

Synthesis, Characterization and Study of Thermal, Magnetic and Electrical Properties of Transition Metals Complexes of Some Newly Synthesized 2, 5-Substituted Oxadiazoles

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Abstract: This paper reports the synthesis and characterization of transition metal complexes of newly synthesized 2,5-substituted-1,3,4-oxadiazoles with Cu(II), VO(IV), Ni(II), Zn(II) and Cd(II). The characterization of complexes were done by elemental analysis, UV-Vis, IR, ESR methods as well as the electrical conductance, magnetic susceptibility and thermal studies. The thermal behaviour provided confirmation of the complex composition as well as the number and the nature of water molecules and the intervals of thermal stability. The *in vitro* qualitative and quantitative antimicrobial activity assay of all the complexes was carried out.

Keywords: Oxadiazoles, Metal complexes, Thermal studies, ESR studies, Antibacterial activity

Introduction

Among the five-membered nitrogen heterocycles, synthesis of 1,3,4-oxadiazoles is of considerable interest as they are known to be associated with a broad spectrum of biological activities¹⁻³. Their derivatives have been known to possess anti-inflammatory⁴, antifungal⁵, cardiovascular⁶, antimicrobial⁷, herbicidal⁸, hypoglycaemic⁹, hypotension¹⁰, antiviral¹¹ and anti-tumour activities¹². The 1,3,4-oxadiazole derivatives are also among the most widely employed electron conducting and hole blocking (ECHB) materials in organic light-emitting diodes (LEDs)¹³.

Several methods have been used for the synthesis of these kinds of compounds from acyclic precursors. Some of them are the oxidative cyclizations of acyl hydrazones, acyl thioureas and acyl thiosemicarbazides¹⁴.

The 1,3,4-oxadiazolyl moiety is present in several pharmacologically active compounds, showing a wide range of biological activities, thus, the behaviour of these oxadiazoles in the presence of metal ions is very important.

In continuation to our work^{15,16}, the biological importance of these organic ligands, we report the synthesis and characterization of complexes of these ligands with transition metals such as Cu(II), VO(IV), Ni(II), Zn(II) and Cd(II).

Experimental

All reagents were of commercial analytical quality and have been used without further purification.

Analytical methods and physical measurements

Elemental analyses were done using CHNS Analyzer at I.R.M.R.A. Pune (MS) India. Metals were estimated after decomposition of known amounts of the complexes by AAS. The magnetic susceptibility measurements were done by Gouy method at room temperature, using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard. The electronic spectra of the ligands and metal complexes in DMSO were recorded on Shimadzu-61 UV-Visible spectrometer in the region 200-700 nm. IR spectra were recorded in KBr pellets with a Perkin Elmer spectrometer at Chandigarh, in the range 400–4000 cm^{-1} . The ^1H NMR and ^{13}C NMR spectra of ligands were recorded at SAIF Punjab University, Chandigarh in DMSO solvent using TMS as an internal standard and in CDCl_3 respectively. EPR spectra were recorded in the solid state at RT, solid state at LNT using Varian E-112 X/Q band spectrophotometer using TCNE as standard at the SAIF, IIT, Mumbai. The Differential Thermal Analysis (DTA) and Thermogravimetric analysis (TGA) were carried out using Perkin Elmer TA/SDT-2960 in the temperature range of 25-1000 $^\circ\text{C}$ at Shivaji University, Kolhapur. X-ray diffraction patterns of the selected metal complexes in powder form were recorded on Philips PW 1050/70 X-ray diffraction machine attached with X-ray Diffractometer which is equipped with Cu- $K\alpha$ target tube ($\lambda = 1.54056\text{\AA}$) at C.F.C Kolhapur. The 1,3,4-oxadiazole derivatives and its complexes were screened for antimicrobial activity by using the well diffusion method reported in the literature by Perez *et al*¹⁷. The structures of ligands are shown in Figure 1.

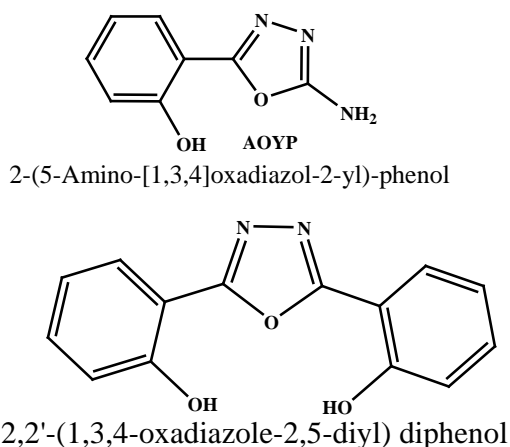


Figure 1. Structures of ligands

The physical and analytical data of the synthesized title compounds are given as follows:

2-(5-Amino-1,3,4-oxadiazol-2-yl) phenol (AOYP)

m. p. 137 °C, molecular formula (C₈H₇N₃O₂), molecular weight 177, recrystallization solvent ethanol, yield 92%, elemental analysis (%) calculated H(3.98), C(54.24), N(23.72), found H(4.02), C(55.23), N(23.80). IR cm⁻¹: 3382(OH), 3273-3251(NH₂), 1597(C=N). 1255 (Phenolic C-O), 1013(C-O-C). ¹H NMR (DMSO-d₆) ppm: 12.14 (2H,s, Ar-NH₂), 7.35-7.75 (4H,m,Ar-H), 5.21 (1H,s,OH).

2,2'-(1,3,4-Oxadiazole-2,5-diyl) diphenol (ODDP)

m. p. 133 °C, molecular formula (C₁₄H₁₀N₂O₃), molecular weight 254, recrystallization solvent ethanol, yield 78%, elemental analysis: (%) calculated H(3.96), C(66.14), N(11.02) found H(4.12), C(66.56), N(11.57). IR cm⁻¹: 3203(OH), 3273-3251(NH₂), 1605(C=N), 1265(Phenolic C-O), 1012(C-O-C). ¹H NMR (DMSO-d₆) ppm: 6.98-7.69 (8H,m,Ar-H), 5.31(2H,s,OH).

Preparation of complexes

General procedure for the synthesis of metal complexes of oxadiazoles

0.02 Moles of ligand (in slight excess) was taken in round bottom flask containing 30 mL of ethanol. 0.01 moles of metal(II) chloride dissolved in 20 mL of ethanol and was gradually added into the solution of ligand. 10% Alcoholic ammonia solution was added drop wise till precipitation of complex was obtained. The precipitated complex was digested for one hour. Any change in pH if observed was readjusted and digested for one more hour. The coloured precipitate of complex was filtered in hot condition. It was washed with alcohol followed by petroleum ether (40-60 °C) and dried in vacuum desiccators over calcium chloride.

Results and Discussion

Examination of elemental analyses data shows that complexes are monomeric, given in Table 1 and also indicates the stoichiometry (metal:ligand). The Cu(II), Ni(II) and the ligands are in the ratio 1:2 for the complexes with AOYP and is 1:1 for the complexes with ODDP. All the complexes are coloured solids, stable to air and moisture. The complexes do not have sharp melting point, but decomposed on heating beyond 269 °C. Complexes are insoluble in water, methanol, ethanol, acetone, ethyl acetate, petroleum ether, 1,4-dioxane but soluble in DMSO, DMF *etc.* The molar conductivity data obtained in DMSO suggest that all the complexes are non-electrolyte in nature.

Magnetic properties

The effective magnetic moment values of the complexes are presented in Table 1. The Cu(II) complex exhibits a value of 1.72 μB, expected for S=1/2 system having an octahedral geometry¹⁸. The results were also consistent with the octahedral¹⁹ structure of complexes for Ni(II), square pyramidal²⁰ for VO(IV) and diamagnetic as expected for a d¹⁰ configuration for Zn(II) and Cd(II) with tetrahedral structures. The subnormal values of the magnetic moments support the binuclear nature of the complexes with ODDP.

Electronic spectra

The electronic spectra of the ligands and all the complexes were recorded in DMSO. The spectra of synthesized Cu(II) complexes consisting of only single broad band in the region 15773-16393 cm⁻¹ has been observed hence it is concluded that all three transitions (²B_{1g} → ²B_{2g}, ²B_{1g} → ²E_g and ²B_{1g} → ²A_g) be within this broad envelope. This band is characteristic of distorted octahedral Cu(II) complexes²¹.

Table 1. Analytical data of complexes

Complex	Mol. Formula	Formula Weight	Temp, °C	Colour	Yield, %	Calculated (Found), %				Λ_m $\text{Scm}^2 \text{mol}^{-1}$	μ_{eff} BM,	λ_{Max} nm
						C	H	Cu	N			
[Cu(AOYP) ₂ (H ₂ O) ₂]	C ₁₆ H ₁₆ CuN ₆ O ₆	451.88	334	Cream	78	42.53 (42.46)	3.57 (3.40)	14.06 (14.98)	18.60 (19.14)	11	1.72	620
[Cu ₂ (ODDP) ₂ (H ₂ O) ₄]	C ₂₈ H ₂₄ Cu ₂ N ₄ O ₁₀	703.60	294	Cream	80	47.80 (47.97)	3.44 (3.78)	18.06 (17.91)	7.96 (8.15)	09	1.54	610
[VO(AOYP) ₂]	C ₁₆ H ₁₂ N ₆ O ₅ V	419.25	269	Green	78	45.84 (45.72)	2.89 (2.93)	11.71 (11.98)	20.05 (19.98)	10	1.75	358, 637, 760
[(VO) ₂ (ODDP) ₂]	C ₂₈ H ₁₆ N ₄ O ₈ V ₂	638.33	294	Greenish-blue	68	52.68 (53.09)	2.53 (2.93)	15.96 (16.13)	8.78 (9.08)	5	1.53	450, 667, 770
[Ni(AOYP) ₂ (H ₂ O) ₂]	C ₁₆ H ₁₆ N ₆ NiO ₆	447.03	358	Yellowish-green	72	42.99 (43.11)	3.61 (3.07)	13.13 (13.54)	18.80 (18.87)	11	2.97	371, 540, 888
[Ni ₂ (ODDP) ₂ (H ₂ O) ₄]	C ₂₈ H ₂₄ N ₄ Ni ₂ O ₁₀	693.90	294	Orange	64	48.47 (47.99)	3.49 (3.97)	16.92 (17.06)	8.07 (7.85)	9	3.18	365, 547, 876
[Zn(AOYP) ₂]	C ₁₆ H ₁₂ N ₆ O ₄ Zn	417.71	314	Pale yellow	75	46.01 (45.97)	2.90 (2.83)	15.66 (15.87)	20.12 (20.66)	18	diamag	-
[Zn ₂ (ODDP) ₂]	C ₂₈ H ₁₆ N ₄ O ₆ Zn ₂	635.27	290	Dull white	83	52.94 (53.06)	2.54 (2.69)	20.59 (20.44)	8.82 (8.92)	9	diamag	-
[Cd(AOYP) ₂]	C ₁₆ H ₁₂ CdN ₆ O ₄	464.72	311	Dull white	72	41.35 (42.01)	2.60 (2.33)	24.19 (25.00)	18.08 (18.34)	8	diamag	-
[Cd ₂ (ODDP) ₂]	C ₂₈ H ₁₆ Cd ₂ N ₄ O ₆	729.27	319	Off white	65	46.11 (46.78)	2.21 (2.76)	30.83 (31.23)	7.68 (7.58)	11	diamag	-

AOYP= 2-(5-amino-1,3,4-oxadiazol-2-yl) phenol, ODDP= 2,2'-(1,3,4-oxadiazole-2,5-diyl) diphenol, diamg= diamagnetic

The oxovanadium(IV) complexes exhibited all the three expected bands which was assigned to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$, ${}^2B_2 \rightarrow {}^2A_1$ transitions respectively. The fourth band may be due to the charge transfer transition, indicating square pyramidal geometry of the complexes²².

The Ni(II) complexes shows a regular pattern of absorption in three regions 11248-11820 cm^{-1} , 18281-19531 cm^{-1} and 26595-29154 cm^{-1} . This pattern of absorption may be assigned to transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) respectively. These observed transitions may be assigned to the characteristic three spin-allowed transitions of octahedral complexes. The ν_2/ν_1 ratio for synthesized Ni(II) complexes occur in 1.60-1.74 range which lie within the range 1.5-1.8 of octahedral complexes²³. The Cd(II) and Zn(II) complexes did not show any d-d transitions.

Infrared spectra

The absence of the band in the region 3300–3200 cm^{-1} assigned to the phenolic –OH groups in the ligand and the shift to lower wave number of $\nu(C-O)$ by $\sim 20 \text{ cm}^{-1}$ confirmed the participation of phenolic oxygen in co-ordination²⁴. The phenolic –OH group on deprotonation forms covalent bond with central metal atom through oxygen atom.

The band at $\sim 1600 \text{ cm}^{-1}$ for free ligands is attributed to $\nu(C=N)$ stretching vibrations of the oxadiazole nucleus is moved towards lower wave numbers by 25-45 cm^{-1} in the spectra of the complexes, which confirms the coordination of the nitrogen atom to the metallic ion²⁵. The presence of broad band for Cu(II) and Ni(II) complexes in the range 3500–3400 cm^{-1} indicates the coordination to water molecule/s. This was evidenced by the formation of two new bands in the range 1160-1190 cm^{-1} corresponding to $\delta(-O-H)$ of the coordinated water²⁶, followed by another band at 720–796 cm^{-1} , assignable to lattice held and/or coordinated water molecules¹³.

The IR spectra of the metal-AOYP complexes show the persistence of two small bands in the region 3200-3300 cm^{-1} for NH_2 stretching is suggestive of its non-coordination. The IR spectral assignments were in accordance to N, O coordination in AOYP and O, N, N, O in ODDP; the coordination takes place through the deprotonated –OH group and azomethine nitrogen. The values of infrared stretching frequencies corresponding to the V=O band are in good agreement with penta-coordinated oxovanadium(IV) complexes. Thus the ligands AOYP acts as monobasic bidentate ligand, the ODDP acts as dibasic tetradentate ligand.

Electronic spin resonance spectra

The EPR spectrum of the mononuclear Cu(II) complex with AOYP in solid state at LNT gives three g values, $g_1 = 1.727$, $g_2 = 1.901$ and $g_3 = 2.129$, indicating a rhombic distortion in the symmetry. Each peak corresponding to the g values is splitted into four well resolved hyperfine lines²⁷. The hyperfine lines is due to the interaction of the electron spin with copper nuclear spin (${}^{63,65}\text{Cu}$, $I = 3/2$). The corresponding A values are $A_1 = 204 \times 10^{-4} \text{ cm}^{-1}$, $A_2 = 134 \times 10^{-4} \text{ cm}^{-1}$ and $A_3 = 169 \times 10^{-4} \text{ cm}^{-1}$.

The EPR spectrum of all the oxovanadium complexes in DMF at 77 K shows typical eight-line splitting pattern, as expected for ${}^{51}\text{V}$ ($I = 7/2$; $n = 2I+1$). The ligand nitrogen or hydrogen superhyperfine splittings are not observed on vanadium line. This indicates the unpaired electrons to be in b_{2g} orbital (dx_{y^2} , 2B_2 ground state) localized in metal, thus excluding the possibility of its interaction with ligands²⁸.

Thermal studies

The TGA-DTA curve (Figure 2) of Cu(II) complex with AOYP shows two step decomposition. The first weight loss 6%, at 220–245 $^\circ\text{C}$ could be correlated with the loss of

coordinated water (Cal. 5.9%). This is supported by an endotherm at 235.98 °C in DTA, corresponding to dehydration step. The anhydrous compound does not remain stable at higher temperature; it undergoes rapid decomposition in the range 250-375 °C with 82% mass loss (Cal. 80.97%) in the second step. A sharp exotherm in DTA in the range 325-400 °C ($\Delta T_{\max} = 334.75$ °C) corresponds to decomposition of the complex. The decomposition is completed at 350 °C leading to the formation of stable residue of metal oxide *i.e.*, CuO (obs. 12%, Cal. 13.03%). The decomposition pattern is shown below:

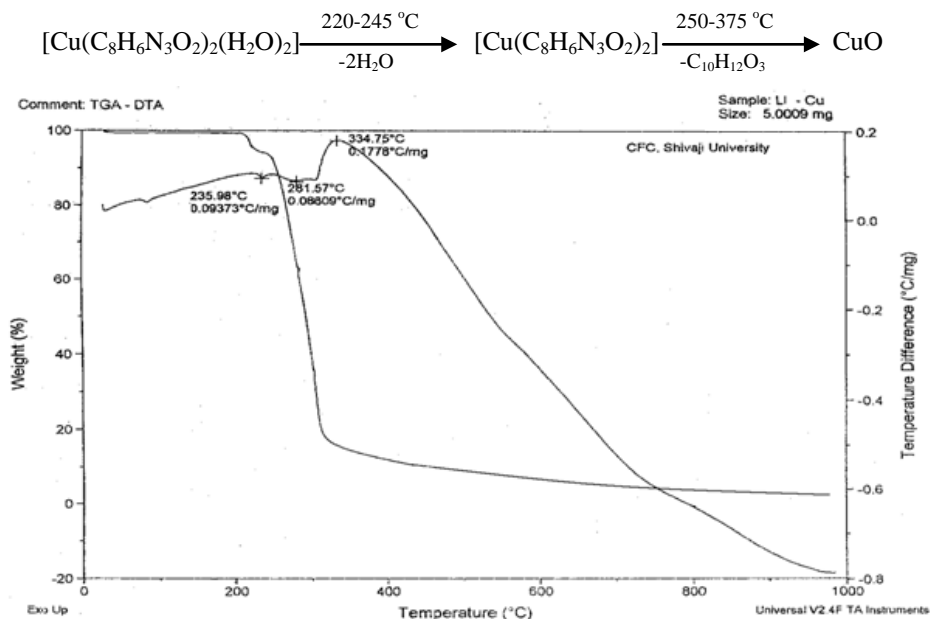
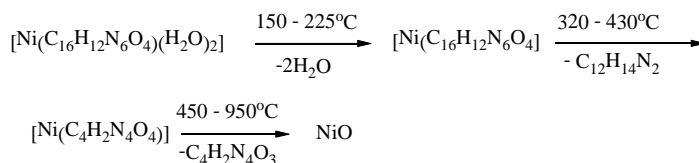


Figure 2. TGA-DTA curve of Cu(II) Complex of (AOYP)

The Ni(II) complex with AOYP (Figure 3) shows five step decomposition. The first and second step in the TG curve may be seen as loss of accidental moisture (water molecules) in the temperature 50-150 °C (obs. 7.5%) supported by DTA curve having two sharp endothermic peaks at 57.44 and 123.29 °C. The third step involves loss of two coordinated water at 187.87 °C (obs. 7.20%, cal. 8.05%), supported by DTA curve having one sharp endothermic peak ($\Delta T_{\min} = 187.87$ °C). The TG curve shows rapid fourth step decomposition in the range 320-430 °C with mass loss 39.50% (Cal. 40.05%), may be attributed to removal of non-coordinated part. The fifth step decomposition is in the range 450-950 °C with mass loss 39.0% (Cal. 39.12%), may be attributed to the oxidative degradation of remaining part of the ligand. The mass of the final residue of 10.0% corresponds to NiO (Cal. 10.25%). The decomposition pattern is shown below:



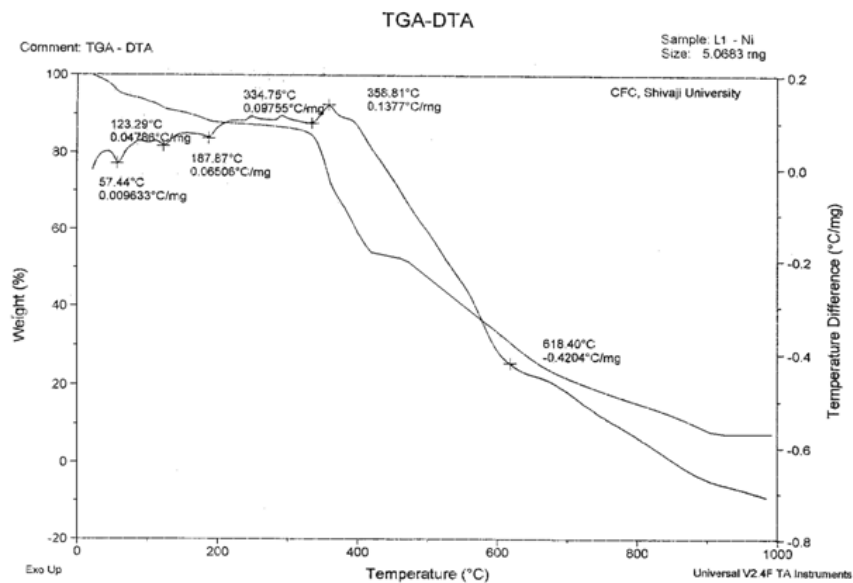
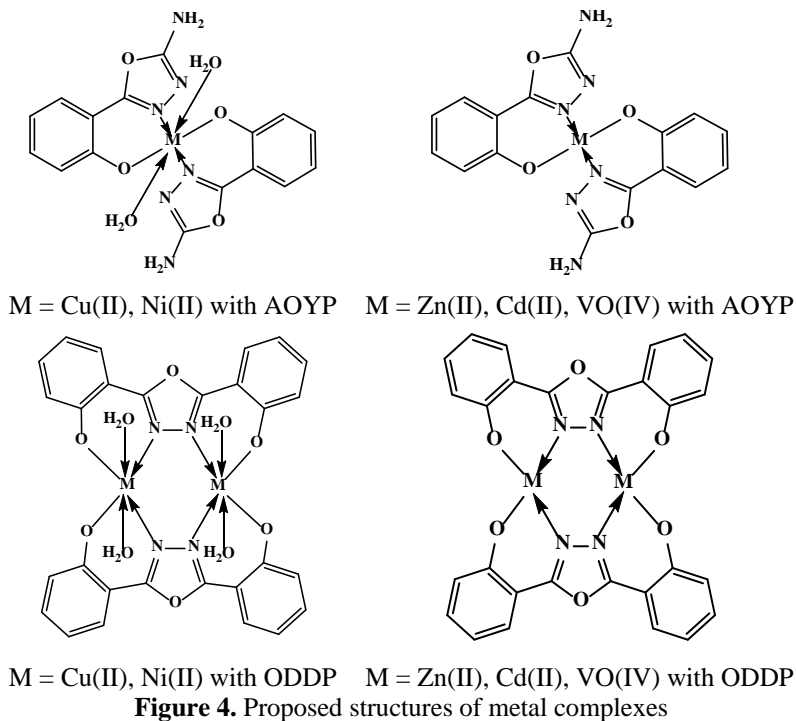


Figure 3. TGA-DTA curve of Ni(II) complex of (AOYP)

On the basis of elemental analysis, UV-Vis, IR, ESR and molar conductivities, magnetic susceptibilities, thermal studies, the structures in Figure 4 are proposed for the reported complexes.



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