New Cerium (III) Complex of Schiff Base (E)-N-Benzylidene-4-Methoxyaniline: Synthesis and Density Functional Theoretical Study of Vibrational Spectra

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ABSTRACT

Complex of cerium (III) with (E)-N-benzylidene-4-methoxyaniline is synthesized through a one-pot three-component reaction from aromatic aldehyde, aromatic amine and the $CeCl_3 \cdot 7 H_2O$, as an efficient catalyst. This cerium (III) complex is characterized by IR, 1H, and 13C NMR-spectroscopy and mass-spectral data. Molecular structure, Mullikan charges, thermodynamic parameters; vibrational frequencies and intensities were calculated by Density Functional theory methods (B3LYP, B3PW91, mPW1PW91 and PBEPBE) using the SDD basis set. The comparison between the calculated and experimental data in order to attain the best quality and to predict the structure, the best performance in the vibration spectra perfected of the title compound, we have found that the harmonic vibration computed are in a good agreement with the observed in IR spectrum, for closest match we calculated optimal scaling factors can recommend for the IR spectral future predictions for unknown compounds of this class. In order to better comparison, we also root mean square values of the experimental and calculated IR bands are 16.64, 16.64, 17.45, 17.66 and the mean absolute percentage error values are 1.33, 1.39, 1.40, and 1.5 for B3LYP, B3PW91, mPW1PW91, and PBEPBE methods respectively.

Keywords: imine complexed, CeCl3, DFT, vibrational frequencies.

INTRODUCTION

Schiff bases[1–7] and their metal complexes represent one of the most areas of material science, catalysis and chemical research[8–21]. The efficiency of these compounds often enhanced upon coordination to a metal has been proven for the drug action acceleration of therapeutic agents[22–26] and for

multi-compounds reaction where these complexes are used as intermediates. Recently, extensive research has surrounded the synthesis of lanthanide complexes and precisely the cerium (III) complexes using cerium (III) heptahydrate (CeCl$_3$ · 7 H$_2$O)[27].

This compounds are prepared by a reaction of a primary amine with an aldehyde and CeCl$_3$ • 7 H$_2$O as a catalyst (Figure 1).   In this present work a cerium (III) complex of new Schiff base (E)-N-benzylidene-4- methoxyaniline noted (P2-CeCl$_3$) has been synthesized and characterized by elemental analysis, IR, NMR and Mass spectral data[28–32].

To our best knowledge no structural data and detailed interpretation of the vibrational spectra of the title compound are mentioned in the literature, this prompted us to look into the vibrational spectroscopy of this molecule more carefully. Therefore, this theoretical study aimed to determine molecular and chemical properties of (P2-CeCl$_3$).

An comprehensive theoretical study carried out for predict the optimized geometric parameters, the Mullikan charges, thermodynamic parameters and vibrational frequencies, involving the cerium (III). The Stuttgrat Dresden (SDD) effective core potential[33,34] basis set was used with four DFT methods including B3LYP, B3PW91, mPW1PW91 and PBEPBE methods. For a comparative performance of these four different DFT methods, commit to the detailed theoretical and experimental investigation of the vibrational spectra of this molecule[35].

So, a detailed interpretation of the vibrational spectra of the title compound has been made, in continuation of our theoretical studies, in the present work, we checked the relative performance of B3LYP, B3PW91, mPW1PW91 and PBEPBE methods at the SDD level taking the title compound as a test compound.

EXPERIMENTAL

In this work, we have found CeCl$_3$ • 7 H$_2$O as an efficient catalyst for the synthesis of the imine complexed with CeCl$_3$ noted (P2-CeCl$_3$) at room temperature through a one-pot reaction of aromatic aldehydes, and aromatic amines in methanol. It is also noteworthy to mention that our environmentally benign reaction does not generate any toxic waste products. A possible mechanism for the formation of the complex proposed by Mazaahir Kidwai et al[21] is shown in Figure 1.

Instrumental Analysis

All reagents used for the synthesis of the compound are commercially available and were used without further purification. IR spectra were recorded on a Shimadzu FTIR-8400 S spectrophotometer as KBr pellets in the frequency range 4000-400 cm^{-1}. 1H NMR and 13C NMR spectra were recorded on Nuclear magnetic resonance spectrometer type "AVANCE 300MHz de BRUKER " . Mass spectra (MS) were obtained by using electrospray ionization (ESI) technique.

Preparation of P2-CeCl$_3$

Benzaldehyde (1 mmol) and para-methoxyaniline (1mmol) in MeOH (5 mL), were mixed and stirred at room temperature. To this, CeCl3 · 7 H$_2$O (cerium chloride heptahydrate) (3 mol%) was added. The progress of reaction mixture was monitored by TLC (using petroleum ether/AcOEt = 80:20 as an eluent). After completion of the reaction, the reaction mixture was evaporated under reduced pressure to give the powder product. The predicted structure of the product is shown in Figure 2, it was unambiguously established on the basis of their spectral analysis (IR, 1H, 13C NMR and MS mass spectral data).

Characterization

P2-CeCl$_3$:(E)-N-benzylidene-4-methoxyaniline CeCl$_3$, C14H13 NO-CeCl$_3$: Yield: 96 % , RMN ^{1}H (CDCl$_3$) δppm: 8.47 (s, 1H, =CH); 7.90 " 7.23 (m, 5H, -C2H5); 6.95"6.59 (m, 5H, O–C2H5)); 3.82 (s, 3H, CH3). RMN^{13}C (CDCl3) äppm: 158.42 (O-CH); 131.05 (=CH-C-CCH); 128.75 (=CH-C-CH); 122.22(O-C-C-CH); 114.77 (O-C-CH); 55.50 (CH3). SM: [M+] (m/z) = 457.73, found: 459.47.

Computational details

In addition to the experimental study, we have used molecular orbital calculations to locate the most stable candidate structure, evaluate the accuracy of the geometries, provide the initial molecule model for structure solutions and investigate spectral properties of the studied complex. The DFT calculation of this com- pound (P2-

CeCl3) were performed using GAUSSVIEW 5.08 molecular visualization program and the Gaussian 09 program package[33]. For calculations, involving the cerium (III), the Stuttgrat Dresden(SDD) effective core potential[34] basis set was used with the B3LYP, B3PW91, mPW1PW91 and PBEPBE methods, the vibrational frequencies were also calculated with these methods.

In the fitting processes performed to correct over estimations at the calculated harmonic frequencies, the values computed at these levels contain known systematic errors and therefore, scaling factors 0.9534, 0.9477, 0.9429 and 0.9795 for B3LYP, B3PW91, mPW1PW9,PBEPBE, respectively[34]. We have also calculated optimal scaling factors for all investigated methods. After this procedure, no imaginary mode was observed.

RESULTS AND DISCUSSION

The prediction of vibrational wave numbers was done at DFT (B3LYP, B3PW91, mPW1PW91, PBEPBE) levels with SDD basis set, as it has been well recognized as an efficient theoretical chemistry tool for studying vibrational properties of variety of molecule, positive wave numbers for each normal mode confirm the stability of the molecular structure obtained with minimum energy. As already known, the wave numbers calculated are almost systematically over estimated compared to the experimentally measured values, these differences are widely corrected by scaling the calculated values with factors corresponding to the methods used. The complex study has 33 atoms, which possess 93 normal mode of vibration where the Gaussview 5.08 package has been considered to get visual animation and also for verification of these normal assignment vibrational modes (IR). The predicted infrared spectra of our com- pound are shown in Figure 3, a comparison between the calculated and the experimental data help us to understand the observed spectral frequencies, which are collected in two Tables 1 and 2. According with results in this Tables, experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for the four methods used, we also calculated the mean absolute deviation, root mean square, TS (tacking signal) and the mean absolute percentage error between the calculated and experimental data. Careful examining and comparison of the experimental and calculated values may conclude the following observations for each vibration mode:

Imine group vibrations

The first type of vibration is the C=N stretching skeletal bands are observed in the range of 1650-1500cm^{-1} [35–38] for the title compound, the strong ab- sorption at 1505 cm^{-1} due to νC=N frequencies. The calculated stretching vibration mode of the C=N (imine) group band of the complex with the four methods (see Figure 3 and Table 1 entry 18 for ν(C=N) at the SDD basis set are 1507, 1519, 1526 and 1531 cm^{-1} (scaled), respectively. The second , the deformation C-H (see Table 1 entry 27) of the imine function , a band at 1363 cm^{-1}, correspond to δC-H,(C=N), it is predicted at 1377, 1371, 1372 and 1385 cm^{-1}, respectively[39].
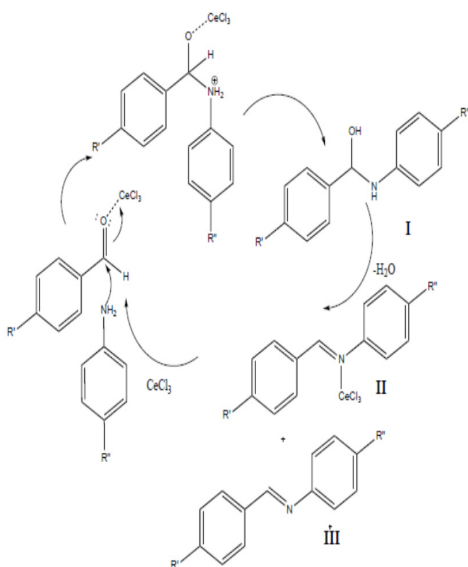

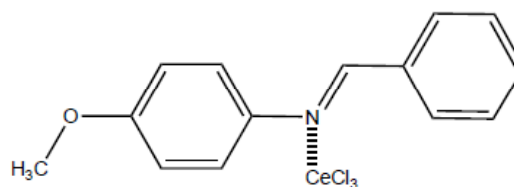**Fig. 1: Proposed mechanism of imines synthesis using CeCl$_3$ · 7 H$_2$O**

Fig. 2: Predicted structure of P2-CeCl$_3$

Methoxy group

32 fundamentals vibrations can be associated to this group. Five stretching, seven deformation, one scis- soring, four umbrella, six rocking and nine torsional vibration modes are motion to the methyl group. The strongest band of CH3 asymmetric and symmetric stretching frequencies are established at 3026 (3037, 3035, 3038, 3055 cm^{-1}), and 2879 (2884, 2879, 2882, 2895 cm^{-1}) in infrared (the SDD calculations using the four methods) spectrum (see Figure 3 and entries 9 and 14 in Table 1). The band observed at 1442 cm^{-1} in the IR and 1442, 1445, 1450 and 1441 cm^{-1} (SDD calculation using the four methods) are assigned as the de- formation mode of CH$_3$ (íCH3 entry 20 in Table 1), the scissoring vibration of this group appear at 1405 cm^{-1} (entry 24 in Table 1) and confirmed by the calculated frequencies in the same rang 1407, 1404, 1407 and 1409 cm^{-1} and 1391 cm^{-1} is attributed to the CH$_3$ umbrella vibration (entry 25 in Table 1), the latter mode is well defined with the SDD calculation, give assignment similar to the experimental value. For the rocking vibrations, many bands observed but the clearest that can identify this vibration mode appears at 1028 cm^{-1} in IR spectrum (entry 44 in Table 1), with values not close enough with SDD calculation at 984, 976, 980, and 980 cm^{-1}. In the vibration spectrum of this compound four bands observed which could be assigned to the following modes with different internals coordinates: 1266 and 1207 cm^{-1} for νC-O vibrations, δO-C at 552 cm^{-1} and torsion vibration at 444 and 410 cm^{-1}, observed in the same range with the calculated vibration.

Aromatic rings

The characteristic νC-H stretching vibrations of the aromatic ring are expected to appear in 3000-3100 cm^{-1}

Frequency range[40,41]. Although nine vibrational bands are predicted in this rang, the νC-H stretching vibration of the title compound is assigned to two strong bands. The first corresponds to the ring para-substituted and the second for the benzene ring at 3093 and 3067 cm^{-1}, in IR, respectively (entry 1 and 2 in Table 1).

For the phenyl ring (ring2), the bands observed at 1207 cm^{-1} in IR spectrum is assigned as C-H deformation. Also SDD calculation give

these mode at 1197, 1199, 1202 and 1211 cm^{-1}, respectively, using the four methods (entry 33 Table 1). They are in agreement with the experimental band. On the other hand, the δC-H of the para substituted (ring2) are seen in the rang[35] 995-1315 cm^{-1}[42,43] band observed at 1266 cm^{-1} observed in the IR spectrum attributed to δC-H of ring2, for this mode the frequencies calculated are 1266, 1261,1263, and 1265 cm^{-1}, respectively, with the four methods (entry 31 Table 1). In general, the C=C stretching vibration in aromatic compound are seen in the region of 1650-1430 cm^{-1}[32,44–46]. A characteristic band appear at 1437 cm^{-1} confirmed by the SDD calculation (1436, 1435, 1439 and 1435 cm^{-1}) attributed to νC-C frequency (entry 21 Table 1). For the modes of deformation in the plan of νC-C-C are observed at 820, 812,778, and 536 cm^{-1}, confirmed by the calculated assignments.

Ce-N and Ce-Cl vibrations modes

There is not far experimental data for this type of complexes, the complexes with Ce(III) ligand bonding is strongly ionic with small donor-acceptor character and supposes weak and not informative bands[47], The Ce-N stretching vibrations are often coupled with other vibrational modes of the ring. For this purpose, the SDD calculation with the four methods offer explicit information and details about these modes vibrations, or you notice the appearance of this mode below 400 cm^{-1}; the νCe-Cl is closest vibration, it appear at (356, 339, 343, and 336 cm^{-1}) (entries 72, 74 and 75 Table 1), whereas the νCe-N stretching and δCe-Cl bending vibration appear in the same band at (145, 148, 150 and 142 cm^{-1}).

Obviously, B3LYP functional give results in closest agreement with the experimental frequency over the other functional and for performance appraisal of the used methods, the Mean Absolute Deviation (MAD), Mean Absolute Percentage Error (MAPE) and Mean Square Values (RMS) were calculated and given in Table2. RMS values of the experimental and calculated IR bands are 16.64, 16.64, 17.45, 17.66 and MAPE values are 1.33, 1.39, 1.40, and 1.5 for B3LYP, B3PW91, mPW1PW91, PBEPBE methods respectively.

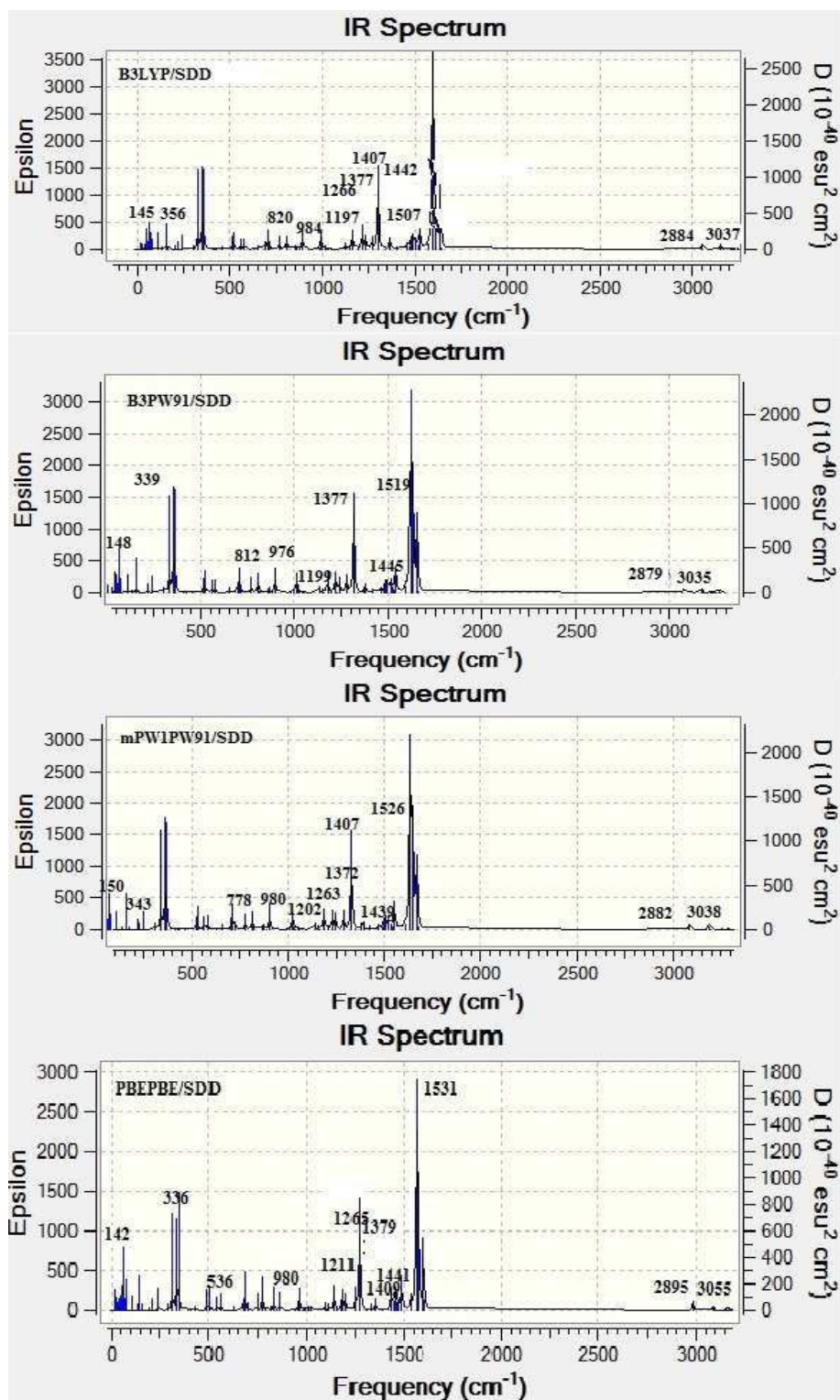These results indicate a good agreement between theoretical and experimental data of the

Fig. 3: The theorethical frequencies (scaled); calculated with B3LYP, B3PW91, mPW1PW91, PBEPBE methods using SDD basis set

Table 1 : Vibrational wave numbers obtained for the title compound at SDD basis set with B3LYP, B3PW91 , mPW1PW91 , PBEPBE methods

N*	Exp. IR	IR. Int	B3LYP/SDD unscaled	scaled	scaled	IR. Int	B3PW91/SDD unscaled	scaled	scaled	IR. Int	MPW1PPW91/SDD unscaled	scaled	scaled	IR. Int	PBEPBE/SDD unscaled	scaled	scaled	IR. Int	Assignements (b)
1	3093	17,73	3263	3111	3080	1,64	3273	3102	3071	3,53	3293	3105	3074	3,69	3184	3119	3088	0,76	νC-H, sym, Ring 2
2	3067	16,40	3252	3101	3070	1,24	3268	3097	3066	0,90	3288	3100	3069	1,24	3181	3116	3085	4,83	νC-H, sym, Ring 1
3			3250	3099	3068	1,65	3264	3093	3062	7,52	3284	3097	3066	5,99	3181	3116	3084	1,64	νC-H, asym, Ring 1
4			3248	3096	3065	9,61	3263	3093	3062	1,94	3284	3096	3065	1,49	3173	3108	3077	6,11	νC-H, asym, Ring 2
5			3234	3083	3053	3,99	3251	3081	3050	3,32	3272	3085	3054	2,56	3161	3096	3066	2,21	νC-H, asym, Ring 2
6			3221	3071	3040	0,00	3238	3069	3038	7,16	3260	3073	3043	0,00	3158	3093	3062	0,63	νC-H, asym, Ring 2
8			3220	3070	3039	9,59	3238	3069	3038	2,07	3259	3073	3042	8,48	3157	3092	3061	7,17	iC-H, asym, CH₃
9	3026	13,87	3218	3068	3037	0,58	3235	3066	3035	0,25	3255	3069	3038	0,16	3150	3086	3055	0,04	νC-H, asym, Ring 1 ;+νC-H, asym, CH₃
10	3013	13,72	3215	3065	3034	0,90	3230	3061	3030	1,00	3249	3064	3033	1,03	3136	3072	3041	0,81	νCH, asym, Ring 1 ;+νC-H, asym, CH₃
11			3205	3055	3025	1,23	3222	3054	3023	1,27	3243	3058	3027	1,12	3136	3072	3041	1,39	νC-H, asym, Ring 2;+νCH(C=N)
12			3166	3019	2989	2,13	3180	3014	2984	2,48	3200	3017	2987	2,42	3098	3034	3004	1,59	νC-H (C=N)
13	2990	13,98	3154	3007	2977	24,61	3171	3005	2975	23,67	3190	3008	2978	23,03	3091	3028	2997	18,97	νC-H, asym, CH₃
14	2879	10,02	3055	2913	2884	37,77	3068	2908	2879	38,59	3087	2911	2882	36,70	2985	2924	2895	31,88	νC-H, sym, CH₃
15	1577	7,52	1647	1570	1554	1,47	1663	1576	1560	2,73	1678	1582	1567	10,33	1609	1576	1560	29,64	νC-C, Ring2 ; +νC=N
16			1637	1561	1546	365,30	1654	1568	1552	23,67	1668	1573	1557	352,80	1604	1571	1555	219,55	νC-C, Ring 1; + δC-H,CH3
17			1613	1538	1522	215,19	1630	1545	1530	349,56	1646	1552	1536	537,25	1572	1540	1524	233,81	νC-C, Ring 2 ;+ ν(C=N)
18	1505	1,12	1597	1522	1507	1093,03	1619	1535	1519	452,10	1635	1542	1526	900,60	1563	1531	1516	685,14	νC-C, Ring 2; + νC=N
19			1576	1502	1487	28,09	1593	1509	1494	924,91	1609	1517	1502	22,32	1534	1503	1488	41,01	νC-C, Ring1; νC-H,CH₃
20	1442	16,72	1528	1457	1442	105,67	1540	1459	1445	26,05	1553	1465	1450	123,85	1486	1456	1441	99,29	νC-C, Ring 1; +νC-C, Ring2; +νC=N+

No.	Exp ν	Exp I	ν	ν	ν	I	ν	ν	ν	I	ν	ν	ν	I	ν	ν	ν	I	Assignment
21	1437	19,64	1521	1451	1436	6,00	1530	1450	1435	113,45	1541	1453	1439	7,35	1480	1449	1435	11,73	νCH,CH₃ / νC-C, Ring 1;+νC-C, Ring2;+νC=N + νC-H,CH₃
22			1517	1447	1432	20,97	1526	1446	1432	7,77	1537	1449	1434	22,39	1466	1436	1422	22,70	νC-H,CH₃,defor,
23			1506	1436	1422	60,91	1514	1434	1420	21,98	1524	1437	1423	59,31	1458	1428	1414	21,70	νCC, Ring1;+δCH, CH₃,sciss,
24	1405	23,41	1491	1422	1407	79,74	1497	1418	1404	57,54	1507	1421	1407	53,98	1453	1424	1409	65,47	νC-C, Ring2; + δC-H,CH₃, umbrella,
25	1391	29,77	1482	1413	1398	58,24	1486	1408	1394	55,49	1496	1411	1397	40,29	1446	1416	1402	24,51	δCH,CH₃, umbrella
26			1469	1401	1387	13,30	1481	1404	1390	41,83	1491	1405	1391	12,07	1434	1404	1390	58,58	νC-C, Ring 1;
27	1363	27,92	1459	1391	1377	30,03	1461	1385	1371	15,96	1469	1385	1372	20,16	1428	1399	1385	15,31	νC-C, Ring2; + δC-H,(C=N)
28	1356	38,29	1400	1335	1321	12,27	1418	1344	1331	21,67	1427	1345	1332	15,24	1388	1360	1346	2,51	νC-C, Ring1;+ δCCH,Ring1
29			1368	1304	1291	19,19	1382	1310	1297	12,71	1391	1312	1299	31,95	1351	1324	1310	29,39	δC-C, Ring2;+ δCCH,Ring2
30			1364	1301	1288	47,86	1373	1302	1289	33,69	1382	1303	1290	21,98	1331	1304	1291	16,73	νC-C, Ring1; +νCC, Ring2,
31	1266	28,90	1341	1279	1266	0,97	1344	1274	1261	19,84	1353	1276	1263	1,56	1305	1278	1265	1,55	δCCH,Ring1 ,+νC=O
32	1222	23,62	1300	1240	1227	377,50	1317	1248	1235	1,07	1330	1254	1241	372,20	1269	1243	1230	275,25	νC-C, Ring1;+ δCCH,Ring1;+ δC-H,CH₃, umbrella,
33	1207	34,78	1268	1209	1197	56,15	1278	1211	1199	370,10	1287	1214	1202	67,97	1249	1223	1211	54,49	νCCH,Ring2;+ νCH,(C=N),+ νOC,
34			1233	1175	1164	58,45	1239	1174	1162	62,46	1246	1175	1163	56,58	1201	1176	1164	37,33	νCCH,Ring2,
35			1220	1163	1152	1,34	1225	1161	1149	55,17	1232	1161	1150	1,05	1185	1161	1149	45,71	νCCH,Ring2,
36			1214	1157	1146	100,60	1219	1155	1144	1,12	1227	1157	1145	66,18	1182	1157	1146	14,09	νCCH,Ring1,
37			1191	1136	1124	8,54	1198	1135	1124	72,03	1207	1138	1126	7,54	1157	1133	1122	5,67	νCCH,Ring2;+ νC-H,CH₃, rocking,

No.																			Assignment
38			1164	1109	1098	74,03	1176	1115	1103	8,10	1186	1118	1107	68,74	1144	1121	1109	53,27	vCCH,Ring1;+ vC-H,(C=N),
39	1073	32,99	1149	1095	1084	0,18	1156	1096	1085	68,69	1166	1100	1089	0,19	1115	1093	1082	13,17	vC-H,CH₃, rocking
40			1147	1093	1082	12,01	1151	1090	1080	0,16	1158	1092	1081	11,62	1109	1086	1075	0,22	vC-C, Ring1; vCCH,Ring1;+ vC-H,CH₃, umbrella,
41	1052	52,86	1124	1071	1061	23,81	1132	1072	1062	11,77	1140	1075	1064	18,01	1098	1075	1065	16,95	vCC, Ring2; +vCCH,Ring2;
42			1065	1016	1005	0,07	1062	1007	997	0,09	1071	1010	1000	0,11	1028	1007	996	8,68	vCCH,Ring2,
43			1045	996	986	1,84	1053	997	988	1,57	1060	1000	990	1,68	1020	999	989	0,06	vCH,Ring2,
44	1028	4,89	1043	994	984	5,33	1040	986	976	4,68	1049	989	980	4,40	1011	990	980	9,45	vCCH,Ring2;+ vC-H,CH₃ , rocking,
45			1032	984	974	0,89	1031	977	967	1,17	1040	980	970	0,84	998	977	968	1,47	vCCH,Ring2,
46	960	42,49	1020	973	963	0,89	1022	969	959	1,07	1030	971	961	4,92	997	976	967	4,25	vCCH,Ring1,
47			1016	969	959	0,64	1018	964	955	10,47	1025	966	957	11,79	984	964	954	5,23	vCCH,Ring1,
48			1013	966	956	12,97	1016	963	953	3,41	1024	965	956	52,07	983	963	953	1,47	vCCC,Ring1; vCCH,Ring1,
49	919	52,92	997	951	941	0,45	1010	957	947	56,48	1023	964	955	1,0826	965	945	936	41,70	vCCH,Ring1; + vC=N,
50	901	57,62	991	945	935	66,22	996	944	935	3,30	1007	950	940	3,03	956	936	927	14,52	vCCH,Ring1; + vCH,CH₃ , rocking,
51			984	938	929	1,05	983	932	922	0,66	991	935	925	0,56	943	924	914	2,61	vCCH,Ring2;+v C-H,CH₃ ,rocking,
52	836	1,54	894	852	843	61,11	897	850	841	60,14	905	853	845	66,53	865	847	839	29,85	vCCH,Ring1,
53			878	837	829	1,15	879	833	825	0,96	887	836	828	0,91	845	827	819	1,27	vCCH,Ring2,
54	820	14,88	864	824	816	8,02	867	822	814	10,70	874	824	816	11,31	835	818	810	37,81	vCCH,Ring2; +vC=N,
55	812	28,42	854	815	806	9,74	856	811	803	9,70	865	815	807	7,30	817	800	792	7,69	vC-C, Ring1; +vCCH,Ring1,
56	778	55,32	807	769	761	33,71	813	771	763	2,48	820	773	766	2,64	788	772	764	2,71	vC-C, Ring2; +vCCH,Ring2,
57	767	50,60	805	768	760	13,85	807	764	757	42,80	813	766	759	42,19	772	757	749	49,25	vCCH,Ring2,

No.	ν	I	ν	ν	ν	I	ν	ν	ν	I	ν	ν	ν	I	ν	ν	ν	I	Assignment
58	715	29,51	766	730	723	34,20	770	730	723	32,12	778	733	726	33,00	747	731	724	23,45	νC-H,CH₃ ; + νCCH,Ring1; + νCCH,Ring1,
59			713	679	673	13,59	715	677	670	13,62	721	680	673	15,91	698	684	677	10,11	νCCH,Ring1; νCCH,Ring2,
60			705	673	666	47,08	707	670	663	49,81	713	672	665	51,27	681	667	661	48,93	νCCH,Ring2,
61	668	33,13	691	659	652	18,09	697	660	654	19,57	703	662	656	21,93	676	662	655	15,01	νC-H3 , rocking; + νCCH,Ring1,
62	633	48,62	650	620	614	7,31	651	617	611	8,09	656	618	612	8,69	627	614	608	4,89	νHCN; + νCCH, Ring1,
63	552	18,58	628	599	593	0,21	627	594	588	0,17	631	595	589	0,15	608	595	589	0,17	νCOC; + νCCH,Ring2,
64			576	550	544	20,70	577	547	541	21,21	581	548	542	22,18	559	547	542	17,48	ν,C-H,CH₃ ; + νCH,Ring1; + νCH,Ring2, νCC,Ring2,
65	536	24,14	557	531	526	18,27	559	530	524	19,50	563	531	526	20,79	539	528	523	13,86	νCH,Ring1;+ νCH,Ring2,
66			521	497	492	28,56	523	496	491	31,57	529	498	493	35,37	503	493	488	23,54	νCC,Ring2, νC-C,Ring1;+ νC-H,Ring1,
67	484	51,04	514	490	485	22,73	516	489	484	20,48	519	490	485	18,98	494	484	479	18,81	νC-C,Ring1;+ νC-H,Ring1;+ νC-C,Ring2;+ νC-H,Ring2,
68	444	57,46	458	437	433	2,86	458	434	430	1,89	462	436	431	1,25	434	425	421	3,94	νOC;+ νC-H, Ring2,
69	410	57,19	425	405	401	0,32	426	404	400	0,22	431	406	402	0,19	409	401	397	0,64	νOC;+ νC-H, Ring2,
70			420	400	396	0,66	421	399	395	0,84	424	400	396	0,90	408	399	395	1,48	ν,C-H,CH₃;+ νC-H,Ring1;+ νC-H,Ring2,
71			409	390	386	0,55	409	388	384	0,56	412	389	385	0,55	393	385	381	0,33	νC-H,Ring2,
72			356	340	336	99,20	361	342	339	104,56	367	346	343	111,23	347	340	336	77,14	ν,asym, Ce-Cl,
73			353	337	333	22,82	359	341	337	26,48	365	344	340	29,67	338	331	327	26,01	ν,CH,CH₃; +

																Assignment
74	349	333	330	99,88	354	335	332	105,85	358	338	335	113,48	336	329	326	58,26	vCH, Ring1, v,asym,Ce-Cl, v,sym,Ce-Cl, v,C-H,CH$_3$;+ vHCN;
75	328	312	309	90,95	333	316	313	91,27	339	320	317	95,46	315	309	306	57,59	
76	302	288	285	4,01	301	286	283	4,44	303	286	283	5,64	291	285	282	3,60	
77	243	232	229	11,56	244	231	229	11,66	246	232	230	12,24	241	236	234	10,02	vC-H,CH$_3$;+ vHCN; + vC-H, -Ring1;-+vCH, Ring2,
78	216	206	204	5,87	217	205	203	5,08	224	211	209	4,25	206	202	200	4,49	vC-H,CH$_3$; +vHCN; + vC-H,Ring1; + vC-H,Ring2,
79	205	195	193	2,00	215	204	202	3,97	218	206	204	5,89	196	192	190	1,00	vC-H,CH$_3$;
80	164	156	155	1,07	169	160	158	0,77	172	162	160	1,10	162	158	157	1,69	vC-H,CH$_3$; + vC-H,Ring1,
81	156	149	148	15,51	158	149	148	15,63	161	152	150	16,48	147	144	142	10,01	v,asym,Ce-N; + vCe-Cl,CeCl$_3$,
82	134	128	127	0,93	134	127	126	0,87	135	128	126	0,67	133	130	129	1,46	vC-H,CH$_3$; + vC-H,Ring1; + vC-H,Ring2,
83	106	101	100	5,92	107	102	101	5,37	109	103	102	5,34	105	102	101	3,02	vC-H,CH$_3$; + vC-H,Ring1,
Mean absolute deveation	77,96899			18,7563	12,419			85,27482	17,8102		12,73	95,6968	19,752		13,232	44,254	21,65	14,173
Root mean square	94,17271			23,0012	16,645			102,6271	22,3462		16,645	113,94	24,555		17,455	56,2961	26,752	17,661
Mean absolute percentage erreur	5,824756			1,63779	1,3308			6,339131	1,60647		1,3864	7,18243	1,7252		1,3975	3,12919	1,8277	1,5383
ts	-36,000			-24,361	1,9211			-36,000	-23,511		4,8440	-36	-26,791		-3,6033	-34,496	-23,973	-2,655
Scaling factor	1,0000			0,9534	0,9439			1,0000	0,9477		0,9382	1,000	0,9429		0,9335	1,000	0,9795	0,9697

a-Harmonic frequencies in (cm^{-1}) and IR intensities (Km.mol^{-1})

b-v,stretching; sym,symmetric; asym,asymmetric; ?,in-plane deformation; ?, out-plane deformation; ?, torsion; ring1,para-substitutedbenzene ring ; ring2, benzene ring

title compound at SDD basis set using B3LYP, B3PW91, mPW1PW91, PBEPBE functional and specially, B3LYP, which have the best agreement with the smallest difference between calculated and experimental frequencies.

Finally, we proposed and calculated the optimal scaling factors, which are recommended to get a very close frequencies. The obtained scaling factors are 0.9439, 0.9382, 0.9335 and 0.9697 for B3LYP, B3PW91, mPW1PW91, PBEPBE, respectively at the SDD basis set.

Molecular geometry

The molecular structure of the compound in the ground state (in vacuo) was optimized using density functional theory, The optimized geometrical parameters: bond length in Å, bond angles and dihedral angles in degree, determined with mPW1PW91, B3LYP, B3PW91 and PBEPBE methods at SDD basis set for molecule are collected in Table 2 in accordance with the atom numbering shown in Fig. 4. The values of the distances be- tween the atoms and valence or torsion angles are very close in any calculation method.

Mulliken Atomic Charges

Mulliken atomic charge calculation in Table 3 has an important role in the application of quantum chemical calculation to molecular system because of atomic charges present a vital insight in the

understanding of several kinds of chemical reactions and they are crucial to the elucidations of a number of other phenomena, effect dipole moment, molecular polarizability, electronic structure and more a lot of properties of molecular systems. In addition to the charge distribution on the molecule has an important influence on the vibrational spectra, they also are important factors in molecular structure-activity and structure-property relations[46,48]. The total atomic charges of the imine complexed with CeCl3 obtained by the Mulliken Population Analysis (MPA), they were calculated using B3LYP, B3PW91, PBEPBE and mPW1PW91 levels with SDD basis set, were listed in Table 3.

Our interest here is the comparison of the performance and assess the sensitivity of the calculated charges using different methods in order to describe electronic distribution in our complex and the influence of the presence of CeCl3, by comparing the MPA charges in the imine(P2) with imine complexed (P2-CeCl3).

In P2 and P2-CeCl3 compounds, more charge density was found at C14 linked to imine function (C=N) than that the other carbon atoms. The high positive charges at C6 is due to effect of oxygen atom (O26) of the methoxy group attached in the para position of ring 1 with C6. The charge distribution of the title compound shows that the carbon atoms attached with hydrogen atoms (C1, C2, C4, C5, C12, C15,C16,C17, C19, C21) are negative whereas the remaining carbon atoms are positively charged. The oxygen and nitrogen atoms have more negative charges whereas all hydrogen atoms have a positive charge. It is very clear from Table 3 that there is large change in Mulliken charges of the nitrogen atom (N11) in P2 and P2-CeCl3, and this variation reveals that there is charge transfer through the N-Ce bond, explained by the appearance of a strongly negative charge noted for the nitrogen atom, which is involved, as acceptor and the bigger positive charge is noticed on the cerium atom, as donor. This donor effect is due to the presence of electronegative nitrogen atoms; while the Cl atoms have a the highest negative charges in P2-CeCl3. All used methods have shown similar charges for each compound (imine and complex), where a change in charges distribution have been observed, for which the complex have the highest charges.
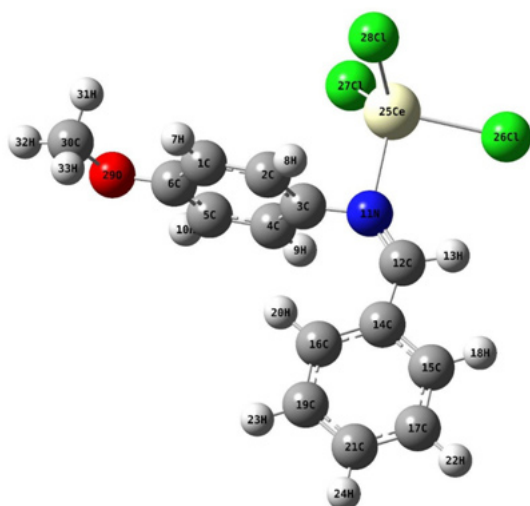

Fig. 4: The optimized structure of P2dCeCl3

Table 2: The selected bond lengths , valence angles and dihedral angles of the compound at SDD basis set with B3LYP, B3PW91, mPW1PW91 ,PBEPBE methods

Bond Lengths (Å)	B3LYP	B3PW91	PBEPBE	mPW1PW91	Bond Angle(°)	B3LYP	B3PW91	PBEPBE	mPW1PW91	Dihedral Angle(°)	B3LYP	B3PW91	PBEPBE	mPW1PW91
C30-H32	1,0896	1,0887	1,09844	1,08691	H31-C30-H33	110,78648	110,77713	110,8201	110,72894	H31-C30-O29-C6	60,8449	61,22227	60,75665	61,3265
C30-H31	1,09656	1,09586	1,10551	1,09418	H32-C30-H33	110,04528	109,93335	110,10183	109,89038	H32-C30-O29-C6	179,29788	179,62474	179,20783	179,74356
C30-H33	1,09666	1,09592	1,10555	1,09424	H31-C30-H32	34,86276	109,89515	110,0796	109,86046	H33-C30-O29-C6	-62,20407	-61,92698	-62,29689	-61,79802
C30-O29	1,47133	1,46394	1,48127	1,45961	H33-C30-O29	110,56695	110,63456	110,54325	110,66617	C30-O29-C6-C5	-179,33911	-179,60474	-179,0573	-179,57024
O29-C6	1,3657	1,36053	1,37366	1,35758	H32-C30-O29	104,72369	104,80848	104,62242	104,88703	C30-O29-C6-C1	0,54607	0,22304	0,60889	0,22809
C6-C1	1,41866	1,41533	1,42486	1,41266	H31-C30-O29	110,53905	110,63323	110,50747	110,65438	O29-C6-C5-H10	0,27482	0,25523	0,48273	0,07535
C6-C5	1,4232	1,41916	1,43089	1,41634	C30-O29-C6	120,70646	120,62681	119,59625	120,57187	O29-C6-C1-H7	0,15666	0,08157	0,95332	-0,10911
C1-H7	1,08421	1,08413	1,09338	1,08237	O29-C6-C1	124,81656	124,79784	125,07405	124,68192	O29-C6-C1-C2	179,84825	179,81059	-179,90609	179,995
C5-H10	1,08495	1,08455	1,09408	1,08278	O29-C6-C5	115,15562	115,16341	114,85106	115,247	O29-C6-C5-C4	179,80049	179,83594	179,61916	179,90731
C5-C4	1,39152	1,38903	1,39604	1,38786	C6-C1-H7	121,11615	121,13103	121,28791	121,11387	C6-C1-C2-H8	-178,15317	-178,15928	-176,53595	-178,63597
C4-H9	1,0868	1,08647	1,09538	1,08486	C6-C5-H10	118,33952	118,38003	118,23857	118,37959	C6-C1-C2-C3	0,01599	0,02839	-0,31298	-0,23528
C1-C2	1,40206	1,39869	1,40894	1,39598	C6-C5-C4	120,29224	120,31297	120,42609	120,30179	C6-C5-C4-H9	179,81883	179,63214	-179,00123	179,2906
C2-H8	1,08711	1,08692	1,0976	1,08524	C6-C1-C2	119,65487	119,68821	119,46311	119,68331	C6-C5-C4-C3	0,70153	0,70479	0,94606	0,46484
C4-C3	1,42596	1,4232	1,43385	1,4207	H10-C5-C4	121,36649	121,30564	121,32956	121,31841	H7-C1-C2-C3	179,71342	179,76271	178,84533	179,86683
C2-C3	1,41951	1,41706	1,42843	1,41431	H7-C1-C2	119,22827	119,18022	119,24348	119,20274	H10-C5-C4-C3	-179,78741	-179,72697	-179,9446	-179,70822
C3-N11	1,44141	1,43558	1,43646	1,43481	C1-C2-H8	119,69317	119,7684	119,514	119,79717	C5-C4-C3-N11	-175,57087	-174,8652	-171,68885	-174,63035
N11-Ce25	2,3453	2,32939	2,3791	2,3159	C1-C2-C3	120,34938	120,32451	120,556	120,32813	H9-C4-C3-N11	5,31008	6,205	8,25866	6,54144
Ce25-Cl27	2,51279	2,49415	2,51989	2,4851	C5-C4-H9	120,12305	120,15109	120,24505	120,17127	C1-C2-C3-N11	175,22922	174,51761	171,63468	174,53554
Ce25-Cl28	2,51398	2,49659	2,52308	2,48999	C5-C4-C3	119,94444	119,91564	119,92161	119,85328	H8-C2-C3-N11	-6,606	-7,29678	-12,15397	-7,06471
Ce25-Cl26	2,5088	2,48972	2,51628	2,48212	H8-C2-C3	119,93215	119,88232	119,82244	119,85542	C2-C3-N11-Ce25	-80,29727	-82,00765	-68,40849	-85,12288
N11-C12	1,31862	1,31477	1,3275	1,31188	H9-C4-C3	119,92663	119,92459	119,83331	119,96503	C4-C3-N11-Ce25	94,31413	91,80956	101,87429	88,59235
C12-H13	1,09155	1,09136	1,10078	1,08967	C2-C3-N11	119,85396	119,83516	118,54314	119,82299	C3-N11-Ce25-Cl26	-168,35627	-171,41883	-165,60543	177,17303
C12-C14	1,44955	1,44596	1,45359	1,44386	C4-C3-N11	120,20196	120,16386	121,20016	120,12207	C3-N11-Ce25-Cl27	-56,74572	-61,91562	-55,16287	-73,29139
C14-C15	1,42689	1,42287	1,43389	1,42	C3-N11-Ce25	93,80107	91,46831	92,83146	90,76267	C3-N11-Ce25-Cl28	80,31045	78,14854	83,13195	68,08914
C14-C16	1,42664	1,42245	1,43303	1,41993	C3-N11-C12	129,58412	129,92999	130,3785	129,84793	C3-N11-C12-H13	177,04618	177,72693	171,82877	179,27395
C15-H18	1,0881	1,08779	1,09731	1,08602	C12-N11-Ce25	136,57452	138,55571	135,75557	139,3649	C3-N11-C12-C14	-3,43002	-2,57768	-9,39387	-0,86257
C16-H20	1,08304	1,08342	1,09358	1,08178	N11-Ce25-Cl26	91,02863	89,93048	89,66628	89,02487	Cl26-Ce25-N11-C12	9,36634	6,11007	3,03663	-4,64644
C16-C19	1,39846	1,39536	1,4046	1,39314	N11-Ce25-Cl27	114,67037	114,84791	110,63423	111,36632	Cl27-Ce25-N11-C12	120,97689	115,61328	113,47918	104,88915

Bond					Angle					Dihedral				
C15-C17	1,3997	1,39659	1,40584	1,39447	N11-Ce25-Cl28	108,17319	110,33119	110,57715	113,95411	Cl28-Ce25-N11-C12	-101,96694	-104,32256	-108,226	-113,73033
C17-H22	1,08545	1,08494	1,09494	1,08308	Cl26-Ce25-Cl27	109,09481	107,6657	109,20258	108,51571	Ce25-N11-C12-H13	-0,00479	0,94906	6,79247	1,64389
C19-H23	1,08582	1,08533	1,09532	1,08347	Cl26-Ce25-Cl28	109,87632	109,13395	109,97122	107,79778	Ce25-N11-C12-C14	179,51901	-179,35555	-174,43017	-178,49263
C19-C21	1,41401	1,4104	1,42067	1,40807	Cl28-Ce25-Cl27	120,12195	120,42658	122,02238	121,13267	N11-C12-C14-C15	178,91645	179,02769	176,32074	179,52509
C17-C21	1,41021	1,40671	1,41689	1,40431	N11-C12-H13	113,64217	113,6598	113,52767	113,68112	N11-C12-C14-C16	-1,82429	-1,4339	-5,40683	-0,59596
C21-H24	1,08661	1,08605	1,09609	1,08421	N11-C12-C14	131,23784	130,9967	130,75291	130,85292	H13-C12-C14-C15	-1,56534	-1,28102	-4,92343	-0,61338
					H13-C12-C14	115,11849	115,34288	115,70937	115,46584	H13-C12-C14-C16	177,69391	178,25738	173,349	179,26556
					C12-C14-C16	125,17923	125,08275	125,06877	125,02625	C12-C14-C15-C17	179,54322	179,7871	179,3819	-179,99959
					C12-C14-C15	115,77898	115,81163	115,96267	115,81535	C12-C14-C15-H18	-0,47561	-0,25432	-0,8717	-0,04077
					C14-C16-H20	120,83385	120,85246	120,67835	120,88892	C12-C14-C16-C19	-179,28408	-179,61611	-178,68132	-179,93269
					C14-C15-H18	119,60636	119,65242	119,443	119,65292	C12-C14-C16-H20	0,51221	0,22826	0,53308	0,03299
					C14-C15-C17	120,69633	120,65137	120,70046	120,63515	C14-C16-C19-H23	179,87723	179,94595	179,59397	-179,98241
					C14-C16-C19	119,91431	119,90264	120,04688	119,86964	C14-C16-C19-C21	-0,15364	-0,08793	-0,3434	-0,03477
					H20-C16-C19	119,25153	119,24473	119,27018	119,24143	C14-C15-C17-H22	179,89209	179,90517	179,56408	179,9319
					H18-C15-C17	119,69731	119,6962	119,85606	119,71192	C14-C15-C17-C21	-0,22042	-0,16465	-0,72668	-0,07666
					H23-C19-C16	119,91702	119,91613	119,96136	119,92168	H18-C15-C17-C21	179,79842	179,87678	179,52797	179,96453
					H22-C17-C15	120,19053	120,18115	120,17367	120,19447	H18-C15-C17-H22	-0,08906	-0,05339	-0,18127	-0,02691
					H22-C17-C21	120,20731	120,20451	120,19483	120,22097	H20-C16-C19-C21	-179,95316	-179,9348	-179,56886	179,99899
					H23-C19-C21	119,72052	119,74673	119,75984	119,74895	H20-C16-C19-H23	0,07772	0,09907	0,36851	0,05134
					C19-C21-C17	120,38648	120,4001	120,38815	120,4229	C16-C19-C21-H24	-179,90295	-179,91618	-179,71102	-179,94342
					C16-C19-C21	120,36246	120,33713	120,27877	120,32935	C15-C17-C21-H24	-179,90879	-179,95662	-179,75058	179,99956
					C15-C17-C21	119,60207	119,6043	119,63086	119,58456	H23-C19-C21-H24	0,06624	0,05	0,35149	0,00431
					C19-C21-H24	119,76451	119,76258	119,76583	119,74972	H23-C19-C21-C17	-179,85961	-179,8888	-179,31107	-179,97902
					C17-C21-H24	119,84897	119,83729	119,84516	119,82738	H22-C17-C21-H24	-0,02133	-0,02646	-0,04141	-0,009
										H22-C17-C21-C19	179,90446	179,91229	179,62088	179,97431

Thermodynamic Properties

The thermodynamic data can be used to compute the other thermodynamic energies according to relation- ships of thermodynamic functions and estimate directions of chemical reactivity according to the second law of thermodynamics in thermo chemical field, from which the relations among energy, structural and reactivity characteristics of the molecules can be clarified. Knowledge of permanent dipole moment of a molecule helps to determine the molecule's conformations[49]. On the basis of vibrational analysis and statistical thermodynamics. The thermodynamic parameters for the title compound were obtained from the theoretical harmonic frequencies namely heat capacity, entropy, rotational constants, vibration and vibrational zero point energies of the compound have also been computed at the DFT-B3LYP, B3PW91,

**Table 3: MPA charges in imine (P2) and imine complexed (P2-CeCl$_3$)
at SDD basis set with B3LYP, B3PW91, mPW1PW91, PBEPBE methods**

Atom	B3LYP/SDD		B3PW91/SDD		PBEPBE/SDD		mPW1PW91/SDD	
	P2-Cl$_3$	P2	P2-Cl$_3$	P2	P2-Cl$_3$	P2	P2-Cl$_3$	P2
H31	0.227	0.205	0.237	0.215	0.244	0.222	0.239	0.218
H32	0.265	0.231	0.271	0.237	0.279	0.245	0.275	0.241
H33	0.224	0.203	0.234	0.213	0.242	0.219	0.235	0.215
C30	-0.47	-0.474	-0.497	-0.449	-0.529	-0.536	-0.504	-0.506
O29	-0.275	-0.313	-0.290	-0.327	-0.225	-0.268	-0.303	-0.338
C1	-0.339	-0.323	-0.356	-0.327	-0.348	-0.333	-0.360	-0.344
C2	-0.291	-0.364	-0.281	-0.367	-0.314	-0.381	-0.275	-0.372
C3	0.223	0.220	0.193	0.227	0.207	0.211	0.181	0.229
C4	-0.258	-0.303	-0.249	-0.304	-0.225	-0.317	-0.257	-0.308
C5	-0.311	-0.333	-0.329	-0.342	-0.324	-0.349	-0.343	-0.349
C6	0.360	0.327	0.395	0.360	0.334	0.311	0.407	0.371
H7	0.269	0.231	0.273	0.237	0.281	0.243	0.278	0.242
H8	0.275	0.242	0.279	0.241	0.292	0.252	0.282	0.247
H9	0.269	0.250	0.274	0.252	0.285	0.262	0.286	0.258
H10	0.283	0.245	0.284	0.246	0.291	0.254	0.292	0.252
N11	-0.341	-0.034	-0.371	-0.067	-0.288	-0.017	-0.387	-0.077
Ce25	0.562		0.576		0.495		0.571	
Cl26	-0.056		-0.062		-0.049		-0.048	
Cl27	-0.043		-0.040		-0.037		-0.035	
Cl28	-0.054		-0.051		-0.044		-0.045	
C12	-0.251	-0.434	-0.213	-0.400	-0.277	-0.461	-0.202	-0.396
H13	0.267	0.208	0.265	0.210	0.273	0.220	0.270	0.215
C14	0.400	0.395	0.399	0.385	0.414	0.413	0.394	0.377
C15	-0.296	-0.354	-0.286	-0.345	-0.311	-0.363	-0.289	-0.350
C16	-0.280	-0.311	-0.275	-0.302	-0.298	-0.321	-0.275	-0.303
C17	-0.221	-0.223	-0.234	-0.231	-0.230	-0.237	-0.242	-0.237
C19	-0.233	-0.231	-0.246	-0.239	-0.240	-0.245	-0.256	-0.246
C21	-0.177	-0.221	-0.185	-0.227	-0.196	-0.236	-0.191	-0.232
H18	0.244	0.224	0.243	0.224	0.255	0.243	0.248	0.229
H20	0.260	0.262	0.262	0.265	0.271	0.274	0.266	0.270
H22	0.259	0.223	0.260	0.224	0.269	0.234	0.266	0.230
H23	0.252	0.225	0.251	0.225	0.262	0.236	0.257	0.231
H24	0.259	0.225	0.260	0.226	0.262	0.236	0.266	0.232

Table 4: Theoretical computed Energy(a.u), Zero Energy, (Kcal/mol), Rotational Constant(GHz), Entropy (cal/mol.K) and Dipole moment D(Kcal/mol.K)

Thermodynamic Pa- rameters	B3LYP/SDD		B3PW91/SDD		PBEPBE/SDD		mPW1PW91/SDD	
	P2-Cl3	P2	P2-Cl3	P2	P2-Cl3	P2	P2-Cl3	P2
Total En-ergy(Thermal): E*tot* (kcal/mol)	165.231	156.944	166.001	157.667	161.658	153.329	167.057	158.735
Heat capacity at const. vol.: C*v*(cal/mol.K)	74.507	52.474	74.253	52.296	76.233	54.144	73.769	51.870
Entropy:S(cal/mol)	169.201	119.397	160.677	119.322	170.727	120.427	167.159	119.007
Vibrational energy: E*vib*(kcal/mol)	163.453	155.167	164.223	155.889	159.881	151.552	165.280	156.958
Zero-point vibrational energy: E$^\psi$(kcal/mol)	151.57885	148.44611	152.39319	149.18289	147.72441	144.61031	153.56278	150.30798
Rotational con- stants(Ghz)								
X	0.20233	1.23352	0.20685	1.22372	0.20395	1.24573	0.20867	1.21809
Y	0.15980	0.24847	0.16106	0.25261	0.15923	0.24380	0.16221	0.25575
Z	0.10552	0.22214	0.10717	0.22559	0.10556	0.21826	0.10818	0.27792
Dipole moment (De- bye)								
μX	-8.7912	-0.4915	-8.6382	-0.5134	-7.1017	-0.2950	-8.5772	-0.5151
μY	3.6801	-1.6588	4.2952	-1.7136	5.8090	-1.6631	4.1951	-1.7213
μZ	1.4217	-1.3257	1.4468	-1.3238	1.5532	-1.2643	-1.3979	-1.3253
μ*total*	9.6359	2.1796	9.7550	2.2254	9.3055	2.1098	9.6500	2.2326
Total energy (a.u)	-2526.910432	-671.1557335	-2526.546118	-670.901587	-2525.447260	-670.355180	-2526.792928	-670.9971721

mPW1PW91 and PBEPBE levels using SDD basis set are presented in Table 4.

To better understand the complex formation, we note that there is a very large differences between the total energies and dipole moments of imine and the complex with used methods, this great difference shows the low reactivity or the high stability behavior, this explains the complex formation further than the imine formation. On un other hand, the high value of dipole moment of the P2-CeCl3 relative to that of the P2, could partly explain the high stability of the complex, which it is due to the presence of the donor effect of cerium which makes the nitrogen atom strongly electronegative. The biggest value of zero-point vibrational energy (ZPVE) is 153.56 kJ/mol obtained with mPW1PW91 whereas the smallest one is 147.72 kJ/mol obtained with PBEPBE, While the total energies calculated by the four levels are very close.

CONCLUSION

The comprehensive studies of the molecular   structure, Mullikan atomic charges and thermodynamic parameters of the complex formed (E)-N-benzylidene-4- methoxyaniline, CeCl3 suggested that the ligand acts as tetradentate one in the Ce(III) complex formation which is favored over the formation of imine, confirming the utility of the this catalyst (CeCl3) in the synthesis of imines and the nitrogen derivatives or imines training in situ. The comparison of the experimental and calculated frequencie , show that the experimental values are in a good agreement with SDD calculation results and obviously B3LYP function which has given the closets results. Optimal uniform factors were also calculated. Taking into account small variations between calculated and experimental data, we can recommend new scaling factors of 0.9439, 0.9382, 0.9353 and 0.9697 for B3LYP, B3PW91, mPW1PW91 and PBEPBE levels, respectively, at SDD basis set, for the IR spectral future predictions for unknown compounds of this class.

REFERENCES

1.   Rezaeivala, M.; Keypour, H. *Coordination Chemistry Reviews* **2014**, *280*, 203.
2.   Hayashi, T.; Shibata, H.; Orita, S.; Akitsu, T. *European Chemical Bulletin* **2012**, *2* 49.
3.   Awual, M. R.; Hasan, M. M.; Shahat, A.; Naushad, M.; waku, H. S.-.; Yaita, T. *Chemical Engineering Journal* **2015**, *265*, 210.
4.   Terzis, A.; Mentzafos, D.; Tajmir-Riahi, H. *Inorganica Chimica Acta* **1984**, *84*, 187.
5.   Afkhami, A.; Madrakian, T.; Shirzadmehr, A.; Tabatabaee, M.; Bagheri, H. *Sensors and Actuators B: Chemical* **2012**, *174* 237
6.   Afshar, S.; Bullock, J. I. *Inorganica Chimica Acta* **1980**, *38*, 145.
7.   Fenton, D. E.; Vigato, P. A. *Chem. Soc. Rev* **1988**, *17*, 69.
8.   A.Mouadili; I.Lakehal; A.Takfaoui; F.Halaimia; H.Nacer; M.L.Hamlaoui; B.Hammouti; M.Messali; R.Touzani *J. Mater. Environ. Sci.* **2014**, *5*, 715.
9.   Takfaoui, A.; Lakehal, I.; Bouabdallah, I.; Halaimia, F.; Nacer, H.; Hammouti, B.; Touzani, R. *J. Mater. Environ. Sci.* **2014**, *5*,

753.
10.   Piro, N. A.; Robinson, J. R.; Walsh, P. J.; Schelter, E. J. *Coordination Chemistry Reviews* **2014**, *260*, 21.
11.   Zamani, H. A.; Ganjali, M. R.; Adib, M. *Sensors and Actuators B: Chemical* **2007**, *120*, 545.
12.   Maity, D.; Chattopadhyay, S.; Ghosh, A.; Drew, M. G.; Mukhopadhyay, G. *Inorganica Chimica Acta* **2011**, *365*, 25.
13.   Kocyigit, O.; Kursunlu, A. N.; Guler, E. *Journal of hazardous materials* **2010**, *183*, 334.
14.   Bhowmik, P.; Drew, M. G.; Chattopadhyay, S. *Inorganica Chimica Acta* **2011**, *366*, 62.
15.   Esmaielzadeh, S.; Azimian, L.; Shekoohi, K.; Esfandiari, H.; Asadi, M.; Zare, Z.; Nejad, A. R.; Mohammadi, K. *Inorganica Chimica Acta* **2013**, *405*, 155.
16.   Ali, M. A.; Haroon, C. M.; Nazimuddin, M.; jumder, S. M.-u.-H. M.-.; Tarafder, M. T.; Khair, M. A. *Transition Metal Chemistry* **1992**, *17*, 133.
17.   Hossain, M. E.; Alam, M. N.; Ali, M. A.; Nazimuddin, M.; Smith, F. E.; Hynes, R. C.

Polyhedron **1996**, *15*, 973.

18. Tan, X.-J.; Liu, H.-Z.; Ye, C.-Z.; Lou, J.-F.; Liu, Y.; Xing, D.-X.; Li, S.-P.; Liu, S.-L.; Song, L.-Z. *Polyhedron* **2014**, *71*, 119.

19. Bagihalli, G. B.; Avaji, P. G.; Patil, S. A.; Badami, P. S. *European journal of medicinal chemistry* **2008**, *43*, 2639.

20. Sathisha, M.; Shetti, U. N.; Revankar, V.; Pai, K. *European journal of medicinal chemistry* **2008**, *43*, 2338.

21. RAIKWAR, K.; AGARWAL, D. D. *Orient. J. Chem.,* **2015**, *31*, 547.

22. ABDULFATAI, A. S.; ADAMU, U.; SULAIMAN, I.; HAMZA2, A. *Orient. J. Chem., Vol. 31(4), (2015)* **2015**, *31*, 1985.

23. AL-KHODIR, F. A. I. *Orient. J. Chem* **2015**, *31*, 1277.

24. Fan, Y.-H.; Wang, A.-D.; Bi, C.-F.; Xiao, Y.; Bi, S.-Y.; Zhang, X.; Wang, Q. *Synthetic Metals* **2011**, *161*, 1552.

25. Silva, C. M. d.; Silva, D. L. d.; Modolo, L. V.; Alves, R. B.; Resende, M. A. d.; Martins, C. V.; Fa´tima, A. d. *Journal of Advanced research* **2011**, *2*, 1.

26. Kidwai, M.; Anwar, J. *Journal of the Brazilian Chemical Society* **2010**, *21*, 2175.

27. Sindhu, Y.; Athira, C.; Sujamol, M.; Joseyphus, R. S.; hanan, K. M.-. *Metal-Organic, and Nano-Metal Chemistry* **2013**, *43*, 226.

28. Wang, Q.; Huang, Y.; Zhang, J.-S.; Yang, X.-B. *Bioinorganic Chemistry and Applications* **2014**, *2014*, 9.

29. Chinthaparthi, R. R.; Gangireddy, C. S. R.; Mudumala, V. R.; Gundluru, M.; Chamarthi, N.; Cirandur, S. R. *Tetrahedron Letters* **2013**, *54*, 6071.

30. Ubani, O. C.; Ngochindo, R. I.; Odokuma, L. O. *J. Chem. Pharm. Res* **2015**, *7*, 720.

31. Adly, O. M.; Taha, A.; Fahmy, S. A. *Journal of Molecular Structure* **2015**, *1093*, 228.

32. El-Wahab, Z. A.; Mashaly, M.; Faheim, A. *Chem Pap* **2005**, *59*, 25.

33. Shebl, M. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2008**, *70*, 850

34. Montazerozohori, M.; Tavakol, H.; Kheiri, S.; Musavi, S.; Joohari, S. *Bulgarian chemical communications* **2014**, *46*, 96.

35. Glendening, E. D.; Feller, D.; Thompson, M. A. *Journal of the American Chemical Society* **1994**, *116*, 10657.

36. Gabal, M.; Elroby, S. A.; Obaid, A. *Powder Technology* **2012**, *229*, 112.

37. Yabalak, E.; Gu¨nay, F.; Kasumov, V. T.; Arslan, H. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2013**, *110*, 291.

38. Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; son, G. P.-. *Gaussian 09, revision a. 02, gaussian, Inc., Walling- ford, CT 200.*

39. Yang, Y.; Gao, H. *Journal of Molecular Structure* **2012**, *1013*, 111.

40. Anto, P.; Panicker, C. Y.; Varghese, H. T.; Philip, D.; Arpaci, O. T.-.; Tekiner-Gulbas, B.; Yildiz, I. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2007**, *67*, 744.

41. Saxena, R.; Kandpal, L.; Mathur, G. *Journal of Polymer Science Part A: Polymer Chemistry* **2002**, *40*, 3959.

42. Bellamy, L. J. *Chapman and Hall London* **1975**, *1*.

43. Xie, J.; Chang, J.; Wang, X. *Application of ir in organic chemistry and medicinal chemistry* **2001**.

44. Li, L.; Cai, T.; Wang, Z.; Zhou, Z.; Geng, Y.; Sun, T. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2014**, *120*, 106.

45. Mary, Y. S.; Jojo, P.; Panicker, C. Y.; Alsenoy, C. V.; Ataei, S.; Yildiz, I. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2014**, *122*, 499.

46. Roeges, N. P. *Wiley* **1994**.

47. Kumar, V.; Panikar, Y.; Palafox, M.; Vats, J.; Kostova, I.; Lang, K.; Rastogi, V. *Indian Journal of Pure & Ap- plied Physics* **2010**, *48*, 85.

48. Kalsi, P. *New Age Inter- national* **2007**.

49. Sathyanarayana, D. N. *New Age International* **2007**.

50. Kostova, I.; Momekov, G. *European journal of medicinal chemistry* **2008**, *43*, 178.

51. Sinha, L.; Prasad, O.; Karabacak, M.; Mishra, H.; Narayan, V.; Asiri, A. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2014**, *120*, 126.

52. Arjunan, V.; Govindaraja, S. T.; Ravindran, P.; Mohan, S. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2014**, *120*, 473.