Journal Homepage: - www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH (IJAR)

Article DOI: 10.21474/IJAR01/15395
DOI URL: http://dx.doi.org/10.21474/IJAR01/15395

ISSN NO. 2320-5407

RESEARCH ARTICLE

SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF BIS(CYCLOPENTADIENYL)- ZIRCONIUM(IV) DERIVATIVES WITH QUINAZOLINONE SCHIFF BASES

Anjali Upadhaya, Om Prakash Pandey and Soumitra Kumar Sengupta

Manuscript Info

Manuscript History
Received: 18 July 2022
Final Accepted: 20 August 2022
Published: September 2022

Abstract

Zirconium(IV) complexes of types [(C5H5)2Zr(L)] and [(C5H5)Zr(L')Cl] (LH2 represents Schiff bases derived from quinazolinone and salycylaldehye or o-hydroxyacetophenone; L' H represents Schiff bases derived from quinazolinone and 4-fluorobenzaldehyde/ 4-fluoro acetophenone /1-(2-fluoro-4-methylphenyl)-2-methylpropan-1-one / 1-(2-fluoro-4-methylphenyl) propan-1-one) have been synthesized by the reactions of bis(cyclopentadienyl)zirconium(IV) dichloride with appropriate ligands in tetrahydrofuran in the presence of triethylamine. All these complexes are soluble in THF, PhNO2, DMF and DMSO. The complexes were characterized by elemental analyses, electrical conductance, magnetic susceptibility, IR, 1H NMR, XRD and SEM spectral techniques. Low molar conductance values indicate non-electrolytic nature of the complexes. The spectral data indicate 5-coordinate geometry for the complexes. XRD pattern evince that the complexes have monoclinic crystal system and particle sizes were found in the range 46.40-49.30 nm (nano-size). In vitro antifungal activity of synthesized compounds was evaluated against fungi Aspergillus niger, Aspergillus fumigatus, Candida albicans and In vitro antibacterial activity was determined by screening the compounds against gram negative (P. aeruginosa, E.coli) and gram positive (S. aureus and B. subtilis) bacterial strains using minimum inhibition concentration method (MIC) by serial dilution technique. The zirconocene(IV) complexes have higher antimicrobial impact than the parent Schiff bases.

Introduction:-

Table 1:- Reactions of bis(cyclopentadienyl)(IV)zirconium(IV) chloride with Quinanzolinone Schiff bases

Corresponding Author:- Anjali Upadhaya

Reactants	Molar Ratio	Stirring\ Reflux time (h)	Solvent	Product	Colour	Yield (%)	Decomp. temp (^{0}C)
Cp_2ZrCl_2 + HBPQ-H_2+ Et_3N	1:1:2	15	THF	[Cp_2Zr(HBPQ)]	Light yellow	68	190
Cp_2ZrCl_2 + HPPQ-H_2+ Et_3N	1:1:2	15	THF	[Cp_2Zr(HPPQ)]	Light yellow	65	140
Cp_2ZrCl_2 + FBPQ-H + Et_3N	1:1:1	15	THF	[Cp_2Zr(FBPQ)Cl]	Brown	65	140
Cp_2ZrCl_2 + FEPQ-H + Et_3N	1:1:1	15	THF	[Cp_2Zr(FEPQ)Cl]	Light yellow	65	135
Cp_2ZrCl_2+ FMPQ-H + Et_3 Cp_2ZrCl_2+ FPPQ-H + Et_3N	1:1:1 1:1:1	15 15	THF THF	[Cp_2Zr(FMPQ)Cl] [Cp_2Zr(FPPQ)Cl]	Light yellow Brown	58 67	168 158

HBPQ-H_2 = Schiff base derived from quinazolinone and salicylaldehyde
HPPQ-H_2 =Schiff base derived from quinazolinone and 2-hydroxyacetophenone
FBPQ-H = Schiff base derived from quinazolinone and 2-fluorobenzaldehyde
FEPQ-H = Schiff base derived from quinazolinone and1-(2-fluoro-4-methylphenyl)butan-1-one
FMPQ-H = Schiff base derived from quinazolinone and 4-fluoroacetophenone
FPPQ-H = Schiff base derived from quinazolinone and 1-(2-fluoro-4-methylphenyl)propan-1-one

Table 2 : Analytical data of zirconium(IV) complexes with Quinazolinone Schiff bases

Complex	**Molecular Formula**	**Elemental Analysis % Found (Calculated)**			
		C	**H**	**N**	**Zr**
[Cp_2Zr(HBPQ)]	$C_{31}H_{24}N_4O_2Zr$	64.22(64.67)	4.01(4.20)	9.45(9.73)	15.65(15.84)
[Cp_2Zr(HPPQ)]	$C_{32}H_{26}N_4O_2Zr$	65.01(65.17)	4.12(4.44)	9.23(9.50)	15.25(15.47)
[Cp_2Zr(FBPQ)Cl]	$C_{31}H_{24}N_4OFZrCl$	60.04(60.62)	3.59(3.94)	8.87(9.12)	14.25(14.85)
[Cp_2Zr(FEPQ)Cl]	$C_{32}H_{26}N_4OFZrCl$	61.02(61.18)	4.01(4.17)	8.54(8.92)	14.23(14.52)
[Cp_2Zr(FMPQ)Cl]	$C_{35}H_{22}N_4OFZrCl$	56.07(62.71)	4.09(4.81)	8.12(8.36)	13.22(13.61)
[Cp_2Zr(FPPQ)Cl]	$C_{34}H_{30}N_4OFZrCl$	62.12(62.22)	4.12 (4.61)	8.18(8.54)	13.35(13.90)

Table 3:- Infrared spectral bands of bis(cyclopentadienyl)zirconium(IV) derivatives.

Complex		**IR Spectra (cm^{-1})**				
	ν(C=N)$_{ring}$	**ν(C=N)**	**ν(C-O)**	**ν(Zr-O)**	**ν(Zr-N)**	**ν(Zr-N)**
$C_{31}H_{24}N_4O_2Zr$	1598	1577	1258	535	454	433
$C_{32}H_{26}N_4O_2Zr$	1604	1580	1260	530	455	435
$C_{31}H_{24}N_4OFZrCl$	1594	1574	1257	536	452	434
$C_{32}H_{26}N_4OFZrCl$	1593	1576	1260	532	450	430
$C_{35}H_{22}N_4OFZrCl$	1601	1581	1256	525	456	438

Table 4:- NMR data (□ , ppm) of zirconium(IV)derivatives with quinazolinone Schiff bases.

Complex	δ, ppm						
	N=C-CH$_3$	-C-CH$_3$ /-CH$_2$-	Ar-CH$_3$	-CH- / CH$_2$-CH$_3$	η^5-C$_5$H$_5$	Ar-H	=CH-
$C_{31}H_{24}N_4O_2Zr$	-	-	-	-	6.85 (s, 10H)	7.16-7.98(m, 13H)	8.61 (s, 1H)
$C_{32}H_{26}N_4O_2Zr$	1.52 (s, 3H)	-	-	-	6.88 (s, 10H)	7.27-7.58(m, 13H)	-
$C_{31}H_{24}N_4OFZrCl$	-	-	-	-	6.80 (s, 10H)	7.26-7.66(m, 13H)	8.68 (s, 1H)
$C_{32}H_{26}N_4OFZrCl$	1.55 (s, 3H)	-	-	-	6.76 (s, 10H)	7.34-7.61 (m, 13H)	-
$C_{35}H_{22}N_4OFZrCl$	-	1.35(d, 6H)	2.36(s,3H)	1.59(sep,1H)	6.82 (s, 10H)	7.42-7.90 (m, 12H)	-
$C_{34}H_{30}N_4OFZrCl$	-	1.58(q, 2H)	2.34(s,3H)	1.21 (t, 3H)	6.87 (s, 10H)	7.47-7.92 (m, 12H)	-

Table 5:- The unit cell parameters, observed and calculated X-Ray diffraction data of organozirconium(IV) complex $[(C_5H_5)_2Zr(C_{21}H_{14}N_4O_2)]$.

S.No.	a =8.26811, b= 9.97733, c= 8.59658, V =694.4696, β=101.683							
	d(obs)	d(cal)	Δd	I/I$_M$X100	2T.obs	2T.calc	Δ2T	h k l
1	6.437	6.434	0.00370	70.03	13.744	13.752	-0.008	0 1 1
2	5.478	5.466	0.01176	20.13	16.167	16.202	-0.0035	-1 1 1
3	4.995	4.988	0.00728	20.57	17.739	17.765	-0.026	0 2 0
4	4.275	4.291	-0.0160	100	20.758	20.679	0.079	0 2 1
5	3.747	3.751	-0.0039	31.77	23.724	23.699	0.025	-2 1 0
6	3.647	3.639	0.0077	33.30	24.384	24.437	-0.053	1 2 1
7	3.458	3.459	-0.0000	24.46	25.735	25.734	0.001	1 0 2
8	3.216	3.217	-0.0007	20.97	27.714	27.707	0.007	0 2 2

Table 6:- Antifungal activities of Bis(cyclopentadienyl)zirconium(IV)complexes with Schiff bases of quinazolinone.

Complex	MICs (μg/mL)			
	C. albicans	A.niger	A. fumigatus	A. Flavus
[Cp$_2$Zr(HBPQ)]	25	25	50	25
[Cp$_2$Zr(HPPQ)]	25	25	12.5	25
[Cp$_2$Zr(FBPQ)Cl]	6.25	12.5	12.5	12.5
[Cp$_2$Zr(FEPQ)Cl]	12.5	12.5	6.25	12.5
[Cp$_2$Zr(FMPQ)Cl]	6.25	12.5	12.5	25
[Cp$_2$Zr(FPPQ)Cl]	12.5	6.25	25	25
Ketoconazole	12.5	6.25	6.25	6.25

Table 7:- Antbacterial activities of Bis(cyclopentadienyl)zirconium(IV)complexes with Schiff bases of quinazolinone.

Complex	MICs (μg/mL)			
	E. coli	P. aeruginosa	S. aureus	B. subtilis
[Cp$_2$Zr(HBPQ)]	25	12.5	12.5	25
[Cp$_2$Zr(HPPQ)]	12.5	12.5	12.5	6.25
[Cp$_2$Zr(FBPQ)Cl]	6.25	6.25	6.25	12.5
[Cp$_2$Zr(FEPQ)Cl]	12.5	6.25	25	12.5
[Cp$_2$Zr(FMPQ)Cl]	25	25	12.5	25

[$Cp_2Zr(FPPQ)Cl$]	12.5	12.5	25	12.5
Ciprofloxacin	6.25	6.25	12.5	6.25