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Vibrational Spectra of the thioglycolate complexes of Zn(II) and Cd(II), structure and natural bond orbitals

Espectro Vibracional dos complexos tioglicolatos de Zn(II) e Cd(II), estrutura e orbitais de ligação natural

Espectros Vibracionales de los complejos de tioglicolato de Zn(II) y Cd(II), estruturas y orbitales naturales de enlace

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Abstract

The objective of this research was to characterize the vibrational spectrum of the Zn(II) and Cd(II) thioglycolate complexes, as well as their structures, vibrational analysis and the natural orbitals of bonds, through the infrared spectrum with Fourier transform (FT -IR) and Raman. The thioglycolate complexes of Zn(II) and Cd(II) were synthesized following procedures given by the graphical method, and structural analysis was performed through a theoretical-experimental method using both, the hybrid RHF/MP2:STO-3G and the experimental FT-IR and FT-Raman spectra. Calculations were performed on the optimized structure and harmonic vibrational wavenumbers for both complexes were obtained. Second derivative of the vibrational spectra and deconvolution analysis were also performed. The infrared and Raman spectra show many combination and overtone bands in both cases. Calculated and experimental spectra confirmed the structural hypothesis considering two ATG (thioglycolic acid) with two water molecules in the coordination sphere of the central atoms. The natural bond orbital analysis (NBO) was also carried out to study the Zn(II) and Cd(II) hybridization leading to a pseudo-octahedral geometry for both complexes.

Keywords: Thioglycolate complexes of Zn(II) and Cd(II); Vibrational spectra; Natural bond orbital analysis (NBO).

Resumo

O objetivo desta pesquisa foi caracterizar o espectro vibracional dos complexos tioglicolatos de Zn(II) e Cd(II), assim como as suas estruturas, análise vibracional e dos orbitais naturais de ligações, por meio dos espectro no infravermelho com transformada de fourier (FT-IR) e Raman. Os complexos de tioglicolato de Zn(II) e Cd(II) foram sintetizados seguindo os procedimentos dados pelo método gráfico, e a análise estrutural foi realizada pelo método teórico-experimental utilizando tanto o híbrido RHF/MP2:STO-3G quanto o experimental FT -Espectros IR e FT-

Raman. Os cálculos foram realizados na estrutura otimizada e os números de onda vibracionais harmônicos para ambos os complexos foram obtidos. A segunda derivada dos espectros vibracionais e a análise de deconvolução também foram realizadas. Os espectros infravermelho e Raman mostram muitas bandas de combinação e sobretons em ambos os casos. Os espectros calculados e experimentais confirmaram a hipótese estrutural considerando dois ATG (ácido tioglicólico) com duas moléculas de água na esfera de coordenação dos átomos centrais. A análise do orbital de ligação natural (NBO) também foi realizada para estudar a hibridização de Zn(II) e Cd(II) levando a uma geometria pseudo-octaédrica para ambos os complexos.

Palavras-chave: Complexos tioglicolatos de Zn(II) e Cd(II); Espectros vibracionais; Análise orbital de ligação natural (NBO).

Resumen

El objetivo de esta investigación fue caracterizar el espectro vibracional de los complejos tioglicolatos de Zn(II) y Cd(II), así como sus estructuras, análisis vibracional y los orbitales naturales de los enlaces, a través del espectro infrarrojo con transformada de Fourier (FT - IR) y Raman. Los complejos de tioglicolato de Zn(II) y Cd(II) se sintetizaron siguiendo los procedimientos dados por el método gráfico, y el análisis estructural se realizó mediante un método teórico-experimental utilizando tanto el híbrido RHF/MP2:STO-3G como el experimental FT -Espectros IR y FT-Raman. Se realizaron cálculos sobre la estructura optimizada y se obtuvieron números de ondas vibratorias armónicas para ambos complejos. También se realizaron la segunda derivada de los espectros vibracionales y el análisis de deconvolución. Los espectros infrarrojo y Raman muestran muchas combinaciones y bandas armónicas en ambos casos. Los espectros calculados y experimentales confirmaron la hipótesis estructural considerando dos ATG (ácido tioglicólico) con dos moléculas de agua en la esfera de coordinación de los átomos centrales. También se llevó a cabo el análisis de orbitales de enlace natural (NBO) para estudiar la hibridación de Zn(II) y Cd(II) que conduce a una geometría pseudo-octaédrica para ambos complejos.

Palabras clave: Complejos de tioglicolato de Zn(II) y Cd(II); Espectros vibracionales; Análisis de orbitales de enlace natural (NBO).

1. Introduction

There are many references on metal complexes with thioglycolic acid as a ligand in the literature. Relevant information about the possible structures of these complexes, are cited in this paper. On the other hand, references on the vibrational spectra are scarce and incomplete.

Ohashi et al., *(1970)* reported a series of hydrated and anhydrous Cu(II) complexes with thioglycolic acid derivatives with methyl, ethyl, and isopropyl chemical groups. In all cases, it was assumed that, in the molecular structures, Cu(II) coordinates with two ATG ligands and two water molecules.

Complexes of iron-thioglycolate were reported in 1953 (Leussing & Kolthof, 1953). The structure of these complexes was shown to be in accordance with the 1:1 molar ratio, ferrous iron/thioglycolic acid.

Soliman et al. (2002) reported on the usefulness of thioglycolic acid as a complexing agent for Cu ions (II), Zn(II) and Hg(II) from natural seawater samples using silica gel (SG) as a matrix. The authors had concluded that the metals make bonds with the –C=O and –SH groups in the ratio metal-ligand 1:1.

In a publication from the 1930s, Michaelis and Schubert (1930), found that the complex nucleus of the cobalt compounds consisted of two molecules of thioglycolic acid distributed around the cobalt atom. The structure was described as the cobalt atom forming an O-bridge and a double OH bridge. In both cases, the cobalt atom coordinates with two –SH groups and two deprotonated sulfur atoms. The kinetics and mechanism of reaction of Pt(II) complexes with thioglycolic acid was discussed in the paper by Bugarčić ND Djordjević (1998). In this paper, the authors claimed that there was no signal of the SH group in the spectrum of the complex $K_2[PtCl_3(SR)]$. From this information, the molar ratio metal-ligand was 1:1.

Loginova et al. (2011) found that the Cu(II), Ni(II), and Fe(II) complexes containing 2-[4, 6-di(tert-butyl)-2, 3-dihydroxyphenylsulfanyl] acetic acid, abbreviated as (HL^I), had the structure of an extremely distorted octahedron, while the structure of the Zn(II) complex underwent a tetrahedral distortion.

A few recent articles on metal ion complexes having thioglycolic acid as a ligand have been reported in the literature. However, a detailed description of the vibrational attribution was absent. Besides, we did not find information on the analysis of natural bond orbitals for this type of complexes with metals using thioglycolic acid as a ligand.

In this article, the synthesis of Zn(II) and Cd(II) complexes with thioglycolic acid was undertaken. But, since metal complexes precipitate as crystalline powders, the X-ray structural determination was not possible. Thus, to determine the structure of the complexes, we used a theoretical-experimental method based on the vibrational assignments of their infrared and Raman spectra, based on the hybrid HF/MP2 with STO-3G basis set for both metallic complexes.

As a first attempt, the structural hypotheses of two complexes of Zn(II) and Cd(II) in the metal-ligand ratio 1:1 was tried, but was discarded because the number of normal modes 3N-6=18 did not match the number of fundamental bands observed in the infrared spectrum. In a second hypothesis, structures of the type $[M(ATG)_3]$ were considered. Nonetheless, instead of having good stabilization energies, the link distances between Cd-S and Zn-S were not well defined and had values above 4 Å, so this hypothesis was also discarded. The third hypothesis considered the ratio of one metal and two ATG ligands, with two water molecules in axial coordination, thus providing the best comparison between the experimental and calculated vibrational spectra, so this is the structure reported in the present work.

This manuscript objective was to characterize the vibrational spectrum of Zn(II) and Cd(II) thioglycolate complexes, as well as their structures, vibrational analysis and natural bond orbitals, through the spectra in the Infrared with Transform of Fourier (FTIR) and Raman.

2. Methodology

2.1 Reagents and solvents were used without further purification

Zinc (II) chloride P. A., cadmium chloride P. A., sodium hydroxide P. A., ethanol P. A., methanol P. A., acetone P. A, and diethyl ether P. A. from VETEC-Química Fina, and thioglycolic acid 70% (w/w) in water from Sigma-Aldrich Co.

2.2 Thioglycolic acid

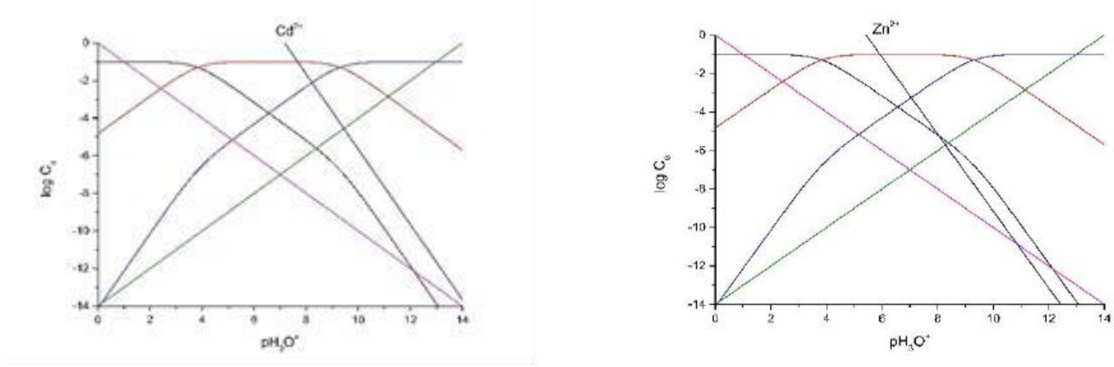
Thioglycolic acid is an organic acid widely used by the pharmaceutical industry for skin treatments. This compound belongs to the class of thiols or mercaptans, also known by the names of 2-mercaptoacetic acid or simply mercaptoacetic acid, its strong unpleasant odor derives from the presence of labile sulfur in its chemical structure.

Physical properties: Molar mass = 92.11 g/mol. Density = 1.32 g/cm3. Melting Point = -16 ºC. Boiling Point = 123 ºC. Ionization constants = pk1 = 3.83; pK2 = 9.3. Solubility in water = completely soluble.

2.3 Equilibrium in aqueous solution – Diagrams

The syntheses of the Zn(II) and Cd(II) complexes with thioglycolic acid (ATG) and two coordination water molecules were carried out according to the conditions based on the Graphic Method (Cabral, 2005; Charlot, 1971; Rossoti & Rossoti, 1961; Ringbom, 1979).

Figure 1 - Overlay of speciation and hydroxide formation graphs for the thioglycolic acid and Cd(II) and Zn(II) systems.



Ca = analytical concentration of ligand and metal. Blue line: $\log H_2A$, red: $\log HA^-$, gray: $\log A^-$, black: $\log H_3O^+$ and $\log OH$.
Source: Authors.

All syntheses were performed in accordance with the logarithmic diagrams presented above. Thioglycolic acid forms stable complexes with various metals so care is needed not to use it in excess.

2.4 Synthesis of the Cd compound with thioglycolic acid

The synthesis of this compound was carried out using 5 mmols of cadmium chloride transferred to a porcelain grate adding a solution of 5 mmols of thioglycolic, with its pH previously adjusted to 7.5 with solid sodium hydroxide (microbeads). After a complete mixing of the compounds, the capsule was heated at 60° C for 5 hours, to complete the reaction and reduce the volume of water. When at room temperature, the capsule was cooled for 24 hours at 4° C. The formed solid was separated and washed with ice water in small portions. After drying in a desiccator under concentrated sulfuric acid, the product was macerated and stored in a container with a calcium chloride cartridge. The product was stored with the calcium chloride cartridge and after approximately two weeks all moisture had been lost.

2.5 Synthesis of Zn Compound with Thioglycolic Acid

The same conditions for the previous synthesis were maintained with the exception of the pH of the thioglycolic acid solution, which was adjusted to 5.

2.6 Experimental vibrational spectra

The IR spectra were obtained at room temperature with a 400 Perkin-Elmer FT-IR spectrophotometer, in the spectral region between 4000 and 370 cm^{-1}, placing a minimal quantity of the crystalline powder in the ATR crystal. The spectra were recorded with a resolution of 4 cm^{-1}, mirror velocity of 0.2 $cm^{-1}s^{-1}$ and 120 scans. The Raman spectra of the solid samples were obtained at room temperature with a Bruker Spectrometer (model RFS 100/S) equipped with a 1064 nm Nd:YAG laser as the excitation source. Adquisition parameters were: 500 mW for laser power, spectral resolution of 4 cm^{-1}, signal gain of 1, 200 scans and 7.0 mm for aperture setting.

2.7 Calculations

Computational calculations: We used the following software: HYPERCHEM, GAUSSIAN 03 and CHEMCRAFT 1.8. Theoretical structural calculations gave the structural parameters which were used to obtain the vibrational spectra of the Cd(II) and Zn(II) complexes. The computations were carried out in a computer with the following specification: Intel® Core™ i5 (1.80 GHz) with 4 GB of RAM.

3.Results and Discussion

3.1 Determination of the geometrical structure of the Zn(II) and Cd(II) thioglycolate

The complexes $[Zn(ATG)_2(OH_2)_2]$ and $[Cd(ATG)_2(OH_2)_2]$ precipitated as crystalline powders in the process of synthesis, making it impossible to determine its structure by X-ray diffraction. Hence, to obtain and confirm its geometry, we opted for the mixed Theoretical-Experimental method, a procedure based on ab initio calculations at RHF (restricted Hartree-Fox) (Scuseria, 1991; Jayatilaka & Lee, 1992; Watts et al., 1993) and MP2 level (Moller- Plesset) (Møller & Plesset, 1934; Head-Gordon et al., 1988) together with the experimental infrared and Raman spectra for both complexes. The agreement between the theoretical and experimental spectral values confirmed the proposed structure for the complex.

The determination of the structure of these complexes was made by choosing between three different models: [M(ATG)], $[M(ATG)_3]$ and $[M(ATG)_2(OH_2)_2]$, with M= Zn(II) and Cd(II). As the number of bands exceeded 3n-6 = 18 corresponding to the structure [M(ATG)], this model was excluded.

The decision between the two remaining structures was made through observation of the active bands in the FT-IR and FT-Raman spectra in the regions between 3600-2500 cm^{-1} and 1800-1500 cm^{-1}. In the first region, the bands and the OH stretch of the coordination water with those corresponding to the CH stretchings of the $-CH_2$ group are present in both complexes; in the second region, the angular variations H-O-H and the vibrations of the carbonyl are in the profile of the bands. This profile did not fit the structural proposal $[M(ATG)_3]$. The spectra of the Zn(II) and Cd(II) complexes are similar and show the corresponding band shifts due to the different atomic masses of the two metal ions. This similarity pointed to the prediction of similar structures.

The confirmation of the proposed structures was done using the experimental theoretical method, placing the proposed structural geometries as a calculation basis and determining the theoretical spectra, whose results were compared with the experimental vibrational spectra, obtaining an excellent agreement. In the calculation procedure, we used the RHF/MP2 functional with STO-3G basis for both complexes.

3.2 Optimization of the geometric parameters

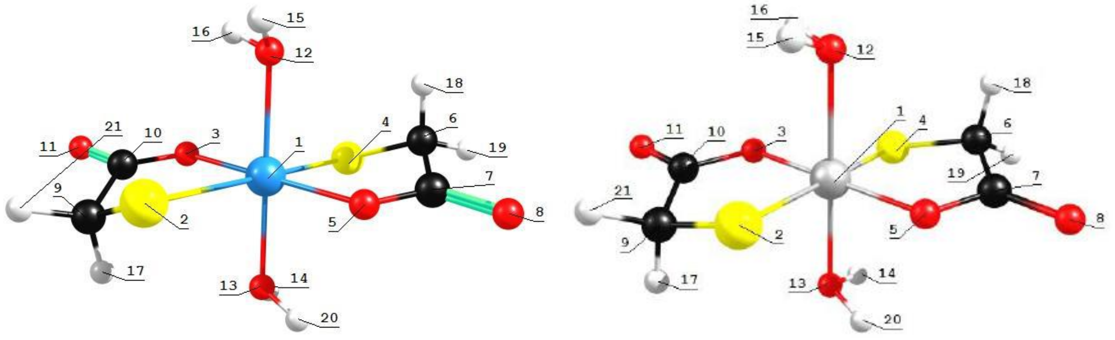
Ab initio optimization of the geometric parameters as well as the structural analysis for $[Zn(ATG)_2(OH_2)_2]$ and $[Cd(ATG)_2(OH_2)_2]$ were carried out employing the methods described above, which are similar to the procedures found in the literature (Costa Jr et al., 2013a; Soto et al., 2015; Costa Jr et al., 2012; Costa Jr et al., 2013b; Ramos et al., 2012). RHF/MP2: STO-3G theoretical values for the $[Zn(ATG)_2(OH_2)_2]$ and $[Cd(ATG)_2(OH_2)_2]$ complexes are given in Table 1. The structure for both complexes are illustrated in Figure 2.

Table 1 - Framework bond distances (Å) and selected bond angles (°) for the $[Zn(ATG)_2(OH_2)_2]$ and $[Cd(ATG)_2(OH_2)_2]$ complexes.

$[Zn(ATG)_2(OH_2)_2]$: HF/MP2:STO-3G		$[Cd(ATG)_2(OH_2)_2]$:HF/MP2:STO-3G	
Bond distances	Bond angles	Bond distances	Bond angles
Zn(1)-O(3) 1.681	S(2)-Zn(1)-O(12) 89.04	Cd(1)-O(3) 1.914	S(2)-Cd(1)-O(12) 88.40
Zn(1)-O(5) 1.681	S(2)-Zn(1)-O(13) 90.96	Cd(1)-O(5) 1.914	S(2)-Cd(1)-O(13) 91.60
Zn(1)-O(12) 2.179	S(4)-Zn(1)-O(12) 90.96	Cd(1)-O(12) 2.324	S(4)-Cd(1)-O(12) 91.60
Zn(1)-O(13) 2.179	O(5)-Zn(1)-O(13) 88.85	Cd(1)-O(13) 2.324	O(5)-Cd(1)-O(13) 86.04
Zn(1)-S(4) 2.208	S(2)-Zn(1)-O(3) 93.07	Cd(1)-S(4) 2.325	S(2)-Cd(1)-O(3) 90.32
Zn(1)-S(2) 2.208	S(2)-Zn(1)-O(5) 86.93	Cd(1)-S(2) 2.325	S(2)-Cd(1)-O(5) 89.68
S(2)-C(9) 1.817	S(4)-Zn(1)-O(5) 93.07	S(2)-C(9) 1.826	S(4)-Cd(1)-O(5) 90.32
S(4)-C(6) 1.817	S(4)-Zn(1)-O(3)86.93	S(4)-C(6) 1.826	S(4)-Cd(1)-O(3) 89.68
O(3)-C(10) 1.388	O(3)-Zn(1)-O(12) 88.85	O(3)-C(10) 1.405	O(3)-Cd(1)-O(12) 86.04
O(5)-C(7) 1.388	O(5)-Zn(1)-O(12) 91.15	O(5)-C(7) 1.405	O(5)-Cd(1)-O(12) 93.96
C(6)-C(7) 1.590	O(3)-Zn(1)-O(13) 91.15	C(6)-C(7) 1.590	O(3)-Cd(1)-O(13) 93.96
C(9)-C(10) 1.590		C(9)-C(10) 1.590	
C(7)=O(8) 1.259		C(7)=O(8) 1.261	
C(10)=O(11)1.259		C(10)=O(11)1.261	

Source: Authors.

Figure 2 - RHF/MP2:STO-3G calculated structure for: $[Zn(ATG)_2(OH_2)_2]$ and $[Cd(ATG)_2(OH_2)_2]$.


a) $[Zn(ATG)_2(OH_2)_2]$

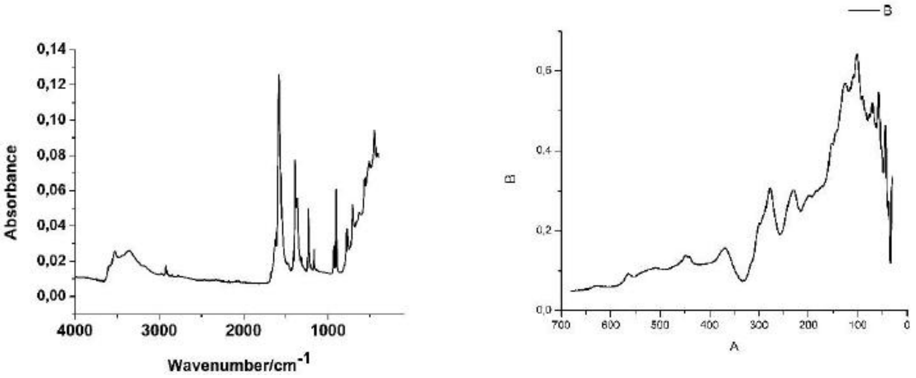
b) $[Cd(ATG)_2(OH_2)_2]$.

Source: Authors.

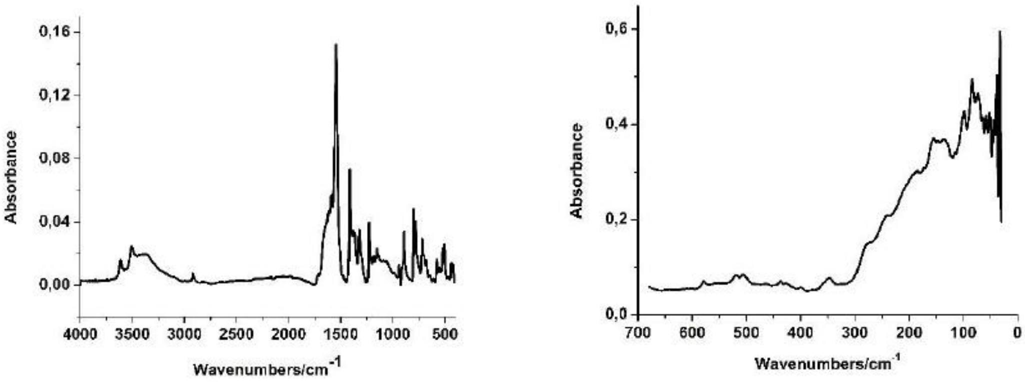
3.3 Vibrational spectra of the [Zn(ATG)$_2$(OH$_2$)$_2$] and [Cd(ATG)$_2$(OH$_2$)$_2$] complexes and vibrational assignments

Figure 3 - FT-IR and FT-Raman spectra of the [Zn(ATG)$_2$(OH$_2$)$_2$] and for [Cd(ATG)$_2$(OH$_2$)$_2$].

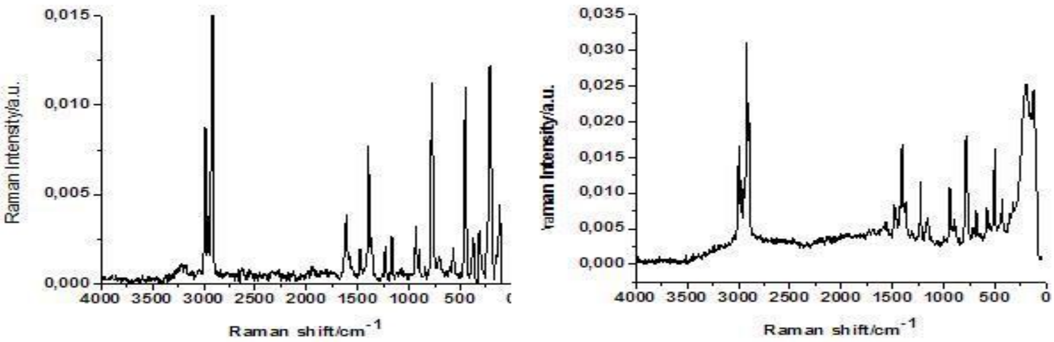
a) FT-IR [Zn(ATG)$_2$(OH$_2$)$_2$]



b) FT-IR [Cd(ATG)$_2$(OH$_2$)$_2$]



c) FT-Raman spectra of the [Zn(ATG)$_2$(OH$_2$)$_2$] (left) and for [Cd(ATG)$_2$(OH$_2$)$_2$] (right)



Source: Authors.

In Figure 3, we can see the similarity of the spectra between the Zn(II) and Cd(II) complexes. This fact suggests similar structures for both complexes.

For the calculation of the vibrational spectra, we used the hybrid RHF/MP2 with basis set STO-3G for both the Zn(II) and Cd(II) complexes. Their stoichiometry corresponds to the brute formula C4H8MdO6S2 (M= Zn, Cd) with 57 degrees of freedom. According to this geometry, the complexes belong to the C_1 point group. The spectrum of the Zn(II) complex was corrected in Table 2 by the scale factor of 0.872 and in Table 3 the Cd(II) complex spectrum was corrected with the same scale factor. The complete vibrational assignments are also presented.

Table 2 - Vibrational assignments for the solid Zn(II)-thioglycolate complex (crystalline powders). Experimental values are within ± 4 cm^{-1}.

Calc. RHF/MP2(0.872)	FT-Raman experimental	FT-IR experimental/Far IR	Mode description
3564		3588-3598	ν_{as}(OH)
3564		3528-3534	ν_{as}(OH)
3347		3440-3466	ν_{s}(OH)
3347		3351-3367	ν_{s}(OH)
		3184-3195	1592x2=3184
3023	2986	2985	ν_{as}(CH)
3023	2977	2976	ν_{as}(CH)
2931	2937	2937	ν_{s}(CH)
2931	2919	2919	ν_{a}(CH)
		2848	1673x2=2346
	1769		881x2=1762
	1752		1147+604=1751
	1738		1231+509=1740
	1712		1147+565 = 1712
1737	1688	1673	δ_{as} (HOH) *
1736	1664	1652	δ_{s} (HOH) *
	1646	1640	1075+568=1643
		1634	1231+404= 1634
	1620	1621	842+778=1620
	1611		1040+564=1613
1570	1592	1593	ν_{as} (C =O) *
1564	1577	1581	ν_{s} (C =O) *
	1557	1558	778x2=1556
		1533	1075+454=1529
	1512		1129+374=1513
1495	1503		δ_{s}(HCH) sciss.
1494	1473		δ_{as}(HCH) sciss.
	1446		1446=778+663=1441
	1439		1439=778+663=1441
	1423		1423=1366+57=1423
(1398) not scaled	1397	1409	δ_{as}(HCH)wagg.
(1398) not scaled	1389	1388	δ_{s}(HCH)wagg.
	1366	1365	842+520=1362
	1354		1592-240=1352
	1331		1331=663x2=1326
(1321) not scaled		1318	ν_{s}(CO)
(1299) not scaled	1307		ν_{as}(CO)
(1278) not scaled	1283		$\delta_{as}(HCH)_{twist}$
(1278) not scaled	1264		$\delta_{s}(HCH)_{twist}$
	1252		1049+200=1249
	1231	1231	727+498=1227

	1217	1221	778+443=1221
	1206		604x2=1208
	1188		1188 = 539+454=1193
	1166	1165	1166 = 631=539=1170
	1147		568x2=1136
	1129		564x2=1129
	1114		663+474=1117
	1091		773+317=1095
	1075		842+232=1074
	1049		526x2=1052; 842+200=1042
	1010		604+404=1008
	994		539+454=993
	971		568+404=972
	932	931	778+156=934
	901	900	778+119=897
862	881		$\rho(CH_2)$
862	842		$\rho(CH_2)$
850		809	$\nu_s(CS)+\nu_s(CC)+\nu_s(CO)$
849		802	$\nu_{as}(CS)+\nu_{as}(CC)$+νas(CO)
812		790	$\nu_s(CS)+\nu_s(CO)$
802	778	773	$\nu_{as}(CS)+\nu_{as}(CO)$
	705	709	663+44=707
642	672		δ(HOH)(OH2)twist
621		663	δ(HOH)(OH2)twist
616		631	δ(HOH)(OH2)twst
614	604		δ(HOH)(OH2twist
566	568	565/564	δ(HOH)(OH2)wagg
		539	300+240=540
528	520	526	δ(HOH)(OH2)wagg
483	498	509	δ(CCO)+δ(HOH)wagg
		501	300+200=500
475		474	ρ(C(C=O)O)↑↓+$\rho(CH_2)$
473	454	449/448	ρ(C(C=O)O)↑↓+$\rho(CH_2)$
442		443/442	ν(ZnO)+δ(CCS)
434		430	ν(ZnS) coupled mode
		425	273+156=429
		419	317+101=418
		415	278+133=411
392		404	ν(*ZnS)+ δ*(CSZn)+δ(SZnO)+δ(OCC)
378	374	/375	ν(ZnO)+δ(SZnS)+$\delta(H_2OZnOH_2)$+δ(CC=O)
359		/369	Ring breathing
322	317		$\nu(Zn\text{-}OH_2)_+$ Ring breathing
308	300	/299	ν(ZnS)+ ν(ZnO)+$\nu(Zn\text{-}OH_2)$
288	273	/278	$\nu(Zn\text{-}OH_2)$+ring breathing
261	240		$\nu_{as}(ZnOH_2)$+ring torsion or $\delta(OZnOH_2)$
252		/232	$\nu_s(Zn\text{-}OH_2) + \nu_s(ZnS)$
191	200	/199	δ(HOH)twist
188		/182	δ(HOH)twist + ring torsion

180		/173	Ring torsion
	156	/152	85+70=155
		/144	70x2=140
134	133		δ(OZnO)+ρ(OH$_2$)
121	119	/125	ρ(OH$_2$)
119		/110	δ(H$_2$OZnOH$_2$)+ δ(SZnS)
108		/101	Ring torsion
97		/90	δ(H$_2$OZnOH$_2$)
73		/85	Ring torsion
58		/70	Ring torsion
54		/57	Ring torsion
38		/37	Ring torsion

(*) according experimental spectra. Source: Authors.

Table 3 - Vibrational assignments for the solid Cd(II)-thioglycolate complex (crystalline powders). Experimental values are within ± 4 cm^{-1}.

Cd(ATG)2(OH2)2 RHF/MP2 (0.872)	FT-Raman	Exp. FT-IR	Mode description
3558		3612	ν_{as}(OH)
3558		3507	ν_{as}(OH)
3343		3404	ν_{s}(OH)
3343		3355	ν_{s}(OH)
3021	2996	2992	ν_{as}(CH)
3021	2975	2972	ν_{as}(CH)
	2947		1566+1370=2936
2923	2921	2915	ν_{as}(CH)
2923		2906	ν_{a}(CH)
	2895	2901	1633+1248=2881
		2836	1458+1370=2828
	1686		920+771=1691
1760		1663	δ_{as} (HOH)
1759	1642	1633	δ_{s} (HOH)
	1613	1617	1592+22=1617
1540	1592	1592	ν_{s} (C =O)
	1566		782x2=1564
1533	1545	1545	ν_{as} (C =O)
1484	1509	1507	δ(HCH)
1484	1478	1475	δ(HCH)
	1458		876+583=1459
(1395)not scaled	1426	1426	δ(HCH)
(1395)not scaled	1406	1413	δ(HCH)
	1370	1375	1091+281=1372
		1364	891+466=1357
	1341		782+554=1336
(1289) not scaled	1315	1320	δ(HCH)
(1286) not scaled	1301	1303	δ(HCH)
	1272		876+398=1274
	1255		891+359=1250

(1244) not scaled	1247	1248	ν_s(C-O)+δ(HCH)
(1218) not scaled	1225	1226	ν_{as}(C-O)+δ(HCH)
	1183	1182	781+398=1179
	1166		583x2=1166
	1151	1150	1247-98=1149
		1139	583+554=1137
	1127		876+243=1119
	1101		579+520=1099
		1091	611+484=1095
	1067	1063	554+505=1059
	1047		520x2=1040
	1025		520+505=1025
	1014		505x2=1010
	998		554+450=1004
	981	987	782+194=976
	939	938	852+83=935
850	920		⍰(CH$_2$)
849	891	889	⍰(CH$_2$)
823	876		⍰$_{as}$(CS)+⍰(CCS)
821	852		⍰$_s$(CS)+⍰(CCS)
		802	398x2=796
763	782	781	⍰$_s$ (SCC)+⍰(OCC)
763	771		⍰$_{as}$ (SCC)+⍰(CSCd)
	718	717	359x2=718
	703	698	347x2=694
	682	679	398+281=679
	649	650	324x2=648
		643	359+281=640
	630		347+281=628
616	613	611	⍰(OCdS)+⍰(OCC)+⍰(CCS)
598	583	579	⍰$_s$(CdO)
543	554		⍰(HOH)twist
543		520	⍰(HOH)twist
488	505	506	⍰$_s$(HOH)wagg + ring torsion
484			⍰$_s$(HOH)wagg + ring torsion
475		466	⍰$_s$(HOH)wagg
470	450		⍰$_{as}$(HOH)wagg
	431	437	281+149=430
416		427	⍰(CCO)+⍰(CH$_2$)
372	358	359	⍰$_{as}$(CdS)
357		347	⍰(OC=O)
357			⍰$_s$(CdS)+⍰(OCS)
300	324		⍰$_{as}$(CdOH$_2$)
290	292	281	⍰$_s$(CdOH$_2$)
287		252	⍰$_s$(CdS)+⍰$_s$(CdOH$_2$)
260		243	⍰(SCdO)+⍰(CCS)
	224		117+106=223
	210	212	2x 102 = 204
197	195	194	⍰$_s$(SCdO)+⍰(CCS)

		184	102+83=185
178	178	173	⍰(H_2O)+ ring torsion
157		161	⍰(H_2O)
156	149	154	⍰(H_2O)
		135	98+39=137
	124	128	61x2=122
	116	117	61+52=113
106		102	Ring torsion
98		98	Ring torsion
96			Ring torsion
88		83	Ring torsion
77		73	⍰(OCdOH$_2$)

Source: Authors.

3.4 Some features of the Zn(II) and Cd(II) thioglyconate complexes

The linear fit between experimental vs calculated spectra gave the following values for the Zn(II) complex: Pearson`s r =0.99984 and the Adj. R-square was equal to 0.99967; for the Cd(II) complex the values were: Pearson`s r = 0.9996 and Adj. R-square = 0.99918. These values are in good agreement between the experimental and calculated wavenumbers, thus indicating that the proposed structures for the Zn(II) and Cd(II) thioglyconate complexes were appropiate.

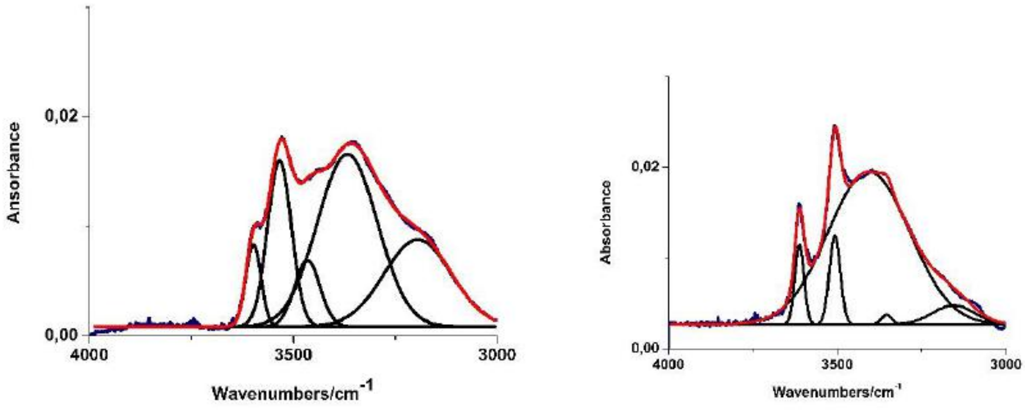
In Tables 2 and 3 the bending H-C-H normal modes were not scaled by the factor 0.872 in the RHF/MP2 procedure with basis set STO-3G, because such scale factor overestimated the wavenumber values of these normal modes.

OH stretching

As both complexes have two H_2O molecules in their structures, there are 4 internal coordinates that define the infinitesimal variations of the distances between the O-H atoms. Hence, there are 4 normal modes defining these variations, with A and B symmetries of the C_1 point group. Figure 4 illustrates the shapes of the observed bands in the infrared spectra, with their respective intensities.

Figure 4 - Deconvolution band in the infrared spectra of the Zn(II)) and Cd(II) thioglycolate complexes.

a) $[Zn(ATG)_2(OH_2)_2]$ b) $[Cd(ATG)_2(OH_2)_2]$



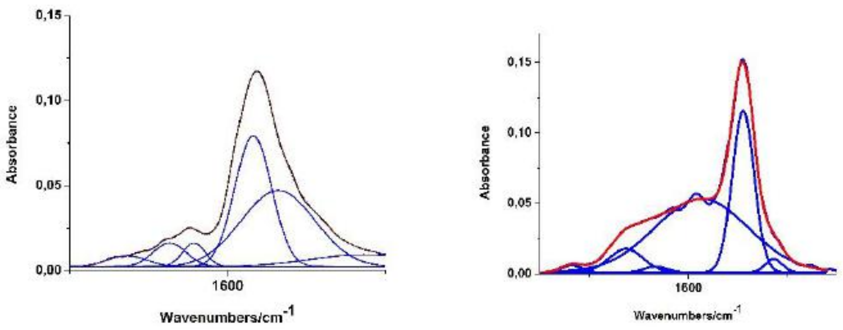
Source: Authors.

From Figure 4 we can appreciate the similarity of the spectra. The four □(OH) bands were assigned at 3598, 3534, 3466, and 3367 cm^{-1} for the Zn(II) complex, and at 3612, 3507, 3406, and 3354 cm^{-1} for the Cd(II) complex.

-C=O stretching

The absorption bands of the symmetric scissoring angular variations □(HOH) of the two water molecules present in the coordination sphere of the Zn(II) and Cd(II) complexes are located between 1750 and 1450 cm^{-1} in the infrared spectrum. The symmetric and asymmetric carbonyl stretchings for each complex appear in the same region of the IR spectrum. For the Zn(II) complex, the calculations indicated that the higher energy bands correspond to the absorption of the carbonyl vibrational modes. The same is not true for the Cd(II) complex. Therefore, we follow the experimental evidence to perform the assignment of these bands. Figure 5 illustrates the infrared spectra for each complex.

Figure 5 - Deconvolution bands in the infrared spectra (1750-1450^{-1}) for the Zn(II) and Cd(II) thioglycolate complexes.



a) [Zn(ATG)$_2$(OH$_2$)$_2$] b) [Cd(ATG)$_2$(OH$_2$)$_2$]

Source: Authors.

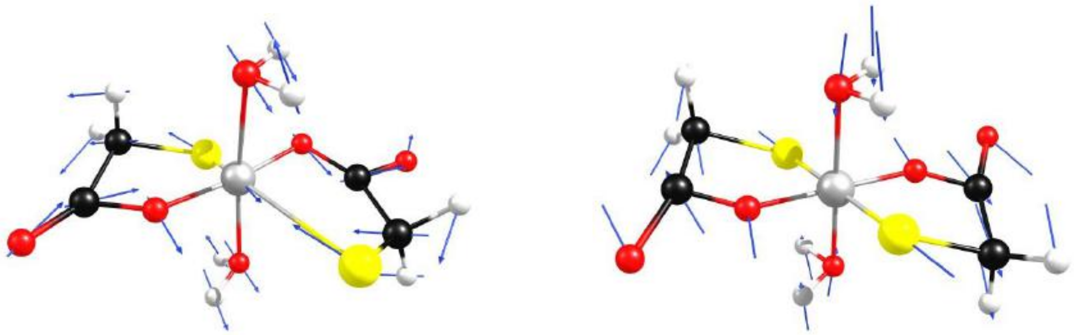
The band assignments were: □(HOH) at 1663 and 1633 cm^{-1} for the Cd(II) complex, and 1673 and 1652 cm^{-1} for the Zn(II) complex; □(C=O) at 1592 and 1545 cm^{-1} for the Cd(II) complex, and 1593 and 1584 cm^{-1} for the Zn(II) complex.

Framework Vibrations

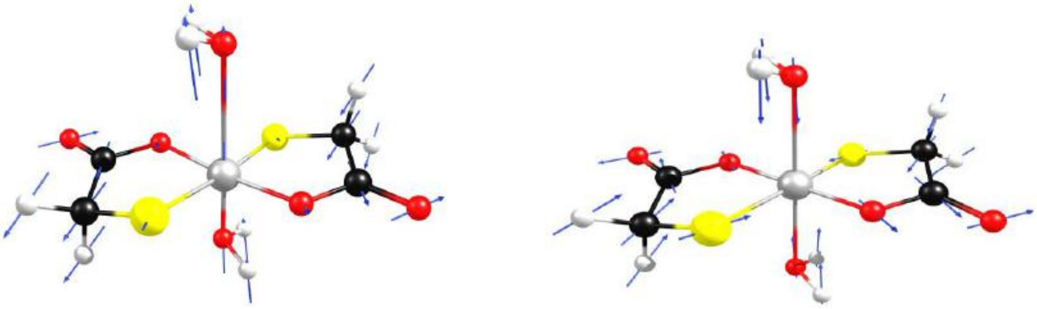
The metal-ligand vibrations of both the Zn(II) and Cd(II) thioglycolate complexes presented a high degree of vibrational coupling between the different internal coordinates participating in the several vibrational modes. However, there were some vibrations that were clearly identified since they had little coupling, as the □$_s$(Cd-OH$_2$) and □$_{as}$(Cd-OH$_2$) stretchings, located at 292 and 324 cm^{-1} respectively. The coupled mode □$_s$(Cd-OH$_2$) + □$_s$(Cd-O) + □$_s$(Cd-S) was located at 252 cm^{-1}. The angle deformation mode □(SCdO) was active at 225.84 cm^{-1}. The coupled mode □$_s$(Cd-S) + □$_s$(Cd-OH$_2$) was active with vibrational energy equal to 357 cm^{-1} as well as the asymmetric stretching mode, □$_{as}$(Cd-S) at 359 cm^{-1}, presenting vibrational coupling. For the Zn(II) thioglycolate complex, we highlight the following vibrational modes: the asymmetric and symmetric stretching modes Zn-S at 430 and 404 cm^{-1}, respectively. At 317 and 278 cm^{-1}, the □$_{as}$(Zn-OH$_2$) and □$_s$(Zn-OH$_2$) vibrational modes, respectively. The □$_{as}$(Zn-S) and □$_s$(Zn-S) coupled modes were observed at 430 and 404 cm^{-1}, respectively. The form of these normal modes is shown in Figure 6.

Figure 6 - Selected skeletal vibrational modes for the Cd(II) and Zn(II) thioglycolate complexes.

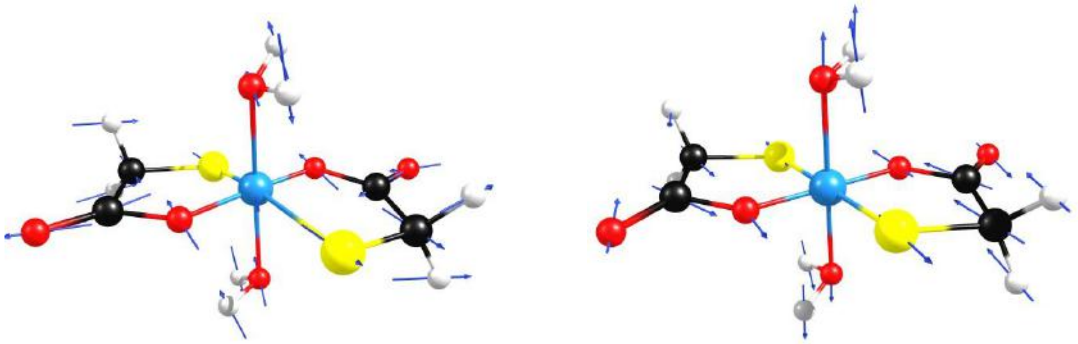
a) □$_{as}$(CdS) 359 cm^{-1} b) □$_{s}$(CdS) 347 cm^{-1}



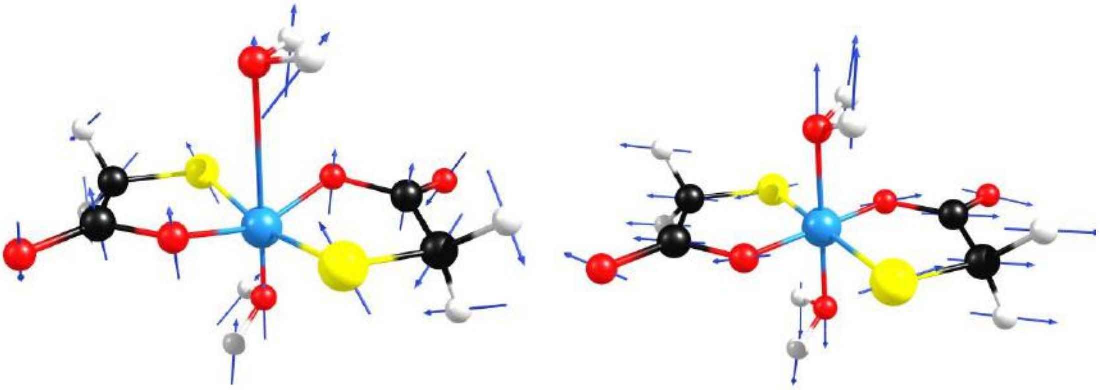
c) □$_{as}$(Cd-OH2) 324 cm^{-1} d) □$_{s}$(Cd-OH$_2$) 292 cm^{-1}



e) □$_{as}$(ZnS) 430 cm^{-1} f) □$_{s}$(ZnS) 404 cm^{-1}



g) □$_{as}$(Zn-OH2) 317 cm^{-1} h) □$_{s}$(Zn-OH$_2$) 278 cm^{-1}



Source: Authors.

3.5 Natural Bond Orbitals of the [Cd(ATG)$_2$(OH$_2$)] and [Zn(ATG)$_2$(OH$_2$)] complexes

An extensive treatment of Natural Bond Orbitals (NBO) [24-29] is currently being carried out by the research group of Professor Dr. Weinhold at the University of Wisconsin-USA. The model is based on the description of atomic orbitals (AO) for the formation of characteristic bonds present in molecules. In principle, the model for the description of the bonds is inserted in the Lewis model that considers single, double or triple bonds by the presence of one, two and three pairs of electrons participating in the bonds. In the Lewis model, the electrons are fixed in chemical bonds, however, in the NBO model, which is dynamic, the electrons can reach Rydberg energy levels. In this work, we provide information about the constitution of the wave functions of the chemical bonds committed in the complexes $[M(ATG)_2(OH_2)_2]$, M=Zn(II), Cd(II), as well as the charge transfer processes.

For the NBO analysis of the $[Cd(ATG)_2(OH_2)]$ and $[Zn(ATG)_2(OH_2)]$ complexes, it is necessary to obtain their geometric structures. For this purpose, we used the quantum mechanical method based on the hybrid RHF/MP2 with STO-3G basis set for both metallic complexes.

Structural geometries of the thioglycolic acid complexes with Zn(II) and Cd(II). The geometries of the complexes are illustrated in Figure 2 and were obtained using the Chemcraft visualization program (Weinhold & Landis, 2005).

The two metal complexes having two thioglycolic acid as ligands, and two water molecules in axial positions have two five-membered rings with single bonds. The only double bond corresponds to the carbonyl (-C=O).

The set of Lewis-type NBOs typically includes a central core (labeled "CR" in the output of the NBO program) and a lone valence pair ("LP"), as well as two-center bonding orbitals ("BD"). The Lewis set includes unbound valence ("LP ∗") and extra valence layer Rydberg Orbitals ("RY ∗"), as well as the valence antibonds ("BD ∗") from the equation ⍰* AB = cBhA – cAhB. Hence, the NBOs form a set of chemical bases of the Lewis type (no star) and orbitals that do not correspond to the Lewis type (stars), with each member closely related to the diagram of the localized Lewis structure or its capacity for chemical alteration (Weinhold & Landis, 2005; Weinhold, Landis & Glendening, 2016; Glendening et al., 2013; Glendening, Landis & Weinhold, 2013; Landis & Weinhold, 2016).

3.6 Natural bond orbitals for the $[Cd(ATG)_2(OH_2)_2]$ complex

The natural atomic orbital occupancies for the valence d orbitals of Cd are: d_{xy}(4d) with 1.46, d_{xz} 1.99, d_{yz} 1.99, d_{x2-y2} 1.95, and d_{z2} with 1.97 electrons, and the natural electronic configurations end as $5s^{0.75}4d^{9.37}5p^{1.71}$.

3.6.1 Framework of natural bond orbitals

BD (1)Cd 1 - O 3 : ⍰$_{CdO}$ = 0.5458(sp$^{2.47}$d$^{1.44}$)$_{Cd}$ + 0.8379(sp$^{6.34}$)$_{O}$

Electron occupancy=1.92264; polarization: 70.21% on O atom and 29.79% on the Cd atom.

BD (1)Cd 1 - O 5 : ⍰$_{CdO}$ = 0.5458(sp$^{2.98}$d$^{1.85}$)$_{Cd}$ + 0.8379(sp$^{6.34}$)$_{O}$

Electron occupancy=1.92342; polarization: 69.81% on the O atom and 30.19% on the Cd atom.

BD (1)Cd 1 - S 4 = BD (1)Cd 1 - S 2 : ⍰$_{CdS}$ = 0.6785(sp$^{0.47}$d$^{0.85}$)$_{Cd}$ + 0.7346(sp$^{18.47}$)$_{S}$

Electron occupancy=1.92915; polarization: 53.97% on the S atom and 46.03% on the Cd atom.

BD (1) S 2 - C 9 : ⍰$_{SC}$ = 0.6849(sp$^{9.99}$)$_{S}$ + 0.7286(sp$^{3.26}$)$_{C}$

Electron occupancy=1.98117; polarization: 46.91% on the S atom and 53.09% on the C atom.

BD (1) S 4 - C 6 : ⍰$_{SC}$ = 0.6836(sp$^{10.98}$)$_{S}$ + 0.7299(sp$^{3.26}$)$_{C}$

Electron occupancy=1.97996; polarization: 46.73% on the S atom and 53.27% on the C atom.

BD (1) O 3 - C 10 = BD (1) O 5 - C 7 : ⍰$_{OC}$ = 0.7658(sp$^{4.39}$)$_{O}$ + 0.6431(sp$^{2.36}$)$_{C}$

Electron occupancy=1.97183; polarization: 58.64% on the O atom and 41.36% on the C atom.

BD (1) C 6 - C 7 = BD (1) C 9 - C 10 : ⍰$_{CC}$= 0.7090(sp$^{3.21}$)$_{C}$ + 0.7052(sp$^{2.07}$)$_{C}$

Electron occupancy=1.97414; polarization: 50.27% on the C(6) atom and 49.73% on the C(7) atom.

BD(1) C(7)-O(8): ⍰$_{C=O}$ = 0.6370(sp$^{5.94}$)$_{C7}$ + 0.7708(sp$^{12.24}$)$_{O8}$

BD(2) C(7)-O(8): ⍰$_{C=O} = 0.6446(sp^{3.32})_{C7} + 0.7645(s^{7.24})_{O8}$

Total electron occupancy=3.98324; total polarization: 82.4% on the C(7) atom and 117.86% on the O(8) atom.

3.7 Second Order Perturbation Theory Energy Analysis on Fock Matrix in NBO basis

A completed bond or a lone electron pair orbital can act as an electron donor and an empty or full anti-ligand orbital, or a lone electron pair orbital can act as an electron acceptor. The strength of a bond can be evaluated through these interactions. Tables 4 and 5 for the Cd(II) and Zn(II) complexes present the donor and acceptor orbitals, electron occupancies and energy values above 10 kcal.mol^{-1}.

Table 4 lists the donor and acceptor orbitals, and the corresponding energies in kcal.mol^{-1}. The most representative interactions obtained by the NBO/RHF/MP2 calculations for the $[Cd(ATG)_2(OH_2)_2]$ complex are shown in the table.

Table 4 - Donor and acceptor orbitals, and energies in kcal.mol^{-1} for the $[Cd(ATG)_2(OH_2)_2]$ complex.

Donor NBO (i)	Acceptor NBO (j)	Energy in kcal/mol
BD*(1)Cd 1 - O 5	BD*(1)Cd 1 - O 3	705.25
LP (3) S 2	LP*(5)Cd 1	447.97
BD*(1) C 10 - O 11	BD*(2) C 10 - O 11	69.49
BD*(1) C 7 - O 8	BD*(2) C 7 - O 8	69.46
LP (2) O 13	LP* (6) Cd 1	64.21
BD*(1)Cd 1 - S 4	BD*(1)Cd 1 - O 5	63.60
LP (2) O 12	LP*(6)Cd 1	63.09
BD*(1)Cd 1 - S 4	BD*(1)Cd 1 - O 3	40.03
LP (2) O 8	BD*(1) O 5 - C 7	37.85
LP (2) O 8	BD*(1) C 6 - C 7	30.28
LP (2) O 11	BD*(1) O 3 - C 10	37.85
LP (2) O 11	BD*(1) C 9 - C 10	30.28
LP*(5)Cd 1	BD*(1)Cd 1 - O 5	32.39
LP (2) O 5	BD*(1) C 7 - O 8	28.04
LP (2) O 3	BD*(1) C 10 - O 11	28.04
LP (1) S 2	LP*(5)Cd 1	23.61
LP (2) O 3	LP*(6)Cd 1	19.93
LP (2) O 5	LP*(6)Cd 1	19.91
BD (1)Cd 1 - O 5	BD*(1)Cd 1 - O 3	15.73
BD (1)Cd 1 - O 3	BD*(1)Cd 1 - O 5	14.17
LP (2) S 4	LP*(6)Cd 1	12.62
LP (2) S 2	LP*(6)Cd 1	12.54
LP (2) O 5	BD*(2) C 7 - O 8	12.36
LP (2) O 3	BD*(2) C 10 - O 11	12.36
BD (1)Cd 1 - S 4	BD*(1)Cd 1 - O 3	11.56
LP (2) O 13	BD*(1)Cd 1 - S 4	10.89
LP (1) O 5	LP*(5)Cd 1	10.42
LP (2) O 12	BD*(1)Cd 1 - S 4	10.18
LP (1) S 2	LP (3) S 2	10.00

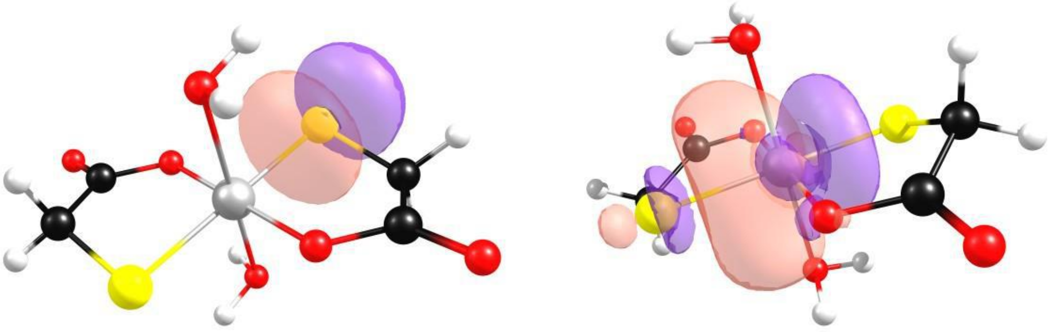
Source: Authors.

The charge transference of the lone pairs of the S and O atoms to Cd* lone pairs have higher stabilization energies. The electrons stabilization i⍰j is estimated as E(2) = ⍰$E_{ij} = q_i[F(I,j)^2/($⍰$_j$ - ⍰$_i)]$ where q_i is the donor orbital occupancy, ⍰$_j$ - ⍰$_I$

are diagonal elements representing orbital energies and F(i, j) is the off-diagonal NBO Fock matrix element (Weinhold & Landis, 2005; Weinhold et al., 2016; Glendening et al., 2013; Glendening et al., 2013; Landis & Weinhold, 2016).

Figure 7 - HOMO and LUMO orbitals for the [Cd(ATG)$_2$(OH$_2$)$_2$] complex.

[Cd(ATG)$_2$(OH$_2$)$_2$]

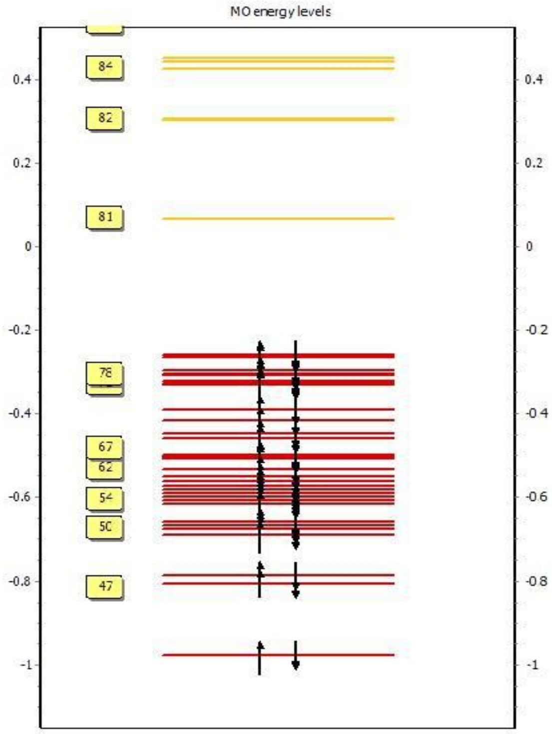


Source: Authors.

The energy gap was of 0.32357 A. U. The energy diagram is shown in Figure 8.

Figure 8 - Energy diagram of the [Cd(ATG)$_2$(OH$_2$)$_2$] complex.

[Cd(ATG)$_2$(OH$_2$)$_2$]



Source: Authors.

3.8 Natural bond orbitals for the [Zn(ATG)$_2$(OH$_2$)$_2$] complex

3.8.1 Framework natural bond orbitals

BD (1)Zn 1 – S 2 = Bd(1) Zn1 – S4 : ⍰$_{ZnS}$ = 0.5954$(sp^{1.85}d^{0.85})_{Zn}$ + 0.8034$(sp^{8.59})_S$

Electron occupancy=1.95815; polarization: 35.46% on Zn atom and 64.54% on the S atom.

BD (1)Zn 1 - O 3= BD(1) Zn1-O5 : ?$_{ZnO}$ = 0.4831(sp$^{2.25}$d$^{1.25}$)$_{Zn}$ + 0.8756(sp$^{2.53}$)$_{O}$

Electron occupancy=1.96709; polarization: 23.34% on the Zn atom and 76.66% on the O atom.

BD (1) S 2 - C 9 = BD(1) S4-C6 : ?$_{SC}$ = 0.6810(sp$^{10.23}$)$_{S}$ + 0.7323(sp$^{3.21}$)$_{C}$

Electron occupancy=1.98135; polarization: 43.38% on the S atom and 53.62% on the C atom.

BD (1) C 6 - C 7= BD(1) C9-C10: ?$_{CC}$= 0.7274(sp$^{3.84}$)$_{C}$ + 0.6862(sp$^{2.91}$)$_{C}$

Electron occupancy=1.96805; polarization: 52.91% on the C6 atom and 47.09% on the C7 atom.

BD(1) O5-C7=BD(1) O3-C10: ?$_{OC}$=0.7744(sp$^{3.63}$)$_{C}$ + 0.6327(sp$^{2.30}$)$_{C}$

Electron occupancy=1.97542; polarization: 59.96% on the O5 atom and 40.04% on the C7 atom.

BD(1) C(7)-O(8)= BD(1)C10-O11: ?$_{C=O}$ = 0.6587(sp$^{1.66}$)$_{C7}$ + 0.7524(sp$^{4.03}$)$_{O8}$

BD(2) C(7)-O(8)= BD(2)C10-O11: ?$_{C=O}$ = 0.6270(sp$^{99.99}$)$_{C7}$ + 0.7790(sp$^{99.99}$)$_{O8}$

Total electron occupancy=3.98687; total polarization: 82.70% on the C(7) atom and 117.30% on the O(8) atom.

Table 5- Donor and acceptor orbitals, and energies in kcal.mol^{-1} for the [Zn(ATG)$_2$(OH$_2$)$_2$] complex.

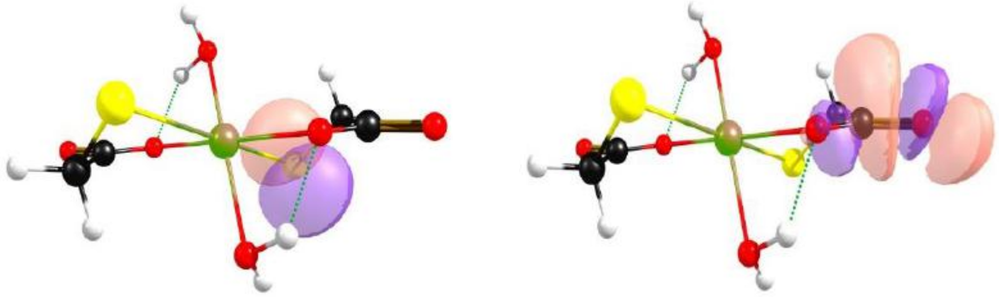
Donor NBO (i)	Acceptor NBO (j)	Energy in kcal/mol
LP (2) O 12	/ 56. LP*(5)Zn 1	85.99
LP (2) O 13	/ 56. LP*(5)Zn 1	85.99
LP (2) O 3	/ 90. BD*(2) C 10 - O 11	60.72
LP (2) O 5	/ 85. BD*(2) C 7 - O 8	60.72
LP (2) O 3	/ 56. LP*(5)Zn 1	48.72
LP (2) O 5	/ 56. LP*(5)Zn 1	48.72
LP (2) O 11	/ 78. BD*(1) O 3 - C 10	37.94
LP (2) O 8	/ 80. BD*(1) O 5 - C 7	37.94
LP (2) O 8	/ 81. BD*(1) C 6 - C 7	30.12
LP (2) O 11	/ 86. BD*(1) C 9 - C 10	30.12
LP (2) S 2	/ 56. LP*(5)Zn 1	22.23
LP (2) S 4	/ 56. LP*(5)Zn 1	22.23
LP (1) O 3	/ 75. BD*(1)Zn 1 - S 4	12.43
LP (1) O 5	/ 73. BD*(1)Zn 1 - S 2	12.43
BD (1)Zn 1 - S 2	/ 74. BD*(1)Zn 1 - O 3	11.36
BD (1)Zn 1 - S 4	/ 76. BD*(1)Zn 1 - O 5	11.36
LP (2) O 12	/ 73. BD*(1)Zn 1 - S 2	10.65
LP (2) O 13	/ 75. BD*(1)Zn 1 - S 4	10.65

Source: Authors.

According to the RHF/MP2 NBO calculations the charge transference of the lone pairs of the S and O atoms to Zn* lone pairs have higher stabilization energies than that determined for the same type of electron transfer to Cd* lone pairs.

Figure 9 - HOMO and LUMO orbitals for the $[Zn(ATG)_2(OH_2)_2]$ complex.

$[Zn(ATG)_2(OH_2)_2$

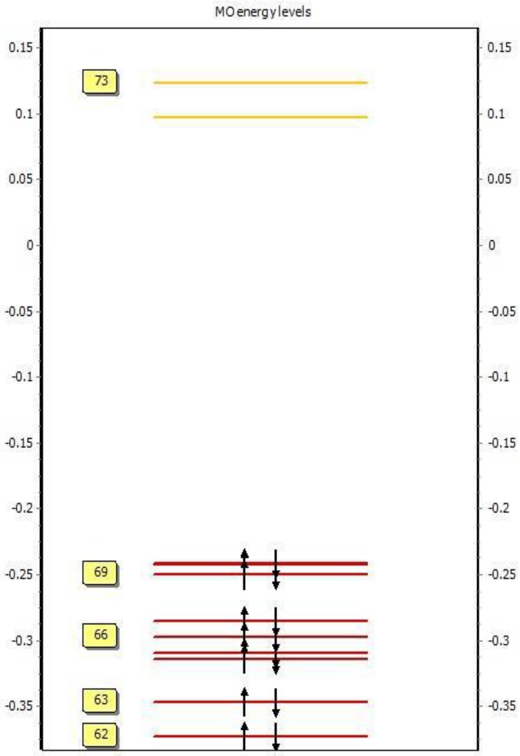


Source: Authors.

The energy gap was of 0.33913 A. U. The energy diagram is shown in Figure 10.

Figure 10 - Energy diagram for the $[Zn(ATG)_2(OH_2)_2]$ complex.

$[Zn(ATG)_2(OH_2)_2$



Source: Authors.

4. Conclusion

We performed the syntheses of the complexes $[Zn(ATG)_2(OH_2)_2]$ and $[Cd(ATG)_2(OH_2)_2]$ applying the graphical method, which allows a rigorous control of the synthesis conditions through the visualization of the strategic zones to avoid experimental problems (low-yield product, contamination with hydroxide, destruction of the binder in an acidic medium), as well as its reproducibility. With the synthesized complexes in hand, the FT-IR and FT-Raman spectra were obtained.

Calculated and experimental spectra confirmed the structural hypothesis considering two ATG (thioglycolic acid) with two water molecules in the coordination sphere of the central atoms. The natural bond orbital analysis (NBO) was also carried out to study the Zn(II) and Cd(II) hybridization leading to a pseudo-octahedral geometry for both complexes. The spectra of the Zn(II) and Cd(II) complexes are similar and show the corresponding band shifts due to the different atomic masses of the two metal ions.

The stretching vibrations corresponding to the metal-S and metal-O bonds, located in the horizontal plane of both metal complexes, showed as medium intensity bands in the region between 500 and 200 cm-1 of the vibrational spectra.

The confirmation of the proposed structures was done using the experimental theoretical method, placing the proposed structural geometries as a calculation basis and determining the theoretical spectra, whose results were compared with the experimental vibrational spectra, obtaining an excellent agreement. The structural analysis through theoretical calculations gave pseudo-octahedral structures with point group C1 for the chromophores MS2O4, M=Zn(II) and Cd(II).

Descriptions of the wave functions in the NBO analysis using the RHF/MP2 method with STO-3G basis set are given in sections 3.6.1 for the Cd(II) complex, and in section 3.8.1. for the Zn(II) complex. The charge transfers between donor and acceptor orbital's in kcal.mol^{-1} values follows correctly the symmetry position of the different bonds in the Zn(II) complex, rather than in the Cd(II) complex, in which we found similar values.

Declaration of interest statements

This paper has no conflict of interest; it is an original research work.

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