. Space group $P2_1/a$ (a non-standard choice of axes for $P2_1/c$, C_{2h}, No. 14); Mo $K(\alpha)$ radiation ($\bar{\lambda} = 0{\cdot}71069$ Å), μ(Mo $K_\alpha = 38{\cdot}00$ cm^{-1}, $F(000) = 856$.

Three-dimensional X-ray diffraction data were collected in the range $3{\cdot}5° < 2\theta < 50°$ partly on a Nicolet R3m and partly on a Stoe Stadi-2 diffractometer by the omega scan technique. The data for which $I/\sigma(I) > 3{\cdot}0$ were corrected for Lorentz and polarization effects and for absorption, and were merged ($R_{\mathrm{merge}} = 0{\cdot}053$) to yield 2063 independent reflections. The structure was solved by standard Patterson and

Table 4. Microanalytical data for the new complexes.

		Calculated (found)				
Complex	Yield (per cent)	C	N	H	Cl	ν(CN)†/cm^{-1}
[PdCl$_2$(5CB)$_2$]	56	64·0 (63·8)	4·1 (4·1)	5·7 (5·8)	10·5 (10·3)	2296
[PdCl$_2$(8CB)$_2$]	90	66·2 (66·4)	3·6 (3·7)	6·4 (6·6)	9·7 (9·3)	2295
[PdCl$_2$(9CB)$_2$]	64	67·1 (66·2)	3·6 (3·6)	6·9 (6·9)	9·0 (9·0)	2298
[PdCl$_2$(9OCB)$_2$]	57	64·4 (64·7)	3·4 (3·7)	6·6 (6·7)	8·6 (7·7)	2294
[PdCl$_2$(10OCB)$_2$]	60	65·1 (64·9)	3·3 (3·0)	6·9 (6·8)	8·4 (8·5)	2297
[PdCl$_2$(CCH3)$_2$]	47	59·7 (59·7)	4·4 (4·4)	8·5 (8·6)	11·0 (11·1)	2305
[PdCl$_2$(CCH5$_2$]	57	61·8 (61·5)	4·0 (4·2)	8·9 (8·9)	10·1 (10·3)	2304
[PtCl$_2$(5CB)$_2$]	32	56·5 (56·1)	3·7 (3·7)	5·0 (5·1)	9·3 (9·1)	2295
[PtCl$_2$(9OCB)$_2$]	37	58·1 (57·2)	3·1 (3·2)	5·5 (6·0)	7·8 (8·4)	2297
[PtCl$_2$(8CB)$_2$]	43	59·4 (58·5)	3·3 (3·4)	5·9 (5·7)	8·4 (9·1)	2290
[RhCl(CO)$_2$(9OCB)]	77	55·6 (55·9)	2·7 (2·6)	5·5 (5·3)	6·9 (6·9)	2272‡
[RhCl(CO)$_2$(10OCB)]	74	56·8 (56·7)	2·7 (2·7)	5·6 (5·5)	7·1 (6·7)	2272‡

† Measured as a nujol mull.

‡ Measured in chloroform; ν(CO) at 2093 and 2035 cm^{-1} (9OCB) and 2094 and 2035 cm^{-1} (10OCB).

Table 5. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $[PtCl_2(8CB)_2]$.

Atom	x	y	z	U_{eq}†
Pt(1)	0	0	0	52(1)
Cl(1)	614(4)	−2878(6)	−421(2)	70(1)
N(1)	1169(9)	1421(18)	−331(5)	56(4)
C(1)	1867(11)	2008(22)	−566(6)	51(5)
C(2)	2757(11)	2603(26)	−895(6)	57(5)
C(3)	2858(11)	4540(22)	−1106(6)	62(6)
C(4)	3716(10)	5013(33)	−1425(5)	63(5)
C(5)	4490(11)	3522(24)	−1546(5)	53(5)
C(6)	4361(12)	1598(23)	−1328(6)	59(5)
C(7)	3501(12)	1167(23)	−1004(6)	64(6)
C(8)	5434(11)	4025(25)	−1881(6)	57(5)
C(9)	5940(13)	2551(29)	−2193(7)	82(7)
C(10)	6811(15)	3129(35)	−2496(7)	83(8)
C(11)	7257(11)	5050(37)	−2484(7)	81(6)
C(12)	6767(14)	6487(31)	−2178(7)	76(7)
C(13)	5878(11)	5996(26)	−1865(6)	64(6)
C(14)	8247(16)	5374(38)	−2814(10)	131(12)
C(15)	8324(16)	7483(33)	−3054(10)	130(13)
C(16)	9315(16)	7679(33)	−3397(10)	140(13)
C(17)	9414(17)	9816(36)	−3620(12)	179(16)
C(18)	10412(18)	10062(38)	−3951(12)	182(17)
C(19)	10526(24)	12237(46)	−4145(17)	250(28)
C(20)	11551(31)	12488(58)	−4452(25)	330(40)
C(21)	11621(36)	14654(72)	−4661(27)	475(60)

† Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fourier techniques and refined by blocked-cascade least squares methods. Hydrogen atoms were detected and refined in riding mode (C–H = 0·95 Å, with U_{iso} 20 per cent greater than that of the attached carbon atom). In view of the high thermal vibrations of the carbon atoms of the *n*-octane chain, geometric constraints were imposed to maintain similar bond lengths (σ = 0·01 Å) and bond angles close to 109·5 (σ = 1·3°). The imposition of these constraints had an insignificant effect on R and substantially improved the geometry.

Refinement converged at R = 0·0553 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of platinum and chlorine. Table 5 lists atomic positional parameters with estimated standard deviations. Unit weights were used throughout the refinement; scattering factors were taken from [16]; computer programs were SHELXTL [17] together with others written locally.

5.4.2. $[PdCl_2(5CB)_2]$

$C_{36}H_{38}N_2Cl_2Pd$, M = 676·0, crystallized from acetone/diethylether (containing free 5CB) as pale yellow/orange plates. Triclinic a = 8·311(4) Å, b = 8·588(8) Å, c = 13·431(11) Å. α = 93·63(7)°, β = 96·93(5)° and γ = 116·97(5)°. U = 860·64 $Å^3$; D_c = 1·30 g cm^{-3}, Z = 1. Space group $P\bar{1}$, confirmed by successful refinement. Mo $K(\alpha)$ radiation (graphite monochromator), $\bar{\lambda}$ = 0·71069 Å, μ = 7·29 cm^{-1}.

Three-dimensional X-ray data were collected in the range 3·5° < 2θ < 45° on a Nicolet R3m diffractometer operating in the omega scan mode with a minimum scan speed of 2° min^{-1}. A crystal measuring approximately 0·25 × 0·08 × 0·4 mm was used. Two check reflections were monitored every 100 reflections and showed no significant decay. 1820 independent reflections with $I > 3\sigma(I)$ were obtained and corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ scans of eight reflections (288 measurements) was also applied. The maximum and minimum transmission factors were 0·895 and 0·846 respectively. The structure was solved by Patterson and difference-Fourier methods and refined by cascade-blocked diagonal matrix least squares with weights $w_i = 1/[(\sigma)^2(F_i) + 0{\cdot}00105\,F_i^2]$ to a final R value of 0·0584 (R_w = 0·0551). All the non-hydrogen atoms were refined with independent positional and anisotropic thermal vibration parameters. Hydrogen atoms were inserted at calculated positions and were all constrained to ride on the adjacent heavy atoms with calculated bond lengths and angles. The (isotropic) vibration parameters for the hydrogen atoms were fixed at 1·2 times the U_{eq} values for their respective heavy neighbours. The parameter shifts obtained from the final cycle of refinement were, in all cases, less than 0·1 of the corresponding e.s.d.s. A final difference Fourier synthesis showed no peaks higher than 0·4 e Å^{-3} and none which could be interpreted as an atom. The final analysis of variance against $\sin\theta$ and against $|F|$ showed no unusual features; neither did the normal probability plot. The SHELXTL [17] suite of crystallographic programs was used on a NOVA 3 computer throughout. The atomic positions are listed in table 6.

Table 6. Atom coordinates ($\times 10^4$) and temperature factors (Å^2 $\times$ 10^3) for [$PdCl_2(5CB)_2$].

Atom	x	y	z	U_{eq}†
Pd(1)	0	0	5000	52(1)
Cl(1)	−1075(3)	−2347(3)	5876(2)	86(1)
N(1)	−2519(9)	−603(7)	4430(4)	69(3)
C(1)	−3996(12)	−991(10)	4120(5)	66(4)
C(2)	−5879(10)	−1554(10)	3763(5)	65(4)
C(3)	−7190(11)	−3088(10)	4031(6)	71(4)
C(4)	−8992(11)	−3656(9)	3675(5)	72(4)
C(5)	−9584(10)	−2727(9)	3042(5)	60(4)
C(6)	−8241(11)	−1161(10)	2816(5)	72(4)
C(7)	−6420(11)	−577(10)	3159(6)	75(4)
C(8)	−11541(10)	−3377(9)	2644(5)	63(4)
C(9)	−12920(11)	−4499(11)	3121(6)	86(5)
C(10)	−14740(12)	−5073(11)	2735(7)	91(5)
C(11)	−15271(12)	−4607(13)	1849(7)	91(5)
C(12)	−13912(13)	−3504(14)	1374(7)	110(6)
C(13)	−12104(12)	−2899(12)	1759(6)	96(5)
C(14)	−17281(13)	−5190(15)	1418(8)	122(7)
C(15)	−18391(14)	−7069(18)	1191(8)	143(8)
C(16)	−20423(18)	−7758(23)	676(10)	194(12)
C(17)	−21567(22)	−7627(28)	1287(13)	276(16)
C(18)	−23345(26)	−8336(24)	965(15)	291(18)

† Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Supplementary material available: anisotropic thermal vibrational parameters with estimated standard deviations, predicted hydrogen atom positional parameters, observed structure amplitudes and calculated structure factors.

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