Synthesis of new water-soluble platinum(II) complexes containing [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. Disodium salt] (HSNQ) by Phase Transfer Catalysis

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Abstract

New water - soluble platinum(II) complexes containing [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] (HSNQ) by using phase transfer catalysis have been prepared. Complexes of the form [(HSNQ)PtL2], where L2 = 2,2'- bipyridine, 1, 10-phenanthroline, (PMe2Ph)2, have been synthesized by the reaction of L2PtCl2 with the corresponding [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] in a two phase system of water and chloroform in the presence of benzyl triphenyl phosphonium chloride. The complexes are characterized by elemental analysis, UV/Vis, IR, mass spectrometry and 1H and 13C NMR spectroscopy.

Keywords: Water - soluble; Platinum; Phase transfer; HSNQ ligand; Nitrogen ligands

Introduction

A great deal of attention has been paid to the search for water-soluble transition metal complexes and related catalysts since water has a variety of properties that set it apart from most organic solvents. Because most organometallic compounds have limited water solubility, the synthesis of novel water soluble transition metal complexes is central to the development of new complexes. Moreover, with growing industrial needs to minimize cost and comply with environmental regulations there is a push to use water as a solvent. For this to occur there needs to be a better understanding of transition metal catalysis in the aqueous phase. In general, square-planar platinum(II) complexes contain stabilizing ligands (such as bipyridine, 1, 10-phenanthroline, 1, 5-cyclooctadiene, tri -alkyl or-aryl phosphines) and halides or organic groups. These complexes are not soluble in water at all. The synthesis of water soluble platinum complexes, as most of Na group for 3 SO and into water soluble ligand having the stabilizing lig to convert is , the work in the literature example. In this work we are modifying this method by replacing the halides by the water soluble ligand [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] (HSNQ). Azo compounds are widely used in industry as textile dyes, coloring agents in foods and pharmaceuticals etc. The studies were mainly concerned with aromatic azo compounds because of (i) the importance of this group in the dyestuff industry (ii) the interest in carcinogenic properties and (iii) the use of azo compound for indirect determination of metal ions. There has been a steady development of interest in [8-hydroxy-7-(4-sulfonaphthylazo)-5-quinoline sulfonic acid. disodium salt] (HSNQ) because it has been used as precursors in the reaction mechanism of biologically important compounds.[1,2]. Based on the complex formation between HSNQ and metal ions, it has been found recently to be useful in determining the metal ions in various samples.[3,4]As the chemical industry strives to increase efficiency, improve process safety, and reduce environmental impact, Phase Transfer Catalysts (PTC) has become recognized as useful tools for achieving these goals [5]. Phase – Transfer Catalysis is useful primarily for performing reaction between anions (and certain neutral molecules and transition metal complexes) and organic substrates. PTC is needed because many anions (in the form of their salts) and neutral compounds are soluble in water and not in organic solvents, whereas the organic reactants are not usually soluble in water. The PTC acts as a shuttling agent b y extracting the anion or neutral compound from the aqueous (or solid) phase into the organic reaction phase (or interfacial region) where the anion or neutral compound can freely react with the organic reactant already located in the organic phase. Reactivity is further enhanced, sometimes by orders of magnitude, because once the anion or neutral compound is in the organic phase, it has very little(if any) hydration or solvation associated with it, thereby greatly reducing the energy of activation [6]. It has been shown [7] that there are several advantages using PTC such as: An increased reaction rate, a lower reaction temperature, avoiding the need for expensive anhydrous or aprotic solvents and the use of water together with an organic solvent as reaction medium. Platinum(II) complexes have been synthesized by many different methods [8]. Recently, using phase transfer catalysis, complexes of the form [(bipy)Pt(OC6H4-4-OMe)2] (X = OCH3, CH3, H, Br, Cl) have been prepared by the reaction of the chloro complex [(bipy)PtCl2] with substituted phenols and KOH in a two phase system of water and chloroform using the phase transfer catalyst benzyl triphenylphosphonium chloride. [9]. We have previously reported the synthesis of platinum phosphine complexes containing N-(substituted aryl or benzyl)-γ-mercaptobutyramides using phase transfer catalysis. Complexes of the form [Pt(PMe2Ph)2{S(CH2)3CON-HC6H4-4-X}2], where X = OCH3, CH3, Cl or benzyl, have been synthesized by the reaction of cis dichlorobis(dimethylphenylphosphine) -platinum(II) with the corresponding N-(substituted aryl or benzyl)-γ-mercaptobutyramide in a two phase system of water and chloroform in the presence of benzyl triphenylphosphonium chloride [10].

In this work we have concentrated on complexes containing [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] (HSNQ). One reason for this interest is that such complexes may have biological importance and reports concerning complexes of this type are still rare if any.

Prior to this work, no platinum complexes of this type had been reported.

Experimental

Material

All solvents were reagent grade. [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid disodium salt] (HSNQ), Potassium tetrachloroplatinum(II) and benzyl triphenylphosphonium chloride (Aldrich) were used as received. Cis-dichlorobis (dimethylphenylphosphine) platinum(II) [11] and (2, 2'-bipyridine) dichloro platinum(II) [12] were prepared as described.

Method

General synthesis of L2Pt(HSNQ):

Recrystallized dichloro (2, 2'-bipyridyl)platinum(II) (1.0 mmol) in chloroform (15 mL) was added to a magnetically stirred solution of [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] (HSNQ) (1.0 mmol) in deionized distilled water (15 mL) containing potassium hydroxide (2.2 mmol) and benzyl triphenyl phosphonium chloride (PTC) (0.1 mmol) at 500 °C in a 100 mL flask, equipped with an N_2 inlet, water – cooled condenser and thermometer. The water layer was separated after stirring for 1h under N_2, and the chloroform layer extracted three times with water. The water fractions were combined and the product was precipitated by diethyl ether to give a red solid. Table (5) shows the physical properties of [(HSNQ)PtL2] complexes. Yield (90%) m.p 346-348 °C. Found: C, 43.14; H, 2.41; N, 8.71 Anal. Calc. for C29H19N5O5PtS2: C, 43.07; H, 2.37; N, 8.66 %.

Measurements

1H and 13C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer in (Methyl sulphoxide)-d6 solution and in D_2O Solution. TMS was used as standard.I.R. Spectra were obtained utilizing CsI window (200 – 4000 cm1) using a Perkin – Elmer 1300 Infrared spectrophotometer. Microanalyses was performed by Centre National de La Recherche Scientifique, Service Central D'Analyse, Vernaison, France.

Results and Discussion

Complexes of the form [(HSNQ)PtL2], where L2 = 2,2'- bipyridine, 1, 10-phenanthroline, (PMe2Ph)2, have been synthesized by the reaction of L2PtCl2 with the corresponding [8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] in a two phase system of water and chloroform in the presence of benzyl triphenyl phosphonium chloride as shown below: Treatment of recrystallized dichloro L2 platinum(II), where L2 = 2,2'- bipyridine, (PMe2Ph)2, 1, 10-phenanthroline, in chloroform with 8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt (HSNQ) in deionized distilled water containing potassium hydroxide (precautions should be taken with reactions containing chloroform and a base) and benzyl triphenyl phosphonium chloride(PTC) under an inert atmosphere and at 500 °C, gave deep orange - red HSNQ complexes which are stable in air and are characterized by elemental analyses,i.r,1H and 13C NMR spectroscopy. The I.R spectra contain bands characteristic of the presence of both reactants as given in Table (1), for L = (PMe2Ph)2 [13].

Table 1: Assignments of Characteristic Frequencies [13] In I.R. –Spectra

Compound	Wavenumber (cm $^{-1}$)	Intensity	Assignment
	1485	s,sh	C = C
	1435	s,sh	P – Ph
Complexes :	1090-1110	s,sh	P – Ph
	1285-1320	s,sh	P – Me
Cis-$PtCl_2(PMe_2Ph)_2$	910-950	s,sh	P –Me
	715-740	s,sh	5 adjacent H
	690-720	s,sh	5 adjacent H
and	845-850	s,sh	2adjacent H
	485-500	s,sh	Pt – P
$[(HSNQ)Pt(PMe_2Ph)_2]$.	440-460	s,sh	Pt - P
	285-315	s,sh	Pt - Cl
	700-820	m,sh	Pt - O
	3493	broad	- OH
	1455	m	N=N

Where: m = medium , s = strong , sh = sharp .

The absorption bands at 285 and 315 cm-1 are attributed to the (Pt - Cl) stretch of the cis –L2 platinum (II) and disappeared after complexation. Instead, new absorptions appeared between (700 -820) cm–1which is attributed to (Pt – O) stretches. The spectra of these complexes are governed by

the absorption of the substituted 8-hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] (HSNQ) units. The comparison of IR spectrum of (2,2'-bipyridyl)HSNQplatinum(II) complex with the IR spectra of the starting materials shows the disappearance of the strong two bands at (300-340) cm-1, which were attributed to the stretching peak of (Pt-Cl) of dichloro bipyridylplatinum(II). This indicates that Pt-Cl bond was broken down and the Pt is attached to other atoms. At the same time a new broad strong band at 3468.27 cm-1appeared which was attributed to the (-OH) band stretch that is attributed to stretching peak of the (HSNQ) ligand. This may confirm the formation of a new complex, which may be a square–planar cis-complex because the bonding of the stabilizing ligand (bipy) is in the cis-form. This suggestion is confirmed by the formation of new two bands of Pt-O which are appeared at (700-820) cm-1. This indicates a success insertion of the HSNQ ligand in the bipyridyl platinum complex. Also a weak band at 550-400cm-1appears in both dichlorobipyridylplatinum(II) and (2, 2'-bipyridyl) HSNQplatinum(II) spectra , which is attributed to (Pt-N) vibration .Whereas there is no such band in the spectrum of HSNQ.

The same trend was found in the IR spectrum of (1, 10-phenanthroline) HSNQ platinum(II) complex.

UV-Visible Spectra for Platinum(II) complexes

The UV–visible spectrum was used mainly to characterize the [(bipyridyl)[HSNQ]platinum(II)] complex by comparison with similar samples prepared earlier.[14].The UV-visible spectra of (2, 2'-bipyridyl)platinum(II) complexes contain two intense MLCT bands, whose energies are strongly dependent on the nature of the ligands bound to platinum and on the solvent. More electronegative substitute on platinum and more polar solvents cause the bands to move to higher energy. We have found this to be so. From the figure(3.2) similar assignment can be made for the (2,2'-bipyridyl)(HSNQ)platinum(II) complex which is synthesized here. There are four bands in the UV -visible spectrum. Two of them are higher in energy which represent Intra ligand transitions (π- π*) and the other two bands are MLCT.

The UV-VIS. spectra of (1,10-phenanthroline) Platinum (II) complexes have been studied and five bands were detected[15]. Two of these were assigned to the π- π* transition within the ligands, and three extra bands assigned as metal to ligand charge transfer transitions (MLCT) from platinum d-orbitals to π* orbitals of the ligand. The third MLCT band is always higher in energy than the other two bands. So, in most cases, the third band was obscured by the first π- π* transition of the ligand. Thus it is usual to study the changes in the lowest energy MLCT band only. We have found this to be the same.

Chemical shifts in the 1H-NMR spectra of the starting materials and complexes are tabulated in Table (2&3).

Figure (1) shows the structural formula of the ligand with numbered hydrogen atoms, and table (2) shows assignment of the characteristic chemical shifts in 1H-NMR spectra of the ligand HSNQ:

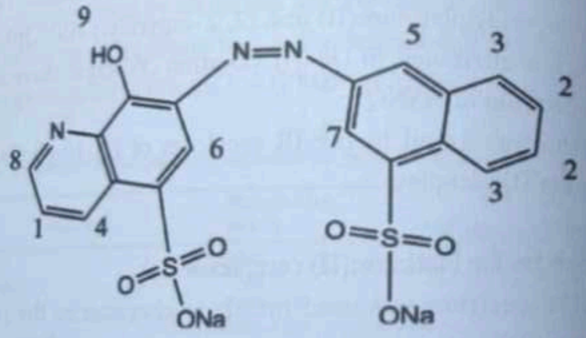


Figure 1: The structure of [HSNQ] ligand with numbered hydrogen atoms.

Table (2) Assignment of the characteristic chemical shifts in ^{1}H-NMR spectra of the ligand HSNQ

Compoud	Chemical shifts of protons,δ(ppm) , multiplicity and J value:
[HSNQ] ligand in D2O solvent	δ =7.26 (t,$H_{(1)}$, J=8.0Hz), δ =7.62 (td, H(2), J=7.8Hz), δ =7.69(dd, H(3), J=8.3Hz), δ =8.01(dd,H(4), J=8.5Hz), δ =8.35(s, H(5)), δ =8.74(s,H(6)), δ =8.80(s, H(7)), δ =8.93(dd,H(8), J=8.7Hz), δ =4.95(s, H(9))

Table 3: Assignment of the characteristic chemical shifts in ^{1}H-NMR spectra

Compound	Chemical shifts of aromatic Proton, δ (ppm)	Chemical shifts of non-aromatic proton, δ (ppm)
cis-Dichlorobis (dimethylPhenyl-phosphine) platinum(II) in $CDCl_3$ solution.	7.1-7.7(10H,m,2Ph)	2.0 6H, 2Me, d, J(PH) = 9Hz, J(PtH) = 16.5 Hz 1.65 6H , 2Me , d , J(PH) = 9 Hz, J(PtH) = 16.5 Hz
[Pt(PMe$_2$Ph)$_2$) (HSNQ)]Complex in methanol-d4 solvent	6.96 6H, Ph,d, J(PPh)=8.3Hz, 8.2 6H, Ph,d, J(PPh)=8.0Hz, 7.32 -7.98(m,HSNQ)	2.20(d,J=7.85, 2Me) 2.34(d,J=7.0,2Me)

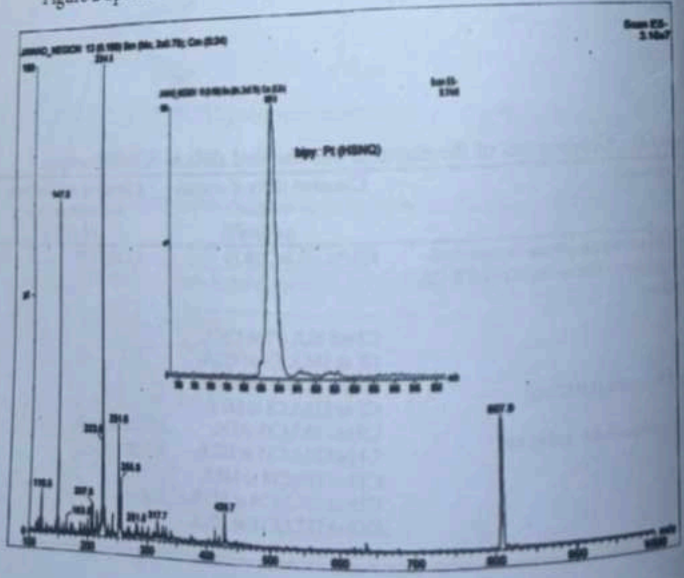
Table (4) Assignment of the characteristic chemical shifts in ^{13}C-NMR spectra

Compound	Chemical shifts of aromatic carbon, δ (ppm)	Chemical shifts of non-aromatic carbon, δ (ppm)
Cis-Dichlorobis(dimethylphenyl-Phosphine)platinum(II) in $CDCl_3$ solution .	131.50,131.04,129.19	15.81,15.37
[Pt(PMe2Ph)2HSNQ] in Methanol-d4 solution	C1 at148.3, C2 at 125.3, C3 at 134.5, C4 at 128.4., C5 at126.5,C6 at126.6, C7 at 131.2,C8 at 141.4, C9 at 119.1,C10 at134, C11at127.0,C12 at 122.5, C13 at 150,C14 at 140.0, C15 at 130.1,C16 at 127.9, C17 at 127.5,C18 at 138.5,	29.66,29.41, 29.22

Mass spectroscopy:

It is possible to determine the masses of individual ions in gas phases. Strictly speaking, it is only possible to measure their mass\charge ration (m/e), but as multi charged ions are very much less abundant than those with single electronic charge(e=1), (m/e) is for all practical purpose equal to the mass of the ion, m. The principle experimental problems in mass spectroscopy are fairly to volatilize the substrate (which implies high vacuum) and secondly to ionize the neutral molecules to charged species. The energy of the electron responsible for the ionization process can be varied. In practical much higher energies are used and this large excess energy causes further fragmentation of the molecular ion. The mass spectrum will show signals due not only from molecular ion but also due to the fragment ions resulting from subsequent fragmentation. As any species may fragment in a varity of ways, the typical mass spectrum consists of many signals. The mass spectrum consists of a plot of masses of ions against their relative abundance. [31]By using the mass spectroscopy we can insure from success of synthesizes of [(2,2'-bipy)[HSNQ]Pt] by comparing the m\z from the spectrum to the exact molecular weight of the compound.

Figure 2 Spectrum of mass spectroscopy of [(2, 2'-bipy)[HSNQ]Pt].

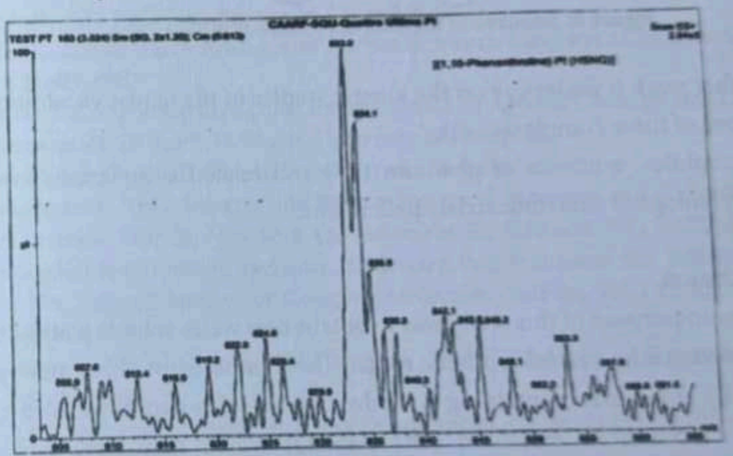


From figure 2 we can observe a sharp signals m\z equal to 807.9 which is the same molecular weight of [(2, 2'- bipy)[HSNQ]Pt]. Also there are other signals appear in the spectrum which represent fragment ions signals that fragment from the original structure.

One more example is the mass spectrum of the complex [(phen)[HSNQ]Pt] we can observe a sharp signals m \z equal to 833 which is the same molecular mass of [(1,10-phenanthroline)[HSNQ]Pt].

Figure 3 shows the mass spectrum of the complex [(phen)[HSNQ]Pt] in the range of 805 – 865 m/z.

Figure 3 Spectrum of mass spectroscopy of [(phen)[HSNQ]Pt]



The elemental analyses of the new complexes were generally in good agreement with theoretical values.

Table 5: Physical Properties of [(HSNQ)PtL$_2$]

Ligand L$_2$	Melting Points(°C)	Yield %	Color	CHN%Calc.(found) C	H	N
PMe$_2$Ph	342-344	92	orange	45.34 (45.28)	3.55 (3.52)	4.52 (4.49)
2,2'-bipyridine	346-348	90	Red	43.07 (43.14)	2.37 (2.41)	8.66 (8.71)
1, 10-phenanthroline	352-354	88	Deep Orange	44.67 (44.58)	2.28 (2.21)	8.41 (8.48)

The I.R, 1H, and 13C, mass spectroscopy and elemental analyses are consistent with complexes of the form shown in Fig (8):

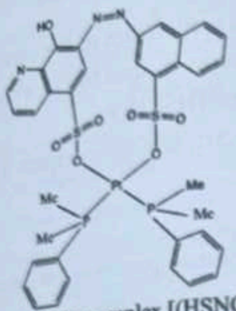


Figure 8: Structure of the complex [(HSNQ)Pt(PMe$_2$Ph)$_2$]

Further work is underway on the kinetic studies of the oxidative addition reactions of these complexes with electrophiles, synthesis of platinum (IV) and related complexes as well as their biological and industrial applications.

Conclusion

The main purpose of this study was to obtain new water soluble platinum (II) complexes using a novel synthetic route. The syntheses of three new platinum(II) complexes containing 8 -hydroxy-7-(4-sulfo-naphthylazo)-5-quinoline sulfonic acid. disodium salt] (HSNQ) which may have biological importance activity have been achieved. The present work describes also the use of phase transfer catalysis as the new method of synthesis.

We have found that using Phase Transfer Catalyst made the reaction faster (increase the reaction rate) and a high yield was obtained (increase in percentage yield) and also decrease the required reaction temperature.

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