Formation of Tin (II) Complexes of Some Macrocyclic Schiff Bases

Kadir ARISOY[1], Ahmet SENER[2],Mehmet TUMER[2]

Abstract: The reaction of benzoine with ethylene or propylene diamines in benzene afforded some new macrocyclic Schiff bases. Some new tin(II) complexes were synthesized by the reaction of the new ligands and tin (II) chloride. Structures of the new macrocycles and their tin(II) complexes were identified based on elemental analyses, ^{1}HNMR and IR.

Key Words: Tin(II) complexes, Schiff bases, benzoine

Bazı Makrosiklik Schiff Bazlarının Kalay-II-Komplekslerinin Oluşumu

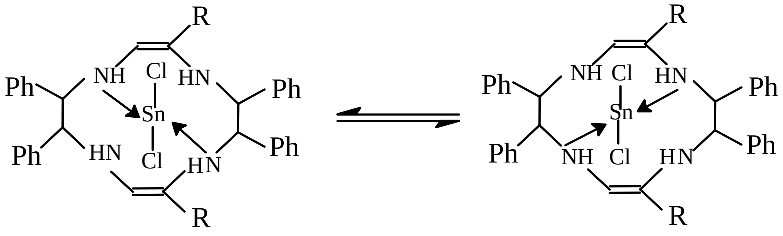
Özet: Benzoinin etilen ve propilendiaminlerle benzende verdiği reaksiyonlar sonucunda ligand olarak kullanılabilecek yeni makrosiklik schiff bazları elde edilir. Bu ligandların kalay -II- klorür ile verdikleri reaksiyon sonucunda yeni kompleksler sentezlendi. Bu komplekslerin yapıları element analizi, ^{1}HNMR, IR ile belirlendi.

Anahtar Kelimeler: Kalay-II-bileşikleri, schiff bazları, benzoin

Introduction

Several papers have been published dealing with tin(II) and tin(IV) adducts of macrocyclic rings such as crown ethers[1-5]. Tin(II) and (IV) complexes of macrocyclic Schiff bases synthesised from benzil were also reported[6]. However no report on the formation of such derivatives from benzoine could be found.

We now wish to report that the formation of macrocyclic rings and their tin(II) complexes from benzoine is also possible.



---

[1] University of Celal Bayar ,Department of Chemistry,Manisa/ TURKEY
[2] University of Yüzüncüyıl ,Department of Chemistry,Van/TURKEY

Experimental

Elemental analysis were carried out by a Perkin Elmer 240 C instrument. IR spectra were recorded on a Matson 1000 FTIR spectrophotometer (4000-400 cm^{-1}) using KBr discs. H-NMR spectra (60 MHz) were run on a Varian spectrometer, in $CDCl_3$

Contents of tin were determined by volumetric analysis (KIO_3 -KI)

All the reactions were carried out under an anhydrous and oxygen-free nitrogen atmosphere. Stannous chloride was dehydrated by dissolving it into acetic anhydride[7].

The ligands (2,3,8,9-tetraphenyl-1,7-diimino-4,10-diaza cyclododeka-3,9-dion and 2,3,8,9-tetraphenyl-5,12-dimethyl-1,7-diimino-4,10-diaza cyclododeka-3,9-dion) were prepared by mixing ethylenediamine(0.60 g, 0.01 mole) or 1,2-propylenediamine (0.74 g, 0.01 mole) with solution of benzoin (2.12 g, 0.01 mole) in benzene (50 mL) in a 1:1 molar ratio. The resulting solution was refluxed for about 3 h on a water-bath and kept overnight. A light yellow crystalline solid precipitated out, which was recrystallized from ethanol. Yield: 2,3,8,9-tetraphenyl-1,7-diimino-4,10-diaza cyclododeka-3,9-dion, % 80, 2.18 g, m.p. 165 ^{o}C,. and 2,3,8,9-tetraphenyl-5,12-dimethyl-1,7-diimino-4,10-diaza cyclododeka-3,9-dion, % 85, 2.43 g , m.p.124 ^{o}C. The ligands were also soluble in CCl_4 , $CHCl_3$,CH_3OH, DMF and DMSO.

To synthesise the complexes, a weighed amount of tin(II) chloride (0.095g, 0.005 mole was added the calculated amount of ethylenediamine(0.60 g, 0.01 mole) or 1,2-propylenediamine (0.74 g, 0.01 mole) and benzoin (2.12 g, 0.01 mole) in a 1:2:2

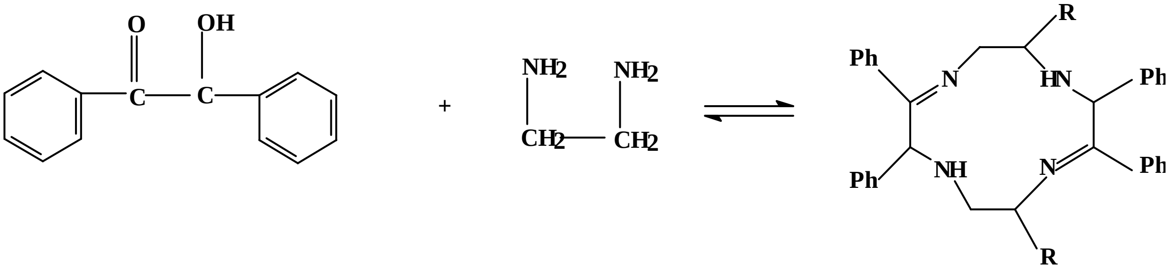
molar ratio, using benzene (100 mL) as the reaction medium. The colour of contents immediately changed from light yellow to dark yellow. The solution was stirred and refluxed using a magnetic stirrer for ca. 3 h. The excess solvent was removed from cooled mixture by decantation and the crude product was finally dried in vacuo at a bath temperature of 60 ± 5 ^{o}C after being repeatedly washed with dry hexane (3 x 25 mL). Yield: 1.69 g, % 60 and 1.92 g, %65)

Amounts of tin(II) in samples were determined by volumetric KIO_3-KI method.

The ligands and complexes were analysed by a Perkin Elmer 240 C model elemental analysis instrument. The IR spectra were recorded on a Matson 1000 FTIR spectrometer in region 4000-400 cm^{-1} using KBr optics. A Varian 60 MHz spectrometer was used for obtaining the PMR spectra employing $CDCl_3$ as solvent and TMS as the internal standard.

Results and Discussion

The equimolar reaction of benzoine with ethylene diamine and propylene diamine gave most probably the macrocyclic ligands, 1,7-diimino-2,3,8,9-tetraphenyl-4,10-diazacyclododeka-3,9-dien (1) and 5,12-dimethyl derivative of 1 (2)respectively.



(1) R: H
(2) R: CH_3

The ligands were soluble in polar and non-polar solvents such as carbontetrachloride, chloroform, methanol, N,N-dimethyl formamide and DMSO. In contrast the tin(II) adducts were normally soluble in polar solvents such as methanol and N,N-dimethyl formamide but insoluble in benzene.

The molecular weigh determinations by the Rast Camphor Method indicate the monomeric nature of the adducts.

The FTIR spectra of the ligands are given in Table 1. The band at 3375 cm^{-1} may be assigned to the imino groups[8]. In the complexes this band splits into two peaks and one of the peaks shifts down to 3020 cm$^{-1,}$, and covers the aromatic and aliphatic C-H bands in this region.

In this study, the macrocyclic schiff bases were synthesized by reactions of diamines with benzoin in 1:1 molar ratio. Reactions of tin(II) chloride with these ligands in 1:1 molar ratio give $SnCl_2$: L type adducts. (L= a macrocyclic schiff base). These adduct are soluble in solvents such as methanol, DMSO, (slightly soluble in $CHCl_3$) but insoluble in benzene.

The molecular weight determinations of the adducts are performed by the Rast Camphor method agree with the formula weight, indicating their monomeric nature.

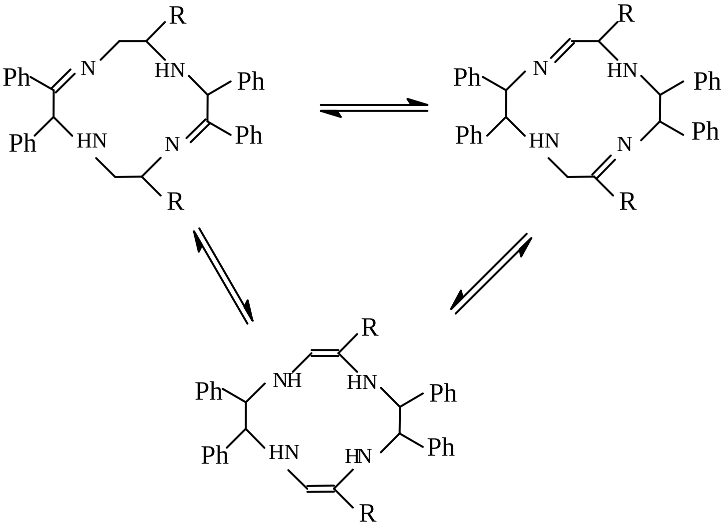
In the FTIR spectra of the ligands a band is observed at ca. 3375 cm^{-1}, which may be assigned to the imino groups[8] This band broadens and splits into two peaks in the complex derivatives. One of these splitted bands undergoes a chemical shift as a result of complex formation and is observed at 3020 cm^{-1}. The other of splitted bands appears at the same frequency. Aromatic and aliphatic C-H bands at the ligands are observed at 2820-3100- cm^{-1}. These bands are shielded the broadened and shifted N-H bands in the complex derivatives (product:). This observation shows that complex has formed in two of four N-H groups in the ligand which is in tautomerised form

Because, the weak intermolecular hydrogen bonding between nitrogen of azometin and hydrogen of imino group have disappeared with complex formation. In this way, N-H band is excluded from co-ordination, and its frequency increase slowly. A new and strong intermolecular hydrogen bonding is formed between chlorine atoms of $SnCl_2$ and hydrogen of imino group , which is occupied in the co-ordination. This hydrogen bonding causes the broadening of the bands arising from imino group.

Ligands have two strong absorption bands at 1550 and 1650 cm^{-1}(because of azometin groups).[9]The bands at 1650 cm^{-1} are not observed in the complex spectra. The band at 1550 cm^{-1} is very weak. The weak bands 1593 cm^{-1} in the ligand spectra are observed strongly in the complex spectra. This indicates co-ordination and tautomerization of the adducts, and co-ordination of ligand through only two nitrogen atoms of equivalent four N-H groups. The new bands around 460 cm^{-1} in the complexes could be assigned to NH-Sn[6].

In the [1] HNMR spectra of the ligands at δ 2.15, 3.75, 4.65, 6, 7-8, and 8.5 ppm have been assigned to methyl, methylene, imino(broad), Ph-CH-N(broad), phenyl and azometin protons, respectively. Signals of methylene, imino and azometin protons disappear in the spectra of complex derivatives and a new weak and broad peak between δ 3.8-4.65 ppm is appeared. (See Table 2)

The complexes have been occurred over tautomeric form. Olefinic structure, which is required for co-ordination is appropriate to spectral data of infrared. On the basis of the evidence given above , the following tentative structures can be assigned to these newly synthesised derivatives:



References

1- Herber R.H., Smelkinson A.E., Inorg. Chem., 17, 1023 (1978)

2- Cusack P.A., Patel B.N., Smith P.J,Inorg. Chim. Acta , 76, 121 (1983)

3- Cusack P.A., Patel B.N., Smith P.J., Allen D.W., Nowell I. J., Chem. Soc. Dalton Trans. , 1239 (1984)

4- Walle G., Casrol A. , Russo U, Inorg. Chim. Acta, 82, 81 (1984)

5. Russo U., Cassol A. , Silvestri A, J.Organomet.Chem., 260, 69 (1984)

6. Varshney A., Tandon J.P, Polyhedron, 5, No:11, pp.1853-1855 (1986)

7. Gull R., Zeldin M, J.Inorg.Nucl.Chem., 37,1133 (1975)

8. Silverstein R.M., Bassler G.C. , Morril T.C. **"Spectrophotometric Identification of Organic Compounds**", Fifth Ed. John Wiley and Sons Inc., New York, pp.123 (1991)

9. Ghose B.N., J.Chem.Eng.Data, 29,237 (1984)

Table 1. The Properties of Tin(II) Complexes of Some Shiff Bases

	Reactives						Analysis					Molecular Weight
Compound			Molar ratio	Yield (%)	Product amp. Formula(colour)	Melting point(°C)	Sn	C	H	N	Cl	calculated
1	Benzoi	Ethylene diamine	1:1	72	$C_{32}H_{32}N_4$ (yellow)	165	-	80.97 (81.32)	7.09 (6.83)	11.98 (11.85)	_	-
2	Benzoi	1,2-propylene diamine	1:1	63	$C_{34}H_{36}N_4$ (yellow)	124	-	81.24 (81.56)	7.35 (7.25)	11.43 (11.19)	_	-
3	SnCl2	C_{32} H_{22} N_4	1:1	80	$SnCl_2.C_{32}H_{32}N_4$ white	216	17.7 (17.9)	58.00 (58.04)	4.79 (4.87)	8.70 (846)	10.85 (10.73)	646(662)
4	SnCl2	C_{34} H_{36} N_4	1:1	68	$SnCl_2.C_{34}H_{36}N_4$ white	185	16.6 (17.2)	58.93 (59.16)	5.52 (5.26)	8.00 (8.12)	10.95 (10.27)	665(690)

Table 2. Spectral Values of Compounds

	FTIR (cm-1)				H-NMR (in $CDCl_3$, ppm)					
Compound No.	γ(NH)	γ(C=N)	γ(C=C)	γ(NH-Sn)	δ(methyl)	δ(methylene)	δ(N-H)	δ(C=CH)	δ(N=CH)	δ(Ph-)
1	3370	1650-1550	1593	-	-	3.75	4.65	6	8.5	7-8
2	3370	1650-1550	1593	-	2.15	3.75	4.65	6	8.5	7-8
3	3385-3018	1550	1593	460	-	3.8-4.65	3.8-4.65	6	-	7-8
4	3385-3000	1440	1593	460	2.15	3.8-4.6	3.8-4.6	6	-	7-8