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PLATINUM GROUP METAL SCHIFF BASE COMPLEXES—I. PLATINUM COMPLEXES

TALAL A. K. AL-ALLAF* and ABEER Z. M. SHEET

Chemistry Department, College of Science, University of Mosul, Mosul, Iraq

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Abstract—Schiff base ligands (L), prepared from benzaldehyde, salicylaldehyde and 2- or 3-aminopyridines or 3-aminoquinoline, have been isolated and reacted with K_2PtCl_4, *cis*-[Pt(DMSO)$_2$Cl$_2$], [Pt(COD)Cl$_2$] and [PtL′Cl$_2$]$_2$ (L′ = C_2H_4, PEt$_3$, PPh$_3$ PMe$_2$Ph) in different molar ratios, to yield complexes of general formula [PtLCl$_2$]$_n$ (n = 1 or 2) and *cis*- or *trans*-[PtLL′Cl$_2$]. The Schiff bases and their platinum complexes have been characterized physicochemically.

Platinum complexes containing nitrogenous ligands have received much attention, especially since Rosenberg's discovery[1] that *cis*-[Pt(NH$_3$)$_2$Cl$_2$] (cisplatin) is an effective antineoplastic agent (first generation) for treating tumours. Thus, *cis*-[Pt(NH$_3$)$_2${(OCO)$_2\overline{\mathrm{C{-}CH_2CH_2C}}\mathrm{H_2}$}] (carboplatin) and *cis*-[Pt(Pr^{i}NH$_2$)$_2$(OH)$_2$Cl$_2$] (iproplatin) were prepared (second generation).[2,3] In view of the importance of such complexes and our intrinsic interest in studying the interaction between platinum and various nitrogen ligands, and the biological activity of such complexes,[4–7] we now describe the reaction of a wide range of Schiff bases (L) (rarely used as ligands to platinum[8,9]) derived from benzaldehyde or salicylaldehyde and 2- or 3-aminopyridines or 3-aminoquinoline (Scheme 1) and K_2PtCl_4, *cis*-[Pt(DMSO)$_2$Cl$_2$], [Pt(COD)Cl$_2$] (COD = 1,5-cyclopentadiene) and [PtL′Cl$_2$]$_2$ (L′ = C_2H_4, PEt$_3$, PPh$_3$, PMe$_2$Ph). To the best of our knowledge this work is novel.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded in (CD$_3$)$_2$CO at 25°C on a Jeol Datum no. Ex-1 90 MHz instrument.

IR spectra were recorded on a Unicam SP 2000 spectrophotometer in the 200–4000 cm^{-1} range using Nujol mulls and CsI discs.

UV–vis spectra were recorded on a Shimadzu UV–vis spectrophotometer UV-160 for 10^{-3} M solutions of the compounds in DMF at 25°C, using a 1 cm quartz cell.

Elemental analyses were carried out on a CHN Analyser, Type 1106 (Carlo Erba) at the Department of Chemistry, College of Science, University of Mosul, Mosul, Iraq.

Conductivity measurements were made on 10^{-3} M solutions of the complexes at 25°C using a conductivity meter model 4070 (Jenway).

Starting materials

K_2PtCl_4 and $PtCl_2$ were used as supplied by Fluka. *cis*-[Pt(DMSO)$_2$Cl$_2$], [Pt(COD)Cl$_2$] (COD = 1,5-cyclooctadiene), [Pt(C_2H_4)Cl$_2$]$_2$, [Pt(PEt$_3$)Cl$_2$]$_2$, [Pt(PPh$_3$)Cl$_2$]$_2$ and [Pt(PMe$_2$Ph) Cl$_2$]$_2$ were prepared according to literature methods.[10,11]

The Schiff bases (Scheme 1) were prepared by using the following standard method.[12]

The aldehyde derivative (benzaldehyde or salicylaldehyde) (0.01 mol) in MeOH (15 cm^3) was mixed with 2- or 3-aminopyridines or 3-aminoquinoline (0.01 mol) in MeOH (15 cm^3) in 100 cm^3 round bottomed flask, and the mixture was boiled

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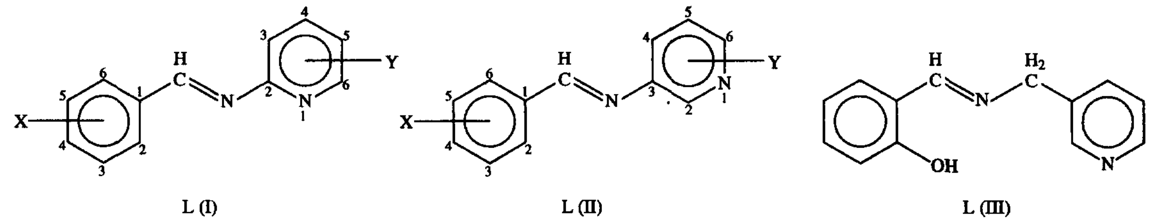
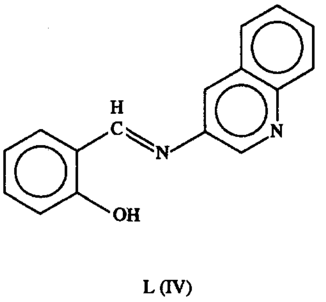
*Author to whom correspondence should be addressed. Present address: The APM Co. Ltd., P.O. Box 42, Sult, Jordan.



I1,	X=2-OH,	Y=H
I2,	$X=2-OCH_3$,	Y=H
I3,	$X=2-OH, 3-OCH_3$,	Y=H
I4,	X=2-OH,	$Y=3-CH_3$
I5,	X=2-OH,	$Y=5-NO_2$
I6,	X=2-Cl,	$Y=4-CH_3$
I7,	X=2-Cl,	$Y=5-NO_2$
I8,	X=2-Cl,	$Y=4,6-(CH_3)_2$
I9,	$X=2-NO_2$,	$Y=4-CH_3$
I10,	$X=2-NO_2$,	$Y=4,6-(CH_3)_2$
I11,	$X=2-SO_3H$,	$Y=4-CH_3$
I12,	$X=2-SO_3H$,	$Y=4,6-(CH_3)_2$
I13,	$X=2-OCH_3$,	$Y=5-NO_2$
I14,	$X=2,4-(OCH_3)_2$,	$Y=5-NO_2$
I15,	$X=3,4-(OH)_2$,	$Y=5-NO_2$
I16,	X=4-OH,	$Y=5-NO_2$

II1,	X=2-OH,	Y=H
II2,	X=2-OH,	Y=2-Cl
II3,	$X=2-OCH_3$,	Y=2-Cl
II4,	X=4-OH,	Y=2-Cl
II5,	X=4-Cl,	Y=H
II6,	$X=3,4(OH)_2$,	Y=2-Cl
II7,	$X=3,4(OCH_3)_2$,	Y=2-Cl



Scheme 1. The Schiff bases used in the complexation with platinum.

under reflux for *ca* 1 h. It was allowed to cool to room temperature and on further cooling (ice bath), the resulting precipitate was removed by filtration, washed separately with H_2O then recrystallized from MeOH. In some cases, the Schiff base was obtained as an oil. It was then treated with petroleum spirit (40–60°C) in an ice bath with continuous stirring until the oil solidified.

Preparation of complexes

Direct reactions giving $[PtLCl_2]_n$. A solution of K_2PtCl_4 (0.5 mmol) in distilled H_2O (5 cm^3) was added to a solution of the Schiff base (L) (0.5 mmol) in EtOH (5 cm^3), and an immediate precipitate formed. The mixture was stirred for several hours to ensure complete reaction. In some cases, precipitation occurs slowly and stirring overnight is necessary. The solid was then filtered off, washed several times with small portions of H_2O, cold EtOH and then with n-hexane and dried *in vacuo* for several hours.

Ligand displacement reactions giving $[PtLL'Cl_2]$: *from* cis-$[Pt(DMSO)_2Cl_2]$ (1 : 1 *molar ratio*). *Cis*-$[Pt(DMSO)_2Cl_2]$ (0.5 mmol) was suspended in $CHCl_3$ (15 cm^3) and to this was added a solution of the Schiff base (L) (0.5 mmol) in $CHCl_3$ (15 cm^3). The reaction mixture was heated to the boiling point of $CHCl_3$ under stirring for *ca* 30 min. The solution became clear, it was filtered through celite while it was hot and $CHCl_3$ was evaporated to a minimal volume, then ether was added to the point of turbidity. The solid thus formed was filtered off, washed several times with ether and dried *in vacuo* for several hours, yielding *cis*-$[PtL(DMSO)Cl_2]$.

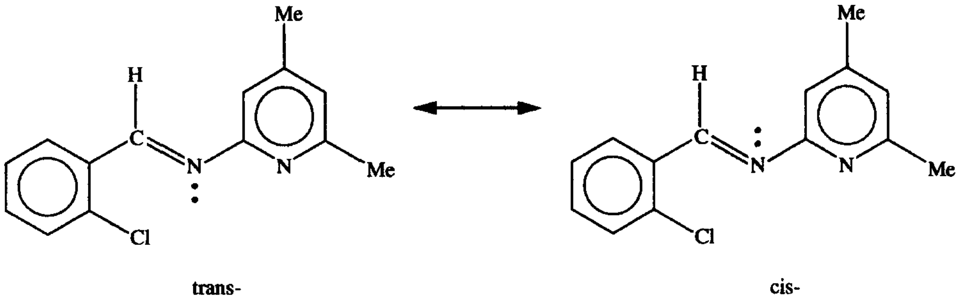
From cis-$[Pt(DMSO)_2Cl_2]$ (1 : 2 *molar ratio*). This type of reaction was carried out in a similar manner to those for 1 : 1 molar ratio but using a 1 : 2 molar ratio of *cis*-$[Pt(DMSO)_2Cl_2]$ to Schiff base respectively, leading to *cis*-$[PtLL'Cl_2]$ (L = L′).

From $[Pt(COD)Cl_2]$. $[Pt(COD)Cl_2]$ (0.5 mmol) was suspended in $CHCl_3$ (10 cm^3) and to this was added a solution of the Schiff base (L) (0.5 mmol) in $CHCl_3$ (10 cm^3). The reaction mixture was heated to the boiling point of $CHCl_3$ under stirring for *ca* 30 min; no odour of COD was detected. The mixture was filtered through celite while hot and $CHCl_3$ was evaporated to leave a minimal volume. Ether was then added until turbidity. The solid thus formed was filtered off, washed several times with ether and dried *in vacuo* for several hours, giving *cis*-$[PtL(COD)Cl_2]$.

Bridge-cleavage reactions giving trans-$[PtLL'Cl_2]$. The $[PtCl_2L']_2$ bridged complex (0.16 mmol) was dissolved in acetone (10 cm^3) and to this was added a solution of the Schiff base (L) (0.32 mmol) in acetone (10 cm^3). The reaction mixture was heated under reflux for *ca* 15 min, then filtered through celite. The filtrate was reduced in volume to *ca* 5 cm^3 and petroleum spirit (40–60°C) was added to the point of turbidity and the sample was left in a cold place overnight. The crystals formed were filtered off, washed several times with petroleum spirit and dried *in vacuo* for several hours, yielding *trans*-$[PtLL'Cl_2]$ (L = C_2H_4, PEt_3, PPh_3, PMe_2Ph).

RESULTS AND DISCUSSION

Physical data for the Schiff bases (**II-16, III-7, III, IV**) (Scheme 1) are listed in Table 1. The ^{1}H NMR spectra data for selected bases (**I8, 13, 14, III, 5, III, IV**) are given in Table 2. In one case (**I8**), the spectrum revealed the presence of signals related to *trans* (76%) and *cis* (24%) isomers. Thus, the *trans* isomer predominates in solution.



trans- cis-

The N-imine (central azomethine) and N-pyridine sites in the Schiff bases are coordinated with platinum metal ion either in bidentate fashion via both sites or monodentate via one site.

The physical properties of the complexes prepared from K_2PtCl_4, *cis*-[Pt(DMSO)$_2$Cl$_2$], [Pt(COD)Cl$_2$] and [PtL′Cl$_2$]$_2$ (L′ = C_2H_4, PEt$_3$, PPh$_3$, PMe$_2$Ph) with Schiff bases (L) are listed in Table 3; ^{1}H NMR data for selected complexes (most of them are poorly soluble) are listed in Table 2.

Direct reactions

The reaction between K_2PtCl_4 with Schiff bases (Scheme 1) in 1 : 1 molar ratio tentatively gave two types of complexes, type A and type B (Scheme 2). The Schiff base in type A coordinated as a bidentate ligand, giving four-membered ring complexes, while in type B, the Schiff base coordinated as a monodentate ligand via the most active site, either the N-imine (type B$_{im}$) or the N-pyridine (type B$_{py}$). These results were confirmed by CHN elemental analyses and by IR spectroscopy (Table 3). The IR spectra of the complexes obtained were compared with those of the free Schiff bases. A new band which appeared in the 492–568 cm^{-1} or 247–313 cm^{-1} regions is tentatively attributed to ν(Pt—N) mode for N-imine or N-pyridine, respectively.[6] The ν(C=N)$_{\mathrm{im\ or\ py}}$ of the free Schiff base is perturbed upon coordination; it either decreases or increases.[13-16] The ν(C=N) values together with ν(Pt—Cl) values are good tools to distinguish between structure types A or B (B$_{im}$ and B$_{py}$), since in types A, the *cis*-Cl$_2$ species gave two clear ν(Pt—Cl) bands at *ca* 310 and 340 cm^{-1},[5,6,17] whereas in type B, the bridged chlorine species also gave two ν(Pt—Cl) values, but the terminal one is at *ca* 330 cm^{-1} and the bridged one is at *ca* 280 cm^{-1} (much less intense than the terminal one).[9,10]

Ligand displacement reactions

The reaction of *cis*-[Pt(DMSO)$_2$Cl$_2$] and [Pt(η^4-COD)Cl$_2$] with Schiff bases (L) in 1 : 1 molar ratio lead to complexes of the general formulae *cis*-[PtL(DMSO)Cl$_2$] and *cis*-[PtL(η^2-COD)Cl$_2$], in which the Schiff base again seems likely to coordinate via the N-imine or N-pyridine site, type C (C$_{im}$ or C$_{py}$) complexes (Scheme 2). This fact was confirmed by the C=N, Pt—N and Pt—Cl stretching frequencies. It seems that complete displacement of 2DMSO or COD by one mole of the ligand did not occur. The presence of the remaining DMSO molecule was confirmed by the ν(Pt—S) and ν(S=O) modes which appeared in the 418–453 and 1155–1177 cm^{-1} regions respectively (sulphur-bonded sulphoxide).[6] Further confirmation was provided by the ^{1}H NMR spectrum of *cis*-[PtL(DMSO)Cl$_2$] (Table 2), which exhibits a methyl resonance at $\delta \cong 3.3$ ppm with $^3J(^{195}\mathrm{Pt{-}S{-}CH}) = 21$ Hz related to coordinated DMSO. The resonance of the organic residue (L) remains almost constant upon coordination, apart from the CH=N resonance, which is shifted downfield by *ca* 1.5 ppm and is assigned to N-imine coordination (*cf* e.g. ligands **III** and **III** with their *cis*-[PtL(DMSO)Cl$_2$] complexes) (Table 2).

Similar behaviour was observed with the complexes *cis*-[PtL(η^2-COD)Cl$_2$], in which COD coordinated more likely as a monodentate ligand with

Table 1. Physical properties of the Schiff bases L **I1-16**, **II1-7**, **III**, **IV** (Scheme 1)

L	Yield (%)	M.p. (°C)	Colour	Found (Calc.) %			Selected IR[a] bands (cm^{-1})				UV–vis
				C	H	N	ν(C=N)$_{py}$	ν(C=N)$_{im}$	ν(C=C)	ν(OH)	λ_{max} (nm)
I1	89	67–69	yellow	72.0 (72.7)	4.9 (5.1)	13.8 (14.1)	1569 m	1623 s	1600 m	3425 b	267,385
I2	80	136–140	white	72.9 (73.6)	5.1 (5.7)	13.1 (13.2)	1578 s	1636 s	1614 m,sh		275
I3	85	96–98	yellow	68.3 (68.4)	5.1 (5.3)	12.2 (12.3)	1575 m	1619 m	1595 m	3401	277.5,370
I4	90	87–89	yellow	73.2 (73.6)	5.1 (5.7)	12.9 (13.2)	1578 s, sh	1620 s	1600 m	3066	295,329
I5	79	156–160	orange	59.0 (59.3)	3.9 (3.7)	17.1 (17.3)	1587 s	1659 s,sh	1600 s	3410	282,380
I6	83	90–94	white	66.1 (67.7)	4.9 (4.8)	12.0 (12.1)	1590 s	1632 s	obscured		290,331
I7	90	158–160	brown	54.8 (55.1)	3.1 (3.1)	16.0 (16.1)	1591 m	1650 m,sh	1605 m		276,385.5
I8	80	130–132	off-white	68.0 (68.7)	5.4 (5.3)	11.2 (11.5)	1585 s	1625 s	1608 s		313,355
I9	75	92–96	off-white	64.5 (64.7)	4.4 (4.6)	17.2 (17.4)	1582 m	1627 s	1602 m		282
I10	81	82–84	yellow	66.0 (65.9)	5.2 (5.1)	16.2 (16.5)	1596 s	1640 s	1596 s		292
I11	76	118–120	white	55.9 (56.5)	4.6 (4.4)	9.8 (10.1)	1596 m	1660 s	1614 s	3200	238,291
I12	80	148–150	pale yellow	58.1 (57.9)	5.0 (4.8)	9.4 (9.7)	1600 w	1650 m	1623 s	3205	282
I13	95	166–168	yellow	60.0 (60.7)	4.4 (4.3)	15.9 (16.3)	1578 s	1632 s,sh	1590 s		309,389
I14	93	165–168	yellow	58.7 (58.5)	4.7 (4.5)	14.2 (14.6)	1591 s,sh	1654 s,sh	1623 s,sh		312,391
I15	71	116–120	grey	54.9 (55.6)	3.7 (3.5)	15.3 (16.2)	1591 m	1659 s	1614 s	3289	314,375
I16	83	89–102	yellow	59.0 (59.3)	4.0 (3.7)	16.8 (17.3)	1591 m	1650 m	1610 m	3207	314,385
II1	85	68–70	orange	72.1 (72.7)	4.9 (5.1)	14.1 (14.1)	1583 m, sh	1641 s	1596 s	3333	305,333

II2	73	60–62	brown	61.0 (61.9)	4.0 (3.9)	11.8 (12.0)	1569 m	1629 s	1592 s	3403	378
II3	79	52–56	off-white	62.8 (63.3)	4.7 (4.5)	11.2 (11.4)	1591 m	1628 m	1600 m		337
II4	83	186–188	grey	61.7 (61.9)	4.0 (3.9)	11.9 (12.0)	1578 s,sh	1620 s,sh	1592 s	3156	358
II5	76	72–74	off-white	65.8 (66.5)	4.3 (4.2)	13.1 (12.9)	1581 s	1632 s	1605 s		237,311
II6	86	192–194	brown	57.0 (57.9)	4.0 (3.6)	10.9 (11.3)	1587 s,sh	1636 s	1609 s	3167	273
II7	81	110–112	off-white	61.2 (60.8)	5.2 (4.7)	10.0 (10.1)	1569 m	1620 s	1587 m		335
III	95	50–54	yellow	73.3 (73.6)	5.4 (5.7)	13.0 (13.2)	1587 m	1632 m	1618 m,sh	3464	277,389
IV	80	198–199	yellow	77.1 (77.4)	4.4 (4.8)	11.0 (11.3)	1587 m	1636 m	1587 m	3495	278,370.5

[a] In Nujol mulls.

Table 2. ^{1}H NMR data[a] for selected Schiff bases and selected complexes

Compound	δ (ppm), *J* values and assignments[b]
I8	*trans* (76% proportion): 2.2 (d, 2CH$_3$), 6.3 (s, Ph), 7.2–7.4 (m, py), 9.7 (s, CH=N) *cis* (24% proportion): 2.4 (d, 2CH$_3$), 7.0 (s, Ph), 7.5–7.9 (m, py), 11.0 (s, CH=N)
I13	4.0 (s, OCH$_3$), 6.5–7.2 (m, Ph), 7.9–8.1 (m, py), 8.7 (s, CH=N)
I14	3.85 (s, CH$_3$CO), 4.0 (s, OCH$_3$), 6.5–7.6 (m, Ph), 7.7–8.9 (m, py), 10.25 (s, CH=N)
II1	6.8–7.9 (m, Ph), 8.4–8.6 (m, py), 8.9 (s, CH=N), 12.75 (s, OH)
II5	7.55 (d), 7.9 (*d*, *J* = 10 Hz, Ph), 8.4–8.6 (m, py), 8.7 (s, CH=N)
III	4.85 (s, CH$_2$), 6.6–8.7 (m, Ph and py), 8.75 (s, CH=N)
IV	6.8–9.05 (m, Ph and quin), 9.2 (s, CH=N), 12.9 (s, OH)
cis-[PtL(DMSO)Cl$_2$]	
L = **I1**	3.45 (s, $^3J(^{195}$Pt–S–CH) = 21.1 Hz, DMSO), 6.5–7.9 (m, Ph and py), 9.05 (s, CH=N)
L = **I10**	2.75 (s, CH$_3$), 2.9 (s, CH$_3$), 3.4 (s, $^3J(^{195}$Pt–S–CH) = 20.7 Hz, DMSO), 6.2–8.2 (m, Ph and py), 10.4 (s, CH=N)
L = **II1**	3.3 (s, $^3J(^{195}$Pt–S–CH) = 21.0 Hz, DMSO), 6.7–9.4 (m, Ph and py), 10.7 (s, CH=N), 12.0 (s, OH)
L = **II5**	3.5 (s, $^3J(^{195}$Pt–S–CH) = 25.3 Hz, DMSO), 7.0–9.1 (m, Ph and py), 10.1 (s, CH=N)
L = **III**	3.3 (s, $^3J(^{195}$Pt–S–CH) = 22.3 Hz, DMSO), 4.93 (s, CH$_2$), 6.5–9.2 (m, Ph and py), 10.2 (s, CH=N)
trans-[PtL(C$_2$H$_4$)Cl$_2$]	
L = **I4**	2.4 (s, CH$_3$), 4.25 (s, $^2J(^{195}$Pt–CH) = 65 Hz, C$_2$H$_4$), 6.8–8.3 (m, Ph and py), 9.4 (s, CH=N)
L = **I13**	4.3 (s, OCH$_3$), 4.3 (s, $^2J(^{195}$Pt–CH) = 66 Hz, C$_2$H$_4$), 7.2–8.85 (m, Ph and py), 9.2 (s, CH=N)
L = **II5**	4.3 (s, $^2J(^{195}$Pt–CH) = 65.5 Hz, C$_2$H$_4$), 7.6–8.6 (m, Ph and py), 9.3 (s, CH=N)
trans-[PtL(PMe$_2$Ph)Cl$_2$]	
L = **II1**	1.6 (d, CH$_3$), 1.8 (d, CH$_3$, *J* = 5.6 Hz), 6.7–8.4 (m, Ph and py), 9.0 (s, CH=N), 10.25 (s, OH)

[a] Downfield from internal TMS, using acetone-d_6 as a solvent.

[b] Multiplicities in parentheses.

Table 3. The properties of platinum complexes of the Schiff bases

Complex	Structural assignment[a]	Colour	M.p. (°C) (Dec.)	Found (Calc.) % C	H	N	Selected IR[b] bands (cm^{-1}) $\nu(C{=}N)_{py}$ (Δ)	$\nu(C{=}N)_{im}$ (Δ)	ν(Pt—Cl)	ν(Pt—N)	ν(others)	UV–vis λ_{max} (nm)	Conductivity Λ (Ω^1 cm^2 mol^{-1}) DMF	MeNO$_2$
[PtLCl$_2$]$_n$														
L = **I3**, $n = 2$	B$_{im}$	yellow–brown	248–250	30.9 (31.6)	2.5 (2.4)	5.5 (5.7)	1573m (−2)	1616s (−3)	299w, 330w	540w		380	25	12
L = **I6**, $n = 2$	B$_{im}$	deep yellow	216–218	31.3 (31.4)	2.4 (2.2)	5.4 (5.6)	1585m (−5)	1632m (0)	288m, 310m	506m		237, 300	16	12
L = **I8**, $n = 1$	A	deep yellow	180–182	33.1 (32.9)	2.7 (2.5)	5.3 (5.6)	1578s (−7)	1641s (+16)	288m, 308m	526m, 261w		325, 420	39	35
L = **I10**, $n = 2$	B$_{py}$	light brown	284–286	32.0 (32.2)	2.7 (2.5)	7.9 (8.1)	1578m (−18)	1632s (−8)	288w, 312m, sh	254w		306, 428	10	5
L = **I11**, $n = 1$	A	yellow	276–278	29.1 (28.8)	2.3 (2.2)	5.4 (5.2)	1564m (−32)	1690s (+30)	285m, 305m	492w, 268w		237, 290	48	10
L = **I13**, $n = 2$	B$_{im}$	yellow	200–204	30.0 (29.8)	2.2 (2.1)	7.9 (8.0)	1580m (+2)	1650s,sh (+18)	291w, 319m	568w		308, 388, 444	22	19
L = **I14**, $n = 2$	B$_{im}$	yellow–brown	120–122	28.9 (30.4)	2.4 (2.4)	7.3 (7.6)	1591s (0)	1650s (−4.5)	295w, 323m	553w		313, 389, 433	16	7
L = **II1**, $n = 2$	B$_{im}$	yellow	262–264	30.8 (31.0)	2.3 (2.2)	5.8 (6.0)	1587w (+4)	1620s (−21)	288w, 322w	547w		236, 293	40	22
L = **II4**, $n = 1$	A	yellow–brown	264–268	29.0 (28.9)	2.0 (1.8)	5.5 (5.6)	1590s (+12)	1600s (−20)	308m, 342s	528w, 252w		208	10	6
L = **II5**, $n = 2$	B$_{py}$	off-white	136–140	30.0 (29.8)	2.0 (1.9)	5.7 (5.8)	1596s (+15)	1632m (0)	288w, 322m	265w		234, 301	40 22	
L = **II6**, $n = 2$	B$_{im}$	brown	288–290	28.1 (28.0)	2.0 (1.8)	5.2 (5.4)	1590s,sh (+3)	1632s (−4)	302w, 326m	496w		327, 412	11	6
cis-[PtLL′Cl$_2$]														
L = **I1**, L′ = DMSO	C$_{im}$	yellow	170–174	30.8 (31.0)	2.7 (3.0)	4.9 (5.2)	1573s (+4)	1618s (−5)	293w, 310w,	524w	449s, 1155m	297, 381	21	3
L = **I10**, L′ = DMSO	C$_{py}$	yellow–brown	140–144	32.0 (32.1)	3.0 (3.2)	7.0 (7.0)	1578m (−18)	1641s (+1)	308m, 331m,sh	274m	453s, 1168s	274	14	5

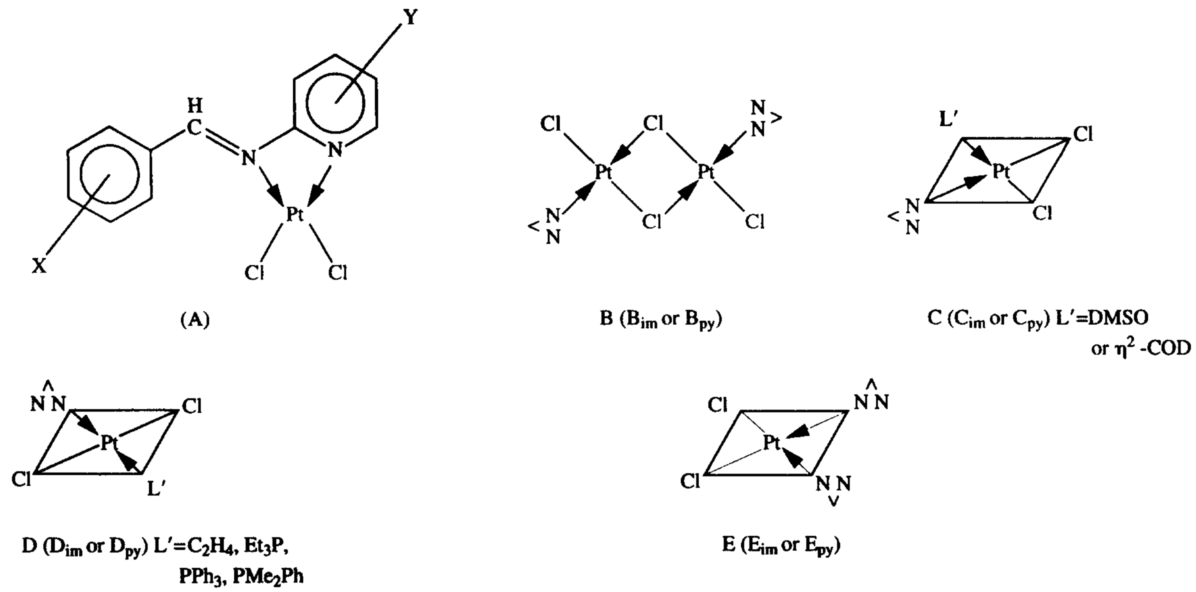
L = **I13**, L′ = DMSO	C_{im}	pale yellow	200–204	29.0 (30.0)	3.0 (2.8)	7.1 (7.0)	1585s (+7)	1652s (+20)	301s, 326s	516m	453s, 1170s	250, 277	13	3
L = **II5**, L′ = DMSO	C_{im}	yellow	67–80	30.1 (30.0)	2.7 (2.7)	5.2 (5.0)	1578m (−3)	1677m (+45)	302w, 330m	502m	427s, 1164m	254, 292	15	4
L = **III**, L′ = DMSO	C_{im}	yellow	100–104	31.1 (32.4)	3.2 (3.2)	4.8 (5.0)	1591s (+4)	1641s (+9)	303w, 336w	547w	418s, 1177s	302	17	5
L = **I6**, L′ = COD	C_{im}	white	128–130	41.2 (41.7)	3.1 (3.8)	4.9 (4.6)	1578m (−12)	1661s (+29)	308s, 320m	553w	451w	255, 301	16	9
L = **II4**, L′ = COD	C_{py}	off-white	180–184	39.3 (39.6)	3.6 (3.5)	4.1 (4.6)	1583m (+5)	1624m (+4)	303s, 316m	248m	442w	295, 360	11	5
L = **III**, L′ = COD	C_{py}	yellow	142–144	42.9 (43.0)	3.9 (4.1)	4.1 (4.8)	1592w (+5)	1636m (+4)	305s, 312m	248m	441w	253, 301	26	2
L = **IV**, L′ = COD	C_{py}	yellow	180–182	45.9 (46.3)	3.5 (3.9)	4.8 (4.5)	1584m (−3)	1635s (−1.5)	308s, 317s	247m	439w	236, 384	10	6
trans-[PtLL′Cl$_2$]														
L = **I4**, L′ = C_2H_4	D_{im}	yellow	80–82	35.4 (35.6)	3.2 (3.2)	5.2 (5.5)	1578s (0)	1663s (+43)	309s	520m,b	444w	247, 289	52	51
L = **II3**, L′ = C_2H_4	D_{im}	yellow	170–172	32.7 (32.7)	2.9 (2.7)	7.4 (7.6)	1578m (0)	1641s (+9)	319s	567m,b	431m	234, 345	72	59
L = **II6**, L′ = C_2H_4	D_{im}	cacao	72–74	30.9 (31.3)	2.8 (2.4)	7.9 (7.8)	1587w (−4.5)	1632w (−18)	315m	543w	431w	251.5, 385	48	45
L = **II5**, L′ = C_2H_4	D_{im}	yellow	120–124	33.0 (32.9)	2.6 (2.5)	5.2 (5.5)	1565w (−16)	1641s (+9)	333s	537w	442w	245, 294	53	50
L = **III**, L′ = C_2H_4	D_{im}	yellow	140–144	35.2 (35.6)	3.0 (3.2)	5.7 (5.5)	1587m (0)	1632m (0)	313m	547w	431m	246, 295	60	54
L = **I4**, L′ = Et_3P	D_{py}	off-white	128–130	38.0 (38.3)	4.9 (4.5)	4.6 (4.7)	1582s (+4)	1628s (+8)	319s	251w	455w	261, 381	7	3
L = **I8**, L′ = Et_3P	D_{py}	off-white	144–148	37.9 (38.2)	4.8 (4.5)	4.4 (4.5)	1587m (+2)	1641s (+16)	302w	248w	458w	261, 316	11	8
L = **II3**, L′ = Et_3P	D_{py}	yellow	108–110	35.5 (35.6)	3.9 (4.1)	6.2 (6.6)	1587w (+9)	1641s (+9)	319m	250w	455m	244, 289, 393	4	1
L = **I13**, L′ = PPh_3	D_{py}	yellow	138–140	47.0 (47.4)	3.4 (3.3)	5.2 (5.4)	1586s (+8)	1641s (+9)	325w	290w	454m	286, 382	4	1
L = **I14**, L′ = PPh_3	D_{im}	yellow	82–86	47.0 (47.1)	3.5 (3.4)	5.2 (5.2)	1592s (+0.5)	1674s (+19.5)	314w	535w	482m	224, 396	21	5
L = **II6**, L′ = PPh_3	D_{im}	brown	90–92	46.3 (46.4)	3.2 (3.1)	3.5 (3.6)	1593m (+6)	1655m (+19)	306w	517m,b	462w	300	20	4

Table 3—*continued*

Complex	Structural assignment[a]	Colour	M.p. (°C) (Dec.)	Found (Calc.) %			Selected IR[b] bands (cm^{-1})					UV–vis λ_{max} (nm)	Conductivity Λ (Ω^1 cm^2 mol^{-1})	
				C	H	N	$\nu(C{=}N)_{py}$ (Δ)	$\nu(C{=}N)_{im}$ (Δ)	ν(Pt—Cl)	ν(Pt—N)	ν(others)		DMF	MeNO$_2$
L = **I5**, L′ = Me$_2$PhP	D_{py}	yellow	130–134	36.9 (37.1)	3.2 (3.1)	6.4 (6.5)	1582s (−5)	1642s (−17)	302m,sh	288m	472m	261, 387	17	10
L = **III**, L′ = Me$_2$PhP	D_{py}	yellow– brown	110–112	39.0 (39.9)	3.6 (3.5)	4.6 (4.7)	1587s (+4)	1632s (−9)	327m	303w	472m	256, 271, 366	13	3
L = **II3**, L′ = Me$_2$PhP	D_{py}	light brown	88–90	39.0 (38.7)	3.9 (3.4)	4.2 (4.3)	1579m (−12.5)	1629s (+1)	323w	313w	439m	304	4	2
cis-[PtLL′Cl$_2$]														
L = L′ = **II1**	E_{im}	pale brown	92–94	44.0 (43.5)	3.5 (3.0)	8.8 (8.5)	1582s (−1)	1632s (−9)	288w, 310w	549m		301, 377	14	9
L = L′ = **II5**	E_{py}	pale yellow	230–234	41.1 (41.2)	2.9 (2.6)	8.1 (8.0)	1596s (+14)	1632s (0)	295w, 302w	247m, 275m		344	17	8

[a] The symbol im represents coordination via the imine site and the symbol py represents coordination via the pyridine site.

[b] In Nujol mulls, ν(others) ; L′ = DMSO, 418–453 cm^{-1} for ν(Pt—S), 1155–1177 cm^{-1} for ν(S=O) ; L′ = COD or C$_2$H$_4$, 431–451 cm^{-1} for ν(HC=CH) ; L′ = PEt$_3$, PPh$_3$ or PMe$_2$Ph, 439–482 cm^{-1} for ν(Pt—P).



(A)

B (B_{im} or B_{py})

C (C_{im} or C_{py}) L'=DMSO or η^2-COD

D (D_{im} or D_{py}) L'=C_2H_4, Et_3P, PPh_3, PMe_2Ph

E (E_{im} or E_{py})

Scheme 2. The suggested structures for the Schiff base/platinum complexes.

platinum and was not totally removed from the coordination sphere. The characteristic odour of COD was not detected from the reaction mixture. Additional confirmation is that a band appeared in the 441–451 cm^{-1} region characteristic of the ν(HC═CH) mode.

In the 1 : 2 molar ratio reaction between *cis*-$[Pt(DMSO)_2Cl_2]$ and Schiff bases (L), the complexes obtained were assigned to the formula *cis*-$[PtL_2Cl_2]$, complex type E (Scheme 2), and no sign of DMSO could be detected by IR spectroscopy.

Bridge-cleavage reactions

These were carried out using the bridge starting complex $[PtL'Cl_2]_2$ (L' = C_2H_4, PEt_3, PPh_3, PMe_2Ph) with Schiff bases (L) in 1 : 2 molar ratio, respectively. The complexes obtained were assigned the general formula *trans*-[PtLL'Cl_2] (type D complexes) and were identified by their CHN elemental analyses, IR and ^{1}H NMR spectra. The ν(Pt—Cl) mode for *trans*-Cl_2 species is well identified by the single band[4,18] in the 310–330 cm^{-1} region for all the complexes obtained (Table 3). The Schiff bases again coordinated via either the N-imine or the N-pyridine and this was confirmed by the significant change in the ν(C═N) values (see below). The ^{1}H NMR of *trans*-$[PtL(C_2H_4)Cl_2]$ (L = **I4, II3, II5**) showed a single resonance at *ca* 4.3 ppm with $^2J(^{195}Pt\text{–}CH) \cong 65$ Hz assignable to coordinated C_2H_4.[4,18] The resonance of the residual organic species (L) was also observed and its significance is that the δ (CH═N) value was shifted downfield by *ca* 0.5 ppm (Table 2) upon coordination. This gave further support to what the IR suggested; namely that the coordination of the N-imine site of the Schiff base had certainly taken place. Additional support for our argument is that the δ (CH═N) value for the free base (**III**) (8.9 ppm) remains almost constant upon coordination in the complex *trans*-$[PtL(PMe_2PH)Cl_2]$ (9.0 ppm) assigning N-pyridine coordination and this is in good agreement with that found by IR spectroscopy, Δ $[\nu(C{=}N)_{py}] = 12.5$ cm^{-1} and Δ $[\nu(C{=}N)_{im}] = 1$ cm^{-1}.

The UV–vis spectra of 10^{-3} M solutions of the complexes showed bands at ~250 and ~370 nm (Table 3) due to the Schiff base, plus a band which appeared, in some cases, at ~400 nm attributed to the *d–d* transitions of platinum.

With few exceptions, the molar conductivities of 10^{-3} M solutions of almost all the complexes $[PtLCl_2]_n$ (n = 1 or 2), *cis*-[PtLL'Cl_2] (L' = DMSO, η^2-COD, L) and *trans*-[PtLL'Cl_2] (L' = PEt_3, PPh_3, PMe_2Ph) indicate that they are non-electrolytes in both $MeNO_2$ and DMF (Table 3). On the contrary, all the complexes *trans*-$[PtL(C_2H_4)Cl_2]$ (L = **14, II3, II6, II5, III**) gave results consistent with some 1:1 electrolytes in both solvents. This may be described on the basis of ligand replacement; C_2H_4 is a labile ligand which can easily be replaced by donor solvents and may give the ionic species $[PtL(solv.)_2Cl]^+Cl^-$.

In one experiment, the complex $[PtLCl_2]_n$ (L = **II5**), with molar conductivity in DMF of 40 Ω^{-1} mol^{-1} cm^2, was left in solution for 24 h; the conductivity increased to 84 Ω^{-1} mol^{-1} cm^2, which is clearly assigned to 1:1 conductivity[19] and this may similarly be described as solvent interaction to give $[PtL(solv.)_2Cl]^+Cl^-$ species.

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