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SYNTHESIS AND CHARACTERIZATION OF PALLADIUM COMPLEXES OF SOME N,N,N’,N’-TETRAKIS(2-PYRIDYLMETHYL)ALKANEDIAMINE LIGANDS

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Abstract. The syntheses and characterization of complexes formed from the reaction of bis(acetonitrile)palladium(II) chloride, $(CH_3CN)_2PdCl_2$, with nitrogen-based ligands of the type N,N,N´,N´-tetrakis(2-pyridylmethyl)alkanediamine {alkane= butane (**L1**), hexane (**L2**) and octane (**L3**)} were investigated. Ligand to metal (L:M) ratios of 1:1 and 1:2 were employed in the preparation of the palladium complexes. **L1** reacted with $(CH_3CN)_2PdCl_2$ in methanol and at a ligand to metal ratio of 1:1 to yield a cream white complex (**A**). Each of the three ligands (**L1**, **L2**, **L3**) reacted with $(CH_3CN)_2PdCl_2$ at a ligand to metal ratio of 1:2 in HCl medium for 24 hours yielding light yellow powders **B**, **C**, and **D**, respectively. Results from IR, ^{1}H-NMR and Mass spectroscopic techniques combined with elemental analyses suggest a mononuclear complex for **A** and dinuclear complexes for **B, C,** and **D.**

Keywords: synthesis, 2-pyridylmethyl, ligands, palladium, complexes

Introduction

Studies on nitrogen- based ligands have continued to attract considerable interest due to their various applications. Some of these ligands have been employed in chelation therapy (Kalinowski & Richardson, 2007; Hider & Zhou, 2005; Xu et al., 2002; Flora et al., 2008; Kalia & Flora, 2005; Walshe, 2003; Blindauer et al., 2006) to assist removal of heavy metals from the body in cases of ingestion. For example, Kalia & Flora (2005) reported the use of EDTA (ethylenediaminetetraacetic acid), TTFD (thiamine tetrahydrofurfuryl disulfide), and DTPA(Diethylene triamine pentaacetic acid) for such chelation therapy. In water and soil treatment of plants, nitrogen based ligands like EDDS (*S,S*-ethylenediaminedisuccinic acid) have been used for restoring metal-contaminated soils (Ocak et al., 2006) while others like EDTA (Marsh et al., 1998; Matsumura & Takeshita, 2008; Oshima et al., 2002) have been employed in resin beds. The use of 3-picolyl and 4-picolyl derivatives in ion exchangers is also known (Marsh et al., 1998). Biomimicry is one area in which the nitrogen based ligands has also been widely investigated (Cotton

& Wilkinson, 1972; Kurzeev et al., 2000; Nagano et al., 1989; Mohamadou & Gerard, 2001; Jubert et al., 2000; Felluga et al., 2000). In this area the complexes are either directly inspired by biology or designed to function in a similar manner, for example, the use of porphyrins to mimic biological systems like haemoglobin and metalloenzymes. The use of nitrogen-based ligands for medicinal purposes have also attracted a lot of interest (Wong & Giandomenico, 1999; Bakalova et al., 2009), the most notable being the use of platinum amine based complexes and their analogues for chemotherapy in cancer patients. Some gold amine based complexes have recently been reported as promising HIV inhibitors (Fonteh et al., 2011). In catalysis, the nitrogen based catalysts have been found to be better than the phosphine based catalysts due to their non-reactivity with oxygen (van Leeuwen, 2004). Brookhart's -α-diimine nickel and palladium complexes have been found to be good catalysts for olefin oligomerisation and polymerization reactions (Sundaravajan, 2002). Nickel allyl complexes containing labile ligands like N,N-tetramethylenediammine (tmed) and pyridine have also been found to display thermolabile and stable characteristics which are good for the α-olefin polymerization catalysis with good yields (King, 2005; Yamamoto, 1999). Nickel and palladium catalysts have also been prepared from pyrazoles and pyrazolyl ligands (Omae, 1998).

Some transition metal (notably platinum) complexes of N,N,N´,N´-tetrakis(2-pyridylmethyl)alkanediamine ligands have been synthesised and characterised earlier (Sato et al., 1992; Hofmann & van Eldik, 2003; Mambanda et al., 2010) but not much is known about the palladium complexes of these ligands. This study reports the synthesis and characterisation of palladium complexes of some N,N,N´,N´-tetrakis(2-pyridylmethyl)alkanediamine ligands.

Experimental

Chemicals

2-pyridyl methyl hydrochloride (2-picolyl chloride), dichloromethane, methanol, chloroform, hexane, sodium hydroxide and sodium perchlorate were supplied by Rochelle Chemicals while CTAB, anhydrous magnesium sulphate, anhydrous sodium sulphate, palladium chloride, *Bis*-acetonitrile dichloride palladium, dimethylsulphoxide and acetonitrile were purchased from Sigma and Aldrich.

Instruments

The infrared spectra for all the synthesised ligands and complexes were recorded in solid state using KBr pellets on a Shimadzu Hyper IR system FT-IR8700 spectrophotometer (made in Japan) in the range of 100 cm^{-1} to

4000 cm^{-1}. The ^{1}H-NMR spectra were recorded at room temperature on a Bruker Avance DPX 300MHz spectrometer (made in Germany) in the range 1-15ppm, respectively. Tetramethylsilane was employed as chemical shift internal starndard for ^{1}H-NMR spectra. For the NMR runs, the ligands solutions were prepared by dissolving the relevant amount (about 5mg) in deuterated methanol (MeOD) as a solvent whereas the palladium complexes were dissovled in deuterated DMSO. The mass spectra analysis was carried out using the ESI technique in the LCQ Deca(made in USA) manufactured by Thermo Finnigan. Solutions of all the ligands and complexes were made to suitable analysis concentration for the instrument (between 5ppm and 10ppm). The solvent used was analytical grade MeOH for the ligands while for the palladium complexes a solvent mixture of DMSO and Acetonitrille (1:1) was used.

The CHN elemental analyses for the ligands and complexes were done using the Vario EL CHNOS Elemental Analyzer, Identity. No. 11.02.5003 (made in Germany). All the samples were analysed in solid state. Each analysis was done in triplicate and the average was obtained and reported. The melting points were recorded using a Stuart Scientific SMP1 melting point apparatus (made in UK).

Synthesis of the ligands

The three ligands N,N,N′,N′-tetrakis(2-pyridylmethyl)1,4-butanediamine **(L1)**, N,N,N′,N′-tetrakis(2-pyridylmethyl)1,6-hexanediamine **(L2)**, and N,N,N′,N′-tetrakis(2-pyridylmethyl)1,8-octanediamine **(L3)** were prepared following modified literature procedures (Sato et al., 1992; Mambanda et al., 2010).

*Synthesis of palladium (II) complexes, **A, B, C** and **D***

[Pd(N,N,N’,N’-tetrakis(2-pyridylmethyl)1,4-butanediamine)Cl](ClO_4) (A)

This complex was prepared by reacting 0.1358g (0.0003moles) of the ligand **L1** with the equimolar amount of 0.0778g (0.0003moles) bis acetonitrille dichloro palladium in 50ml of methanol. The reaction mixture was stirred for 48 hours and then filtered. The product was precipitated by addition of 1ml of saturated $NaClO_4$ solution to the filtrate. The resulting cream white powder was filtered off followed by washing with H_2O, EtOH and Et_2O, and then dried in vaccum.

*[Pd_2(N,N,N’,N’-tetrakis(2-pyridylmethyl)1,4-butanediamine)Cl_2](ClO_4)$_2$ **(B)***
*[Pd_2(N,N,N’,N’-tetrakis(2-pyridylmethyl)1,6-hexanediamine)Cl_2](ClO_4)$_2$ **(C)***
*[Pd_2(N,N,N’,N’-tetrakis(2-pyridylmethyl)1,8-octanediamine)Cl_2](ClO_4)$_2$ **(D)***

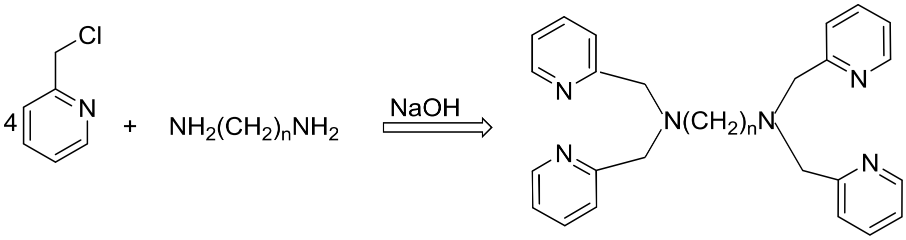
These complexes were synthesised following the procedures used to prepare the analogous dinuclear platinum complexes (Sato et al., 1992; Mambanda et al., 2010).

124.5mg (0.48mmol) of $(CH_3CN)_2PdCl_2$ in 50 ml of 0.01 M HCl, and a solution of 0.24 mmol of **L1, L2,** or **L3** in 50 ml of 0.01M HCl were mixed together. The mixture was refluxed for 24 hours and then filtered. The product was precipitated by addition of 1 ml of saturated $NaClO_4$ solution to the filtrate. The resulting light yellow powder was filtered off, washed with H_2O, EtOH and Et_2O, and dried in vacuum.

Results and discussion

Ligands (L1, L2, L3)

The preparation of 2-pyridylmethyl substituted diamine ligands by the reaction of 2-(chloromethyl)pyridinium chloride with the respective diamines can be represented by Scheme 1 below**.** All reactions were at room temperature.



Scheme 1. General reaction route for the preparation of the ligands (where n=4 for **L1,** n=6 for **L2** and n=8 for **L3**)

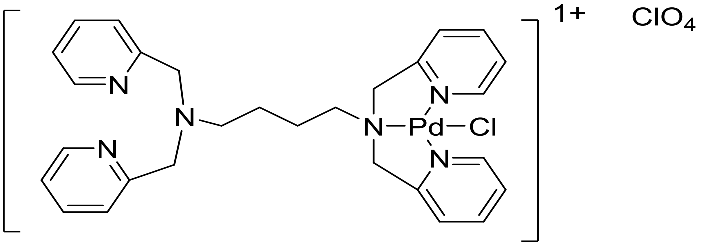
The three ligands were obtained as brown solids which after recrystallisation gave **L1** as white crystals**, L2** as light yellow crystals and cream white crystals for **L3.** The calculated yields were found to be 65, 81 and 62%, respectively, for **L1, L2** and **L3**.

Results from detailed characterisation of these ligands using melting points, IR, NMR, Mass Spectrometry and CHN analysis are in agreement with what is expected based on earlier studies (Sato et al., 1992; Hofmann & van Eldik, 2003; Mambanda et al., 2010).

Palladium complexes

[Pd(L1)Cl]ClO$_4$ [A]

An equimolar reaction of N,N,N’,N’-tetrakis(2-pyridylmethyl)1,4-butanediamine **(L1)** with bis acetonitrile palladium dichloride in methanol afforded a new complex $[Pd(L1)Cl]ClO_4$ in the form of a cream white powder after precipitation with saturated $NaClO_4$. The percentage yield was 54% while the melting point ranged from 250 to 254 °C. The complex was then analysed and characterised by spectroscopic methods. The ^{1}H-NMR spectrum showed the presence of a pair of singlets at 1.51 and 2.81 ppm, doublets at 4.40 due to methylene bridge of the diamine and 5.42 ppm due to the CH_2 in the 2-pyridylmethyl group of the complex. The pyridyl ring protons appeared down field showing three signals at 7.61, 8.16 and 8.53ppm as a multiplet, triplet and doublet, respectively. The ^{1}H-NMR spectra of both the free ligand and the metal complex were very similar in pattern, but a downfield shift of the proton ortho(position 6) to the pyridine ring nitrogen was observed upon complexation (from 8.50 to 8.53 ppm) as expected on attachment of the ligand to the electron deficient metal ion. Another down field shift occurred for the proton at position 4 (para to the pyridyl nitrogen) from 7.14 ppm to 7.61 ppm. Generally, the pyridyl proton signals were shifted down field due to the coordination of electron deficient Pd ion to the nitrogen atom of the pyridyl ring. The mass spectrum showed a molecular peak at *m/z* value 595.1 a.m.u deviating from the calculated expected exact molecular mass of 693.93 a.m.u. showing that the complex gave a positive ion(+1) $[Pd(\mathbf{L1})Cl]^+$ after losing one perchlorate ion in solution. The mass spectrum analysis was done in solution hence it is convenient to say the perchlorate ion (ClO_4^-) dissociates in solution leaving a positive ion as shown in Fig.1 below. The IR spectra showed the presence of the peaks characteristic of the perchlorate in the complex at 1091cm^{-1} (broad) and 623cm^{-1} (weak), due to the symmetric and asymmetric stretching frequencies of the perchlorate ion. The observation of these peaks in the IR spectrum was because the analysis was performed in solid state as opposed to the mass spectrum which was done in solution.



Pd[N,N,N,N-Tetrakis(2-pyridyl methyl)1,4-butanediamine]Cl(ClO_4)

Fig. 1. Proposed structure of the mononuclear palladium complex A

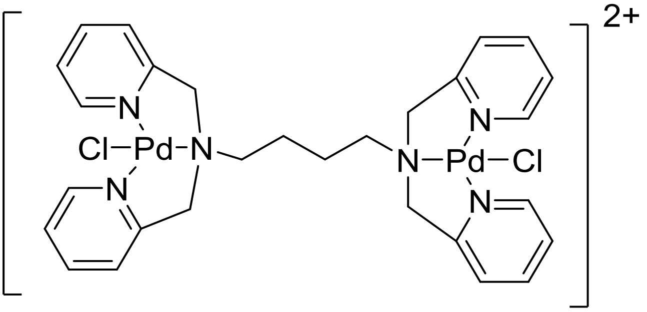
Dinuclear Palladium complexes: ***B, C, D***

$[Pd_2(L1)Cl_2](ClO_4)_2$ ***[B]***
$[Pd_2(L2)Cl_2](ClO_4)_2$ ***[C]***
$[Pd_2(L3)Cl_2](ClO_4)_2$ ***[D]***

The refluxing of bis acetonitrile palladium dichloride with the ligands **L1, L2** and **L3** in 0.01M HCl as represented in Scheme 2 yielded light yellow powders of **B, C** and **D**, respectively, after precipitation with saturated $NaClO_4$. All the three products were obtained as light yellow powders soluble in DMSO. The calculated yields were found to be 90%, 87% and 91% for complexes **B, C and D,** respectively.

$$2(CH_3CN)_2PdCl_2 \quad + \underset{\mathbf{(L1,\ L2,\ L3)}}{\mathbf{L}} \xrightarrow[\text{reflux 24 hrs} \atop NaClO_4]{\text{50 ml HCl}} \underset{\mathbf{B,\ C,\ D}}{[Pd_2\,(L)\,Cl_2]\,(ClO_4)_2} \quad \text{(light yellow powder)}$$

Scheme 2. Reaction scheme for the formation of dinuclear palladium complexes **B, C, D**



Pd_2[N,N,N',N'-Tetrakis(2-pyridylmethyl)1,4-butanediamine]Cl_2

Fig. 2. Structure of the dinuclear palladium complex

Fig. 2 shows the proposed structure of the dinuclear palladium complex **B**. The other two complexes **C** and **D** have similar structures.

Table 1. Physical and spectroscopic properties of the palladium complexes

Name	M:L ratio	colour	^{1}H-NMR phenyl region (ppm)	^{1}H-NMR methylene region (ppm)
$[Pd(L1)Cl]ClO_4$ **[A]**	1:1	Cream white	7.61 (m, 8H) 8.16 (t, 4H) 8.53 (d, 4H)	1.51 (s, 4H) 2.81 (t, 4H) 4.40 (d, 4H) 5.42 (d, 4H)
$[Pd_2(L1)Cl_2](ClO_4)_2$ **[B]**	2:1	Light yellow	7.62 (m, 8H) 8.17 (t, 4H) 8.53 (d, 4H)	1.52 (s, 4H) 2.81 (t, 4H) 4.41 (d, 4H) 5.43 (d, 4H)
$[Pd_2(L2)Cl_2](ClO_4)_2$ **[C]**	2:1	Light yellow	7.66 (m, 8H) 8.21 (t, 4H) 8.57 (d, 4H)	1.07 (s, 4H) 1.42 (s, 4H) 2.88 (t, 4H) 4.44 (d, 4H) 5.47 (d, 4H)
$[Pd_2(L3)Cl_2](ClO_4)_2$ **[D]**	2:1	Light yellow	7.67 (m, 8H) 8.22 (t, 4H) 8.58 (d, 4H)	0.95 (s, 4H) 1.10 (s, 4H) 1.12 (s, 4H) 2.92 (t, 4H) 4.49 (d, 4H) 5.58 (d, 4H)

The ^{1}H-NMR spectrum for all the three complexes (Table 1) showed the presence of some methylene shifts from 1.07 ppm to 4.44 ppm as protons from the diamine chain. On the other hand there was a peak around 5.40 ppm assigned to the CH_2 of the pyridyl ring. The shifts due to the pyridyl ring protons in each of the above complexes appeared down field showing three signals around 7.60, 8.10 and 8.50 ppm as multiplet, triplet and doublet respectively. These spectral observations are consistent when compared to the ones reported for the analogous dinuclear platinum complexes (Sato et al., 1992; Hofmann & Van Eldik, 2003; Mambanda et al., 2010). The ^{1}H-NMR spectra of both the free ligand and the complex showed a similar pattern in shifts because the compounds are symmetrical. However. there was an increase of 0.03 ppm, 0.33 ppm, 0.04 ppm and 0.14 ppm in chemical shift of the proton ortho (position 6) to the pyridine nitrogen observed upon complexation to the Pd ion for complexes **A, B, C** and **D,** respectively. Another down field shift occurred for the proton at position 4 (para to the pyridyl nitrogen) by a magnitude of 0.47 ppm, 0.48 ppm, 0.50 ppm and 0.34ppm for complex **A, B, C** and **D**, respectively, as in Table 2.

Table 2. Comparison of the proton shifts at position 4 and 6 of the pyridyl ring in a free ligand and upon complexation

Compound	C6 shift (ppm)	C4 shift (ppm)	C6 Shift magnitude	C4 Shift magnitude
L1	8.50	7.14		
A	8.53	7.61	0.03	0.47
B	8.83	7.62	0.33	0.48
L2	8.53	7.16		
C	8.57	7.66	0.04	0.50
L3	8.44	7.28		
D	8.58	7.62	0.14	0.34

Infrared spectroscopic results showed the presence of the peaks characteristic of the perchlorate ion in all the complexes around 1085cm^{-1} to 1093 cm^{-1}(broad) and around 623 cm^{-1} (weak), due to the symmetric and asymmetric stretching frequencies, respectively. However, there were also various peaks below 500 cm^{-1} some corresponding to the Pd –N and others correspond to Pd -Cl stretching frequencies observed between 437 cm^{-1} and 260 cm^{-1}. The IR spectra of the complexes also showed the presence of the pyridyl nitrogen stretch at about 763 cm^{-1}, but with reduced intensity as compared to the one observed in the IR spectrum of the free ligand (Table 3). These results suggest that the pyridyl nitrogen has been involved in the bonding with the palladium ion.

Table 3. IR data for palladium complexes A, B, C and D

Name	Assignment	Frequency (cm^{-1})
[Pd(L1)Cl]ClO$_4$ **[A]**	v (C-H)	2935
	v (C=N and C=C)	1610-1558
	v (Pyridine shift)	1440-1286
	v (ClO$_4$)	1091
	v (Pyridyl Nitrogen)	765
	δ (ClO$_4$)	623
	v (Pd-N)	308
	v (Pd-Cl)	273-177
[Pd$_2$(L1)Cl$_2$](ClO$_4$)$_2$ **[B]**	v (C-H)	2952
	v (C=N and C=C)	1610
	v (Pyridine shift)	1446-1276
	v (ClO$_4$)	1085
	v (Pyridyl Nitrogen)	765
	δ (ClO$_4$)	623
	v (Pd-N)	437
	v (Pd-Cl)	298-268

$[Pd_2(L2)Cl_2](ClO_4)_2$ **[C]**	v (C-H)	2925
	v (C=N and C=C)	1608
	v (Pyridine shift)	1442-1280
	v (ClO4)	1091
	v (Pyridyl Nitrogen)	763
	δ (ClO4)	624
	v (Pd-N)	337
	v (Pd-Cl)	308
$[Pd_2(L3)Cl_2](ClO_4)_2$ **[D]**	v (C-H)	2929
	v (C=N and C=C)	1608
	v (Pyridine shift)	1440-1288
	v (ClO4)	1093
	v (Pyridyl Nitrogen)	767
	δ (ClO4)	623
	v (Pd-N)	420
	v (Pd-Cl)	307

The mass spectra of the complexes showed molecular peaks at *m/z* value 836.9 a.m.u for complex **B** for instance, deviating from the calculated exact molecular mass of 935.25 a.m.u. This shows that the complex has formed its positive ion $[Pd_2(\mathbf{L1})Cl_2](ClO_4)]^+$ after losing one perchlorate ion in solution. Similar results were obtained for the other complexes showing the loss of a chloride ion for **A** and loss of one perchlorate ion for each of **C** and **D** as shown in Table 4.

The results from elemental analysis of the complexes (Table 4) show fairly close agreement between the experimental and calculated values for the elements except in complex **A** where there is a fairly significant disparity between the two sets of values. This disparity could arise from solvent effects and/or presence of un-reacted ligand. The ^{1}H-NMR spectrum of **A** actually shows presence of some un-reacted ligand.

Table 4. Mass spectral and CHN analysis results for the complexes

Complex	Molar mass	**m/z value**	**Molecular peak ion [for m/z]**	***Elemental Analysis results**
$[Pd(C_{28}H_{32}N_6)Cl](ClO_4)$ **A**	693.93	595.1	$[Pd(C_{28}H_{32}N_6)Cl]$	C 47.81 (48.46) N 11.35 (12.11) H 3.72 (4.66)
$[Pd_2(C_{28}H_{32}N_6)Cl_2](ClO_4)_2$ **B**	935.25	836.9	$[Pd_2(C_{28}H_{32}N_6)Cl_2]ClO_4$	C 35.68 (35.96) N 8.89 (8.98) H 3.34 (3.44)
$[Pd_2(C_{30}H_{36}N_6)Cl_2](ClO_4)_2$ **C**	963.36	863.4	$[Pd_2(C_{30}H_{36}N_6)Cl_2]ClO_4$	C 37.62 (37.40) N 8.61 (8.73) H 3.88 (3.77)
$[Pd_2(C_{32}H_{40}N_6)Cl_2](ClO_4)_2$ **D**	991.42	893.1	$[Pd_2(C_{32}H_{40}N_6)Cl_2]ClO_4$	C 38.42 (38.76) N 8.46 (8.48) H 3.91 (4.07)

* *calculated values are in brackets*

Conclusions

Different N,N,N′,N′-tetrakis(2-pyridylmethyl)alkanediamine complexes of palladium have been prepared with reasonable yields and characterised by spectroscopic techniques. The spectral data for the mononuclear and the dinuclear complexes are consistent with the expected products. The results show that in both the mononuclear and dinuclear complexes, the ligands are coordinated to the metal ions through the pyridinyl nitrogen atoms.

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