COMPARATIVE STUDY BETWEEN N,N'-BIS (ACETYLACETONE)-O-PHENYLENEDIAMINE AND (MONOACETYLACETONE)-O-PHENYLENEDIAMINE SCHIFF BASE COMPLEXES

AMINA A.SOAYED* AND HEBA M.REFAAT

Chemistry Department, Faculty of Science, Alexandria University, Egypt.

P.O. Box 426-Ibrahimia, Alexandria 21321, Egypt. Fax: +203 39 11 794

(Received: September 25, 2012 - Accepted: January 12, 2013)

ABSTRACT

Co(II), Ni(II) and Cu(II) complexes formed from the Schiff base [(2Z,4Z)-4-[(2-aminophenyl)imino]-pent-2-en-2-ol], were prepared in situ and characterized on the basis of elemental analyses, magnetism, UV-vis., IR and ESR spectra. Thermal analyses of the complexes were studied in order to confirm the proposed structures and determine their thermal stability. Comparison between geometries, ESR and thermal studies obtained from direct condensation and in situ preparation of complexes were discussed. The in situ data show that the Schiff base form complexes with 1:1 (metal : ligand) stoichiometry with Cu(II) and Ni(II) ions compared to 2:1 (metal : ligand) formed from direct condensation between Schiff base and metal ions. However, the Co(II) in situ complex formed 1:2 (metal: ligand) stoichiometry. Square-planar geometry was suggested for the Cu(II) and Ni(II) in situ complexes, while, octahedral geometry was suggested for the Co(II) complex. The ESR spectrum of the in situ Cu(II) complex was isotropic to suggest a geometry involving grossly misaligned tetragonal axes. The thermal behavior of the complexes showed good agreement with the formulae suggested from the analytical data. Thermal decomposition of the complexes took place in several stages. The order of stability was $[\text{Cu L}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O} > \text{NiL} \cdot \text{H}_2\text{O} > \text{CoL}_2 \cdot \text{H}_2\text{O}$. The thermodynamic parameters, energy of activation ΔE^* , enthalpy of activation ΔH^* , order of reaction n and entropy of activation ΔS^* of the complexes were calculated. All the reactions were found to be first order. The high values of activation energies reveal the high stability of these complexes.

Key words: Schiff-base, IR, UV-Vis., ESR, TG, DTA.

INTRODUCTION

The chelating abilities of Schiff bases and their analytical applications have attracted remarkable attention [1-5]. o-Phenylene diamine (o-PDA) is used in the copper catalyzed synthesis of quinoxalines [6]. o-PDA is also suitable for removing elemental sulfur in mining ores, and removing aldehyde color formers in polymers. Polymeric plasticized membrane electrode based on Bis-(o-phenylenediamine)-Cu(II) (Cu(II)BOPD) complex has been investigated as iodide selective electrode exhibiting anti-Hofmeister selectivity pattern [7]. Moreover, it is used as a pharmaceutical intermediate in pharmaceuticals industry [8]. Schiff bases of (o-PDA) are used in the synthesis of insecticides, dyestuff fungicides, corrosion inhibitors and pigments. A large number of Schiff bases and their complexes are of significant interest and attention are drawn to them because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties [1,9].

The wide range of uses of o-PDA and its Schiff bases urged us to study its Schiff base with acetyl acetone by using a different method of preparation, the in situ method, which was successfully performed by others [10], in order to throw light on the structure, mode of bonding, spectral and thermal properties of this type of compounds and to compare between this study and previous studies.

EXPERIMENTAL

All the chemicals and solvents used for the syntheses were reagent grade. All solvents were dried and purified before being used. Elemental analyses (C, H, N) were performed by the Micro analytical unit at Cairo University using HP Model MS-5988. The metal ion content was determined using atomic absorption spectrophotometer 850-Fisher Jarrell ash computer controlled. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wavenumber region 4000-200 cm^{-1} . The spectra were recorded as KBr pellets. The nujol mull electronic absorption spectra in the 200-1000 nm range were obtained using a Shimadzu AA-6800 spectrophotometer. The thermo-gravimetric analyses (TGA and DTA) was carried out in a dynamic nitrogen atmosphere (20 $\text{mL} \cdot \text{min}^{-1}$), with a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$ using LINSOLS STA PT 1000 thermal analyzer. The ESR (X-band) spectrum for the poly-crystalline sample was recorded at room temperature using a Varian E-12 spectrometer and DPPH as an external standard.

Preparation of the Schiff base ligand:
(monoacetylacetone-o-phenylenediamine Schiff base)

The ligand ($\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$) was prepared by condensation of 0.108 g (1.00 mmol) o-phenylenediamine dissolved in EtOH to 0.100 g (1.00 mmol) of acetyl acetone dissolved in EtOH solvent and the reaction mixture stirred for 3h at 60 $^\circ\text{C}$. A brown precipitate was separated, filtered, washed several times with ethanol and dried in vacuum (m.p. 150 $^\circ\text{C}$).

(mono acetylacetone-o-phenylenediamine Schiff base)

Preparation of the metal complexes

All the complexes were prepared in situ using the following method. To a 0.108 g (1.00 mmol) of the o-phenylenediamine dissolved in 30 mL of EtOH was added a solution of 0.100 g (1.00 mmol) of acetylacetone dissolved in 30 mL EtOH and the reaction mixture was refluxed for 1hour. A (1.00 mmol) of the metal salts $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$, 0.20 g, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 0.24 g and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 0.25g in 15 ml ethanol was added drop wise with continuous stirring. The mixtures were stirred further for 1.5-2.5 h. at 80 $^\circ\text{C}$. The precipitated solids were then filtered off, washed with cold ethanol, followed by diethylether and dried in vacuum desiccators.

The colors and elemental analyses of all the compounds are presented in Table 1.

RESULTS AND DISCUSSION

Infrared spectra

In order to clarify the mode of bonding and the metal ion effect on ligand, the IR spectra of the free ligand and its metal chelates were studied, Figure 1, Table 2. FT-IR spectrum of the ligand revealed absorption bands in the region of stretching vibrations of O-H and N-H bonds. Thus, the absorption band at 3449 cm^{-1} was assigned to O-H bond [11] while the absorption band at 3396 cm^{-1} was assigned to a free NH_2 group, which depicts the condensation of one acetyl acetone molecule (and not two molecules) to phenylene-diamine, thus forming monoacetylacetone-o-phenylenediamine Schiff base (I). The Schiff base ligand is characterized by strong bands at 1634 and 1298 cm^{-1} which are ascribed to the stretching vibrations of C=N (imine) and C-O groups, respectively [12,13], beside bands at 1430 and 1264 cm^{-1} which are attributed

to -OH bending [12,14]. The out-of-plane C-H deformation of the phenyl ring was observed at 756 cm^{-1} [14]. Comparing the IR spectrum of Schiff base ligand prepared by that prepared by Sadek et.al [9] and Ismail et.al [15] where there was a lack of NH_2 band and thus attributed to the formation of (N,N'-bis (acetylacetonate)-o-phenylenediamine) and behaving as a dianionic tetradentate ligand [15].

Table 1. Elemental analyses of the metal complexes.

Complexes	Elemental Analyses Calculated (Found) %			
	C	H	N	% M
$[\text{CuL}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_4\text{Cu}$ (Brown)	40.798 (41.022)	6.182 (5.901)	8.654 (8.907)	19.638 (20.026)
$[\text{CoL}_2\cdot\text{H}_2\text{O}]$ $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_3\text{Co}$ (violet)	58.287 (58.472)	5.740 (6.117)	12.364 (12.292)	13.010 (13.428)
$[\text{NiL}(\text{H}_2\text{O})]$ $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{Ni}$ (green)	49.865 (50.210)	5.288 (5.382)	10.577 (10.214)	22.179 (21.680)

Figure (1): Infrared spectra of: (a) Ligand (b) $[\text{CoL}_2\cdot\text{H}_2\text{O}]$ (c) $[\text{NiL}(\text{H}_2\text{O})]$ (d) $[\text{CuL}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$

Table (2). Characteristic IR and electronic absorption spectral data of the ligand and its metal complexes.

Compound	$\nu\text{ O-H}$ cm^{-1}	$\nu\text{ NH}_2$ cm^{-1}	$\nu\text{ C=N}$ cm^{-1}	$\nu\text{ C-O}$ cm^{-1}	$\nu\text{ N-H}$ bending cm^{-1}	$\nu\text{ M-O}$ or M-N	λ_{max} nm
L	3449	3396(b)	1634	1298	1504	-	-
$[\text{CuL}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$	3460(b)	-	1630	1322	1518	364, 393	525
$[\text{CoL}_2\cdot\text{H}_2\text{O}]$	3444	-	1637 1601	1278	1519	356 394	513,635, 677
$[\text{NiL}(\text{H}_2\text{O})]$	3448	-	1654	1256	1518	364 393	430, 590

The Cu(II), Co(II) and Ni(II) complexes gave broad bands at 3460, 3444 and 3448 cm^{-1} respectively, assigned either to coordinated water [16,17], or to -OH group, whereas, the band at 3396 cm^{-1} disappeared, together with the shifting of $\nu\text{ N-H}$ bending band from 1504 cm^{-1} in the ligand to 1518 cm^{-1} upon complexation indicating the contribution of the NH_2 group in complex formation. Two $\nu\text{ C=N}$ bands were observed in the Co(II) complex, one of them is at about the same position as that in the ligand, whereas the second band is blue shifted indicating the coordination of one of the two C=N groups of the two ligands to the metal ion. $\nu\text{ C=N}$ band is red shifted in the Ni(II) complex, also indicating its coordination to the metal ion. The $\nu\text{ C-O}$ band at 1298 cm^{-1} is shifted to lower frequency by $\sim (20\text{--}42\text{ cm}^{-1})$, thus it is suggested that the -OH group is deprotonated and oxygen atom of this (C-O) group is bonded to the metal ions. New bands in the ranges $356\text{--}420\text{ cm}^{-1}$ for the Cu, Co and Ni complexes, due to $\nu\text{ M-N}$ and $\nu\text{ M-O}$ [18] were detected. The IR suggests that (mono acetylacetonate-o-phenylenediamine) coordinates to the metal ions in a tridentate fashion through NNO; whereas N,N'-bis (acetylacetonate)-o-phenylenediamine coordinated through NNOO tetradentate mode [15]. Ismail et.al have shown that metal ions have coordinated to water, enolic -OH and C=N (imino N atoms).

Electronic Absorption Spectra

The UV-visible absorption spectrum of the $[\text{CuL}(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ prepared in situ, showed a band at 525 nm which may be assigned to ${}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{1g}$ and is consistent with a square-planar [19,20] or a distorted tetragonal [21] geometry for this complex. The $[\text{NiL}(\text{H}_2\text{O})]$ showed two bands at 430 and 590 nm assigned as ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ attributed to the presence of this complex in the square-planar structure [12,20,22]. As for the cobalt complex $[\text{CoL}_2\cdot\text{H}_2\text{O}]$, three bands were observed at 513 , 635 and 677 nm respectively assignable to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ [23] transitions in an octahedral

structure. The Ni(II) complex reported in this work, is diamagnetic confirming consequently, four coordinate, square planar geometry [24,25] ruling out the presence of paramagnetic, tetrahedral form. The room temperature magnetic moments of the copper(II) complexes are expected to be higher than the spin-only value of 1.73 B.M. as a result of an orbital contribution and spin-orbit coupling, which mixes in the higher terms into the ground term. As a result, $1.90\text{--}2.20\text{ B.M.}$ moment values are usually observed for mononuclear copper(II) complexes, regardless of stereo-chemistry [26]. A magnetic moment was found to be 1.884 B.M. which lies within the expected value for one electron. The Co(II) complex has a magnetic moment of 5.12 B.M. corresponding to an octahedral geometry.

On the other hand, Ismail et.al [15], prepared complexes from N,N'-bis(acetylacetonate)-o-phenylenediamine having the $[\text{Ni}_2(\text{L})\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ (1) and $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_6](\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$ (2) stoichiometries, assigning a tetrahedral, tetrahedral and octahedral geometries around Ni(II) and Cu(II) ions, respectively. From these data, it can be concluded that by changing the method of preparation, different structures are obtained.

Thermogravimetric (TGA) and differential thermal analysis (DTA):

Thermogravimetric (TG) and differential thermal analyses (DTA) for the metal complexes were carried out within the temperature range from $25\text{--}1000^\circ\text{C}$ at a heating rate of 10°C/min in N_2 atmosphere. It was noted that the thermal behaviour of Co(II), Ni(II) and Cu(II) complexes depends on the nature of the metal ion, Figure 2., Table 3.

The thermal behavior of the complexes showed good agreement with the formulae suggested from the analytical data, Table 3, Figure 2. The thermal decomposition of the complexes took place in several stages.

The TG curve of $[\text{CuL}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ complex showed a mass loss of 16.300% (calc. 16.690%) between $55\text{--}240^\circ\text{C}$ due to the loss of three water

molecules in the first stage. Between the temperature 240-350 °C, a percentage loss of 45.551 was observed (calculated 45.743 %) due to the loss of $C_8H_6N_2$ + the coordinated water molecule and the corresponding activation energy amounted to 103.925 KJ/ mol and finally a percentage loss of 32.770 (calculated 33.00 %) due to the decomposition of the complex to $CuO + 2C$ in the temperature range 350-480 °C, , with corresponding activation energy amounting to 189.143 KJ/mol. A remaining of 5.380 % is attributed to the evolution of a CH_4 molecule (4.95%) during the process of decomposition.

Table (3): TGA of the studied complexes.

Complex	T / °C	% mass loss Found (calc.)	Assignment
[CuL.(H ₂ O)] 3H ₂ O	55-240	16.300 (16.690)	3 H ₂ O
	240-350	45.551 (45.743)	$C_8H_6N_2 + H_2O$
	350-480	32.770 (33.00)	$CuO + 2C$
[CoL ₂ .H ₂ O]	68-269	28.030 (27.150)	$C_6H_3N_2 + H_2O$
	269-450	24.913 (25.607)	$C_6H_4N_2 + C$
	450-617	46.720 (47.365)	$Co + C_8H_{16} + CO_2$
[NiL.H ₂ O]	204 -289	45.332 (46.055)	$C_6H_4N_2 + H_2O$
	289 -434	38.380 (38.840)	$NiO + C_2H_4$

Figure (2): TGA and DTA of metal complexes

On the other hand, The TGA of Cu(II) complex $[Cu_2(L)(H_2O)_6](SO_4)_2 \cdot 2H_2O$ (2) prepared by Ismail et.al [15] shows loss in weight within the temperature range 50–180 °C, due to removal of the lattice and coordinated water molecules. The dehydrated complex is thermally stable up to 360 °C, after which SO_4^{2-} ions were removed. Finally the complex undergoes decomposition of the organic ligand at 800 °C, whereupon the final product $[Cu_2(O)_2(CO)_2]$ is formed.

Comparing the decomposition pattern of the two different copper complexes, it seems that the latter complex is decomposed at a higher temperature due to its presence as a dimer.

The DTA of $[CuL(H_2O)] \cdot 3H_2O$ showed one broad splitted endothermic peak centered at 90 and 150 °C, together with two small exothermic peaks at 170

and 200 °C which is in accord with the dehydration of outer and decomposition of the coordinated water molecules. Two other strong exothermic peaks were observed at 325°C and 420 °C due to the decomposition of the rest of the complex.

The TG of $[NiL.H_2O]$ showed the mass loss in two steps only. The first between 204 -289 °C owing to the loss of $C_6H_4N_2$ + coordinated H_2O (found: 45.288 %, calculated: 46.055 %). The second step between the temperature range 289-434 °C attributed to the loss of $NiO + C_2H_4$ molecule (found: 38.380 %, calculated 38.840 %). A (16.338%) which is remaining is attributed to the evolution of C_3H_6 molecule (15.850%).

The DTA curve exhibits two exothermic peaks. The first is at 117 °C is due to the loss of the coordinated water molecule to the Ni(II) ion [27,28]

together with the loss of part of the organic ligand. The second peak which is a splitted one centered at 210, 240° C is due to the decomposition of the rest of the complex.

As for the cobalt complex $\text{CoL}_2 \cdot \text{H}_2\text{O}$, three steps were detected. In the first step, between 68-269 °C, the loss was found to be 28.030 % (calculated: 27.150 %) due to the loss of $\text{C}_6\text{H}_5\text{N}_2$ + the coordinated H_2O molecule with activation energy 156.968 KJ/mol. Then between 269-450 °C, the % loss was found to be 24.983% (calculated 25.607 %) owing to the loss of the second $\text{C}_6\text{H}_5\text{N}_2$ + C molecule, with an activation energy of 149.984KJ/mol. The third step between 450-617°C was attributed to the decomposition of the rest of the complex to $\text{Co} + \text{CO}_2 + \text{C}_8\text{H}_{16}$ molecules, (found: 47.850%, calculated 47.395 %) with

activation energy 76.455 KJ/mol.

The DTA of $\text{CoL}_2 \cdot \text{H}_2\text{O}$ gave exothermic peaks at 80, 150, 220, 340, 425, 510 and 680 °C due to the decomposition of the complex [29].

There were no data available in the literature to compare between them and the prepared Co(II) and Ni(II) complexes.

From the DTA data, the thermodynamic parameters ΔE_a^* (activation energy), ΔH^* (enthalpy of activation), n (order of the reaction) and ΔS^* (entropy) were calculated by the Horowitz-Metzger equations [30,31] and the results are shown in Table 4. The values of the collision factor, Z , were calculated based on the following relation :

Table (4): Thermodynamic parameters of the complexes.

Complex	T_m /K	n	Z (min^{-1})	ΔE_a^* (KJ/mol)	ΔH^* (KJ/molK)	ΔS^* (KJ/mol)
$[\text{CuL}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$	320	1.14	7.355	103.925	-73.252	-0.229
	400	1.47	10.928	189.143	-90.990	-0.228
$[\text{CoL}_2 \cdot \text{H}_2\text{O}]$	430	1.26	8.104	156.968	-99.141	-0.230
	535	1.02	5.985	149.984	-125.671	-0.234
	610	1.19	2.575	76.455	-148.230	-0.243
$[\text{NiL} \cdot \text{H}_2\text{O}]$	140	1.49	4.395	26.147	-31.684	-0.226
	290	1.06	6.857	89.874	-78.199	-0.230
	340	1.54	7.064	104.34	-66.244	-0.228

$$Z = (\Delta E_a^* / RT_m) \varphi \exp. (\Delta E_a^* / RT_m^2) = KT_m / h \exp (\Delta S^* / R),$$

where R = molar gas constant, φ = the rate of heating (10 K/min), ΔS^* = the entropy of activation, K and h are the Boltzman and Planck's constants, respectively. The change of the entropy ΔS^* values for all complexes are of the same magnitude within the range

(-0.226 - 0.243 KJ / mol K). The negative values for the entropies of activation indicate that the activated complexes have more ordered structure than the reactants and the reactions are slower than normal [32]. The negative values of ΔS^* make the dissociation process non-spontaneous. All the reactions were found to be approximately first order. The high values of activation energies reveal the high stability of chelation in these complexes [33]. Comparing ΔE_a^* of $[\text{CuL}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ with that of $[\text{NiL} \cdot \text{H}_2\text{O}]$, it was found that the former possess a higher value, since as the radius of the metal ion decreases, the binding between it and the ligand increases. ΔE_a^* of the Co(II) complex is the greatest as two ligand molecules are coordinated to the metal ion. ΔH values are negative, indicating exothermic decomposition processes.

Ismail et.al [15], have also shown that ΔS^* values for $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ complex were negative indicating that either the activated complex is more ordered than the reactants and/or the reactions are slow, whereupon, they obtained positive ΔH^* values which means that the decomposition processes are endothermic.

X-band EPR:

The X-band EPR spectrum of the $[\text{CuL}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ complex in the solid-state was measured at room temperature and gave a dissymmetric isotropic broad band having no hyperfine structure, Figure 3. When there is a slow-motion regime, the rotational diffusion is slow, so that the spectrum loses its similarity to the isotropic limiting case. The lines broaden and distort [34]. Also, the broadening can be due to dipolar exchange and unresolved hyperfine interactions in the solid state [35] or due to the tumbling motion of the molecules [36]. The calculated g -value was found to be equal to 2.145, Figure (2), to suggest a geometry involving grossly misaligned tetragonal axes [37]. $A_1 = 139 \times 10^{-4} \text{ cm}^{-1}$. On the other hand, $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_6](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ (2) [15], prepared by Ismail et. al, gave two g -values, $g_1 > g_2$ which indicates that the unpaired electron is predominantly in the $d_{x^2-y^2}$ orbital giving 2B_g as the ground state. The observed data show that the $g_{\parallel}$ values are > 2.0023 and hence the metal-ligand bonding in this complex is essentially covalent.

The proposed structures for the in situ prepared complexes are shown in Figure 4.

Figure (3) : X-band EPR spectrum of the $[\text{CuL}(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ complex in the solid-state.

CONCLUSION

- 1- Preparation of Schiff base and its complexes derived from o-phenylenediamine and acetylacetone were performed in situ in order to compare between them and those prepared previously by normal condensation method.
- 2- It was found that the in situ method gives (monoacetylacetone)-o-phenylenediamine Schiff base compared to N,N'-bis (acetylacetone)-o-phenylenediamine obtained by condensation method.
- 3- The activation energy for decomposing the in situ (mono) copper (II) complex is lower than that of the dimeric complex prepared by condensation which was expected due to the presence of two Cu(II) ions.

Figure (4) : The proposed structures for complexes:

(a) [CuL.H₂O].3H₂O (b) [CoL₂.H₂O] (c) [NiL.H₂O]

REFERENCES

- N. Ramana., L.Mitub, A. Sakthivela , M.S.S. Pandia , *J. Iran.Chem. Soc.*, **6(4)** ,738, (2009).
- A.S. Munde , A. Jagdale , S.M. Jadhav , T.K. Chondhekar , *J. Serb. Chem. Soc.*, **75(3)**, 349, (2010).
- B. Theis, S. Metz, F. Back, C. Burschka, R. Tacke, *Z anorg. allg. Chem.*, **635**, 1306 (2009).
- B. Sindhukumari , G. Rijuulal , K. Mohanan , *Synth. React. Inorg., Met.-Org. Nano-Met. Chem.*, **39** , 24, (2009).
- M.B. Dai , Q.L. Zhang; X.C. Zhu , Y.Q. Zhang; B.X. Zhu, *Wuji Huaxue Xuebao (Chin.J.Inorg.Chem.)*, **24** , 1381, (2008).
- W. Wang , Y. Shen , X. Meng , M. Zhao , Y. Chen , B. Chen , *Org. Lett.*, **13(17)**, 4514, (2011).
- A. Rawat , S. Chandra , A. Sarkar , *Sensor Letters* , **8(6)** , 753, (2010).
- B.J. Gangani , P.H. Parsania , *Spectrosc. Lett.*, **40** , 97, (2007).
- S.A. Sadeek , M.S. Refaat., *Journal of the Korean Chemical Society*, **50(2)** , 107, (2006).
- Y.Q Jiang , Z.H. Zhou , Z.B. Wei, *JIEGOU HUAXUE, (Chinese J. Struct. Chem.)* **24 (4)**, 457 (2005).
- M. Jadrijevic , M. Takac , D.V. Topic , T. Govorciovic , *Acta Pharm.*, **54(3)**, 163, (2004).
- R.L. De , M. Mandal , L. Roy, J. Mukherjee , R. Bhawal , K. Maiti , *Indian Journal of Chemistry*, **47(A)** , 1480, (2008).
- M. Sonmez , *Erciyes Üniversitesi Fen Bilimleri Enstitüsü Dergisi* , **24(1-2)** , 308, (2008)..
- M. Tumer , H. Koksall , S. Serin , M. Digrak., *Trans.Met.Chem.*, **24** , 13, (1999).
- T.M.A. Ismail , A.A. Saleh , M.A. El Ghamry , *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **86** , 276, (2012)..
- M. Gaber , M.M. Ayad , Y.S.Y. El-Sayed , *Spectrochim. Acta, A*, **62** , 694, (2005).
- B. Dede , F. Karipcin , M. Cengiz , *J. Chem. Sci.*, **121(2)** , 163, (2009).
- N. Raman, A. Kulandaisamy , C. Thangaraja , P. Manisankar , S. Viswanathan , C. Vedhi , *Trans.Met.Chem*, **29 (2)**, 129, (2004).
- a) N. Gupta, R. Gupta, S. Chandra, S.S. Bawa , *Spectrochim. Acta Part A* , **61(6)**, 1175, (2005), (b) A.B.P. Lever , *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.
- A.A. Osowole , *Bull. Chem. Soc. Ethiop.*, **22(2)**, 219, (2008).
- S. karabocek , N. Karabocek , *Polyhedron*, **17** , 319, (1998).
- N. Raman, J.D. Raja, A. Sakthivel., *J. Chem. Sci.*, **119(4)**, 303, (2007).
- M. Sonmez , *Turk. J. Chem.*, **25** , 181, (2001) .
- M. Lashanizadegan, D.M. Boghaei., *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1519, (2001).
- A.A. Osowole , G.A. Kolawole , O.E. Fagade , *Synth. React. Inorg. Met.-Org. Chem. and Nano-Metal Chem.*, **35** , 829, (2005).
- A. Earnshaw , “The Introduction to Magnetochemistry”, Academic Press: London; 1980.
- S.L. Stefan , *J. Thermal Analysis*, **42**, 1299, (1994)..
- J.C. Pessoa , J.A.J. Silva , A.L. Vieira , L. Vilas-Boas, P.O. Brien, P. Thomson , *J. Chem. Soc., Dalton Trans.*, 1745, (1992)..
- A. Reiss A., S. Florea , T. Caproui , N. Stanic , *Turk. J. Chem.*, **33** , 775, (2009).
- H.H. Horowitz , G. Metzger , *Anal. Chem.*, **35(10)** , 1464, (1963).
- M.L. Dhar , O. Singh , *J. Thermal Analysis*, **37** , 259, (1991) .
- N. Raman , S. Ravichandran , C. Thangaraja , *J. Chem. Sci.* , **116(4)** , 215, (2004).
- M.S. Refat, *J. Therm. Anal. Calorim*, **102(3)** , 1095, (2010).
- S. Stoll ; A Schweiger , *J Magn Reson*, **178** , 42, (2006).
- K.K. Narang , V.P. Singh, *Transition Met. Chem.*, **21(6)** , 507, (1996)..
- A.A. Frost , R.G. Pearson , *Kinetics and Mechanism*, 2nd edition, Wiley, New York , 1961.
- V.P. Singh , P. Gupta , N. Lal , *Russian Journal of Coordination Chemistry*, **34(4)**, 270, (.2008).