DFT calculations on N,N'-1,2-Cyclohexylene-bis(2-Hydroxyacetophenonylideneimine) and Its Ni(II) Complex

Alireza Akbari*, Majid Jalili Rasti

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

*Corresponding Author: a_akbari@pnu.ac.ir

Copyright © 2013 Horizon Research Publishing All rights reserved.

Abstract The N,N'-1,2-cyclohexylenebis(2-hydroxyacetophenonylideneimine) Ligand (H_2L) was synthesized by condensing 1,2-diaminocyclohexane with 2-hydroxyacetophenone in ethanol as solvent. Preparation of the related complex was carried out using Ni (OAc) $_2$ in the methanol as solvent. The composition and properties of the ligand and its complex were established by elemental analysis, molar conductance and FTIR, and UV/Vis spectrophotometry. The fully optimized geometries were calculated using ADF 2009.01 package. A combined experimental and theoretical studies were conducted on the molecular structure and vibrational spectra of mentioned Schiff base and its Ni(II) complex. The pw91 functional method invoking DZP basis set were used in all calculations. The optimized geometric bond lengths and bond angles were showed good agreement with the reported experimental values. The calculated HOMO and LUMO energies were showed that the charge transfer occurred within the molecule. The UV absorption spectrum was recorded in methanol and compared with the calculated one in gas phase, as well using DFT/DZP basis set.

Keywords DFT Calculations, PW91, Vibrational Frequencies, Electronic Spectra, Schiff Base, ADF

1. Introduction

Catalytic abilities of the optically active Schiff base complexes in stereoselective synthesis have been one of the main interests of scientists [1-3]. Schiff-base ligands derived from salicylaldehyde and chiral amines have been widely applied in various organic reactions as catalyst [4-8]. Cilastatin, an antibacterial drug, can prepare in a special process using a chiral copper (II) Schiff-base complexes derived from salicylaldehyde and chiral amine [9-10]. A nickel complex of such Schiff-base ligand has been synthesized and fully characterized [11]. Theoretical characterization coupled with experimental are widely used

after the synthesis of not only various Schiff-base ligands but also too many complexes [12-19].

This article was focused on the preparation and characterization of a Ni(II) complex with a Schiff base, N,N'-1,2-cyclohexylenebis(2-hydroxyacetophenonylideneimine), an NNOO type ligand. Moreover, the DFT calculations were done for both ligand and its Ni(II) complex for comparing with the experimental results.

2. Experimental and Calculations

2.1. Synthesis of

N'-1,2-cyclohexylenebis(2-hydroxyacetophenonylideneimine), H_2L

This compound was synthesized as reported [20]. 2-hydroxyacetophenone (5.5g, 2 mmol) was added to a solution of 1,2-diaminocyclohexane (2.3g, 1mmol) in absolute ethanol. The resulting mixture was then refluxed for 24 h. After cooling to room temperature, the precipitate was filtered off, washed several times with ethanol and finally dried in a desiccator. The precipitate was re-crystallized from methanol. Yield (4.6mg, 66%); mp: 144 °C; IR (KBr) cm^{-1} : 3421 (OH), 1616.2 (C=N), 1230.5 (C-O); 1H -NMR(DMSO, ppm): 16.49-16.27 (s, 2H, OH), 7.64-6.69 (m, 8H, Ar-H), 4.15-3.92 (d, 2H, CH), 2.34-2.28 (s, 6H, CH $_3$), 1.83-1.52 (m, 8H, CH $_2$ CH $_2$); Anal.: Calcd. for C $_{22}$ H $_{26}$ N $_2$ O $_2$: C, 75.40; H, 7.48; N, 7.99; Found: C, 75.43; H, 7.28; N, 7.94.

2.2. Synthesis of NiL

A mixture of the H_2L ligand (0.1 g, 1 mmol) in ethanol (10 mL) and an ethanolic solution (10mL) of the Ni(II) acetate (0.07 g, 1 mmol) was stirred for 30 min at room temperature. The resulting precipitate was separated by filtration and re-crystallized from ethanol and air-dried. Yield (60mg, 46%); mp: 245°C; IR (KBr) cm^{-1} : 1596 (C=N), 1338 (C-O); 1H -NMR(DMSO, ppm): 7.464-6.398 (m, 8H, Ar-H), 3.947, 3.794 (d, 2H, CH), 2.377 (s, 6H, CH $_3$), 1.79-1.375 (m, 8H, CH $_2$ CH $_2$); Anal. Calc: for C $_{24}$ H $_{36}$ N $_2$ NiO $_2$:

C, 66.83; H, 7.77; N, 6; Found: C, 66.26; H, 7.26; N, 5.65.

2.3. Physical Methods

All chemicals and solvents obtained from Merck or Fluka and used without further purification. The infrared spectra of the ligand and complex were recorded on a Shimadzu Prestige 8400 FT-IR spectrometer as KBr disks. Elemental CHN analyses were performed using a Heraeus CHN-O-FLASH EA 1112 elemental analyzer. The conductivity measurements were carried out in DMSO at room temperature using a Metrohm 712 conduct meter. The electronic spectra of the compounds were recorded in DMSO on a Shimadzu 2550 (UV-Vis) spectrophotometer.

Figure 1. The molecular structure with atomic numbering for the H2L ligand and its Ni complex

2.4. Computational Methods

The quantum chemical calculations were performed using the Amsterdam Density Functional (ADF) 2009.01 package. Geometry of the ligand and complex were optimized at pw91 level and DZP basis set (Fig. 1). Calculations of harmonic frequencies at the fully optimized geometries of the ligand and its Ni (II) complex were performed at the same level and basis set. The UV-Vis spectra properties were explained and illustrated from the frontier molecular orbital orientation. Finally, the calculated vibrational spectra were assigned based on vibrational mode analysis with the aid of the ADF program. Here, the scale factors of 0.96 and 0.72 were used for calculated harmonic vibrational wave numbers and singlet-singlet calculated excitations, respectively.

3. Results and Discussions

3.1. Optimized Structures

The molecular structures with atomic numbering for the ligand and the complex are shown in Figure 1. Some selected calculated structure parameters with those obtained experimentally from the X-ray data of the same or similar geometric structures [20, 21] are compared in Table 1. From the theoretical values, we can find that most of the optimized bond lengths are slightly longer than the experimental values and the optimized bond angles are slightly different from the experimental values, due to the difference of the studied molecular state. The isolated molecules in gas phase are considered in the theoretical calculations, while the experimental results are related to molecular packing in solid state.

Table 1. Comparison of the calculated structure parameters with X-ray data for the geometric same or similar structures.

	Data from ref. 12	NiL (calculated)	Data from ref. 11	H2L (calculated)
	X-ray	DZP	X-ray	DZP
Bond length (Å)				
Ni--O1		-	1.849	1.811
Ni--O2	-	-	1.859	1.824
Ni--N2	-	-	1.854	1.857
Ni--N1	-	-	1.861	1.873
C15--N2	1.277	1.288	1.316	1.290
N1--C7	1.281	1.284	1.32	1.326
Bond angle (°)				
O1--Ni--O2	-	-	84	85.2
O1--Ni--N2	-	-	176.2	177.9
O2--Ni--N2	-	-	93.6	92.8
O1--Ni--N1	-	-	95	94.9
O2--Ni--N1	-	-	175.3	175.8
N2--Ni--N1	-	-	87.6	87.2

Jason et al, reported that the distances of N1-C7(1.284 Å) and N2-C15(1.288 Å) show double and C9-N1(1.477 Å) and C14-N2(1.475 Å) single-double bonds characteristics in the ligand, respectively. In our calculations the distances of N1-C7(1.281 Å) and N2-C15(1.277 Å) and C9-N1(1.453 Å) and C14-N2(1.457 Å) were obtained. They reported the O1-C1(1.346 Å) and O2-C22(1.340 Å) bond distances, while the O1-C1(1.373 Å) and O2-C22(1.372 Å) bonds in our calculations are slightly longer.

Both The crystal structure analysis of complex and computation results reveal that the complex contain a tetradentate ligand in which two nitrogen and two oxygen are coordinated to the nickel atom[2]. The square-planar N2O2 coordination sphere is slightly tetrahedrally distorted [11]. the O1-Ni-O2, O1-Ni-N2, O2-Ni-N2, O1-Ni-N1, O2-Ni-N1, N2-Ni-N1 bond angles are found to have values of 85.2°, 177.9°, 92.8°, 94.9°, 175.8° and 87.2°, and in our calculations were 84.1°, 177.9°, 93.6°, 95.1°, 175.3° and 87.6°, respectively, which indicating the square-planar geometry for our complex. The Ni-N distances found in crystallography structures, 1.857 and 1.873 Å, are similar to those of Å found in our calculations 1.854 and 1.861 Å.

3.2. Chemistry

3.2.1. HOMO and LUMO Analysis

The Figure 2(a) show isodensity plots of HOMO and LUMO for the ligand, in which the LUMO surface mostly is delocalized on the aromatic ring. In the surface shown for the HOMO level, the C=N group is overlapped.

Figure 2. The isodensity plots of the ligand (a) and complex (b) frontier orbitals.

The LUMO surface of the complex mostly delocalized within the non-metallic atoms (Figure 2(b)), and the for the HOMO level, the metal atom is overlapped. HOMO, which

can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. LUMO can be thought the innermost orbital containing free places to accept electrons. Owing to the interaction between HOMO and LUMO orbitals, transition of $\pi \rightarrow \pi^*$ type was observed with regard to the molecular orbital theory. The energy difference between HOMO and LUMO orbitals, so called as energy gap, is an important stability for structures [22]. The HOMO-LUMO energy gap of the ligand and the complex calculated at the PW91/dzp level are shown in Table 2 and reveal that the energy gap reflect to the chemical activity of the molecule.

Table 2. The HOMO-LUMO energy gap of the ligand and the complex (PW91/DZP)

	E HOMO(ev)	E LUMO(ev)	HOMO/ LUMO Gap(ev)
Ni(II) Complex	-4.467	-2.907	-1.56
Ligand	-5.628	-1.712	-3.916

3.2.2. UV-Vis Spectra

The electronic spectra of the ligand and its Ni(II) complex were recorded in methanol and shown in Figures 3 and 4, respectively.

Figure 3. UV-Vis spectrum of the Ligand. (a) Experimental, (b) Calculated (PW91/DZP)

Figure 4. UV-Vis spectrum of the Ni(II) complex. (a) Experimental, (b) Calculated (PW91/ DZP)

In the ligand spectrum, four (mainly absorption) bands appear at 214, 252, 320 and 390 nm. The first and second bands correspond to the transitions of phenyl ring. The third band corresponds to the $\pi \rightarrow \pi^*$ transition within the C=N group, and the last broad band, which was observed at 390 nm, is due to the $n \rightarrow \pi^*$ transition from the phenyl ring to the azomethine.

A detailed analysis of orbitals and excitation energies and oscillator strengths for the various absorption bands in the ligand are presented in Tables 3 and 4 respectively. Regarding with main calculated transitions and considering of the largest oscillator strength (Table 4), the absorption found experimentally at 390 nm belongs to HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 transitions, while the 320 nm absorption basically is due to HOMO-1 $\rightarrow$ LUMO+1 and HOMO-2 $\rightarrow$ LUMO transitions. The absorption found at 252 nm belongs to four transitions, HOMO-3 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+2, HOMO-2 $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO+2. The absorption found at 214 nm mainly occurred due to HOMO-4 $\rightarrow$ LUMO+1, with 50% probability [20]. L+1 or H-1 and so on, means the immediately level upper or lower than LUMO and HOMO respectively.

Table 3. A detailed analysis of the ligand orbitals

Orbital	N%	O%	C%
HOMO-4	6.49P _x + 4.65P _y + 3.12P _z	1.73P _x	44.81P _x +1.21P _y + 57.35P _z
HOMO-3		12.77P _x +7.65P _z	42.41P _x +22.85P _z
HOMO-2	24.26P _x + 1.19P _y + 24.26P _z +1012	1.25P _x	5.67P _x +6.64P _y +1.26S
HOMO-1	3.14P _x + 3.71P _y + 4.27P _z	13.16P _x +P _y +2.47P _z	43.3P _x +10.54P _z
HOMO	3.49P _x +38.60P _y + 10.22P _z +10.80S		2.45P _x +7.23P _y +1.85P _z
LUMO	10.97P _x +6.64P _z		37.38P _x + 21.99P _y + 4.74P _z
LUMO+1			73.01P _x +37.43P _z
LUMO+2	9.33P _y	2.25P _x +1.59P _z	35.30P _x +11.03P _y + 31.27P _z +1.20S
LUMO+3	22.89P _y +2.38P _z		16.55P _x +29.71P _y + 17.65P _z
LUMO+4	1.59P _x	2.10P _x +1.48P _y	49.82P _x +34.03P _y + 2.24P _z

Table 4. The calculated composition of excitations in ligand. F is the oscillator strength

Excitation	Composition	F ($\times 10^{-5}$)	$\lambda_{\text{calc.}}$ (nm)	λ_{exp} (nm)
1	H $\rightarrow$ L (%76), H $\rightarrow$ L+1(%22)	250	334	
2	H $\rightarrow$ L+1 (%77), H $\rightarrow$ L(%20)	113	324	390
3	H -2 $\rightarrow$ L(%86), H-1 $\rightarrow$ L (%11)	466	319	
4	H-1 $\rightarrow$ L+1 (%79), H-1 $\rightarrow$ L (%15)	1537	313	320
5	H-3 $\rightarrow$ L(%88), H -1 $\rightarrow$ L(%4)	1643	301	
6	H $\rightarrow$ L+2 (%97)	242	300	
7	H-2 $\rightarrow$ L+1(%80), H-1 $\rightarrow$ L(%5), H-1 $\rightarrow$ L+1(%4)	1442	299	252
8	H-1 $\rightarrow$ L (%39), H-2 $\rightarrow$ L+1(%13)	5426	295	
9	H-1 $\rightarrow$ L+2(%86), H $\rightarrow$ L+3 (%4)	275	285	
10	H-4 $\rightarrow$ L+1 (%50), H-4 $\rightarrow$ L (%16), H-2 $\rightarrow$ L+2 (%14), H $\rightarrow$ L+4(%10), H-3 $\rightarrow$ L+1(%5)	1285	276	214

Table 5. A detailed analysis of the complex orbitals

Orbital	N%	O%	C%	Ni%
H-4		2.57p _x +4.06p _y	22.24p _x +15.05p _y	25.67d _{xz} +12.14d _{yz} +1.19 dx ² -y ²
H-3	3.15p _x	4.66p _y	13.47p _x +3.06p _y	3.10d _{xz} +31.49d _{xy} +6.34d _z ² +22.09 dx ² -y ²
H-2		5.06p _x +9.95p _y	9.06p _x +5.51p _y	2.52d _{xy} +29.49 dx ² -y ² +5.42d _z ²
H-1		1.72p _x +1.09p _y		40.92d _{xy} +1.64d _{xz} +9.13d _x ² -y ² +30.79d _z ²
H	3.17p _x	10.83p _x +7.76 p _y	14.05p _x +7.74p _y	28.49d _{xz} +13.82d _{yz} +1.92dx ² -y ²
L	2.91s+9.07p _x +1.54p _y +1.98p _z	2.72p _x +5.33p _y +1.22p _z	2.90p _x +6.39p _y	11.57dxz+26.89dyz+2.30dz ²
L+1	16.50p _x	1.44p _x +2.91p _y	38.62p _x +7.89p _y +2.61p _z	1.19dxz+1.87dyz+3.79dx ² -y ²
L+2	5.26p _x +9.07p _y +4.9p _z	4.37p _x	21.15p _x +20.85p _y +2.59p _z	4.78dxz+4.68dyz+1.13dz ²

Table 6. The calculated composition of excitations in complex. F is the oscillator strength

Excitation	Composition	F (×10-5)	λ calc. (nm)	λ exp (nm)	Assignment
1	H → L (%93)	1001	366		MLCT
2	H → L+1 (%92)	1494	330	390	MLCT
3	H → L+2 (%86)	407	310	316	MLCT
4	H-1 → L (%51), H-1 → L+2 (%36)	295	289		MLCT
5	H-1 → L+1 (%87), H-1 → L+2 (%9)	92	280	256	MLCT
6	H-2 → L (%81)	546	272		ILCT
7	H-2 → L+1 (%65), H-2 → L+2 (%16), H-4 → L+1 (%9)	4087	240	246	ILCT
8	H-1 → L+2 (%38), H-1 → L (%25)	666	235		MLCT
9	H-2 → L+2 (%49), H-4 → L (%13), H-2 → L+1 (%11)	1784	234		ILCT LMCT
10	H-3 → L (%69)	1341	224		MLCT

The scale factor (0.76) was used for all calculated excitations in both ligand and complex. The Complex was shown one absorption in 246nm which is assign to the $\pi \rightarrow \pi^*$ transition associated with of C=C band. The two bands at 256 nm and 316 nm are due to the ligand coordination bond band. A broad band at 390 nm assigned to the transition between the nitrogens and metal, N→M, typically in the forming stage of ligand band coordination bond[19]. A detailed analysis of orbitals and excitation energies and oscillator strengths for the various absorption bands in the ligand and complex are presented in Tables 5 and 6. The transition with the largest oscillator strength was considered as main transfers. Total percentage of atoms contribution in each orbital and oscillator strengths were considered for assignment of transitions. The transition energies of the complex as well as their characters, MLCT, LMCT, LLCT (ligand to ligand charge transfer) were collected in Table 6.

The UV-Vis spectrum of the complex exhibits a broad low-energy absorption band attributed to MLCT transitions from the Ni center to the π -anti bonding orbitals of the chelating ligand. The experimental absorption bands at 390 nm and 316 nm belong to Metal-Ligand Charge Transfer (occurring from the M to the π -antibonding orbitals of the C=N on ligand or π -antibonding orbitals of the ring group) because the main contribution in L+1 and L+2 is for carbon atoms of ligand, while in the case of H (or HOMO), the main contribution is in Ni.

The experimental band at 246 nm can be attributed to H-2 → L+1 (%65) and H-2 → L+2(%16) transitions, with maximum oscillator strength compared four possible excitations, 8-10. Normally, the oscillator strengths of the LLCT transitions are larger than those of MLCT transitions [21].

Table 7. Selected experimental and calculated vibrational frequencies of the ligand and its Ni (II) complex. ^a scale factor = 0.96

Experimental frequencies		Calculated frequencies (cm ⁻¹)				assignment
		Ligand		Ni(II) Complex		
Ligand	Complex	unscaled	^a scaled	unscaled	^a scaled	
3421	-	3637	3492	-	-	ν (O-H)
1616.2	1596	1665	1598.4	1603	1539	ν(C=N) _{imini}
1231	1338	1290	1238	1427	1370	ν(C- O) _{phenolic}
-	597	-	-	626	601	ν (Ni-O)
-	474	-	-	470	451	ν (Ni-N _{imin})

3.2.3. Vibrational spectroscopy

Selected experimental and calculated FTIR vibrational frequencies (cm⁻¹) of the ligand and its Ni (II) complex were listed in Table 7, which showed the agreement between the experimental and scaled calculated frequencies. The C=N stretching vibration in the ligand is appeared at 1598.4 cm⁻¹, which is in accordance with the experimental values (1616.2 cm⁻¹). This value is shifted to lower frequency in the complex, indicate the coordination of azomethin nitrogen to central atom which was appeared at 1596 cm⁻¹. In calculated frequencies, the related peak was appeared at 1539 cm⁻¹. In the theoretical and experimental frequencies, the O-H stretching was assigned at 3491 cm⁻¹ and 3421 cm⁻¹ respectively. In the complex, the O-H peak disappeared which indicating coordination of phenolic oxygens to central atom. The experimental and calculated C-O vibration of H₂L were found at 1231 cm⁻¹ and 1238 cm⁻¹ respectively. After complexation, this band was shifted to higher frequency which is in agreement with removing of proton and coordination of the ligand from the oxygen to central atom. The mentioned vibration was appeared and calculated at 1338 cm⁻¹ and 1370 cm⁻¹ respectively [22].

4. Conclusion

The H₂L ligand and Ni(II) complex were synthesized and characterized by elemental analysis, molar conductances and UV-Vis and FTIR spectroscopies. The geometry of the H₂L ligand and Ni(II) complex were optimized with PW91 method and DZP basis set. The IR frequencies were computed with PW91 method and DZP basis set as well. The calculated structural parameters for the H₂L ligand and its Ni(II) complex are in good agreement with experimental data, confirming the obtained geometries for them. The FTIR spectra of them were recorded and the important bands were identified and compared. They can use for analysis of ligand and complexes, help to explain the behavior of their vibrational modes. The results were showed that the H₂L was acted as a dianionic tetra dentate salen ligand in N, N, O-, O- manner. The phenyl rings were not in the same plane in ligand, but

were essentially in the same plane in Ni(II) complex, due to coordination sphere condition. The square-planar NNOO coordination sphere was slightly distorted. Electronic spectra of Ni(II) complexes were dominated by charge transfer and intraligand bands at experimental and DFT calculations, showed the LUMO surfaces mostly are localized within the non-metallic atoms in the complex, and in the HOMO level, the metal atom were overlapped.

Acknowledgments

Special thanks to Dr. M. A. Naseri (from Birjand university) and Dr R. Khalifeh (from Industrial university of Shiraz) for their kindly helps for our ligand synthesizing. We gratefully acknowledge the financial support of this work by the Payame Noor University Research Council. We are also grateful to Dr. S.Y. Ebrahimi, Dr. M. Ahmadi, and Mis. Z. Alinia and all of other our research group members for their useful cooperation.

REFERENCES

- [1] A.E. Martell and D. T. Sawyer ;Oxygen Complexes and Oxygen Activation by Transition Metal, Plenum, New York, 1988, p. 87.
- [2] L. Casella, M. Gulotti, A. Pintar, L. Messori, A. Rockenbauer, M. Gyor, Inorg. Chem. 26 (1987) 1031.
- [3] M. Tabche, A. El-Achqar, L. Pappalardo, M.-L. Roumestant, P. Viallefont, Tetrahedron 47 (1991) 4611.
- [4] Z. Li, G. Liu, Z. Zheng, Tetrahedron, 2000, 56, 7187-7191.
- [5] J.O. Kenneth; J.W. Shiow; J.B. Cynthia, Tetrahedron Lett., 1992, 33, 1001-1004.
- [6] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, P. Iyer, J. Mol. Catal., 1999, 150, 175-183.
- [7] Kim, G.J.; Shin, J.H., Cat. Lett., 1999, 63, 83-89.
- [8] Waldemar, A.; Rainer, T.; Veit, R.S. J. Am. Chem. Soc.,

- 1998, 120, 708-714.
- [9] T. Aratani, Y. Yoneyoshi, T. Nagase, *Tetrahedron Lett.*, 1982, 23, 685.
- [10] Aratani, T., *Pure Appl. Chem.*, 1985, 57, 1839.
- [11] E. Szlyk, A. Wojtczak, E. Larsen, A. Surdykowski, J. Neumann, , *Inorganica Chimica Acta* 293 (1999) 239–244.
- [12] H. Eshtiagh-Hosseini, M. R. Housaindokht, S. A. Beyramabadi, S. H. Mir Tabatabaei, A. A. Esmaili, M. Javan Khoshkholgh, , *Spectrochimica Acta Part A* 78 (2011) 1046–1050.
- [13] S. Muthu, E. I. Paulraj, , *Solid State Sciences* 14 (2012) 476-487.
- [14] M. Ramalingama, V. Sethuraman, N. Sundaraganesan, , *Spectrochimica Acta Part A* 78 (2011) 660–669.
- [15] I. Sheikhshoaie, H. Stoeckli-Evans, A. Akbari, S. A. Yasrebi, S. Y. Ebrahimipour, , *Arabian Journal of Chemistry* (2012) 5, 173–178.
- [16] I. Sheikhshoaie, A. Akbari, S. Y. Ebrahimipour, , *Arabian Journal of Chemistry* (2013), 6, 407–411.
- [17] A. Akbari, I. Sheikhshoaie, L. Saghatforoush, S. Y. Ebrahimipour, and Z. Amiri, , *E-Journal of Chemistry*, (2012), 9(4), 2114-2118.
- [18] S. Y. Ebrahimipour, J. T. Mague, A. Akbari, R. Takjoo, , *Journal of Molecular Structure* (2012), 1028 ,148–155.
- [19] A. Akbari, M. Ahmadi, R. Takjoo and F. W. Heinemann, , *J. of Coord. Chem.* 65, (2012), 4115–4124.
- [20] J.C. Cannadine, J.P. Corden, W. Errington, P. Moore and M.G. H. Wallbrige, , *Acta Cryst.* (1996). C52, 1014-1017.
- [21] M. Lashanizadegan, D.M. Boghaei, , *Synth. React. Inorg. Met. Org. Chem.*, 32(2), 345–355 (2002).
- [22] D.F.V. Lewis, C. Ioannides, D.V. Parke, *Xenobiotica* 24 (1994) 401-408.