

Theoretical Vibrational Analysis of Bidentate and Unidentate Coordination of Carbonate, Nitrate, Sulfate, and Perchlorate Ions to a Metal

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ABSTRACT: *In this study, firstly, the vibrational analysis of the bidentate coordination of the title ions to metal was theoretically performed as combined with group-theoretical analysis. In the calculation, the DFT method with B3LYP functional was used at the DEF2-TZVP level set and, cobalt, nickel, and copper were chosen as metal. As expected, the coordination of the ions to the metal atom lowered the symmetry and so, the splitting of degenerate modes occurred together with the appearance of IR inactive modes. The calculated frequencies for all the modes were given together with their symmetry species in tables. These results showed that all the splitting bands of the degenerate modes are nearly center-out, and if the intensity of degenerate mode is high the intensities of its splitting bands are also high or vice versa. Then, to compare, some metal complexes with bidentate and unidentate ligands were optimized and, their calculated frequencies were given together with their corresponding experimental data in tables. From these results it was concluded that the vibrational frequency value of the M-O stretching mode is lower in the unidentate than in the bidentate complexes due to the decreasing of the force constant, and the splitting bands of degenerate modes are larger in the bidentate than in the unidentate complexes.*

KEYWORDS: *Bidentate; Unidentate; Group theory; IR; DFT.*

INTRODUCTION

Ligands can play an important role in the stabilities of their complexes due to the chelate effect which is highly beneficial and desirable in transition metal chemistry [1-4]. The title ligand ions can coordinate to a metal with one of the ways of bidentate, unidentate or bridged bidentate. It is not easy to decide which of these ways exists in the formed complexes. But infrared spectra can help to determine the structures of coordination complexes since the coordination usually causes the appearance of inactive

bands, the splitting of the degenerate modes and, the frequency shifts of the vibrational modes [5-7].

Bidentate ligands donate two pairs ("bi") of electrons to a metal atom and, are often referred to as chelating ligands ("chelate" is derived from the Greek word for "claw") because they can "grab" a metal atom in two places. So, the effect of coordination is undoubtedly stronger in bidentate than in unidentate (monodentate) ligands. Some authors have concluded that as the metal-ligand

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bond becomes stronger, the frequency shifts of the ligand to lower or higher increase [8,9]. In an early study, the normal coordinate calculations were made for nitrate and carbonate ions, assuming them to act as bidentate ligands [10]. The authors in their study have focused on variations of infrared and Raman frequencies of the ligand. Today, with the help of the contemporary advanced programs the structures of coordination complexes can more easily be understandable. So, in the present study the vibrational analysis of the bidentate and unidentate coordination of the title ions to a metal was theoretically performed in detail as supported with their group theory analysis.

COMPUTATIONAL METHODS

The optimized structures and vibrational frequencies of the ions and formed complexes were calculated by using DFT(B3LYP) method with DEF2-TZVP basis set level. All the computations were performed using Gaussian 09 program package on personal computer [11]. The vibrational modes were assigned on the basis of visual inspection of each of the vibrational modes by Gauss-View 5.0 molecular visualization program [12]. The calculated vibrational frequencies were not scaled since the obtained results are sufficiently close to the experimental ones in the comparison.

RESULTS AND DISCUSSION

The calculated vibrational frequencies of the free title ions and their metal coordination complexes are given in Tables 1 and 2, with together the experimental ones [13-19]. The symmetry numbers and species of all the vibrational modes are also written in the tables. When CO_3^{2-} or NO_3^- ion is present as a free ion they will exhibit a molecular point group of D_{3h} . Group theoretical analysis of these ions predicts the four normal modes. While the bending non-planar (A_2''), asymmetrical stretching (E_1') and bending planar (E_1') modes are observed in IR, the symmetric stretching mode (A_1') is IR inactive. Except from the bending non-planar mode (A_2''), all these modes are Raman active. Similarly the free SO_4^{2-} or ClO_4^- ion belong to T_d group. While the asymmetrical stretching (T_2) and bending (T_2) modes are both Raman and IR active, the symmetric stretching (A_1) and bending (E) modes are only Raman active (see Tables 1 and 2).

The bidentate coordination of the ions to the metal changes the symmetry to the C_{2v} point group and so, all the vibrations modes become IR and Raman active

except from the mode of A_2 symmetry (only Raman active). By the coordination, the double degenerate modes of species E_1' or E split into two bands while the triplet degenerate mode of species T_2 split into three bands. These calculated frequencies can be seen in the Tables 1 and 2, with together their symmetry species. In Fig. 1, the splitting bands of the degenerate modes are shown in the IR spectra of CoCO_3 and CoSO_4 complexes. As seen all the splitting bands are nearly center-out, namely, the frequency value of the degenerate mode is nearly at the center of the frequency values of the splitting bands. In addition, if the intensity of the degenerate mode is high the intensities of the splitting bands are also high, or vice versa.

In Tables 1 and 2 the calculated metal-ligand frequencies for some bidentate and unidentate complexes were given together with their corresponding experimental data. In Fig. 2 the optimized structures of the bidentate and unidentate carbonate complexes of $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{Cl}$ and $\text{Co}(\text{NH}_3)_5\text{CO}_3\text{Br}$, respectively, are given. Fig. 3 shows their IR spectra together with the ones of $\text{Cu}(\text{ClO}_4)_2$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ complexes. As seen from the figure the most imported difference between the bidentate and unidentate complexes is the vibrational frequency value of the M-O stretching mode. As example, in the Co complexes this frequency value of Co-O stretching mode was calculated as 457 cm^{-1} for the bidentate structure whereas it was calculated as 325 cm^{-1} for the unidentate structure. This can be attributed to the decreasing of the force constant (calculated as $0.953 \text{ mDyne/A}^\circ$ for the bidentate and, $0.657 \text{ mDyne/A}^\circ$ for the unidentate carbonate complexes, respectively). This effect has also been recorded in Ref [16]. The other imported difference between the bidentate and unidentate complexes is that the splitting bands of the degenerate modes are larger in the bidentate than in the unidentate complexes. This can easily be understandable from Fig. 3. As it is said before, some studies have shown that while the metal-ligand bond becomes stronger, the frequency shifts of the ligand to lower or higher increase [8,9].

CONCLUSIONS

In this study the vibrational analysis of the bidentate coordination of the title ions to a metal which is chosen as cobalt, nickel and copper, was theoretically performed together with their group theoretical analysis. The

Table 1: Assignments and, calculated and experimental frequencies of vibrational modes together with their symmetries for carbonate and sulfate ions, and some bidentate complexes.

Ion or complex	Point group, Sym. of vib. modes	Assignments and, calculated and experimental frequencies (cm ⁻¹) v; stretching, δ ; planar bending, γ ; non-planar bending or symmetric bending, τ ; torsion, β ; breathing.						
		$\frac{v_{\text{sym}}(\text{C-O})}{1016 (\text{A}')} \text{----} 1063^{\text{a}} (\text{R})$	$\frac{\gamma(\text{OCO})}{879 (\text{A}'') \text{----} 880^{\text{a}} (\text{IR})}$	$\frac{v_{\text{asym}}(\text{C-O})}{1383 (\text{E}') \text{----} 1415^{\text{a}} (\text{R})}$	$\frac{\delta(\text{OCO})}{662 (\text{E}'') \text{----} 680^{\text{a}} (\text{IR}) \text{----} 680^{\text{a}} (\text{R})}$			
CO ₃ ²⁻	D _{3h} A ₁ ' + A ₂ ' + 2E'							
CoCO ₃	C _{2v} 4A ₁ + 2B ₁ + 3B ₂	$\frac{v_{\text{sym}}(\text{C-O}) + \delta(\text{OMO})}{950 (\text{A}_1)}$	$\frac{\gamma(\text{OCO})}{792 (\text{B}_1)}$	$\frac{v_{\text{asym}}(\text{C-O})}{1845 (\text{A}_1) \text{----} 1077 (\text{B}_2)}$	$\frac{\delta(\text{OCO}) + v(\text{M-O})}{773 (\text{A}_1) \text{----} 665 (\text{B}_2)}$	$\frac{v(\text{M-O}) + \delta(\text{OCO})}{451 (\text{B}_2)}$	$\frac{\beta_{\text{cmplx}}}{472 (\text{A}_1)}$	$\frac{\tau_{\text{cmplx}}}{174 (\text{B}_1)}$
NiCO ₃		967	786	1833 1088	771 662	433	482	176
CuCO ₃		972	803	1580 1165	580 534	303	321	146
Co(NH ₃) ₄ CO ₃ Cl		903 (1030 ^b)	789 (834 ^b)	1826 (1593 ^b) 1055 (1265 ^b)	744 (760 ^b) 672 (673 ^b)	455 (430 ^b)	419	300
Co(NH ₃) ₃ CO ₃ Br	unidentate complex	952 (1070 ^b)	785 (850 ^b)	1807 (1453 ^b) 1119 (1373 ^b)	736 (756 ^b) 665 (678 ^b)	325 (362 ^b)	413	285
SO ₄ ²⁻	T _d A ₁ + E + 2T ₂	$\frac{v_{\text{sym}}(\text{S-O})}{925 (\text{A}_1) \text{----} 981^{\text{a}} (\text{R})}$	$\frac{\gamma(\text{OSO})}{428 (\text{E}) \text{----} 451^{\text{a}} (\text{R})}$	$\frac{v_{\text{asym}}(\text{S-O})}{1082 (\text{T}_2) \text{----} 1104^{\text{a}} (\text{IR}) \text{----} 1104^{\text{a}} (\text{R})}$	$\frac{\delta(\text{OSO})}{599 (\text{T}_2) \text{----} 613^{\text{a}} (\text{IR}) \text{----} 613^{\text{a}} (\text{R})}$			
CoSO ₄	C _{2v} 5A ₁ + A ₂ + 3B ₁ + 3B ₂	$\frac{v_{\text{sym}}(\text{S-O}) + \delta(\text{OMO})}{796 (\text{A}_1)}$	$\frac{\gamma(\text{OSO})}{569 (\text{A}_1) \text{----} 342 (\text{A}_2)}$	$\frac{v_{\text{asym}}(\text{S-O}) + \delta(\text{OSO})}{1221 (\text{A}_1) \text{----} 1405 (\text{B}_1) \text{----} 772 (\text{B}_2)}$	$\frac{\delta(\text{OSO}) + v(\text{M-O})}{729 (\text{A}_1) \text{----} 532 (\text{B}_1) \text{----} 428 (\text{B}_2)}$	$\frac{v(\text{M-O}) + \delta(\text{OSO})}{597 (\text{B}_2)}$	$\frac{\beta_{\text{cmplx}}}{351 (\text{A}_1)}$	$\frac{\tau_{\text{cmplx}}}{119 (\text{B}_1)}$
NiSO ₄		810	570 338	1219 1399 761	734 523 423	608	354	107
CuSO ₄		800	523 344	1197 1369 704	656 522 356	574	281	88
Co(en) ₂ SO ₄ Br		870 (827 ^c)	534 (515 ^c) 393	1179 (1176 ^c) 1352 (1211 ^c) 861 (806 ^c)	669 (647 ^c) 575 (585 ^c) 455	612 (632 ^c)	427	216
Co(en) ₂ SO ₄ Br 2H ₂ O	unidentate complex	1026 (978 ^c)	612 (625 ^c) 422	1195 (1130 ^c) 1251 (1282 ^c) 839 (794 ^c)	667 (645 ^c) 575 (585 ^c) 492	325	384	218

^a Ref. [15], ^b [16], ^c [17].

Table 2: Assignments and, calculated and experimental frequencies of vibrational modes together with their symmetries for nitrate and chlorate ions, and some bidentate complexes.

Ion or complex	Point group, Sym. of vib. modes	Assignments and, calculated and experimental frequencies (cm ⁻¹) v; stretching, δ; planar bending, γ; non-planar bending or symmetric bending, τ; torsion, β; breathing.						
		$\frac{v_{\text{sym}}(\text{N-O})}{1069 \text{ (A)}} \quad 1049^{\text{a}} \text{ (R)}$	$\frac{\gamma(\text{ONO})}{851 \text{ (A"')} \quad 830^{\text{a}} \text{ (IR)} \quad \text{----}}$	$\frac{v_{\text{asym}}(\text{N-O})}{1401 \text{ (E')} \quad 1350^{\text{a}} \text{ (IR)} \quad 1355^{\text{a}} \text{ (R)}}$	$\frac{\delta(\text{ONO})}{715 \text{ (E')} \quad 680^{\text{a}} \text{ (IR)} \quad 690^{\text{a}} \text{ (R)}}$	$\frac{v(\text{M-O}) + \delta(\text{OCO})}{421 \text{ (B}_2)}$	$\frac{\beta_{\text{emplx}}}{461 \text{ (A}_1)}$	$\frac{\tau_{\text{emplx}}}{197 \text{ (B}_1)}$
NO ₃ ⁻	D _{3h} A ^u +A ^u + 2E ^g							
CoNO ₃ ⁺	C _{2v} 4A ₁ +2B ₁ + 3B ₂	$\frac{v_{\text{sym}}(\text{N-O}) + \delta(\text{OMO})}{937 \text{ (A}_1)}$	$\frac{\gamma(\text{ONO})}{758 \text{ (B}_1)}$	$\frac{v_{\text{asym}}(\text{N-O})}{1795 \text{ (A}_1) \quad 1077 \text{ (B}_2)}$	$\frac{\delta(\text{ONO}) + v(\text{M-O})}{785 \text{ (A}_1) \quad 646 \text{ (B}_2)}$			
NiNO ₃ ⁺		953	755	1797 1078	791 652	396	467	195
CuNO ₃ ⁺		953	774	1717 1047	724 653	287	323	170
Ni(en) ₂ NO ₃ I		1029	798 (805 ^b)	1649 (1480 ^b) 1239 (1292 ^b)	775 (740 ^b) 697 (702 ^b)	401	371	206
Ni(en) ₂ (NO ₃) ₂	unidentate complex	1018	815 (818 ^b)	1578 (1420 ^b) 1297 (1305 ^b)	777 (728 ^b) 708 (708 ^b)	289	389	191
ClO ₄ ⁻	T _d A ₁ +E+2T ₂	$\frac{v_{\text{sym}}(\text{Cl-O})}{918 \text{ (A}_1) \quad \text{----}} \quad 928^{\text{a}} \text{ (R)}$	$\frac{\gamma(\text{OCIO})}{449 \text{ (E)} \quad \text{----}} \quad 460^{\text{a}} \text{ (R)}$	$\frac{v_{\text{asym}}(\text{Cl-O})}{1107 \text{ (T}_2) \quad 1128^{\text{a}} \text{ (IR)} \quad 1128^{\text{a}} \text{ (R)}}$	$\frac{\delta(\text{OCIO})}{618 \text{ (T}_2) \quad 645^{\text{a}} \text{ (IR)} \quad 645^{\text{a}} \text{ (R)}}$			
CoClO ₄ ⁺	C _{2v} 5A ₁ +A ₂ + 3B ₁ +3 ₂	$\frac{v_{\text{sym}}(\text{Cl-O}) + \delta(\text{OMO})}{744 \text{ (A}_1)}$	$\frac{\gamma(\text{OCIO})}{555 \text{ (A}_1) \quad 340 \text{ (A}_2)}$	$\frac{v_{\text{asym}}(\text{Cl-O}) + \delta(\text{OCIO})}{1205 \text{ (A}_1) \quad 1382 \text{ (B}_1) \quad 755 \text{ (B}_2)}$	$\frac{\delta(\text{OCIO}) + v(\text{M-O})}{673 \text{ (A}_1) \quad 530 \text{ (B}_1) \quad 392 \text{ (B}_2)}$	$\frac{v(\text{M-O}) + \delta(\text{OCIO})}{527 \text{ (B}_2)}$	$\frac{\beta_{\text{emplx}}}{357 \text{ (A}_1)}$	$\frac{\tau_{\text{emplx}}}{127 \text{ (B}_1)}$
NiClO ₄ ⁺		753	565 340	1205 1380 745	693 524 385	543	359	118
CuClO ₄ ⁺		848	505 406	1144 1245 890	650 586 170	596	253	66
Cu(ClO ₄) ₂		831	534 (497 ^c) 390	1160 (1130 ^c) 1291 (1270 ^c) 868 (920 ^c)	659 (665 ^c) 574 (600 ^c) 353	596 (624 ^c)	358	152
Cu(ClO ₄) ₂ ·2H ₂ O	unidentate complex	813	489 (480 ^c) 436 (460 ^c)	1155 (1030 ^c) 1251 (1158 ^c) 988 (948 ^c)	653 (648 ^c) 597 (620 ^c) 450	307	245	160

^a Ref. [15], ^b [18], ^c [19].

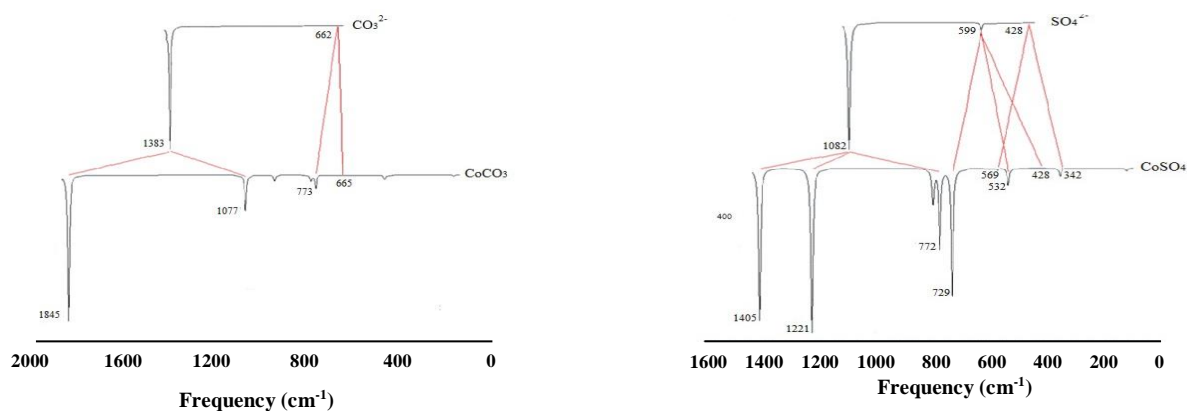


Fig. 1: Calculated IR spectra of free ions and their cobalt complexes, and splitting bands of degenerate vibrational modes.

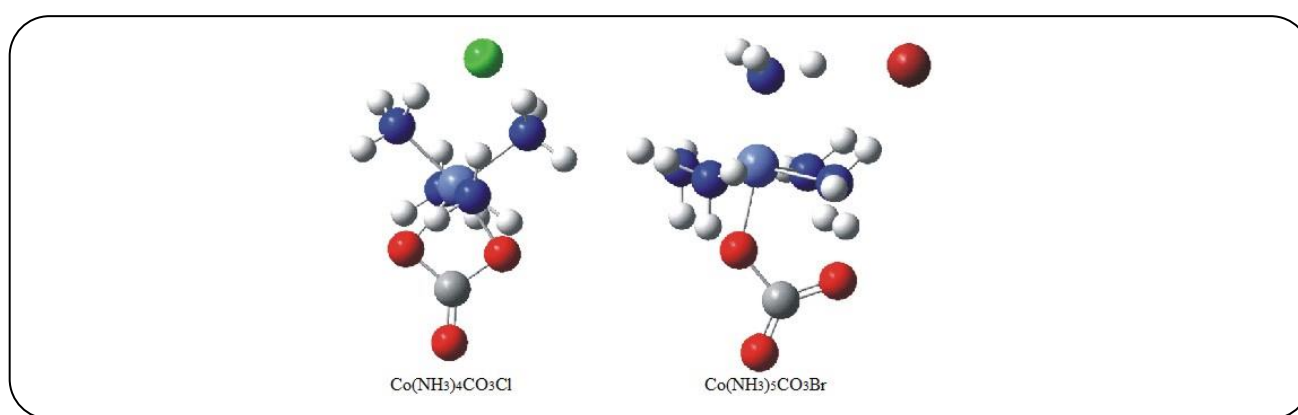


Fig. 2: Optimized structures of $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{Cl}$ and $\text{Co}(\text{NH}_3)_5\text{CO}_3\text{Br}$ complexes with bidentate and unidentate ligands, respectively.

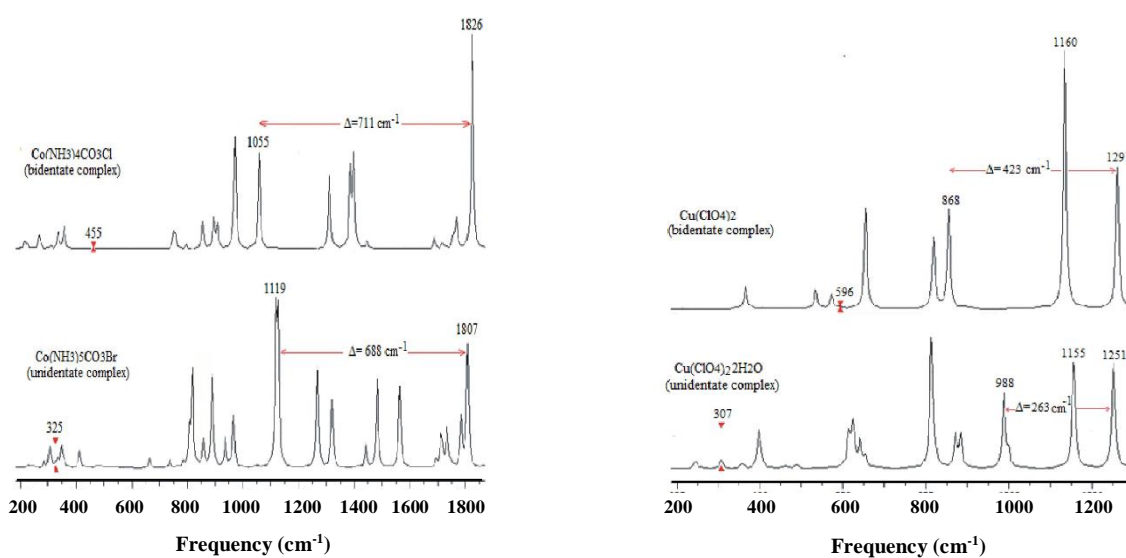


Fig. 3: Calculated IR spectra of some bidentate and unidentate complexes, and splitting bands of degenerate asymmetrical stretching mode.

coordination of the ions to the metal atom changes the symmetry to the C_{2v} point group. So, in this symmetry of the formed complexes, all the vibrations modes become both IR and Raman active except the mode of A_2 symmetry (only R active). After the coordination, the symmetric stretching vibrational mode of carbonate or nitrate ion, which is forbidden in free ions (D_{3h}) becomes IR active, and each of the doubly degenerate asymmetric stretching and bending planar modes split into two bands. Similarly, the symmetric stretching and bending modes of sulfate or perchlorate ion which are forbidden in free ion (T_d) become IR active, and while the doubly degenerate symmetric bending mode splits two bands, the triplet degenerate asymmetric stretching, and bending modes split into three bands. These calculated frequencies were given in tables. It was concluded that all the splitting bands of the degenerate modes are center-out and, that the more intensity the degenerate mode is the more intensities the splitting bands are, or vice versa. Some bidentate and unidentate complexes were optimized as an example. Their calculated frequencies showed that the vibrational frequency value of the M-O stretching mode is lower in the unidentate than in the bidentate complexes depending on the decreasing of force constant and, the splitting bands of the degenerate modes are larger in the bidentate than in the unidentate complexes. It is expected that the calculated and commented data this study will help the experimental researchers in the determination of the structures of their complexes.

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