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Synthesis, structural and fungicidal studies of hydrazone based coordination compounds

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HIGHLIGHTS

- ► Synthesis of hydrazone based imine.
- ▶ Complexes of Co(II), Ni(II) and Cu(II) with [M(L)X₂] and [M(L)]X₂ compositions.
- Structural elucidation by the Physicochemical and spectral studies.
- ► Fungicidal screening.
- Activation of the pharmaceutical action of the antipathogen by the metal ions.

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ABSTRACT

The coordination compounds of the Co(II), Ni(II) and Cu(II) metal ions derived from imine based ligand, benzil bis(carbohydarzone) were structurally and pharmaceutically studied. The compounds have the general stoichiometry $[M(L)]X_2$ and $[Co(L)X_2]$, where M = Ni(II) and Cu(II), and X = NO_3^- and Cl⁻ ions. The analytical techniques like elemental analyses, molar conductance measurements, magnetic susceptibility measurements, IR, UV/Visible, NMR, ESI mass and EPR were used to study the compounds. The key IR bands, i.e., amide I, amide II and amide III stretching vibrations accounts for the tetradentate metal binding nature of the ligand. The electronic and EPR spectral results suggest the square planar Ni(II) and Cu(II) complexes ($g_{iso} = 2.11-2.22$) and tetragonal geometry Co(II) complexes ($g_{iso} = 2.10-2.17$). To explore the compounds in the biological field, they were examined against the opportunistic pathogens, i.e., *Alternaria brassicae, Aspergillus niger* and *Fusarium oxysporum*. The partial covalent character of metalligand bond is supported by the orbital reduction factor k (0.62–0.92) and nephalauxetic parameter β (0.55–0.57).

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SPECTROCHIMICA ACTA

Introduction

The mechanisms of DNA replication and protein synthesis in fungi are similar to the mammalian cell. Consequently, it is a challenge to the Biochemists for designing the drugs that are selectively toxic to fungal cells but not to the human host [1]. When a compound is found to be biologically active, it is chemically modified to improve its properties. Consequently, the advance synthetical and separation methodologies and biochemical techniques are followed for designing of the drug.

Imines constitute one of the most interesting and widely used families of the hydrazones. The interaction of imines and modified imines with the transition metal ions as well as lanthanides is worth a great interest due to synthetical and applicative causes in array of pharmaceutical, analytical, biochemistry, etc. Further, the endogenous availability of metal ions and strict regulation of their intracellular concentration have stimulated the synthesis of metal-based drugs. A number of drugs do not show purely mode

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of pharmaceutical action, they are activated by the metal ions [2–4].

Preceding our work in the coordination and biological research, we report here the synthesis, structural and biological studies of the hydrazone based imine and transition metal complexes derived from it.

Experimental

Materials and measurements

Metal salts and chemicals (Fluka, S.D. Fine, E. Merck and Thomas Backer) were commercial products and were used as supplied. Benzil and carbohydrazide (AR grade) were obtained from Sigma-Aldrich. NMR spectra were recorded with a model Bruker advance DPX-300 spectrometer operating at 300 MHz using DMSO-d₆ as a solvent and TMS as an internal standard. ESI mass spectrum was recorded on a model Q Star XL LCMS-MS system. The stoichiometric analyses were carried out on a Carlo-Erba 1106 analyser. IR spectra were recorded as KBr and CsI₂ pellets in the region 4000-200 cm⁻¹ on a FT-IR spectrum BX-II spectrophotometer. The electronic spectra were recorded on Shimadzu UV mini-1240 spectrophotometer. EPR spectra were recorded for solids and solutions on an E4-EPR spectrometer at room temperature and liquid nitrogen temperature operating at X-band region using DPPH as a standard. The molar conductance of complexes was measured in DMSO at room temperature on an ELICO (CM 82T) conductivity bridge. The magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as calibrant.

Synthesis of ligand, benzil bis(carbohydrazone), (L)

A solution of carbohydrazide (1.8018 g, 0.02 mol) in water (15 mL) was heated for 15 min in presence of few drops of acetic acid and then was added to a hot solution of benzil (2.1023 g, 0.01 mol) in ethanol (15 mL). The reaction mixture was refluxed for 2 h at 65 °C, allowed to stay at room temperature and then kept in refrigerator overnight. The white product was precipitated out, which was filtered off, washed several times with ethanol and dried under *vacuum* over P_4O_{10} . Yield 80%, m.p. 206 °C. Elemental analyses, Found (Calcd.) For $C_{16}H_{18}N_8O_2$: C, 54.29 (54.24); H, 5.12 (5.08); N, 31.70 (31.64)%. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 4.29 (S, 4H, 2 NH₂), 9.68 (S, 4H, 4NH), 7.15–7.95 (m, 10H, 2Ph); ¹³C NMR (300 MHz, DMSO-d₆): δ (ppm): 125.98–135.54 (m, 12C, 2 Ph), 151.09 and 151.27 (2C, -C=N-), 160.22 and 161.20 (2C, -C=ONH-).

Synthesis of the complexes

A hot solution of metal salt (nitrate or chloride) (1 mmol) in ethanol (10 mL) was added slowly to a hot solution of ligand (1 mmol) in ethanol (15 mL) with constant stirring. The mixture was refluxed for 8–10 h at 80–85 °C. On keeping the resulting mixture overnight at 0 °C, the colored product was separated out, which was filtered off, washed with ethanol and dried under *vacuum* over P_4O_{10} .

Biological screening

The Food Poison Technique was employed to examine the synthesized compounds against the fungi, i.e. *Alternaria brassicae*, *Aspergillus niger* and *Fusarium oxysporum* for their fungicidal investigations [5]. The stock solutions of the compounds were prepared in DMSO solvent. The fungicidal capacity of the compounds was determined in percentage terms from the growth of the fungus in the test plate to the respective control plate. DMSO and captain were employed as a control and a standard fungicide, respectively.

Results and discussion

The hydrazone based Schiff's base ligand L was obtained in good yield by reacting benzil and carbohydrazide in 1:2 ratio (Supplementary material). The complexes with Cu(II), Ni(II) and Co(II) metal ions were also obtained in the satisfactory yield on reaction of the ligand with metal salts.

Physical properties

The complexes are insoluble in the nonpolar solvents but soluble in the polar solvents like DMSO. The elemental, molar conductivities studies of the complexes suggest the $[M(L)]X_2$ and $[Co(L)X_2]$ compositions, where M = Ni(II) and Cu(II), and X = NO₃⁻ and Cl⁻ [6]. The analytical data of ligand and its complexes with their physical properties are given in Table 1 in supporting information, which indicates 1:1:2 metal:ligand:anion stoichiometry for all the complexes. Measured values of magnetic moments indicate that the nickel(II) complexes are paramagnetic having the magnetic moments 1.86–1.93 and 4.80–4.92 BM respectively.

IR spectra

The important IR bands of the compounds along with their assignment are given in Table 2. The IR spectrum of the free ligand displays the bands at 3420 and 3317 cm⁻¹ corresponding to the $v_{as}(NH_2)$ and $v_s(NH_2)$ stretching vibrations, respectively, which suggests the presence of free NH₂ groups in the ligand. The spectrum exhibits the bands at 1686, 1620 and 1509 cm⁻¹ corresponding to the amide I, amide II and amide III stretching vibrations, respectively, due to the presence of the amide groups in the ligand [7]. On complex formation, the position of these bands is altered, which indicates that the ligand coordinates to the metal ion through the amide oxygen and azomethine nitrogen atoms. This NO binding of the ligand is also supported by the appearance of new IR bands at 405–428 and 500–529 cm⁻¹ due to v(M–N) and v(M–O) vibrations, respectively [8,9]. This discussion reveals that the Schiff base ligand coordinates to metal ions as tetradentate chelate to give the complexes.

Mass spectrum

ESI mass spectrum was recorded on a LCMS–MS system. The mass spectrum of the ligand gives the peak at m/z = 354 due to molecular ion (M⁺). The weak peaks at m/z = 355 and 356, are also observed in the spectrum which are due to the (M + 1)⁺ and (M + 2)⁺ isotopes. The maximum intensity peak (base peak, 100% intensity) is observed at m/z = 77 is due to the phenyl cation and another intense peak at m/z = 177 is also appeared in the spectrum due to the six membered cyclic positive ion ($C_8H_9N_4O^+$), which is plausibly the resultant of the $\gamma\delta$ C—C bond cleavage and followed by cyclization. The other structural units present in the ligand gives peaks at various mass numbers with variable intensity like at m/z = 59 due to amide group and 41, 118, 295, etc. corresponding to the different fragments (Supplementary material) [10].

Electronic spectra

The UV/Visible spectra of complexes were recorded in DMSO solvent. The data of electronic spectra are summarized in Table 3.

Table 1

Microanalytical data of complexes with their physical properties.

S. no.	Complex	Color	m.p. (°C)	Molar conductance	Yield (%)	Microanalytical data (%) calcd. (found)				
				$(\Omega^{-1} \operatorname{cm}^2 \operatorname{mol}^{-1})$		М	С	Н	Ν	
1	$\begin{array}{l} [Cu(L)]Cl_2\\ CuC_{16}H_{18}N_8O_2Cl_2 \end{array}$	Green	216	130	68	12.99 (13.04)	39.30 (39.35)	3.68 (3.72)	22.93 (22.98)	
2	$[Cu(L)](NO_3)_2$ $CuC_{16}H_{18}N_{10}O_8$	Brown	162	120	60	11.73 (11.78)	35.46 (35.50)	3.32 (3.37)	25.85 (25.89)	
3	$[Ni(L)]Cl_2 \\ NiC_{16}H_{18}N_8O_2Cl_2$	Orange	230	128	65	12.14 (12.19)	39.69 (39.75)	3.72 (3.76)	23.15 (23.20)	
4	[Ni(L)](NO ₃) ₂ NiC ₁₆ H ₁₈ N ₁₀ O ₈	Brown	>300	140	70	10.94 (10.99)	35.77 (35.82)	3.35 (3.40)	26.08 (26.14)	
5	$ \begin{bmatrix} Co(L)Cl_2 \end{bmatrix} \\ CoC_{16}H_{18}N_8O_2Cl_2 $	Brown	188	11	62	12.17 (12.22)	39.68 (39.74)	3.72 (3.76)	23.14 (23.18)	
6	$[Co(L)(NO_3)_2]$ $CoC_{16}H_{18}N_{10}O_8$	Brown	230*	14	64	10.97 (10.92)	35.76 (35.81)	3.35 (3.39)	26.08 (26.14)	

* Decomposition temperature.

Table 2	
Comparative IR data of compounds.	

Compound	Amide I	Amide II	Amide III	v(M-O)	v(M-N)
Ligand	1686	1620	1509	-	-
[Cu(L)]Cl ₂	1617	1595	1444	519	420
$[Cu(L)](NO_3)_2$	1664	1595	1446	510	418
[Ni(L)]Cl ₂	1664	1590	1542	500	405
[Ni(L)](NO ₃) ₂	1663	1609	1445	508	415
$[Co(L)Cl_2]$	1719	1569	1446	529	423
[Co(L)(NO ₃) ₂]	1660	1590	1442	504	428

The copper(II) complexes show the electronic spectral bands in the region 11,248–11,547, 14,814–16,140 and 24,450–25,360 cm⁻¹. These transitions may be assigned to the ${}^{2}B_{1g} \leftarrow {}^{2}A_{1g}$ $(d_{x^2-y^2} \leftarrow d_{z^2})v_1$, ${}^{2}B_{1g} \leftarrow {}^{2}B_{2g}$ $(d_{x^2-y^2} \leftarrow d_{xy})v_2$ and ${}^{2}B_{1g} \leftarrow {}^{2}E_g$ $(d_{x^2-y^2} \leftarrow d_{xz},d_{yz})v_3$ transitions, respectively [11–13]. The transitions suggest the D_{4h} symmetry and square planar geometry for the complexes (Fig. 1a).

The absorption spectra of nickel(II) complexes give the d-d transitions in the range 11,185–11,210, 22,883 and 30,864 cm⁻¹. The lowest energy transition corresponds to the transition ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g} (d_{xy} \rightarrow d_{x^2-y^2})v_1$ which suggest the energy levels order $d_{z^2} < d_{xy}$. The other transitions correspond to the ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g} (d_{z^2} \rightarrow d_{x^2-y^2})v_2$ and intraligand band, respectively [11–13]. These transitions reveal that the nickel(II) complexes possess square planar geometry (Fig. 1a).

The electronic spectra of cobalt(II) complexes display the d–d transition bands in the region 10,341–10,649 and 18,621 cm⁻¹. These transitions may be assigned to the ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)v_{1}$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)v_{2}$, respectively [11–13]. The band at 29325 cm⁻¹ is due intraligand transition. The transitions correspond to the tetragonal geometry of the complexes (Fig. 1b).

The complexes exhibit the high energy bands in the range $33,003-36,900 \text{ cm}^{-1}$ which may be attributed to the charge transfer transitions. The ligand field parameters like Racah inter-electronic repulsion parameter B, ligand field splitting energy Dq,



Fig. 1. Structure of the complexes (a) $[M(L)]X_2$ and (b) $[Co(L)X_2]$, where M = Cu(II) and Ni(II), and X = NO₃⁻ and Cl⁻.

covalency factor β and ligand field stabilization energy (LFSE) have been calculated for the Co(II) complexes. The values of B and Dq of Co(II) complexes were calculated from the transition energy ratio diagram using v_3/v_1 ratio. The value of β (0.55–0.57) for the Co(II) complexes accounts for the covalent nature of the complexes [14]. The evaluated parameters are listed in Table 3.

EPR spectra

The EPR spectra of copper(II) and cobalt(II) complexes were recorded at room temperature as well as liquid nitrogen temperature in polycrystalline form and DMSO frozen. The data are given in Table 4.

The spectra of the Cu(II) complexes show only one signal (Supplementary material) at $g_{iso} = 2.11-2.22$. The calculated values of $g_{||}$ and g_{\perp} for the complexes at room temperature and liquid nitrogen temperature show the order as $g_{||} > g_{\perp} > 2.0023$ which is consistent with the $d_{x^2-y^2}$ ground state [15–18]. The odd electron is located in the B_{1g} antibonding orbital. The spectral studies reveal that the Cu(II) ion in the present complexes is in square planar field. The approximate antibonding wave functions are

Table 3
Electronic spectral data and Ligand field parameters of the complex

sectione spectral data and ligand new parameters of the complexes.											
Complex	μ_{eff} (BM)	λ_{max} (cm ⁻¹)	$D_q ({ m cm}^{-1})$	<i>B</i> (cm ⁻¹)	β	LFSE (kJ mol ⁻¹)					
[Cu(L)]Cl ₂	1.86	11,248, 14,814, 24,450, 36,496	-	-	-	-					
$[Cu(L)](NO_3)_2$	1.93	11,547, 16,140, 25,360, 36,900	-	-	-	-					
[Ni(L)]Cl ₂	Dia.	11,185, 22,883, 30,864, 35,714	-	-	-	-					
[Ni(L)](NO ₃) ₂	Dia.	11,210, 33,222	-	-	-	-					
$[Co(L)(NO_3)_2]$	4.92	10,341, 18,621, 36,900	1155	642	0.57	110					
[Co(L)Cl ₂]	4.80	10,669, 18,621, 29,325, 33,003	1241	620	0.55	118					

Table 4EPR and bonding parameters of the complexes.

Complex	Medium	g_{\perp} (RT)	g (RT)	g _{iso} (RT)	g_{\perp} (LNT)	g (LNT)	g _{iso} (LNT)	k_{\perp}^{2} (RT)	$rac{k_{ }^2}{(RT)}$	k (RT)	k_{\perp}^{2} (LNT)	$k_{ }^2$ (LNT)	k (LNT)	G (RT)	G (LNT)
[Cu(L)]Cl ₂	Solid DMSO	2.07 2.09	2.42 2.37	2.18 2.18	2.06 2.06	2.26 2.28	2.12 2.13	0.76 0.98	0.93 0.82	0.82 0.92	0.65 0.64	0.58 0.62	0.62 0.64	6.16 4.19	4.47 4.81
[Cu(L)](NO ₃	Solid DMSO	2.05 2.06	2.29 2.37	2.13 2.22	2.05 2.06	2.27 2.24	2.12 2.11	0.73 0.88	0.70 0.90	0.72 0.89	0.73 0.88	0.65 0.58	0.70 0.78	6.03 6.37	5.61 4.12
$[Co(L)Cl_2]$	Solid DMSO	_	-	-	1.91 1.87	2.62 2.78	2.14 2.17	_	-	-	-	-	-	-	-
[Co(L)(NO ₃) ₂]	Solid DMSO	-	-	-	1.86 1.85	2.59 2.62	2.10 2.10	-	-	-	-	_	-	-	_

$$\begin{split} \psi B_{1g} &= \alpha (d_{x^2-y^2}) - \alpha' [-\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}]/2 \\ \psi B_{2g} &= \beta (d_{xy}) - \beta' [p_y^{(1)} - p_x^{(2)} - p_y^{(3)} - \sigma_x^{(4)}]/2 \\ \psi A_{1g} &= \alpha_1 (d_{z^2}) - \alpha'_1 [\sigma_x^{(1)} + \sigma_y^{(2)} - \sigma_x^{(3)} - \sigma_y^{(4)}]/2 \\ \psi E_{1g} &= \gamma (d_{xz}) - \gamma' [p_z^{(1)} - p_z^{(3)}]/\sqrt{2} \\ \psi E_{1g} &= \gamma (d_{yz}) - \gamma' [p_z^{(2)} - p_z^{(4)}]/\sqrt{2} \end{split}$$

For the copper(II) ion in tetragonal field, the spin-Hamiltonian is given by

$$\mathbf{H} = \beta [\mathbf{g}_{\parallel} \mathbf{H}_z \mathbf{S}_z + \mathbf{g}_{\perp} (\mathbf{H}_x \mathbf{S}_x + \mathbf{H}_y \mathbf{S}_y)] + \mathbf{A} \mathbf{I}_z \mathbf{S}_z + \mathbf{B} (\mathbf{I}_x \mathbf{S}_x + \mathbf{I}_y \mathbf{S}_y)$$

where β is the Bohr magneton. H is the applied magnetic field and the last term in expression represents the ligand hyperfine term.

The geometric parameter *G*, is calculated by using the expression:

$$G = \frac{(g_{||} - 2.0023)}{(g_{\perp} - 2.0023)} = \frac{4k_{||}^2 \cdot \Delta E_{xz}}{k_{\perp}^2 \Delta E_{xy}}$$

The complexes show the *G* values greater than four (Table 4), which indicate that the exchange interaction between the copper(II) ions in the polycrystalline form is negligible. The EPR parameters and the d-d transition energies are used to evaluate, the orbital reduction factor k by using the expression: $k^2 = k_{\parallel}^2 + 2k_{\perp}^2/3$, where k_{\parallel} and k_{\perp} are the parallel and perpendicular components of the orbital reduction factor. The low values of k (0.62–0.92) indicate the partial covalent nature of the complexes (Table 4) [15–18].

The X-band EPR spectra of the Co(II) complexes were recorded at liquid nitrogen temperature in polycrystalline form and solution form. Due to the fast spin-relaxation of high-spin cobalt(II) ion, the signals are observed only at low temperature. The EPR spectra give the one signal with $g_{iso} = 2.10-2.17$ (Table 4). The spectra of the complexes do not display any hyperfine splitting. Because this hyperfine splitting is resolved only in magnetically diluted Co(II)

Table 5					
Fungicidal	activity	data	of th	ie con	pounds.

complexes. The spectral features correspond to the tetragonal symmetry around the Co(II) ion [15–18].

Antimicrobial activities

The low lipophilicity is a typical problem because that leads to poor permeability through membrane of organism. Several modifications like pharmacodynamics and pharmacokinetics lead the improved lipophilicity of the drug through the target cell. Moreover, the pharmaceutical action of the antipathogen is activated by the metal ions. This improvement in the antipathogenic activity of ligand on complexation is based on the Overtone's Concept and Chelation Theory. The polarity of the metal ion is reduced on complexation by the partial sharing of its positive charge with lewis base, which causes the delocalization of the charge over the whole ring. Consequently, the lipophilicity of the compound is improved [19,20].

Further, the biological activity of a drug is related to its affinity for the receptor, i.e., the stability of the drug-receptor complex. This stability is commonly measured its K_d , the dissociation constant for the drug-receptor complex at equilibrium:

$$K_{d} = \frac{[drug][receptor]}{[drug - receptor \ complex]}$$

Smaller the K_d , the larger the concentration of the drug-receptor complex, the stable is that complex and the greater is the affinity of the drug for the receptor. Solvated compound (drug) and solvated proteins (receptor) generally exist as an equilibrium mixture of several conformers each. The solvent molecules that occupy the binding site of the receptor must be displaced by the drug to produce a solvated complex. The interactions between the drug and the receptor are stronger than the interaction between the drug and the receptor with solvent molecule. The noncovalent interactions are generally weak. However, other several types of interactions like electrostatic, dipole–dipole, hydrogen bonds, hydrophobic, Charge transfer complexes, Van der Waals or London

Compound	Fungal inl	hibition (%) (con	c. in $\mu g m L^{-1}$)							
	A. brassicae			A. niger			F. oxysporum			
	100	200	300	100	200	300	100	200	300	
Ligand	30	42	50	28	38	45	25	32	44	
$[Cu(L)]Cl_2$	45	60	72	42	55	70	36	50	60	
$[Cu(L)](NO_3)_2$	48	62	75	40	52	72	38	52	65	
$[Ni(L)]Cl_2$	40	60	70	36	45	58	35	44	52	
[Ni(L)](NO ₃) ₂	45	68	76	38	45	60	34	46	55	
$[Co(L)Cl_2]$	46	70	78	35	42	54	32	40	50	
$[Co(L)(NO_3)_2]$	48	70	80	36	45	55	34	40	52	
Standard (Captan)	70	80	100	75	90	100	65	75	100	



Fig. 2. Graph showing the activation of the pharmaceutical action of the antipathogen by the metal ions.

dispersion forces, are also taking place during the formation of drug-receptor complex. These several weak interactions may combine to produce a strong interaction to form drug –receptor complex [21].

The results of the antifungal investigations of the ligand and complexes are given in Table 5. After investigations, it has been found that the compounds have fungicidal potential (Supplementary material) and the antipathogenic potential of the metal free ligand is positively modified by the coordination (Fig. 2) [22–25].

Conclusion

The hydrazone based Schiff's base has been synthesized and its coordination behavior with Cu(II), Ni(II) and Co(II) metal ions has also been studied. Formation of the hydrazone and its structural studies reveal that it exhibits in fully protonated form in solid as well as in solution form. Cu(II) and Ni(II) complexes were found to have square planar geometry whereas the Co(II) complexes were of tetragonal geometry. The ligand coordinates to metal ions in tetradentate fashion to give the stable complexes. The low value of orbital reduction factor k and covalency factor β reveals the partial covalent nature of complexes. Analytical data correspond to the monomeric composition of the complexes. The fungicidal examination of the compounds led to the conclusion that the metal free ligand has growth inhibition capacity against the tested fungal strains and this efficacy is positively affected by the complex formation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.11.012.

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