



Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 8(5), 2013 [141-146]

Synthesis, structural characterization and antimicrobial activity of zirconium (iv) complexes with schiff bases rearranged from benzothiazolines

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ABSTRACT

Zirconium (IV) complexes of the type $[(EtO)_2Zr(Bzt)_2]$ where Bzt = anion of Schiff base of monofunctional bidentate benzothiazoline, have been synthesized by the reaction of zirconium ethoxide with sulfur containing ligands in 1:2 molar ratio using dry benzene as reaction medium. Benzothiazolines are prepared by the reaction of 2-acetylfluorene, 4-acetylbiphenyl, 4-tolualdehyde, 4-fluoroacetophenone, 9-acetylanthracene and 9-anthraldehyde with 2-aminothiophenol which on reaction with metal ion rearranges to Schiff bases. These compounds have been characterized by the elemental analysis, conductance and magnetic measurements. Octahedral geometry of the resulting complexes has been proposed on the basis of UV, IR, 1H , ^{13}C spectral studies. Some of these compounds were screened for antifungal and antibacterial activities to access the potency of the compounds.

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KEYWORDS

Zirconium (IV) complexes;
Benzothiazolines;
2-aminothiophenol;
Antimicrobial activity.

INTRODUCTION

Schiff bases are well known for different types of biological activities^[1]. But much interest has been shown in the synthesis of metal complexes with sulfur containing ligands. The condensation of 2-aminothiophenol with aldehydes/ketones normally does not lead to the formation of Schiff bases but a benzothiazoline is isolated. These benzothiazolines rearranges in Schiff bases in presence of metal ions. It is reported that equilibrium may exist between benzothiazoline and Schiff base even in the absence of metal ions and cyclic form of the benzothiazoline rearranges to give the Schiff base metal complex in presence of metal ion^[2-3].

The sulfur containing ligands and their complexes have become more important due to their wide biologi-

cal activities and it is proved that the existence of metal ions bonded to biologically active ligands can enhance their activity^[4-6]. Metal complexes having such type of ligands are drawing much attention due to their activity against viruses, malaria, tuberculosis cancer and tumor^[7-9].

Zirconium (IV) tetradentate Schiff base (salphen) complex has been successfully used for efficient synthesis of wide variety of indole derivatives in EtOH as a standard green solvent under mild conditions^[10]. The role of ligand effects on the stability and redox properties of the zirconium(IV) complexes have been reported by Al-Mohanna *et al.*^[11]. Therefore the present study was focused on the synthesis of such type of complexes by the reaction of zirconium (IV) ethoxide with some new benzothiazolines.

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EXPERIMENTAL

Analytical methods and Physical measurements

All the reactions were carried out under strictly anhydrous conditions. To attain anhydrous conditions all the apparatus used during the reactions were fitted with quick fit interchangeable standard ground joints. All the chemicals used were of AR grade and obtained commercially which were used without further purification. Solvents were dried by standard methods.

Nitrogen and sulfur were estimated by Kjeldahl and Messengers method respectively^[12-13]. The analysis of Carbon and hydrogen were carried out on a Coleman 5612 analyzer at CDRI, Lucknow and molecular weights were determined by the Rast method. Measurement of molar conductance was carried out in dry DMF at $30 \pm 1^\circ\text{C}$ using a model 305 Systronics digital conductivity bridge. The IR spectra in the range $4000-200\text{ cm}^{-1}$ were recorded on FTIR spectrophotometer using Shimadzu A-8400S model in KBr optics and electronic spectra were recorded with a Toshniwal spectrophotometer using dry methanol as a solvent. A Jeol AL 300 MHz spectrophotometer was used to obtain ^1H and ^{13}C spectra using DMSO-d_6 as a solvent and zirconium was estimated gravimetrically as their oxides.

Synthesis of ligands

Benzothiazolines of 2-acetyl fluorene, 4-acetyl biphenyl, 4-tolualdehyde, 4-fluoro acetophenone, 9-acetyl anthracene and 9-anthraldehyde were prepared by adding ice cold ethanolic solution of 2-aminothiophenol (1 mole) to the precooled ethanolic solution of aldehydes/ketones (1 mole). After stirring the solution the mixture was refluxed for one hour and then allowed to stand overnight at room temperature. The crystalline solid obtained was filtered off, washed with ethanol and dried in vacuum over phosphorous pentoxide. The general structure of benzothiazoline ligands used during the present study is represented in Figure 1. The main physical properties and analysis of these ligands are enlisted in TABLE 1.

Synthesis of complexes

For the synthesis of zirconium (IV) complexes required amount of zirconium ethoxide and benzothiazoline (1:2 molar ratio) was added in dry benzene and refluxed under a fractionating column for about 8 hours. After

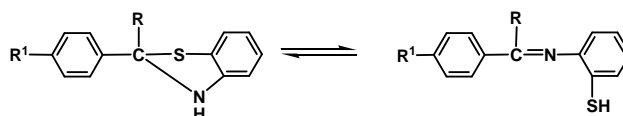


Figure 1: Structure of benzothiazoline

TABLE 1 : Physical properties and Elemental analysis of monofunctional bidentate benzothiazolines

S. No.	Ligands	Colour & State	Yield (%)	M.P. ($^\circ\text{C}$)	Molecular Wt. Found (Calcd.)	Elemental Analysis (%)			
						C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)
1	2-Acetylfluorene benzothiazoline ($\text{C}_{21}\text{H}_{17}\text{NS}$)	Creamy Powdered solid	80	85	309.20 (315.43)	79.90 (79.96)	5.40 (5.43)	4.25 (4.44)	10.10 (10.17)
2	4-Acetylbiphenyl benzothiazoline ($\text{C}_{20}\text{H}_{17}\text{NS}$)	Light yellow powder	75	65	300.10 (303.42)	79.12 (79.17)	5.59 (5.65)	4.60 (4.62)	10.40 (10.57)
3	4-Tolualdehyde benzothiazoline ($\text{C}_{14}\text{H}_{13}\text{NS}$)	Light yellow Powdered Solid	78	135	224.30 (227.32)	73.84 (73.96)	5.70 (5.76)	6.10 (6.16)	14.05 (14.10)
4	4-Fluoroacetophenone benzothiazoline ($\text{C}_{14}\text{H}_{12}\text{FNS}$)	Yellow Crystalline solid	85	130	240.20 (245.31)	68.51 (68.54)	4.85 (4.93)	5.56 (5.70)	13.01 (13.07)
5	9-Acetylanthracene benzothiazoline ($\text{C}_{22}\text{H}_{17}\text{NS}$)	Brown Powdered solid	88	154	315.40 (327.44)	80.60 (80.69)	5.18 (5.23)	4.20 (4.27)	9.70 (9.79)
6	9-Anthraldehyde benzothiazoline ($\text{C}_{21}\text{H}_{15}\text{NS}$)	Dark yellow Crystalline solid	81	81	310.30 (313.41)	80.34 (80.47)	4.75 (4.82)	4.35 (4.46)	10.10 (10.23)

completion of the reaction the excess of solvent was removed under reduced pressure. Complexes formed were washed and dried under vacuum for 2-3 hours and then were purified by recrystallization with same solvent. The purity of complexes was further checked by TLC on silica gel G. The complex formation can be represented

by the following general equation.



Where BztH = Schiff base of monofunctional bidentate benzothiazoline.

The physical properties and analytical data of complexes are given in TABLE 2.

TABLE 2 : Physical properties and elemental analysis of zirconium (IV) complexes with monofunctional bidentate benzothiazolines

S. No.	Reactants		Molar Ratio	Product (Colour & State)	M.P. (°C)	Molecular wt. Found (Calcd.)	Elemental Analysis (%)		
	Zirconium Compound	Ligand					N Found (Calcd.)	S Found (Calcd.)	Zr Found (Calcd.)
1.	Zr(OEt) ₄	C ₂₁ H ₁₇ NS	1:2	(EtO) ₂ Zr(C ₂₁ H ₁₆ NS) ₂ Light Red Crystalline Solid	190	805.12 (810.19)	3.40 (3.46)	7.85 (7.92)	11.30 (11.26)
2.	Zr(OEt) ₄	C ₂₀ H ₁₇ NS	1:2	(EtO) ₂ Zr(C ₂₀ H ₁₆ NS) ₂ Light Brown Solid	145	775.10 (786.17)	3.55 (3.56)	8.20 (8.16)	11.50 (11.60)
3.	Zr(OEt) ₄	C ₁₄ H ₁₃ NS	1:2	(EtO) ₂ Zr(C ₁₄ H ₁₂ NS) ₂ Light Brown Solid	95 (d)	635.40 (633.98)	4.40 (4.42)	10.10 (10.12)	14.21 (14.39)
4.	Zr(OEt) ₄	C ₁₄ H ₁₂ FNS	1:2	(EtO) ₂ Zr(C ₁₄ H ₁₁ NSF) ₂ Light Brown Solid	140	665.00 (669.96)	4.20 (4.18)	9.50 (9.57)	13.75 (13.62)
5.	Zr(OEt) ₄	C ₂₂ H ₁₇ NS	1:2	(EtO) ₂ Zr(C ₂₂ H ₁₆ NS) ₂ Brown Crystalline Solid	165	830.20 (834.21)	3.30 (3.36)	7.85 (7.69)	10.85 (10.94)
6.	Zr(OEt) ₄	C ₂₁ H ₁₅ NS	1:2	(EtO) ₂ Zr(C ₂₁ H ₁₄ NS) ₂ Brown Solid	185	810.10 (806.16)	3.46 (3.47)	7.90 (7.95)	11.25 (11.32)

BIOLOGICALACTIVITY

Antifungal activity

Antifungal activity of some ligands and their corresponding zirconium complexes were screened in vitro against *Aspergillusflavus* and *Fusariumoxysporum* by the linear growth method^[14]. Solutions of the compounds in different concentrations in DMF were mixed with medium. Micostatin was used as reference compound.

The growth^[14] of the fungus colony was recorded by measuring the diameter of the colony after 96 hours and the percentage inhibition was calculated by the formula^[15].

$$\text{Percentage Inhibition} = \frac{100(C - T)}{C}$$

Here C = diameter of the fungus colony in the control

T = diameter of the fungus colony in the test plates.

The data have been given in TABLE 3.

Antibacterial activity

Synthesized ligands and their corresponding zirconium (IV) complexes were tested against gram positive

(*Bacillus thuringiensis*) and gram negative (*Escherichia coli*) bacteria by disc plate method^[16-17]. The nutrient agar medium (beef extract, peptone agar agar and NaCl), 5 mm diameter paper discs and the reference compound (Streptomycin) were used.

The compounds used were dissolved in methanol to prepare different concentration viz. 500 and 1000 ppm. The paper discs were dipped in solutions of compounds, dried and then placed in petri dishes which

TABLE 3 : Antifungal screening data of benzothiazolines and their zirconium(IV) complexes

Compounds	Percent Inhibition after 96h (conc. In ppm)			
	Organism <i>Apergillusflavus</i>		Organism <i>Fusariumoxysporum</i>	
	50 ppm	100 ppm	50 ppm	100 ppm
C ₂₁ H ₁₇ NS (Bzt ₁ H)	38	72	65	70
C ₂₀ H ₁₇ NS (Bzt ₂ H)	55	65	55	58
C ₁₄ H ₁₃ NS (Bzt ₃ H)	50	65	46	66
C ₁₄ H ₁₂ FNS (Bzt ₄ H)	52	60	52	56
Zr(OEt) ₂ (Bzt ₁) ₂	43	75	66	75
Zr(OEt) ₂ (Bzt ₂) ₂	60	68	57	60
Zr(OEt) ₂ (Bzt ₃) ₂	55	70	50	68
Zr(OEt) ₂ (Bzt ₄) ₂	54	67	54	70
Micostatin	69	86	72	82

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were already seeded with test organism. These dishes were incubated for 24h at $28 \pm 2^\circ\text{C}$ and inhibition zone was measured around each disc. The results of antibacterial activity are given in TABLE 4.

TABLE 4 : Antibacterial screening data of benzothiazolines and their zirconium (IV) complexes

Compounds	Diameter (mm) of inhibition zone after 24h (conc. in ppm)			
	Bacillus thuringiensis(+)		Escherichia coli(-)	
	500 ppm	1000 ppm	500 ppm	1000 ppm
C ₂₁ H ₁₇ NS(Bzt ₁ H)	6	6	6	7
C ₂₀ H ₁₇ NS(Bzt ₂ H)	5	5	7	8
C ₁₄ H ₁₃ NS(Bzt ₃ H)	6	6	8	9
C ₁₄ H ₁₂ FNS(Bzt ₄ H)	5	5	7	8
Zr(OEt) ₂ (Bzt ₁) ₂	9	9	11	12
Zr(OEt) ₂ (Bzt ₂) ₂	7	7	12	14
Zr(OEt) ₂ (Bzt ₃) ₂	8	8	10	13
Zr(OEt) ₂ (Bzt ₄) ₂	10	10	12	15
Streptomycin	14	14	17	18

RESULTS AND DISCUSSION

Zirconium (IV) complexes of the type [(EtO)₂Zr(Bzt)₂], where Bzt = anion of Schiff base of monofunctional bidentate benzothiazoline were prepared from zirconium ethoxide and respective benzothiazoline schiff bases (1:2 molar ratio) in refluxing anhydrous benzenewhich proceeds with rearrangement of benzothiazolines ring.



Where BztH = Schiff base of benzothiazoline

The newly synthesized Zr(IV) complexes are colored solid crystals susceptible to hydrolysis and soluble in common organic solvents viz. acetone, chloroform and THF. The complexation occurs by the loss of proton from the ligands. The molecular weight determination shows that these complexes are monomeric and diamagnetic in nature. The lower value of molar conductivity ($\approx 10^{-15} \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of the complexes in DMF shows them to be non electrolytes^[18].

Spectral characterization

Electronic spectra

Two intense bands near 250 nm and 315 nm were observed in the electronic spectra are consistent with the typical spectrum of benzothiazoline (cyclic form) moiety^[19]. These bands may be attributed to the $n-\pi^*$ ^[20]

and $\pi-\pi^*$ benzenoid transitions in the corresponding zirconium complexes, an additional band at about 402-412 nm is also observed which can be assigned to the charge transfer band according to $(n-1) d^0 ns^0$ electronic configuration of zirconium(IV)^[21].

Infrared spectra

The IR spectra of ligands and corresponding zirconium complexes have been obtained and important bands are recorded in TABLE 5. In the IR spectra of the benzothiazolines the -NH stretching and deformation bands appears at 2930-3150 cm^{-1} and absence of $\nu(>\text{C}=\text{N})$ band at 1620-1600, and $\nu(\text{SH})$ at about 2500-2600 cm^{-1} is indicative of the existence of benzothiazoline ring structure rather than the Schiff base structure^[22]. In the spectra of metal derivatives, the $\nu(\text{NH})$ band disappears, which suggests the deprotonation of the ligands on chelation and a new band at $1600 \pm 10 \text{ cm}^{-1}$ is also observed which may be ascribed to the coordinated $>\text{C}=\text{N}$ group and supports the fact that the complexes formed are metal azomethine derivatives, as the benzothiazoline ring rearranges to give the azomethine form in presence of metal ion and act as a monobasic bidentate ligand. The medium to strong intensity bands in the region 510-530 cm^{-1} and 350-330 cm^{-1} in zirconium complexes may be assigned to $\nu(\text{Zr}-\text{N})$ and $\nu(\text{Zr}-\text{S})$ vibrations respectively.

TABLE 5 : IR spectral data (in cm^{-1}) of the ligands and their metal complexes

Compound	$\nu(\text{N}-\text{H})$	$\nu(>\text{C}=\text{N}-)$	$\nu(\text{Zr}-\text{N})$	$\nu(\text{Zr}-\text{S})$
C ₂₁ H ₁₇ NS(Bzt ₁ H)	2930	-	-	-
Zr(OEt) ₂ (Bzt ₁) ₂	-	1601	515	350
C ₂₀ H ₁₇ NS(Bzt ₂ H)	2950	-	-	-
Zr(OEt) ₂ (Bzt ₂) ₂	-	1595	520	345
C ₁₄ H ₁₃ NS(Bzt ₃ H)	3150	-	-	-
Zr(OEt) ₂ (Bzt ₃) ₂	-	1590	510	330
C ₁₄ H ₁₂ FNS(Bzt ₄ H)	3100	-	-	-
Zr(OEt) ₂ (Bzt ₄) ₂	-	1595	530	340

¹H NMR spectra

To confirm the bonding pattern in the complexes proton magnetic resonance spectra of the ligands and their metal complexes were recorded in DMSO-d₆ using TMS as internal reference. The ¹H NMR spectra of the free benzothiazolines shows the N-H proton signal at $\delta 4.50$ to $\delta 5.20$ ppm which disappears on complexation indicates the deprotonation of the functional group^[23]. The presence of benzothiazoline ring in the

ligands are supported by the absence of SH signals. Free ligands show a complex multiplet in the region

TABLE 6 : ¹H NMR chemical shifts (δ ppm) of the ligands and their metal complexes

Compound	NH	Aromatic protons (m)	O-CH ₂ -CH ₃
Bzt ₁ H(C ₂₁ H ₁₇ NS)	4.55	6.40-8.70	-
Zr(OEt) ₂ (Bzt ₁) ₂	-	6.50-7.80	1.50s
Bzt ₂ H(C ₂₀ H ₁₇ NS)	4.50	6.44-7.20	-
Zr(OEt) ₂ (Bzt ₂) ₂	-	6.70-8.15	1.55s
Bzt ₃ H(C ₁₄ H ₁₃ NS)	4.60	6.70-8.20	-
Zr(OEt) ₂ (Bzt ₃) ₂	-	6.50-8.40	1.52s
Bzt ₄ H(C ₁₄ H ₁₂ FNS)	5.20	6.50-8.00	-
Zr(OEt) ₂ (Bzt ₄) ₂	-	6.75-8.60	1.60s
Bzt ₅ H(C ₂₂ H ₁₇ NS)	4.80	6.75-8.10	-
Zr(OEt) ₂ (Bzt ₅) ₂	-	6.70-8.00	1.58s
Bzt ₆ H(C ₂₁ H ₁₅ NS)	5.10	6.65-8.30	-
Zr(OEt) ₂ (Bzt ₆) ₂	-	6.60-8.25	1.56s

6.40-8.70 ppm for the aromatic protons and it remains at almost same position in the spectra of the complexes. The spectra of complexes shows proton signal at 1.50-

1.60 ppm due to methyl protons of the ethyl groups (TABLE 6).

¹³C NMR spectra

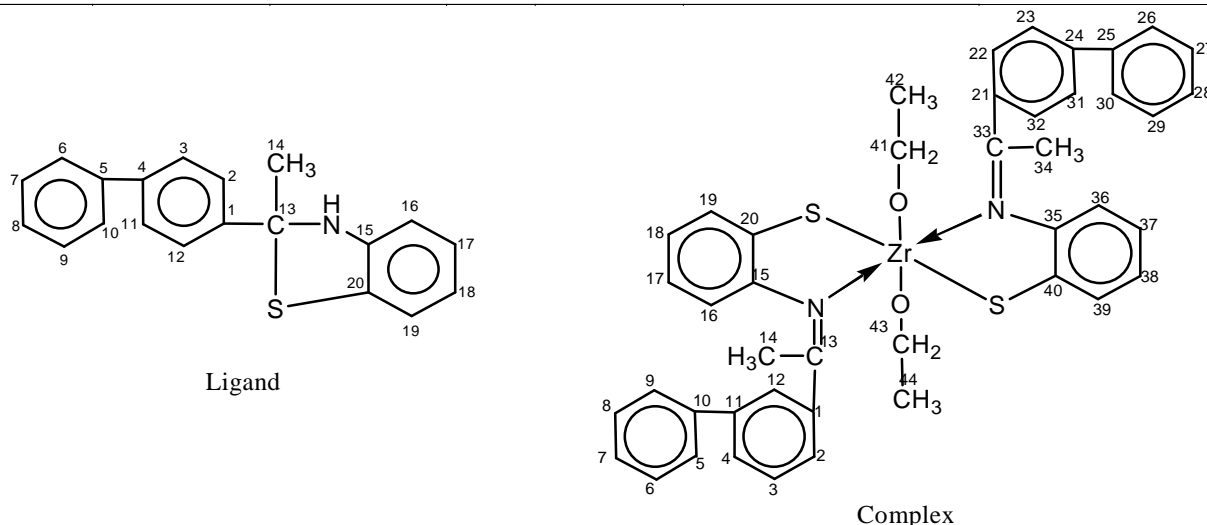
The ¹³C NMR spectra of one ligand and their corresponding zirconium complex have been recorded in dry DMSO and given in TABLE 7. The shifts in the signals of carbon atom attached to nitrogen and sulphur indicates their coordination with the zirconium atom. Thus on the basis of above spectral data the following structure is suggested for the zirconium (IV) complex with benzothiazoline.

Antimicrobial activity

The antimicrobial activity of few ligands and their metal derivatives under investigation have been screened which are given TABLE 3 and 4. The results reveal that ligands and complexes have found to be active in inhibiting the growth of fungi even at lower concentration. The inhibi-

TABLE 7: ¹³C NMR chemical shift of the ligand and their metal complex

Ligand	C ₁ /C ₂	C ₃ /C ₄	C ₅ /C ₆	C ₇ /C ₈	C ₉ /C ₁₀
		139.9/128.4	127.4/135.4	136.8/127.4	129.0/127.4
Complex	C ₁₁ /C ₁₂	C ₁₃ /C ₁₄	C ₁₅ /C ₁₆	C ₁₇ /C ₁₈	C ₁₉ /C ₂₀
	127.4/128.4	66.1/32/8	141.4/112.5	125.6/117.0	127.4/119.2
Complex	C ₁ /C ₂	C ₃ /C ₄	C ₅ /C ₆	C ₇ /C ₈	C ₉ /C ₁₀
	129.2/127.2	129.2/127.4	127.0/129.2	127.1/129.1	127.2/136.2
	C ₁₁ /C ₁₂	C ₁₃ /C ₁₄	C ₁₅ /C ₁₆	C ₁₇ /C ₁₈	C ₁₉ /C ₂₀
	137.1/128.0	154.0/18.0	129.0/129.2	125.1/127.1	127.0/132.0
	C ₂₁ /C ₂₂	C ₂₃ /C ₂₄	C ₂₅ /C ₂₆	C ₂₇ /C ₂₈	C ₂₉ /C ₃₀
	127.2/129.0	127.2/137.4	136.2/127.1	129.1/127.1	127.2/127.2
Complex	C ₃₁ /C ₃₂	C ₃₃ /C ₃₄	C ₃₅ /C ₃₆	C ₃₇ /C ₃₈	C ₃₉ /C ₄₀
	129.1/128.0	154.0/18.0	129.7/128.2	125.1/129.1	129.1/132.4
	C ₄₁ /C ₄₂	C ₄₃ /C ₄₄			
	35.2/16.4	35.1/16.2			

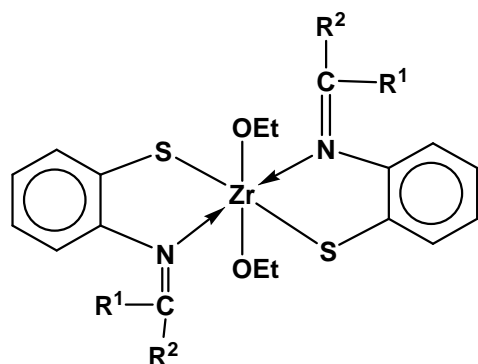


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tion of growth was dependent on the concentration of the compounds^[24]. The results shows that zirconium (IV) complexes were active against gram positive and gram negative bacteria^[25] and complexes were found to be more active than Schiff bases which indicates that metallation increases the activity.

CONCLUSION

Octahedral geometry have been proposed for zirconium (IV) complexes (Figure 2) on the basis of various spectral studies (electronic, IR, ¹H NMR and ¹³C NMR).



where, R = H, CH₃

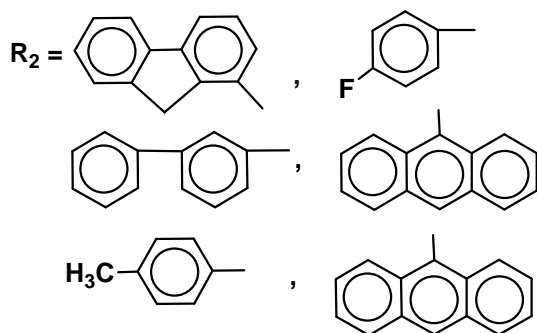


Figure 2 : Proposed structure of the 1:2 complexes

ACKNOWLEDGEMENT

The authors are thankful to the Head, Deptt. Of Chemistry and Deptt. Of Botany, UOR jaipur for providing laboratory facilities. Monika gupta is thankful to CSIR, New Delhi for providing financial assistance.

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