

Transition metal complexes with a new tridentate ligand, 5-[6-(5-mercapto-1,3,4-oxadiazol-2-yl)pyridin-2-yl]-1,3,4-oxadiazole-2-thiol

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Abstract: A new ligand 5-[6-(5-mercapto-1,3,4-oxadiazol-2-yl)pyridin-2-yl]-1,3,4-oxadiazole-2-thiol (L) and its Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes were synthesized. The authenticity of the ligand and its transition metal complexes were established by elemental analyses, conductance and magnetic susceptibility measurements, as well as spectroscopic (IR, ¹H- and ¹³C-NMR, electronic, mass, ESR) and thermal studies. The IR and ¹H-NMR spectral studies revealed the existence of the ligand in the thiol form in the solid state, whereas in the thione form in the dissolved state. The magnetic and electronic spectral studies suggest an octahedral geometry for all the complexes. The ligand acts as a tridentate ligand coordinating through the pyridine nitrogen and the nitrogen atoms (N-3' and N-3'') of the two oxadiazole rings. Antimicrobial screening of the ligand and its metal complexes were determined against the bacteria *Escherichia coli* and *Bacillus cirroflagellosus*, as well as against the fungi, *Aspergillus niger* and *Candida albicans*.

Keywords: oxadiazole, transition metal complexes, magnetic moments, IR spectra, electronic spectra, biological activity.

INTRODUCTION

1,3,4-Oxadiazoles are of considerable pharmaceutical and material interest. They have been shown to possess muscle relaxant, antimitotic, analgesic, anti-inflammatory, anticonvulsive, diuretic and anti-emetic properties.¹ They also possess tranquilizing, antitubercular, hypoglycaemic, herbicidal, antiviral, amoebicidal, insecticidal, hypnotic and sedative activities. Some material applications of 1,3,4-oxadiazole derivatives lie in the field of liquid crystals.¹

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). The oxadiazole ring is electron deficient, resulting in poor hole transport but good electron transport properties. Although some types of metal com-

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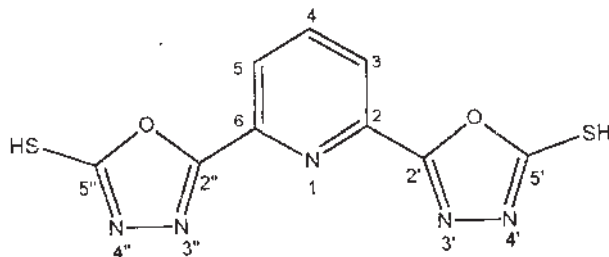


Fig. 1. Ligand.

plexes have found to be good emitters and/or excellent electron transporters with excellent thermal properties, no oxadiazole metal complexes were employed in light emitting-diodes until recently.² Yang *et al.*³ studied a new conjugated polymer chemosensor functionalized with 2,6-bis(1,3,4-oxadiazol-2-yl)pyridine for metal ion recognition. Franski⁴ prepared Cu(II) and Cu(I) complexes of 2,5-disubstituted 1,3,4-oxadiazoles, namely 2,5-diphenyl-1,3,4-oxadiazole, 2,5-bis(2-pyridyl)-1,3,4-oxadiazole and 2,5-bis(4-pyridyl)-1,3,4-oxadiazole. The compounds studied tend to form both 1:1 and 2:1 chelate complexes with both Cu(II) and Cu(I). The complexes with Cu(I) are formed in the electrospray ionization process. Al-Obaidi *et al.*⁵ prepared mono- and dinuclear Cu(I) and Cu(II) complexes of mercapto-1,3,4-oxadiazoles and also studied their microbial activity.

Influenced by these various properties of 1,3,4-oxadiazoles and their complexes, a programme to design and study the title ligand (Fig. 1), which has an appropriate architecture to interact directly with metal centres was commenced. In order to reveal the conformational changes of the newly synthesized ligand upon coordination with transition metals, a study on the synthesis, characterization and spectroscopic evidence for their structural elucidation was undertaken.

EXPERIMENTAL

Materials

All the employed chemicals were of reagent grade. 2,6-Dipicolinic acid (Spectrochem), thionyl chloride (BDH), hydrazine hydrate (s. d. fine) and carbon disulphide (BDH) were used. All the metal chlorides ($\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$) were purchased from s. d. fine chemicals.

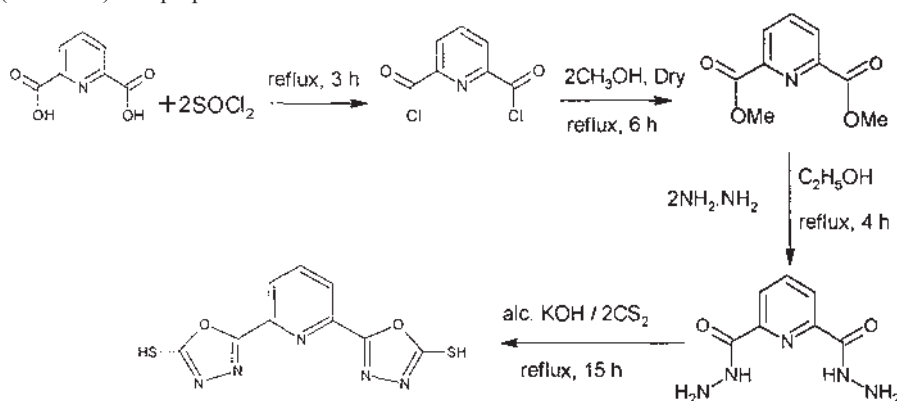
Analytical methods and physical measurements

C, H and N were analyzed on a Thermoquest Elemental Analyzer. The molar conductance measurements were made in DMSO with 10^{-3} M solutions using an Elico Conductivity Bridge, Type CC-01 with a cell constant of 0.53. All the metal contents were determined by the gravimetric method,⁶ *i.e.*, Mn(II) as manganese pyrophosphate, Ni(II) as nickel dimethylglyoximate, Co(II) as cobalt oxinate, Cu(II) as copper salicylaldoximate and Zn(II) as zinc ammonium phosphate. Chloride was determined gravimetrically as AgCl .⁶ The IR spectra were recorded on a Nicolet FT-IR spectrometer Impact 410 using KBr pellets. The ^1H - and ^{13}C -NMR spectra were scanned in $\text{DMSO}-d_6$ on a Bruker Avance 300 MHz spectrometer and the chemical shifts are given in ppm relative to TMS. The UV-Vis spectra were recorded in DMSO on a Hitachi 150-20 spectrophotometer. The magnetic susceptibilities were measured at room temperature using a Faraday balance with $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant.⁷ The mass spectrum was recorded on an Auto spec EI-Mass Spec-

trometer using 70 eV with a source temperature of 150 °C. The ESR spectra were recorded on an EPR-E-4 spectrometer, operating in the X-band region, with TCNE as the reference material, at both 300 and 77 K. The thermal studies of the complexes were performed on a Mettler Toledo TGA/SDTA851^e with star^e software, under a nitrogen atmosphere at a heating rate of 10 °C/min in the temperature range of 50 to 1000 °C.

Preparation of the ligand

The new ligand 5-[6-(5-mercapto-1,3,4-oxadiazol-2-yl)pyridin-2-yl]-1,3,4-oxadiazole-2-thiol (Scheme 1) was prepared as follows:



Scheme 1. Preparation of the ligand.

A mixture of 2,6-dipicolinic acid hydrazide⁸ (10 mmol, 1.95 g) dissolved in ethanol (50 mL), KOH (20 mmol, 0.112 g) in 60 ml ethanol and CS₂ (20 mmol, 1.2 mL) was refluxed on a water bath for ≈ 8 h, until the evolution of H₂S gas ceased. The excess CS₂ was removed under reduced pressure. The resultant mixture was acidified with acetic acid and the white solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel.

Yield: 80 %, m. p. 340 °C.

Preparation of complexes

The Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes were prepared by refluxing the respective hydrated metal chloride (10 mmol) in 15 mL ethanol with 50 mL of an ethanolic solution of the ligand (10 mmol, 2.79 g) for ≈ 4 h. The resultant solids which separated were filtered, washed with ethanol and dried in air.

Yield: 75 – 80 %.

RESULTS AND DISCUSSION

Examination of elemental analyses data, given in Table I for all the complexes indicate their 1:1 (metal:ligand) stoichiometry. They are insoluble in chloroform, carbon tetrachloride, methanol and ethanol but soluble in DMF and DMSO. The molar conductivity data obtained in DMSO suggest that all the complexes are non-electrolyte in nature.

Mass spectrum of L

The mass spectrum of the ligand exhibits a molecular ion peak [M+1] at *m/z* 280.04 and [M+NH₄⁺] at *m/z* 297.04 (Fig. 2).

TABLE I. Analytical, conductance and magnetic data of the ligand and its complexes

Compound	Molecular Formula	C/%	H/%	N/%	S/%	M/%	Cl/%	Λ S cm ² mol ⁻¹	μ_{eff} μ_{B}
L	C ₉ H ₅ N ₅ O ₂ S ₂	38.54 (38.70)	1.60 (1.80)	25.02 (25.07)	22.01 (22.96)	–	–	–	–
[MnCl ₂ (H ₂ O)]	MnC ₉ H ₇ N ₅ O ₃ S ₂ Cl ₂	24.44 (24.48)	2.00 (2.05)	15.66 (15.87)	14.35 (14.53)	12.22 (12.45)	15.99 (16.07)	13.46	5.90
[CoCl ₂ (H ₂ O)]	CoC ₉ H ₇ N ₅ O ₃ S ₂ Cl ₂	25.11 (25.30)	2.10 (2.12)	16.22 (16.39)	14.95 (14.98)	13.50 (13.79)	16.20 (16.59)	12.60	3.38
[NiCl ₂ (H ₂ O)]	NiC ₉ H ₇ N ₅ O ₃ S ₂ Cl ₂	25.11 (25.32)	1.55 (1.65)	16.28 (16.40)	15.00 (15.02)	13.00 (13.74)	16.80 (16.60)	15.47	2.90
[CuCl ₂ (H ₂ O)]	CuC ₉ H ₇ N ₅ O ₃ S ₂ Cl ₂	25.00 (25.03)	1.58 (1.63)	16.12 (16.22)	14.66 (14.85)	14.65 (14.71)	16.00 (16.41)	4.87	1.78
[ZnCl ₂ (H ₂ O)]	ZnC ₉ H ₇ N ₅ O ₃ S ₂ Cl ₂	22.92 (22.99)	2.31 (2.36)	14.50 (14.90)	13.48 (13.65)	14.00 (13.92)	15.15 (15.09)	12.42	Diamag.

The values in the parentheses are calculated. Diamag. = Diamagnetic.

Infrared spectra

In the IR spectrum (Table II) of the ligand, the band at 1619 cm⁻¹ was assigned to $\nu(\text{C}=\text{N})$,⁹ while that at ≈ 2540 cm⁻¹ to $\nu(\text{SH})$. These observations suggest that the ligand exists in the thiol form (Fig. 3) in the solid state. A strong band at 1084 cm⁻¹ was attributed to $\nu(\text{N}-\text{N})$ of the oxadiazole ring.¹⁰ Bands located at ≈ 1563 ,

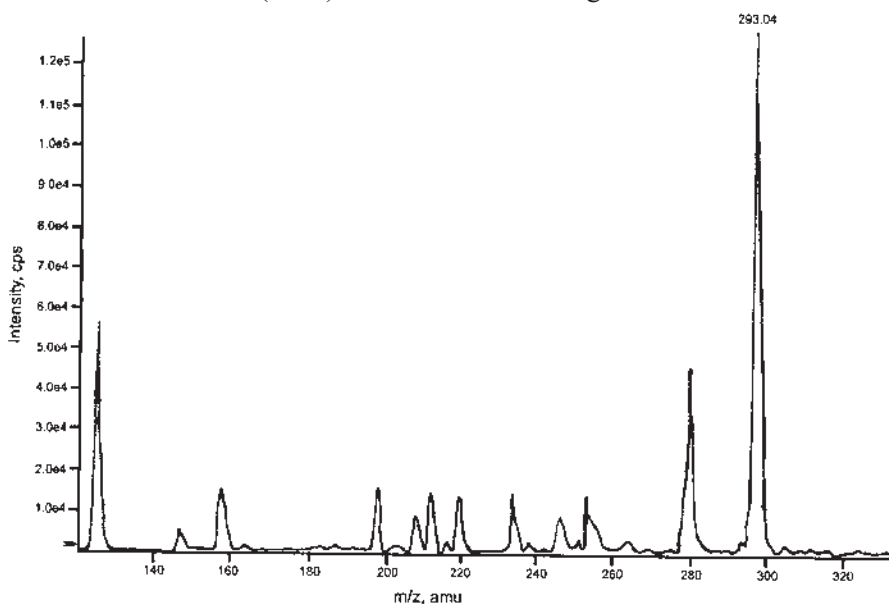


Fig. 2. Mass spectrum of the ligand.

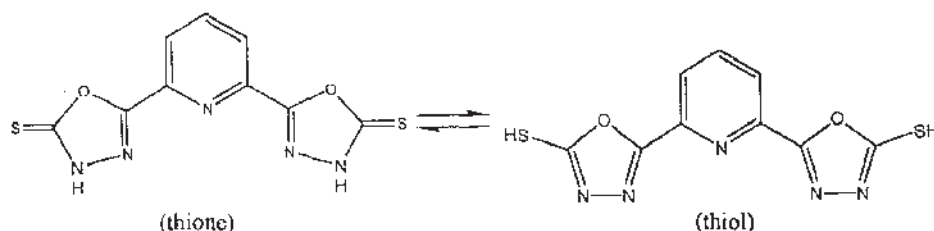


Fig. 3. Tautomeric forms of the ligand.

689 and 490 cm^{-1} were assigned to the pyridine ring deformation, in-plane deformation and out-of-plane deformation,¹¹ respectively.

In the spectra of the complexes, a band due to $\nu(\text{SH})$ is visible in the region 2540–2548 cm^{-1} , suggesting the non-involvement of $-\text{SH}$ in coordination. The shift of $\nu(\text{N}-\text{N})$ to lower energy and the weakening of the $\nu(\text{C}=\text{N})$ band indicates the coordination of $\text{C}=\text{N}$ to the metal centre through the nitrogen atoms, N-3' and N-3'' of the two oxadiazole rings (Fig. 1). This view is further supported by the appearance of a band corresponding to the metal–nitrogen stretching vibration¹² at 554–579 cm^{-1} in the complexes. All the complexes exhibit a broad band at 3500–3400 cm^{-1} followed by another band at 723–790 cm^{-1} , assignable to lattice held and / or coordinated water molecules.¹³

¹H- and ¹³C-NMR spectra

The ¹H-NMR spectrum of the ligand exhibits a sharp singlet at 10.37 ppm due to NH, indicating the thione form of the ligand in the solution state. The aromatic protons were observed in the region 8.18–8.28 ppm. The ¹³C-NMR spectrum shows peaks at 143.19 (C-2,6), 125.50 (C-3,5) and 140.67 (C-4) ppm for the pyridine ring.¹⁴ The peaks observed at 159.71 and 178.81 ppm are due to C-2', 2''¹⁴ and C-5', 5'' (C=S),¹⁵ respectively, of the oxadiazole ring (Fig. 1).

In the ¹H-NMR spectrum of the $[\text{ZnLCl}_2(\text{H}_2\text{O})]$ complex, the signal due to $-\text{NH}$ is no longer present and a new peak at 4.3 ppm due to $-\text{SH}$ is observed. This suggests the existence of ligand in the thione form in the complexes (Fig. 3) and the non-involvement of $-\text{SH}$ in the coordination. The aromatic protons are observed in the region 8.20–8.29 ppm.

Magnetic properties

The effective magnetic moment values of the complexes are presented in Table I. The Mn(II) complex has a μ_{eff} value of 5.90 μ_{B} , which suggests a spin-free complex. The Co(II) complex has a magnetic moment of 3.38 μ_{B} which is typical of Co(II) ion in an octahedral environment.¹⁶ A magnetic moment value of 2.90 μ_{B} is observed for the Ni(II) complex, expected for octahedral geometry.¹⁶ The Cu(II) complex exhibits a value of 1.78 μ_{B} , expected for S=1/2 system having an octahedral geometry. The Zn(II) complex is diamagnetic as expected for a d^{10} configuration.

TABLE II. IR spectral data (cm^{-1}) of L and its complexes

Compound	$\nu(\text{O-H})$ (H_2O)	$\nu(\text{S-H})$	$\nu(\text{C=N})$	$\nu(\text{N-N})$	Pyridine ring deformation	Pyridine in-plane deformation	Pyridine out-of-plane deformation	$\nu(\text{M-N})$	$\delta(\text{O-H})$ (H_2O)
L	-	2540	1619	1084	1563	689	490	-	-
$[\text{MnLCI}_2(\text{H}_2\text{O})]$	3413	2542	1574	1066	1593	696	515	579	782
$[\text{CoLCI}_2(\text{H}_2\text{O})]$	3407	2540	1554	1066	1603	695	520	572	733
$[\text{NiLCI}_2(\text{H}_2\text{O})]$	3431	2548	1557	1066	1603	695	516	572	733
$[\text{CuLCI}_2(\text{H}_2\text{O})]$	3437	2540	1547	1010	1616	702	480	566	782
$[\text{ZnLCI}_2(\text{H}_2\text{O})]$	3419	2540	1560	1029	1597	708	545	554	795

Electronic spectra

The electronic spectra of the ligand and all the complexes were recorded in DMSO. The $n-\pi^*$ transition associated with azomethine group in the ligand was found in the region 31250 cm^{-1} . Co(II) complex exhibits bands at 11574 cm^{-1} and 15360 cm^{-1} , which are assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{2g}$ transitions. The Ni(II) complex exhibits bands at 13106 , 20790 and 26881 cm^{-1} , assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively, in an octahedral field. The ligand field parameters, such as the Racah interelectronic repulsion parameter, B (556.8 cm^{-1}), the nephelauxetic ratio, β (0.53) and the ν_2/ν_1 ratio (1.58), are in good agreement with the reported values for an octahedral Ni(II) complex.¹⁷ The Cu(II) complex shows a broad band peaking at 11682 cm^{-1} . This band may arise from the ${}^2E_g \rightarrow {}^2T_{2g}$ transition in an octahedral field.¹⁸ The Zn(II) complex did not show any d-d transitions.

Electronic spin resonance spectra

The ESR spectrum of the Cu(II) complex at both 300 K and 77 K shows one intense absorption band at high field, which is isotropic due to the tumbling motion of the molecules. The " g_{iso} " values at 300 and 77 K are 2.07 and 2.08 , respectively. The mononuclear nature of the complex was also evident from the absence of a half field signal due to the $m_s = \pm 2$ transitions, ruling out any Cu-Cu interaction.¹⁹

Thermal studies

The $[\text{CoLC}_2(\text{H}_2\text{O})]$ complex shows a first weight loss of 4.00% (calcd. 4.21%) at $150\text{--}220\text{ }^\circ\text{C}$, indicating the loss of one coordinated water molecule. The second weight loss of 81.90% (81.98%) between $220\text{--}500\text{ }^\circ\text{C}$ corresponds to the loss of a ligand and two chloride molecules. When heated above $500\text{ }^\circ\text{C}$, a plateau is obtained due to the formation of stable CoO. The residue 13.50% (calcd. 13.81%) agrees with the analytical result for the metal content.

Biological activity

The antibacterial and antifungal activity of the ligand, transition metal salts and the corresponding complexes were assayed against two bacteria, *Escherichia coli* and *Bacillus cirroflagellosus* and two fungi, *Aspergillus niger* and *Candida albicans*, by the cup plate method. The results were compared against the standards norfloxacin and griseofulvin, which were screened simultaneously. Norfloxacin is an antibacterial drug and griseofulvin is an antifungal drug currently in use.

The activity was measured by measuring the diameter of the inhibition zone in millimeters and the results are compiled in Table III in terms of the percent of inhibition with respect to the standards. The percentage inhibition was calculated using the formula:

$$\text{Relative inhibition (\%)} \text{ of the test substance} = 100 (X - Y) / (Z - Y),$$

where X = the area of inhibition in the sample plate,

Y = the area of inhibition in the control (DMSO) plate, and

Z = the area of inhibition in the standard plate.

The ligand was weakly active against the bacteria and inactive against the fungi used. The Cu(II) and Zn(II) complexes were found to be more active, while the Mn(II), Co(II) and Ni(II) complexes were moderately active.

TABLE III. Antimicrobial activities of L and its metal complexes

Compound	Zone in inhibition in mm (% inhibition)							
	Antibacterial				Antifungal			
	B. C.		E. C.		A. N.		C. A.	
	mm	%	mm	%	mm	%	mm	%
MnCl ₂ ·6H ₂ O	20	52.63	20	52.63	21	55.00	21	55.00
CoCl ₂ ·4H ₂ O	28	94.73	28	94.73	28	90.00	28	90.00
NiCl ₂ ·6H ₂ O	26	84.21	26	84.21	22	60.00	22	60.00
CuCl ₂ ·2H ₂ O	16	31.57	21	57.89	28	90.00	27	85.00
ZnCl ₂ ·2H ₂ O	22	63.15	25	78.94	32	–	35	–
L	14	21.05	14	21.05	13	15.00	13	15.00
[MnLCl ₂ (H ₂ O)]	16	31.57	16	31.57	15	25.00	14	20.00
[CoLCl ₂ (H ₂ O)]	16	31.57	16	31.57	17	35.00	16	30.00
[NiLCl ₂ (H ₂ O)]	16	31.57	16	31.57	17	35.00	18	40.00
[CuLCl ₂ (H ₂ O)]	22	63.15	22	63.15	29	95.00	29	95.00
[ZnLCl ₂ (H ₂ O)]	22	63.15	22	63.15	22	60.00	22	60.00
Norfloxacin	29	–	29	–	–	–	–	–
Griseofulvin	–	–	–	–	30	–	30	–
DMSO (Control)	10	–	10	–	10	–	10	–

E. C. = *Escherichia coli*, B. C. = *Bacillus cirroflagellus*, A. N. = *Aspergillus niger*, C. A. = *Candida albicans*

The increased activity of the Cu(II) and Zn(II) chelates can be explained on the basis of the Overtone concept and the Tweedy chelation theory.²⁰ According to the Overtone concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only lipid-soluble materials, for which reason liposolubility is an important factor controlling antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with the donor groups. Furthermore, it increases the delocalisation of the π -electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into the lipid membranes and the blocking of the metal binding sites of the enzymes of the microorganisms.

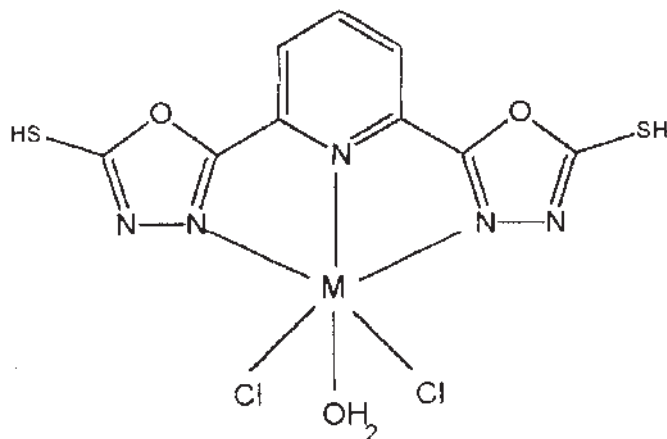


Fig. 4. Proposed structure of $[MLCl_2(H_2O)]$, where $M = Mn(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$.

These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism.

On the basis of the elemental analyses, molar conductances, magnetic susceptibilities, electronic, IR, 1H -NMR and thermal studies, the structure in Fig. 4 is proposed for the reported complexes.

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ИЗВОД

КОМПЛЕКСИ ПРЕЛАЗНИХ МЕТАЛА СА НОВИМ ТРИДЕНТАТНИМ ЛИГАНДОМ, 5-[6-(5-МЕРКАПТО-1,3,4-ОКСАДИАЗОЛ-2-ИЛ)-ПИРИДИН-2-ИЛ]-1,3,4-ОКСАДИАЗОЛ-2-ТИОЛОМ

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Синтетисан је нови лиганд 5-[6-(5-меркапто-1,3,4-оксадиазол-2-ил)-пиридин-2-ил]-1,3,4-оксадиазол-2-тиол и његови $Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ и $Zn(II)$ комплекси. Аутентичност лиганда и његових комплекса прелазних метала утврђена је елементарном анализом, мерењем проводљивости и магнетне суспектибилности, спектроскопским (IR, 1H - и ^{13}C -NMR, електронским, масеним, ESR) и термичким студијама. IR и 1H -NMR спектрално проучавање потврдило је да је лиганд у тиолном облику у чврстом стању, док је у тионском облику у раствору. Проучавање магнетизма и електронских спектра указују на октаедарску геометрију у свим комплексима. Лиганд је тридентат, координујући се преко пиридинских азота и азотових атома (N-3' и N-3'') са два оксадиазолова прстена. Антимикробни тест лиганда и његових комплекса метала одређен је на бактеријама *Escherichia coli*, *Bacillus cirroflagellosus* и гљивицама *Aspergillus niger* и *Candida albicans*.

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