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### HIGHLIGHTS

• Ni and Zn with 4-chloro-2-nitrobenzenesulfonamide complexes have been prepared.

• The structure of the nickel complex was determined by X-Ray diffration methods.

• FTIR, Raman and UV-VIS spectra have been assigned on the basis of DFT calculation.

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#### ABSTRACT

Two new complexes of Ni and Zn with 4-chloro-2-nitrobenzenesulfonamide (ClNbsa) have been synthesized and characterized. The structure of the [Ni(ClNbsa)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>] complex was determined by X-ray diffraction methods. It crystallizes in the monoclinic P2<sub>1</sub>/c space group with *a* = 12.8679(3) Å, *b* = 7.7254(1) Å, *c* = 12.2478(2) Å,  $\beta$  = 109.899(2)°, *V* = 1144.85 (4)Å<sup>3</sup> and *Z* = 4 molecules per unit cell. The coordination geometry of the Nickel (II) ion in the complex can be described as a distorted octahedron with two N-sulfonamide and four NH<sub>3</sub> groups in opposite vertices. Due to the poor solubility of the Zn(II) complex, their cell parameters were determined by indexing the powder X-ray pattern using the successive dichotomy method implemented in the Fullprof Suite software package. A triclinic cell was determined with cell parameters *a* = 18.3724(1) Å, *b* = 7.9468(8) Å, *c* = 10.2212(9) Å  $\alpha$  = 63.061(6)  $\beta$  = 108.754(6)  $\gamma$  = 109.153(6) and *V* = 1229.97(2)Å<sup>3</sup>. Nuclear magnetic resonance (NMR) spectroscopy of <sup>1</sup>H and <sup>13</sup>C have been used for support the structure of the Zn complex. Vibrational and electronic spectroscopy have been used to characterize the compounds, using theoretical calculations for the assignment of the experimental bands. The thermal behavior was investigated by thermogravimetric analyses (TG) and differential thermal analysis (DT).

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#### 1. Introduction

The use of metal based therapeutics for both diagnosis and treatment of diseases constitutes a new field of increasing interest. Metal ions have been always relevant in biological systems, [1,2] with several diverse features determining the characteristics of metal coordinated systems, as the spatial arrangement of the ligands around the metal ion.

The coordination chemistry of simple and N-substituted sulfonamides has also undergone noticeable development in recent years due to their interesting properties. They are recognized as antitumor, antibacterial, diuretic, hypoglycaemic and anti-thyroid pro-drugs and protease inhibitors [3–6]. In general, metal complexes of heterocyclic sulfonamides possess much stronger carbonic anhydrase (CA) inhibitory properties than the sulfonamides from which they were prepared [7,8]. On the other hand, binary and ternary complexes of transition metals are usually found in biological media and might play important roles in processes as diverse as the catalytic interaction of viruses with bacterial cell walls, or the transport and storage of oxygen [9]. In view of the versatile importance of metal complexes and in order to identify their coordination properties, we have previously reported the results of the structural and electronic investigations

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of p-cyanobenzenosulfonamide (L), and its copper(II) complex [10]. We also prepared and characterized a new copper(II) complex,  $[Cu(L)_2(NH_3)_2]$ , with the 4-chloro-2-nitrobenzenesulfonamide as ligand [11].

The structures of both were analyzed computationally, rendering stable conformations for the free sulfonamide and for the copper complex, and suggesting for the latter a distorted square planar geometry. In light of the interesting coordination chemistry of these compounds, herein we describe the synthesis of two complexes with 4-chloro-2-nitrobenzenesulfonamide (in further text denoted as L) with formula Ni(L)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub> and Zn(L)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>. Their characterization by means of X-ray diffraction, thermogravimetry, FTIR, Raman, NMR and UV–VIS spectra is also discussed. The assignment of experimental electronic, infrared and Raman bands was accomplished with the aid of theoretical results based in density functional theory.

#### 2. Experimental

#### 2.1. Materials and methods

The FTIR spectra were carried out with an EQUINOX 55 spectrophotometer, in the range from 4000 to 400 cm<sup>-1</sup> using the KBr pellet technique, with a spectral resolution of 4 cm<sup>-1</sup>. The Raman spectra were recorded with a Bruker IFS 66 FTIR spectrophotometer provided with the NIR Raman attachment, with a resolution of 4 cm<sup>-1</sup>. The electronic absorption spectra of the compounds were measured in two different conditions: on freshly prepared DMSO solutions in the 200–800 nm spectral range, and in solid sate with KBr reference pellet. They were recorded with a Hewlett–Packard 8452-A diode array spectrometer, using 10 mm quartz cells. DT and TG analyses were performed using Shimadzu TGA-50 and DTA-50H units at a heating rate of 5 °C/min. and oxygen flow of 50 ml/min. NMR spectra were carried out with an Spectrophotometer 500 MHz multinuclear, Bruker Avance II 500

#### 2.2. X-ray diffraction data

The data for the Nickel complex were collected on an Agilent Gemini Diffractometer with an EOS CCD detector equipped with a graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. X-ray diffraction intensities were collected ( $\omega$  scans with  $\theta$  and  $\kappa$ -offsets), integrated and scaled with CrysAlisPro [12] suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro Data were corrected empirically for absorption employing the multi-scan method implemented in CrysAlisPro. The structure was solved by direct methods with SHELXS-97 [13] and the molecular model refined by full-matrix least-squares procedure on  $F^2$  with SHELXL-97 [14,15].

The hydrogen atoms were positioned stereo-chemically and refined with the riding model. The angular locations of the ammonia groups were optimized during the refinement by treating them as rigid bodies allowed to rotate around the Ni-NH<sub>3</sub> bond. Crystal data and refinement results are summarized in Table 1.

The X-ray powder diffraction data (XRPD) were collected on a Philips PW1710 powder diffractometer with a scintillation counter and an exit beam graphite monochromator using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å). The 2 $\theta$  range covered was from 4° to 95° with a step interval of 0.02° and a counting time of 3 s. The XRPD pattern was analyzed using the DICVOL4 program as implemented in the Fullprof code [16].

#### Table 1

Crystal data and structure refinement for [Ni (ClNbsa)<sub>2</sub>(NH3)<sub>4</sub>] complex.

Empirical formula	$C_{12}H_{20}Cl_2N_8NiO_8S_2$
Formula weight	598.09
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 12.8679(3) Å
	b = 7.72540(10) Å
	c = 12.2478(2) Å
	$\beta = 109.90(2)^{\circ}$
Volume	1144.85(4) Å3
Z, Density (calculated)	4, 1.735 Mg/m3
Absorption coefficient	1.320 mm-1
F(000)	612
Crystal size	$0.337 \times 0.278 \times 0.189 \text{ mm}^3$
Crystal shape/color	Prism/bluish
$\theta$ -range for data collection	3.18-28.95°
Index ranges	$-17 \leqslant h \leqslant 16, -10 \leqslant k \leqslant 10, -15 \leqslant l \leqslant 16$
Reflections collected	19379
Independent reflections	2841 [ <i>R</i> (int) = 0.0206]
Observed reflections $[I > 2\sigma(I)]$	2390
Completeness to $\theta$ = 26.50°	93.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.97369
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	2841/0/157
Goodness-of-fit on F2	1.007
Final $R^{d}$ indices $[I > 2\sigma(I)]$	R1 = 0.0251, wR2 = 0.0654
R indices (all data)	R1 = 0.0319, wR2 = 0.0672
Largest diff. peak and hole	0.230 and $-0.425 \text{ e A}^{-3}$

<sup>a</sup>  $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ ,  $wR_2 = [\Sigma w (|F_0|^2 - |F_c|^2)^2 / \Sigma w (|F_0|^2)^2]^{1/2}$ .

#### 2.3. Computational methods

The computational study of the complexes was performed using the density functional theory (DFT) methods implemented in Gaussian 09 [17].

The systems studied herein were subjected to unrestrained energy minimizations using the (B3LYP [18] functional with the 6-31 + G\*\* basis set [19,20] for non-metal atoms and the Los Alamos effective core potentials LANL2DZ [20,21] for the metal. The vibrational frequencies were calculated from the second derivatives and on this basis the vibrational modes have been assigned. In order to model the UV–VIS spectra experimentally determined in DMSO, the geometries were optimized, at the same level, under the solvent condition (Polarizable Continuous Model, PCM) [21–23]. The same solvent model was used in the time dependent DFT calculations (TDDFT). 90 electronic transitions were analyzed using the Merz–Kollman electron density.

#### 2.4. Synthesis of the complexes

4-Chloro-2-nitrobenzenesulfonamide (L) was purified by several crystallizations from ethyl acetate /hexane.

The metal complexes were prepared by direct reaction of ethanol solutions of sulfonamide and metal(II) chloride in the 2:1 M ratio, followed by drop wise addition of 2 ml of 2 M NH<sub>3</sub>, under continuous stirring. The resulting mixture was stirred during ca. 4 h. and was then left to stand at room temperature. Slow evaporation of the solution of the Ni complex provided well-developed violet crystals that were suitable for X-ray diffraction. They were collected by filtration washed and dried. For Zn complex, slow evaporation of the solution provided a white powder.

Analytical calculation for  $C_{12}H_{20}Cl_2N_8NiO_8S_2$  (%) C, 24.08%; H, 3.34%; N, 18.73%; S: 10.70%. Found: C, 24.12%; H, 3.35%; N, 18.75%, S 10,72%.

 $C_{12}H_{16}Cl_2ZnN_6O_4S_2(\%)$  C, 25.4%; H, 2.8%; N, 14.8%; S, 11,20% Found: C, 25.61%; H, 2.6%; N, 14.3%; S, 11.23%

#### 3. Results and discussion

#### 3.1. Structure

The experimentally determined bond distances and angles around the Ni(II) cation in the [Ni (L)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>] complex are listed in Table 2. Fig. 1 shows the coordination sphere and the labeling scheme used. The Ni(II) cations are located on an inversion center octahedrally coordinated by four equatorial ammonia at a N···Ni distances of 2.113(1) and 2.146(1) Å and two axial sulfonamide nitrogen atoms at a N···Ni distance of 2.151(1) Å forming a C1-S1-N1-Ni torsional angle of 112.9(1)°. These values are in good agreement with those observed in other similar sulfonamide nickel(II) complex where the Ni(II) cation coordinates also with four ammonia molecules, at distances N-Ni of 2.092 Å and 108.8(5) respectively [24]. The C1-S1-N1-Ni torsional angle values observed in these systems are larger than those found by the same authors in the hydrated methazolamide and pyridine nickel complex, 86.2(2)° [25]. The lower value might be attributed to the fact that the thiadiazole and pyridine rings [24] are in a paralallel arrangement at a distance of 3.683(2) Å. The sulfonamide nitrogen



**Fig. 1.** Plot of Ni[(ClNbsa)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>] complex showing the labeling of the independent non-H atoms and their displacement ellipsoids at the 30% probability level. The H-bonding structure is denoted by dashed lines. Os: Oxygen atoms belonging to sulfonamide groups of another molecule.

atom is located very close to the benzene ring plane, forming the N1–S1–C1–C6 torsional angle of  $6.3(1)^\circ$ , with a S–N bond distance of 1.534(1)Å (see Table 2). These values are similar to those

#### Table 2

Angles and Interatomic Distances Observed and Calculated.

Bond distances (Å)	X-Ray observed	B3LYP Ni (II) Complex	B3LYp Zn(II) Complex
S-0	1.4602 (13)	1.4838	1.4742
	1.4412 (12)	1.4846	1.4867
S–N	1.5340 (13)	1.61069	1.6089
S–C	1.7932 (15)	1.82893	1.8357
C–Cl	1.7336 (17)	1.7498	1.3748
N-O	1.215 (2)	1.22959	1.2245
N-O	1.204	1.22322	1.2356
C–C	1.388 (2)	1.40138	1.3980
C–C	1.373 (2)	1.3923	1.3955
C–C	1.385 (2)	1.39273	1.3953
Ni–NH3	2.1128 (13)	2.16622	2.1283
Ni–NH3	2.1464 (15)	2.17016	2.1671
Ni–NH	2.1508 (13)	2.19479	2.0371
O-N	1.215	1.22322	1.2249
N-C	1.478 (2)	1.47941	1.4763
Angles (Deg)			
0-S-0	114.89	117.560	119.491
O–S–N	110.21 (8)	113.322	111.478
0–S–C	102.21	104.537	103.590
0-N-0	125.36 (18)	125.944	124.608
C–C–C	123.31(14)	121.589	122.381
C–C–C	116.96(14)	117.700	117.329
C–C–S	122.58 (11)	124.351	125.370
C-C-N	120.67	122.890	122.822
S–NH–Ni	136.92 (8)	114.500	124.830
O(3)-N(2)-C(2)	118.19 (16)	117.43	117.70
N(1)-S(1)-C(1)	109.14 (7)	105.960	105.859
N(3)–Ni(1)–N(3)	180.00 (10)	179.999	103.248
N(3)-Ni(1)-N(4)	88.76 (6)	86.909	114.214
Torsion (Deg)			
C-C-S-N	6.303	159.143	159.692
O–S–N–Me	52.943	56.790	21.207
O–S–N–Me	32.360	74.842	110.735
O-S-C-C	96.763	137.438	137.02
0-S-C-C2	34.519	92.975	39.119
S–N–Me–N	128.120	161.536	166.235
Cl-C-C-Cl	179.80	179.997	164.995

observed by Alzuet et al. [24,25]). The NO<sub>2</sub> plane is rotated an angle of 78.0(1)° from the benzene ring plane, which is larger than the one calculated in gas phase for Cu(II) complex  $29.56^{\circ}$  [11]. The structure is further stabilized by a network of hydrogen bond interactions involving NH3 and the benzene hydrogen atoms with sulfonamide oxygen atoms see Table 3 and Fig. 1.

The geometry of the Ni complex optimized at the B3LYP/ level is shown in Fig. 2(a front view and b lateral view). The gas phase optimized structure is in close agreement with the experimentally determined one (Table 2). The optimization in solvent keeps the octahedral coordination and does not change significantly the overall structure of the complex. A slight difference was observed in the shortening of S–N distances, 1.58 Å in a solvent and 1.61 in gas phase

We were not able to obtain crystals of the Zn(II) complex. Conversely, a powder X-ray diffraction pattern was recorded (Fig. 3). The cell parameters were determined by indexing the X-ray powder pattern, employing the program DICVOL04 [16], included in the Fullprof Suite software package: a = 18.372(8)Å, b = 7.947(3)Å, c = 10.221(3)Å,  $\alpha = 63.06(2)^{\circ}$ ,  $\beta = 108.75(2)^{\circ}$ ,  $\gamma = 109.15(2)^{\circ}$ , and cell volume = 1230(2)Å<sup>3</sup> (figure of merit M(20) = 10.5). The measured and calculated peak intensities are shown in Fig. 3 together with the expected Bragg positions. The cell volume, 85 Å<sup>3</sup> larger than the one determined for the Ni(II) complex, is consistent with two Zn(L)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> formula in the unit cell.

The structure of the Zn(II) complex was analyzed using computational techniques, after geometry optimizations using the B3LYP functional. Two different geometries have been obtained in this case, holding a tetrahedral coordination around the Zn center (Fig. 4) but differing in the spatial distribution of the substituent groups. In both cases the zinc ion is tetracoordinated by four N atoms, two of them belonging to the NH<sub>3</sub> ligands and the other two belonging to the N–H of the sulfonamide deprotonated groups. The calculated parameters of the complex in the optimized geometry (see Fig. 4a) are in good agreement with those previously reported for a similar cupper complex having a distorted square planar geometry [11] and they are very close to the X ray structure of another sulfonamide-Zn complexes [26].

In the gas phase optimization, B3LYP favors the linear structure (see Fig. 4a) by 1.2 kcal/mol. This difference is not large enough to disregard any of the structures. Moreover, in the packed crystal, the linear structure shown in Fig. 4a would be more likely, as can also be confirmed by the analysis of the IR spectra. The agreement with the experimental FTIR bands is better when the linear structure is used for the calculations (See Table 2). The geometry optimization in solvent favors the non-linear structure (Fig. 4b) by 6.27 kcal/mol.

#### 3.2. Spectroscopic properties

#### 3.2.1. FTIR and Raman spectra

The observed FTIR and Raman bands are shown in Fig. 5a and d for the Ni(II) complexes, and in Fig. 5b and c for Zinc(II) complex. The most significant IR and Raman data are reported in Table 4, together with the theoretically derived ones. The IR data for the

 Table 3

 Hydrogen bonds distances and angles for 4-chloro-2-nitrobenzenosulfonamide.

Atoms	D-H	$H{\cdots}A$	$D{\cdot}{\cdot}{\cdot}A$	$D{-}H{\cdots}A$
$N1-H1\cdots O1^i$	0.81	2.33	3.129(2)	167.3
N3−H3A····O1 <sup>i</sup>	0.89	2.30	3.180(2)	170.1
N3−H3B···O1 <sup>ii</sup>	0.89	2.29	3.148(2)	160.6
N3−H3C· · ·O2 <sup>iii</sup>	0.89	2.16	2.933(2)	145.4

Symmetry transformations used to generate equivalent atoms: (i) -x + 1, -y + 1, -z; (ii) x, -y + 1/2, z-1/2; (iii) -x + 1, -y, -z.



Fig. 2. Geometry optimized structures for Ni complex in gas phase using B3LYP level. (a) front view and (b) lateral view.



Fig. 3. Measured and calculated X-ray diffraction profiles and their difference plot for the Zn complex.

ligand has been previously reported [11] and it is compared here with those of the complexes in order to confirm which groups are involved in chelation.

In the spectra of both complexes new bands are attributed to the NH stretching vibrations of ammonia molecules. The positions of the stretching bands due to NH<sub>2</sub> groups are modified with regard to the ligand, suggesting that this amino group is involved in the coordination with the metal centre [11,12,25,26]. The strong band observed at  $3372 \text{ cm}^{-1}$  and the shoulder at  $3355 \text{ cm}^{-1}$  in the IR spectrum of the Ni(II) complex are indicative of the presence of coordinating NH<sub>3</sub> as can be observed in the Fig. 1. This result is consistent with the weak band observed at 1612 cm<sup>-1</sup> assigned to the bending mode of this group and with the strong one at 662 cm<sup>-1</sup> associated with its torsion mode. These modes are observed at 3380, 3347, 1592 and 668 cm<sup>-1</sup> respectively, in the infrared spectrum of the Zn(II) complex. The assignment of the ammonia bands is bases on standard references [28] and in good agreement with those for Ni(II) and Zn(II) mixed-ligand saccharinato complexes containing ammonia as the second ligand [29]. The bands assigned to the SO<sub>2</sub> groups are usually shifted to lower frequencies under complexation, associated with the binding of the sulfonamides through the deprotonated sulfonamido group [11,12,24–27]. In the free ligands the assimetric and symmetric



Fig. 4. Two different geometries optimized structures for Zn complex in gas phase.



**Fig. 5.** (a) FTIR and (d) Raman spectrum of the Zn complex, (b) FTIR and (c) Raman spectrum of the Ni complex,

stretching of these modes appear at 1348 and 1060 cm<sup>-1</sup>, respectively [11]. In the spectrum of the nickel(II) complex the  $v_{asymm}(SO_2)$  and  $v_{symm}(SO_2)$  are shifted to 1255 and 1056 cm<sup>-1</sup> respectively. These modes are observed at 1243 and 1058 cm<sup>-1</sup> in the case of the Zn(II) complex. In the Raman spectra the asymmetric mode of the nickel(II) complex is not observed after complexation, but it develops as a very weak band at 1242 cm<sup>-1</sup> in the zinc(II) spectrum. The symmetric one is observed at 1058 cm<sup>-1</sup> for both complexes.

The v(S-N) vibration is observed in the ligand at 923 cm<sup>-1</sup>, and shifted to 988 and 994 cm<sup>-1</sup> in the spectra of the Ni(II) and the Zn(II) complexes, respectively. This is in agreement with the shortening of the S–N bond length (and increase of the bond order) relative to that of the uncoordinated ligand, shifting the v(S-N) band to higher frequency. The S–N bond distance calculated for the ligand is 1.69 Å, and it shortens in the Ni(II) and Zn(II) complexes to 1.61(13) Å and 1.60 Å respectively

The nature of the metal–NH<sub>3</sub> bond is confirmed by a new band that develops at 380 cm<sup>-1</sup> in the Raman spectrum of the complex, which appears at 391 and 377 cm<sup>-1</sup> (for Ni and Zn complexes, respectively). The bands associated with the N–H corresponding modes are observed at 362 and at 352 cm<sup>-1</sup>.

3.2.2. Electronic absorption spectra

The electronic absorption spectra of the complexes were measured in DMSO and compared with that of the ligand, previously reported [11]. Two intense bands appear in the spectrum of the ligand at 286 and 266 nm, which can be assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively [11]. An intense peak develops in the Ni(II) UV-VIS spectrum at 260 nm with shoulders at 290 nm and 340 nm, which are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions centered in the sulfonamide ligand on the basis of the theoretical calculations. At the present level of theory, bands are calculated at 266 nm, 288 nm and 340 nm, with relative intensities of f = 0.11, 0.0198, 00.628 respectively. The poorly resolved band observed in the visible region at 616 nm ( $\varepsilon$ . = 96026 cm<sup>-1</sup> M<sup>-1</sup>) is calculated at 653 nm (f = 0.0) and assigned to d-d transitions. This band is absent in the Zn complex, while the  $\pi \to \pi^*$  and  $n \to \pi^*$ transitions bands are observed at 320, 290 and 262 nm for the structure shown in Fig. 4a. As previously mentioned, the geometry optimization in solvent favors the non-linear structure (Fig. 4b) by 3.77 kcal/mol. Nevertheless, the position of the bands do not change markedly, and are calculated at 330, 295 and 260 nm (*f* = 0.053, 0.005, 0.030), They are also assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions.

3.2.3. NMR spectroscopy

<sup>1</sup>H and <sup>13</sup>C NMR spectra of the Zn complex in DMSO-d<sub>6</sub> have been measured to support the structural assignment and compared to the ligand [11]. The <sup>1</sup>H NMR spectrum shows three groups of signals for the three different hydrogen atoms of the benzene rings sulfonamide. The three groups are doublet and appear at 7.99 ppm (J = 1.9 Hz) 7.93 ppm (J = 8.5 Hz) and 7.61 ppm (J = 7.7 Hz) slightly shifted respect to the ligand (8.15 ppm, 7.92 ppm and 7.73 ppm, respectively). The ligand signal at 5.4 ppm, due to the protons of the sulfonamide moiety does not appear in the complex. The remaining signal as a broad doublet at 3.03 ppm could be assigned to the hydrogen of the NH and NH<sub>3</sub> groups.

The <sup>13</sup>C NMR spectrum shows six singlet signals at 147.95 ppm, 138.94 ppm, 135.43 ppm 132.16 ppm 130.73 ppm and 123.72 ppm assigned to the six aromatic carbon of the sulfonamide. Unfortunately, the NMR spectra of the paramagnetic Ni(II) complex could not be measured in solution and no comparison with the Zn complex has been possible.

Table 4	4
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FTIR and Raman frequencies observed and calculated in 4-chloro-2-nitrobenzenesulfonamide of nickel and zinc complexes. Observed FTIR bands of ligand are also included.

Ligand <sup>a</sup>	Ni 4-Chloro-2-niti	robenzenesulfo	namide	Zn 4-Chloro-2-nitrobenzenesulfonamide			Assignments	
Infrared	Infrared	Raman	B3LYP	Infrared	Raman	B3LYP (linear)	B3LYP (non-linear)	
3368 vs	3372 vs	3370 (133)	3407 (81)	3380 sh	3372 vs	3443 (61)	3442 (27)	v <sub>as</sub> NH <sub>3</sub> v <sub>as</sub> NH <sub>2</sub>
	3355 sh		3389 (133)	3347 vs	3355 sh	3412 (70)	3439 (20)	$v_{as}N-H_3$
3272 vs	3280 vs	3299 (6.8)	3316 (6.8)	3279 sh		3376 (15)	3389 (25)	v <sub>s</sub> NH
	3235 sh		3298 (85)			3302 (25)	3249 (61)	$v_s N - H_3$
			3232 (565)				3241(184)	
3089 m	3092 m	3094 w	3105 (11)	3094 vw		3105(4)	3106(4)	vC-H
		3077 m		3075 vw	3078 w	3090 (1)	3091(2.7)	vC-H
			1652 (135)	1621 w		1651 (17)	1667 (33)	δNH3
1592 m	1587 m	1585w	1601 (341)	1592 m	1588w	1575 (123)	1576 129)	$v_{as}NO_2$ + ring
1533 s	1535 vs	1542 w	1546 (77)	1543 s	1542 w	1536(127)	1536(127)	
1564 w	1562 m	1566 w	1566 (188)	1560 w	1562 w	1558 (164)	1558(167)	Ring
1365 s 1348 s	1365 vs	1363 w	1354 (369)	1361 s	1363 s	1355 (215)	1349(200)	$v_sC-NO_2 + v_sNO_2$ $v_{as}SO_2$
1282 m	1280 sh		1286 (40)	1281 m		1279 (22)	1282 (12)	Ring vCH + vNH
1263 m				1271 m		1251(31)	1258 (77)	
	1255 br		1224 (50)	1243 m	1242 w	1237 (224) 1219(220)	1232(322)	$\rho NH_3 + \rho NH$
	1235 sh 1193 vs		1211 (506) 1194 (365)	1190 m	1193 vw	1219 (270) 1206 (173)	1215(245) 1207(130)	$\rho NH_3 + \rho NH$
1164 s	1166 s			1159 m	1159 m	1164 (182)	1170(89)	$(ONH_2)^a ONH_2$
	1157 vs	1150 w	1139 (157)	1142 sh	1144 m	1145 (39)	1157(174)	$\delta NH + Ring$
1136 w	1133 vs	1132 w	1129 (167)	1134 vs	1135 m	1130 (24)	1134 (21)	$\delta NH + ring$
	1100 m		1103 (143)	1105 m		1102 (64)	1102 (59)	Ring
1060 w	1056 m	1058 m	1044 (290)	1058 m	1058 m	1054 (137)	1051(251)	v <sub>s</sub> SO2
920 m	988 vs	993 m	851 (713)	994 s	998 m	883 (122)	892 (301)	vS–N
885 m	886 m		858 (142)	887 m		856 (508)	858 (31)	$\delta NO_2$ + ring
875 m	873 m		858 (142)	875 m		818 (22)	819 (19)	Ring
776 m	770 s	769 m	746 (81)	773 s	772 s	816 (22)	817 (19)	Ring
	747 m	744 w	738 (78)	752 m		744 (34)	745(31)	$\rho NO_2$ + ring
662 w	662 s	666 w	643 (166)	668 w		660 (134)	678 (162)	$\rho NH + \rho NH_3$
	619 s		600 (392)	637 m		622 (66)	636 (129)	$\omega NH_3 + \omega N - H ring$
	577 w		579 (237)	555 m	559 w	606 (150)		$\omega N-H + \omega NH_3$
560 w	551 m		537 (55)			575 (230)	564 (120)	$\rho SO_2 + \omega NH_3 + \omega N-H$
450 m	485 s	480 w	411 (117)	481 w		476 (113)	450 (70)	vC–Cl + ring
		391 w	372 (11)		377 w	349 (3.1)	340 (12)	$vM-NH_3 + ring$
		362 w	319 (6)		352w	347 (3)	346 (5)	vM-NH

<sup>a</sup> Ref. [11].

#### 3.3. Thermogravimetric study of the complexes, TG-DT

The TG curve of the complex reveals that the decomposition takes place in three steps. The first one corresponds to a weight loss of 11.70% which is consistent with the evolution of the four NH<sub>3</sub> groups (loss of weight calculated 11.36%). This process takes place with one endothermic peak observed in the DTA curve at 120 °C and an exothermic peak at 155 °C. The second step occurs with a weight loss of 51.45% probably due to the evolution of the two sulphonamide ligands with their substituents except one SO<sub>2</sub> group (expected 51.4%). The third step shows an incomplete reaction until 800 °C. This feature may be assigned to the oxidation of the other SO<sub>2</sub> group, loss of weight observed 9.75%, calculated 10.70%.

As for the case of the nickel complex, the Zn complex TG curve shows three steps. The first one corresponds to a weight loss of 39.57% consistent with the evolution of the two NH<sub>3</sub> and one of the sulfonamide ligands (loss of weight calculated 38.89%). In the DTA curve two endothermic peaks are observed at 187 and at 197 °C. The second step of the TG curve is compatible with a weight loss of 25.79% and might be attributed to the decomposition of the benzene ring with their substituents except the SO<sub>2</sub> group (calculated 23.98%). This process takes place with one endothermic peak observed in the DTA curve at 234 °C. The last incomplete step probably corresponds to the decomposition of the remaining SO<sub>2</sub> group, loss of weight observed 11.26%, calculated 9.78% with an exothermic peak observed in DTA at 410 °C.

#### 4. Conclusions

This study reports the synthesis and characterization of  $Ni(L)_2(NH_3)_4$  and  $Zn(L)_2(NH_3)_2$  complexes with L = 4-chloro-2nitrobenzenesulfonamide. The Ni(II) complex was structurally characterized by single crystal X-ray diffractometry while the Zn(II) complex was characterized by powder X-ray method. The structural data derived from IR and Raman spectroscopies are in a good agreement with those determined by X-ray diffraction methods. Electronic structure calculations have been used to analyze the structural characteristics of the Zn complex, for which the crystal structure was not obtained, and to better assign the spectroscopic features. The agreement of the calculated data with the experimental excitation energies and intensities supports the accuracy of the theoretical description.

### Supplementary material

Tables of fractional coordinates and equivalent isotropic displacement parameters of the non-H atoms (Table S4), full bond distances and angles (Table S5), atomic anisotropic displacement parameters (Table S6), hydrogen atoms positions (Table S7), and H-bond distances and angles (S8). A CIF file with details of the crystal structure reported in the paper has been deposited with the Cambridge Crystallographic Data Centre, under deposition number CCDC 923214. Tel.: +54 221 4246062/4247201/4230122; E-mail address: geche@fisica.unlp.edu.ar. 88

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