Studies on palladium(II) complexes containing multidentate *N*-heterocycles

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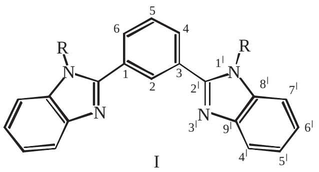
Palladium dihalides/perchlorate react with the multidentate *N*-heterocycles (I), 1,3-bis(benzimidazol-2-yl)benzene (L^1) 1,3-bis(1-methylbenzimidazol-2-yl)benzene (L^2), 2,6-bis(benzimidazol-2-yl)pyridine (L^3) and 2,6-bis(1-methylbenzimidazol-2-yl) pyridine (L^4) in ethanol/tetrahydrofuran in presence of hydrohalic acid to yield complexes of the compositions, $[PdX_2L{\cdot}nH_2O]$ (X = Cl, L = L^1 or L^2, $n = 1$; X = Cl, L = L^3 or L^4, $n = 0$; X = Br, L = L^1 or L^3 $n = 0$; X = Br, L = L^2, $n = 3$; X = Br, L = L^4, $n = 2$), $PdL_2(ClO_4)_2{\cdot}nH_2O$ (L = L^1, $n = 2$; L = L^2, $n = 1$) and $[Pd_2L_3(ClO_4)_4{\cdot}nH_2O]$ (L = L^3, $n = 2$; L = L^4, $n = 0$). The complexes were characterised by elemental analysis, molar conductance measurements, IR, electronic, ^1H, ^{13}C NMR and FAB-mass spectral studies.

Keywords: palladium complexes, *N*-heterocycles, NMR and FAB-mass spectra

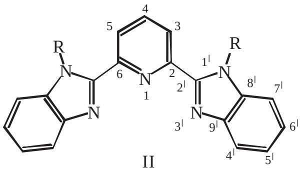
A variety of complexes of transition and post-transition metal ions containing multidentate bis-benzimidazole derivatives have been investigated. Investigations on Pd(II) complexes containing multidentate bis-benzimidazole derivatives have been scanty. Jutzi and Heusler have synthesised dichlorobis (1-methylbenzimidazol-2-yl)methylsilane palladium(II) complex.[1] Uson and collaborators have isolated a few mono and homo/hetero bi- and polynuclear palladium complexes containing the bibenzimidazolate dianion.[2] Williams and coworkers have reported the synthesis and X-ray crystal structure of a trinuclear cyclometallated palladium complex, $[Pd_3(L^2)_3(OAc)_3]{\cdot}9CH_3CN$ with a hydrophobic cavity.[3] Recently, we have reported the synthesis and characterisation of organopalladium(II) complexes containing bis-benzimidazole derivatives.[4]

Imidazole, benzimidazole and their derivatives are of considerable importance as they exhibit pharmacological properties. It has been reported that the 2-substituted benzimidazole drug cytostasan, showed considerable antitumor activity.[5] Palladium complexes containing 2-aminomethylbenzimidazole have been used as vehicles of biological alkylating agents and have been investigated for antitumor activity.[6] Palladium complexes containing imidazole and benzimidazole moieties are also known to exhibit catalytic activity. Herein, we report the synthesis and characterisation of halo and perchlorate complexes containing bis-benzimidazole derivatives, L^1 through L^4 (I and II).



I

L^1, L^2



II

L^3, L^4

	R	Compound
L^1	H	1,3-bis(benzimidazol-2-yl)benzene
L^2	CH_3	1,3-bis(1-methylbenzimidazol-2-yl)benzene
L^3	H	2,6-bis(benzimidazol-2-yl)pyridine
L^4	CH_3	2,6-bis(1-methylbenzimidazol-2-yl)pyridine

Experimental

Reagents

The *N*-heterocycles, L^1, L^2, L^3 and L^4 were prepared as per published methods.[7-9] Aqueous $Pd(ClO_4)_2$ was made by dissolving $Pd(OH)_2$ (obtained by treating dilute HCl solution of $PdCl_2$ with Na_2CO_3) in 1:1 $HClO_4$. $PdCl_2$ and $PdBr_2$ were procured from Arora-Matthey Ltd. The solvents used were distilled prior to their use.

Measurements

C, H and N analyses were carried out on a Carlo Erba analyser. IR (in nujol) spectra were recorded on a Shimadzu IR–435 spectrophotometer. Palladium analysis was carried out by atomic absorption spectroscopy using a Spectr AA-30 spectrometer equipped with a Varian DS-15 computer on solutions obtained by digestion of the complexes in concentrated nitric acid or aqua regia (the reading of the blank solution was subtracted from that of the sample concentration followed by the calculation of percentage of metal). The molar conductivity measurements were made using a Elico CM-82T conductivity bridge with a conventional dip-type conductivity cell. Electronic spectra were recorded on a Hitachi 150-20 spectrophotometer. NMR spectra were recorded at ambient temperature in DMSO-d_6 on Bruker WH-270 or AMX 400 MHz spectrometers using TMS as the internal standard. The FAB-mass spectra were recorded at room temperature on a JOEL SX 102/DA-6000 mass spectrometer (using xenon as the FAB gas and *m*-nitrobenzyl alcohol as the matrix).

Preparation of the complexes

$[PdX_2L]nH_2O$ (X = Cl or Br, L = L^1, L^2, L^3 or L^4)

To palladium halide (1 mmol) dissolved in the corresponding hydrohalic acid (0.3 ml), the N-heterocycle (1 mmol) in ethanol (20 ml) was added and the mixture was refluxed for 4 hours during which time coloured solid separated. The solid was filtered, washed with alcohol, ether and water and dried in a vacuum.

$[PdL_2(ClO_4)_2]nH_2O$ (L = L^1 or L^2) and $[Pd_2L_3(ClO_4)_4.]nH_2O$ (L = L^3 or L^4)

To an aqueous solution of palladium perchlorate (1 mmol) was added a solution of the N-heterocycle (2 mmol) dissolved in tetrahydrofuran (30 ml). The resulting mixture was refluxed for 6 hours when a cream, brown or yellow coloured solid separated. The solid was filtered, washed with tetrahydrofuran, ether and water and dried in a vacuum.

Results and discussion

The halide complexes are insoluble in common organic solvents but are soluble in DMF and DMSO, the solutions of which are non-conducting. The perchlorate complexes exhibit uni-bivalent electrolytic behaviour in DMF and CH_3CN (L^1 and L^2 containing complexes) or nitrobenzene (L^3 and L^4 containing complexes).[10] Some physical properties of the complexes together with their analytical data are deposited in Table 1.

The IR spectra (Nujol mull) of the complexes are comparable with those of the un-coordinated N-heterocycles. The complexes of L^1 displayed a ν(NH) band in the range 3180–3250 cm^{-1} and this was lowered by 20–60 cm^{-1} compared to that of the uncoordinated heterocycle. On the other hand, the complexes of L^3 display a ν(NH) band in the range 3200–3375 cm^{-1} and this has increased by 20–195 cm^{-1} relative to that of the uncoordinated heterocycle. The shifts imply the coordination of pyridine nitrogens rather than the pyrrole ones of the benzimidazolyl moieties.[11] The ν(C=N) and ν(C=C) bands have appeared as weak bands at *ca*1630 and 1600 cm^{-1}. Symmetrical deformation of the CH_3 group of N–CH_3 occurs in the range 1405–1420 cm^{-1}. The peaks due to δ(NH) and ν(C–N) are in the range

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Table 1 Physical properties, electronic spectral and analytical data of the complexes

Complex	Colour	Yield/%	Δ M/Ω^{-1} cm^2 mol^{-1}	Electronic spectral data[†]/cm^{-1}	Found/calcd. %			
					Pd	C	H	N
$[PdCl_2L^1]\cdot H_2O$	Yellow	58	11[a]	23,669 (173)	20.6 (21.0)	47.5 (47.5)	3.2 (3.2)	11.0 (11.1)
$[PdBr_2L^1]$	Brownish green	60	12[a]	23,513 (433)	–	40.5 (40.4)	2.6 (2.7)	9.3 (9.4)
$[Pd(L^1)_2](ClO_4)_2\cdot 2H_2O$	Cream	60	116[a] 293[d]	23,747 (63)	–	49.7 (49.9)	3.4 (3.3)	11.3 (11.6)
$[PdCl_2L^2]\cdot H_2O$	Bluish green	59	49[a]	23,480[e]	20.6 (19.9)	49.3 (49.5)	3.6 (3.8)	10.1 (10.5)
$[PdBr_2L^2]\cdot 3H_2O$	Bluish green	58	49[a]	20,547[e]	–	39.7 (40.1)	3.4 (3.6)	8.8 (8.5)
$[Pd(L^2)_2](ClO_4)_2\cdot H_2O$	Brown	56	149[a] 264[d]	23,596[e]	–	52.9 (52.8)	3.9 (3.8)	11.1 (11.2)
$[PdCl_2L^3]$	Yellow	70	26[b]	22,952[e]	22.5 (21.8)	46.4 (46.7)	2.7 (2.7)	14.1 (14.3)
$[PdBr_2L^3]$	Yellow	71	27[b]	23,047[e]	18.9 (18.4)	39.7 (39.8)	2.2 (2.3)	11.7 (12.1)
$[Pd_2(L^3)_3](OClO_3)_2](ClO_4)_2\cdot 2H_2O$	Yellow	55	50[c]	24,667 (1,118)	–	43.1 (43.3)	2.6 (2.7)	13.0 (13.2)
$[PdCl_2L^4]$	Yellow	65	25[a]	23,419 (1,780)	–	47.9 (48.8)	3.7 (3.3)	13.2 (13.5)
$[PdBr_2L^4]\cdot 2H_2O$	Reddish brown	69	66[a]	23,272 (2,406)	18.4 (17.6)	39.0 (39.3)	2.8 (3.3)	11.2 (10.9)
$[Pd_2(L^4)_3(OClO_3)_2](ClO_4)_2$	Yellow	54	60[c] 220[d]	23,480 (888)	–	46.6 (46.4)	3.3 (3.1)	12.8 (12.9)

[a]Molar conductance of ~ 10^{-3} M solutions around 25 °C in DMF; [b]in DMSO; [c]in nitrobenzene; [d]in acetonitrile; [e]spectra recorded in nujol; [†]spectra recorded from DMF solution; Molar extinction coefficients (dm^3 mol^{-1} cml^{-1}) are in parentheses.

1325–1345 cm^{-1}. The perchlorate complexes (L^1 and L^2) show strong bands at *ca.*1100 and 620 cm^{-1} ascribable to ionic perchlorates.[12] In the spectrum of the L^3-containing perchlorate complex, the higher wavenumber band is split (1112 and 1045 cm^{-1}) implying that one of the perchlorates per metal ion is coordinated. The molar conductance data of the perchlorate complex of L^4 indicates the coordination of one perchlorate per metal ion, but the coordination is not easily discernible from its infrared spectrum. It is likely that the band corresponding to the ionic groups has masked the one due to coordinated perchlorates.[13]

Electronic spectra of the complexes recorded in nujol or dimethylformamide solution display absorption bands in the range 23,000–24,700 cm^{-1} (Table 1). The bands may be assigned to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition arising out of four-coordinate square planar stereochemistry.[14-16]

Table 2 ^{1}H NMR spectral data of the *N*-heterocycles and complexes in DMSO-d_6 (δ in p.p.m.)

Compound	Benzene ring/pyridine ring			Benzimidazole ring				
	H–2	H–4, 6	H–5	H–4'	H–5'	H–6'	H–7'	NH/N–CH_3
L^1	9.07 s	8.28d	7.75 t	7.65 s	7.24 m	7.24 m	7.64 s	13.14 bs
$[PdCl_2L^1]\cdot H_2O$	8.64 s (–0.43)	8.55d (0.27)	8.49 s (0.74)	8.29 m (0.65)	7.96 m (0.72)	7.6 m (0.26)	8.05 m (0.41)	14.13 m (1.0)
$[PdBr_2L^1]$	9.69 s (0.62)	9.05dd (0.77)	8.31 m (0.56)	7.97 m (0.33)	7.48 m (0.24)	7.48 m (0.24)	7.73 m (0.09)	14.10 m (1.0)
$[Pd(L^1)_2](ClO_4)_2\bullet H_2O$	9.07 s (0.00)	8.40d (0.12)	8.02 t (0.27)	7.83 m (0.19)	7.51 m (0.27)	7.51 m (0.27)	7.83 m (0.19)	ND
L^2	8.31 s	8. (1.7)	7.80 t	7.73 d	7.30 m	7.30 m	7.65 d	3.96 s
$[PdCl_2L^2]\cdot H_2O$	9.23 s	8.4 m	8.11 m	7.77 m (0.04)	7.41 m (0.11)	7.41 m (0.11)	7.77 m (0.06)	4.0 m (0.04)
$[PdBr_2L^2]\cdot 3H_2O$	9.19 s	8.89 m	8.12 m	7.72 m (0.01)	7.34 m (0.04)	7.34 m (0.04)	7.72 m (0.01)	4.01 s (0.05)
$[Pd(L^2)_2](ClO_4)_2\cdot H_2O$	8.39 s (0.08)	8.20dd (0.16)	7.96 t (0.16)	7.85 qd (0.12)	7.51 m (0.21)	7.51 m (0.21)	7.85 qd (0.14)	4.04 s (0.08)
		H–3, 5	H–4					
L^3	–	8.37 d	8.19 t	7.78 m	7.34 m	7.34 m	7.78 m	13.04 s
$[PdCl_2L^3]$	–	8.52 d (0.15)	8.52 t (0.33)	7.83 m (0.05)	7.38 m (0.04)	7.38 m (0.04)	7.63 d (–0.15)	ND
$[PdBr_2L^3]$	–	8.25 dd (–0.12)	8.60 t (0.41)	7.82 m (0.04)	7.40 m (0.06)	7.40 m (0.06)	7.67 d (–0.11)	ND
$[Pd_2(L^3)_3](OClO_3)_2](ClO_4)_2\cdot 2H_2O$	–	8.48 d (0.11)	8.39 t (0.20)	7.89 m (0.11)	7.50 m (0.16)	7.50 (0.11)	7.89 (0.11)	ND
L^4	–	8.40 d	8.20 t	7.77 d	7.37 t	7.31 t	7.69 d	4.26 s
$[PdCl_2L^4]$	–	8.66 d (0.26)	8.51 m (0.31)	7.99 dd (0.22)	7.62 m (0.25)	7.62 m (0.31)	7.99 dd (0.30)	4.36 s (0.10)
$[PdBr_2L^4]\cdot 2H_2O$	–	8.42 d (0.02)	8.55 t (0.35)	7.70 d (–0.07)	7.14 m (–0.23)	7.14 m (–0.17)	7.68 d (–0.01)	3.93 s (–0.33)
$[Pd_2(L^4)_3(OClO_3)_2](ClO_4)_2$	–	8.55 m (0.15)	8.19 m (–0.01)	7.50 m (–0.27)	7.99 t (0.62)	7.69 t (0.38)	7.18 m (–0.51)	4.37 d (0.11)

Values in parentheses are coordination induced shifts; c.i.s. = $\delta_{complex} - \delta_{ligand}$; ND – not detected.

Table 3 ^{13}C NMR spectral data of the *N*-heterocycles and complexes in DMSO-d_6 (δ in p.p.m.)

Compound	Benzene ring/ Pyridine ring				Benzimidazole ring							
	C–1,3	C–2	C–4, 6	C–5	C–2'	C–4'	C–5'	C–6'	C–7'	C–8'	C–9'	N–CH_3
L^1	124.84	129.82	127.65	131.03	150.85	119.03	122.04	122.95	111.67	135.21	143.84	–
$[Pd(L^1)_2](ClO_4)_2 \cdot 2H_2O$	125.75	129.57	128.85	130.39	150.20	115.22	123.74	123.74	115.22	137.7	137.7	–
	(0.91)	(–0.25)	(1.20)	(–0.64)	(–0.65)	(–3.81)	(1.70)	(0.79)	(3.55)	(2.49)	(–6.14)	
L^2	129.11	129.82	130.36	130.57	152.33	119.08	122.00	122.50	110.61	136.63	142.46	31.69 s
$[Pd(L^2)_2](ClO_4)_2 \cdot H_2O$	127.00	129.89	132.46	130.86	150.38	116.64	124.59	124.59	112.14	134.87	136.19	32.28 s
	(–2.11)	(0.07)	(2.10)	(0.29)	(–1.95)	(–2.44)	(2.59)	(2.09)	(1.53)	(–1.76)	(–6.27)	(0.59)
	C–2, 6		C–3, 5	C–4								
L^3	147.86	–	121.47	139.42	150.71	119.86	122.64	124.13	112.08	134.50	144.20	–
$[Pd_2(L^3)_3](OClO_3)_2](ClO_4)_2 \cdot 2H_2O$	144.43	–	125.69	134.57	148.05	115.15	126.10	126.10	115.15	140.69	140.69	–
	(–3.43)		(3.95)	(–4.85)	(–2.66)	(–4.71)	(3.46)	(1.97)	(3.07)	(6.20)	(–3.51)	
L^4	149.66	–	122.90	137.98	150.19	120.24	123.68	125.32	109.96	137.26	142.70	32.45 s
$[Pd_2(L^4)_3(OClO_3)_2](ClO_4)_2$	136.77	–	134.20	146.30	162.43	115.80	121.60	125.40	112.78	151.05	157.0	34.0 s
	(–12.89)		(11.3)	(8.32)	(12.24)	(–4.44)	(–2.08)	(0.08)	(2.82)	(13.79)	(14.30)	(1.55)

Values in parentheses are coordination induced shifts; c.i.s. = $\delta_{complex}$ - δ_{ligand}

The ^{1}H NMR spectra of the complexes recorded in DMSO-d_6 show resonances due to protons of the coordinated N-heterocycles. The spectral data for the complexes along with the assignments are compiled in Table 2. Coordination induced shifts (c.i.s.) for protons of coordinated L^1 and L^2 are observed to be positive and are in the δ0.1–0.74 range. The c.i.s for the protons of coordinated L^3 and L^4 are observed to be both positive and negative. The resonance due to the imine proton of L^1 in the halide complexes has shifted to downfield by 1.0 ppm. Furthermore, the N*H* (in the halide complexes of L^1) and N–CH_3 (in the chloride complex of L^2) signals, which appear as singlets in the spectra of uncoordinated heterocycles are observed as multiplets in those of the complexes. The NH resonance has not been located,[17] in the spectra of the complexes of L^3 and that of the perchlorate complex of L^1. Perhaps the peak has broadened as the proton is bound to the quadrupolar ^{14}N nucleus. The resonance due to N–CH_3 of L^4, which is a singlet in the spectrum of the uncoordinated heterocycle, is split into a doublet at δ4.37 in the perchlorate complex.

The ^{13}C NMR spectra of the perchlorate complexes have been recorded in DMSO-d_6 and the data are collected in Table 3. The resonances due to C-2', C-4' and C-9' (L^1 and L^2 complexes) and C-1,3, C-2' and C-9' (L^3 complexes) shows an upfield shift as compared to those of the free heterocycles and hence the negative c.i.s. values imply metal-to-ligand π-back donation as these carbons are in close proximity to the coordinated nitrogens. For the other carbons, positive c.i.s. values are observed and the results are attributable to predominant ligand-to-metal σ-donation.[18]

The FAB-mass spectra of $[Pd_2(L^3)_3](OClO_3)_2](ClO_4)_2 \cdot 2H_2O$ and $[Pd_2(L^4)_3(OClO_3)_2](ClO_4)_2$ support the binuclear nature of the complexes. They exhibit the molecular ion peaks at *m/z* 1581 due to $[Pd_2(L^3)_3](OClO_3)_2](ClO_4)_2 \cdot 2H_2O$ and *m/z* 1635 for $[Pd_2(L^4)_3(OClO_3)_2](ClO_4)_2$ + 6H. Further, *m/z* values higher than the molecular weights are also observed and these may be due to association of fragments. Several peaks due to the products of fragmentation have also been observed.

The coordination of the N-heterocycles to the metal ion is evident from the analytical data, IR and NMR spectral studies. The electronic spectral results suggest a four-coordinate square planar stereochemistry for the complexes with the N-heterocycles acting as bidentate ligands including the potential tridentate N-heterocycles, L^3 and L^4. The perchlorate complexes containing L^3 and L^4 may be suggested to be binuclear and square planar with one of the heterocycle molecules serving as bridging bidentate, while each of the other two molecules as chelating bidentate (each coordinated to an independent palladium metal ion), leaving a pendant nitrogen. The coordination of potentially tridentate, L^4 in a bidentate manner has been established by Addison and co-workers by X-ray crystal structure study of $[Cu(L^4)_2](ClO_4)_2 \cdot H_2O$[19]. In the said complex, one of the molecules of L^4 is bound to the metal ion in a chelating bidentate fashion while the other in a tridentate manner. Such a varied coordination mode of L^4 has also been reported from this laboratory earlier.[9]

The authors thank Prof. B. K. Sadashiva, Raman Research Institute, Bangalore, India for CHN analyses, the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India for recording the NMR spectra. Shivakumaraiah gratefully acknowledges the financial support received from the Sree Siddaganga Education Society, Sree Siddaganga Math, Tumkur, India.

Received 18 February 2005, accepted 22 April 2005
Paper 05/3075

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