

Vibrational and DFT Studies of Creatinine and Its Metal Complexes

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Article Info

Article history:

Received
March 4, 2010

Received in revised form
April 27, 2010

Accepted
March 14, 2010

Available online
June 12, 2010

Key Words

Creatinine,
Metal-halogen
complexes,
FT-IR,
DFT,
SQM

Abstract

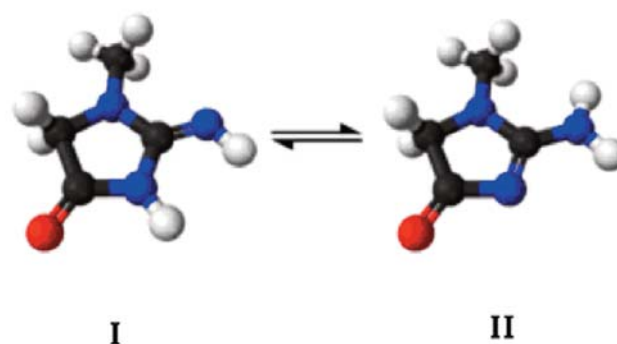
Creatinine (2-amino-1-methyl-5H-imidazol-4-one) is an amino acid that occurs in vertebrate tissues and in urine. The mid and far infrared spectra of creatinine were recorded in the solid phase. The optimized structure of creatinine was obtained using DFT/B3LYP method with 6-311+G(d,p) and LANL2DZ basis sets. The harmonic frequencies of creatinine were calculated using DFT/B3LYP/6-311+G(d,p) method. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The creatinine-metal {cadmium [Cd(II)], zinc [Zn(II)] and mercury [Hg(II)]} halogen [chloride (Cl⁻) and bromide (Br⁻)] complexes were synthesized. DFT calculations, DFT-B3LYP/LANL2DZ were performed for the determination of geometrical structure and vibrational assignment for metal-complexes.

INTRODUCTION

Creatinine (C₄H₇N₃O) is produced from creatine, a molecule of major importance for energy production in muscles. Creatinine (creat) is transported through the bloodstream to the kidneys. The kidneys filter out most of the creatinine and dispose of it in the urine [1,2]. An abnormal level of creatinine in biological fluids is an indicator of various disease states [3].

Creatinine has two tautomeric forms, the imine (I) and the amine (II) (Figure 1). *Ab initio* calculations

have shown that in the gas phase, the imine form is preferred but the solid state, the amine form is observed, and is predicted theoretically [4-7]. Creatinine is an important biological molecule thus theoretical studies on its various physical and chemical properties in the solution and solid state have been reported [8-10].



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Figure 1. Imine (I) and amine (II) tautomeric forms of creatinine.

The fundamental vibrations for the creatinine molecule have assigned using the generalized valence force field approximation [11]. Literature survey reveals that, to the best of our knowledge, the quantum chemical calculations for creatine and its complexes have not been reported so far. Hence, this study has been undertaken to record and study the mid and far FT-IR spectra of the title compound and to assign the normal modes of vibrations.

More recently, the study of complexes of this bioligand are attracting considerable interest. The X-ray crystal structure and the coordination chemistry with transition metal ions of creatinine have been widely studied [12-29]. Although the infrared spectra of $\text{Pt}(\text{creat})_2(\text{NO}_2)_2$, $\text{Pt}(\text{creat})_2(\text{ClO}_4)_2$ have been completely analyzed [11], no complete spectral characterizations have been done on the other complexes.

Muralidharan et al [24] investigated $\text{M}(\text{creat})_2\text{X}_2$ ($\text{M}=\text{Zn}$, Cd or Hg , $\text{X}=\text{Cl}$, Br or I) complexes using IR, NMR and TG. They only reported M-N and M-Cl frequencies for these complexes.

The aims of this study are to give a complete description of the molecular geometry and molecular vibrations of the free creatinine experimentally (FT-IR) and theoretically. The complete experimental FT-IR spectra, vibrational assignments and DFT calculations of $\text{M}(\text{creat})_2\text{Cl}_2$ and $\text{M}(\text{creat})_2\text{Br}_2$ complexes ($\text{M}=\text{Cd}$, Zn and Hg) were also reported for the first time.

MATERIAL AND METHODS

Experimental

Metal chloride or bromide was dissolved in absolute methanol. The methanolic solution of creatinine (metal to ligand ratio of 1:2) was added to the

solution and mixed with stirring. The precipitated complex was filtered, washed with ether and dried. Infrared spectra of the samples in KBr pellet in the range of $4000\text{-}400\text{ cm}^{-1}$ were recorded on a Perkin-Elmer Spectrum One FT-IR Spectrometer. The far infrared spectra in the frequency range $400\text{-}50\text{ cm}^{-1}$ were recorded on a Bruker IFS 66v/S FT-IR spectrometer.

Theoretical

The basic sets 6-311++G(d,p) and LANL2DZ were employed in the B3LYP [30] calculations and the geometry optimizations of amine and imine forms of creatinine were performed without symmetry constrain. The harmonic wave numbers of the amine form of creatinine was calculated at B3LYP/6-31++G (d,p) theory level. The DFT hybrid B3LYP functional method tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. In the fitting processes performed to correct overestimations at the calculated harmonic wave numbers, we applied two different scaling procedures. In the first procedure, scale factor 0.98 was used for lower than 1800 cm^{-1} . In the second procedure, scale factor 0.96 was used for higher than 1800 cm^{-1} . The total energy distributions (TED %) of the vibrational modes were calculated with the scaled quantum mechanics (SQM) force field method [32]. SQM calculations were carried out using SQM v.1.0.

Geometrical structures of creatinine complexes with $\text{M}(\text{creat})_2\text{Cl}_2$ ($\text{M}=\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Hg}(\text{II})$) were carried out using the Becke's three parameter exchange functional with the Lee-Yang-Parr correlation functional (B3LYP) using the LANL2DZ split-valence basis set. The basis set LANL2DZ [31] was chosen to include the pseudopotential of the core electrons in atoms of heavy elements like mercury and it is compatible with all other organic elements (C, N, H, O). The X-ray crystallographic

structure of $\text{Cu}(\text{creat})_2\text{Cl}_2$ [12] was used as the initial guess for optimization. Geometrical structure of this complex was also calculated for comparison purpose. All computations were performed with the GAUSSIAN 03 program [33].

RESULTS AND DISCUSSION

Structure of Creatinine

As mentioned before creatinine have two tautomeric forms, the imine (I) and the amine (II) (Figure 1). We calculated that the amine form 6.907 kJ/mol higher than the amine form in the gas phase. However we investigated solid form of creatinine and its complexes, experimentally. Therefore, we focused on the amine form of creatinine in this paper.

The optimized geometric parameters are listed in Table 1. The optimized bond lengths and bond angles of creatinine are in good agreement with X-ray data [14] with the exception of some bonds. In the gas phase, N1-C2 is shorter and C2-N3 is longer than as expected. From the theoretical values, we can find that most of the optimized bond length is slightly different than the experimental values, due to that the theoretical calculations belong to isolated molecule in gaseous phase and experimental results belongs to molecules in the solid state. Two creatinine molecules bound by hydrogen bridges

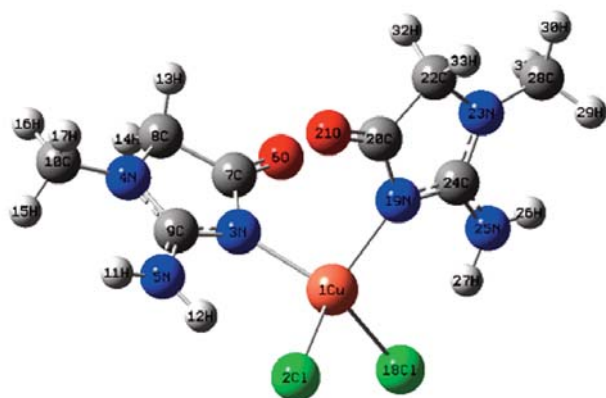


Figure 2. Optimized structure and atom numbering scheme of $\text{M}(\text{creat})_2\text{Cl}_2$.

($\text{N3-O}'=2.85\text{\AA}$ and $\text{N1-N3}'=2.92\text{\AA}$) in the crystal structure [14]. This would be understandable, since the environment of the molecules is different (because of the absence of the hydrogen bonds in the calculated structure). The creatinine is planar in the experimental structure. We also found nearly planar in the gas phase.

Structure of Metal Complexes

Atomic numbering for geometrical data of all studied complexes is illustrated in Figure 2.

The B3LYP/LANL2DZ-optimized geometrical data for the creatinine complexes with Cd(II), Zn(II), Hg(II) and Cu(II) metal (in forms of $[\text{M}(\text{creat})_2\text{Cl}_2]$) are listed in Table 1. The calculated total energies and dipole moments of complexes are also given bottom of the Table 1. The X-ray crystallographic structures of these complexes were compared with their corresponding B3LYP/LANL2DZ optimized structures. The optimized geometry parameters for the creatinine complexes with Cu (II), Zn (II) and Cd (II) are in good agreement with the X-ray crystallographic data [12,28,29].

The creatinine molecules are held together by intermolecular hydrogen bond involving the amino H atoms and the carbonyl O atoms in the crystal structure of complexes. It should be remembered that the comparison is between theoretical calculations in gaseous phase (not involved H-bonds) and experimental results in the solid state.

Comparing the free creatinine with corresponding metal complexes, the bond lengths in the imidazole ring are changed. The C7-C8 and N4-C8 bond lengths increase from 1.40 to 1.46 Å. In contrast, the lengths of the N3-C9 and N4-C9 bonds decrease. A comparison of the bond lengths of the free ligand with that of the complex shows that the N3-C7 and C=O bond lengths are not altered much upon coordination. Based on the crystal and optimized

Table 1. Optimized geometrical parameters of creatinine and metal obtained by DFT-B3LYP/LANL2DZ.

Parameters	Cu(creat) ₂ Cl ₂		Zn(creat) ₂ Cl ₂		Cd((creat) ₂ Cl ₂		Hg(creat) ₂ Cl ₂	Creatinine		
	Exp. ^a	Calc.	Exp. ^b	Calc.	Exp. ^c	Calc.	Calc.	Exp. ^d	Calc.	
Bond length(Å)										
M-N3	1.982	2.038	2.022	2.072	2.226	2.291	2.393			
M-Cl1	2.238	2.346	2.249	2.377	2.433	2.538	2.611			
M-Cl18							2.611			
N3-C9	1.368	1.370	1.37	1.366	1.365	1.366	1.365	1.40	1.344	
N3-C7	1.367	1.401	1.36	1.402	1.367	1.399	1.398	1.37	1.387	
N4-C9	1.329	1.369	1.32	1.369	1.325	1.370	1.371	1.34	1.371	
N4-C10	1.450	1.461	1.46	1.461	1.451	1.461	1.461	1.46	1.459	
N4-C8	1.453	1.468	1.45	1.471	1.456	1.471	1.471	1.40	1.423	
N5-C9	1.310	1.337	1.32	1.341	1.322	1.342	1.342	1.30	1.356	
O6-C7	1.217	1.246	1.22	1.244	1.221	1.246	1.247	1.22	1.209	
C7-C8	1.507	1.544	1.50	1.546	1.513	1.546	1.547	1.47	1.532	
Bond Angle (°)										
N3-M-Cl	100.25	100.76	110.5	103.82	101.76	98.33	96.40			
N3-M-N19	92.31	95.05	106.5	104.21	112.28	98.99	95.14			
N3-M-Cl	137.32	135.89	109.0	115.79	115.10	122.94	126.24			
Cl-Cu-Cl	97.55	95.86	110.5	113.43	111.95	115.52	117.26			
C9-N3-C7	107.1	107.97	107.7	108.23	107.0	108.09	108.22	107	106.70	
C9-N3-M	131.8	131.12	130.3	129.64	133.6	129.80	129.18			
C7-N3-M	117.5	120.28	121.1	121.86	119.2	121.02	120.90			
C9-N4-C10	126.9	125.87	128.3	126.14	127.1	126.08	126.14	123	125.87	
C9-N4-C8	109.3	108.99	108.5	108.87	108.8	108.78	108.70	107	107.34	
C10-N4-C8	123.8	125.02	123.1	124.64	123.7	124.70	124.65	129	125.03	
O6-C7-N3	125.0	127.27	125.6	126.66	124.9	126.45	126.66	127	127.48	
O6-C7-C8	125.7	124.59	126.1	125.43	126.1	125.42	125.30	124	124.15	
N3-C7-C8	109.3	108.13	108.2	107.89	109.0	108.10	108.03		108.54	
N4-C8-C7	101.3	101.86	102.5	101.85	101.5	101.75	101.78	107	101.53	
N5-C9-N4	124.8	123.02	123.9	123.61	124.5	123.48	123.38		121.25	
N5-C9-N3	122.2	123.96	123.1	123.34	121.8	123.36	123.47	120		
N4-C9-N3	112.9	113.01	113.0	113.04	113.7	113.14	113.14	112	115.83	
Total Energy (H)		-1018.34		-887.84		-870.29	-864.92			-396.06
Dipole Moment (D)		12.35		9.66		11.28	11.76			9.00

^{a, b, c} and ^d taken from Refs. [12,28,29,14], respectively.

geometrical data, the bond lengths between metal and N3 atom are in the sequences: Hg-N3>Cd-N3>Zn-N3>Cu-N3.

In the crystal M(creat)₂Cl₂, the M=Cd or Zn atom is four-fold coordinated (distorted) tetrahedral) by the endocyclic N atoms from two imidazole rings and by

two Cl atoms [28,29]. There is a difference concerning central angles the two Cl-M-N3 angles in complexes. These angles were calculated as 100.76° and 135.89° for Cu complex while the corresponding angles for Zn complex are 103.82° and 115.79°.

We probed creat-HgCl₂ interactions with all three donors, the carbonyl oxygen, the ring nitrogen N, and the amino nitrogen atom. Three possible structures were investigated. We also calculated their infrared spectra. The M-L, NH₂, C=O stretching vibrations have been used as a good marker of the metal binding. However, the calculated metal-induced shifts are in disagreement with the observed ones. Using calculated results and the observed data in the literature, we proposed Hg(creat)Cl₂ has distorted tetrahedral structure. The creatinine ligands coordinate the Hg atom via the N3 atoms in Hg(creat)₂Cl₂ and with the Cl atoms define a tetrahedral environment in the predicted structure. In this structure Hg-Cl distance is 2.611 Å, Hg-N distance is 2.393 Å, the Cl-Hg-Cl angle is 117.26° and N-Hg-N angle is 95.154°. The energy of complex formation for Cu (II) is much lower than the others (Table 1).

Infrared spectra of creatinine

To our best knowledge, no quantum mechanical calculations have been reported for creatinine. The detailed vibrational assignments of fundamental modes of creatinine along with the calculated IR intensities at B3LYP levels using the triple split valence basis set along with diffuse and polarization functions, 6-311++G (d, p) and normal mode descriptions (characterized by TED) based on SQM

force field calculations are reported in Table 2 together with the the relevant experimental data of Trendafilova et al. [11]. The FT-IR spectrum of creatinine is illustrated in Figure 3.

Our calculation results given in Table 2 have demonstrated that some of the fundamental bands of creatinine are different assigned by Trendafilova et. al [11] and Costa et.al [12]. Creatinine has 15 atoms and 39 normal modes. It has methyl, methylene, amino and C=O groups. The methyl group as a united atom in the creatinine molecule considered by Trendafilova et. al [11] and 30 vibrational modes discussed. Costa et al [12] reported some selected IR bands of creatinine.

The fundamental modes involving the amino group are stretching and bending of NH bonds. The creatinine molecule possesses one NH₂ group and hence one expects one symmetric and one asymmetric N-H stretching vibrations. In all the primary aromatic amines the N-H stretching frequency occurs in the region 3300-3500 cm⁻¹ [34]. The asymmetric ν_{as} stretching mode appears to be calculated at a higher wavenumber 3565 cm⁻¹ than the symmetric ν_s one 3455 cm⁻¹, and was related to the FT-IR bands observed experimentally at 3254 cm⁻¹ and 3030 cm⁻¹, respectively. These bands indicate the presence of the amine form in the

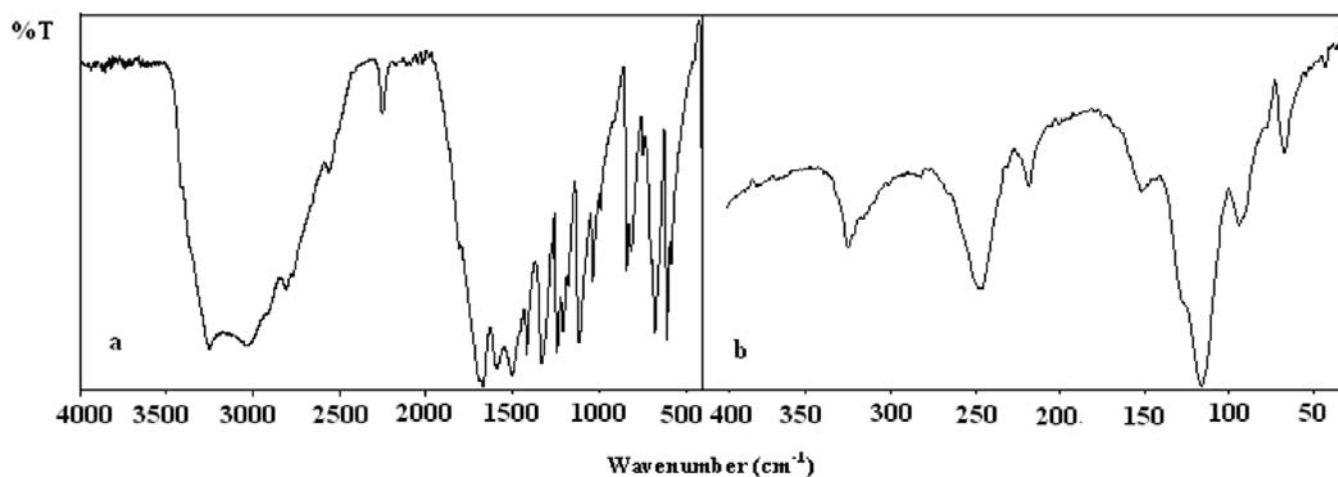


Figure 3. The mid- (a) and far- (b) infrared spectra of solid creatinine.

Table 2. Detailed assignment of fundamental vibrations of creatinine based on SQM force field.

Modes	Observed ^a	Observed	Calculated	Scaled ^c	TED %	
		KBr	Harmonic			
39	3254vs	3252vs	3714	51.54	3565	100 $\nu_a(\text{NH}_2)$
38	3040s	3030vs	3599	67.27	3455	100 $\nu_s(\text{NH}_2)$
37	2980sh	2980vw	3115	12.97	2990	100 $\nu_a(\text{CH}_3)$
36			3089	10.75	2965	100 $\nu_a(\text{CH}_2)$
35		2922w	3082	26.38	2959	100 $\nu(\text{CH}_3)$
34			3030	19.01	2909	100 $\nu_s(\text{CH}_2)$
33		2809w	2995	62.51	2875	100 $\nu_s(\text{CH}_3)$
32		1692sh	1802	55.89	1730	65 $\nu(\text{C=O})$ 11 $\nu(\text{CN})_{\text{ring}}$
31	1669vs	1670vs	1698	364.56	1664	51 $\delta(\text{NH}_2)$ 27 $\delta(\text{HNC})$ 11 $\nu(\text{C-NH}_2)$
30		1590s	1614	260.85	1581	37 $\nu(\text{CN})_{\text{ring}}$ + 20 $\nu(\text{CNH}_2)$ 13 $\nu(\text{C=O})$ 10 $\delta(\text{HNC})$
29	1503s	1503s	1549	186.01	1518	50 $\nu(\text{CN})_{\text{ring}}$ 15 $\nu(\text{C-NH}_2)$ 10 $\delta(\text{C-NH}_2)$
28	1440sh	1457sh	1504	14.66	1474	64 $\nu(\text{CH}_2)$ 12 δ_{ring} 10 $\tau(\text{H}_2\text{C-NC-CH}_3)$
27			1492	3.09	1462	55 $\delta(\text{CH}_3)$ 32 $\tau(\text{CN-CH}_3)$
26	1420s	1418s	1472	26.74	1443	53 $\delta(\text{CH}_3)$ 30 $\tau(\text{CN-CH}_3)$
25	1334s	1331s	1420	66.38	1391	50 $\delta(\text{CH}_3)$ 46 $\delta(\text{N-CH}_3)$
24	1268w	1269w	1316	2.05	1290	35 $\delta(\text{CH}_2)$ 32 $\tau(\text{CN-CH}_2)$ 17 $\nu(\text{N-CH}_3)$
23	1244s	1243s	1280	58.14	1254	38 ν_{ring} 30 $\nu(\text{N-CH}_3)$ 18 $\delta(\text{N-CH}_3)$
22	1205m	1208m	1224	57.64	1200	45 ν_{ring} 28 $\delta(\text{CH}_2)$ 13 $\delta(\text{C=O})$
21	1176w	1177w	1206	6.18	1182	33 ν_{ring} 17 $\delta(\text{C-NH}_2)$ 15 $\delta(\text{N-CH}_3)$ 14 $\nu(\text{N-CH}_3)$
20	1119s	1118s	1167	48.07	1143	46 $\delta(\text{CH}_2)$ 30 $\tau(\text{NC-CH}_2)$
19	1037w	1036m	1119	17.89	1096	72 $\delta(\text{N-CH}_3)$ 15 $\tau(\text{CN-CH}_3)$
18			1108	44.35	1086	60 $\delta(\text{C-NH}_2)$ 15 ν_{ring} 10 $\delta(\text{C=O})$
17			1036	10.37	1015	44 $\delta(\text{N-CH}_3)$ 35 $\nu(\text{CN})_{\text{ring}}$
16		992w	999	1.87	979	26 $\tau(\text{C=O})$ 21 $\delta(\text{C-CH}_2)$ +16 τ_{ring} 13 $\tau(\text{ring-CH}_2)$
15	830m	841s	866	19.15	849	63 ν_{ring} 16 δ_{ring} 10 $\delta(\text{C-NH}_2)$
14	815m	813m	817	25.16	801	40 $\nu(\text{CN})_{\text{ring}}$ 17 $\nu(\text{N-CH}_3)$ 14 δ_{ring} 10 $\nu(\text{C-NH}_2)$
13		747mw	748	22.10	733	50 $\omega(\text{NH}_2)$ 30 τ_{ring}
12	679w	677vs	674	1.02	661	43 δ_{ring} 15 $\nu(\text{C-NH}_2)$ 11 ν_{ring} 10 $\nu(\text{C=O})$
11	609s	608vs	618	28.14	606	32 δ_{ring} 18 $\nu(\text{N-CH}_3)$ 10 ν_{ring} 10 $\delta(\text{C=O})$
10		583mw	589	4.10	577	30 $\delta(\text{C=O})$ 28 $\tau(\text{ring-CH}_2)$ 14 $\tau(\text{C=O})$ 12 $\delta(\text{NC-NH}_2)$
9		455vw 422vw	542	5.32	531	20 $\delta(\text{NC-NH}_2)$ 17 $\tau(\text{ring-NH}_2)$ 13 $\tau(\text{ring-CH}_2)$ 10 $\tau(\text{C=O})$
8	428vw	406m	421	57.62	412	71 $\tau(\text{ring-NH}_2)$
7	324s	325m	357	122.84	350	87 $\tau(\text{ring-NH}_2)$
6	248s	246s	321	28.60	314	48 $\delta(\text{NC-NH}_2)$ 20 $\delta(\text{C=O})$ 13 ν_{ring}
5	218w	218m	297	4.72	291	58 $\delta(\text{CN-CH}_3)$ 15 $\tau(\text{ring-NH}_2)$
4		151mw	164	15.99	160	27 $\tau(\text{ring-CH}_3)$ 24 $\tau(\text{ring-CH}_2)$ 15 $\tau(\text{ring-NH}_2)$
3	116s	116vs	126	0.56	123	37 $\tau(\text{C=O})$ 22 τ_{ring} 13 $\tau(\text{ring-NH}_2)$
2	94w	94mw	103	5.83	101	90 $\tau(\text{ring-CH}_3)$
1	67w	67mw	87	3.20	85	46 $\tau(\text{ring-CH}_3)$ 28 $\tau(\text{H}_3\text{C-ring-NH}_2)$

^a Vibrational modes: n, stretching; d, deformation; τ , torsion; r, rock superscript; s, symmetric; superscript a, asymmetric. ^b Taken from [11] ^c Calculated IR intensities km/mol; ^c Scaling factor: 0.98 below 1800 cm^{-1} and 0.96 up 1800 cm^{-1} .

structure. They are rather broad. The observed low values of bands are due to the participation in the H-bonding interactions.

The band observed at 1690 cm^{-1} in solid phase infrared spectrum is assigned by Trendafilova et al [11] as the fundamental due to the scissoring modes of the amino group while the corresponding band observed at 1670 cm^{-1} is assigned by Costa et al. [12] as the C=O stretching mode. This assignment by Trendafilova is in disagreement with our calculation results. We assigned a strong band at 1670 cm^{-1} to the NH_2 scissoring mode.

The NH_2 out-of-plane deformation frequency is found in the $665\text{-}900\text{ cm}^{-1}$ region (NH_2 wag) for primary amines [34]. The bands observed at 841 and 813 cm^{-1} are assigned by Costa et al. [12] as the fundamental due to the wagging modes of the amino group. Trendafilova et al [11] assigned these bands to C-N and C-C stretching modes, respectively. This mode assigned at c.a. 700 cm^{-1} , aminopyridine [35] and aminopyrazine [36]. The corresponding bands were observed by us at 747 cm^{-1} considering our calculation results; we propose to assign this band as the fundamentals due to the NH_2 wagging mode of the creatinine.

The C-H stretching wavenumbers of N bonded methyl group are lower than methyl groups attached

to carbon atom [37]. The N-methyl symmetric CH stretch occurs from $2805\text{-}2780\text{ cm}^{-1}$. The bands at 2809 (2771) and 2980 cm^{-1} in the solid phase were assigned to the C-H symmetric and antisymmetric stretching modes of N-CH_3 group, respectively.

Infrared spectra of metal-creatinine complexes

The infrared spectra of the ZnCl_2 and ZnBr_2 complexes are shown in Figure 4 (a and b) as representative illustration. Creatinine can coordinate through the ring nitrogen, the C=O and/or $-\text{NH}_2$ groups. In metal complexes, creatinine typically coordinates to the metal *via* the ring nitrogen [11-13,17,28,29].

The N-H stretching vibration of NH_2 group is much affected and found to shift to lower wavenumbers on coordination [38-40]. The shifts to lower wavenumbers of the $\nu(\text{C=O})$ in the complexes can be attributed to the effect of coordination through the oxygen atoms of these groups to the metal [41]. When the aromatic ring nitrogen coordinates to metal, the ring stretching wavenumbers shift to higher wavenumbers [41]. In order to determine the coordination site of creatinine in $\text{M}(\text{creat})_2\text{Cl}_2$ complexes, the wave numbers of creatinine in complexes are compared with those of free creatinine. Some selected fundamental modes of complexes are reported in Table 3.

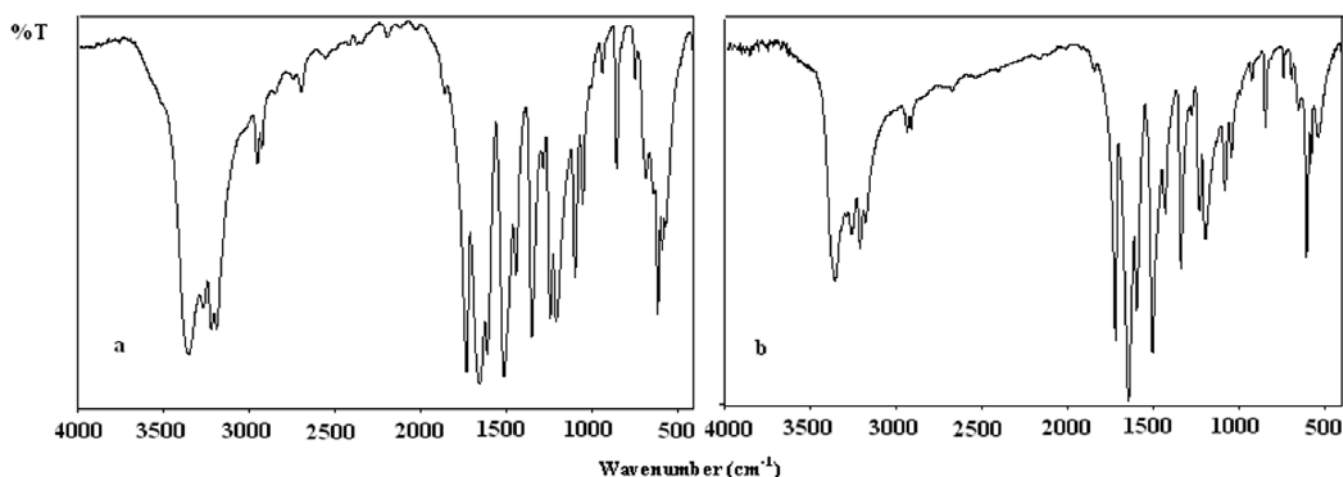


Figure 4. FT-IR spectra of solid $\text{Zn}(\text{creat})_2\text{Cl}_2$ (a) and $\text{Zn}(\text{creat})_2\text{Br}_2$ (b) in the $4000\text{-}400\text{ cm}^{-1}$ region.

Table 3. Selected vibrational wavenumbers (cm⁻¹) of creatinine complexes with their assignment.

Observed ^a	Cu(creat) ₂ Cl ₂			Zn(creat) ₂ X ₂			Cd(creat) ₂ X ₂			Hg(creat) ₂ X ₂			TED % [*]
	Calc.	Observed	Calc.	Br	Cl	Cl	Observed	Calc.	Cl	Br	Cl	Cl	
145sh	146	133m	136	135m	133m	136	128mw	128vwv	131	125mw	128m	121	54 δ(ring-MX)13 ν(M-N) 12 δ(C=O)
154m	177	149m	158	176vw	149m	158	166m		139	145 m	148w	124	33 τ(N-M-X) 20 τ(ring-NH ₂) 12 δ(N-CH ₃)
241s	181	203m	159	203m	205m	159	192vs	209m	143	175ms	148w	130	53 δ(X-M-X)19 ν(M-X) 15 τ(N-M-X)
253s	184	233m	192	233m	241m	192	245m	250m	166	217ms	246vs	153	48 ν _s (M-N) 24 ν(M-X)14 δ(N-CH ₃)
169/178m	196	233m	218	233m	241m	218	386m		171	381mw	386s	163	61 ν _a (M-N) 15 δ(N-M-X)
287vs	259	251w	252	251w	293s	252	267m	267m	238	260m	278mw	233	33 δ(M-N)15 τ(N-M-X) 10 τ(ring-NH ₂)
304vs	283	394w	266	395m	394w	266	283mw	362m	254	348m	386s	242	62 ν _a (M-X) 12 ν(M-X) 18 δ _{ring}
402s	287	1600s	283	1600s	1600s	283	391	391	268	406ms	386s	248	85 ν _s (M-X)
1598vs	402	1595	396	1595	1600s	396	1589s	1594m	391	1595s	1593ms	388	69 τ(ring-NH ₂)
1648vs	1631	1642vs	1633	1642vs	1645vs	1633	1639vs	1642vs	1630	1665	1643vs	1629	37 ν(CN) _{ring} + 20 ν(CNH ₂) 13 ν(C=O)
1715vs	1680	1719vs	1693	1719vs	1722vs	1693	1714s	1714s	1693	1650vs	1670vs	1693	10 δ(HNC)
3178s	1731	3260	1736	3260	3312m	1736	3270	3265m	1732	3268m	3261	1730	51 δ(NH ₂) 27 δ(HNC) 11 ν(CNH ₂)
		3211	1736	3211	3312m	1736	3255	3206m	1732	3216w	3202	1691sh	65 ν(C=O) 11 ν(CN) _{ring}
		3180	3255	3180	3181m	3255	3172w	3172w	3244	3176w	3260	3030s	100 ν _s (NH ₂)
3212s	3222	3358	3358	3358	3345s	3358	3391m	3368ms	3244	3379m	3362m	3260	
		3291	3356	3291	3345s	3356	3356	3314m	3705	3315w	3316mw	3260	100 ν _a (NH ₂)
		3258m	3707	3258m	3258m	3707	3311	3705	3705	3315w	3705	3706	

* Vibrational modes: n, stretching; d, deformation; t, torsion; superscript s, symmetric; superscript a, asymmetric. The numbers before the mode symbols indicate % contribution (10 or more) of a given mode to the corresponding normal vibration, according to the TED total energy distribution. v = very, s = strong, w = weak, sh = shoulder, br = broad.

We observed four broad bands corresponding to stretching vibrations $\nu(\text{NH}_2)$ and their wave numbers are found to be higher in value than those of free creatinine. A positive shift of these absorptions is usually regarded as signifying that the ligand is not NH_2 -bonded. This band indicates the presence of creatinine in the metal halogen complexes in its amine form and the rather broad character of the NH_2 vibration bands is suggestive of H bond participation [42]. In addition, NH_2 scissoring mode of creatinine is observed at 1670 cm^{-1} for creatinine and around 1644 cm^{-1} for complexes. These results suggested that the NH_2 groups of creatinine are not involved in the coordination with the metal ions and are in good agreement with those reported in the literature [11,12].

The $\nu(\text{C}=\text{O})$ mode is observed at 1692 cm^{-1} for free creatinine and around 1710 cm^{-1} in the infrared spectra of complexes, indicating that the ligand does not coordinate to the metal ions through (C=O) group. The bands at 1590, 1418 and 1331 and 677 cm^{-1} with ring contribution exhibit intensity changes

and shift to higher wavenumbers in complexes. All of these data suggest binding between the metal (II) and the ring N atom of the creatinine (The complete infrared data of metal complexes may be obtained from the authors).

The frequency region below 500 cm^{-1} is particularly interesting since it can provide information on metal–ligand vibrations. The infrared spectra in the $400\text{--}20\text{ cm}^{-1}$ region of $\text{Zn}(\text{creat})_2\text{Cl}_2$ and $\text{Zn}(\text{creat})_2\text{Br}_2$ are shown in Figure 5a and b, respectively. In the far-IR spectra, the new bands due to M-N, M-X and X-M-X modes appear in addition the free creatinine. The coordination environmental at the M atom is distorted tetrahedral in the crystal. Two M-N and two M-Cl are expected in infrared spectra of tetrahedral complexes [43]. It is known that the M-X (M = heavy transition metal, X = halogen) stretching vibrations are sensitive to the structure of the complex. The M-Cl stretching vibrations appear generally in the range of $400\text{--}200\text{ cm}^{-1}$.

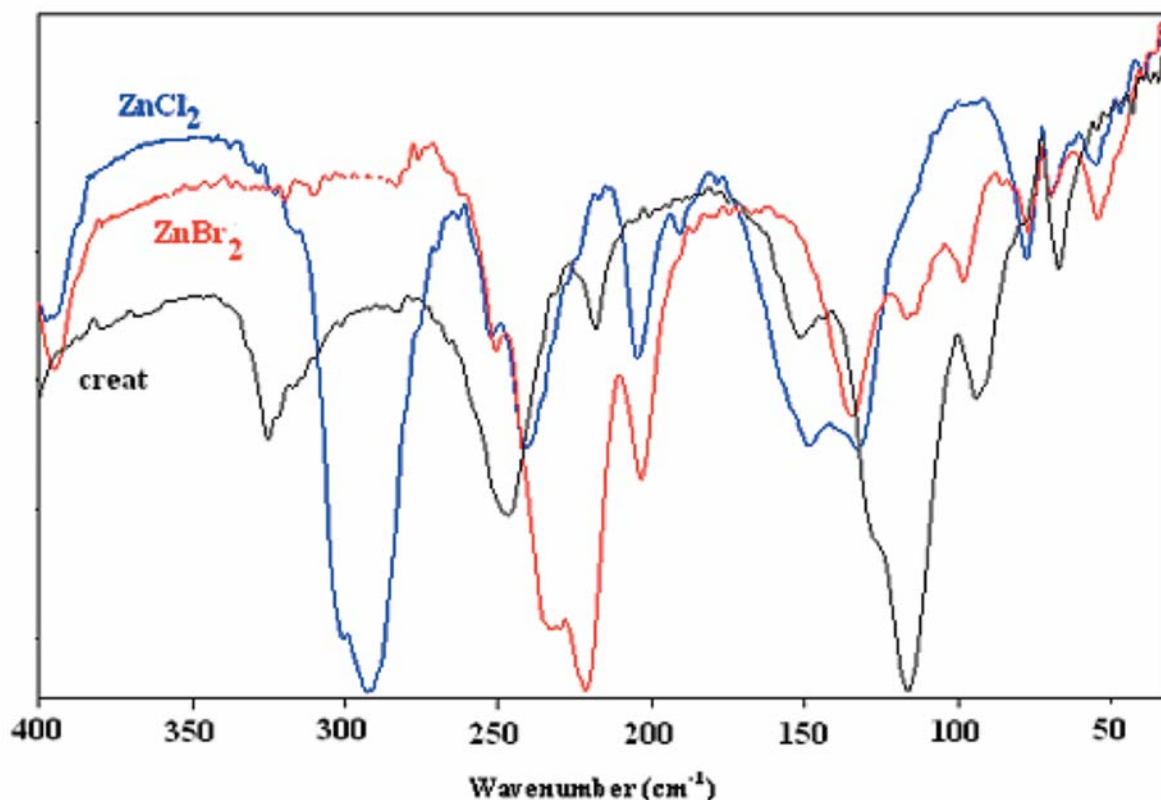


Figure 5. FT-IR spectra for creatinine, $\text{Zn}(\text{creat})_2\text{Cl}_2$ and $\text{Zn}(\text{creat})_2\text{Cl}_2$ (b) in the $400\text{--}50\text{ cm}^{-1}$ region.

As mentioned before the calculated M-N bond lengths increase in the order Hg>Cd>Zn>Cu in the complexes. We can expect that the M-N stretching frequencies decrease in this order.

However, in the metal complexes, the M-N stretching frequencies were calculated at (153/163) cm^{-1} for Hg, 166/171 cm^{-1} for Cd, 184/196 cm^{-1} for Cu and 192/218 cm^{-1} for Zn (Hg<Cd<Cu<Zn).

The above order for Hg(II) and Cd(II) is in agreement with the calculation results. However, the order for Cu(II) does not agree. These results may be due to the differences in two Cl-M-N angles in the calculated structure of complex.

The DFT method predicts two infrared bands for the Hg-N stretching vibrations. The second M-N stretching frequency of the Hg(creat)₂Cl₂ complex is not observed in the infrared spectrum is probably masked by the ligand bands or the complex may have a dimeric structure in which Hg(II) ions are in a distorted tetrahedral environment. The M-Cl (symmetric/asymmetric) stretching frequencies were calculated at 242/248 cm^{-1} for Hg, 254/268 cm^{-1} for Cd, 283/287 cm^{-1} for Cu and 266/283 cm^{-1} for Zn. Corresponding observed values are given in Table 3.

We observed new strong bands at 386 cm^{-1} for Hg(creat)₂Cl₂ complex. Muradlihan et al [24] assigned these bands due to the Hg-N(creat) mode. However, this band was also observed in the infrared spectra of the other metal-creatinine complexes. According to calculation, we propose to assign this band as the fundamentals due to the NH₂ torsion mode of the creatinine.

ACKNOWLEDGEMENT

The authors thank Prof. Dr. Mustafa Korkmaz for providing the creatinine sample.

CONCLUSIONS

The geometry of the ligand (creat) was computed and optimized with the DFT/B3LYP/6-311++G(d,p) and DFT/B3LYP/LANL2DZ. The vibrational assignments for the creatinine molecule were performed with the help of the observed IR spectra and DFT/B3LYP/6-311++G(d,p) calculations. Based on the SQM force field, a complete vibrational analysis of creatinine was performed. The 39 fundamentals were reassigned in the present work, revising the assignment of earlier studies for several fundamentals.

The geometry of creatinine complexes with Cd(II), Zn(II) and Hg(II) were optimized, using the hybrid DFT method B3LYP with LANL2DZ basis set. This method gave good results, comparable with the experimental data from the literature for similar compounds.

The metal-ligand binding mode in the complexes was confirmed from the calculations. In all complexes, metal(II) coordinates through the ring nitrogen atom. B3LYP/LANL2DZ was also used for predicting IR spectra for the complexes.

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