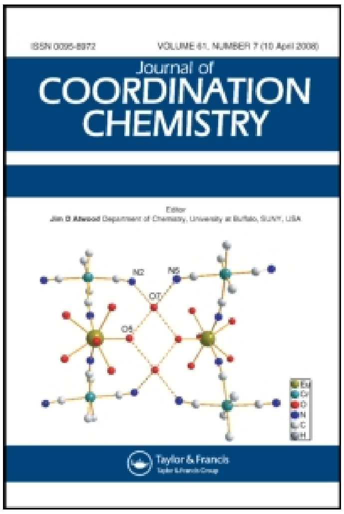

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Theoretical study of inner and outer mononuclear complexes of Co(II), Ni(II), and Cu(II) with a compartmental hexadentate Schiff base derived from 3-formylsalicylic acid

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Theoretical study of inner and outer mononuclear complexes of Co(II), Ni(II), and Cu(II) with a compartmental hexadentate Schiff base derived from 3-formylsalicylic acid

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Density functional theory (B3LYP/6-31G(d)) has been applied for optimization and calculation of the vibrational spectra of the compartmental hexadentate Schiff base derived from 3-formylsalicylic acid and 4,5-dichloro-1,2-phenylenediamine and 12 of its mononuclear complexes with Co(II), Ni(II), and Cu(II). Six of these complexes have the metal ion occupying the inner, N_2O_2, or the outer, O_2O_2, coordination sites in square planar geometry. The other six complexes possess octahedral geometry, occupying the inner or the outer coordination sites coordinating, additionally, to two waters. Significant changes in the ligand geometry have been observed in all complexes to permit efficient complexation with the metal. Assignments of the infrared bands are proposed based on calculations. Vibrational frequencies that are important for assignment and confirmation of the coordination sites are reported. Comparison of the total energies of the complexes reveals that inner complexes are more stable than corresponding outer complexes. Selectivity of metal ions to the coordination sites is also discussed.

Keywords: 3-Formylsalicylic acid; Compartmental ligand; Mononuclear complexes; DFT; Vibrational spectra

1. Introduction

Schiff bases form stable complexes with most transition metal ions [1–21]. 3-Formylsalicylic acid (3-fsa) serves as a basic building unit for designing polypodal Schiff bases [5–21]. Amines/diamines/amino acids and substituted aromatic amines with suitable donor centers produce compartmental Schiff-base ligands with 3-fsa. These are Salen-type ligands [22] which are one of the most important coordinating systems [23]. They are effective agents for synthesizing multimetallic compounds [5–18] and are gaining ground in catalysis, magnetic materials, optical devices and bioinorganic chemistry. Recently, Schiff-base complexes were investigated as inhibitors in prostate cancer cells [24] and tumor cells [25], and some of the salen-type Schiff-base complexes were reported to possess inhibitory activities against xanthine oxidase and excellent antibacterial activities [26, 27]. These compartmental ligands possess different coordination sites, usually known as inner and outer sites.

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Mononuclear complexes of these Schiff bases can have the metal in the inner coordination site [28–41] or in the outer coordination site [34–41]. Considerable difference in ligand field strength exists between the two centers and thus mononuclear complexes with metals occupying different coordination sites would have different spectroscopic properties [28, 41]. In a previous study, Zude *et al.* [41] found that occupancy of the outer coordination site of the Schiff-base ligand of 3-fsa with 1,2-diaminoethane by Cu(II) results in less fluorescence intensity, while presence of the metal in the inner coordination site results in complete quenching of intensity. The difference in ligand field strength of the two sites also affects the stability which may affect their catalytic activity and/or bioactivity. Identification of the coordination site and factors affecting its type, inner or outer, are thus important.

Vibrational spectra have been used to determine the coordination sites by comparison of the vibrational frequencies of the coordinating groups in the two sites before and after complexation to metal ions. Theoretical studies on these ligands and their complexes have not been reported. In continuation to our studies on 3-fsa [42–44] and its Schiff base with 4,5-dichloro-1,2-phenylenediamine [45], we present density functional theory (DFT) studies on this Schiff base and 12 of its mononuclear complexes with Co(II), Ni(II), and Cu(II) in order to determine their characteristic vibrational frequencies, their relative stability, and factors affecting the coordination site.

2. Theoretical procedure

Density functional calculations were carried out by the program package of Gaussian 03 [46] using the hybrid B3LYP functional [47–49]. Geometries of the ligand and its complexes were optimized with 6-31G(d) basis sets without symmetry constraint. In all systems, the stability check of the DFT wavefunction showed a stable wavefunction under the perturbations considered. Frequency calculations on all final optimized structures have not found any imaginary frequency, indicating that the obtained structures are energy minima. The resulting theoretical frequencies were scaled with a uniform scaling factor of 0.9613 that has been recommended for B3LYP/6-31G(d) level of theory [50, 51]. For the sake of spectral analysis, the calculated frequencies are transformed into Lorentz line shape bands with a small line-width of $5\,\text{cm}^{-1}$ for clearly distinguishing close frequencies.

3. Results and discussion

3.1. *Optimized ground-state structures*

The labeling diagram of the ligand and its four different types of complexes used in this article are displayed in figure 1. Some selected geometric parameters of the optimized structures are listed in table 1. Geometry optimization led to similar structural features for certain type of complexes and thus only the optimized structures of the ligand and its four mononuclear complexes with Cu(II) are shown in figure 2.

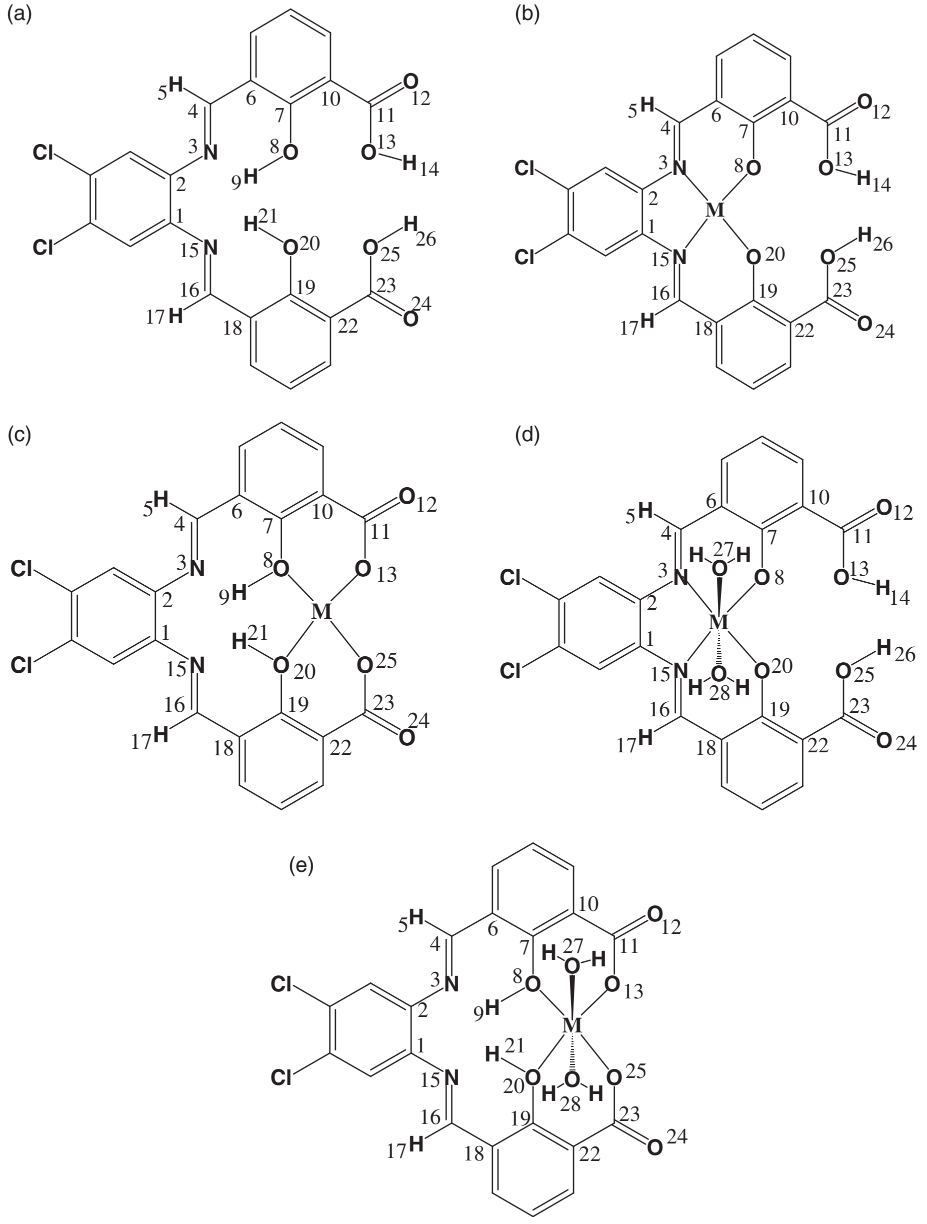

Figure 1. Labeling diagram of the ligand (a), inner square planar complexes (b), outer square planar complexes (c), inner octahedral complexes (d), and outer octahedral complexes (e). M represents Co(II), Ni(II), or Cu(II).

The characteristic feature of the optimized ligand structure is the orientation of the two salicylic acids with respect to the dichlorobenzene; one bends up and the other bends down (figure 2a). This bending is large as shown by distance between O_{13} and O_{25}, 5.64 Å, and the dihedral $C_1C_2N_3C_4$ angle, 145.5°, and results in a larger outer coordination site in comparison to the inner one. This structural feature results in inner

Table 1. Selected structural parameters of the ligand and its 12 complexes by theoretical prediction.

Structural property	Ligand (H_4fsacph)	Inner square planar complexes			Outer square planar complexes			Inner octahedral complexes			Outer octahedral complexes		
		Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)
Bond distances (Å)													
C_1–C_2	1.42	1.41	1.41	1.42	1.42	1.42	1.42	1.41	1.41	1.42	1.42	1.42	1.42
C_2–N_3	1.40	1.41	1.41	1.41	1.40	1.40	1.40	1.41	1.41	1.41	1.40	1.40	1.40
N_3–C_4	1.29	1.32	1.32	1.31	1.30	1.30	1.30	1.31	1.31	1.31	1.30	1.30	1.30
C_4–H_5	1.1	1.09	1.09	1.09	1.09	1.10	1.10	1.09	1.09	1.09	1.10	1.10	1.10
C_4–C_6	1.45	1.41	1.41	1.42	1.44	1.44	1.44	1.43	1.42	1.43	1.45	1.45	1.45
C_6–C_7	1.43	1.45	1.45	1.45	1.42	1.42	1.42	1.45	1.44	1.45	1.42	1.42	1.42
C_7–O_8	1.33	1.29	1.28	1.28	1.37	1.37	1.37	1.29	1.29	1.29	1.37	1.37	1.37
O_8–H_9	1.00	–	–	–	1.06	1.05	1.04	–	–	–	1.03	1.04	1.04
C_7–C_{10}	1.42	1.44	1.44	1.44	1.39	1.39	1.40	1.44	1.44	1.44	1.40	1.40	1.40
C_{10}–C_{11}	1.49	1.49	1.49	1.49	1.53	1.52	1.53	1.49	1.49	1.49	1.53	1.52	1.52
C_{11}–O_{12}	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22
C_{11}–O_{13}	1.35	1.35	1.35	1.35	1.30	1.30	1.30	1.36	1.36	1.36	1.31	1.31	1.31
O_{13}–H_{14}	0.98	0.98	0.98	0.98	–	–	–	0.98	0.98	0.98	–	–	–
$N_3 \cdots N_{15}$	2.75	2.56	2.54	2.61	2.75	2.74	2.74	2.58	2.55	2.62	2.75	2.74	2.74
$O_8 \cdots O_{20}$	3.83	2.52	2.48	2.12	2.65	2.62	2.68	2.69	2.55	2.83	2.75	2.66	2.73
$O_{13} \cdots O_{25}$	5.64	3.66	3.52	4.16	2.57	2.51	2.72	4.51	4.25	4.62	2.74	2.58	2.80

N_3–H_9	1.71	–	–	–	1.50	1.52	1.54	–	–	–	1.57	1.55	1.56
N_{15}–H_{21}	1.71	–	–	–	1.56	1.51	1.56	–	–	–	1.57	1.52	1.56
N_3–M	–	1.87	1.85	1.94	–	–	–	1.90	1.87	1.97	–	–	–
O_8–M	–	1.84	1.83	1.89	1.91	1.89	1.89	1.90	1.86	1.94	1.97	1.90	1.99
O_{13}–M	–	–	–	–	1.84	1.81	1.85	–	–	–	1.91	1.84	1.91
O_{27}–M	–	–	–	–	–	–	–	2.40	2.57	2.58	2.41	2.59	2.59
O_{28}–M	–	–	–	–	–	–	–	2.40	2.57	2.58	2.39	2.55	2.54
Bond angles (°)													
$C_1C_2N_3$	118.4	113.9	113.7	115.1	118.2	118.1	118.2	114.4	113.7	115.2	118.2	118.2	118.2
$C_2N_3C_4$	121.5	121.5	121.5	123.2	124.1	123.7	123.9	121.6	121.7	122.7	123.4	123.5	123.4
$N_3C_4H_5$	121.0	118.4	118.2	118.7	121.5	121.3	121.4	118.8	118.6	118.7	121.3	121.2	121.4
$N_3C_4C_6$	122.6	125.8	126.0	126.2	124.2	121.2	121.3	125.9	125.8	126.6	121.6	121.3	121.6
$C_4C_6C_7$	121.4	121.4	120.9	122.5	121.2	121.1	121.2	122.0	121.3	122.8	121.3	121.1	121.4
$C_6C_7O_8$	120.7	122.2	122.2	122.6	117.3	118.1	117.8	122.5	122.5	122.8	118.1	118.3	117.9
$C_7O_8H_9$	108.0	–	–	–	106.7	106.5	106.6	–	–	–	107.0	106.9	106.9
$C_{10}C_{11}O_{13}$	115.3	115.0	115.0	115.3	118.7	118.7	118.4	114.6	114.4	114.7	118.1	118.3	117.9
Dihedral angles (°)													
$C_1C_2N_3C_4$	145.5	177.9	175.1	177.7	156.4	149.6	152.2	174.0	178.1	169.7	150.8	146.0	151.6
$C_2N_3C_4H_5$	4.3	3.0	2.5	5.3	4.0	2.9	4.1	3.3	2.0	0.5	3.4	2.8	3.3
$C_2N_3C_4C_6$	176.6	176.3	177.1	173.9	176.8	179.0	176.6	175.3	176.0	177.2	178.0	179.2	178.1
$C_4C_6C_7C_{10}$	179.7	175.5	175.9	174.9	179.6	178.4	179.6	170.7	171.6	171.5	180.0	177.6	179.3
$C_6C_7O_8H_9$	179.9	–	–	–	0.9	1.9	0.6	–	–	–	0.9	2.2	0.6
$C_7C_{10}C_{11}O_{13}$	2.0	18.2	17.1	15.3	9.5	11.0	13.7	24.0	25.1	22.7	21.1	9.4	21.4

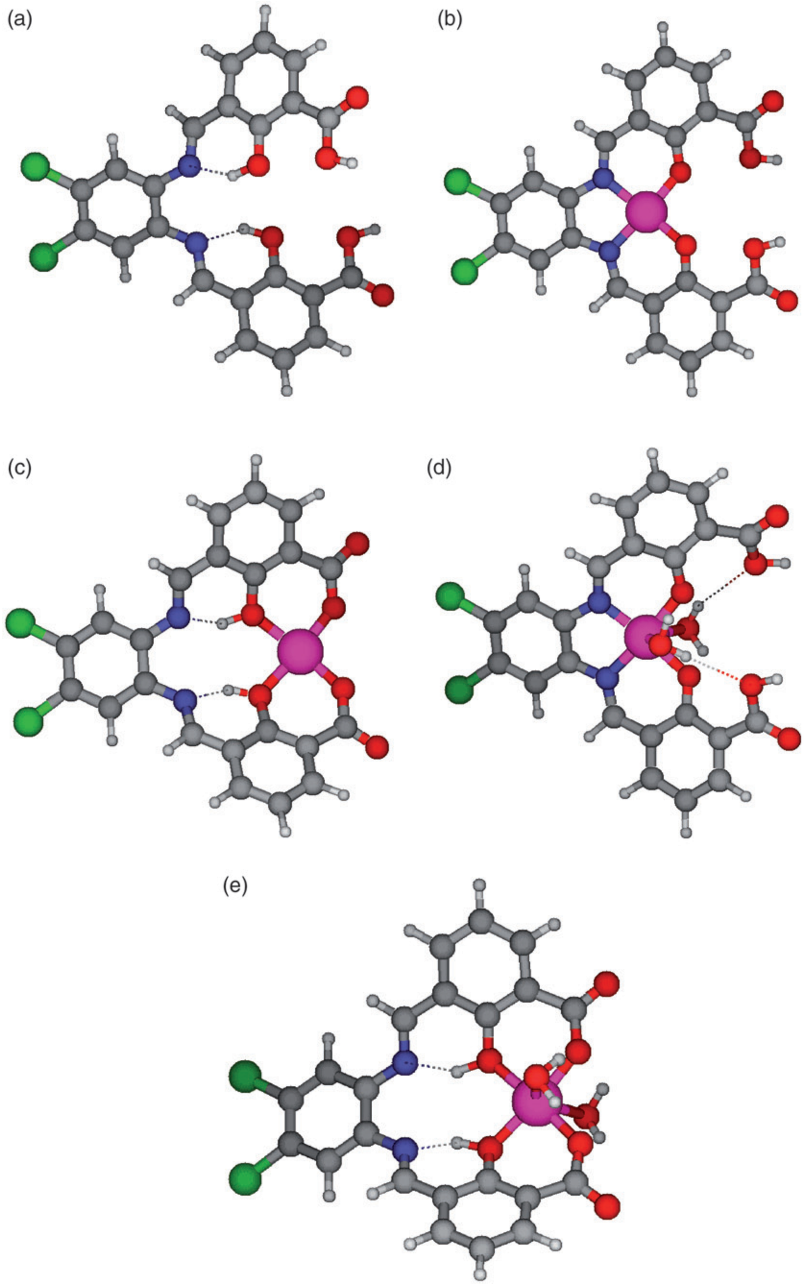

Figure 2. Optimized structures of the ligand (a), inner square planar Cu(II) complex (b), outer square planar Cu(II) complex (c), inner octahedral Cu(II) complex (d), and outer octahedral Cu(II) complex (e).

type complexes with small metal ions and outer type complexes with large metal ions, as will be discussed in detail in section 3.3. Another structural feature for the ligand is the formation of hydrogen bonds between phenolic hydrogens and neighboring nitrogens, in agreement with the experimental infrared (IR) spectrum of the ligand; a broad band with a maximum intensity at $3280\,\mathrm{cm}^{-1}$ has been observed and assigned to the stretching vibration of the phenolic group, υ_{str} (O–H_{ph}) [45]. Such a broad and lower energy band confirms the intramolecular hydrogen bonding of the phenolic hydrogen.

The complexation of metal ions in the inner coordination site results in a square planar geometry. Figure 2(b) shows the optimized structure of the inner square planar Cu(II) complex. This figure together with the data in table 1 clearly shows the change in the ligand structure on complexation with metal. Major structural changes involve atoms surrounding the metal ion while atoms away from the metal tend to retain their structural parameters (bond distances, bond angles, and dihedral angles). C_2–N_3, N_3–C_4, C_6–C_7, and C_7–C_{10} increase by 0.01, 0.02−0.3, 0.02, and 0.02 Å, respectively, while C_4–H_5, C_4–C_6, and C_7–O_8 decrease by 0.01, 0.03−0.04, and 0.04–0.05 Å, respectively, upon complexation. One atom forming these bonds is either in direct complexation with the metal or is separated from the metal by only one atom. Bonds between atoms that are separated from the metal ion by more than one atom are almost unaffected by the complexation; C_{10}–C_{11}, C_{11}–O_{12}, C_{11}–O_{13}, and O_{13}–H_{14}, in which all atoms are in the outer coordination sphere, undergo no change in bond length upon complexation. The change in bond lengths is responsible for change in vibrational frequency. Absorption bands that correspond to vibrations of atoms in the inner coordination sphere are thus expected to shift vibrational frequencies while absorptions that arise from vibrations involving atoms in the outer sphere are expected to be unaffected by complexation of the metal to the inner site. Other structural changes are: (1) The three benzene rings are almost in the same plane with dihedral angle $C_1C_2N_3C_4$, 175.1–177.9°. This planarity permits efficient complexation of the phenolic oxygens with the metal. (2) The two carboxylates are not in the same plane as the benzene rings, bending in opposite directions but not to a large degree as shown by the $O_{13}\cdots O_{25}$ distance, 3.52–4.16 Å, and the dihedral $C_7C_{10}C_{11}O_{13}$ angle, 15.3–18.2°.

The outer square planar complexes also have large structural differences in comparison with the free ligand. The optimized structure of the outer square planar Cu(II) complex is shown in figure 2(c). In contrast to the inner complexes, C_2–N_3, N_3–C_4, C_4–H_5, and C_4–C_6, away from the metal ion, are negligibly affected by complexation. O_8–H_9, C_{10}–C_{11}, and C_{11}–O_{13} are strongly affected by the metal coordination; the first two increase in the range 0.03–0.04 and 0.04–0.06 Å, respectively, while the third decreases by 0.05 Å. In all complexes, the phenolic hydrogen is hydrogen bonded to the neighboring nitrogen, responsible for the slight change in bond lengths and angles in the inner coordination site; however, these differences are less than changes due to direct interaction with the metal. In contrast to the inner complexes, the outer complexes are less planar, as indicated from the value of the dihedral $C_1C_2N_3C_4$, ∼150°, *versus* ∼177° in the inner complexes.

The inner octahedral complexes have similar structural features to the inner square planar complexes (figure 2d). Changes in bond lengths, bond angles, and dihedral angles occur in similar directions and in comparable values to those observed in the inner square planar complexes (table 1). The slight increase in C_{11}–O_{13} bond, 0.01 Å, is a result of hydrogen bond formation between coordinated water and carboxylate oxygens. The higher symmetry of the complexes around the two waters results in equal separation of water molecules from the metal.

The outer octahedral complexes are also structurally similar to the outer square planar complexes (figure 2e). As observed in the inner octahedral complexes, changes in the structural properties occur in similar directions and in comparable values to those observed in the outer square planar complexes (table 1). In contrast with the inner octahedral complexes, the coordinated waters are not involved in hydrogen bonding and their bonds with the metal are not equal. This is a result of the electronic environment around the two waters, one in contact with two aromatic moieties more than the other.

3.2. *Calculated vibrational spectra*

Frequency calculations on all final optimized structures at the B3LYP/6-31G(d) level of theory have not found any imaginary frequencies. Complexation of the ligand with the metal results in modification of the vibrational spectrum of the ligand. Such modifications include: (1) increase or decrease in vibrational frequencies of vibrations involving atoms coordinating to the metal, (2) absence of some vibrational frequencies due to complexation, and (3) appearance of new vibrational frequencies corresponding to vibrations involving new bonds and angles. The changes in IR spectra of the ligand on complexation with metals are a major function of the coordination site and a slight function of the type of metal. The geometry around the metal has a negligible effect, as shown by the similarity between calculated IR spectra of the square planar and octahedral complexes, except for bands resulting from coordinated water. The shift in frequencies of the stretching vibrations is related to changes in bond length with a decrease in bond length accompanied by increase in its vibrational frequency and vice versa. Bonds between atoms separated from the metal by more than one atom undergo minimal change in bond length and are thus found at similar frequencies. Calculated IR spectrum of the ligand is given in figure 3 and calculated spectra of its four Cu(II) complexes can be found in Supplementary material (figures S1–S4). The resulting theoretical frequencies were scaled with a uniform scaling factor of 0.9613, as recommended for B3LYP/6-31G(d) level of theory [50, 51].

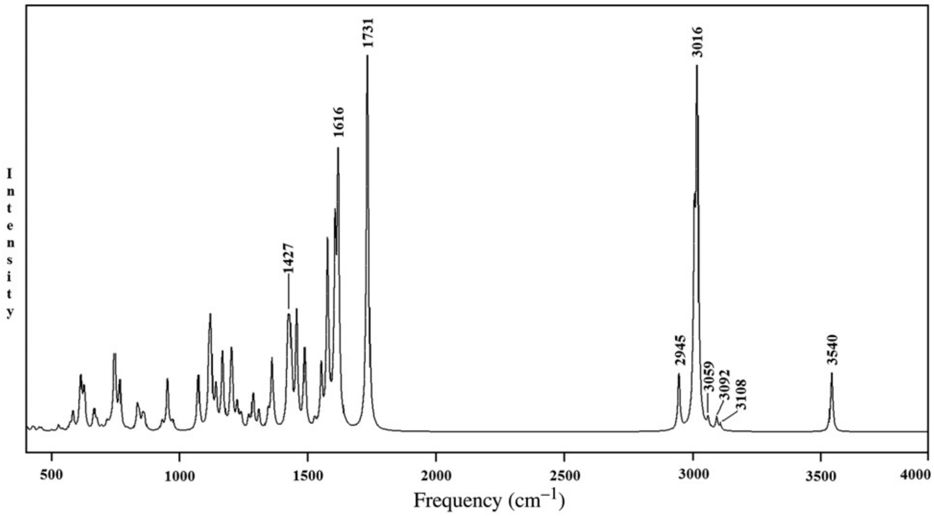

Figure 3. Calculated IR spectrum of the ligand, scaled by 0.9613.

3.2.1. Vibrational spectrum of the ligand. The calculated IR spectrum of the optimized ligand structure is shown in figure 3. The frequencies of the stretching vibrations involving phenolic oxygen, ν_{str}(C–O$_{ph}$) and ν_{str}(O$_{ph}$–H), are 1427 and 3016 cm^{-1}, respectively [2, 3, 45]. Frequencies of the stretching vibrations of the carboxylic group, ν_{str}(C=O) and ν_{str}(O$_{car}$–H), occur at 1731 and 3540 cm^{-1} [12, 28, 33, 41, 45]. The stretching vibrations in the azomethine group, ν_{str}(C=N) and ν_{str}(C–H$_{az}$), occur at 1616 and 2945 cm^{-1} [1, 3, 12, 28, 33, 41, 45]. Stretching vibrations involving aromatic hydrogen, ν_{str}(C–H$_{ar}$), occur at different frequencies, 3059, 3092, and 3108 cm^{-1} [1], due to different chemical environments.

3.2.2. Vibrational spectra of inner square planar complexes. Table 2 shows frequencies of the most important vibrations of the inner square planar complexes. Complexation of the metal ion in the inner coordination site results in deprotonation of the phenol [28–41]. The stretching vibration involving phenolic oxygen, ν_{str}(C–O$_{ph}$), occurs at 1437–1452 cm^{-1}. The ν_{str}(C=N) is at 1579–1586 cm^{-1}, 30–37 cm^{-1} lower than free ligand [4, 12, 21, 28, 33, 41]. The ν_{str}(C–H$_{az}$) occurs at 3039 cm^{-1} in the Co(II) and Ni(II) complexes and at 3001 cm^{-1} in the Cu(II) complex showing an increase in vibrational energy in comparison with free ligand. The data in table 2 show that the stretching vibrations involving the carboxylic oxygens, ν_{str}(C=O) and ν_{str}(O–H$_{car}$), and aromatic hydrogen, ν_{str}(C–H$_{ar}$), are almost the same as in the free ligand indicating that vibrations of atoms in the outer complexation site behave almost the same before and after complexation, in agreement with the observed structural features of the inner square planar complexes. Experimentally reported frequencies of ν_{str}(C=O) for inner complexes of similar ligands [1, 12, 28, 33, 40, 41] are close to the calculated frequencies.

3.2.3. Vibrational spectra of outer square planar complexes. The frequencies of some selected vibrations in the outer square planar complexes are given in table 3. The stretching vibration, ν_{str}(C–O$_{ph}$), results in a very weak band near 1404 cm^{-1} in all the complexes, which, in contrast to the inner square planar complexes, is shifted to lower energy than the free ligand. The ν_{str}(C=N) occurs at 1596 cm^{-1} in the three complexes,

Table 2. Selected vibrations and their frequencies (cm^{-1}) in inner square planar complexes.

Complex	ν_{str}(C–O$_{ph}$)	ν_{str}(C=N)	ν_{str}(C=O)	ν_{str}(C–H$_{az}$)	ν_{str}(C–H$_{ar}$)	ν_{str}(O–H$_{car}$)
Co(II)	1437	1579	1727	3039	3055, 3090, 3102	3541
Ni(II)	1449	1580	1727	3039	3054, 3089, 3102	3542
Cu(II)	1452	1586	1725	3001	3052, 3090, 3102	3539

Table 3. Selected vibrations and their frequencies (cm^{-1}) in outer square planar complexes.

Complex	ν_{str}(C–O$_{car}$)	ν_{str}(C–O$_{ph}$)	ν_{str}(C=N)	ν_{ben}(O–H$_{ph}$)	ν_{str}(C=O)	ν_{str}(O–H$_{ph}$)	ν_{str}(C–H$_{az}$)	ν_{str}(C–H$_{ar}$)
Co(II)	1277	1406	1595	1669	1692	2089, 2379	2982	3066, 3091, 3108
Ni(II)	1284	1403	1596	1669	1690	2142, 2242	2988	3066, 3091, 3108
Cu(II)	1282	1407	1596	1668	1692	2266, 2383	2981	3059, 3092, 3108

Table 4. Selected vibrations and their frequencies (cm^{-1}) in inner octahedral complexes.

Complex	ν_{str} (C–O_{ph})	ν_{str} (C=N)	ν_{ben} (wat)	ν_{str} (C=O)	ν_{str} (C–H_{az})	ν_{str} (C–H_{ar})	ν_{str} (O–H_{car})	ν^{as}_{str} (wat)
Co(II)	1421	1596	1651, 1670	1735	3026	3052, 3088, 3100	3539	3659, 3669
Ni(II)	1425	1600	1641, 1664	1738	3035	3054, 3088, 3100	3540	3654, 3665
Cu(II)	1417	1602	1649, 1673	1736	3000	3052, 3089, 3101	3538	3637, 3667

20 cm^{-1} lower than the vibrational frequency in the free ligand and in agreement with experimental values [41, 45]. In comparison with free ligand, ν_{str}(C–H_{az}) shifts to slightly higher value, 2981–2988 cm^{-1}. The frequency of ν_{str}(C=O) in the three complexes at 1692 cm^{-1} is lower than that in the free ligand [40, 41]. In the three complexes, ν_{str}(C–H_{ar}) is at the same frequency as in the free ligand. Two bands for ν_{str}(O–H_{ph}) have been observed, the first in the range 2089–2266 cm^{-1} and the second at 2242–2383 cm^{-1}. Both occur at lower vibrational frequency than the free ligand, as expected, due to hydrogen bond formation. A new band in all spectra at 1669 cm^{-1} corresponds to bending of the phenolic group, ν_{ben}(O–H_{ph}). A new strong vibrational band in all complexes at 1277–1284 cm^{-1} is assigned to ν_{str}(C–O_{car}), in which O is the carboxylic oxygen that bonds to the metal. These two new bands are characteristics to the outer complexes and are thus important in the assignment of coordination site.

3.2.4. Vibrational spectra of inner octahedral complexes. The frequencies of some selected vibrations in the inner octahedral complexes are given in table 4. Similar to the inner square planar complexes, ν_{str}(C–O_{ph}) and ν_{str}(C–H_{az}) increase [12, 28, 33, 34], ν_{str}(C=N) decreases [12, 28, 33, 34], and both ν_{str}(C=O) and ν_{str}(O_{car}–H) are unchanged [12, 28, 32]. The ν_{str}(C–H_{ar}) occurs very close to the free ligand. Other characteristic vibrations involve coordinated water. Two sets of very weak close bands have been found in all complexes at 1641–1673 and 3637–3667 cm^{-1}, which correspond to bending and asymmetric stretching vibrations in the coordinated water, respectively [2, 32]. Tables 2 and 4 clearly show that only bands corresponding to vibrations in coordinated water can determine the geometry of the coordination site. However, water can exist as crystalline water and similar IR spectra can result. The intensity of the vibrational bands of water is also problematic and they are sometimes difficult to assign in the IR spectrum. Thus, IR spectrum can distinguish between different coordination sites but may not be accurate enough for investigation of the geometry around the metal ion which, instead, can be determined from the electronic spectra or magnetic moment measurements.

3.2.5. Vibrational spectra of outer octahedral complexes. Frequencies of some selected vibrations in the outer octahedral complexes are given in table 5. We see that ν_{str}(C–O_{ph}), ν_{str}(C=N), ν_{str}(C–H_{ar}), ν_{str}(C–H_{az}), ν_{ben}(O–H_{ph}), and ν_{str}(C=O) occur at values very similar to those in the outer square planar complexes. Also similar to outer square planar complexes, the stretching frequencies of the phenolic group, ν_{str}(O–H_{ph}), appear at lower frequency. Two bands at 3503–3536 and 3523–3555 cm^{-1} correspond to symmetric stretching vibrations of complexed water, ν^{s}_{str}(wat) [45]. Two other bands at 3609–3635 and 3638–3655 cm^{-1} are assigned to asymmetric vibrations, ν^{as}_{str}(wat).

Table 5. Selected vibrations and their frequencies (cm^{-1}) of outer octahedral complexes.

Complex	ν_{str} (C–O_{car})	ν_{str} (C–O_{ph})	ν_{str} (C=N)	ν_{ben} (O–H_{ph})	ν_{str} (C=O)	ν_{str} (O–H_{ph})	ν_{str} (C–H_{az})	ν_{str} (C–H_{ar})	ν^{s}_{str} (wat)	ν^{as}_{str} (wat)
Co(II)	1278	1409	1597	1666	1689	2404, 2474	2977	3066, 3091, 3109	3512, 3523	3609, 3638
Ni(II)	1278	1407	1597	1667	1688	2176, 2365	2986	3066, 3091, 3109	3536, 3555	3635, 3655
Cu(II)	1278	1409	1601	1665	1691	2366, 2433	2980	3066, 3092, 3109	3503, 3525	3626, 3650

Table 6. Total energy, E (Hartree) and energy difference, ΔE ($kcal\,mol^{-1}$) between the inner and outer types of complexes.

Metal	E (inner square planar)	E (outer square planar)	$\Delta E = E_{inner} - E_{outer}$	E (inner octahedral)	E (outer octahedral)	$\Delta E = E_{inner} - E_{outer}$
Co(II)	−3709.58033171	−3709.52263110	−36.21	−3862.44033236	−3862.39467704	−28.65
Ni(II)	−3835.09906577	−3835.03750867	−38.63	−3987.94079413	−3987.88859158	−32.76
Cu(II)	−3967.21862617	−3967.17463237	−27.61	−4120.07472496	−4120.04026529	−21.6

Similar to outer square planar complexes, the strong band at 1278 cm^{-1} in all complexes is assigned to ν_{str}(C–O_{car}). IR spectra are thus similar to those of the outer square planar complexes except for bands due to vibrations in water; again, care must be taken in investigation of the geometry around the metal ion from IR spectra.

3.3. ***Inner* versus *outer complexes***

Complexation of metal ions with structurally similar Schiff bases have been reported to occur in the inner coordination site [28–41] and in the outer coordination site [34–41, 45]. Table 6 shows the total electronic energy of the optimized complexes and the energy difference between the inner and the corresponding outer complexes. The data in table 6 show that the inner complexes are more stable in both square and octahedral complexes than the corresponding outer complexes. The inner square planar complexes of Cu(II), Co(II), and Ni(II) are 27.61, 36.21, and 38.63 $kcal\,mol^{-1}$, lower in energy than the corresponding outer complexes, respectively. Similarly, the inner octahedral complexes of these ions, in respective, are 21.6, 28.65, and 32.76 $kcal\,mol^{-1}$, lower than the corresponding outer complexes, respectively. The stability of the inner complexes in comparison with the outer complexes is a reason for the large number of inner complexes [28–41]. Other factors that control coordination of the metal to the coordination sites are structural features of the ligand and the experimental conditions. The geometry of the ligand affects the coordination site. The structural properties of the ligand (section 3.1) suggest that neutral ligand will favor formation of the inner complexes with small metal ions since the orientation of the carboxylic groups does not permit their complexation to the same metal. In contrast, large metal ions have been reported [34, 37–40] to occupy the outer coordination sites, which confirm the theoretically determined ground state structure of the ligand, large outer *versus* inner coordination site.

The pH of the medium is the experimental factor that affects the type of coordination. In acidic media where the ligand exists in the molecular form, formation of inner complexes will dominate for small metal ions while large metal ions will occupy the outer coordination site based on the structural properties. At pH values where ligand is dibasic, *via* deprotonation of the two carboxylic groups, the formation of outer complexes will be favored [41, 45]. The electrostatic attraction between the positive metal ion and the negative charges on the carboxylic groups can be a driving force for bringing the carboxylic groups in position for complexation. At much higher pH values, the ligand is tetrabasic and complexation to both sides can occur; however, in equimolar mixtures, formation of the more stable inner complexes will dominate for small metal ions. The effect of the pH can be confirmed from previous experimental studies. Casellato *et al.* [38] synthesized inner square planar complex of Cu(II) with the Schiff base obtained from condensation of 3-fsa and 1,2-diaminoethane, through direct interaction between the metal ion and the ligand. Zude *et al.* [41] synthesized the outer isomer *via* mixing the ligand with the metal ion followed by addition of LiOH in 2 : 1, LiOH : ligand. We ware also able to synthesize outer complexes of the metal ions and the ligand reported in this study through reacting the metal ions with the dilithium salt of the ligand [45].

4. Conclusion

The complexation of three divalent transition metals with the compartmental Schiff-base ligand derived from 3-formylsalicylic acid showed considerable change in the structural and vibrational features of the ligand. Major changes in the vibrational frequencies occur for atoms coordinated with the metal or separated from it by only one atom. The change in IR spectrum of the ligand due to complexation with metal ions depends largely on the coordination site in comparison to the type of metal and the coordination geometry. The most important vibrational frequencies for determination of coordination site are reported. Inner complexes are more stable than the corresponding outer complexes. The site selection by the metal has been concluded to be function of the pH, the configuration of the ligand, and the size of the metal.

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