Synthesis and Characterization of Palladium (II) and Platinum(II) Complexes with Quinazoline and Thiolate Derivatives

Samir S. Ezzat
Department of Chemistry
College of Science
Mosul University

(Received 8\1\2008 ; Accepted 17\3\2008)

ABSTRACT

A number of Pd^{+2} and Pt^{+2} complexes with 2-methyl-3-aminoquinazoline 4-one (L_1) and 2-methyl-3-hydroxyquinazoline-4-one (L_2) have been synthesized by direct reaction of Na_2PdCl_4 or K_2PtCl_4 with the ligands. Complexes of the general formula $[M(L)(SC_6H_4.p\text{-}Me)_2]$ were also prepared through neucleophilic substitution reaction. The prepared complexes were characterized by IR and UV/Vis spectroscopy, conductivity, magnetic measurement and the metal content were determined spectrophotometrically. The electronic spectra and magnetic susceptibility indicates that the complexes have a square planer geometry in which the ligands behave as bidentate.

تحضير وتشخيص عدد من معقدات البلاديوم والبلاتين مع مشتقات الكوينازولين والثايوليت

الملخص

تم تحضير عدد من معقدات Pd^{+2} و Pt^{+2} مع 2-مثيل -3-أمينو كينوزولين-4-اون (L_1) و2-مثيل-3-هيدروكسي كوينازولين-4-اون (L_2) بالتفاعل المباشر بين Na_2PdCl_4 أو K_2PtCl_4 مع الليكاندات. كذلك تم تحضير المعقدات التي تمتلك الصيغة العامة $[M(L)(SC_6H_4.p\text{-}Me)_2]$ خلال تفاعل الاستبدال النيكلوفيلي. تم تشخيص المعقدات المحضرة بوساطة أطياف IR و UV/Vis والقياسات المغناطيسية وقياسات التوصيل الكهربائي. تبين من نتائج الطيف الالكتروني والقياسات المغناطيسية بان جميع المعقدات تتخذ شكل المربع المستوي وان ارتباط الليكاندات (L_1 و L_2) بالايونات الفلزية بشكل ثنائي السن.

INTRODUCTION

Substituted quinazolinones were known to possess various biological activities, such as antimicrobial (Abdel-Fattah et al., 1999; Dandia et al., 2001) traumatic brian treatment(Chenard et al., 1999) and as muscle relaxants (Mathieson, 1965).

New lanthanide(III)complexes (Gudasi et al., 2005) with 2-pyridine-2-yl-3-[pyridine-2-carboxylideneamine]-2-dihydroquinazolin-4-(3H)-one have been prepared and characterized by different physico-chemical techniques, also the ligand and complexes have been evaluated for their antibacterial and antifungal activities Palladium(II) and platinum (II) complexes containing mixed ligands N-(2-pyridyl) acetamide or N-(2-primidyl) acetamide and the diphosphines $Ph_2P(CH_2)_nPPh_2$ (n=1,2,3) have been prepared and characterized (AL-Jibori et al., 2007). Substitution reactions have been used to prepare complexes of the type $[Pt(OAc)(SR)_2]$ and $[Pt_2LCl_4]$, which are used as versatile precursors for other products (Kujper, 1979; Buttrus et al., 2007) to prepare complexes of the type $[Pt_2LCl_4]$ which are used as versatile precursors for other products $[Pt_2(L)(L`)_4]$ where L= 1,1,2,2-tetrakis (substituted phenylthio) ethylene, L`= thiophenoxide or *p*-aminothiophenoxide.

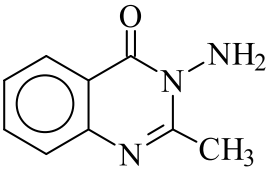
We presenting here the preparation and characterization of some new mono complexes of Pd^{+2} and Pt^{+2} with the ligands 2-methyl-3-aminoquinazoline-4-one (L_1) and 2-methyl-3-hydroxy quinazoline-4-one (L_2), as well as the mixed ligand complexes with above ligands and the thiolate ion.

EXPERIMENTAL

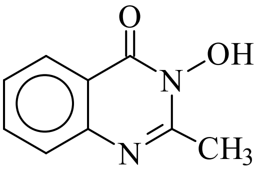
IR spectra were recorded on F.T. thermo Mattson 300 spectrophotometer in the 200-4000 cm^{-1} range using CsI discs. Electronic spectra were obtained using Shimadzu UV/Vis. spectrophotometer UV-160 for 10^{-3} M solution of the complexes in dimethyl sulfoxide using 1cm quartz cell. The metal content was estimated spectrophotometrically using Shimadzu AA670. Conductivity measurements were made on 10^{-3} M solution of the complexes in (DMSO) solvent at ambient temperature using conductivity model 4070 Jenway. Magnetic measurements were recorded on a Bruker BM6 instrument at room temperature following the Faraday method. Melting points were recorded on electrothermal 9300 melting point apparatus and were uncorrected.

Starting material

The compounds K_2PtCl_4,Na_2PdCl_4 and *p*-tolylthiol were commercial products (Fluka) and used as supplied. The ligands (L_1 &L_2) were prepared by condensation of benzoxazinone with primary amine according to literature (Tiwari and Pandey, 1975) as shown below:



(L_1)



(L_2)

Preparation of $[M(L)Cl_2]$ were ($L=L_1$ or L_2, M= Pd or Pt)

To an ethanolic solution (15 cm^3) of the ligand (L_1) (0.16 g , 0.001 mol) or (L_2) (0.16 g, 0.001 mol) was added to an ethanolic solution (10 cm^3) of K_2PtCl_4 or Na_2PdCl_4 (0.42 g, 0.001 mol) or (0.29 g, 0.001 mol) with stirring at 70 ºC. A distinct change in colour was observed. The mixture was stirred under reflux for 1hr. to ensure the completion of the reaction. The solid products were filtered out, washed with ethanol and diethylether, and then dried under vacuum for several hours.

Preparation of $[M(L)(SPh\text{-}Me\text{-}p)_2]$ complexes

The complexes of the general formula $[Pt(L)(SC_6H_4\text{-}p\text{-}Me)_2]$ were prepared by mixing of (1 mmol) of the complexes $[M(L)Cl_2]$ in (15 cm^3) dimethylformamide (DMF) with (0.002mol) of (20 cm^3) ethanolic solution containing equimolar quantities of p-Me-C_6H_4SH and KOH. Then the mixture was refluxed for 2hr. with continous stirring KCl was removed by filtration. The precipitate was obtained after evaporation of the residue solution to about 1/3 of its volume, which was filtered off to remove the KCl, washed with DMF, ethanol and diethylether. Then dried under vacuum for several hours.

RESULTS AND DISCUSSION

The complexes of the general formula $[M(L)Cl_2]$ were prepared by the direct reaction of the ligands (L_1 and L_2) with Na_2PdCl_4 or K_2PtCl_4 in 1:1 ligand to metal molar ratio, in which the ligands behaves as bidentate to form chelates of Pd or Pt via carbonyl oxygen and nitrogen or oxygen atom of the amine or the hydroxyl group of the ligands. The reaction of these complexes with equimolar quantities of KOH and *p*-Me-C_6H_4SH gave the complexes of general formula $[M(L)(SC_6H_4\text{-}p\text{-}Me)_2]$.

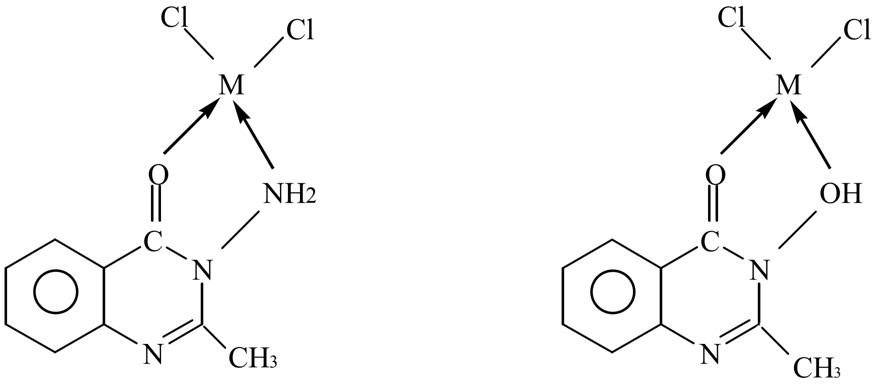
Physico-chemical properties of the complexes are tabulated in Table (1). These data were in a good agreement with the proposed formula. All the complexes are stable at room temperature and insoluble in common organic solvents. They are however, soluble in (DMF) and (DMSO). The electrical molar conductance of the complexes as 10^{-3} M DMSO solution are within the range 5-25 $ohm^{-1}.mol^{-1}.cm^2$, indicating the neutral nature of the complexes (Geary, 1971). This is consistent with the stoichiometry assumed for the complexes on the basis of the analytical data. The most important IR assignment of the ligands as well as its bonding sites (Table 2) have been determined by careful comparison of the spectra of the ligands with those of metal complexes.

The IR spectrum of the ligands showed medium bands at 1670-1675, 3380 and 3400 cm^{-1} assigned to υ(C=O), υ(NH_2) and υ(OH) were observed at lower frequencies in all complexes, indicating that these groups were shared in coordination with Pd or Pt through oxygen or nitrogen atoms (AL-Jibori et al., 2007). The IR spectra of metal complexes showed new bands at 400-420 and 480-510 cm^{-1} assigned to υ(M – O) or υ(M–N). They also showed a band in the region 290-320 cm^{-1} assigned to υ(M – Cl) in the complexes(1-4). This band is splitted in to two bands in the spectrum of $[M(L)Cl_2]$ complexes; this can be taken as evidence for square planer of these complexes (Buttrus et al., 2003).

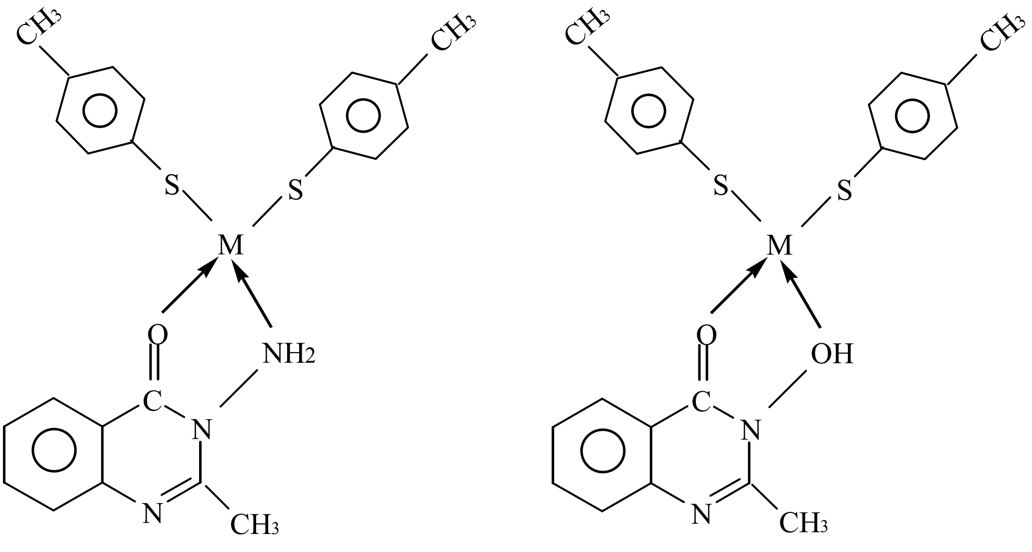
In the complexes of the formula $[M(L)(SC_6H_4\text{-}p\text{-}Me)_2$(5-8) similar observation was found in the IR spectra as above as well as the band at 340-360 cm^{-1} which assigned as υ(M–S). The absence of any band due to υ(M–Cl) absorption indicates complete substitution of thiophen-oxide in the complexes. This observation is also confirmed by sodium test.

The tentative assignments of the absorption bands from the electronic spectra of the complexes are listed in Table 2. The π- π* transition in the spectrum of the ligands is observed at 270-310 nm. In the spectra of the complexes, this band was shifted to a higher value within 350-390 nm region. The d-d bands from the spectra of the complexes having low intensities appeared at 400-450 nm and were assigned to the $^1A_1g \rightarrow {}^1A_2g$ transition in square planar environment around Pd or Pt (Gürol et al., 1992). Other bands from the spectra of the complexes are too intense to be assigned to d-d transition. Based upon position and intensity, we can assign these band to L–M or M–L charge transfer.

The magnetic moment of Pd^{+2} and Pt^{+2} complexes (Table 1) indicate that these complexes are diamagnetic. The complexes may have a square planar geometry. The following structures are suggested for the present complexes, as in Fig 1.



Complexes (1-4)



Complexes (5-8)

$M = Pd^{+2}$ or Pt^{+2}

Fig 1: Probable structures of Pd^{+2} and Pt^{+2} complexes.

Table 1: Physical properties of the complexes.

Comp. No.	Complex	m.p (°C)	Colour	Yield %	Analysis % found (calc.)	Ω $ohm^1.cm^2.mol^{-1}$	μ_{eff} (B.M)
					M		
1	$[Pd(L_1)Cl_2]$	220-222	Brown	80	30.51 (30.75)	8	0.3
2	$[Pt(L_1)Cl_2]$	278-280	Black	75	45.39 (45.45)	25	0.5
3	$[Pd(L_2)Cl_2]$	242-244	Dark oleive	78	34.49 (34.63)	10	0.1
4	$[Pt(L_2)Cl_2]$	260-262	Violet	82	45.28 (45.35)	14	0.7
5	$[Pd(L_1)(SC_6H_4\text{-p-Me})_2]$	202-205	Dark red	75	18.21 (18.13)	8	0.1
6	$[Pt(L_1)(S\ C_6H_4\text{-p-Me})_2]$	220-223	Dark orange	81	28.73 (28.88)	6	0.3
7	$[Pd(L_2)(S\ C_6H_4\text{-p-Me})_2]$	268-270	Dark blue	85	18.01 (18.09)	5	0.0
8	$[Pt(L_2)(S\ C_6H_4\text{-p-Me})_2]$	248-250	Dark red	80	29.23 (29.28)	12	0.1

Table 2: Selected IR bands and electronic spectra data for the ligands and their complexes.

Comp. No.	IR band (cm^{-1})								λ_{max} U.V.Vis. (nm)
	υ(C=O)	$υ(NH_2)$	υ(OH)	υ(C–S)	υ(M–S)	υ(M–N)	υ(M–O)	υ(M–Cl)	
L_1	1670	3380_m	---	---	---	---	---	---	270,290
L_2	1675	---	3400_b	---	---	---	---	---	280,310
1	1636	3120_m	---	---	---	400_m	480	290	300,380,410
2	1638	3240	---	---	---	420	480	295	320,360,400
3	1637	---	3310_w	---	---	---	490	300	300,375,410
4	1640	---	3300_w	---	---	---	510	290	330,380,440
5	1632	3210	---	1030_s	340_m	410	485	---	
6	1635	3200	---	1022_s	355_m	415	495	---	320,360,450
7	1632	---	3300_w	1020	360_m	420	500	---	300,380,440
8	1635	---	3310_w	1015	350_m	400	510	---	310,375,450

s = strong, m = medium, w = weak

REFERENCES

Abdel-Fattah, M.E., Soliman, E.A. and Soliman, S.M.A., 1999. Synthesis and Reaction of 2-[2-(3,4,6-trimethylbenzyl)vinyl-4H-3,1-benzoxazine-4-one] and atrtimicrobial acivity. Indian J. Heterocyclic Chem. Vol. 8, No. 3, 177 p.

AL-Jibori, S.A., Abdullah, A.I. and AL-Allaf, T.A.K., 2007. Mononuclear and Heterobimetallic Pd^{+2} and Pt^{+2} complexes containing the mixed ligands (2-pyridyl or 2-pyrimidol) acetamide and tertiary phosphine. Transition Met.Chem. 32, 398 p.

Buttrus, N.H., Hussain, A.K. and AL-Allaf, T.A.K., 2003. Synthesis and characterization of new trinuclear Palladium (II) and Platinum (II) complexes containing phosphorus-sulphur Ligands. Asian J. Chem.,15, 1617 p.

Buttrus, N.H., Abd-Alrazaq, E.A. and AL-Sger, A.K., 2007. Synthesis and characterization of some new semiconducting dinnclear Platinum (II) complexes containing 1,1,2,2-tetrakis (substituted phenylthio) ethylene. Int. J. Chem. Sci., Vol. 5, No. 3, 1111 p.

Chenard, B.L. and Shenk, K.D., 1999. Methods of preparing substitutes-3-phenyl and 3-pyridyl-4(3H)-quinozolines and atropisomers there of useful as AMPA inhibitors or their intermediates. Eur. Pat Appl. Ep934, 934(Cl. co7D 239/91). Chem.Abst.131(11).

Dandia, A., Sanan, S., Bhagat, S. and Arya, K., 2001. Synthesis of some bioactive heterocycles investigation of the reaction of indol-2,3-dione derivatives with 2,3-diamine-4(3H)-quinozolon. Internet.

Geary, W.J., 1971. Use of conductivity measurement inorganic solvent for characterization of coordination compounds. Coord. Chem. Rev., Vol. 7, p.8.

Gudasi, K.B., Shenoy, R.V., Vadavi, R.S., Patil, M.S. and Patil, S.A., 2005. New Lanthanide (III) complexes of biologically active 2,3-disubstituted quinazoline-4(3H)-one.Indian J.Chem.,44A, 2255 p.

Gürol, I., Ahsen, V. and Bekâroğlu, Ö., 1992. Synthesis of soluble complexes from a tetradentate dithioglyoxime ligand. J. Chem. Soc. Dalton Trans., p.2283.

Kujper, J., 1979. A versatile starting material: Substitution reactions of bis (acetate) bis (diethyl sulfide) platinum with phosphines, thiols, o-hydroquinones and dihydroxy benzoquinones. Inorg. Chem., 18, 1484 p.

Mathieson, O., 1965. 3-Phenyl quinazolinones. Chem. Abst., 62, 1672a.

Tiwari, S.S. and Pandey, V.K., 1975. Synthesis of possible antiparkinsonian compounds part X: synthesis of 2,6,8-trisubstituted benzoxazinones and their corresponding 3-hydroxy-quinazolinones. J. Indian Chem. Soc., LII, 73 p.