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# DFT: B3LYP/6-311G (d, p) vibrational analysis of bis-(diethyldithiocarbamate)zinc (II) and natural bond orbitals

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#### HIGHLIGHTS

- Synthesis of bisdiethyldithiocarbamate Zn(II) was carried out.
- ► The FT-IR and Raman spectra of [Zn(DDTC)<sub>2</sub>] were carried out.
- The calculated FT-IR and FT-Raman spectra were performed using DFT/ B3LYP method.

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#### G R A P H I C A L A B S T R A C T



# ABSTRACT

Theoretical and experimental bands have been assigned for the Fourier Transform Infrared (FT-IR) and Fourier Transform Raman (FT-Raman) spectra of the bis-(diethydithiocarbamate)Zn(II) complex,  $[Zn(DDTC)_2]$ . The calculations and spectra interpretation have been based on the DFT/B3LYP method, infrared and Raman second derivative spectra as well as band deconvolution analysis. To assign the metal-ligand normal modes the deviation percentage of the geometrical parameters was used. Results confirms a pseudo tetrahedral structure around the Zn(II) cation. The calculated infrared and Raman spectra has an excellent agreement with the experimental spectra. The Natural Bond Orbital analysis (NBO) was carried out as a way to study the Zn(II) hybridization leading to the pseudo tetrahedral geometry of the framework of the  $[Zn(DDTC)_2]$  complex, and to study also which are the donor NBO and the acceptor NBO in meaningful charge transfer through the Second Order Perturbation Theory Analysis of Fox Matrix in NBO basis.

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# Introduction

There are many reports on literature about the use of bis(diethyldithiocarbamate)zinc(II) complex and his importance in medicine. By example, Rathore et al. [1] had studied the fungicidad activity of  $[Zn(DDTC)_2]$ , and Siling et al. [2] carried out an investigation on ocular drug delivery system containing  $[Zn(DDTC)_2]$  and HPbetaCD inclusion complex-corneal permeability, anticataract effects and mechanism. In literature we find also studies on contact urticaria to  $[Zn(DDTC)_2]$  [3,4] and protective effects of Zinc on

\* Corresponding author. *E-mail address:* tellez@vm.uff.br (C.A. Téllez Soto). diethyldithiocarbamate cytotoxicity on rat astrocytes in vitro [5]. Concerning cancer research according to Cveck et al. [6], Ni(II), Cu(II), and Zn(II) diethyldithiocarbamate complexes show various activities against the proteasome in breast cancer cells. By other hands Daniel et al. [7] studied complexes with clioquinol and pyrrolidine dithiocarbamate of copper to form proteasome inhibitors and apoptosis inducers in human breast cancer cells, and Neslund-Dudas et al. [8] carried out a study about association of metals and proteasome activity in erythrocytes of prostate cancer patients and control. The interaction of Zn as an element of biological importance is put in evidence recently by Dhawan and Chadha [9] sustaining that Zinc is an essential element that is integral to many proteins and transcription factors which regu-

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late key cellular functions such as the response to oxidative stress, DNA replication, DNA damage repair, cell cycle progression, and apoptosis. Zinc has been ascribed roles in the metabolism and interaction of malignant cells, particularly in apoptosis.

Due to the wide applicability of the  $[Zn(DDTC)_2]$  complex we thing that it is necessary to have a total interpretation of the vibrational spectra, and to put in evidence almost some important molecular characteristic, such as an analysis of the natural bond orbitals. Related papers on a vibrational study of  $[Zn(DDTC)_2]$ , the assignment are not complete and normal coordinate analysis were based on reduced models [10,11]. Taken these considerations in account ours purposes are: achieve the synthesis of a Zn[DDTC\_2] using the graphic method to determine initial synthesis conditions; to obtain the FT-infrared and the FT-Raman spectra, achieve the total vibrational assignment, and to study bond characteristic of this Zn(II) complex.

To achieve this goal we must overcome some difficulties which arise from the band shape of some fundamentals which are large and overlap other bands. Hence it is important to obtain the second derivative spectrum that gives an appropriate indication of the position of overlapped fundamental bands, combinations and overtones which are active according the selection rules.

The results of this experimental work are summarized in Table 2. Fig. 2 shows the experimental infrared spectra of [Zn(DDTC)<sub>2</sub>]. In spite of the remarkable coincidence between the experimental and calculated scaled wave numbers, the spectral differences are due to the different nature between the calculated spectrum which supposes only one molecule without interactions in the gas phase, and the experimental one's where interactions of the solid phase are present.

#### Experimental

#### General

Zinc(II) nitrate, sodium diethyldithiocarbamate trihydrate salt and HNO<sub>3</sub> were purchased from Vetec Co. All solvents and reagents were used as received without further purification. Elemental analysis (CHN) was carried out in a Sinc EA 1110 analyzer. For the FT-IR measurements, the samples were prepared in KBr and polyethylene pellets. The spectra were collected at room temperature, in range of 4000–370 cm<sup>-1</sup> with 4 cm<sup>-1</sup> of resolution, scanning speed of 0.2 cm<sup>-1</sup> s<sup>-1</sup> and 120 scans, using a Perkin Elmer 2000 FT-IR spectrometer.

The FT-Raman spectra were measured at room temperature using a Bruker Spectrometer (model RFS 100/S), in the range of 4000–100 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 120 scans. The samples were measured in the solid state. The excitation light source was a Nd:YAG laser at 1064 nm. The laser spot size was 200  $\mu$ m in diameter and the power was kept at 30 mW to prevent

any degradation. The percentage of zinc was determined by atomic absorption spectrometry using a Varian-1106 spectrophotometer. The  $pH_3O^+$  control during the synthesis of the complex was carried out with the potentiometer Micronal B 375.

#### Synthesis of bis-diethyldithiocarbamate Zn(II)

To a solution of diethyldithiocarbamate (5 mmol) in 50 mL of deionizated water was stirred by 20 min obtaining a  $pH_3O^+$  = 10. The  $pH_3O^+$  was adjusted to 6.0 with HNO<sub>3</sub> 6 mol L<sup>-1</sup>. Then zinc(II) nitrate (5 mmol) was added to this solution and the  $pH_3O^+$  was maintained around 6.0. This control was done using a potentiometer and all the synthesis was carried out under stirring at room temperature. The agitation was kept constant for 10 min until a white solid precipitate. This precipitate was filtered under reduced pressure and washed for three times with deionized water. [Zn(DDTC)<sub>2</sub>] solid was kept under vacuum in a desiccator with sulfuric acid. Elemental analysis (CHN) and atomic absorption, for C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>S<sub>4</sub>Zn: Found C, 32.85%; N, 7.67%; H, 5.51% and Zn 18.22%. Calculated: C, 33.18%; N, 7.74%; and H, 5.57% and, Zn 18.07%.

#### Calculations

The calculations were carried out for the neutral complex,  $[Zn(DDTC)_2]$ , considered it as no interacting independent units. For geometry optimization, the density functional theory method B3LYP was used in the Gaussian 03 program [12]. For all calculations, we used the 6-311G (d, p) basis set for all atoms. All calculations have been optimized from several initial geometries, being the complex with C1 symmetry more stable. After this procedure, the vibrational calculations were performed. No imaginary mode was observed. Characteristic normal stretching and bending modes from the  $-C_2H_5$  groups were visualized using the graphical Chemcraft program [13]. The skeletal or framework normal modes were determinate using the percentage deviation of the geometrical parameters (PDPG), from its equilibrium position.

#### Results

# General

Monosodium DDTC salt is easily prepared by treatment of carbon disulfide with diethylamine in the presence of sodium hydroxide. This compound is a stable reagent in solid state, but the most important property of this ion is its protonation in acid solution and subsequent decomposition into carbon disulfide and protonated amine. The composition is favored when the  $pH_3O^*$  of the reactional mean is lower than  $pK_a$  of the R'RNH<sub>2</sub><sup>+</sup> ion. The  $pK_a$  of diethyldithiocarbamate acid derived from diethylamine is 3.95 at

Table	1
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Calculated parameters with B3LYP using 6-311G (d, p) base set for [Zn(DDTC)2] complex of  $C_1$  symmetry (Bonamico experimental values are between parentheses [25]).

Atoms i, j	Bond lengths (Å)	Atoms i, j, k	Bond angles (°)	Atoms i, j, k	Bond angles (°)
R(1-2)	2.40 (2.36)	A(2-1-3)	77.39 (75.78)	A(1-10-12)	81.83 (93.93)
R(1-3)	2.40 (2,44)	A(2-1-10)	127.90	A(1-11-12)	81.83 (78.27)
R(1-10)	2.40 (2.33)	A(2-1-11)	127.15 (93.62)	A(2-4-3)	118.95 (117.53)
R(1-11)	2.40 (2.82)	A(1-2-4)	81.83 (84.48)	A(2-4-5)	120.53 (121.42)
R(2-4)	1.74 (1.73)	A(3-1-10)	127.18 (106.87)	A(3-4-5)	120.53 (121.00)
R(3-4)	1.74 (1.72)	A(3-1-11)	127.89	A(10-12-11)	118.95 (117.78)
R(10-12)	1.74 (1.73)	A(1-3-4)	81.83 (81.88)	A(10-12-13)	120.53 (119.67)
R(11-12)	1.74 (1.74)	A(10-1-11)	77.39 (69.57)	A(11-12-13)	120.53 (122.52)
R(4-5)	1.34 (1.34)				
R(12-13)	1.34 (1.31)				

Table 2

Experimental FT-IR and FT-Raman. DFT:B3LYP/6-311G (d, p) calculated spectra for [Zn(DDTC)<sub>2</sub>] complex (wavenumbers in cm<sup>-1</sup>).

Wn <sub>calc</sub> B3LYP	$I_{IR}^{(*)}$	$I_R^{(**)}$	Wn <sub>cor</sub>	IR Wn <sub>Exp</sub> (Abs.)	IR DBA	Raman Wn <sub>Exp</sub>	Raman DBA	Assignment (internal coordinate)
3128	1.49	9.03	3007			-		$_{2}(CH)(CH_{2}) + v_{2}(CH)(CH_{2})$
3127	64.32	0.99	3006					$v_{as}(CH)(CH_3) + v_{as}(CH)(CH_2)$
3125	3.06	5.57	3004					$v_{as}(CHv)(CH_3) + v_{as}(CH)(CH_2)$
3125	5.18	1.02	3004				2991	$v_{as}(CH)(CH_3) + v_{as}(CH)(CH_2)$
3114	5.26	64.64	2993	2984 (0.12)	2988			$v_s(CH)(CH_3) + v_{as}(CH)(CH_2)$
3114	13.66	56.94	2993					$v_s(CH)(CH_3) + v_{as}(CH)(CH_2)$
3113	20.62	128.56	2993					$v_{s}(CH)(CH_{3}) + v_{as}(CH)(CH_{2})$
3113	4./1	23.75	2993	2070 (0 12)	2070			$V_{s}(CH)(CH_{3}) + V_{as}(CH)(CH_{2})$
3095	52.38 10.20	224.06	2975	2979 (0.12)	2979	2072 (0.14)	2072	$V_{as}(CH)(CH_3) + V_{as}(CH)(CH_2)$
3094	0.63	94 50	2973	2970 (0.11)	2969	2373 (0.14)	2373	$v_{as}(CH)(CH_3) + v_{as}(CH)(CH_2)$ $v_{as}(CH)(CH_3) + v_{as}(CH)(CH_2)$
3094	3.09	48.48	2974	2938 (0.08)	2505	2936 (0.23)	2937	$v_{as}(CH)(CH_2) + v_{as}(CH)(CH_2)$
3062	0.99	499.02	2944	2000 (0.00)	2933	2000 (0.20)	2007	$v_{as}(ch)(ch_2)$
3062	74.75	14.55	2944					v <sub>s</sub> (CH)(CH <sub>2</sub> )
3054	21.11	52.41	2936	2931 (0.09)	2930			$v_{as}(CH)(CH_2)$
3054	21.91	21.91	2936	2921 sh		2918 sh.	2917	$v_{as}(CH)(CH_2)$
				(0.05)		(0.11)		
3036	21.91	263.68	2919	2900			2890	$v_{s}(CH)(CH_{3})$
2026	24.22	202 62	2010	sh.(0.05)	2070	2971 (0.07)	2860	
3036	6.44	203.02	2919	2872 (0.04)	2070	2871 (0.07)	2009	$v_{as}(CH)(CH_3)$
3036	51 36	17.55	2919					$v_{as}(CH)(CH_3)$
1535	0.00	77.17	1476	1507 (0.50)		1507 (0.04)	1515	$v_{as}(C=N) + \delta(HCH)(CH_2)_{resize}$
1533	370.59	5.23	1474	1503 (0.53)	1501	1500 (0.03)	1504	$v_{as}(C=N) + \delta(HCH)(CH_2)_{sciss}$
1508	18.51	0.56	1450	1494 (0.20)	1498			$\delta(\text{HCH})(\text{CH}_3) + v_s(\text{C=N})$
1508	8.44	0.46	1450	. ,			1470	$\delta(\text{HCH})(\text{CH}_3) + v_{as}(\text{C}=\text{N})$
1504	0.23	22.36	1446				1464	$\delta(HCH)(CH_3),(CH_2)$
1504	19.39	16.24	1446	1459(0.13)			1461	$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2)$
1496	0.00	53.10	1438		1458			$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2)$
1496	0.22	0.75	1438			1452 (0.04)	1455	$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2)$
1494	4.86	2.03	1436	1449 (0.13)	1450	1 427 (0.04)	1447	$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2)$
1494	1.57	11 24	1430	1438 (0.33)	1/22	1437 (0.04)	1/22	0(HCH)(CH <sub>3</sub> ),(CH <sub>2</sub> ) S(HCH)(CH <sub>2</sub> )(CH <sub>2</sub> )
1486	13.64	33 34	1428	1429 (0.28)	1452	1420 (0.01)	1455	$\delta(\text{HCH})(\text{CH}_3)(\text{CH}_2)$
1400	0.01	23.97	1414	1422 (0.11)	1422	1420 (0.01)	1417	$\delta(\text{HCH})(\text{CH}_2) + v_2(C=N)$
1470	362.66	1.46	1413			1408 (0.01)	1409	$\delta(\text{HCH})(\text{CH}_2) + v_{3}(\text{C}=\text{N})$
1417	37.66	0.42	1362	1399 (0.06)			1392	$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2)$
1417	3.97	5.28						δ(HCH)(CH <sub>3</sub> ),(CH <sub>2</sub> )
1413	0.00	13.29	1358	1377 (0.13)	1377	1380 sh.	1377	δ(HCH)(CH <sub>3</sub> ),(CH <sub>2</sub> )
						(0.01)		
1413	14.38	1.36	1358			1373 (0.01)	1370	$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2)$
1399	0.00	5./2	1345	1356 (0.15)	1353	1355 (0.01)	1354	$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2) + v_s(\text{C=N})$
1399	4 81	2.50	1345	1545 (0.07)	1542	1345(0.01) 1320(yw)	1345	$\delta(HCH)(CH_3)(CH_2) \neq V_{as}(C=N)$
1383	4 99	3.72	1329	1299 (0.14)	1297	1290(0.01)	1299	$\delta(\text{HCH})(\text{CH}_2)$
1339	15.59	14.06	1287	1200 (0111)	1207	1200 (0.01)	1284	$\delta_{as}(HCH)(CH_3)(CH_2)$
1339	22.70	2.38	1287	1273 (0.36)	1271	1276 (0.02)	1275	$\delta_{as}(HCH)(CH_3),(CH_2)$
1304	0.00	83.00	1254				1267	$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2) + v_s(C=N)$
1302	311.72	0.08	1252			1247 (0.01)		$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2) + v_{as}(\text{C}=\text{N})$
1230	44.96	1.78	1182	1207 (0.22)	1208	1211 (0.02)	1204	$\delta(CNC) + \delta(HCH)(CH_3),(CH_2)$
1229	69.42	1.77	1181	1202 (0.15)	1201		1192	$\delta(CNC) + \delta(HCH)(CH_3),(CH_2)$
1170	142.07	21.10	1126		1190		11//	$\delta(\text{HCH})(\text{CH}_3), (\text{CH}_2) + V_s(\text{C}=\text{N})$
1115	20.86	0.15	1072	1147 (0.16)	1146	1147 (ww)	1100	$\delta(HCH)(CH_3)_{i}(CH_2) \neq v_{as}(C-N)$
1115	3 78	2.54	1072	1147(0.10) 1147(0.16)	1140	1147 (vw) 1147 (vw)		$\delta(\text{HCH})(\text{CH}_2)$
1097	3.78	2.94	1055		1131	1127 (vw)		$\delta(\text{HCH})(\text{CH}_3)(\text{CH}_2)$
1096	0.00	9.97	1054	1097 (0.08)	1095	1095 (0.01)		$\delta(\text{HCH})(\text{CH}_3),(\text{CH}_2))$
1083	39.53	1.03	1041	1080 (0.10)	1078	1076 (0.02)		$\rho(CH_3) + \rho(CH_2)$
1083	41.52	0.03	1041	1074 (0.12)	1072			$\rho CH_3$ ) + $\rho (CH_2)$
1007	7.59	7.57	968	1062 (0.07)	1063	1064 (0.01)		ρ(CH <sub>3</sub> )
1007	0.32	16.71	968	995 (0.19)	993	998 (0.02)	992	ρ(CH <sub>3</sub> )
990	5.75	5.24	952	984 (0.06)	0.00	983 (0.02)	978	$\rho(CH_3)$
990	51.55	2.82	952	960 (0.02)	968	972 (0.01)	964	$\rho(CH_3)$
916	30.55	7.80	881 881			864 (104)	884 873	$\delta(N(CS)_{S} + v(C(S) + v(CN))$
852	32.70	14 08	819	847 (0.06)		845 (VW)	848	$O(CH_2) + O(CH_2)$
852	0.05	5.50	819	517 (0.00)		842 (vw)	837	$\rho(CH_3) + \rho(CH_2)$
794	30.08	0.12	763	792 (0.01)		790 (0.01)	798	$\rho(CH_3) + \rho(CH_2)$
793	2.39	0.08	763	777 (0.04)		770 (vw)	765	$\rho(CH_3) + \rho(CH_2)$
788	1.79	3.98	758			750 (vw)	747	$\rho(CH_3) + \rho(CH_2)$
787	0.01	5.56	757			723 (vw)	726	$\delta(\text{HCH})(\text{CH}_3)_{\text{wagging}} + \delta(\text{HCH})(\text{CH}_2)_{\text{twisting}}$
617	1.13	0.69	593	565 (0.06)	565	566 (0.03)		$\rho(S_2C\uparrow N) + \rho(C_2N\downarrow C)$
617	0.96	0.03	593			558 (0.02)		$\rho(S_2C\downarrow N) + \rho(C_2N\uparrow C)$

Table 2 (continued)

Wn <sub>calc</sub> B3LYP	$I_{IR}^{(*)}$	$I_R^{(**)}$	Wn <sub>cor</sub>	IR Wn <sub>Exp</sub> (Abs.)	IR DBA	Raman Wn <sub>Exp</sub>	Raman DBA	Assignment (internal coordinate)
566	0.32	0.24	544	507 (0.03)	507	507 (vw)		$\delta(H_5C_2N^{\wedge}C_2H_5)s + v(CS) 38.4\% + \delta(SZnS)24.4\%$
566	0.01	2.34	544	. ,		487 (vw)	493	$\delta(H_5C_2N^{\wedge}C_2H_5)ass + v(CS) 44.9\% + \delta(SZnS)16.0\%$ .
502	25.81	2.35	483		477		470	$v(CS)$ 38.6% + $\delta(SCN)$ 30.2%
501	11.38	0.04	482	466 (0.02)	466			$v(CS)$ 37.5% + $\delta(SCN)$ 26.0% + $\delta(ZnSC)$ 15%.
439	0.31	0.17	422		459			$\delta(ZnSC)29.2\% + v(CS) 19.5\% + v(ZnS) 13\%$
436	2.77	4.17	419	427 (0.04)		434 (0.01)		$\delta$ (ZnSC)28.2% + $\delta$ (SZnS) 23.5% + $\nu$ (CS) 17.0%
397	50.40	0.82	382	400 (0.07)	396	399 (0.01)		v(ZnS) 31.5% + δ(ZnSC) 21.4% + δ(SCN) 18.5% + δ(SCS) 18.6%, including
								τ(H <sub>3</sub> CH <sub>2</sub> CNCH <sub>2</sub> CH <sub>3</sub>
395	3.77	0.57	380	379 (0.07)	379			$v(CS) 25.1\% + \delta(ZnCS) 21.3\% + v(ZnS) 16.5\%$
395	24.76	0.46	380			373 (0.01)	373	$\delta(SCN) 36.8\% + v(CS) 35.9\% + \delta(ZnCS) 13.2\%$
386	0.00	13.74	371			312 (0.01)	306	$\delta(ZnSC) 30.7\% + v(ZnS) 23.7\% + \delta(SCS) 19.9\% + \delta(SCN) 19.7\%$
322	25.63	0.10	310	335 (0.05)				v(ZnS) 41.3% + δ(SZnS) 21.2% + δ(SCS) 10.1%, including
								$\tau(H_3CH_2CNCH_2CH_3)$
317	0.00	1.36	305	296 (0.03)	294	302 (0.01)		$\delta$ (ZnSC) 17.8% + v(ZnS) 27.9% + $\delta$ (SCN 16.6% + $\delta$ (SCS) 16.5%
317	0.06	0.66	305				289	δ(SCN) 32.2% + v(ZnS) 31.2% + δ(ZnSC) 23.9%
316	0.00	0.72	304	281 (0.03)	281			δ(SCN) 33.1% + v(ZnS) 30.5% + δ(ZnSC) 22.8%
244	70.41	0.05	235		248		246	τ(CH <sub>3</sub> )
232	2.38	0.24	223	241 (0.06)	240	240 (0.01)		τ(CH <sub>3</sub> )
231	1.75	0.09	222				235	τ(CH <sub>3</sub> )
222	0.00	0.02	213	225 (0.04)	223	217 (0.01)		τ(CH <sub>3</sub> )
221	1.11	0.04	212				211	τ(CH <sub>3</sub> )
161	12.16	0.94	155			187 (0.01)		$\tau(C_2H_5)$
159	9.34	1.30	153			162 (0.02)		$\tau(C_2H_5)$
149	2.08	0.19	143					$\tau(C_2H_5)$
148	1.07	0.10	142			131 (0.02)		$\tau(C_2H_5)$
138	0.00	7.46	133	119 (0.10)		116 (0.03)		$\tau(C_2H_5)$
100	6.71	0.38	96					$\tau(C_2H_5)$
91	0.03	0.00	87					$\tau(C_2H_5)$
89	4.42	0.12	86					$\tau(C_2H_5)$
82	0.00	5.18	79					$\tau(C_2H_5)$
81	0.62	0.30	78					$\tau(C_2H_5)$
78	0.00	4.46	75					δ(ring)wagg.
74	0.02	0.22	71					δ(ring)wagg.
67	0.39	0.45	64					$\tau(C_2H_5)$
27	0.00	4.04	26					$\tau(C_2H_5)$
22	1.76	1.04	21					$\tau(C_2H_5)$
20	1.35	0.75	19					$\rho(C_2H_5)_2$

Symbols:  $Wn_{calc} = Calculated wavenumber; Wn_{cor} = Calculated wavenumber scaled by 0.9613; I_{IR} = Infrared intensity in (KM/mol); I_R = Raman scattering activities (Å<sup>4</sup>/ AMU); IR Wn_{exp} (Abs) = Experimental infrared wavenumbers (Absorbance); IR DBA = Infrared deconvolution band analysis; Raman Wn_{exp} = Experimental Raman wavenumbers; Raman DBA = Raman deconvolution band analysis; v = stretching; <math>\delta$  = bending; r = out of plane bending or rocking;  $\tau$  = torsion.

19 °C [14]. Thus, the synthesis must be performed in optimum  $pH_3O^+$  range between 5.0 and 7.0. This prevents the decomposition of DDTC and the metal hydroxide formation. The definition of these optimal conditions of synthesis was evaluated in different  $pH_3O^+$  conditions. These data were obtained from the graphical method [15], presented in Fig. 1S of the supplementary material. The graph shows the region of optimum  $pH_3O^+$  to performer the synthesis of the complex around 6.5. This allowed us to obtain the complex with a adequate yield and a purity satisfactory.

The solid obtained after purification was characterized through typical bands of the ligand in the infrared region, as vC–H stretching between 3000 and 2900 cm<sup>-1</sup> and vC=N stretching between 1500 and 1400 cm<sup>-1</sup>, presented in Fig. 2 for the IR and Raman spectra.

# Optimization of the geometrical parameters

Ab initio optimization of the geometrical parameters, and the structural analysis of the  $[Zn(DDTC)_2]$  complex, was carried out employing the methods described above which are similar to the works found in the literature [16–19].

The B3LYP theoretical values for the Zn—S, C=N and C–S bond lengths were of 2.40, 1.34 and 1.74 Å, without symmetry restrictions. The bond angles S(10)–Zn–S(2) and S(11)–Zn–S(3) were of 127.90° and 127.89°, respectively. The bond angles S(10)–Zn–(S11)and S(3)–Zn(S2) were of 77.39°, and the angles S(10)–Zn–S(3) and S(11)—Zn—S(2) were of 127.18° and 127.15° showing a pseudo-tetrahedral structure for the ZnS<sub>4</sub> framework. Another important structural parameter is the distance S···S that is responsible for the bite angle of the ligand to the metal. The theoretical calculations show an average value of 3.00 Å. This average value is higher than the values found in dithiolates, which were reported between 2.781 and 2.811 Å [20,21], as well as for S<sub>8</sub><sup>+</sup> cations which have S···S distances of 2.83 Å [22]. Calculated selected bond lengths and bond angles for the C<sub>1</sub> symmetry are given in Table 1, and were compared with experimental data obtained by Bonamico et al. [23], whom had informed that the four shortest bond by any zinc atom are directed to the corners of a very distorted tetrahedron, and that the crystal structure of [Zn(DDTC)<sub>2</sub>] has Z = 4 in the monoclinic cell with space group  $P2_1/c$ . The complete structure of the [Zn(DDTC)<sub>2</sub>] complex is represented in Fig. 1.

#### Vibrational assignments

Vibrational assignments were carried out with support of Density Functional Theory (DFT) calculations, using the B3LYP method with a 6-311-G (d, p) basis set having the structural geometry obtained by the same method as the starting point. The calculated values for C<sub>1</sub> symmetry of the  $[Zn(DDTC)_2]$  complex did not present imaginary frequencies and they are described in Table 2. The simulated IR and Raman spectra are shown in Fig. 2S (supplementary material). For the discussion of the vibrational assignment, we



Fig. 1. DFT:B3LYP/6-311G (d, p) calculated structure for the [Zn(DDTC)<sub>2</sub>] complex (1 = Zn; 2, 3, 10 e 11 = S; 5, 13 = N; 4, 6, 7, 8, 9, 12, 14, 15, 16, 17 = C; other atoms = H).



Fig. 2. FT-IR (a) and FT-Raman (b) spectra of [Zn(DDTC)<sub>2</sub>] complex.

took the DFT values corrected by a scale factor of 0.9613 as a base for comparison [24] in all fundamental vibrational modes, 3n - 6 = 105. This adjusting in the data were associated with the second derivative spectrum and with DBA of the infrared bands of the [Zn(DDTC)<sub>2</sub>] complex. For an accurate description of the normal modes in the metal-ligand spectral range, we use the percentage of deviation of the geometrical parameters (PDGPs) from the equilibrium position as described in others works [25-28]. The PDGP can also be normalized to obtain the percentage of participation of each internal vibrational coordinate that describes the framework vibrations, at all 26 coordinates (10 stretching and 16 bending). With  $C_1$  symmetry for the  $[Zn(DDTC)_2]$  complex, the vibrational irreducible representation is  $\Gamma_{\text{vibrational}}$  = 105 a (type symmetry), where all vibrational modes are active in the infrared spectrum and Raman spectra. The results were compatible with the experimental data. The intensity variations between calculated and experimental FT-IR and FT-Raman spectra could be explained by the nature of the experimental measurement in the solid state (anharmonic spectrum) compared to the calculations (harmonic spectrum), which was carried out in the vacuum, neglecting molecular interactions.

# CH stretching

In the  $[Zn(DDTC)_2]$  complex, there are four  $-CH_3$  groups and four  $-CH_2$  groups totalizing 20 stretching v(CH) vibrational

modes. In the FT-IR spectrum of Fig. 3a, we visualize in the region between 3000 and 2800 cm<sup>-1</sup> three large bands with three peaks at 2984, 2979 and 2970 cm<sup>-1</sup>; 2938 and at 2931 cm<sup>-1</sup> with shoulders at 2921 and at 2900 cm<sup>-1</sup>, and at 2872 cm<sup>-1</sup>, respectively. In the FT-Raman spectrum shown in Fig. 3b there were three bands defined at 2973, 2936 with a shoulder at 2919, and at 2871 cm<sup>-1</sup>. For both spectra, the second derivative were obtained and it was followed by DBA to achieve the maximum intensity of the observable bands. Fig. 3a and b shows nine fundamentals bands in both spectra obtained by this procedure. The calculated and experimental wave numbers of the —CH stretching are given in Table 2.

#### C=N stretching

The C=N bands stretching bands were observed in the infrared and FT-Raman spectra at 1507(IR, R), 1503(IR) and at 1500(R) cm<sup>-1</sup>, which were corroborated by the second derivative spectra and DBA at 1515(R), 1504(R), and at 1501(IR) cm<sup>-1</sup>, (Fig. 4) and these bands were assigned with aid of the calculated DFT vibrational spectrum. The comparison between calculated bands without correction by scale factor and experimental values for the v(C=N) stretching was excellent. Calculations has also showing that these modes are coupled modes among different internal coordinates in which the scissoring mode  $\delta$ (HCH)(CH<sub>2</sub>) participates in the normal mode description.



Fig. 3. Band deconvolution analysis of the FT-IR (a) and FT-Raman (b) spectra in the region of the v(C-H) stretching.



Fig. 4. Infrared (a) and Raman (b) BDA in the region of 1550–1480 cm<sup>-1</sup> for the [Zn(DDTC)<sub>2</sub>] complex.

# HCH bending

In general terms, the HCH bending vibrations are considered as characteristic wavenumbers. In the infrared and FT-Raman spectra, Fig. 2, we can observe 31 bands in the region between 1492 and 1069 cm<sup>-1</sup>, and one additional band at 723(R) cm<sup>-1</sup>. With aid of DBA, all of them assigned to HCH bending and are listed in Table 2. The rocking vibrations were found in the region between 1075 and 960 cm<sup>-1</sup> (six bands) and between 850 and 750 cm<sup>-1</sup> (five bands), also with the DBA support, and the assignments are also presented in Table 2. A plot between bending and rocking experimental vibrations versus the calculated modes give the following results: correlation coefficients *R* = 0.99432, with SD = 25.34. The graphic representation between the calculated and experimental bending vibrations obtaining with aid of the Origin six program [29] is depicted in Fig. 5.

#### Skeletal framework vibrations

The identification of the metal-ligand vibrations was not straightforward as we have pointed out in other publications [22–25]. This is due to the higher mixture of the different internal coordinates that take part in the description of the normal modes. Thus, we studied the distorted geometry of each normal mode,



**Fig. 5.** Plot between calculated and experimental FT-IR and FT-Raman bending vibrations of the  $-CH_2CH_3$  groups of the  $[Zn(DDTC)_2]$  complex.



**Fig. 6.** FT-infrared (a) and FT-Raman (b) spectra in the region of 600–180 cm<sup>-1</sup>.

observing the extension to which the equilibrium configuration parameters are dislocated. This procedure helps us to assign the low-energy bands, whose spectra are depicted in Fig. 6.

The results presented below obey the following nomenclature: in bold characters we wrote (IR exp.) for experimental observation in the infrared spectrum, and (R exp.) for the FT-Raman spectrum. The Deconvolution Band Analysis was written concisely as (DBA/ IR; R). The abbreviation corr., means that the calculated wave number by the DFT:B3LYP/6-311G (d, p) procedure was scaled by 0.9613. The percentage (%) indicates the percentage variation of the bond lengths and bond angle. Stretching, bending and torsion internal coordinates are represented by the Greek letters v,  $\delta$ , and  $\tau$ , respectively.

In this approach, we used 10 stretching and 16 bending internal coordinates, which are inside of the skeletal framework of the complex in the description of the normal modes.

- 483 corr., 477 (DBA/IR), 470 (DBA/R): v(CS) 38.6% +  $\delta(SCN)$  30.2%.
- 482 corr., 466 (exp.IR/DBA/IR): ν(CS) 37.5% + δ(SCN) 26.0% + δ(ZnSC) 15%.
- 422 corr. 459 (DBA/IR): δ(ZnSC)29.2% + ν(CS) 19.5% + ν(ZnS) 13%.
- 419 corr. 427 (IR exp.), 434 (R exp.): δ(ZnSC)28.2% + δ(SZnS) 23.5% + ν(CS) 17.0%
- 382 corr. 400 (IR exp.), 396 (DBA/IR), 399 (R exp.): v(ZnS)31.5% +  $\delta(ZnSC)$  21.4% +  $\delta(SCN)$  18.5% +  $\delta(SCS)$  18.6%, including  $\tau(H_3CH_2CNCH_2CH_3)$ .
- 380 corr. 379 (IR exp.), 379 (DBA/IR)
- v(CS) 25.1% +  $\delta(ZnCS)$ 21.3% + v(ZnS) 16.5%.
- 380 corr. 373 (exp.R; DBA/R).
- $\delta(SCN)$  36.8% +  $\nu(CS)$  35.9% +  $\delta(ZnCS)$  13.2%.
- 371 corr. 312 (R exp.), 306 (DBA/R): δ(ZnSC) 30.7% + ν(ZnS) 23.7% + δ(SCS) 19.9% + δ(SCN) 19.7%.
- 310 corr. 335 (exp. IR): ν(ZnS) 41.3% + δ(SZnS) 21.2% + δ(SCS) 10.1%, including τ(H<sub>3</sub>CH<sub>2</sub>CNCH<sub>2</sub>CH<sub>3</sub>).
- 305 corr. 296 (exp. IR), 294 (DBA/IR), 302 (exp. R): δ(ZnSC) 17.8% + ν(ZnS) 27.9% + δ(SCN 16.6% + δ(SCS) 16.5%.
- 305 corr. 289 (R exp.): δ(SCN) 32.2% + ν(ZnS) 31.2% + δ(ZnSC) 23.9%.
- 304 corr. 281 (exp.IR; DBA/IR): δ(SCN) 33.1% + ν(ZnS) 30.5% + δ(ZnSC) 22.8%.

In the [Zn(DDTC)<sub>2</sub>] complex we expected four main contributions of the Zn–S stretching internal coordinates in the normal modes, and the above assignment shows that the principal contributions of the v(ZnS) appears as v<sub>as</sub>(ZnS) at 353(R) cm<sup>-1</sup> and at 323 (IR)/329(R) cm<sup>-1</sup>, and as v<sub>s</sub>(ZnS) at 287(DBA/IR) cm<sup>-1</sup> and at 227(DBA/R) cm<sup>-1</sup>. Fig. 3S shows the displacement vectors of the framework of the [Zn(DDTC)<sub>2</sub>] complex of these four vibrational modes.

#### Torsional vibrations

The characterization of these torsional modes using the DFT results of the normal modes was rather complicated. To obtain an approximate assignment of these normal modes, we used the 3D computerized visualization. Eighteen torsional internal coordinates were defined in [Zn(DDTC)2]. From the infrared and Raman spectra we were able to associate 18 bands of weak intensity. All the torsional modes presents coupling with other stretching and bending internal coordinates whose description are given in Table 2.

#### Natural Bond Orbitals Analysis (NBO)

NBO analysis [30], at the B3LPY/6-311G (d, p) level was carried out to rationalize the factors contributing to the total conformational energy. Using B3LYP/6-311G (d, p) procedure, The Zn—S bonds were formed by interaction between a  $sp^{2.99}d^{0.01}$  (24.97% s, 74.67% p and 0.36% d) orbital centered on the zinc ion and a  $sp^{4.68}d^{0.01}$  (17.57% s, 82.33% p and 0.10% d) orbital on the sulfur atom. The occupancy of the electrons in the four Zn—S bonds was 1.94 electrons for each other. The polarization coefficient for the formation of the bonding was 11.78% on the zinc ion and 88.22% on the sulfur atom of the Zn—S bond, showing a higher polarization through the sulfur atom indicating a strong ionic character for the bond.

The four S–C bonds were formed by interaction between a  $sp^{4.10}d^{0.03}$  (19.46% s, 79.89% p and 0.65% d) orbital and a  $sp^{2.06}$  on the sulfur atom and a  $sp^{2.06}d^0$  (32.61% s, 67.25% p, 0.65% d) orbital on the carbon atom. The occupancy of electrons in the four S–C bonds was 1.98 electrons for each other. The polarization coefficient for the formation of the bonding was 43.64% on the sulfur atom and 56.36% on the carbon atom, showing a little polarization through the carbon atom.

Results obtained by the method DFT/B3LYP show one bridge interaction with 1.43418 electron occupancy between the 3pz orbitals from the sulfur atoms of the diethyldithiocarbamate anion. This bridge interaction is illustrated in Fig. 4S. The description of this interaction follows as: NBO: S(2)–S(3) equal to S(10)–S(11)

bridge giving an hybrid orbital s<sup>0</sup>p<sup>1</sup>d<sup>0</sup> with 99.96% orbital p participation without polarization between the two sulfur atoms.

For the double bond C(4)=N(5) and C(12)=N(13) the molecular orbital can be described as  $\sigma_{CN} = 0.6064(sp^{1.95})_C + 0.7951(sp^{163})_N$  with occupancy of 1.98760 eletrons and  $\pi_{CN} = 0.5006(sp^1d^0)_C + 0.8476(sp^{91}d^0)_N$ , with occupancy of 1.96278 electrons. The polarization coefficients for the C and N atoms were of 32.46% for carbon and 67.54% for nitrogen. This shows a strong polarization directed toward the N atom.

The four C—S bonds can be described as follows: interaction between an orbital sp<sup>4.10</sup><sub>d</sub><sup>0.03</sup> (19.46% s, 79.89% p, 0.65% d) on the sulfur atom, and with the orbital sp<sup>2.02</sup>d<sup>0.0</sup> (32.61% s, 67.25 p, 0.13% d) centered on the carbon atom, with occupancy of 1.98461 electrons. The polarization coefficients were: 43.64% for the sulfur atom, and 56.36% for the carbon atom, showing polarization in his direction. The gap of energy between the HOMO and LUMO orbitals was of -0.9327 a.u.

#### Conclusions

Synthesis, elementary CHN analysis, FT-Infrared and FT-Raman spectra of the  $[Zn(DDTC)_2]$  complex were presented. Theoretical calculations concerning structural analysis show a tetrahedral framework structure for the  $ZnS_4$  chromosphere. Vibrational assignments of bands in the infrared spectrum of the  $[Zn(DDTC)_2]$  complex have been done based on the DFT: B3LYP/6-311G (d, p) quantum mechanical calculation. The most probable assignment for the skeletal vibrations was based on the interpretation of the distorted geometry of the normal modes, having as focus the study of the percentage of deviation of the geometrical parameters. The results suggest the structure depicted in Fig. 1 as the most probable, and the full assignment for the complex is presented in Table 2. The NBO results also indicate an interaction between S—S atoms in each diethyldithiocarbamate ligands.

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# **Appendix A. Supplementary material**

Species distribution diagram for the [Zn(DDTC)<sub>2</sub>] synthesis, calculated infrared and Raman spectra. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.11.097.

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