Synthesis and Thermal Degradation Kinetics of Co(II), Ni(II), Cd(II), Zn(II), Pd(II), Rh(III) and Ru(III) Complexes with Methylquinolino[3,2-b]benzodiazepine

BENNEHALLI BASAVARAJU* and HALEHATTI S. BHOJYA NAIK[#]

*Department of Biotechnology, GM Institute of Technology,
Davangere-577 006, Karnataka, India.
E-mail: basavaraju_b@yahoo.co.in

[#]Department of PG studies and Research in Industrial Chemistry,
School of Chemical Sciences, Kuvempu University,
Shankaraghatta-577451, Shimoga, Karnataka, India.
E-mail: hsb_naik@rediffmail.com

Received 3 October 2006; Accepted 1 November 2006

Abstract: A series of new complexes formed by the interaction of a new ligand Methylquinolino[3,2-b]benzodiazepine (L) with various transition metal ions have been isolated and characterized by elemental analysis and electronic, IR, magnetic moment and conductivity measurements. Thermogravimetric (TG) studies of the complexes have been performed in order to establish the mode of their thermal degradation. The thermal degradation was found to proceed in two steps. The kinetics and thermodynamic parameters were computed from the thermal decomposition data.

Keywords: Thermogravimetric studies, Thermodynamic parameters, Entropy, Enthalpy, Activation energy, Free energy of activation.

Introduction

In the last decade, much attention has been given to the organic ligands and transition metal complexes because of their biological relevance, interesting spectral and magnetic properties. The fused aromatic heterocyclic ligands and their metal complexes are being used extensively as pharmaceutical and chemotherapeutic agents¹⁻⁴. On the other hand, quinoline and their derivatives form an interesting class of compounds which display attractive applications as pharmaceuticals⁵⁻⁸ and are general synthetic building blocks, due to their chemical and biological relevance. Therefore, it was thought worthwhile to isolate and characterize some novel quinoline derivatives containing different donor atoms.

Experimental

Physical measurements

All necessary precautions were taken to exclude oxygen and moisture during the synthesis of compounds. Analytical reagent grade chemicals were used as received for all the experiments. Infrared spectra of the ligand and its metal complexes in KBr pellets were recorded in the spectral range $4000\text{--}250\text{ cm}^{-1}$ range with SHIMADZU FTIR-8400S spectrometer. UV-Visible spectra were recorded on a SHIMADZU double beam spectrophotometer. The C, H, N and S content analyses were determined by using Carlo-Erba 1106 model 240 Perkin Elmer analyzer at University of Mysore, Mysore. Magnetic susceptibilities were measured on a Guoy Balance at room temperature using $\text{HgCo}(\text{NCS})_4$ as calibrant. ^1H NMR spectra were recorded in DMSO-d_6 solution on a JEOL 300 MHz spectrometer and TMS was used as an internal reference. The molecular weight of the complexes was determined by Rast's method using biphenyl⁹.

Thermogravimetric analysis

The thermogravimetric (TG) curves of complexes were recorded in static air atmosphere. Dupont 9900 computerized thermal analyzer with 951 TG module thermo balance was used for recording TG curves. The temperature scale of the instrument was calibrated with high purity calcium oxalate $[\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}]$. The operational range of instrument is from ambient to $970\text{ }^\circ\text{C}$. About 6-8 mg of pure sample was subjected for dynamic TGA scans at heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The kinetic parameters for the degradation steps on TG curves were determined using the methods reported elsewhere¹⁰⁻¹².

Synthesis of Ligand (L)

The mixture of 2-Chloro-6-methylquinoline-3-carboxaldehyde (1.569 g, 5 mmol) dissolved in small amount of acetic acid and *o*-Phenylenediamine (0.541 g, 5 mmol) was taken in a 100 mL borosil beaker and a pinch of potassium iodide was then added. The whole mixture was made into slurry and was irradiated by placing the beaker in a microwave oven for about 10 minutes. The product obtained was poured into ice-cold water; the solid separated was filtered and dried. The product was separated on an alumina column (3x20 cm) using methylenechloride/acetonitrile (5:1) as an eluant (Scheme 1).

Scheme 1. Preparation of methylquinolino[3,2-b]benzodiazepine (L)

Synthesis of Cobalt(II) and Nickel(II) complexes

An alcoholic solution of **L** (2 mmol, 50 mL) and Metal chloride (1 mmol) was refluxed for 8 h and its volume was reduced in a rotary evaporator until a precipitate appeared. After cooling, the solid was filtered off, washed with water, methanol and ether, and then dried under reduced pressure at room temperature.

Synthesis of Cadmium(II) and Zinc(II) complexes

The Metal salt (10 mmol) was added to a solution of **L** (10 mmol) in dry ether (30 mL) with continuous stirring and stirring was continued for 1h at 0 °C and 18 h at room temperature. The resulting solution was concentrated to give a white compound. The compound was recrystallized by using chloroform/hexane (1: 1) mixture to give the desired complex.

Synthesis of Pd(II), Rh(III) and Ru(III) complexes

The complexes were prepared by mixing an ethanolic solution of PdCl₂/ RhCl₃.3H₂O/ RuCl₃.3H₂O (2.5 mmol) with **L** in hot ethanol in 1:1 metal-ligand ratio for Pd(II) and 1:2 for Rh(III) and Ru(III) complexes, respectively. The resultant solution was refluxed at 110 °C for three hours. When the complex precipitated, it was filtered, washed several times with ethanol and dried under reduced pressure.

Results and Discussion

The complexes were microcrystalline coloured powder. They are stable at room temperature and soluble in DMSO and DMF. The elemental analyses agree well with a 1:1 metal-to-ligand stoichiometry for Cd(II), Zn(II) and Pd(II) and 1:2 for Co(II), Ni(II), Rh(III) and Ru(III) complexes (Table 1). The conductivity values measured in DMF at room temperature fell in the range 14.52-34.3 mhos cm² mol⁻¹, which indicates the non-electrolytic nature of all the complexes except Rh and Ru complexes, which show conductivity value of 47.04 and 46.05 respectively¹³.

Magnetic moments

The room temperature magnetic moment value (Table 1) support octahedral geometry for Co(II), Ni(II), Rh(III) and Ru(III), square planar for Zn(II) and Pd(II) and tetrahedral for Cd(II) complexes¹³⁻¹⁶.

Spectral study

The octahedral Co(II) complex exhibit three bands at 14380, 14766 and 16393 cm⁻¹, pertaining to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively. The absorption spectra of Ni(II) complex show two bands at 16240 cm⁻¹ and 23251 cm⁻¹ due to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions, respectively supporting the octahedral stereochemistry. The reflectance spectra of Zn(II) and Cd(II) complexes show no bands due to *d-d* transition. This phenomenon is natural as there is no possibility of transition due to non availability of empty *d*-orbital¹⁶. By considering the spectral data, the tetrahedral geometry for Cd(II) complex and square planar geometry for Zn(II) complex have been proposed¹⁶⁻¹⁸. The electronic bands observed at 16582, 21276 and 30284 cm⁻¹ for Pd(II) complex ion are due to the transitions ${}^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1), ${}^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2) and ${}^1A_{1g} \rightarrow {}^1E_{1g}$ (ν_3) respectively in a square planar configuration. In the present investigation of Rh(III) complex, the observed electronic bands around 16580, 19370 and 22280 cm⁻¹ are due to the transitions ${}^1A_{1g} \rightarrow {}^3T_{1g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, respectively in an octahedral structure around Rh(III) ion¹⁶. The UV-Visible spectra of Ru(III) complex exhibit octahedral absorption band at 24560 cm⁻¹ attributed to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ charge transfer transitions¹⁹.

Table 1. Physical constants of ligand and its complexes

Compound	Yield (%)	Found (Calcd) (%)					Molar conductivity (mhos cm ² mol ⁻¹)	Magnetic moment (μ_{eff} BM)	Mol.wt. found (Calcd)
		C	H	N	M	Cl			
Ligand(L)	74	78.89 (78.7)	5.25 (5.0)	16.35 (16.2)	--	--	--	--	256.21 (259.30)
[CoL ₂ Cl ₂]	82	60.27 (63.0)	4.23 (4.0)	13.01 (12.9)	9.20 (9.1)	11.21 (10.9)	22.4	4.84	645.35 (648.44)
[Co(L) ₂ (NO ₃) ₂]	78	50.22 (58.2)	3.65 (3.7)	15.98 (15.9)	8.35 (8.4)	--	24.6	4.63	697.25 (701.55)
[Co(L) ₂ (ClO ₄) ₂]	69	54.38 (52.5)	3.52 (3.3)	11.92 (10.8)	7.36 (7.6)	--	25.4	4.96	770.26 (776.54)
[NiL ₂ Cl ₂]	75	64.4 (63.0)	4.2 (4.0)	13.0 (12.9)	8.9 (9.0)	11.1 (10.9)	23.4	2.99	642.89 (648.21)
[Ni(L) ₂ (NO ₃) ₂]	68	57.2 (58.2)	3.4 (3.7)	15.7 (15.9)	8.4 (8.3)	--	32.0	3.12	696.57 (701.31)
[Ni(L) ₂ (ClO ₄) ₂]	65	50.2 (52.5)	3.4 (3.3)	11.0 (10.8)	7.6 (7.5)	--	34.3	3.19	770.94 (776.31)
[CdLCl ₂]	82	42.89 (46.3)	2.86 (3.0)	9.58 (9.5)	26.4 (25.4)	16.15 (16.0)	14.52	--	439.87 (442.62)
[CdLSO ₄]	75	41.03 (43.6)	3.10 (3.0)	9.18 (9.0)	24.2 (23.9)	--	17.89	--	468.78 (464.87)
[ZnLCl ₂]	75	55.38 (57.6)	3.35 (3.3)	10.72 (10.6)	16.6 (16.5)	17.86 (17.9)	15.25	--	392.35 (395.60)
[ZnLSO ₄]	82	47.26 (48.4)	3.38 (3.3)	9.89 (9.96)	15.0 (15.5)	--	18.92	--	421.76 (419.98)
[PdLCl ₂]	81	46.76 (45.8)	3.00 (3.1)	9.62 (9.6)	24.37 (24.5)	16.24 (16.1)	28.5	--	432.59 (436.63)
[RhL ₂ Cl ₂]Cl	82	58.98 (57.9)	3.78 (3.7)	12.14 (12.3)	14.86 (13.7)	10.24 (10.3)	47.04	1.86	689.36 (692.42)
[RuL ₂ Cl ₂]Cl	79	59.13 (58.3)	3.79 (3.9)	12.17 (12.2)	14.64 (14.6)	10.27 (10.4)	46.05	1.85	688.84 (690.59)

IR Spectra

The IR spectral data of ligand and its metal complexes are presented in Table 2. IR spectroscopy can provide valuable information as to whether or not a reaction has occurred. The ligand **L** shows bands at 1662 cm^{-1} and 3332 cm^{-1} due to $\nu(\text{C}=\text{N})$ and $\nu(\text{NH})$ vibrations respectively²⁰. These bands are shifting in the complexes indicates the coordination of nitrogen atom of quinoline and azepine moiety with the metal ions. On the basis of the above interpretation, it is concluded that the ligand behaves as a bidentate.

Table 2. Some important IR and ^1H NMR data of ligand and its complexes

Compound	Infrared spectral data, (cm^{-1})				^1H NMR spectral data (δ , ppm)
	$\nu(\text{C}=\text{N})$	$\nu(\text{NH})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{X})$	
Ligand(L)	1662	3332	--	--	10.80 (s, 1H, NH), 8.6 (s, 1H, H-C=N), 7.1-8.2 (m, 11H, Ar-H), 2.7 (s, 3H, CH_3)
$[\text{CoL}_2\text{Cl}_2]$	1616	3318	438	352	10.95 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-8.8 (m, 9H, Ar-H)
$[\text{NiL}_2\text{Cl}_2]$	1622	3312	468	252	10.90 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-8.8 (m, 9H, Ar-H)
$[\text{CdLCl}_2]$	1612	3300	432	348	10.85 (s, 1H, NH), 8.3 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)
$[\text{ZnLCl}_2]$	1624	2990	428	348	10.90 (s, 1H, NH), 8.1 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)
$[\text{PdLCl}_2]$	1620	3304	406	310	10.85 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)
$[\text{RhL}_2\text{Cl}_2]\text{Cl}$	1636	3294	408	340	10.9 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)
$[\text{RuL}_2\text{Cl}_2]\text{Cl}$	1624	3310	404	318	10.8 (s, 1H, NH), 8.4 (s, 1H, H-C=N), 7.2-7.8 (m, 9H, Ar-H)

^1H NMR spectra

All the compounds show the ^1H NMR signals for different kinds of protons at their respective positions. The data are shown in Table 2. The ^1H NMR spectra of the ligand MQBD exhibit a singlets at $10.80\text{ }\delta$ (s, N-H) and $8.6\text{ }\delta$ (s, H-C=N). The ^1H NMR spectra of complexes slightly changed compared to those of the corresponding ligand, and the signals appeared downfield, as expected, due to the coordination of nitrogen atoms to the metal ion²²⁻²⁴.

Thermal Analysis

The temperature of decomposition, the pyrolyzed products, the percentage weight loss of the ligand, and the percent ash are given in Table 3. TG curves of the complexes show two significant steps in the decomposition. In the first step, the loss of organic ligand moiety occurred in the range $190\text{--}450\text{ }^\circ\text{C}$ with a mass loss of $61.97\text{--}80.26\%$. The decomposition temperature of second stage lies in the range $400\text{--}690\text{ }^\circ\text{C}$, which represents the loss of corresponding inorganic ligand with a mass loss in the range $7.89\text{--}14.65\%$. These experimental values are in agreement with the expected value. This observation suggests that these complexes do not have water molecule either inside or outside the coordination sphere. The ash from the complexes obtained in each case has been chemically identified as pure metal oxide. The experimental values of the ash content are in the expected range ($8.57\text{--}30.58\%$).

Table 3. Thermogravimetric characteristics of complexes

Complex	Process	Temp. Range (°C)	Product	No of moles	Weight (%)		*Residue (%)	
					Found	Calcd	Found	Calcd
[CoL ₂ Cl ₂]	Decomposition of coordination sphere Ligand & Cl	200-400	Ligand	2	77.56	79.0	11.53	12.10
		425-625	Cl	2	10.85	11.43		
[Co(L) ₂ (NO ₃) ₂]	Decomposition of coordination sphere Ligand & NO ₃	210-410	Ligand	2	71.25	72.75	10.53	11.10
		415-610	NO ₃	2	16.86	18.41		
[NiL ₂ Cl ₂]	Decomposition of coordination sphere Ligand & Cl	220-410	Ligand	2	78.12	79.01	10.76	11.40
		435-694	Cl	2	10.59	11.43		
[Ni(L) ₂ (NO ₃) ₂]	Decomposition of coordination sphere Ligand & NO ₃	205-395	Ligand	2	70.89	72.80	17.58	18.40
		410-710	NO ₃	2	17.67	18.40		
[CdLCl ₂]	Decomposition of coordination sphere Ligand & Cl	220-436	Ligand	1	56.28	57.16	31.24	30.00
		491-776	Cl	2	15.64	16.54		
[CdLSO ₄]	Decomposition of coordination sphere Ligand & SO ₄	218-440	Ligand	1	52.68	53.90	27.85	28.23
		460-680	SO ₄	1	21.89	21.10		
[ZnLCl ₂]	Decomposition of coordination sphere Ligand & Cl	225-460	Ligand	1	63.56	64.20	20.43	21.32
		480-760	Cl	2	17.54	18.58		
[ZnLSO ₄]	Decomposition of coordination sphere Ligand & SO ₄	220-440	Ligand	1	58.76	60.10	20.45	19.96
		450-680	SO ₄	1	22.15	23.54		
[PdLCl ₂]	Decomposition of coordination sphere Ligand & Cl	216-395	Ligand	1	56.54	57.97	26.91	28.96
		395-545	Cl	2	15.94	16.78		
[RhL ₂ Cl ₂]Cl	Decomposition of coordination sphere Ligand & Cl	218-434	Ligand	2	69.86	71.20	32.80	34.90
		440-585	Cl	3	9.73	10.32		
[RuL ₂ Cl ₂]Cl	Decomposition of coordination sphere Ligand & Cl	210-398	Ligand	2	68.97	71.40	33.12	34.50
		420-550	Cl	3	9.86	10.38		

*Residue: CoO/NiO/ CdO/ ZnO/ PdO/ Rh₂O₃/ Ru₂O₃

The thermograms obtained during TGA scans were analysed to give the percentage weight loss as a function of temperature. T_0 (temperature of onset of decomposition), T_{10} (temperature for 10 % weight loss), T_{20} (temperature for 20 % weight loss) and $T_{\max}$ (temperature of maximum rate of degradation) are the main criteria to indicate the heat stability of the complexes. The higher the values of T_0 , T_{10} , T_{20} and $T_{\max}$, higher the heat stability.

Broido's method¹⁰ was used to evaluate the kinetic parameters from TG curve. Using Broido's method, plots of $\ln[\ln(1/y)]$ vs $1/T$ (where y is the fraction not yet decomposed) for different stages of the thermal degradation process of the complexes were made. The plots were linear over the conversion range of about 0.1 – 0.9, supporting the assumption of first order kinetics.

In order to determine the thermal stability trend, the parameters T_0 , T_{10} , T_{20} , $T_{\max}$, activation energy (E_a) and frequency factor ($\ln A$), were evaluated and are given in Table 4. The kinetic parameters were obtained by applying the methods of Broid's for each step of transition. The activation energy E_a and pre exponential factor $\ln A$ data reveal that the reactivities of all the systems differ significantly as shown from the different values of activation energy. All the complexes show the least activation energies in the first stage decomposition and maximum in second stage decomposition. The values of pre-exponential factor $\ln A$ of complexes indicate that the decomposition reaction of the complexes with the ligand can be classified as a slow reaction²⁶.

Table 4. Temperature characteristics, activation energies and frequency factors of decomposition process of complexes

Complex	T_0 (°C)	T_{10} (°C)	T_{20} (°C)	$T_{\max}$ (°C)	Process	E_a (KJ mol ⁻¹)	$\ln A$ (min ⁻¹)
[CoL ₂ Cl ₂]	198	240	280	610	I	36.20	16.20
					II	144.90	34.12
[Co(L) ₂ (NO ₃) ₂]	200	260	300	630	I	46.90	20.14
					II	161.20	35.42
[NiL ₂ Cl ₂]	198	240	278	620	I	37.20	17.82
					II	146.00	35.13
[Ni(L) ₂ (NO ₃) ₂]	200	258	290	620	I	48.10	20.24
					II	162.20	36.63
[CdLCl ₂]	208	270	340	690	I	25.43	14.21
					II	106.47	26.13
[CdLSO ₄]	220	292	318	705	I	21.23	11.56
					II	97.87	24.53
[ZnLCl ₂]	212	285	310	705	I	24.56	14.32
					II	104.97	26.52
[ZnLSO ₄]	220	290	315	715	I	21.45	12.15
					II	98.37	25.87
[PdLCl ₂]	208	265	317	528	I	24.2	15.28
					II	115.5	29.51
[RhL ₂ Cl ₂]Cl	152	210	265	620	I	23.42	14.65
					II	118.95	30.93
[RuL ₂ Cl ₂]Cl	167	262	295	628	I	28.45	11.39
					II	122.59	30.67

The thermodynamic parameters, enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) of activation were calculated using standard equations and the values are given in Table 5. The present complexes show positive enthalpy values for two steps degradation. The first step enthalpy values compared with second step show that, in the first step the values are low, which may be due to the fact that the metal-organic bond is weaker than the inorganic ligand-metal ion bond. The entropy values obtained are negative for first step degradation (except Co(II) and Ru(III) complexes) and they become progressively positive for second step of degradation. This indicates that on decreasing the size of the group in the complex, gain rotational and transitional freedom decreases and hence entropy increases progressively. The free energies of complexes in both the steps are positive. The above results clearly show that the basic steps in the thermal degradation are similar for all new complexes.

Table 5. Thermodynamic parameters for the thermal degradation of the complexes

Complex	Process	ΔH (KJ mol ⁻¹)	ΔS (J K ⁻¹)	ΔG (KJ mol ⁻¹)
[CoL ₂ Cl ₂]	I	32.15	-0.83	32.00
	II	132.14	128.28	38.28
[Co(L) ₂ (NO ₃) ₂]	I	42.34	18.42	30.98
	II	153.73	147.83	40.80
[NiL ₂ Cl ₂]	I	32.51	-0.85	33.00
	II	133.94	129.28	39.82
[Ni(L) ₂ (NO ₃) ₂]	I	43.34	19.42	32.23
	II	155.63	148.93	41.70
[CdLCl ₂]	I	19.35	-27.28	36.34
	II	99.54	63.98	46.24
[CdLSO ₄]	I	15.68	-40.25	25.69
	II	92.46	56.74	43.62
[ZnLCl ₂]	I	20.13	-26.08	35.84
	II	100.14	64.18	47.02
[ZnLSO ₄]	I	16.13	-39.75	26.02
	II	91.64	55.14	44.14
[PdLCl ₂]	I	20.01	-17.66	28.90
	II	109.81	90.85	41.33
[RhL ₂ Cl ₂]Cl	I	19.17	-19.95	29.35
	II	112.99	104.16	39.03
[RuL ₂ Cl ₂]Cl	I	24.11	-11.42	30.07
	II	116.40	89.12	41.16

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