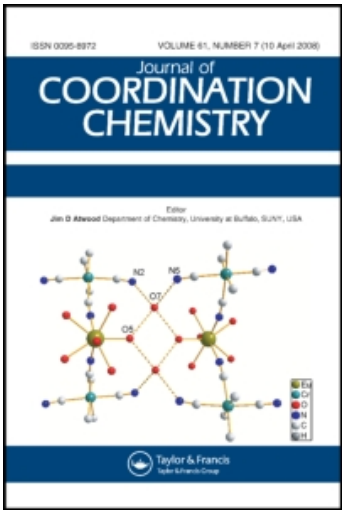

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Biological and spectral studies of transition metal complexes with a quinquedentate Schiff base, 2,6-diacetylpyridine bis(thiocarbohydrazone)

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First published on: 10 December 2009

To cite this Article Chandra, Sulekh and Sharma, Amit Kumar(2009) 'Biological and spectral studies of transition metal complexes with a quinquedentate Schiff base, 2,6-diacetylpyridine bis(thiocarbohydrazone)', Journal of Coordination Chemistry, 62: 22, 3688 — 3700, First published on: 10 December 2009 (iFirst)
To link to this Article: DOI: 10.1080/00958970903121305
URL: http://dx.doi.org/10.1080/00958970903121305

Journal of Coordination Chemistry
Vol. 62, No. 22, 20 November 2009, 3688–3700

Biological and spectral studies of transition metal complexes with a quinquedentate Schiff base, 2,6-diacetylpyridine bis(thiocarbohydrazone)

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(*Received 16 March 2009; in final form 4 May 2009*)

Manganese(II), cobalt(II), and copper(II) complexes with a quinquedentate Schiff base, 2,6-diacetylpyridine bis(thiocarbohydrazone), have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, and IR, ^{1}H NMR, ^{13}C NMR, mass (for ligand), UV and Electron Paramagnetic Resonance spectroscopies. The complexes are [M(L)X]X, where M=Mn(II), Co(II), and Cu(II), L = 2,6-diacetylpyridine bis(thiocarbohydrazone), and X=NO_3^- and Oac^-. The ligand with five coordination sites forms six-coordinate complexes with octahedral geometry for manganese(II), whereas the cobalt(II) and copper(II) complexes were of tetragonal geometry. The A_{iso} values, nephelauxetic parameter (β), and orbital reduction factor (k) indicate the covalent nature of the metal–ligand bond. The compounds have been screened for their antipathogenic activities against *Alternaria brassicae*, *Aspergillus niger*, *Fusarium oxysporum*, *Xanthomonas compestris*, and *Pseudomonas aeruginosa*.

Keywords: Transition metal complexes; 2,6-Diacetylpyridine bis(thiocarbohydrazone); Spectral characterization; Biological activities

1. Introduction

Hydrazone-based Schiff bases are versatile ligands capable of generating a variety of molecular architectures, coordination compounds, and polymerization catalysts [1–9]. Ease in synthesis, steric and electronic modularity, luminescence, and diversity in the biological properties like antibacterial, antifungal, herbicides, insecticides, rotenticides, plant growth regulators [10–15] and their usage in the treatment of diseases such as antitumor, leprosy, mental disorders, etc. [16] have sustained the interest of researchers in these compounds.

To further explore hydrazone-based ligands, in this article, we report the synthesis, and IR, ^{1}H NMR, ^{13}C NMR, mass, UV, and Electron Paramagnetic Resonance (EPR) spectroscopic characterization of a quinquedentate Schiff base ligand, 2,6-diacetylpyridine bis(thiocarbohydrazone) and its Mn(II), Co(II), and Cu(II) complexes. The synthesized compounds have been screened for antipathogenic activity.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970903121305

2. Experimental

2.1. *Materials and measurements*

2,6-Diacetylpyridine and thiocarbohydrazide of AR grade were obtained from Sigma-Aldrich. Metal salts (E. Merck), other chemicals (Fluka and Thomas Baker), sterile discs (Himedia), and solvents (S.D. Fine and Sisco International) were commercial products and used as received. Microanalytical analyses were performed on a Carlo-Erba 1106 analyzer. NMR spectra were recorded with a Bruker Avance DPX-300 spectrometer operating at 300 MHz using DMSO-d_6 and D_2O as solvents and TMS as an internal standard. IR spectra were recorded as KBr pellets from 4000 to 200 cm^{-1} on a FT-IR spectrum BX-II spectrophotometer. ESI mass spectrum was recorded on a model Q Star XL LCMS–MS system. Electronic spectra were recorded on a Shimadzu UV mini-1240 spectrophotometer using DMSO/DMF. EPR spectra were recorded in solid and solution form on an E4-EPR spectrometer at room temperature and liquid nitrogen temperature, operating at X-band region with 100 KHz modulation frequency, 5 MW microwave power and 1 G modulation amplitude using DPPH as standard. The molar conductances of complexes were measured in DMSO/DMF at room temperature on an ELICO (CM 82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as calibrant.

2.2. *Synthesis of 2,6-diacetylpyridine bis(thiocarbohydrazone) (L)*

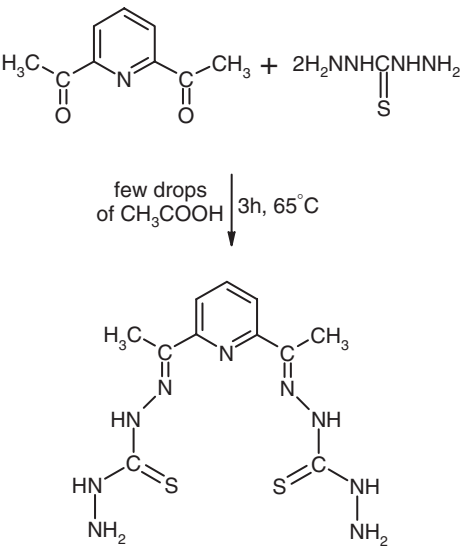
A solution of thiocarbohydrazide (2.123 g, 0.02 mol) in 30 mL water was heated for 15 min in the presence of a few drops of acetic acid. To this solution, a hot solution of 2,6-diacetylpyridine (1.6318 g, 0.01 mol) in absolute ethanol (20 mL) was added dropwise with constant stirring. The resulting mixture was refluxed for 3 h at 65°C and then cooled overnight at 0°C. The yellow precipitate was filtered, washed with cold ethanol, and dried under vacuum over P_4O_{10} (scheme 1) [17]. Yield 78%, m.p. 250°C (dec.). Anal. Calcd for $C_{11}H_{17}N_9S_2$ (%): C, 38.94; H, 5.01; N, 37.17. Found: C, 38.89; H, 4.98; N, 37.13.

2.3. *Synthesis of the complexes*

A hot ethanolic (15 mL) solution of the Schiff base (1 mmol) was added slowly to a hot ethanolic (10 mL) solution of the corresponding metal salts (nitrate and acetate) (1 mmol) with continuous stirring. The resulting solution was refluxed for 8–15 h. On cooling overnight at 0°C, a colored product was precipitated, filtered, washed with cold ethanol, and dried under vacuum over P_4O_{10}.

2.4. *Biological screening*

The compounds were screened against the fungi, namely *Alternaria brassicae*, *Aspergillus niger*, and *Fusarium oxysporum* and the bacteria viz., *Xanthomonas compestris* and *Pseudomonas aeruginosa* by using Disc Diffusion Method and Food Poison Technique [18–20]. Stock solutions of the compounds were prepared in DMSO and serial dilutions of the stock solutions were made with sterile distilled water to determine the Minimum Inhibition Concentration (MIC).



Scheme 1. Synthesis of ligand.

To determine the antibacterial activity by employing disc diffusion method, the nutrient agar medium was poured in Petri plates and kept overnight. The suspension of the tested microorganism (0.5 mL) was spread over the solid nutrient agar plates using a spreader. Fifty microliters of the stock solutions were applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plate. The Petri plates were sealed with parafilm and first placed at low temperature for 2–3 h for the diffusion of the chemical and then incubated at $29 \pm 2^{\circ}C$ for 30–36 h. The diameters of the inhibition zones were measured in millimeters.

For antifungal activity, the Food Poison technique was employed. The stock solution of the tested concentration of the compound was directly added to the Potato Dextrose Agar (PDA) medium. The mixture was poured into the Petri plate and kept overnight for solidification. A disc of 5 mm of test fungal culture is then cut with a sterile cork borer and placed at the center of the Petri plate with the help of inoculums' needle. The plates were sealed with parafilm and incubated at $29 \pm 2^{\circ}C$ for 6–7 days.

The inhibition percentage of the fungal growth was determined from the growth in the test plate to the respective control plate by using the expression:

$$\text{Inhibition } (\%) = (C - T) \times 100/C$$

where C = diameter of fungal growth in the control plate and T = diameter of fungal growth in the test plate. DMSO was used as a control. Streptomycin and Captan were used as a standard bactericide and fungicide, respectively.

3. Results and discussion

The analytical data and physical characterization of the complexes, summarized in table 1, correspond to $M(L)X_2$, where M=Mn(II), Co(II), and Cu(II), L = ligand, and $X = NO_3^-$ and Oac^-. Molar conductivity measurements of complexes in DMF/DMSO

Table 1. Analytical data and physical properties of complexes.

Complex	Color	m.p. (°C)	Molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$)	Yield (%)	Elemental analysis data (%) calculated (found)			
					M	C	H	N
$[Mn(L)NO_3]NO_3$ $MnC_{11}H_{17}N_{11}S_2O_6$	Yellow	>300	93	65	10.61 (10.56)	25.49 (25.43)	3.28 (3.23)	29.73 (29.67)
[Mn(L)OAc]OAc $MnC_{15}H_{23}N_9S_2O_4$	Yellow	>300	88	59	10.73 (10.65)	35.16 (35.09)	4.49 (4.43)	24.61 (24.56)
$[Co(L)NO_3]NO_3$ $CoC_{11}H_{17}N_{11}S_2O_6$	Brown	282	118	68	11.29 (11.22)	25.29 (25.36)	3.26 (3.20)	29.51 (29.42)
[Co(L)OAc]OAc $CoC_{15}H_{23}N_9S_2O_4$	Brown	>300	122	58	11.42 (11.35)	34.89 (34.81)	4.46 (4.40)	24.42 (24.34)
$[Cu(L)NO_3]NO_3$ $CuC_{11}H_{17}N_{11}S_2O_6$	Brown	>300	109	53	12.06 (11.99)	25.07 (25.01)	3.23 (3.17)	29.25 (29.18)
[Cu(L)OAc]OAc $CuC_{15}H_{23}N_9S_2O_4$	Brown	>300	103	61	12.20 (12.14)	34.58 (34.53)	4.42 (4.35)	24.21 (24.16)

indicates that the complexes are 1 : 1 electrolytes with [M(L)X]X composition [21]. The magnetic moments are 5.98–6.00, 4.88–5.03, and 1.89–1.91 B.M. for Mn(II), Co(II), and Cu(II) complexes, respectively.

Owing to the presence of thioamide bonds in the Schiff base, it may show thione and thiol tautomerism. However, in the IR spectrum of the ligand no band is observed in the range 2500–2600 cm^{-1} due to SH, which is in agreement with the existence of the ligand in thione form in solid state [22]. Moreover, the ^1H NMR spectrum shows two broad signals at δ:10.010 (s, br, 2H, 2C=SNH) and 10.333 ppm (s, br, 2H, 2C=NNH) due to NH protons and there is no sharp singlet at $\delta \approx 4$ ppm due to SH, which is in agreement with the thione form in solution. Thus, the ligand exists in the thione form in solid and solution [22]. The complexes are 1 : 1 electrolytes, suggesting that the ligand coordinates to metal in protonated form [23, 24].

3.1. *NMR spectra*

^1H and ^{13}C NMR spectra of the ligand were recorded in DMSO-d_6 and D_2O, respectively. The ^1H NMR spectrum displays a singlet at *ca* δ 2.502 ppm (s, 6H, $2CH_3$) due to six protons of two methyl groups, a broad signal at *ca* δ 5.222 ppm (s, br, 4H, $2NH_2$) due to four protons of two amino groups, a triplet (t, 1HPy) and a doublet (d, 2HPy) at δ 7.904–8.524 ppm due to two types of protons of pyridine ring and two broad signals at *ca* δ 10.010 (s, br, 2H, 2C=SNH) and 10.333 ppm (s, br, 2H, 2C=NNH) due to two kinds of thioamide groups [22, 25, 26].

The ^{13}C NMR spectrum (Supplementary material) displays six signals at δ 10.17 ppm due to carbon of methyl, δ 128.72, 130.73, 131.15 ppm due to three types of pyridine ring carbon, *ca* δ 145.17 ppm due to C=S and *ca* δ 159.29 ppm due to azomethine (C=N) [27].

3.2. *Mass spectrum*

The ESI mass spectrum of the ligand (Supplementary material) displays the molecular ion peak at $m/z = 339$. Peaks at $m/z = 340$ and 341 also appeared, which may be due to ^{13}C, ^{15}N, and ^{34}S isotopes, respectively. The base peak at $m/z = 159$ is due to $C_9H_9N_3^+$ stabilized by pyridine. A high-intensity peak at $m/z = 131$ in the spectrum may be due to cyclic cation. Peaks at $m/z = 77$ and 79 correspond to thioamide and pyridine ring cations, respectively. Peaks at $m/z = 15$, 16, 59, 119, 189, 208, 218, 264, 277, 292, 307, and 323 are due to different fragments [28].

3.3. *IR spectra*

Key IR spectral bands are summarized in table 2. The ligand gives characteristic bands at 1695, 1357, 1288, and 814 cm^{-1} due to thioamide I [ν(C=N)], thioamide II [ν(C=N) +δ(NH)], thioamide III [δ(NH)], and thioamide IV [ν(C=S)], respectively. These bands shift upon coordination to metal suggesting that the sulfur of thioamide and nitrogen of azomethine coordinate to the metal [29–31]. Pyridine ring vibrations mostly affecting the coordination of pyridine are pyridine ring-stretching, in-plane-ring-bending, and

Table 2. Selected IR bands of ligand and complexes.

Compound	Thioamide I	Thioamide II	Thioamide III	Thioamide IV	Pyridine ring	ν(M–N)	ν(M–S)	Anion bands
Ligand	1695	1357	1288	814	1569, 593, 430	–	–	–
$[Mn(L)NO_3]NO_3$	1664	1343	1273	781	1578, 618, 510	388	348	1410, 1384, 1290, 1073
[Mn(L)OAc]OAc	1680	1388	1275	802	1584, 605, 510	361	329	1590, 1438, 1256
$[Co(L)NO_3]NO_3$	1616	1450	1257	795	1582, 616, 456	383	352	1411, 1384, 1309, 1073
[Co(L)OAc]OAc	1663	1348	1254	804	1577, 599, 503	369	343	1596, 1452, 1286
$[Cu(L)NO_3]NO_3$	1686	1384	1270	811	1587, 612, 500	380	366	1448, 1384, 1317, 1077
[Cu(L)OAc]OAc	1664	1378	1256	799	1577, 610, 498	477	368	1610, 1483, 1299

out-of-plane-ring-bending. These vibrations are at 1569, 593, and 430 cm^{-1} in the IR spectrum of ligand and shift upward upon coordination to metal [32].

New bands in the IR spectra of complexes are in the range 361–477 and 329–368 cm^{-1} (table 2) assigned to ν(M–N) and ν(M–S) stretching vibrations [33], confirming coordination of the ligand to metal through NS donors.

Nitrato complexes show IR bands in the range 1410–1448 (ν_5), 1290–1317 (ν_1), and 1073–1077 cm^{-1} (ν_2) due to NO stretches. The value of $\Delta(\nu_5-\nu_1)$, i.e., 102–131 cm^{-1}, suggests monodentate coordination. For monodentate coordination of NO_3^-, the separation of first NO stretching vibrations is low ($\approx$100–130 cm^{-1}), whereas these bands show larger separation ($\approx$180–225 cm^{-1}) when NO_3^- is bidentate. IR spectra also show a band at 1384 cm^{-1} due to ionic nitrate [34]. The acetato complexes show bands in the regions 1438–1483 and 1256–1299 cm^{-1} due to ν_{as}(OAc) and ν_s(OAc). The $\Delta\nu$ of 166–184 cm^{-1} suggests unidentate coordination of the Oac^-. The oxygen of –COO that is not coordinated to metal is hydrogen bonded to the free amino groups of the ligand. Thus, the –COO stretching frequencies of acetate group are affected by coordination as well as intermolecular interactions. On coordination, the antisymmetric frequency [ν_{as}(OAc)] shows the positive shift, whereas the symmetric frequency [ν_s(OAc)] shows the negative shift, and the separation of these two frequencies depends upon the nature of M–O bonding. These complexes also have IR bands at 1590–1610 cm^{-1} from uncoordinated acetate [32, 35].

3.4. *Electronic spectra*

Electronic spectra were recorded in DMSO/DMF solution and the data are given in table 3. The ligand displays two absorption bands at 26,246 and 29,940 cm^{-1} due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transitions. The complexes show the transitions in the range 34,125–42,194 cm^{-1} due to the charge transfer and intraligand bands.

The electronic spectra of Mn(II) complexes display absorption bands in the range 17,094–18,691, 23,848–24,630, 26,975–28,868, and 33,333–37,313 cm^{-1} which may be assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G), $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$(^4G), $^6A_{1g} \rightarrow {}^4E_g$($^4D$), and $^6A_{1g} \rightarrow {}^4T_{1g}$(P) transitions, respectively [36], suggesting octahedral Mn(II).

The electronic spectra of Co(II) complexes show transitions at 9280–9540, 17,180–17,890, and 20,358–20,545 cm^{-1}, assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ν_1, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ν_2, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ν_3, respectively. The transitions reflect to the tetragonal distortion from regular octahedral geometry of the Co(II) complexes [36, 37].

Electronic spectra of Cu(II) complexes show transitions at 10,741–10,878, 21,180–22,522, and 26,410–27,472 cm^{-1} due to the $^2B_{1g} \leftarrow {}^2A_{1g}$ ($d_{x^2-y^2} \leftarrow d_{z2}$) ν_1, $^2B_{1g} \leftarrow {}^2B_{2g}$ ($d_{x^2-y^2} \leftarrow d_{xy}$) ν_2, and $^2B_{1g} \leftarrow {}^2E_g$ ($d_{x^2-y^2} \leftarrow d_{xz}$, d_{yz}) ν_3, respectively [36, 38], suggesting Cu(II) possesses D_{4h} symmetry from Jahn–Teller distortion.

The ligand field parameters like B, C (Racah parameters), 10 D_q, covalency factor β and LFSE have been calculated and are summarized in table 3. The Slater–Condon parameters F_2 and F_4 for Mn(II) complexes have also been evaluated as a function of Racah parameters B and C (table 3).

3.5. *EPR spectra*

EPR spectral data of the complexes are presented in table 4. The X-band EPR spectra of Mn(II) complexes in polycrystalline form give only one signal at

Table 3. Magnetic, electronic spectral data and ligand field parameters of complexes.

Complex	μ_{eff} (B.M.)	λ_{max} (cm^{-1}), ε (L $mole^{-1}$ cm^{-1})	D_q (cm^{-1})	B (cm^{-1})	C (cm^{-1})	β	LFSE (kJ mol^{-1})	F_4	F_2
Ligand	–	26,246 (105), 29,940 (140)	–	–	–	–	–	–	–
$[Mn(L)NO_3]NO_3$	5.98	18,691 (40), 23,848 (68), 26,975 (92), 33,333 (150)	1869.1	446	3876	0.46	–	110.7	999.7
[Mn(L)OAc]OAc	6.00	17,094 (28), 24,630 (55), 28,868 (85), 37,313 (175)	1709.4	605	3715	0.63	–	106.1	1135.7
$[Co(L)NO_3]NO_3$	4.88	9280 (30), 17,890 (70), 20,545 (105), 36,743 (198)	1090.1	838	–	0.75	104.20	–	–
[Co(L)OAc]OAc	5.03	9540 (55), 17,180 (80), 20,358 (95), 34,125 (168)	1117.7	798	–	0.71	106.83	–	–
$[Cu(L)NO_3]NO_3$	1.89	10,741 (45), 22,522 (86), 27,472 (70), 42,194 (110)	–	–	–	–	–	–	–
[Cu(L)OAc]OAc	1.91	10,878 (56), 21,180 (65), 26,410 (112), 36,298 (180)	–	–	–	–	–	–	–

Table 4. EPR spectral data and orbital reduction parameters of complexes.

Complex	Polycrystalline form					Solution form						
	$g_{\perp}$ (LNT/RT)	$g_{\|\|}$ (LNT/RT)	g_{iso} (RT)	g_{iso} (LNT)	G	g_{iso} (RT)	A_{iso} (RT)	g_{iso} (LNT)	A_{iso} (LNT)	$K_{\perp}^2$	$K_{\|}^2$	k
$[Mn(L)NO_3]NO_3$	–	–	1.9932	2.2041	–	1.9920	90.5	2.0531	94.5	–	–	–
[Mn(L)OAc]OAc	–	–	2.0099	2.3096	–	1.9351	80.0	2.0382	91.7	–	–	–
$[Co(L)NO_3]NO_3$	2.0255	3.0962	–	2.3824	–	–	–	–	–	–	–	–
[Co(L)OAc]OAc	1.9934	2.8066	–	2.2645	–	–	–	–	–	–	–	–
$[Cu(L)NO_3]NO_3$	2.0192	2.3730	2.14	–	21.71	–	–	–	–	0.28	1.26	0.78
[Cu(L)OAc]OAc	2.0319	2.2576	2.11	–	8.64	–	–	–	–	0.47	0.82	0.76

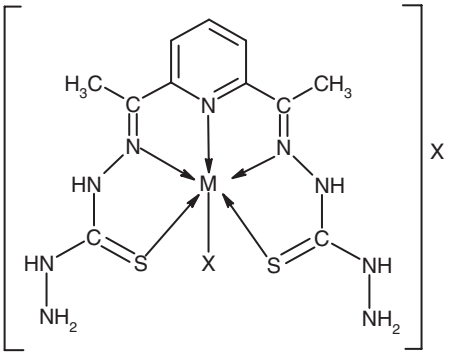


Figure 1. Structure of [M(L)X]X, where M=Mn(II), Co(II), and Cu(II), and X= NO_3^- and OAc^-.

$g_{iso} = 1.9932–2.3096$, observed even at room temperature, which suggests that the spin-system is effectively coupled with the lattice vibrations and the spin relaxation time is very small [39]. The EPR spectra of Mn(II) complexes in solution at both temperatures, i.e., room temperature and liquid nitrogen temperature, give six lines (Supplemental Material) at $g_{iso} = 1.9351–2.0531$, due to electron spin-nuclear spin coupling (^{55}Mn, $I = 5/2$). The coupling constants A_{iso} are consistent with octahedral coordination around Mn(II). The A_{iso} values (80.0–95.5) reflect covalent metal-ligand bonding [40, 41].

X-band EPR spectra of Co(II) complexes at liquid nitrogen temperature display a broad signal with g in the range $g_{\|} = 2.8066–3.0962$, $g_{\perp} = 1.9934–2.0255$ and $g_{iso} = 2.2645–2.3824$, corresponding to tetragonal Co(II) complexes [42, 43]. Owing to fast spin-relaxation of high-spin Co(II), the signals are observed only at low temperature.

X-band EPR spectra of Cu(II) complexes at room temperature in polycrystalline form show only one broad signal at $g_{iso} = 2.11–2.14$ (Supplementary material) [42] for tetragonal Cu(II). The calculated g values show the order $g_{\|} > g_{\perp} > 2.0023$, consistent with $d_{x^2-y^2}$ ground state [38, 44] and the B_{1g} orbital accommodating the odd electron. The exchange interaction parameter G is greater than 4 (table 4), reflecting negligible interaction between metal centers [38].

The EPR parameters and the d–d transition energies are used to evaluate the orbital reduction factor k by using the expression $k^2 = k_{\|}^2 + 2k_{\perp}^{2/3}$, where $k_{||}$ and $k_{\perp}$ are the parallel and perpendicular components of the orbital reduction factor. The values of k (0.76–0.78) less than unity suggest covalent complexes [44]. The structures are given in figure 1.

3.6. *Antimicrobial activities*

The antipathogenic activities of ligand and its complexes are summarized in tables 5 and 6. The complexes have moderate antipathogenic activities, more than the free ligand (Supplementary material). This improvement in antipathogenic activity of ligand on complexation is based on Overtone's Concept and Chelation Theory [45, 46].

Table 5. Antifungal activity of the compounds.

	Fungal inhibition (%) (conc. in μg mL^{-1})								
	A. brassicae			*A. niger*			*F. oxysporum*		
Compound	100	200	300	100	200	300	100	200	300
Ligand	32	41	60	30	45	59	35	50	60
$[Mn(L)NO_3]NO_3$	40	56	62	40	49	64	42	55	65
[Mn(L)OAc]OAc	40	52	62	38	48	64	41	54	66
$[Co(L)NO_3]NO_3$	54	65	72	50	66	77	54	66	80
[Co(L)OAc]OAc	52	64	70	50	62	75	54	66	80
$[Cu(L)NO_3]NO_3$	58	68	80	55	70	84	58	71	88
[Cu(L)OAc]OAc	55	66	75	54	68	80	56	70	85
Standard (Captan)	70	80	100	75	90	100	65	75	100

Table 6. Antibacterial activity of compounds.

	Bacterial inhibition zone (mm) (conc. in μg mL^{-1})					
	X. compestris			*P. aeruginosa*		
Compound	250	500	1000	250	500	1000
Ligand	8	10	14	6	9	12
$[Mn(L)NO_3]NO_3$	9	12	16	8	13	15
[Mn(L)OAc]OAc	9	13	15	7	11	14
$[Co(L)NO_3]NO_3$	12	15	19	11	15	18
[Co(L)OAc]OAc	13	15	20	12	14	19
$[Cu(L)NO_3]NO_3$	18	22	25	17	23	28
[Cu(L)OAc]OAc	19	21	26	16	23	27
Standard (Streptomycin)		30			35	

The copper(II) complexes are most active, redox processes and high affinity of these complexes to DNA of microorganisms may be involved [47–49].

4. Conclusions

The physicochemical and spectral studies reveal that 2,6-diacetylpyridine bis(thiocarbohydrazone) provides quinquedentate coordination to metals in six-coordinate complexes. Mn(II) complexes have octahedral geometry, whereas the Co(II) and Cu(II) complexes were tetragonally distorted. The A_{iso} values, nephelauxetic parameter (β) and orbital reduction factor (k) indicate covalent metal–ligand bonding. The complexes have enhanced antipathogenic activity in comparison to the free ligand.

Acknowledgments

The authors are thankful to the UGC, New Delhi, for financial assistance and Dr Pratibha Sharma, Principal Scientist, IARI, Pusa, New Delhi, for providing laboratory facilities for screening the biological activities.

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