Research Article

Synthesis of New Zirconium(IV) Complexes with Amino Acid Schiff Bases: Spectral, Molecular Modeling, and Fluorescence Studies

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New zirconium(IV) complexes were synthesized with bidentate ligands and characterized by elemental analysis, molar conductance measurements, molecular weight determinations, IR, electronic, NMR (^1H and ^{13}C), fluorescence and molecular modeling studies. All the complexes are 1:2 electrolytes in nature and may be formulated as $[\text{Zr}(\text{L})_2\text{Cl}_2]$ (where L is Schiff bases of amino acids and substituted isatin). The analytical data showed that the Schiff-base ligand acts as bidentate toward zirconium ion via the azomethine nitrogen and carboxylate oxygen. The conductivity values between $8.5\text{--}12.6\ \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ in DMF imply the presence of nonelectrolyte species. On the basis of spectral and molecular modeling studies, the resulting complexes are proposed to have octahedral geometries.

1. Introduction

The coordination chemistry of Schiff bases has been widely explored, though its use in supramolecular coordination chemistry remains largely unexplored. The Schiff-base moiety is potentially ambidentate and can coordinate through nitrogen with either oxygen or sulfur atoms. The vast literature on structural studies of Schiff-base complexes reveals some interesting features of their coordination behavior [1–6]. Schiff-base metal chelates have played a central role in the development of coordination chemistry. Metal complexes with Schiff-base ligands have been receiving considerable attention due to the pharmacological properties of both ligands and complexes [7–10]. Schiff-base derivatives exhibit a great variety of biological activities, such as antitumor [11, 12], antifungal [13, 14], antibacterial [15, 16], anticonvulsant [17] and antiviral [18] properties. The interest in the construction of Schiff-base coordination complexes by reacting transition metal ions with bidentate has been constantly growing over the past years [19–21]. Within this understanding lies an increased knowledge of molecular self-assembly, metal-ligand complexation, and disposition of metal binding sites.

By mastering these areas, new improved systems related to the fields of catalysis, supramolecular chemistry, and bioengineering can be achieved. Although the chemistry of zirconium complexes has been extensively studied, particularly in relation to their application as polymerization catalysts, the coordination chemistry of these oxophilic metals has concentrated on the use of oxygen donors. Many researchers have conducted on Schiff-base complexes; most of these complexes were found to be biologically active [22–25] as there has been considerable interest in the study of first-row transition metal Schiff-base complexes. However, relatively less work has appeared on the complexes of 2nd and 3rd rows transition metal ions. There is not much information on zirconium(IV) complexes from the available literature; therefore this paper reports the synthesis and characterization of zirconium(IV) complexes of Schiff bases derived from amino acids and isatins.

2. Experimental

2.1. Starting Materials. All chemicals used in the present work, 1H-indole-2,3-dione, 5-chloro-1H-indole-2,3-dione,

TABLE 1: Various Bond Lengths of Compound $[\text{Zr}(\text{L}^4)_2\text{Cl}_2]$.

S. No.	Atoms	Actual (Å)	Optimal (Å)
1	Zr(4)-N(3)	2.1381	
2	C(41)-H(66)	1.1131	1.113
3	C(41)-H(65)	1.1126	1.113
4	C(39)-H(64)	1.1137	1.113
5	C(39)-H(63)	1.1153	1.113
6	C(38)-H(62)	1.1125	1.113
7	C(38)-H(61)	1.1135	1.113
8	C(38)-H(60)	1.1127	1.113
9	C(36)-H(59)	1.1132	1.113
10	C(36)-H(58)	1.1141	1.113
11	C(35)-H(57)	1.1142	1.113
12	C(35)-H(56)	1.1132	1.113
13	C(34)-H(55)	1.0939	1.1
14	C(33)-H(54)	1.1023	1.1
15	C(32)-H(53)	1.1023	1.1
16	C(31)-H(52)	1.1016	1.1
17	N(27)-H(51)	1.0444	1.05
18	C(25)-H(50)	1.1159	1.113
19	C(25)-H(49)	1.1146	1.113
20	C(24)-H(48)	1.1012	1.1
21	C(23)-H(47)	1.1061	1.1
22	C(22)-H(46)	1.1049	1.1
23	C(21)-H(45)	1.1012	1.1
24	N(17)-H(44)	1.0446	1.05
25	C(8)-H(43)	1.1138	1.113
26	C(2)-H(42)	1.1165	1.113
27	S(40)-C(41)	1.8167	1.815
28	C(39)-S(40)	1.8236	1.815
29	C(25)-C(39)	1.5388	1.523
30	S(37)-C(38)	1.8142	1.815
31	C(36)-S(37)	1.8255	1.815
32	C(35)-C(36)	1.5393	1.523
33	N(9)-Zr(4)	2.1345	
34	Zr(4)-O(5)	2.0916	
35	C(2)-C(35)	1.5486	1.523
36	C(34)-C(29)	1.4014	1.42
37	C(33)-C(34)	1.3978	1.42
38	C(32)-C(33)	1.3994	1.42
39	C(31)-C(32)	1.3929	1.42
40	C(28)-C(31)	1.3971	1.42
41	C(26)-O(30)	1.2293	1.208
42	C(29)-C(15)	1.4774	1.503
43	C(28)-C(29)	1.4077	1.42
44	N(27)-C(28)	1.3928	1.462
45	C(26)-N(27)	1.3678	1.462
46	C(15)-C(26)	1.5141	1.517
47	C(8)-C(25)	1.5398	1.523
48	C(24)-C(19)	1.4832	1.42
49	C(23)-C(24)	1.5134	1.42
50	C(22)-C(23)	1.5149	1.42
51	C(21)-C(22)	1.5092	1.42

TABLE 1: Continued.

S. No.	Atoms	Actual (Å)	Optimal (Å)
52	C(18)-C(21)	1.4845	1.42
53	C(16)-O(20)	1.3098	1.208
54	C(19)-C(14)	1.5193	1.503
55	C(18)-C(19)	1.374	1.42
56	N(17)-C(18)	1.3476	1.462
57	C(16)-N(17)	1.3903	1.462
58	C(14)-C(16)	1.5503	1.517
59	N(3)-C(15)	1.2988	1.26
60	N(9)-C(14)	2.1882	1.26
61	C(1)-O(13)	1.2142	1.208
62	C(7)-O(12)	1.2117	1.208
63	Zr(4)-Cl(11)	2.4423	
64	Zr(4)-Cl(10)	2.4453	
65	C(8)-N(9)	1.4968	1.47
66	C(7)-C(8)	1.5279	1.509
67	O(6)-C(7)	1.3594	1.338
68	C(41)-H(67)	1.1129	1.113
69	O(5)-C(1)	1.3551	1.338
70	Zr(4)-O(6)	2.0914	
71	C(2)-N(3)	1.5032	1.47
72	C(1)-C(2)	1.5292	1.509

FIGURE 1: Emission spectra of the ligand (L^3H).

amino acids (glycine, alanine, valine, methionine, phenylalanine, and tryptophan), and oxozirconium(IV) chloride, were of analytical grade. The ligands were prepared by the condensation of isatins with amino acids as described earlier [9, 26].

2.2. Analytical Procedures. Solvents used were dried and purified by standard methods and moisture was excluded from the glass apparatus using CaCl_2 drying tubes. The melting points of the compounds were determined on a capillary melting point apparatus and were not corrected. The purity of the compounds was confirmed by thin layer chromatography using silica gel-G glass plates as the stationary phase and

TABLE 2: Various Bond Angles of Compound $[\text{Zr}(\text{L}^4)_2\text{Cl}_2]$.

S. No.	Atoms	Actual (°)	Optimal (°)
1	H(67)-C(41)-H(66)	109.418	109
2	H(67)-C(41)-H(65)	108.9614	109
3	H(67)-C(41)-S(40)	110.3566	109.3
4	H(66)-C(41)-H(65)	108.7912	109
5	H(66)-C(41)-S(40)	109.9408	109.3
6	H(65)-C(41)-S(40)	109.3437	109.3
7	C(41)-S(40)-C(39)	97.5564	96.3
8	H(64)-C(39)-H(63)	107.5686	109.4
9	H(64)-C(39)-S(40)	110.1883	112
10	H(64)-C(39)-C(25)	110.4229	109.41
11	H(63)-C(39)-S(40)	109.8119	112
12	H(63)-C(39)-C(25)	109.1207	109.41
13	S(40)-C(39)-C(25)	109.6938	106.5
14	H(62)-C(38)-H(61)	109.6623	109
15	H(62)-C(38)-H(60)	109.0937	109
16	H(62)-C(38)-S(37)	110.3571	109.3
17	H(61)-C(38)-H(60)	108.6879	109
18	H(61)-C(38)-S(37)	110.0128	109.3
19	H(60)-C(38)-S(37)	108.9946	109.3
20	C(38)-S(37)-C(36)	98.533	96.3
21	H(59)-C(36)-H(58)	107.1198	109.4
22	H(59)-C(36)-S(37)	110.417	112
23	H(59)-C(36)-C(35)	109.5515	109.41
24	H(58)-C(36)-S(37)	110.7645	112
25	H(58)-C(36)-C(35)	110.8347	109.41
26	S(37)-C(36)-C(35)	108.1586	106.5
27	H(57)-C(35)-H(56)	104.9845	109.4
28	H(57)-C(35)-C(36)	108.6578	109.41
29	H(57)-C(35)-C(2)	110.8409	109.41
30	H(56)-C(35)-C(36)	108.9072	109.41
31	H(56)-C(35)-C(2)	109.5018	109.41
32	C(36)-C(35)-C(2)	113.5779	109.5
33	H(55)-C(34)-C(29)	122.3033	120
34	H(55)-C(34)-C(33)	117.5306	120
35	C(29)-C(34)-C(33)	120.1661	
36	H(54)-C(33)-C(34)	119.6447	120
37	H(54)-C(33)-C(32)	119.4129	120
38	C(34)-C(33)-C(32)	120.9424	
39	H(53)-C(32)-C(33)	119.7786	120
40	H(53)-C(32)-C(31)	120.1954	120
41	C(33)-C(32)-C(31)	119.9868	
42	H(52)-C(31)-C(32)	121.1904	120
43	H(52)-C(31)-C(28)	120.678	120
44	C(32)-C(31)-C(28)	118.1313	
45	C(34)-C(29)-C(15)	134.3781	120
46	C(34)-C(29)-C(28)	117.1629	120
47	C(15)-C(29)-C(28)	108.4549	120
48	C(31)-C(28)-C(29)	123.0239	120
49	C(31)-C(28)-N(27)	126.8775	120
50	C(29)-C(28)-N(27)	110.0936	120
51	H(51)-N(27)-C(28)	126.0741	118

TABLE 2: Continued.

S. No.	Atoms	Actual (°)	Optimal (°)
52	H(51)-N(27)-C(26)	125.3088	118
53	C(28)-N(27)-C(26)	108.5425	
54	O(30)-C(26)-N(27)	120.8581	122.6
55	O(30)-C(26)-C(15)	129.2063	123
56	N(27)-C(26)-C(15)	109.9356	122
57	H(50)-C(25)-H(49)	106.678	109.4
58	H(50)-C(25)-C(39)	108.7135	109.41
59	H(50)-C(25)-C(8)	108.393	109.41
60	H(49)-C(25)-C(39)	111.2794	109.41
61	H(49)-C(25)-C(8)	109.454	109.41
62	C(39)-C(25)-C(8)	112.1296	109.5
63	H(48)-C(24)-C(19)	117.3341	120
64	H(48)-C(24)-C(23)	117.009	120
65	C(19)-C(24)-C(23)	119.9311	
66	H(47)-C(23)-C(24)	113.9434	120
67	H(47)-C(23)-C(22)	114.0848	120
68	C(24)-C(23)-C(22)	118.3693	
69	H(46)-C(22)-C(23)	115.8207	120
70	H(46)-C(22)-C(21)	115.0649	120
71	C(23)-C(22)-C(21)	118.1479	
72	H(45)-C(21)-C(22)	119.4891	120
73	H(45)-C(21)-C(18)	118.9569	120
74	C(22)-C(21)-C(18)	118.0658	
75	C(24)-C(19)-C(14)	124.1732	120
76	C(24)-C(19)-C(18)	120.434	120
77	C(14)-C(19)-C(18)	114.4563	120
78	C(21)-C(18)-C(19)	123.9331	120
79	C(21)-C(18)-N(17)	126.1831	120
80	C(19)-C(18)-N(17)	109.7946	120
81	H(44)-N(17)-C(18)	126.029	118
82	H(44)-N(17)-C(16)	126.0518	118
83	C(18)-N(17)-C(16)	107.8705	
84	O(20)-C(16)-N(17)	122.4042	122.6
85	O(20)-C(16)-C(14)	123.6108	123
86	N(17)-C(16)-C(14)	113.7879	122
87	C(29)-C(15)-C(26)	101.2183	117.6
88	C(29)-C(15)-N(3)	129.5068	120
89	C(26)-C(15)-N(3)	129.128	120
90	C(19)-C(14)-C(16)	93.7144	117.6
91	C(19)-C(14)-N(9)	101.1826	120
92	C(16)-C(14)-N(9)	103.5499	120
93	Zr(4)-N(9)-C(14)	104.5285	
94	Zr(4)-N(9)-C(8)	111.1129	
95	C(14)-N(9)-C(8)	111.1476	
96	H(43)-C(8)-C(25)	108.1727	109.39
97	H(43)-C(8)-N(9)	109.7641	107.5
98	H(43)-C(8)-C(7)	106.4941	107.9
99	C(25)-C(8)-N(9)	111.9987	
100	C(25)-C(8)-C(7)	113.8847	109.9
101	N(9)-C(8)-C(7)	106.3523	
102	O(12)-C(7)-C(8)	125.0648	122.5

TABLE 2: Continued.

S. No.	Atoms	Actual (°)	Optimal (°)
103	O(12)-C(7)-O(6)	124.6366	122
104	C(8)-C(7)-O(6)	110.2827	107.1
105	Zr(4)-O(6)-C(7)	111.3282	
106	Zr(4)-O(5)-C(1)	114.0377	
107	N(3)-Zr(4)-O(5)	80.1135	
108	N(3)-Zr(4)-O(6)	128.6218	
109	N(3)-Zr(4)-N(9)	149.0865	
110	N(3)-Zr(4)-Cl(11)	88.0663	
111	N(3)-Zr(4)-Cl(10)	84.2757	
112	O(5)-Zr(4)-O(6)	148.2304	
113	O(5)-Zr(4)-N(9)	78.2701	
114	O(5)-Zr(4)-Cl(11)	85.1672	
115	O(5)-Zr(4)-Cl(10)	116.7647	
116	O(6)-Zr(4)-N(9)	78.9572	
117	O(6)-Zr(4)-Cl(11)	82.9908	
118	O(6)-Zr(4)-Cl(10)	83.2655	
119	N(9)-Zr(4)-Cl(11)	111.6987	
120	N(9)-Zr(4)-Cl(10)	86.0092	
121	Cl(11)-Zr(4)-Cl(10)	154.9219	
122	Zr(4)-N(3)-C(15)	121.0647	
123	Zr(4)-N(3)-C(2)	107.937	
124	C(15)-N(3)-C(2)	120.234	
125	H(42)-C(2)-C(35)	110.432	109.39
126	H(42)-C(2)-N(3)	106.5807	107.5
127	H(42)-C(2)-C(1)	102.9891	107.9
128	C(35)-C(2)-N(3)	118.1743	
129	C(35)-C(2)-C(1)	109.8863	109.9
130	N(3)-C(2)-C(1)	107.6576	
131	O(13)-C(1)-O(5)	124.3628	122
132	O(13)-C(1)-C(2)	123.8243	122.5
133	O(5)-C(1)-C(2)	111.734	107.1

FIGURE 2: Emission spectra of the $\text{Zr}(\text{L}^3)_2\text{Cl}_2$ complex.

benzene and ethanol (9:1) as the mobile phase. Zirconium was determined gravimetrically as its oxide, ZrO_2 . Nitrogen and sulfur were determined by Kjeldahl's and Messenger's methods, respectively. Molecular weight determinations were carried out by the Rast camphor method.

2.3. Physical Measurements. The IR spectra of samples in KBr pellets were recorded on an FTIR spectrophotometer model SP-2, Perkin Elmer in the range of $4000\text{--}400\text{ cm}^{-1}$. The electronic spectra of the ligands and their metal complexes were recorded in dry DMSO, on a thermo-, double-beam spectrophotometer UV 1, in the range of $800\text{--}200\text{ nm}$. The fluorescence studies of Schiff base and its metal complexes were recorded on Shimadzu RF-5301PC spectrophotometer. The molar conductance of the complexes was measured on 10^{-3} M DMF solutions using Systronics conductivity bridge model 305. ^1H and ^{13}C NMR spectra were recorded on Bruker avance II (400 MHz) FTNMR spectrometer at the SAIF, Punjab University, Chandigarh, using $\text{DMSO-}d_6$ as the solvent and tetramethylsilane (TMS) as an internal standard.

2.4. Molecular Modeling Studies. The molecular modeling of a representative compound is carried out on a CS Chem 3D ultramolecular modeling and analysis programme, interactive graphics programme that enables rapid structure building and geometry optimization with minimum energy and molecular display.

2.5. Preparation of Zirconium Complexes. The complexes were prepared by treating oxozirconium(IV) chloride (1.61 mmol) in methanol with the corresponding Schiff bases (3.22 mmol) in the same solvent. The mixture was refluxed for three hours on a water bath after which the crystals of the complex separate out on cooling; the mixture was concentrated on a steam bath until about one-third of the solution remained. The concentrated solution was cooled after which the crystals were filtered, washed with methanol, and then dried in vacuum at $45 \pm 5^\circ\text{C}$ after repeated washing with dry cyclohexane. The compounds were purified by recrystallization from the same solvent. The purity of the compounds was checked by TLC using silica gel G as adsorbent.

Compound $\text{Zr}(\text{L}^1)_2\text{Cl}_2$ was prepared by reacting zirconium(IV) dichloride with ligand (L^1H); colour, red; yield, 0.218 g; mp, 170°C (d) and elemental analysis (%), calcd. for $\text{C}_{20}\text{H}_{14}\text{Cl}_2\text{N}_4\text{O}_6\text{Zr}$: C, 42.26; H, 2.48; N, 9.86; found, C: 42.33; H, 2.57; N, 9.81; molecular weight: found, 580.12, calcd. 568.48. Molar conductance (DMF , 10^{-3} , Ω^{-1} , molL^{-1} , cm^2): 10.8; ^1H NMR ($\text{DMSO-}d_6$, δ ppm, 400 MHz): 4.28 (s, 2H, $\text{N-CH}_2\text{-}$), 8.06 (s, 1H, NH), 7.18–7.78 (m, 4H, aromatic); ^{13}C NMR (DMSO , δ ppm): 186.3 (COO), 52.1 ($\text{-CH}_2\text{-}$), 153.8 (C=N), 167.3 (C=O), 148.65, 131.2, 129.9, 125.3, 122.7, 119.5 (aromatic carbons); UV-visible (λ_{max} , nm): 220, 260, 320, 370; infrared (KBr, cm^{-1}): $\nu(\text{C=N})$, 1610; $\nu(\text{C=O})$, 1722; $\nu_{\text{asym}}(\text{COO})$, 1595; $\nu_{\text{sym}}(\text{COO})$, 1325; $\nu(\text{Zr} \leftarrow \text{N})$, 535; $\nu(\text{Zr-O})$, 465.

Compound $\text{Zr}(\text{L}^2)_2\text{Cl}_2$ was prepared by reacting zirconium(IV) dichloride with ligand (L^2H); colour, reddish

brown; yield, 0.317 g; mp, 200°C (d) and elemental analysis (%), calcd. for $C_{22}H_{18}Cl_2N_4O_6Zr$: C, 44.30; H, 3.04; N, 9.39; found, C, 44.46; H, 3.10; N, 9.33; molecular weight: found, 590.68, calcd. 596.53. Molar conductance (DMF, 10^{-3} , Ω^{-1} , $molL^{-1}$, cm^2): 11.5; 1H NMR (DMSO- d_6 , δ ppm, 400 MHz): 4.70 (q, 1H, N-CH-); 8.32 (s, 1H, NH); 1.50 (d, 3H, C-CH₃); 7.00–7.86 (m, 4H, aromatic); ^{13}C NMR (DMSO, δ ppm): 180.7 (COO), 63.6 (–CH–), 150.2 (C=N), 159.6 (C=O), 1502.7, 138.3, 133.6, 131.7, 130.5, 129.3, 124.9, 121.1 (aromatic carbons); UV-visible (λ_{max} , nm): 220, 260, 320, 370; infrared (KBr, cm^{-1}): ν (C=N), 1617; ν (C=O), 1728; ν_{asym} (COO), 1585; ν_{sym} (COO), 1322; ν (Zr ← N), 537; ν (Zr–O), 460.

Compound Zr(L³)₂Cl₂ was prepared by reacting zirconium(IV) dichloride with ligand (L³H); colour, brown; yield, 0.179 g; mp, 144°C (d) and elemental analysis (%), calcd. for $C_{26}H_{26}Cl_2N_4O_6Zr$: C, 47.85; H, 4.02; N, 8.58; found, C, 47.89; H, 4.14; N, 8.54; molecular weight: found, 640.96, calcd. 652.64. Molar conductance (DMF, 10^{-3} , Ω^{-1} , $molL^{-1}$, cm^2): 8.5; 1H NMR (DMSO- d_6 , δ ppm, 400 MHz): 4.26 (d, 1H, N-CH-); 8.40 (s, 1H, NH); 2.16–2.30 (m, 1H, –CH–); 1.22 (d, 3H, –CH₃) 7.11–7.65 (m, 4H, aromatic); ^{13}C NMR (DMSO, δ ppm): 183.1 (COO), 67.5 (–CH–), 18.4 (–CH₃), 152.5 (C=N), 161.2 (C=O), 150.68, 140.7, 132.85, 131.5, 131.3, 129.4, 123.7, 121.2 (aromatic carbons); UV-visible (λ_{max} , nm): 220, 260, 320, 370; infrared (KBr, cm^{-1}): ν (C=N), 1616; ν (C=O), 1725; ν_{asym} (COO), 1588; ν_{sym} (COO), 1322; (Zr ← N), 530; ν (Zr–O), 462.

Compound Zr(L⁴)₂Cl₂ was prepared by reacting zirconium(IV) dichloride with ligand (L⁴H); colour, reddish brown; yield, 0.120 g; mp, 160°C (d) and elemental analysis (%), calcd. for $C_{26}H_{26}Cl_2N_4O_6S_2Zr$: C, 43.57; H, 3.66; N, 7.82; found, C, 43.15; H, 3.70; N, 7.70; molecular weight: found, 723.11, calcd. 716.77. Molar conductance (DMF, 10^{-3} , Ω^{-1} , $molL^{-1}$, cm^2): 12.2; 1H NMR (DMSO- d_6 , δ ppm, 400 MHz): 4.62 (t, 1H, N-CH-), 2.20–2.30 (m, 4H, –CH₂–), 1.56 (s, 3H, –CH₃), 8.00 (s, 1H, NH), 7.10–7.72 (m, 4H, aromatic); ^{13}C NMR (DMSO, δ ppm): 185.6 (COO); 62.3 (CH); 26.8, 30.2 (CH₂); 17.9 (CH₃); 153.7 (C=N); 158.1 (C=O); 144.86, 136.2, 132.5, 128.24, 122.6, 117.3 (aromatic carbons); UV-visible (λ_{max} , nm): 218, 260, 378; infrared (KBr, cm^{-1}): ν (C=N), 1608; ν (C=O), 1722, ν (NH), 3130, ν_{asym} (COO), 1582; ν_{sym} (COO), 1310; ν (Zr ← N), 542; ν (Zr–O), 468.

Compound Zr(L⁵)₂Cl₂ was prepared by reacting zirconium(IV) dichloride with ligand (L⁵H); colour, brown; yield, 0.194 g; mp, 254°C (d) and elemental analysis (%), calcd. for $C_{22}H_{16}Cl_4N_4O_6Zr$: C, 39.71; H, 2.42; N, 8.42; found, C, 39.56; H, 2.40; N, 8.34; molecular weight: found, 660.29, calcd. 665.42. Molar conductance (DMF, 10^{-3} , Ω^{-1} , $molL^{-1}$, cm^2): 11.9; 1H NMR (DMSO- d_6 , δ ppm, 400 MHz): 4.15 (q, 1H, N-CH-); 1.40 (d, 3H, –CH₃); 8.00 (s, 1H, NH), 7.02–7.60 (m, 3H, aromatic); UV-visible (λ_{max} , nm): 220, 260, 320, 370; infrared (KBr, cm^{-1}): ν (C=N), 1612; ν (C=O), 1720; ν_{asym} (COO), 1585; ν_{sym} (COO), 1315; ν (Zr ← N), 530; ν (Zr–O), 460.

Compound Zr(L⁶)₂Cl₂ was prepared by reacting zirconium(IV) dichloride with ligand (L⁶H); colour, brown; yield, 0.203 g; mp, 180°C (d) and elemental analysis (%), calcd. for $C_{26}H_{24}Cl_4N_4O_6Zr$: C, 43.28; H, 3.35; N, 7.77; found, C,

42.97; H, 3.41; N, 7.62; molecular weight: found, 708.58, calcd. 721.53. Molar conductance (DMF, 10^{-3} , Ω^{-1} , $molL^{-1}$, cm^2): 10.6; 1H NMR (DMSO- d_6 , δ ppm, 400 MHz): 4.00 (t, 1H, N-CH-); 2.25–2.28 (m, 1H, –CH₂–); 8.40 (s, 1H, NH), 7.01–7.70 (m, 3H, aromatic); UV-visible (λ_{max} , nm): 220, 260, 320, 370; infrared (KBr, cm^{-1}): ν (C=N), 1615; ν (C=O), 1722; ν_{asym} (COO), 1590; ν_{sym} (COO), 1320; ν (Zr ← N), 538; ν (Zr–O), 466.

Compound Zr(L⁷)₂Cl₂ was prepared by reacting zirconium(IV) dichloride with ligand (L⁷H); colour, brown; yield, 0.332 g; mp, 210°C (d) and elemental analysis (%), calcd. for $C_{34}H_{26}Cl_2N_4O_6Zr$: C, 54.54; H, 3.50; N, 7.48; found, C, 54.44; H, 3.55; N, 7.54; molecular weight: found, 755.64, calcd. 748.72. Molar conductance (DMF, 10^{-3} , Ω^{-1} , $molL^{-1}$, cm^2): 12.6; 1H NMR (DMSO- d_6 , δ ppm, 400 MHz): 4.26 (t, 1H, N-CH-CH₂–), 3.06 (d, 2H, –CH₂–Ph), 8.00 (s, 1H, NH), 7.12–7.80 (m, 9H, aromatic); ^{13}C NMR (DMSO, δ ppm): 185.8 (COO), 66.7 (–CH–), 38.3 (–CH₂–), 15.9 (C=N), 166.4 (C=O), 149.6, 135.7, 133.1, 128.5, 127.6, 126.3, 124.5, 122.7, 120.8 (aromatic carbons); UV-visible (λ_{max} , nm): 220, 260, 320, 370; infrared (KBr, cm^{-1}): ν (C=N), 1609; ν (C=O), 1725; ν_{asym} (COO), 1585; ν_{sym} (COO), 1320; ν (Zr ← N), 540; ν (Zr–O), 460.

Compound Zr(L⁸)₂Cl₂ was prepared by reacting zirconium(IV) dichloride with ligand (L⁸H); colour, dark brown; yield, 0.127 g; mp, 218°C (d) and elemental analysis (%), calcd. for $C_{38}H_{28}Cl_2N_6O_6Zr$: C, 55.20; H, 3.41; N, 10.16; found, C, 55.03; H, 3.36; N, 10.21; molecular weight: found, 821.15, calcd. 826.80. Molar conductance (DMF, 10^{-3} , Ω^{-1} , $molL^{-1}$, cm^2): 12.4; 1H NMR (DMSO- d_6 , δ ppm, 400 MHz): 4.36 (t, 1H, N-CH-CH₂–); 3.22 (d, 2H, –CH₂–); 8.06 (s, 1H, NH), 6.98–7.76 (m, 9H, aromatic); UV-visible (λ_{max} , nm): 220, 260, 320, 370; infrared (KBr, cm^{-1}): ν (C=N), 1614; ν (C=O), 1726; ν_{asym} (COO), 1594; ν_{sym} (COO), 1318; ν (Zr ← N), 535; ν (Zr–O), 470.

3. Results and Discussion

The reactions of zirconium(IV) dichloride with the monofunctional bidentate Schiff bases were carried out in dry methanol in 1 : 2 stoichiometric ratios and can be represented by the equation in Scheme 1.

All these compounds are coloured solids, insoluble in common organic solvents and soluble in DMSO, DMF, CHCl₃, MeOH, and so forth and insoluble in n-hexane and petroleum ether. The conductivity values for the $Zr(L)_2Cl_2$ complexes (in DMF, 10^{-3} molL, 25°C), ranging in the 8.5–12.6 Ω^{-1} , $molL^{-1}$, cm^2 region, indicate that the nonelectrolytic nature of the compounds suggests that the anions are covalently bonded. The molecular weight determination by the Rast camphor method shows that the products are monomeric in nature.

3.1. IR Spectra. The IR absorption frequencies for the ligands and their zirconium complexes were recorded in the range 4000–400 cm^{-1} . The assignment of important infrared data for ligand and complexes are listed in experimental section.

SCHEME 1: Representative equation illustrating the formation of Schiff bases and their zirconium(IV) complexes.

A strong band (due to the azomethine group) at 1620–1635 cm^{-1} in the spectra of the free ligands [27, 28] is shifted to lower wavenumber in the complexes studied, showing the coordination of azomethine nitrogen to the metal atom [26, 29]. The coordination of azomethine nitrogen to the metal atom is supported by the appearance of a new absorption band at 535 cm^{-1} , which may be assigned to $\nu(\text{Zr} \leftarrow \text{N})$ vibrations [30].

The infrared spectra of all the zirconium complexes do not show the strong band in the region 3105–2740 cm^{-1}

due to $\nu(\text{COOH})$, indicating the deprotonation of the carboxylate group of the Schiff bases with zirconium metal as expected. It is further confirmed by the appearance of sharp band at 465 cm^{-1} in the spectra of all the complexes assignable to the $\nu(\text{Zr}-\text{O})$ stretching vibrations [31]. In the spectra of the complexes two sharp bands are observed at 1590 and 1320 cm^{-1} and are assigned to the $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$, respectively. Furthermore, the separation between asymmetric and symmetric vibrations is about 270 cm^{-1} , indicating the covalent nature of the metal-oxygen

FIGURE 3: (a) HOMO orbitals of the MM2 geometry-optimized structure of the ligand (L^4H). (b) LUMO orbitals of the MM2 geometry-optimized structure of the ligand (L^4H).

FIGURE 4: 3D molecular structure of $Zr(L^4)_2Cl_2$.

bond as unidentate manner. Ionic bonding and also bridging or chelation can therefore be excluded. Sandhu and Verma in their studies and reports have shown that the $\Delta\nu$ value of complexes greater by $65\text{--}90\text{ cm}^{-1}$ than in their sodium salts indicates either asymmetric or monodentate bonding of the carboxylate group to metal atom [32]. Moreover, $\Delta\nu$ values of complexes below 200 cm^{-1} would be expected for bridging or chelating carboxylates, but greater than 200 cm^{-1} for the monodentate bonding carboxylate anions [33]. The $C=O$ band of the indole group appears in the range of $1720\text{--}1740\text{ cm}^{-1}$ in the ligands. However, a strong band at 1740 cm^{-1} due to the vibration of $C=O$ group remains unchanged in the spectra of complexes showing thereby the noninvolvement of

this group in coordination and thus confirms that the $C=O$ from indole is not involved in the complexation.

3.2. Electronic Spectra. The electronic spectra of Schiff bases and its zirconium complexes have been recorded in methanol. In spectrum of the ligand, three bands are observed at 280, 300, and 380 nm. The bands at 280 and 300 nm are due to the $\pi\text{--}\pi^*$ transitions within the aromatic ring and remain almost unchanged in the spectra of zirconium complexes. Another band at 380 nm is due to the $n\text{--}\pi^*$ transitions within the $>C=N\text{--}$ chromophore and shows a bathochromic shift in the spectra of zirconium complexes due to the coordination of azomethine nitrogen to the zirconium atom. This band shifts slightly to the higher-energy region in the spectra of zirconium complexes due to the polarization within the $>C=N$ chromophore caused by the zirconium-ligand electron interaction.

3.3. 1H NMR Spectra. The characteristic resonance peaks for the synthesized compounds have been recorded in $DMSO\text{-}d_6$ and data are given in experimental section. The expected resonances are assigned by their peak multiplicity, intensity patterns, and integration. The 1H NMR spectral data of the ligands show single resonance at $\delta\ 11.4 \pm 0.10$ ppm, which is absent in the spectra of the metal complexes, indicating the replacement of the carboxylic acid proton by the $Zr(IV)$ moiety. The ligands give a complex multiplet signal in the region $\delta\ 7.20\text{--}7.82$ ppm for the aromatic protons and these remain almost at the same position in the spectra of the metal complexes. The appearance of signals due to NH protons at the same positions in the ligand and its complexes shows the non-involvement of this group in coordination.

Schiff bases derived from glycine, alanine, valine, and methionine display four/three aromatic protons, as expected. In the spectrum of phenylalanine, the integral of the aromatic

region corresponds to nine protons; five protons on the phenyl ring are recognizable at 7.4 ppm. Methylene (for glycine, alanine, valine, and methionine) protons on the α -carbon of the carboxylic acid moieties appear at 3.96–4.30 ppm. This signal is a singlet for (1), a doublet for (3) and (6), a triplet for (7) and (8), and a quartet for (2) and (5) all of which arise from the nonequivalent methylene protons in structures (1–8). In general, the complexes obtained were found to exhibit no additional resonances and thus reflect the purity of the complexes. The integration of peaks concurs with the number of protons postulated from the structures proposed for the complexes.

3.4. ^{13}C NMR Spectra. The ^{13}C NMR spectral data for ligands and their corresponding metal complexes have been recorded in experimental part. Evidence of the formation of the complexes is clearly displayed in the ^{13}C NMR spectra. The ^{13}C NMR spectra of complexes showed that the $\delta(\text{COO})$ signal shifted to the downfield region which is lower compared to that of the ligand (176.1–178.5 ppm) indicating the carboxylate anion is bonded to zirconium atom upon complexation. The signals due to the carbon atom attached to the azomethine group in the ligands appear at δ 162.3 $\pm$ 0.90 ppm. However, in the spectra of the corresponding metal complexes, these appear at $\sim\delta$ 154.2 ppm. The considerable shifts in the resonance of the carbon atom attached to nitrogen indicate the involvement of azomethine nitrogen atom of coordination. The occurrence of eight resonances in the range of δ 118.3–150.7 ppm in the ^{13}C NMR spectra of the complexes and ligands is defined as aromatic carbons signals. Generally, the ^{13}C NMR spectra of the complexes obtained were found to exhibit no additional resonances and thus reflected the purity of the complexes.

Though, it is also possible that the shifting of azomethine carbon is due to the change in hybridization of nitrogen attached to carboxylate group, but in the light of IR, UV, and ^1H NMR spectral studies it seems more plausible that the shifting in these carbons is due to the involvement of carboxylate oxygen and azomethine nitrogen in bonding.

3.5. Fluorescence Spectral Studies. Metal-ligand coordination may lead to significant changes of the fluorescence properties of the ligand, including increase of the intensity, shift of the emission wavelength, appearance of new emissions, or quenching of the fluorescence. The fluorescence spectra of the Schiff base HL^1 and HL^3 and their metal complexes were recorded in DMF with excitation wavelength 380 nm at room temperature (298 K). The fluorescence emission spectrum of HL^1 with its metal complexes is depicted in Figures 1 and 2. HL^1 exhibits a strong fluorescence emission at 430 nm; in contrast with this partial fluorescence quenching phenomena are observed in its metal complexes with weak fluorescence emission at 432 nm for zirconium(IV). HL^3 shows strong fluorescence band at 435 nm and its Zr(IV) complexes exhibit weak emission bands at 436 nm, respectively. The maximum emission wavelength of Schiff bases is red-shifted about 10–20 nm owing to the formation of complex, which may be tentatively assigned to the ligand to metal charge transfer

(LMCT). It is evident from the fluorescence spectra that fluorescence emission intensity of Schiff bases decreased dramatically on complex formation with transition metal ions. The decrease in fluorescence intensity with formation of metal complexes is due to decrease in electron density on Schiff bases [34, 35]. All these fluorescent emissions may be assigned to the intraligand fluorescence since the free ligand exhibited a similar emission at 430 and 435 nm, respectively, under the same condition.

3.6. Molecular Modeling and Analysis. The ligand (L^4H) has 50 filled molecular orbitals, and the orbitals of the HOMO and LUMO levels are shown in Figures 3(a) and 3(b). Notice that the HOMO orbitals are concentrated on the oxygen and nitrogen atoms while the LUMO orbitals are concentrated on the carbons of the indole rings. The HOMO and LUMO energy was found to be -8.268 eV and -4.368 eV. All the synthesized compounds have hexa-coordination and distorted octahedral geometry. Molecular modeling was performed for $[\text{ZrCl}_2(\text{L}^4)_2]$, as representative compound. Tables 1 and 2 list selected interatomic distances and bond angles. The structure of the complex with atomic numbering scheme is shown in Figure 4. The complex consists of two units of ligand molecule with metal ion Zr(IV) . The complex is of six coordinates with distorted octahedral environment around the metal ion. The metal ion Zr(IV) is coordinated to one azomethine nitrogen atom and one carboxylate oxygen atom of Schiff-base ligand and Cl ion. The Zr-O and Zr-N bond lengths are 2.092 Å and 2.138 Å, respectively, and the bond distance between Zr-Cl is 2.444 Å. The two chloride groups are equidistant from Zr (2.44 Å) and complete the coordination sphere of Zr. The Cl-Zr-Cl angles are 154.92° . The O-Zr-N , N-Zr-N , and O-Zr-O angles are 80.11 , 149.08 , and 148.23° , respectively, for both the Schiff-base ligands. These angles and distances are in good agreement with the X-ray structure of a similar zirconium complex [36]. The Zr-Cl distances for the metal bound chloride groups are also similar in both complexes and are comparable with reported zirconium compounds [37].

In all, 205 measurements of the bond lengths (72 in numbers) plus the bond angles (133 in numbers) are listed. Except for a few cases, optimum values of both the bond lengths and the bond angles are given in the tables, with the actual values. The actual bond lengths/bond angles given in Tables 1 and 2 are calculated values as a result of energy optimization in Chem3D Ultra, and the optimum bond length/bond angle values are the standard bond lengths/bond angles established by the builder unit of CHEM 3D. Some values of standard bond lengths/bond angles are missing, possibly because of limitations of the software; we have already noticed this when modeling other systems. In most cases, the actual bond lengths and bond angles are close to the optimum values, confirming the proposed structure of the compound $[\text{Zr}(\text{L}^4)_2\text{Cl}]$.

4. Conclusion

New Schiff bases and their zirconium complexes have been successfully synthesized. Elemental analysis data obtained

are in good agreement with the predicted formula. Distorted octahedral geometries have been proposed for Zr(IV) complexes with the help of various physicochemical studies. The infrared spectra of these complexes show the presence of monofunctional and bidentate ligands. The Schiff base exhibits a strong fluorescence emission; in contrast with this partial fluorescence quenching phenomena is observed in its metal complexes. The proposed structures of metal complexes are presented in Figure 4. The ^1H NMR spectra showed that the calculated number of protons for each functional group in the complexes is equal to the number predicted from the molecular formula. Moreover, the ^1H and ^{13}C NMR spectra of the complexes obtained were found to exhibit no additional resonances and thus reflected the purity of the metal complexes.

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