

Study and Synthesis Metal Complexes with 5-(4-Aminophenyl)-3-((Dipropylamino) Methyl)-1,3,4-Oxadiazol-2(3H)-Thione

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Abstract: A compound 5-(4- amino phenyl)-3-((dipropyl amino)methyl)-1,3,4-oxadiazole-2(3H)-thione was synthesized and characterized to gether with its metal ions complexes of Co^{+2} , Ni^{+2} and Cu^{+2} . This ligand and its metal complexes were characterized by means different techniques, FTIR, IR UV-Vis spectra, magnetic susceptibility, (C.H.N) analysis ,atomic absorption and mole ratio(jobs method). The proposed structure of the complex in all case is ML_2X_2 [where M: is Co^{+2} , Ni^{+2} and Cu^{+2} ,L is the ligand and x is chloride.

Keywords: 4-minobenzoic acid, dipropylamine and oxadiazole complex

1. Introduction

Oxadiazoles are five-membered heterocyclic compounds with two nitrogen and one oxygen atoms. They are synthesized by ring condensation and rearrangement reactions. Some of the recent studies have shown that 1,3,4-oxadiazoles and its derivatives were reported to possess antimicrobial⁽¹⁾ anti-inflammatory⁽²⁾ antibacterial⁽³⁾ anticancer⁽⁴⁾ antifungal⁽⁵⁾ tuberculostatic and analgesic⁽⁶⁾ activities.

2. Experimental

2.1 Materials

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

2.2 Physical Measurements

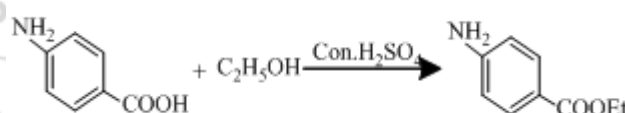
Metal point was obtained on abuchi SMP-20 capillary melting point apparatus and is uncorrected. Infrared spectra were recorded as (KBr) disc using (8400) (FTIR) shimadzu spectrophotometer in the range $(4000-400)\text{cm}^{-1}$. UV-vis spectra for the compounds were measured in the region $(200-900)\text{nm}$ for (10^{-3}M) solution in ETOH at (RT) by using (Uv-vis) spectrophotometer type Shimadzu. Metal were determined using ashimadzu(A.A)680 G atomic absorption spectrophotometer. Conductivity measurements were made with ETOH solution using a PW 9526 digital conductivity meter, and room temperature magnetic moment were measured with amagnetic susceptibility balance (Jonson Matthey Catalytic System Division).

3. Synthetic Procedures

Preparation of Compound [1]

To stirred ethanolic solution of 4-aminobenzoic acid (5g, 0.01mole) was added slowly H_2SO_4 (20ml). The reaction mixture was refluxed for 2hrs. The white precipitate that separated on cooling and filtered off., and dried at room

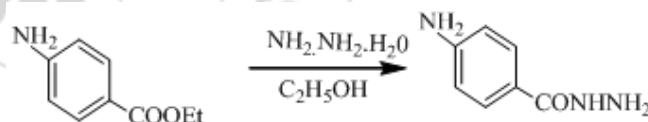
temperature. Yield= 75%.



Scheme (1): The preparation of compound [1]

Preparation of Compound [2]

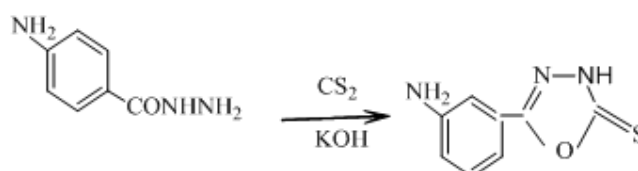
A mixture of compound(1) (0.4g, 0.1mole) and hydrazine hydrate(10ml, 0.5 mole) was heated under reflux for 1hrs in abs. ethanol (15ml). Then left to cool, the white precipitate was collected by filtration and dried at room temperature. Yield= 72%.



Scheme 2: The preparation of compound [2]

Preparation of Compound [3]

To stirred ethanolic solution of KOH(0.2 g, 0.56mol) in abs. ethanol (15ml) and compound [2](0.4g, 0.2 mole), was added slowly CS_2 (10ml). The reaction mixture was refluxed for 2hrs, the yellow precipitate that separated on cooling and filtered off.



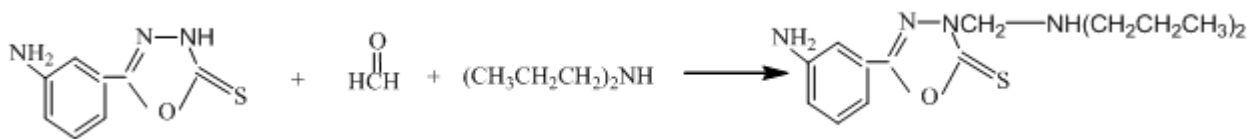
Scheme 3: The preparation of compound [3]

Preparation of 5-(4- amino phenyl)-3-((dipropyl amino)methyl)-1,3,4-oxadiazole-2(3H)-thione

A mixture of compound [3] (2.92 g, 0.5 mole), dipropylamine(1.6g,0.7mole) and formaldehyde(8ml) was a

stirred in the water bath of a snow for 3hrs in hexane(10ml). The white precipitate that separated on cooling and filtered off., and dried at room temperature. Physical data for the

ligand are given in Table(1).



Scheme 4: The preparation of 5-(4- amino phenyl)-3-((dipropyl amino)methyl)-1,3,4-oxadiazole-2(3H)-thione
Preparation of the Ligand Complexes

Co(II) ,Ni(II) and Cu(II) complexes were prepared as follows:-

(0.02)mole of metal (II) chloride was dissolved in 30ml of methanol and add to ligand solution (0.04mole dissolved in 25 ml of methanol) the mixture refluxed at room temperature; the solid product was then filtered and re-crystallized with ethanol.Physical data for the complexes are given in Table(1).

Table 1: The physical data ,elemental analysis and molar conductance of 5-(4- amino phenyl)-3-((dipropyl amino)methyl)-1,3,4-oxadiazole-2(3H)-thione and its complexes.

Compound	color	Yield%	M.P	Found (Calcu.)%				Molar conductance Ohm ⁻¹ cm ² mole ⁻¹
				M	C	H	N	
C ₁₅ H ₂₁ N ₃ OS	white	65	180-182	-	63.83(63.50)	4.25(4.20)	14.89(14.62)	-
Co(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	brown	70	210-212	8.50(8.80)	51.95(51.80)	3.46(3.55)	12.12(12.30)	4.10
Ni(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	red	55	250-252	8.46(8.50)	51.95(51.20)	3.46(3.40)	12.12(12.22)	3.2
Cu(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	green	72	280-282	9.10(9.25)	51.61(51.80)	3.44(4.60)	12.04(12.15)	0.25

4. FT-IR Spectra of the Ligand and its Metalcomplexes

The ligand prepared in this work exhibit characteristic band due to (C=N) stretching vibration which appears around (1602)cm⁻¹. Band appears in the region (839)cm⁻¹ is due to the (C=S). The spectra of the prepared complexes showed some changes regarding the position , shape, and intensity of the peaks , of (C=N)and (C=S) peaks, is an indication of the

coordination through sulfur atom of the (C=S) group with the metal ion the peak at (465 - 475)cm⁻¹ are assigned to the (M-S) stretching vibration (7-9). up on the coordination of the ligand with ion, the absorption of -C=N- (azomethine groups) undergoes shift to lower frequency,again this change is an indication for the coordination process; and the peak at (501-543) cm⁻¹ is assigned to the (M-N)cm⁻¹ stretching vibration(10-12) the peak at (403- 412) is assigned to the (M-Cl) stretching vibration of the complexes.

Table 2: The most diagnostic FT-IR bands (in cm⁻¹) of 5-(4- amino phenyl)-3-((dipropylamino) methyl)-1,3,4-oxadiazole-2(3H)-thione and its complexes

Compound	U(C=N)	U (C=S)	U(M-N)	U(M-S)	U(M-Cl)
C ₁₅ H ₂₁ N ₃ OS	1602	839	-	-	-
Co(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	1592	822	520	470	403
Ni(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	1585	825	501	465	410
Cu(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	1569	828	543	475	412

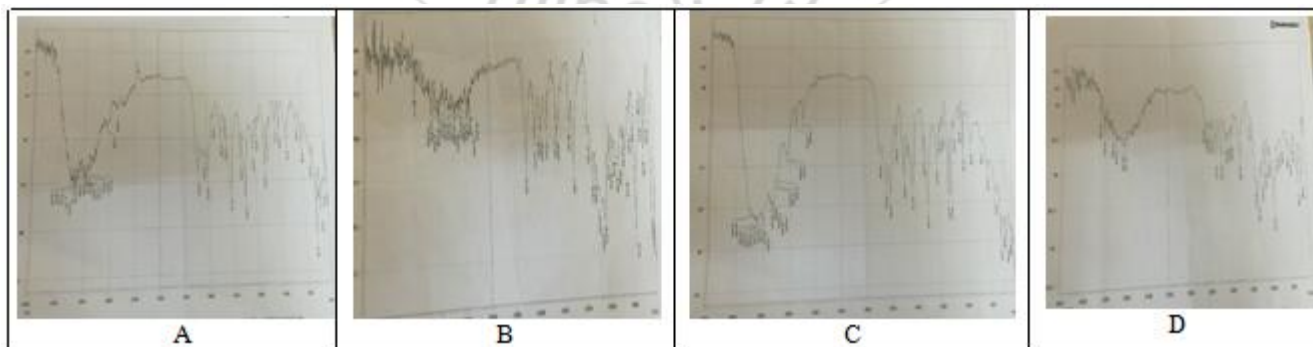


Figure 1: FTIR spectra of (A) C₁₅H₂₁N₃OS ,(B) Co(C₁₅H₂₁N₃OS)₂Cl₂ , (C) Ni(C₁₅H₂₁N₃OS)₂Cl₂ and (D) Cu(C₁₅H₂₁N₃OS)₂Cl₂

5. Electronic Spectra and Magnetic Properties

The electronic spectra of the ligand 5-(4- amino phenyl)-3-((dipropyl amino) methyl)- 1,3,4-oxadiazole-2(3H)-thione showed two well distinguished absorption bands at 242 nm (41322 cm⁻¹) and 365 nm (27397 cm⁻¹). The spectra of the Co(II) complex was showed three

bands can be assigned at(14705, 17123 and 26178) cm⁻¹ these to electronic transition of ⁴T_{1g}^F→⁴T_{2g}^F (V₁), ⁴T_{1g}^F→⁴A_{2g}^F (V₂),⁴T_{1g}^F→⁴T_{1g}^P (V₃).

The measured magnetic susceptibility and electronic spectra showed that the cobalt adapt an octahedral structure with brown color⁽¹³⁻¹⁴⁾.The electronic spectra of the Ni(II) complex red in color showed three bands at (13157, 15243 and 27624)

cm⁻¹ these assigned to electronic transition
³A_{1g}^F → ³T_{2g}^F (V₁), ³A_{2g}^F → ³A_{2g}^F (V₂), ³A_{2g}^F → ⁴T_{1g}^P (V₃).

The measured magnetic susceptibility was (2.86)B.M which indicate that the complex is paramagnetic, and octahedral geometry, the value of magnetic susceptibility correspond to the resulted of the Ni(II) octahedral geometry complexes⁽¹⁵⁾. Magneticsusceptibilityof Ni(II) complexes in square planar complexes is zero, while it takes certain values in case of octahedral⁽¹⁶⁻¹⁸⁾. The spectra of the green Cu(II) complex was characterize by the band at (16339)cm⁻¹ to be due to ²E_g → ²T_{2g} transition . Magneticsusceptibility measurement give the value (1.56)B.M this is not far away from the value of (M_{s,0}=1.7 B.M). It is quite obvious that no the complex doesn't adapt the square planar structure.

Table 3: Electronic spectra for complexes of 5-(4- amino phenyl)-3-{(dipropyl amino) methyl} -1,3,4-oxadiazole-2(3H)-thione

Compound	μ _{eff}	Band position (cm ⁻¹)	Assignment
C ₁₅ H ₂₁ N ₃ OS	-	27397 41322	
Co(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	4.93	14705 17123 26178	⁴ T _{1g} ^F → ⁴ T _{2g} ^F ⁴ T _{1g} ^F → ⁴ A _{2g} ^F ⁴ T _{1g} ^F → ⁴ T _{1g} ^P
Ni(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	2.86	13157 15243 27624	³ A _{1g} ^F → ³ T _{2g} ^F ³ A _{2g} ^F → ³ A _{2g} ^F ³ A _{2g} ^F → ⁴ T _{1g} ^P
Cu(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	1.56	16339	² E _g → ² T _{2g}

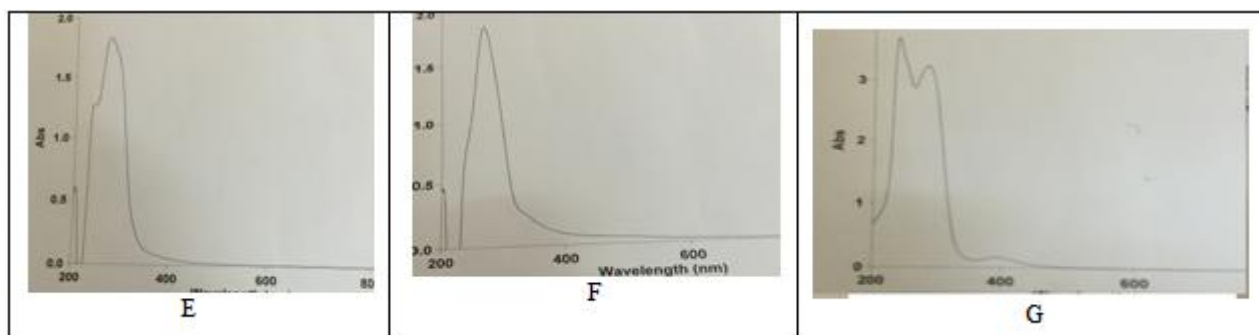


Figure 2: UV-Vis spectra of (E) C₁₅H₂₁N₃OS, (F) Co(C₁₅H₂₁N₃OS)₂Cl₂ and (G) Ni(C₁₅H₂₁N₃OS)₂Cl₂

6. Study of the Complexes Inorganic Solvent

The widely applied method used to study the nature of complex formation in solution is that of mole ratio plot of job⁽¹⁹⁾. Mixtures of ligands with the metal ions mentioned above which give colored solution in acetone. Fig.3 to Fig.5 shows the change in optical density of the observed light with the ratio of L/M . Table (4): showed value of M:L and maximum lumda ; which is in comply with the isolated metal complexes in the solid complexes

Table 4: Ratio of ligand to the metal of the complex in solution

Complex	λ _{max} (nm)	M:L
Co(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	332	1:2
Ni(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	350	1:2
Cu(C ₁₅ H ₂₁ N ₃ OS) ₂ Cl ₂	445	1:2

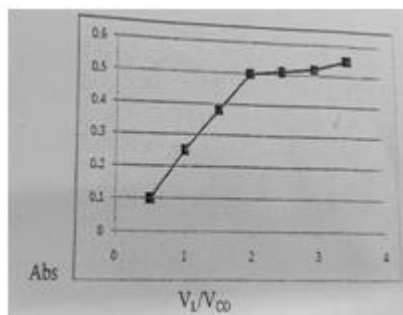


Figure 3: Mole ratio plot of Co(C₁₅H₂₁N₃OS)₂Cl₂,

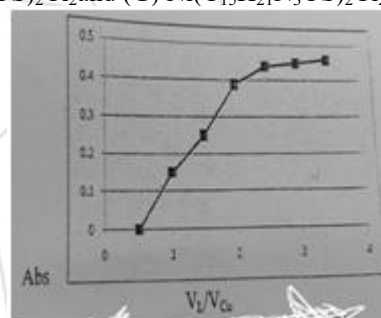


Figure 4: Mole ratio plot of Cu(C₁₅H₂₁N₃OS)₂Cl₂

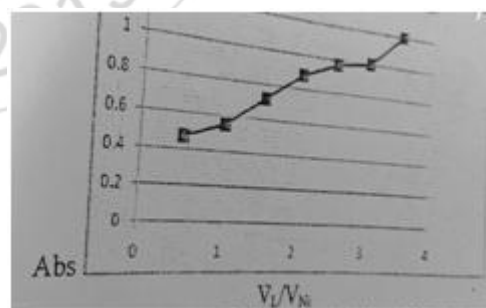


Figure 5: Mole ratio plot of Ni(C₁₅H₂₁N₃OS)₂Cl₂

References

- [1] Ingole SP, Mohane SP, Berad BN. Synthesis and antimicrobial activity of 2-alkyl-5-(Pyrid-4-yl)-1,3,4-oxadiazole. Asian J Chem. 2007; 19;2683-6.
- [2] Amir M, Javed SA, Kumar H. Synthesis of some 1,3,4-oxadiazole derivatives as potential

- anti-inflammatory agents. Indian J Chem. 2007;46B: 1014-9.
- [3] Siddiqui N, Khan SA, Bhat MA. Synthesis and antibacterial activity of coumarin incorporated 1,3,4-oxadiazoles. Indian J Het Chem. 2005; 14:271-2.
- [4] ShivaramaHolla B, Poojary KN, SubrahmanyaBhat K, Ashok M, Poojary B. Synthesis and anticancer activity studies on some 2-Chloro-1,4-bis-(substituted-1,3,4-oxadiazole-2-ylmethyl enoxy) phenylene derivatives. Indian J Chem. 2005; 44B: 1669-73.
- [5] Mishra A, Singh DV, Mishra RM. Synthesis, antifungal activity of new 1,3,4-oxadiazole(3,2-b)-s-triazine-5-ones and their thiones analogues. Indian J Het Chem. 2005; 14 :289-92.
- [6] Franski R. Biological activities of the compound
- [7] J.R. Ferraro and W.R. Walker. Inorg Chem. 4. 1382, (1967).
- [8] M.M., Mostava. A.M. Shallaby and A.A. el-Asmy. J. Inorg Nucl. Chem. 43. 2992. (1981).
- [9] C.B. Mahto. J Indian Chem. Soc. 57. 481 (1980).
- [10] V.J. Babar. D.V. Khasnis and V.M. Shinde. J. Indian chem. Soc. 58. 970. (1978).
- [11] B. Dash and S.K. Mahapatra. J. Inorg. Nucl. Chem., 37, 271, (1975).
- [12] N. C. Mishra. J. Indian Chem. Soc., 55, 839, (1978).
- [13] N.N. Greenwood and A. Eamshaw. Chemistry of the Elements Pergamon press. (1986).
- [14] D. Nicholas. Pergamon Texts in Inorganic Chemistry Pergamon Press. Oxford. 1st Ed., 24, 1087-1090. 1152-1154 (1973).
- [15] M.S. Patial and J.T. Shah. J. Indian Chem. Soc. 58. 944. (1981).
- [16] C.B. Mahto. Indian Chem. Soc. 57. 481. (1980).
- [17] B. Singh and H. Missra. J. Indian Chem. Soc. LXIII, 692m (1986).
- [18] M. S. Patial and J. T. Shah. J. J. Indian Chem. Soc. 58. 944. (1981).
- [19] P. Jop. Ann. Chem, 9, 113, (1926).