International Journal of Chemical Synthesis & Chemical Reactions
Vol. 3: Issue 1
www.journalspub.com

Preparation and Characterization of Mixed Ligand Complexes of Cobalt(II) and Ni(II) Salt of Phthalimide With Some Oxamic Acids

Ajay Agarwal, Virendra Mishra*
B.S.A College of Engineering and Technology, Mathura, UP, India

ABSTRACT

The mixed ligand complexes of oxamic acids with Co(II) and Ni(II) salt of phthalimide were prepared, where oxm = N-phenyl thio urea oxamic acid(NPTUOA), m-tolumide oxamic acid (m-TOA), N-pyrrazole oxamic acid and phth= Co(II) and Ni(II) salt of phthamlimide. These all mixed ligand complexes examined by their elemental analysis, melting points, UV–visible analysis, I.R studies, magnetic susceptibility measurements and thin layer chromatography. Elemental analysis of the complexes shows 1:2 (metal:ligand) stiochiometry for all the complexes having the general formula of $K_2[M(oxm)_2(phth)_2]$*. On the basis of above studies an octahedral geometry is proposed for all above complexes.*

Keywords: Co(II) and Ni(II) salt of phthalimide and octahedral geometry, oxamic acids

Corresponding Author
E-mail: dr.ajay0206@gmail.com

INTRODUCTION

Oxamic acids are the N-amine derivatives of aliphtatic dibasic acids. A wide range of oxamic acids can be prepared by changing the dibasic acids. Oxamic acids as a ligand offers several potential sites [1] containing nitrogen and oxygen as donor atoms [2].

Oxamic acids has been recognized that many of these complexes may serve as models for biologically [3, 4] important species having N and O as bonding sites [5–7]. Oxamic acids and its derivatives, which are useful in the treatment destroying cells and as a anticancer agents [8–10], inhibitor of tumour growth [11].

The mixed ligand complexes of oxamic acids with Co (II) and Ni (II) salt of phthalimide increases its importance because of pharmacological and other industrial applications. These have been proved to be important medicinal agents and have been suggested for use in the treatment of arthritis, tuberculosis and Epilepsy [12, 13] etc. The literature survey has revealed that a very little attention have been given on mixed ligand metal complexes of the oxamic acids with phthalimide.

EXPERIMENTAL

All chemicals used were of AR grade. The solvents were purified before use.

Physico-Chemical Measurements

The C, H and N were analyzed on Carlo–Erba-1106 elemental analyser. The nitrogen content of the complexes was determined using Kjeldahl's method. The magnetic susceptibility measurement was made at 300 K by Guy's Method using Hg [Co $(NCS)_4$] as calibrant. The standard and diamagnetic corrections were applied using Pascal's constants. IR spectra of the ligands and complexes were recorded in KBr in the range 4000–300 cm^{-1} on Beckmann-IR-5A spectrophotometer.

Synthesis of Simple Complex

An alcoholic solution of potassium hydroxide was mixed with a saturated solution of phthalimide. White crystals were at once separated which were filtered at the pump, washed well with alcohol and then dried in the oven at 25°C.

Synthesis of Metal (II) Phthalimide

The alcoholic solution of metal chloride ($CoCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$) and potassium phthalimide were mixed in 1:2 molar ratio and the coloured precipitate formed, were filtered, washed several times with distilled water and then dried in an oven at 50°C. The results of chemical analyses were in accordance with the general formula: $[M(phth)_2(H_2O)_2]$, where phth=deprotonated phthalimide.

Synthesis of m-Tolumide Oxamic Acids

0.02 M of recrystallised m-tolumide and 0.02 M freshly distilled diethyl oxalate were mixed and refluxed for half an hour in an round bottom flask about 60–100°C. On cooling the contents of the flask, 100 ml of absolute alcohol was added to dissolve the ester. The insoluble oxamide formed during the condensation reaction, was filtered out. The filtrate was then treated by saturated solution of $NaHCO_3$ in distilled water. The mixture was then distilled for about 1 hour. The solution of sodium salt of the formed acid was filtered out. On keeping the filtrate at room temperature for 1 or 2 days, the sodium salt of desired acid crystallized out as a chocolate coloured product. The free oxamic acid was obtained by adding concentrated HCl to the solution of sodium salt. Purity of the product was checked by TLC.

Synthesis of m-Tolumide-Oxamato-bis-pthalimide metal (II)

The ethanolic solution bis-phthalimidato [Co (II) and Ni (II)] and m-tolumide oxamic acid (m-TOA) were mixed together in 1:2 molar ratio. The mixture was refluxed on water bath for half an hour, and then allowed to stand for 5–6 hours. The colored precipitates formed, were the dried in the desiccators over silica gel. Purity of the complex was checked by T.L.C.

RESULTS AND DISCUSSION

Analytical Data

Analytical data reveal 1:2 (metal:ligand) stoichiometry for the Co (II) and Ni (II) complexes of N-phenyl thio urea oxamic acid (NPTUOA), m-tolumide oxamic acid (m-TOA), N-pyrrazole oxamic acid. These compounds have high melting points and are soluble in DMF, DMSO and 1,4-dioxane. These compounds are insoluble in common organic solvents.

Magnetic Moment Studies and Molar Conductance

The magnetic moment for synthesized Co (II) and Ni (II) complexes were calculated at room temperature from the magnetic susceptibility measurements and found 5.04–5.08 and 3.67–3.70 B.M., respectively, which is quite closer with spin only value of 3.87 and 2.83 B.M., favour the octahedral geometry of the metal complexes. The molar conductance of the reported complexes was 177–255 $Ohm^{-1}cm^2mol^{-1}$, respectively. These values indicate the presence of two ions respectively in the solution of the complexes (Table 1).

Infra-red Spectroscopy

In the case of oxamic acids, a sharp band has been observed at 3140–3170 cm^{-1} probably due to ν_{NH} stretching vibration, which is shifted towards positive side as a single sharp peak in the I.R. spectra of its metal complexes, showing its coordination during complex formation [14–16]. This stretching vibration is replaced by a strong single sharp band at 3175–3190 cm^{-1}. The spectra of ligands also exhibits bands in the region 1650–1640 and 1415–1400 cm^{-1} corresponding to $\nu_{asmm}coo^-$ and $\nu_{symm}coo$–, respectively, while in their complexes

$\nu_{smm}coo^{-}$ gets shifted to lower region 1340–1385 cm^{-1}.

Table 1. *Chemical analysis of the ligand/mixed ligand complexes.*

S. no.	**Ligand/complexes**	**Colour**	**M.P./dec. temp (°C)**	**Elemental analysis (%)**								**μ eff**	**Molar Conductance ($mol^{-1}cm^2mol^{-l}$)**
				Metal		**C**		**H**		**N**			
				Cal.	**Obs.**	**Cal.**	**Obs.**	**Cal.**	**Obs.**	**Cal.**	**Obs.**		
1	m-TOA	Chocolate	140	-	-	57.97	57.99	4.34	4.30	6.76	6.72	-	-
2	NPTUOA	Shinning violet	110	-	-	48.21	48.25	3.57	3.55	12.50	12.30	-	-
3	$NP_{Zole}OA$	Pink white	120	-	-	38.90	38.70	3.52	3.22	26.94	27.09	-	-
4	$K_2[Co(m\text{-}TOA)_2(phth)_2]$ $K_2[Co(C_{10}H_9O_3N_2S)_2(phth)_2]$	Brown	285	8.21	8.23	43.51	43.49	2.78	2.80	7.81	7.79	5.08	188
5	$K_2[Co\ (NPTUOA)_2(phth)_2]$ $K_2[Co\ (C_8H_6O_4N)_2(phth)_2]$	Dark green	245	7.84	7.90	38.34	38.40	2.39	2.42	11.18	11.21	5.06	177
6	$K_2[Co(NP_{Zole}OA\ )_2(phth)_2]$ $K_2[Co(C_{10}H_9O_3N_2S)_2(phth)_2]$	Light green	260	8.91	8.94	47.20	47.26	2.72	2.75	16.94	16.96	5.04	186
7	$K_2[Ni\ (\ m\text{-}TOA)_2\ (phth)_2]$ $K_2[Ni\ (C_{10}H_8O_4N)_2(phth))_2]$	Parrot green	195	8.22	8.30	43.51	43.53	2.78	2.77	7.81	7.87	3.70	255
8	$K_2[Ni(\ NPTUOA\ )_2(phth)_2]$ $K_2[Ni(C_9H_7O_3N_2S)_2(phth)_2]$	Green	240	7.85	7.89	38.34	38.39	2.39	2.37	11.18	11.21	3.68	205
9	$K_2[Ni(\ NP_{Zole}OA\ )_2(phth)_2]$ $K_2[Ni(C_{10}H_9O_3NS)_2(phth)_2]$	Light brown	240	8.91	8.93	47.20	47.24	2.72	2.74	16.94	16.98	3.67	225

Thus, a shift of 30–60 cm^{-1} in $\nu_{smm}coo^{-}$ suggests the deprotonated oxygen of carboxylic acid take part in complex formation with metal [17] and also it is observe that in the case of primary amide group, an increased ν_{CN} and decreased ν_{CO} frequencyhave almost seen. Furthermore, the separation value Δ (ν_{symCOO}^{-}- $\nu_{asym}coo^{-}$) in the range of 230–245 cm^{-1} displays unidentate bonding by carboxylic group [18–21]. The presence of ν_{CO} of the ionization of the amidic hydrogen, since a similar change occurs when a primary amide is converted to a secondary amide [14, 22].

Another bands were also present in the I.R. spectra of metal complexes of Co (II) and Ni (II), which are due to another linkage of primary ligand of phthalimide.Phthalimide molecule has two interesting –NH and –CO stretching frequency regions. The imide nitrogen is directly linked to the carbonyl group hence any change in the –NH frequency will alter the molecular environment and accordingly the frequency of –CO is shifted towards lower side even if it is not coordinated. Hence, I.R. spectra cannot make a sharp and clear cut distinction between the two coordinated viz. the coordination of imide through the nitrogen or the oxygen of the carbonyl group. However, on the basis of Lewis concept, it may be expected that the negatively charged imide nitrogen will have better possibilities of being coordinated than oxygen [23]. There is steric hindrance also if coordination is through. In free phthalimide the carbonyl frequency is obtained in the form of two bands at 1780 and 1750 cm^{-1} which get shifted by 30–45 cm^{-1} toward lower side on complexation due to mass effect [24] and secondly, the filled orbital of the imide nitrogen is made available by a quasi-aromatic delocalization, which would give a lower band order to $\nu_{C=O}$ and lower frequency. On the basis of shifting of $\nu_{C=O}$ stretching frequency towards the lower side it can be said that the coordination involves the keto form of the imide, nevertheless it is possible that the enol form may be the coordination species [25]. In this case, relative donor capacities of carbonyl oxygen and nitrogen become reversed and give rise to a large difference in the fundamental stretching frequencies of the two carbonyl groups with the decrease in their capacity for coordination with metal. This fact also confirms that the frequencies of the bands are lowered by an equivalent amount of 50–60 cm^{-1} on coordination, confirms that coordination would be through the nitrogen of the phthalimide not through the oxygen of carbonyl group of the phthalimide [26]. A strong band due to ν_{NH} observed at 3300 cm^{-1}in the spectrum of phthalimide is changed in to a band of negligible intensity in the spectrum of metal phthalimide indicating thereby, the deprotonation of –NH. The stretching frequency at 1460–1599 in the spectra of the complexes indicating the coordination through nitrogen of phthalimide [27]. It was concluded that oxamic acids coordinated through the nitrogen of –NH of secondary amine and oxygen of deprotonated carboxylic group. The absorption bands of the metal-oxygen and metal nitrogen are the characteristic bands of metal complexes.

The bands appearing in the spectra of metal complexes in the region $\nu_{M–N}$ 430–460 cm^{-1} and $\nu_{M–O}$ 370–396 cm^{-1} indicate the presence of M–O and M–N bands which show the coordination of metal ion with nitrogen and oxygen atoms of the ligands (Table 2).

Table 2. *I.R. spectral data of oxamic acids/mixed ligand complexes (cm^{-1})*

S. no.	**Ligand/complex**	**Oxamic acid/mixed ligand complexes**				**Metal salt of phthalimide**			**ν_{M-N}**	**ν_{M-O}**
		ν_{N-H}	**$\nu_{asym}COO^-$**	**$\nu_{sym}COO^-$**	**$\Delta(\nu_{asym}COO^- – \nu_{sym}COO^-)$**	**$\nu_{C=O}$**	**ν_{N-H}**	**ν_{C-N}**		
1	$[M(phth)_2(H_2O)_2]$	-	-	-		1750	3300	1480	-	-
2	m-TOA	3140	1650	1400	-	-	-	-	-	
3	NPTUOA	3170	1645	1420	-	-	-	-	-	-
4	$NP_{Zole}OA$	3160	1640	1415	-	-	-	-	-	-
6	$K_2[Co(m\text{-}TOA)_2(phth)_2]$	3178	1640	1370	240	1715	3290	1500	460	370
7	$K_2[Co(NPTUOA)_2(phth)_2]$	3190	1592	1360	232	1710	3295	1500	455	390
8	$K_2[Co(NP_{Zole}OA)_2(phth)_2]$	3195	1625	1385	240	1710	3290	1500	440	395
9	$K_2[Ni(m\text{-}TOA)_2(phth)_2]$	3175	1635	1340	245	1715	3295	1500	435	390
10	$K_2[Ni(NPTUOA)_2(phth)_2]$	3180	1610	1380	230	1710	3290	1500	430	395
11	$K_2[Ni(NP_{Zole}OA)_2(phth)_2]$	3182	1615	1370	245	1720	3295	1500	440	396

**1 Metal (Co and Ni) salt of phthalimide, *2,3,4, are oxamic acids and *6,7, 8, 9, 10 and 11 are mixed ligand complexes.*

Electronic Spectral Studies

The electronic spectra of mixed ligand complexes of m-tolumide oxamic acid (m-TOA), N-phenyl thio urea oxamic acid (NPTUOA), N-pyrrazole oxamic acid ($NP_{Zole}OA$) & phth=Co(II) salt of phthamlimide in tetra hydro furan showed two bands at 16000–16500 cm^{-1} (ν_2) and 18200–18400 cm^{-1} (ν_3) assigned as${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_2) ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3), respectively. Due to limted range of spectral instrument used, the transition ${}^4T_{1g} \rightarrow {}^4T_{2g}(F)$ (ν_1) could not be observed, hence ν_1 was calculated assuming the transition $\nu_2/\nu_1=2.10$ [28]. These bands clearly indicates that the complexes have octahedral geometry [29, 30]. The electronic spectra of complexes in 1,4-dioxane showed three spin allowed bands due to splitting of ground terms at 8900–9500 cm^{-1} (ν_1), 15,100–16,000 cm^{-1} (ν_2) and 27,400–28,900 cm^{-1} (ν_3) assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ ν_1, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ν_2 and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) ν_3. These bands clearly indicates that reported Ni(II) complexes are octahedral in nature [31, 32]. The energies of these transitions may be reported as a function of 10 Dq and parameters B_{35}. The calculated values of ν_2 and ν_3 were found in close agreement with the observed values. This indicates the octahedral structure of the complexes is also supported by the ratio

ν_2/ν_1, which comes in the range 1.68–1.69 in each case. The values of 10Dq, B, β β_{35} are presented [31] in (Tables 3 and 4).

Table 3. *Electronic spectra of Co (II) complexes.*

Complex no.	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_2/ν_1=2.1 (cm^{-1})	B	β35	10Dq (cm^{-1})	L.F.S.E. (kJ/Mole)
6	16500	18400	7857	759	0.67	8662	47.14
7	16000	18400	7619	798	0.71	8523	45.71
8	16400	18200	7809	753	0.67	6832	46.85

Table 4. *Electronic spectra of Ni (II) complexes.*

Complex no.	Observed bands position (cm^{-1})			Calculated bands position (cm^{-1})		$(\nu_3\text{-}\nu_2)_{cal}–(\nu_3–\nu_1)_{obs}$	B	ν_2/ν_1	β35	L.F.S.E. (kJ/Mole)
	ν_1	ν_2	ν_3	ν_2	ν_3					
9	8900	15,100	27,400	14,923	27,571	348	1053	1.69	0.97	25.42
10	9500	16,000	28,700	15,870	28,830	260	1080	1.68	1.00	27.14
11	9400	15,800	27,900	15,651	28,049	298	1033	1.68	0.96	26.85

CONCLUSION

The reported mixed ligand complexes of oxamic acids and phthalimide with Co(II) and Ni(II) shows octahedral geometry.

REFERENCES

[1] P. Arrizabalaga, P. Caston, J.P. Laurent. *Transit Metal Chem*. 1980; 5(1): 204–6p.
[2] S. Zagan, T. Negreanu. Pirjol Ovidius, *Univ Ann Med Sci – Pharm*. 2006; IV(1).
[3] S.J. Lippard. *Angew. Chem. Engl*. 1988; 27: 344p.
[4] R.L.Carrol, C.B.Gorman. *Angew Chem Int*. 2002; 41: 4378p.
[5] M.N. Hughes. *The Inorganic Chemistry of Biological Processes*. 2nd Edn., New York: John Wiley & Sons; 1981.
[6] S.C. Lemos, S.J.S. Franchi, A.V.G. Netto, A.E. Mauro, O. TreuFilho, R.C.G. Frem, E.T. Almeida, C. Torres. *J Therm Anal Calorim*. 2011. doi:10.1007/s10973-011-1494-9.
[7] C.T. Carvalho, F.J. Caires, L.S. Lima, M. Ionashiro. *J Therm Anal Calorim*. 2011. doi:10.1007/410973-011-1679-2.
[8] S.E. Livingstone, J.D. Nolan, A.E. Mihkelson. *Inorg Chem*. 1968; 7: 1447p.
[9] S.E. Livingstone, J.D. Nolan, A.E. Mihkelson. *Inorg Chem*. 1970; 9: 2545p.
[10] B. Rosenberg, L. Van Camp. *Cancer Res*. 1970; 30: 1799p.
[11] S.P. Perlepes, Th.F. Zafiropoulos, J.K. Kouinis, A. Galinos. *Z Naturforsch*. 1981; 36b: 697–703p.
[12] D.S. Goldman. *Biochem Biophys Acta*. 1960; 45: 27Ap.
[13] British Patent,730910 (1955), invs.: Parke-Davis & Co.
[14] J.K. Kouinis, J.M. Tsangaris, A.G. Galinos. *Z Naturforsch*. 1978; 33b: 987p.
[15] K.A. Hoffmann, U. Enrhardt, Ber. 1913; 46: 1457p.
[16] R.M. Burger. *Struct Bonding*. 2000; 97: 287p.
[17] O. Kahn. *Adv Inorg Chem*. 1995; 43: 180p.
[18] S. Wafa, M. Abu, M. Rafat. *J Ind Chem Soc*. 1990; 29A: 285p.
[19] G.B. Decon, R.J. Philips. *Coord Chem Rev*. 1980; 33: 227p.
[20] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. New York: John Wiley; 1980.
[21] L.J. Bellamy. *The Infrared Spectra of Complex Molecules*. London: Methuen; 1962.

[22] A.G. Galinos, J.M. Tsangaris, J.K. Kouinis. *Z Naturforsch.* 1977; 32b: 645p.

[23] P.C. Bailer, Jr. *Reinhold.* New York; 1956, 180p.

[24] G.F. Svatos, C. Curran, J.V. Quaglino. *J Am Chem Soc*. 1955; 77: 23,6159p.

[25] N.P. Stabbert, D.A.Thronton. *Spectrosc Lett*. 1970; 3: 83p.

[26] A. Agarwal, V. Mishra, S. Arora. *IJTCK*. 2017; 3(1): 5p.

[27] P.C.H. Mitchell. *J Iinorg Nucl Chem*. 1963; 25: 9639p.

[28] A.B.P. Lever, D.ogden. *J Chem Soc. A*. 1967; 2041p.

[29] ABP Lever. *Inorganic Electronic Spectroscopy*. Amsterdam: Elsevier; 1968.

[30] O. Bostrup, C.K. Jorgensen. *Acta Chem Scand*. 1957; 11: 1223p.

[31] R.L. Carlin. *Trans Met Chem*. 1968; 4: 211p.

[32] R.L.Carlin. *Trans.Met.Chem*. Vol. I, NY: Marcel-Dakker; 1965, Chap I, 20p.