



Synthesis and Characterization of Co (II) And Ni (II) Complexes of 2, 5-Substituted 1, 3, 4-Oxadiazole Derivatives

Subha C and Selvaraj A

Department of Chemistry, CBM College, Coimbatore-641 042, INDIA

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Abstract

Eight new Co(II) and Ni(II) complexes with variously substituted 1,3,4-oxadiazoles (L_1 - L_8) have been prepared and characterized by magnetic susceptibility, molar conductance, molecular weight determination and spectral studies. All the cobalt complexes exhibit the composition $Co(L)_2Cl_2 \cdot 2H_2O$ and the formula $Ni(L)_2(SO_4) \cdot 2H_2O$ has been assigned to Ni(II) complexes. Although 1,3,4-oxadiazoles have three coordinating sites, namely two ring nitrogen and one oxygen, the spectral studies indicate that only the two ring nitrogen involved in the coordination. Electronic spectral data reveal that these complexes have octahedral geometry.

Keywords: Complexes, 1,3,4-oxadiazole, magnetic property, octahedral geometry.

Introduction

The coordination chemistry of Co(II) and Ni(II) are well established and they form complexes with a variety of organic ligands. 1,3,4 - Oxadiazole, considered as an important five member compound among the huge heterocyclic families, has been studied as an excellent candidate for material applications during the past years due to its excellent thermal, chemical stabilities and high photoluminescence quantum yields. These properties combined with its electron deficient nature and good electron accepting ability, have led to many potential applications in organic light emitting diodes¹⁻³. The wide range of applications of the ligand and its metal complexes are used our interest to prepare a new series of some of those metal complexes. We describe in this paper, the synthesis and characterization of Cobalt(II) and Ni(II) complexes with eight differently substituted 1,3,4- Oxadiazoles.

Material and Methods

Reagents: The variously substituted 1, 3, 4-Oxadiazoles (L_1 - L_8) were prepared, following the reported procedures⁴. Purified EtOH (95%) was used as solvent. Cobalt (II) chloride and Nickel (II) sulphate was of Analar grade.

Synthesis of metal complexes: A solution of [M (II)] salt [Cobalt (II) chloride for Co (II), Nickel (II) sulphate for Ni (II)] (5mmol) in ethanol (30ml) was added to a solution of Oxadiazole (15 mmol) in ethanol (30ml) and the mixture was boiled under reflux on a water bath for 3 – 4hrs. The solvent was then removed by vacuum distillation and the pasty residue was thoroughly washed with acetone and dry ether to remove unreacted M(II) and oxadiazole. The complex obtained was dried over P_2O_5 in vacuum.

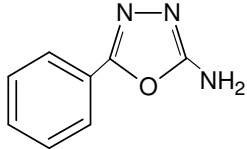
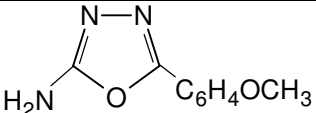
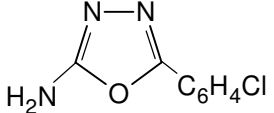
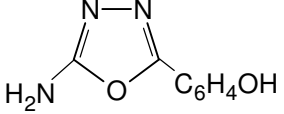
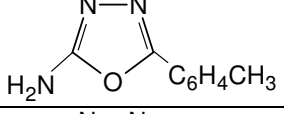
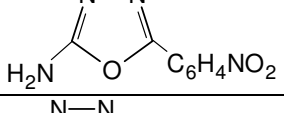
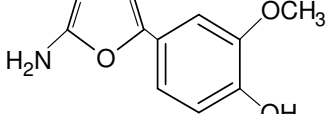
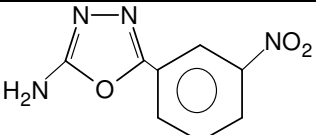
Physical measurements: Molecular weight determinations were carried out by the freezing point depression method, using camphor as solvent. The metal content of each complex was estimated by complexometric EDTA titration^{5,6} using xylenol orange as an indicator. Conductance measurements were performed on 10^{-3} mol dm^{-3} solutions of the complexes in acetonitrile using CM-82 Eli co Digital Conductivity meter with a dip type conductivity cell fitted with platinum electrodes. (Cell constant = 1.0 cm^{-1}). The effective magnetic moments of the complexes were determined by Guoy method at room temperature. The IR spectra of the ligands and the complexes were recorded on Shimadzu FT-IR 8000 spectrophotometer in the $4000 - 400 \text{ cm}^{-1}$ region using the KBr disc technique.

Results and Discussion

The colour of the cobalt (II) oxadiazole complexes ranges from yellow to dark brown whereas the colour of the Nickel (II) oxadiazole complex ranges from yellow to Orange. All the complexes were found to be solids, insoluble in water and soluble in ethanol, DMSO, Acetonitrile etc., the complexes were non-hygroscopic and stable in air. A perusal of the conductivity values for the complexes of Ni(II)-oxadiazole reveals that all the complexes synthesized have very low conductivities in the range of 10^{-6} mho.

Conductivity studies: The molar conductance values of cobalt (II) chloride complexes are found to be in the range of 10^{-6} mho indicating that these complexes are non-electrolytes. This observation suggests that the complex molecule is neutral with the sulphate ions held tightly within the coordination sphere along with the oxadiazole ligands.

Table-1
The structures of the synthesized ligands are as follows

	L₁	2-Phenyl 5-amino 1,3,4-oxadiazole
	L₂	2'-methoxy phenyl 5-amino 1,3,4-oxadiazole
	L₃	2'-chlorophenyl 5-amino 1,3,4-oxadiazole
	L₄	2'-hydroxyphenyl 5-amino 1,3,4-oxadiazole
	L₅	2'-methylphenyl 5-amino 1,3,4-oxadiazole
	L₆	2'-nitrophenyl 5-amino 1,3,4-oxadiazole
	L₇	3'-methoxy-4'-hydroxyphenyl 5-amino 1,3,4-oxadiazole
	L₈	3'-nitrophenyl 5-amino 1,3,4-oxadiazole

Molecular weight determination: The observed molecular weights of all the complexes show that one metal atom coordinates with two oxadiazole ligand molecules indicating that they behave as 1:2 non-electrolyte. The results of both molar conductance studies and molecular weight determinations complement each other. The most probable molecular formulae of complexes studied in this work are derived from the metal content and the corresponding experimental molecular mass. The molecular formula for the cobalt (II) oxadiazole and Ni (II) oxadiazole complexes, their molecular weight, Conductivity, colour and Magnetic moment are given in Table 1 and 2 respectively.

Magnetic Properties: The effective magnetic moments (μ_{eff}) of Cobalt(II) and Nickel(II) complexes were calculated from their magnetic susceptibilities obtained by Guoy's method and the data are given in table-2 and 3 respectively. The μ_{eff} values of Cobalt (II) complexes are found to be in the range of 4.13-6.68

BM. These values are in agreement with the high spin d^7 complexes. For Ni (II) complexes, when the values of μ_{eff} are compared with μ_{obs} value, the μ_{obs} values are higher than μ_{eff} . The μ_{obs} value ranges from 4-5 BM. This may be due to the following reasons the orbital angular momentum is quenched for $(t_{2g})^6 (e_g)^2$ configurations, spin-orbit coupling is greater because of positive quantity of α , Δ and negative quantity of λ . Hence the observed magnetic moment is higher than the predicted magnetic moment. These higher values are in accordance with high spin d^8 complex⁷.

IR spectral studies: The IR spectra of the ligands were compared with those of the cobalt (II) complexes in order to confirm the binding mode of the 2, 5-disubstituted 1, 3, 4-oxadiazoles ligands to the cobalt (II) ion in the complexes. The characteristic IR bands of the complex differ from free ligand providing significant indications about the co-ordination and bonding sites of the ligand. FTIR spectral analysis of

complexes in general reveals that C=N stretching has shifted from 1511 to 1548 cm^{-1} . The upward shift in the C=N stretching frequency indicates the formation of coordinate covalent bond involving the nitrogen of azomethine group C=N with the metal atom. IR spectra of the complexes synthesized in the present studies indicate the absence of the three additional vibrational modes that would have arisen had there been an M-OH₂ bond. Hence it can be concluded that all the complexes synthesized in the present investigation do not contain H₂O molecule within the coordination sphere. Cobalt (II) complexes show an absorption band at 265 cm^{-1} which proves beyond doubt

that the existence of M-Cl bond in the complexes and the presence of Cl⁻ inside the co-ordination sphere. For Ni (II) oxadiazole complexes, the appearance of a strong absorption band at 1580-1600 cm^{-1} is due to ν (C=N). The coordination of the azomethine nitrogen to the metal center was confirmed in the IR spectra of the complex by a shift of the ν (C=N) band to lower frequency. Additional evidence for the coordination of the azomethine nitrogen is the presence of ν (M-N) bands in the frequency range of 300-500 cm^{-1} . The IR spectral absorption band values of Co (II) and Ni (II) oxadiazole complexes are given in tables-4 and 5 respectively.

Table-2
Physical and Analytical data of Co (II) – Oxadiazole complexes

Complex formula	Molecular Weight found (theor.) (Cal)	Conductivity $\nu \times 10^{-6}$	Colour	Magnetic moment $\mu \times 10^{-2}$
[Co(L ₁) ₂ Cl ₂].2H ₂ O	486.83 (511.8)	08.51	Light Brown	6.68
[Co(L ₂) ₂ Cl ₂].2H ₂ O	536.83 (548.23)	12.50	Dirty Yellow	4.36
[Co(L ₃) ₂ Cl ₂].2H ₂ O	555.83 (541.29)	10.53	Dirty Yellow	6.05
[Co(L ₄) ₂ Cl ₂].2H ₂ O	518.83 (503.70)	32.60	Dark Brown	5.24
[Co(L ₅) ₂ Cl ₂].2H ₂ O	515.83 (515.83)	14.90	Brown	4.94
[Co(L ₆) ₂ Cl ₂].2H ₂ O	577.83 (579.96)	17.19	Brown	5.71
[Co(L ₇) ₂ Cl ₂].2H ₂ O	579.83 (553.56)	25.90	Pale Brown	4.69
[Co(L ₈) ₂ Cl ₂].2H ₂ O	577.83 (553.01)	15.22	Yellow	4.13

Table-3
Physical and Analytical data of Ni (II) – Oxadiazole complexes

Complex formula	Molecular Weight found (thert) (Cal)	Conductivity $\nu \times 10^{-6}$	Colour	Magnetic moment $\mu \times 10^{-2}$
[Ni(L ₁) ₂ (SO ₄) ₂].2H ₂ O	512.71 (502.02)	03.70	Yellow	5.30
[Ni(L ₂) ₂ (SO ₄) ₂].2H ₂ O	572.71 (585.06)	07.58	Dirty yellow	4.87
[Ni(L ₃) ₂ (SO ₄) ₂].2H ₂ O	580.71 (585.06)	08.55	Pale orange	4.96
[Ni(L ₄) ₂ (SO ₄) ₂].2H ₂ O	544.71 (535.99)	16.75	Dark brown	4.69
[Ni(L ₅) ₂ (SO ₄) ₂].2H ₂ O	540.71 (541.29)	11.70	Dark orange	5.64
[Ni(L ₆) ₂ (SO ₄) ₂].2H ₂ O	602.71 (593.10)	15.21	Orange	5.53
[Ni(L ₇) ₂ (SO ₄) ₂].2H ₂ O	604.71 (586.23)	12.18	Pale brown	5.29
[Ni(L ₈) ₂ (SO ₄) ₂].2H ₂ O	602.71 (604.51)	07.14	Light yellow	5.61

Table-4
IR absorption bands (in cm^{-1}) of the ligands and Co (II)-Oxadiazole complexes

Name of the complex	γ (C=N) ^a	γ (C=N) ^b	γ (-NH ₂)	Aromatic γ (=C-H)	γ (O-H) water of crystallization	γ (M-Cl)
Co-L ₁	1511	1605.34	3460.23	3065.52	3287.51	278
Co-L ₂	1510.11	1593.89	3469.20	3061.77	3281.74	265
Co-L ₃	1594.02	1619.96	3464.26	3070.29	3278.09	261
Co-L ₄	1529.82	1548.03	3469.11	3062.96	3286.41	301
Co-L ₅	1511.14	1548.08	3467.23	3066.78	3203.47	273
Co-L ₆	1535.94	1556.00	3452.67	3001.75	3203.83	269
Co-L ₇	1513.49	1522.16	3462.35	3077.08	3238.08	264
Co-L ₈	1513.28	1593.78	3463.41	3069.87	3278.16	264

^a-for free ligand, ^b-for complexes

Table-5
IR absorption bands (in cm⁻¹) of the ligands and Ni (II)-Oxadiazole complexes

Name of the complex	ν (C=N) ^a	ν (C=N) ^b	ν (-NH ₂)	Aromatic ν (=C-H)	ν (O-H) water of crystallization	ν (M-SO ₄ ²⁻)
Ni-L ₁	1511	1605.68	3460.45	3064.26	3281.74	1029.22
Ni-L ₂	1510.11	1594.08	3474.26	3061.74	3280.94	1032.24
Ni-L ₃	1594.02	1609.56	3464.24	3074.34	3276.09	1012.85
Ni-L ₄	1529.82	1600.90	3489.93	3026.75	3277.89	1036.73
Ni-L ₅	1511.14	1535.89	3467.12	3063.13	3273.17	1030.64
Ni-L ₆	1535.94	1557.76	3466.89	3000.10	3203.01	1022.87
Ni-L ₇	1513.49	1522.27	3463.80	3071.95	3287.99	1040.40
Ni-L ₈	1513.28	1590.45	3463.73	3067.39	3278.72	1067.77

^a-for free legend, ^b-for complexes

UV spectral studies: To understand the UV-visible spectral behaviour of Cobalt (II)-oxadiazole complexes, typical spectrum of Cobalt (II)-L₂ complex has been recorded and interpreted. The UV-visible spectrum of Co(II)-L₂ complex contains one well resolved absorption band around 8500cm⁻¹ and a multiple absorption band around 21,000 cm⁻¹. The absorption band observed around 8500cm⁻¹ for the cobalt (II)-L₂ complex can be assigned to ⁴T_{1g} → ⁴T_{2g} transition. The multiple band observed around 21,000cm⁻¹ can be assigned to the two transitions, viz, ⁴T_{1g} → ⁴A_{2g} (γ₂), ⁴T_{1g} → ⁴T_{2g} (P) (γ₃) and the third are to the spin-orbit coupling effects or transitions to doublet state. The three absorption bands noticed for the Nickel (II)-L₂ complex in the present studies can be assigned to ³A_{2g} → ³T_{2g} (γ₁= 9,000cm⁻¹), ³A_{2g} → ³T_{1g} (F) (γ₂=17,000cm⁻¹) and ³A_{2g} → ³T_{1g} (P) (γ₃= 28,000cm⁻¹).

Table-6
Electronic Absorption Spectral data for Metal (II)-L₂ complexes

Complex	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)
Cobalt(II)-L ₂	8,500	Multiple absorption band around 21,000	
Nickel(II)-L ₂	9,000	17,000	28,000

Conclusion

Based on the foregoing observations, the following conclusions have been drawn: i. All the Cobalt (II) and Nickel (II) oxadiazole complexes synthesized are 1:2 non-electrolytes. ii. Oxadiazole ligand acts as a bidentate ligand. iii. Although, 2,5-disubstituted 1,3,4-oxadiazoles contain three potential co-ordinating sites, namely the two ring nitrogen and the oxygen, it has been shown by IR and UV spectral studies that it is the two ring nitrogen atoms that are involved in complexation and not the oxygen atom. Thus, 2, 5-disubstituted 1, 3, 4-oxadiazoles act as bidentate ligands. iv. IR spectral studies confirm the presence of two water molecules in all the complexes as water of crystallization. v. Magnetic moments and electronic spectra of the complexes reveal that the complexes are spin-free and have octahedral geometry.

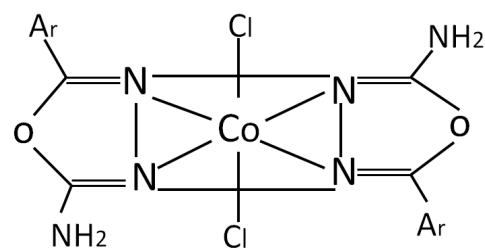


Figure-1
The most probable structure of Cobalt (II) –oxadiazole complexes

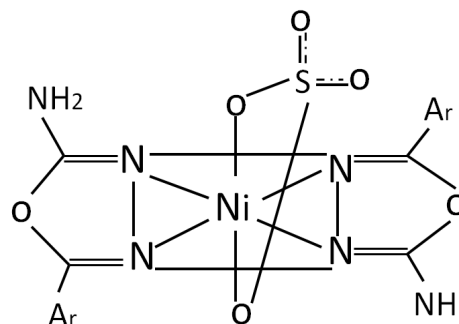


Figure-2
The most probable structure of Nickel(II)-oxadiazole complexes

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