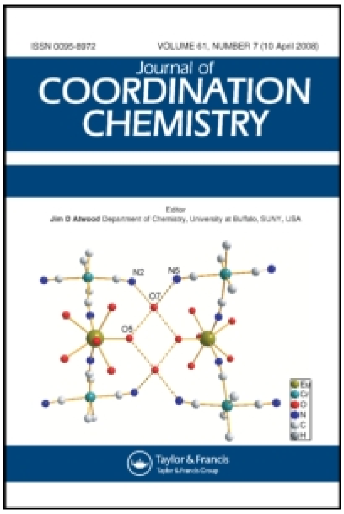

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Spectroscopic and Magnetic Studies on Metal Complexes of 5-Methyl-3-(2-Hydroxyphenyl)Pyrazole

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To cite this Article Khalil, Saied M. E.(2003) 'Synthesis, Spectroscopic and Magnetic Studies on Metal Complexes of 5-Methyl-3-(2-Hydroxyphenyl)Pyrazole', Journal of Coordination Chemistry, 56: 12, 1013 — 1024
To link to this Article: DOI: 10.1080/0095897031000135289
URL: http://dx.doi.org/10.1080/0095897031000135289

J. Coord. Chem., Vol. 56, No. 12, 15 August 2003, pp. 1013–1024

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SYNTHESIS, SPECTROSCOPIC AND MAGNETIC STUDIES ON METAL COMPLEXES OF 5-METHYL-3-(2-HYDROXYPHENYL)PYRAZOLE

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(Received 10 July 2002; Revised 27 December 2002; In final form 8 April 2003)

A tridentate ONN donor ligand, 5-methyl-3-(2-hydroxyphenyl)pyrazole; H_2L, was synthesized by reaction of 2-(3-ketobutanoyl)phenol with hydrazine hydrate. The ligand was characterized by IR, ^{1}H NMR and mass spectra. ^{1}H NMR spectra indicated the presence of the phenolic OH group and the imine NH group of the heterocyclic moiety. Different types of mononuclear metal complexes of the following formulae $[(HL)_2M]\cdot xH_2O$ (M=VO, Co, Ni, Cu, Zn and Cd), $[(HL)_2M(H_2O)_2]$ (M=Mn and UO_2) and $[(HL)LFe(H_2O)_2]$ were obtained. The Fe(III) complex, $[(HL)LFe(H_2O)_2]$ undergoes solvatochromism. Elemental analyses, IR, electronic and ESR spectra as well as thermal, conductivity and magnetic susceptibility measurements were used to elucidate the structures of the newly prepared metal complexes. A square-pyramidal geometry is suggested for the VO(IV) complex, square-planar for the Cu(II), Co(II) and Ni(II) complexes, octahedral for the Fe(III) and Mn(II) complexes and tetrahedral for the Zn(II) and Cd(II) complexes, while the UO_2(VI) complex is eight-coordinate. Transmetallation of the UO_2(VI) ion in its mononuclear complex by Fe(III), Ni(II) or Cu(II) ions occurred and mononuclear Fe(III), Ni(II) and Cu(II) complexes were obtained. IR spectra of the products did not have the characteristic UO_2 absorption band and the electronic spectra showed absorption bands similar to those obtained for the corresponding mononuclear complexes. Also, transmetallation of the Ni(II) ion in its mononuclear complex by Fe(III) has occurred. The antifungal activity of the ligand and the mononuclear complexes were investigated.

Keywords: Mononuclear metal complexes; Pyrazole ligand; Hetero trinuclear complexes; Transmetallation reactions

INTRODUCTION

The properties of pyrrole, pyrazole and imidazole are of interest because of the widespread occurrence of these heterocycles in compounds of biological importance [1]. Aromatic nitrogen heterocycles play an important role in coordination chemistry. Neutral donor ligands such as pyridine, 2,2′-bipyridine or polydentate macrocycles stabilize a variety of transition metal complexes [2]. Monoanionic monodentate ligands

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0095897031000135289

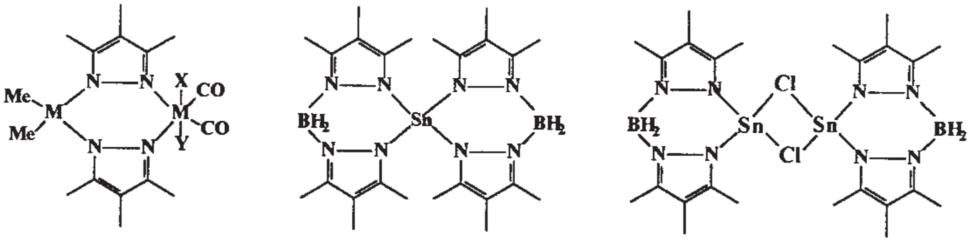


FIGURE 1 Bi- and trinuclear complexes of the pyrazole ligand.

such as pyrazolyl or imidazolyl are able to bridge two transition metal centers, resulting in bi- and multinuclear complexes [3–10]. Figure 1 shows three examples.

The aim of this work was to synthesize and characterize new mononuclear complexes of a variety of transition metal cations of a new ligand derived from the pyrazole nucleus. In addition, transmetallation reactions were used to check replacement of one metal by other metals and the probability of obtaining species with more centers.

EXPERIMENTAL

Materials

The acetate salts of Mn(II), Co(II), Cu(II), Ni(II), Zn(II), Cd(II) and UO_2(VI), $FeCl_3 \cdot 6H_2O$, $VOSO_4 \cdot H_2O$, hydrazine hydrate, 2-hydroxyacetophenone, ethylacetate and DMF were purchased from Merck. Organic solvents were reagent grade. 2-(3-keto-butanoyl)phenol was prepared according to the Wittig method [11].

Measurements

Visible spectra of the metal complexes, as DMF solutions, were recorded on a Jasco 550 spectrophotometer. IR spectra of the ligand and its metal complexes, as KBr discs, were recorded on a Perkin-Elmer 598 spectrometer. Polystyrene was used as a calibrant. The ^{1}H NMR spectra of the ligand and its UO_2(VI) complex in DMSO-d_6, were recorded on a Bruker WP 200 SY spectrometer at room temperature using TMS as internal standard. Mass spectra were recorded at 300°C and 70 eV on a Hewlett-Packard mass spectrometer model MS-5988 at the Microanalytical Center, Cairo University, Giza, Egypt. TGA-DTG and DSC measurements were carried out on a Shimadzu-50 thermal analyzer. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alfa Products, Model MKI magnetic susceptibility balance. The effective magnetic moments were calculated from the expression $\mu_{\mathrm{eff}} = 2.828\ (\chi_M T)^{1/2}$ BM, where χ_M is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the compounds. ESR spectra of the complexes were recorded on a JEOL microwave unit, JES-FE_2XG spectrometer at the Central Laboratories, Tanta University, Tanta, Egypt. The magnetic field was calibrated with a 2,2-diphenyl-1-picryl-hydrazyl sample purchased from Aldrich. Molar conductances of 10^{-3} M solutions of the complexes in DMF were measured on a Corning conductivity meter NY 14831 model 441 (USA). Microanalyses of carbon, hydrogen, nitrogen and chlorine were carried out at the

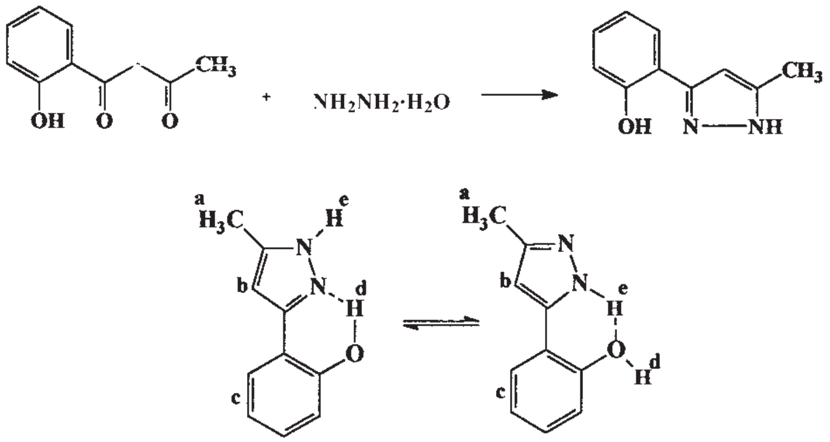


FIGURE 2 Formation of the tridentate pyrazole ligand, H_2L and its tautomeric forms.

Microanalysis Center, Cairo University, Giza, Egypt. Analyses of the metals in the mononuclear complexes followed the dissolution of the solid complex in conc. HNO_3 neutralizing the diluted aqueous solutions with ammonia and titration of the metal solutions with EDTA. Antifungal activity were evaluated at the Botany Dept., Faculty of Education, Ain Shams University, Egypt.

Preparation of the 5-Methyl-3-(2-hydroxyphenyl)pyrazole Ligand, H_2L

The ligand H_2L, Fig. 2, was prepared by heating to reflux 2-(3-ketobutanoyl)phenol (2 g, 11.2 mmol) and hydrazine hydrate (2.24 g, 44.8 mmol) in ethanol (100 mL) for 0.5 h. The solution was poured into water and a precipitate obtained. The precipitate was filtered, washed with ethanol, air-dried then recrystallized from water–ethanol mixture and a colorless crystalline product was obtained. The crystals were dried in a desiccator over calcium chloride. m/z Calcd. for ($C_{10}H_{10}N_2O$): 174. Found: 174 amu.

Preparation of Metal Complexes

Ethanolic solutions of the metal salt and the ligand were mixed and stirred for 2–3 h. The uranyl complex was prepared in methanol as uranyl acetate is more soluble in this solvent. The resulting precipitates were filtered, washed with ethanol then ether and finally air-dried. The complexes are air stable in the solid state, soluble in dimethylformamide and slightly soluble in some other organic solvents except the mononuclear Fe(III) complex, which is soluble in a variety of organic solvents.

Mononuclear Complexes

Method A: By Direct Metallation

*Preparation of [(HL)LFe(OH_2)$_2$] Complex (**4**)* An ethanolic solution (20 mL) of $FeCl_3 \cdot 6H_2O$ (0.388 g, 1.44 mmol) was added gradually to an ethanolic solution (40 mL) of the ligand (0.5 g, 2.88 mmol). The solution was stirred for 3 h and a deep violet precipitate was obtained. The precipitate was filtered, washed with ethanol then diethyl ether and finally air-dried. Yield, 0.45 g (65.0%).

*Preparation of [(HL)$_2$Ni] Complex (**6**)* An ethanolic solution (20 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.36 g, 1.44 mmol) was added gradually to an ethanolic solution (40 mL) of the ligand (0.5 g, 2.88 mmol). The solution was stirred for 5 h and a green precipitate was obtained. The precipitate was filtered, washed with ethanol then diethyl ether and finally air-dried. Yield, 0.55 g (95.0%).

*Preparation of [(HL)$_2$UO$_2$(H$_2$O)$_2$] Complex (**10**)* A methanolic solution (20 mL) of $UO_2(OAc)_2 \cdot H_2O$ (0.975 g, 2.3 mmol) was added gradually to a methanolic solution (40 mL) of the ligand (0.8 g, 4.6 mmol). The solution was stirred for 3 h and a reddish orange precipitate was obtained. The precipitate was filtered, washed with methanol then diethyl ether and finally air-dried. Yield, 0.82 g (55.0%).

Method B: By Transmetallation

*Preparation of [(HL)(L)Fe(H$_2$O)$_2$] Complex (**4**)* An ethanolic solution (20 mL) of $FeCl_3 \cdot 6H_2O$ (0.667 g, 2.47 mmol) was added gradually to a suspended solution (20 mL) of the yellowish-green [(HL)$_2$Ni] complex (1.0 g, 2.47 mmol). The solution was heated to reflux for 2 h and the color changed from green to dark violet. The solution was concentrated (ca. 10 mL) and cooled. A precipitate was obtained, filtered, washed with ethanol then diethyl ether and finally air-dried. Yield, 0.89 g (75.0%).

Preparation of [(HL)$_2$Cu] Complex (7) An ethanolic solution (20 mL) of $CuCl_2 \cdot 2H_2O$ (0.26 g, 1.53 mmol) was added gradually to a suspended solution (20 mL) of the orange [(HL)$_2$UO$_2$(H$_2$O)$_2$] complex (1.0 g, 1.53 mmol). The solution was refluxed for 2 h and a green precipitate was obtained. The precipitate was filtered, washed with ethanol then diethyl ether and finally air-dried. Yield, 0.52 g (88.0%).

RESULTS AND DISCUSSION

Synthesis

The pyrazole ligand was synthesized by the addition of hydrazine hydrate in excess to *o*-acetoacetylphenol. The mononuclear complexes were synthesized by reaction of the ligand with the metal acetate, nitrate or chloride. Conversion of the uranyl complex **(10)**, [(HL)$_2$UO$_2$(H$_2$O)$_2$], to the mononuclear complexes [(HL)$_2$M] (M=Cu(II), Ni(II)) and [(HL)LFe(H$_2$O)$_2$] by transmetallation was achieved in good yields.

Characterization

Table I indicates the analyses and physical properties of the ligand and its metal complexes. The electronic spectral data, conductance values and magnetic moments of the complexes are given in Table II.

The Ligand

The ^{1}H NMR spectrum of the ligand in DMSO-d$_6$ (Table III) showed signals at δ (ppm) 2.3 (3H, CH_3^a); 6.45; (H, CH^b); 6.6–7.6 (4H, Ar-H^c); 10.8 (1H, OH phenolic);

TABLE I Analytical and physical data for the ligand and its metal complexes

No.	*Complexes M.F. (F.Wt.)*	*Color*	*Yield* (%)	*M.P.* (°C)	*Elemental analysis* (%) *Found/(Calc.)*			
					C	*H*	*N*	*M*
1	H_2L $C_{10}H_{10}N_2O$ (174.2)	Colorless	91.0	130.0–131.0	68.7 (69.0)	6.1 (5.8)	16.4 (16.1)	–
2	$[(HL)_2VO]$ $C_{20}H_{18}N_4O_3V$ (413.3)	Sky blue	89.0	388.0	57.7 (58.1)	4.6 (4.4)	13.2 (13.6)	12.5 (12.3)
3	$[(HL)_2Mn(H_2O)_2]$ $C_{20}H_{22}N_4O_4Mn$ (437.4)	Green	60.0	314.0	55.2 (54.9)	4.9 (5.1)	12.9 (12.8)	12.8 (12.6)
4	$[(HL)LFe(H_2O)_2]$ $C_{20}H_{21}N_4O_4Fe$ (438.4)	Deep violet	65.0	352	54.6 (54.8)	4.6 (4.8)	12.9 (12.8)	13.2 (12.7)
5	$[(HL)_2Co]2 \cdot 5H_2O$ $(C_{20}H_{23}N_4O_{4.5}Co)$ (450.4)	Brown	81.0	> 400	53.6 (53.3)	4.8 (5.2)	12.1 (12.4)	13.3 (13.1)
6	$[(HL)_2Ni]$ $(C_{20}H_{18}N_4O_2Ni)$ (405.1)	Yellowish green	95.0	362	58.9 (59.3)	4.8 (4.5)	13.6 (13.8)	14.6 (14.5)
7	$[(HL)_2Cu]$ $(C_{20}H_{18}N_4O_2Cu)$ (409.9)	Olive green	88.0	330	58.5 (58.6)	4.7 (4.4)	13.8 (13.7)	15.3 (15.5)
8	$[(HL)_2Zn] \cdot H_2O$ $(C_{20}H_{20}N_4O_3Zn)$ (429.4)	Colorless	85.0	240	55.8 (55.9)	4.6 (4.7)	13.0 (13.1)	14.9 (15.2)
9	$[(HL)_2Cd]$ $(C_{20}H_{18}N_4O_2Cd)$ (458.4)	Colorless	90.0	> 400	52.4 (52. 4)	3.9 (3.9)	12.1 (12.2)	24.3 (24.5)
10	$[(HL)_2(UO_2)(H_2O)_2]$ $(C_{20}H_{22}O_6N_4U)$ (652.4)	Orange	55.0	> 400	37.1 (36.8)	3.3 (3.4)	8.4 (8.6)	–

TABLE II Electronic spectra, magnetic moments and molar conductivity data of metal complexes

No.	*Complex*	*Electronic spectral bands* (nm)	$\mu_{eff}{}^{a}$ BM	*Conductance* $(Ohm^{-1}cm^3\,mol^{-1})$
1	H_2L	240, 365	–	3.0
2	$[(HL)_2VO]$	640	1.52	6.0
3	$[(HL)_2Mn(H_2O)_2]$	450, 640	5.83	4.0
4	$[(HL)LFe(H_2O)_2]$	500	5.70	8.0
5	$[(HL)_2Co]2.5H_2O$	410, 580	2.20	5.0
6	$[(HL)_2Ni]$	475, 605	Diamagnetic	7.0
7	$[(HL)_2Cu]$	550	1.96	10.0
8	$[(HL)_2Zn] \cdot H_2O$	310	Diamagnetic	4.0
9	$[(HL)_2Cd]$	360	Diamagnetic	4.0
10	$[(HL)_2(UO_2)(H_2O)_2]$	470	Diamagnetic	6.0

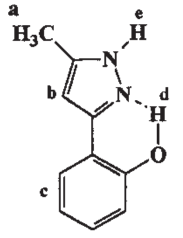
[a] μ_{eff} is the magnetic moment of one cationic species in the complex; [b]Solution in DMF (10^{-3} M).

12.5 (1H, NH) [12]. The IR spectrum of the ligand showed a broad band at 3280 cm^{-1} due to overlap of the stretching vibrational mode of the heterocyclic NH and phenolic OH groups. The low frequency of the OH group in the IR spectrum of the ligand and the upfield shift of the OH signal in its ^{1}H NMR spectrum indicate the presence of intramolecular hydrogen bonds linking the hydroxyl proton with the pyrazole nitrogen lone pair [12] (Fig. 2). The UV spectrum of a solution of the free ligand (10^{-3} M in DMF) shows bands at 240 and 365 nm due to π–π* and n–π* transition(s) within the phenyl group and C=N group of the heterocyclic ring with a certain degree of conjugation between the pyrazole and the benzene ring.

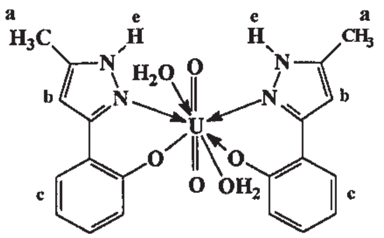
TABLE III ^{1}H NMR data of the free ligand H_2L (A) and its $UO_2(VI)$ complex (B)

	H^a	H^b	H^c	H^d	H^e
(A) H_2L	2.3 (s) (3H)	6.45(s)	6.6–7.6 (m) (4H)	10.8 (s, br)	12.5
(B) $[(HL)_2UO_2(H_2O)_2]$	2.6 (s) (6H)	6.45, (1H)[a] 6.55, (1H)	6.6–7.7 (m) (8H)	–	12.8, (1H)[a] 13.3, (1H)

s = singlet, m = multiplet, br = broad; [a]Two separate signals appeared for both the two hydrogen atoms linked to the carbon atom of the heterocyclic ring (H^b) and those of the NH group (H^e). This may be due to the occurrence of the heterocyclic ligand in different planes.



(A)
pyrazole ligand, H_2L



(B)
$[(HL)_2UO_2(H_2O)_2]$

The Mononuclear Metal Complexes

IR Spectra

The reactions of the pyrazole ligand, H_2L, with different metal ions produce a new series of mononuclear metal complexes $[(HL)_2M]\cdot xH_2O$ (M=VO, Co, Ni, Cu, Zn and Cd), $[(HL)_2M(H_2O)_2]$ (M=Mn or UO_2) and $[(HL)LFe(H_2O)_2]$. The IR spectra of some complexes exhibit a broad band around 3400–3480 cm^{-1} assigned for ν(O–H) of water molecules associated with the complexes which are confirmed by elemental analyses and thermoanalyses. The disappearance of the δ(O–H) frequency which appears at 1320 cm^{-1} for the ligand, and shift ν(C–O) by 15–20 cm^{-1} to higher frequency compared to the band at 1245 cm^{-1} in the spectrum of the free ligand [13] are observed. In addition, the IR spectra of all mononuclear complexes showed a shift of the strong band of ν(N–H) towards higher frequencies by 20–115 cm^{-1} compared to the free ligand spectrum (3280 cm^{-1}) following the order Ni (3300 cm^{-1}) $<$ Cu (3320 cm^{-1}) $<$ Co (3350 cm^{-1}) $<$ Mn (3360 cm^{-1}) $<$ Fe (3370 cm^{-1}) $<$ VO (3380 cm^{-1}) $<$ UO_2 (3395 cm^{-1}). The observed shift in the latter frequency may be due to hydrogen bonding with the OH group (Fig. 2). New bands between 515–560 and 410–460 cm^{-1} assigned to ν(M–O) and ν(M–N) [14] respectively, support the view that bonding of metal ions to the ligand is achieved through the phenolic oxygen atom and nitrogen atoms of the heterocyclic pyrazole ring.

The IR spectrum of the $UO_2(VI)$ complex shows a strong absorption band at 910 cm^{-1}, which is assigned to the antisymmetric ν_3(O=U=O) vibration [15]. Also, the characteristic band of ν(V=O) is observed in the IR spectrum of the VO(IV) complex at 950 cm^{-1} [16].

Electronic and ESR Spectra, Conductance and Magnetic Moments

Based on the electronic spectral and magnetic moment data, Table II, the nickel(II) complex has square-planar geometry with its characteristic features: the complex is yellowish green in color, diamagnetic and has an electronic spectral band at 605 nm assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition [17]. The complex was obtained whether the Ni(II) salt was chloride, sulfate, acetate or perchlorate. The chemical formula of the complex is supported by a TGA study. The thermogram was recorded for the complex in the temperature range 21–798.5°C. The thermogram of the complex does not show any inflections to 330°C indicating the absence of both hydrated and coordinated water molecules. The molar conductance of the complex in DMF (10^{-3} M solution) was 7.0 $\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ (Table II), which indicates that the complex is a non-electrolyte.

The reaction of $Co(OAc)_2 \cdot 4H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ with the ligand H_2L yielded a brown complex. The visible spectrum of the Co(II) complex showed two d–d bands at 580 and 410 nm which may be assigned to $^2A_{1g} \rightarrow {}^2B_{2g}$ and $^2A_{1g} \rightarrow {}^2E_g$ transitions, respectively, for Co(II) in a square-planar geometry [18]. The magnetic moment of the complex, 2.2 BM, supports this geometry [18]. TGA of the complex indicated that 2.5 hydrated water molecules are lost at 110°C. The molar conductance of the complex in DMF (10^{-3} M) was 5.0 $\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$, which indicates a non-electrolyte.

The electronic spectrum of $[(HL)_2Cu]$ shows a band at 532 nm corresponding to the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition in square-planar geometry [19]. Its magnetic moment was 1.92 BM consistent with a square-planar structure [20]. The ESR spectrum of the complex at room temperature showed one broad signal with $g_{\text{eff}} = 1.90$ in the powder form consistent with square-planar geometry.

The Fe(III) complex, $[(HL)LFe(H_2O)_2]$, was obtained from reaction of the ligand and $FeCl_3 \cdot 6H_2O$ or $Fe_2(SO_4)_3$. The molar conductance of the complex was 8.0 $\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ (Table II) indicating a non-electrolyte. The magnetic moment of the complex was 5.7 BM, consistent with octahedral geometry [21]. The electronic spectrum of the Fe(III) complex shows an absorption band at 500 nm corresponding to $^6A_1 \rightarrow {}^4T_2$ transition [16], suggesting an octahedral arrangement around the Fe(III) ion. The octahedral geometry of the iron(III) complex is achieved by two additional water molecules. The thermogram of the complex shows two inflections; at 170°C the loss of weight corresponds to two coordinated water molecules and the second inflection at 380°C is due to degradation of the complex. The visible spectra of the Fe(III) complex in a number of organic solvents showed the d–d transition band undergoes a red shift with increase of the DN value (Gutmann's Donor Number) [22, 23] of the solvent. These spectral changes are mainly due to changes in the degree of axial solvation of the complex. The complexes of Ni(II), Co(II) and Cu(II) did not show solvatochromism, owing to the rigidity of their pyrazole groups and the stability of the square-planar geometry.

Most of the mononuclear oxovanadium(IV) complexes with square-pyramidal coordination are green while the polynuclear linear chain octahedral structures (V=O–V=O–) are usually orange [24]. Also, the IR spectra of the VO(IV) complexes generally show ν(V=O) around 850 cm^{-1} for the polymeric form and around 970 cm^{-1} for the monomeric form [25]. The electronic absorption spectrum of the prepared blue VO(IV) complex, $[(HL)_2VO]$, shows a d–d transition band at 640 nm and is IR spectrum shows νV=O at 970 cm^{-1}. These data indicate that the VO(IV) cation is monomeric with square-pyramidal geometry. The magnetic moment of the complex is 1.52 BM which agrees with the presence of one unpaired electron. An ESR spectrum of the solid complex at room temperature showed one strong signal with $g_{\mathrm{eff}} = 1.901$. The lack of hyperfine structure may be due to strong spin exchange in the magnetically concentrated samples. Thermal analysis of the complex did not show weight loss to 350°C.

The magnetic moment of the complex, $[(HL)_2Mn(H_2O)_2]$ is 5.83 BM due to the spin-free value for five unpaired electrons, indicating that the Mn(II) is high-spin six-coordinate. The electronic spectrum of the Mn(II) complex shows weak bands at 640 and 450 nm assigned to the transitions $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(^4G)$, respectively, in an octahedral field [26]. TGA of the Mn(II) complex shows a loss in weight corresponding to two coordinated water molecules at 180°C supporting an octahedral geometry. The ESR spectrum of the solid complex at room temperature showed a broad band with $g_{\mathrm{eff}} = 1.909$. The broadening of the spectrum in the powdered sample is analogous to that observed in the case of immobilized free radicals [27]. Broadening is thus due to immobilization of Mn(II) ions with the ligand restricting rotational motion of Mn(II). Spin relaxation may also contribute.

The electronic spectral features of the complexes, $[(HL)_2UO_2(OH_2)_2]$, $[(HL)_2Zn] \cdot H_2O$ and $[(HL)_2Cd]$, (Table II) exhibit absorption bands at 470, 310 and 360 nm, respectively. The high-energy band of the UO_2(VI) complex is attributed to an electronic transition from the apical oxygens to f orbitals of the uranium(VI) or to a charge transfer transition from ligands to the uranium(VI) ion [28, 29], while the spectra of the Zn(II) and Cd(II) complexes are dominated only by the ligand band. ^{1}H NMR spectral data of the UO_2(VI) complex (Table III) showed the disappearance of the signal of the proton of the phenolic OH group indicating that deprotonation took place during complex formation. The signal from the NH group which was found in the spectrum of the free ligand at $\delta = 12.5$ is shifted downfield in the spectrum of the UO_2(VI) complex. Thermal analysis of the Cd(II) complex showed that it is stable up to 250°C while the Zn(II) complex showed weight loss at 102°C corresponding to elimination of one hydrated water molecule. The UO_2(VI) complex had weight loss at 220°C indicating elimination of two coordinated water molecules. This dehydration process appeared as an endothermic peak in the DSC curve with $\Delta H = -131.6\,\mathrm{J\,g^{-1}}$. Also, the DSC curve shows an exothermic peak at 268°C ($\Delta H = 15.9\,\mathrm{J\,g^{-1}}$) without loss of weight, assigned to change of the geometry from eight-coordinate to six-coordinate. The final weight loss of the complexes agreed well with the calculated weights of ZnO, CdO and U_3O_8 as residues. The IR spectra and thermal data indicated that the UO_2(VI) cation is eight-coordinate while the Zn(II) and Cd(II) cations are four-coordinate.

Mass Spectra

Mass spectra of the complexes provide good evidence for their molecular formulas. Complexes **6**, **7**, **8** and **9**, $[(HL)_2Ni]$ (F.Wt. 405.1), $[(HL)_2Cu]$, (F.Wt. 409.9), $[(HL)_2Zn] \cdot H_2O$ (F.Wt. 429.4) and $[(HL)_2Cd]$ (F.Wt. 458.4) were taken as representative complexes. The mass spectra of these complexes showing the highest mass peak with *m*/*z* 404, 409, 412 and 456 agree with the formula weights of the complexes. The parent peak of the Zn(II) complex agrees with its anhydrous formula. The

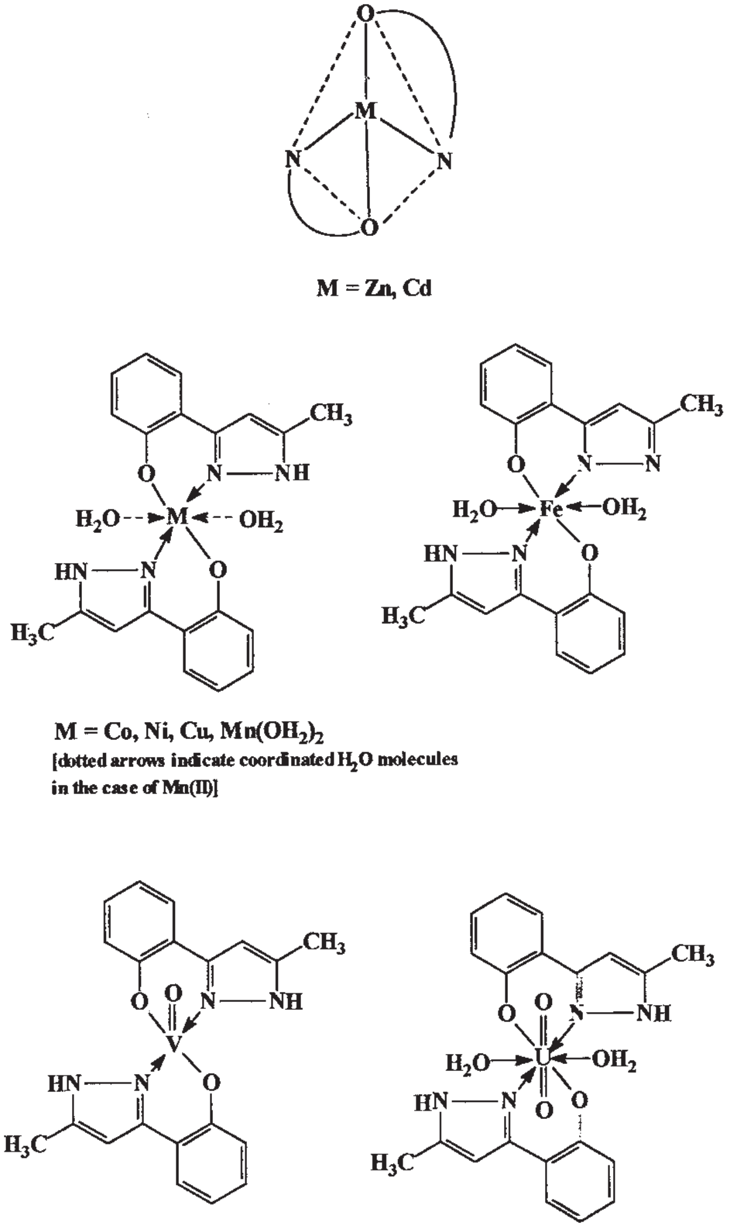


FIGURE 3 The suggested structures of the mononuclear complexes.

fragmentation patterns of the complexes show a fragment with m/z 174 due to the pyrazole ligand, H_2L.

On the basis of the microanalytical data, IR, ^{1}H NMR, ESR, electronic and mass spectra and magnetic moments, the suggested structures of the mononuclear complexes are shown in Fig. 3.

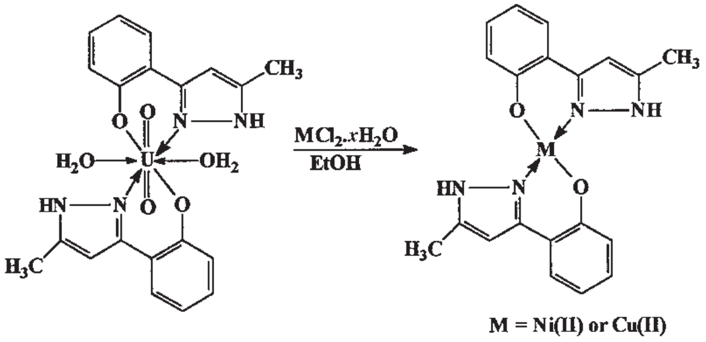


FIGURE 4 Transmetallation reaction.

Transmetallation Reactions

Reaction of the mononuclear UO_2(VI) complex, $[(HL)_2UO_2(OH_2)_2]$, with $MCl_2 \cdot xH_2O$; M = Cu(II) or Ni(II) and $FeCl_3 \cdot 6H_2O$ yielded mononuclear Fe(III), Ni(II) and Cu(II) complexes, $[(HL)LFe(H_2O)_2]$, Complex **4** and $[(HL)_2M]$, M = Ni(II) or Cu(II) Complexes **6** and **7**. These ions are incorporated in the N_2O_2 sites of the ligand, Fig. 4. Complex **4** was also obtained from a transmetallation reaction of the Ni(II) complex, $[(HL)_2$ Ni] and $FeCl_3 \cdot 6H_2O$. These complexes are identical in all respects to the previously obtained mononuclear complexes by the direct reaction of the ligand with either Fe(III) chloride, Cu(II) or Ni(II) acetates. IR spectra of the products did not have the UO_2 vibration absorption band.

The heats of degradation (ΔH) obtained from the first peak of DSC curves of the mononuclear complexes are −137.2, −98.0, −74.2 and −26.8 J g^{-1} for Fe(III), Cu(II), Ni(II) and UO_2(VI), respectively. These data indicate the order of stability to be Fe(III) > Cu(II) > Ni(II) > UO_2(VI). This order thus supports transmetallation and explains the inability of Ni(II) to displace Cu(II) or Fe(III).

Biological Activity of the Mononuclear Complexes

The fungicidal activities of the mononuclear complexes were evaluated against *Fusarium oxysparium* by the agar plate technique at three concentrations, 1000, 500 and 250 ppm. The average percentage inhibition after 96 h by various mononuclear complexes was calculated from the expression:

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

where C = diameter of fungus colony in control plate after 96 h and T = diameter of fungus colony in tested plates after 96 h.

The results are recorded in Table IV. The following conclusions can be derived: All the mononuclear complexes have significant toxicity at 1000 ppm against *Fusarium oxysparium* and the complexes are more active than the pyrazole ligand. Also, it is clear that neither the Cu(II) nor the Mn(II) complexes have activity against

TABLE IV Fungicidal screening data of the mononuclear complexes

		Inhibition (%)		
No.	*Compound*	*1000* ppm	*500* ppm	*250* ppm
1	H_2L	46.6	22.2	14.4
2	$[(HL)_2VO]$	66.7	38.9	20.0
3	$[(HL)_2Mn(H_2O)_2]$	0.0	0.0	0.0
4	$[(HL)LFe(H_2O)_2]$	62.2	28.9	11.1
5	$[(HL)_2Co]2.5H_2O$	66.7	37.8	25.6
6	$[(HL)_2Ni]$	50.0	22.2	20.0
7	$[(HL)_2Cu]$	0.0	0.0	0.0
8	$[(HL)_2Zn] \cdot H_2O$	50.0	25.6	21.1
9	$[(HL)_2Cd]$	41.1	23.3	6.7
10	$[(HL)_2(UO_2)\ (H_2O)_2]$	51.1	27.8	15.6

fungi. The VO(IV) and Co(II) complexes exhibited the maximum fungicidal activity and the activity of the metal chelates was found to be in the order VO(IV)=Co(II) > Fe(III) > UO_2(VI) > Zn(II)=Ni(II) > Cd(II).

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