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Journal of the Serbian Chemical Society

JSCS@tmf.bg.ac.yu • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. *73* (11) 1073–1082 (2008)
JSCS–3788

UDC 661.8+547.362–32+549.766.321:615.281
Original scientific paper

Transition metal complexes with oxygen donor ligands: a synthesis, spectral, thermal and antimicrobial study

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(Received 14 November 2007, revised 6 June 2008)

Abstract: Transition metal complexes of chalcones derived from the condensation of 3-acetyl-6-methyl-2*H*-pyran-2,4(3*H*)-dione (dehydroacetic acid) and *p*-methoxybenzaldehyde (HL^1) or *p*-nitrobenzaldehyde (HL^2) were synthesized and characterized by elemental analysis, conductometry, thermal analysis, magnetic measurements, IR, ^{1}H-NMR, UV–Vis spectroscopy and a microbial study. From the analytical and thermal data, the stoichiometry of the complexes was found to be 1:2 (metal:ligand). The molar conductance data revealed that all the metal chelates were non-electrolytes. The thermal stability of the complexes was studied by thermogravimetry and the decomposition schemes of the complexes are given. The ligands and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*, and fungicidal activity against *Aspergillus flavus*, *Curvularia lunata* and *Penicillium notatum*.

Keywords: dehydroacetic acid; chalcones; thermal study; ligand field parameters; antimicrobial study.

INTRODUCTION

A number of β-dicarbonyl compounds in which the carbonyl function(s) is bonded to C=C linkage(s) have gained considerable importance,[1] mainly because such compounds are associated with many biological activities due to the presence of the α,β-unsaturated system, as evidenced from their antimalarial,[2] antituberculosis,[3] antiplasmodial,[4] antitrichomonal,[5] anti-oxidant[6] and analgesic[7] activities, as well as their use as anti-inflammatory and cancer chemopreventive agents.[8]

Therefore, the synthesis and characterization of such unsaturated carbonyl system and their metal complexes are of tremendous importance. Continuing earlier research[9–11] on biologically active complexes of dehydroacetic acid chalcones containing β-dicarbonyl moieties and a carbonyl group directly linked to a C=C group, the present paper reports a synthetic, spectral, thermal and biological study.

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doi: 10.2298/JSC0811073P

EXPERIMENTAL

Dehydroacetic acid was purchased from Merck and was used as supplied. *p*-Methoxybenzaldehyde and *p*-nitrobenzaldehyde, used for the preparation of the ligands, were from Aldrich. Metal chlorides used for the preparation of the complexes were from BDH. A.R. grade solvents were used for the spectral measurements. The carbon, hydrogen and sulphur content in each sample were determined using a Perkin Elmer 2400 CHNS analyzer. The IR spectra (nujol) were recorded on a Perkin Elmer C-75430 IR spectrometer in the range 4000–450 cm^{-1}. The ^{1}H-NMR spectra were recorded in $CDCl_3$ at room temperature using TMS as the internal standard on a Varian Mercury YH 300 MHz instrument. The metal contents were determined by AAS on a Perkin Elmer PE-Analyst 300. The TG–DTA measurements were performed on a Perkin ElmerTA/SDT-2960 instrument in a dry nitrogen atmosphere and at a heating rate of 10 °C min^{-1}. The electronic spectra were recorded in DMF solution on a Shimadzu UV-1601 spectrophotometer. The magnetic susceptibility measurements of the complexes were performed using a Gouy balance at room temperature with $Hg[Co(SCN)_4]$ as calibrant. The molar conductivity was measured on an Elico CM180 conductivity meter with a dip-type cell using a 1.0×10^{-3} M solution of complexes in DMF.

Synthesis of ligand

A solution of 0.010 mol of dehydroacetic acid, 10 drops of piperidine and 0.010 mol of aldehyde (*p*-methoxybenzaldehyde or *p*-nitrobenzaldehyde) in 25 ml chloroform was refluxed for 8–10 h. 10 ml of the chloroform–water azeotrope mixture was separated by distillation. Crystals of the product separated on slow evaporation of the remaining chloroform, which were recrystalised from ethyl acetate.

Synthesis of metal complexes

To a chloroform solution (30 ml) of the ligand (10 mmol), a methanolic solution (20 ml) of metal chloride (5.0 mmol) was added under constant stirring. The pH of the reaction mixture was maintained around 7–8 by adding a 10 % methanolic solution of ammonia. It was then refluxed for 2 h. The resulting metal complex was filtered hot and washed with chloroform, methanol and petroleum-ether and dried over calcium chloride in a desiccator.

Antimicrobial screening

The ligands and their metal complexes were screened for *in vitro* antibacterial activity against gram positive bacteria, *i.e.*, S*taphylococcus aureus* and gram negative bacteria, *i.e.*, *Escherichia coli* by the paper disc plate method.[12] The compounds were tested at a concentration of 0.50 mg ml^{-1} in DMF and compared with a known antibiotic, *viz.* ciproflaxin at the same concentration.

To evaluate the fungicidal activity of the ligands and the corresponding metal complexes, their effect on the growth of *Aspergillus flavus*, *Curvularia lunata* and *Penicillium notatum* was studied. The ligand and their corresponding metal chelates in DMF were screened *in vitro* by the disc diffusion method.[13] The ligands and complexes were dissolved separately in DMF to obtain concentration of 125 and 250 μg/disc. The linear growth of the fungus was recorded by measuring the diameter of colony after 96 h. The diameters of the zone of inhibition produced by the complexes were compared with griseofulvin antifungal drug.

RESULTS AND DISCUSSION

Elemental analyses show 1:2 (metal:ligand) stoichiometry for all the complexes (Fig. 1). The analytical data of the ligand and the complexes are given in

Table I. They correspond well with the general formula $[M(L^{1\text{ or }2})_2(H_2O)_2]$, where M = Mn(II), Co(II), Ni(II) and Cu(II), and $[M(L^{1\text{ or }2})_2(Cl)(H_2O)]$, where M = Fe(III), and $L^1 = C_{16}H_{14}O_5$ and $L^2 = C_{15}H_{11}NO_6$. The presence of coordinated water was confirmed by TGA–DTA analysis. The low conductance of the chelate solution supports the non-electrolytic nature of the metal complexes. Since a single crystal of the complexes could not be isolated from any common solvent, the possible structure was predicted based on analytical, spectroscopic, magnetic and thermal data.

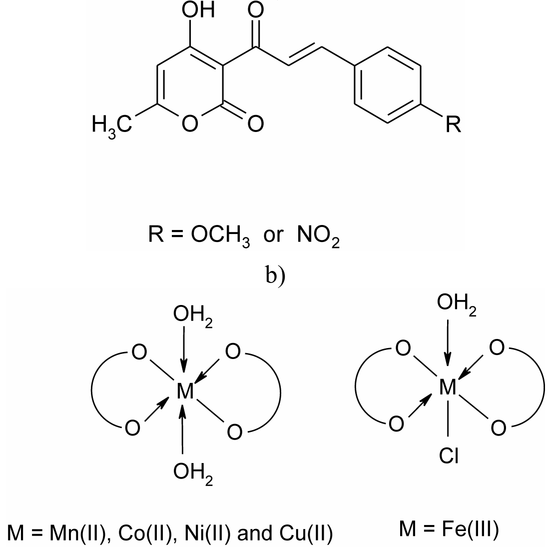

Fig. 1. The proposed structures of ligands (a) and complexes (b).

TABLE I. Physical characterization, analytical and molar conductance data of the compounds

Compound	M_r g mol^{-1}	M.p. °C	Yield %	Color	Found (Calcd.), % M	C	H	N	Λ_m MΩ^{-1} cm^2 mol^{-1}
Ligand HL^1 $C_{16}H_{14}O_5$	286.3	208	52	Yellow	–	67.54 (67.13)	4.89 (4.93)	–	–
$[C_{32}H_{30}O_{12}Mn]$	661.5	272	59	Brown	8.11 (8.30)	57.92 (58.10)	4.32 (4.57)	–	12.7
$[C_{32}H_{28}O_{11}ClFe]$	679.91	268	68	Dark brown	8.20 (8.21)	56.12 (56.52)	4.00 (4.15)	–	13.3
$[C_{32}H_{30}O_{12}Co]$	665.5	>300	61	Light brown	8.71 (8.85)	57.31 (57.75)	4.44 (4.54)	–	15.1
$[C_{32}H_{30}O_{12}Ni]$	665.3	258	57	Pale green	8.80 (8.82)	57.07 (57.77)	4.65 (4.55)	–	13.7
$[C_{32}H_{30}O_{12}Cu]$	670.1	296	58	Green	9.32 (9.48)	58.01 (57.35)	4.44 (4.51)	–	17.5
Ligand HL^2 $C_{15}H_{11}NO_6$	301.3	246	54	Yellow	–	59.52 (59.80)	3.51 (3.68)	4.57 (4.65)	–

TABLE I. Continued

Compound	M_r	M.p.	Yield	Color	Found (Calcd.), %				Λ_m
	g mol^{-1}	°C	%		M	C	H	N	MΩ^{-1} cm^2 mol^{-1}
[$C_{30}H_{24}N_2O_{14}Mn$]	691.5	>300	52	Brown	7.79	51.79	3.36	3.97	10.1
					(7.94)	(52.10)	(3.49)	(4.05)	
[$C_{30}H_{22}N_2O_{13}ClFe$]	709.7	>300	63	Red	7.91	51.22	3.22	3.87	13.1
					(7.87)	(50.77)	(3.12)	(3.95)	
[$C_{30}H_{24}N_2O_{14}Co$]	695.5	>300	61	Light brown	8.32	52.32	3.39	3.89	11.2
					(8.47)	(51.81)	(3.48)	(4.03)	
[$C_{30}H_{24}N_2O_{14}Ni$]	695.2	>300	57	Pale green	8.36	51.20	3.55	3.91	10.1
					(8.44)	(51.82)	(3.48)	(4.03)	
[$C_{30}H_{24}N_2O_{14}Cu$]	700.1	>300	63	Green	9.23	51.08	3.59	4.11	12.2
					(9.07)	(51.46)	(3.45)	(4.00)	

^{1}H-NMR spectroscopy

Ligand HL^1. ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 2.27 (3H, *s*, C_6–CH_3), 3.85 (3H, *s*, –OCH_3), 5.93 (1H, *s*, C_5–H), 6.9–8.43 (6H, *m*, phenyl ring and –CH=CH–), 16.65 (1H, *s*, –OH).

Ligand HL^2. ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 2.35 (3H, *s*, C_6–CH_3), 6.03 (1H, *s*, C_5–H), 6.9–8.3 (6H, *m*, phenyl ring and –CH=CH–), 16.77 (1H, *s*, –OH).

IR Spectroscopy

The IR spectra of the ligands show bands at 3164–3120, 1739–1720, 1705–1675 and 1257–1222 cm^{-1}, assignable to ν(OH) (phenolic hydrogen bonded), ν(C=O) (lactone carbonyl), ν(C=O) (acetyl carbonyl) and ν(C–O) (phenolic) stretching mode, respectively (Table II).[14,15] In the IR spectra of all the metal chelates, no band was observed in the region 3164–3120 cm^{-1}. Instead, in its place, a broad band characteristic of ν(OH) of coordination water was observed in the region 3500–3200 cm^{-1}.The presence of coordinated water was further confirmed by the appearance of a non-ligand band in the region 830–840 cm^{-1}, assignable to the rocking mode of water.[16] This was also established and supported by TG and DTA analysis. The absence of ν(OH) (phenolic) at 3164–3120 cm^{-1} suggests subsequent deprotonation of the phenolic group and coordination of the phenolic oxygen to the metal ion. This was supported by an upward shift in ν(C–O) (phenolic)[17] by 20–40 cm^{-1}. The ν(C=O) (acetyl carbonyl) was shifted to lower energy with respect to the free ligand, suggesting the participation of the acetyl carbonyl in the coordination.[14,15,17] The IR spectra of all the compounds showed a prominent band at ≈ 1377 and ≈ 970 cm^{-1}, typical of ν(C–O–C) and *trans*–CH=CH– absorption. The presence of new bands in the region 600–450 cm^{-1} can be assigned to ν(M–O) vibrations.[16]

Hence, the ligands coordinated with the metal ions as monodeprotonated bidentate and the coordination occurs *via* the acetyl and phenolic oxygen of dehydroacetic acid moiety, as shown in Fig. 1.

TABLE II. Magnetic and electronic spectral data of the complexes and their ligand field parameters

Complex	ν(OH) cm^{-1}	ν(C=O) (lactone carbonyl) cm^{-1}	ν(C=O) (acetyl carbonyl) cm^{-1}	ν(C–O) (phenolic) cm^{-1}	ν(NO$_2$) cm^{-1}	ν(M-O) cm^{-1}	μ_{eff} / μ_B	10 Dq cm^{-1}	B / cm^{-1}	β	ν_2/ν_1	LFSE kcal mol^{-1}
HL^1 $C_{16}H_{14}O_5$	3164(*b*)	1709(*m*)	1705(*m*)	1257(*m*)	–	–	–	–	–	–	–	–
HL^2 $C_{15}H_{11}NO_6$	3126(*b*)	1722(*s*)	1679(*m*)	1224(*m*)	1575(*m*)	–	–	–	–	–	–	–
[Mn(L^1)$_2$(H$_2$O)$_2$]	3375(*b*)	1740(*m*)	1634(*m*)	1253(*m*)	–	566(*m*)	5.77	–	–	–	–	–
[Mn(L^2)$_2$(H$_2$O)$_2$]	3373(*b*)	1719(*s*)	1645(*s*)	1254(*m*)	1574(*s*)	585(*m*) 533(*m*)	5.81	–	–	–	–	–
[Fe(L^1)$_2$(Cl)(H$_2$O)]	3379(*b*)	1723(*s*)	1620(*s*)	1279(*m*)	–	597(*m*) 537(*m*)	5.92	–	–	–	–	–
[Fe(L^2)$_2$(Cl)(H$_2$O)]	3375(*b*)	1719(*m*)	1647(*m*)	1250(*m*)	1573(*m*)	586(*m*) 533(*w*)	5.79	–	–	–	–	–
[Co(L^1)$_2$(H$_2$O)$_2$]	3348(*b*)	1698(*s*)	1625(*s*)	1297(*m*)	–	563(*m*) 549(*m*)	4.66	8779	821.1	0.84	1.91	25.08
[Co(L^2)$_2$(H$_2$O)$_2$]	3365(*b*)	1721(*s*)	1640(*m*)	1255(*m*)	1571(*s*)	555(*m*) 532(*w*)	4.70	9298	874.8	0.90	1.93	26.41
[Ni(L^1)$_2$(H$_2$O)$_2$]	3348(*b*)	1698(*m*)	1624(*m*)	1297(*m*)	–	562(*m*) 549(*m*)	3.03	9372	781.5	0.75	1.66	26.77
[Ni(L^2)$_2$(H$_2$O)$_2$]	3365(*b*)	1718(*m*)	1628(*m*)	1243(*m*)	1566(*m*)	580(*m*)	3.02	9910	701.0	0.67	1.55	28.31
[Cu(L^1)$_2$(H$_2$O)$_2$]	3363(*b*)	1729(*m*)	1620(*m*)	1299(*m*)	–	534(*m*)	2.09	15122	–	–	–	43.22
[Cu(L^2)$_2$(H$_2$O)$_2$]	3370(*b*)	1716(*m*)	1625(*m*)	1252(*m*)	1572(*m*)	598(*m*) 489(*w*)	1.95	15138	–	–	–	43.25

Magnetic and electronic absorption spectroscopy

The magnetic and electronic spectral data are given in Table II. The data is of relevance for the proposed structure of the complexes (Fig. 1). The electronic spectra of the Cu(II) complexes in DMF revealed one broad band at 15128 and 25126 cm^{-1} for ligand HL^1 and at 15138 and 25000 cm^{-1} for ligand HL^2, assignable to a $^2E_g \rightarrow {}^2T_{2g}$ transition and charge transfer, respectively. The observed magnetic moment value for the Cu(II) complexes was in the range 1.95–2.09 μ_B. The electronic spectral data[18] coupled with the magnetic moment value suggest a distorted octahedral geometry for the Cu(II) complexes.[19] The electronic spectra of Ni(II) complexes display three bands at 9372, 15625 and 24213 cm^{-1} for HL^1 and at 9910, 15360 and 24885 cm^{-1} for HL^2, assignable to $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3) transitions, respectively. This is in accordance with earlier reported values for octahedral Ni(II) complexes.[21,22] The reductions of the Racah parameter (B) and the nephelauxetic effect (β) from the value of the free ion suggest an appreciable amount of covalent character in the metal ligand bonds.[20,21] The calculated values of 10 Dq, B, ν_2/ν_1 and β (Table II) lie in the range reported for octahedral geometry. The normal magnetic moment 2.99–3.19 μ_B confirms the proposed geometry. The Co(II) complexes show three transitions at 9569, 18348 and 22675 cm^{-1} for HL^1 and at 9900, 19182 and 23640 cm^{-1} for HL^2, assignable 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) transitions, respectively.[19,20] The calculated values of 10 Dq, B, ν_2/ν_1 and β together with the magnetic moment value of the Co(II) complexes (Table II) suggest octahedral geometry. The obtained values of LFSE determine the stability of the complexes and follows the order in terms of metal ion Cu(II) > Ni(II) > Co(II) for ligand HL^1 and HL^2.

The Fe(III) complexes of ligands HL^1 and HL^2 show three bands at, respectively, 14556, 21692, 24450 cm^{-1} and 14484, 22322, 24196 cm^{-1}, assignable to $^6A_1 \rightarrow {}^4T_1$ (G), $^6A_1 \rightarrow {}^4T_2$ (G) and $^6A_1 \rightarrow {}^4E$ (G) transitions, respectively. The spectra suggest distorted octahedral geometry.[19,21,23] The electronic spectrum of Mn(II) complex of HL^1 displays weak bands at 17794, 19569 and 31056 cm^{-1}, whereas Mn(II) complex of HL^2 displayed weak bands at 18382 and 24671 cm^{-1}. These bands are both Laporte and spin-forbidden. However, due to instantaneous distortion of the octahedral structures around the metal cation, weak bands sometimes do appear.[19,21]

Thermal analysis

The Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of ligand HL^1 were chosen for a thermal study. The TG curve of the complexes of ligand HL^1 shows three decomposition steps. On the TG curve of the Mn(II) complex, the first step shows a steep slope between 150–200 °C with a mass loss of 5.0 % (calculated 5.4 %), indicating the removal of two molecules of coordinated water. An endothermic peak in the range 150–200 °C ($\Delta t_{\min}$ = 175 °C) on the DTA curve corresponds to the dehydration step. The anhydrous compound in second step decomposes within a short temperature range from 220–330 °C, with a 37.0 % mass loss (calculated 36.3 %). An exotherm between 240 and 400 °C with a $\Delta t_{\max}$ = = 270 °C on the DTA curve corresponds to this mass loss. This step may be attributed to the removal of the non-coordinated part of the ligand, *i.e.*, [$C_{16}H_{16}O_2$]. The third mass loss step in the range 400–790 °C corresponds to the decomposition of the coordinated part of the ligand, with a mass loss 47.0 % (calculated 47.6 %). A broad endotherm is observed for this step. The mass of the final residue corresponds to stable MnO, 11.0 % (calculated, 10.7 %).

In the thermal study of the Fe(III) complex, an inclined slope from 175–195 °C on the TG curve, with a mass loss of 7.0 % (calculated 7.9 %), indicates the removal of one molecule of water and one chloride ion. An endothermic peak in the range 180–240 °C was observed on the DTA curve ($\Delta t_{\min}$ = 192 °C). The complex continues to decompose in a second step between 210 and 300 °C, with 37.0 % mass loss (calculated 35.2 %). A corresponding exothermic peak between 250–280 °C ($\Delta t_{\max}$ = 265 °C) on the DTA is attributed to the removal of the non-coordinating part of the ligand. The third step corresponds to the decomposition of remaining part of the ligand with a mass loss 47.0 % (calculated 46.3 %). The mass of the final residue was 9.0 % (calculated 10.6 %), corresponding to FeO.

The thermal decomposition profile of the Co(II) complex showed no weight loss up to 140 °C. A mass loss of 5.0 % (calculated 5.4 %) was observed in the range 140–175 °C. The endothermic peak between 140–165 °C ($\Delta t_{\min}$ = 152 °C) correspond to the loss of two molecules of water. The second step of decomposition was between 265 and 400 °C with a 37.0 % mass loss (calculated 36.1 %). The broad exothermic peak between 270–375 °C ($\Delta t_{\max}$ = 346 °C) on the DTA curve is attributed to the removal of the non-coordinating part of the ligand. The mass loss continued with the slow decomposition of remaining part of the ligand 45.5 % (calculated 47.2 %). The mass of the final residue corresponded to CoO, 12.5 % (calculated 11.3 %).

The thermal decomposition profile of the Ni(II) complex showed a mass loss of 5.0 %(calculated 5.4 %) in the range 150–175 °C, indicating the removal of two coordinated water molecules. An endothermic peak on the DTA curve between 160–185 °C ($\Delta t_{\min}$ = 162 °C) also corresponds to dehydration. The second step of the decomposition was between 190 and 325 °C with a 37.0 % mass loss (calculated 36.1 %). A broad exothermic peak between 200–350 °C ($\Delta t_{\max}$ = 260 °C) on the DTA curve is attributed to the removal of the non-coordinating part of the ligand. The mass loss continued with the slow decomposition of the remaining part of the ligand up to 900 °C with a 46.0 % (calculated 47.3 %) mass loss. A broad endothermic peak between 450–850 °C was observed on the DTA curve. The mass of the final residue of 12.0 % (calculated 11.2 %) corresponds to NiO.

On the TG curve of the Cu(II) complex, the mass loss commences at 120 °C with an inclined slope from 155–185 °C with a mass loss of 6.0 % (calculated 5.4 %), indicating the removal of two molecules of coordinated water. An endothermic peak in the range 150–200 °C (Δt_{min} = 158 °C) on the DTA curve also corresponds to the dehydration. The second step of the decomposition continues on the TG curve from 275 up to 375 °C, with a mass loss of 37.0 % (calculated 35.7 %) and the exothermic peak (Δt_{max} = 299 °C) on the DTA curve may be attributed to the removal of the non-coordinated part of the ligand. The third step in the range 420–880 °C with a mass loss of 46.0 % (calculated 47.0 %) corresponds to the decomposition of the coordinated part of the ligand. A broad endotherm was also observed for this step. The mass of the final residue corresponded to stable CuO, 11.0 % (calculated 11.9 %).

Antimicrobial activity

The results of the antimicrobial study, Table III, showed that the ligand HL^1 had no antibacterial activity whereas the ligand HL^2 exhibited weak activity. This may be due to the presence of the electron withdrawing group ($-NO_2$) on the phenyl ring. The Cu(II) and Co(II) complexes of ligand HL^2 showed moderate antibacterial activity against both of the bacteria.

TABLE III. Antibacterial and antifungal activities of ligands and their metal complexes

Compound	Antibacterial activity		Antifungal activity					
	Inhibition zone of bacterial growth, mm		*A. flavus*		*C. lunata*		*P. notatum*	
	S. aureus 0.50 mg ml^{-1}	*E. coli* 0.50 mg ml^{-1}	I^a	II^b	I	II	I	II
HL^1 $C_{16}H_{14}O_5$	1.1	1.2	7	15	7	14	7	14
HL^2 $C_{15}H_{11}NO_6$	3.6	4.1	8	16	8	15	8	15
$[Mn(L^1)_2(H_2O)_2]$	1.6	1.8	9	17	8	17	8	17
$[Mn(L^2)_2(H_2O)_2]$	4.2	4.5	11	24	11	22	10	22
$[Fe(L^1)_2(Cl)(H_2O)]$	2.1	2.1	8	16	7	19	7	15
$[Fe(L^2)_2(Cl)(H_2O)]$	4.5	4.9	9	20	9	19	9	20
$[Co(L^1)_2(H_2O)_2]$	5.1	5.6	10	20	10	20	10	20
$[Co(L^2)_2(H_2O)_2]$	8.9	9.3	14	33	13	32	13	33
$[Ni(L^1)_2(H_2O)_2]$	4.2	4.6	9	19	9	19	9	19
$[Ni(L^2)_2(H_2O)_2]$	6.3	6.8	13	30	12	29	12	30
$[Cu(L^1)_2(H_2O)_2]$	6.1	6.5	11	22	11	21	11	19
$[Cu(L^2)_2(H_2O)_2]$	9.2	10.7	15	37	14	34	14	36
Ciproflaxin	12.0	13.5	–	–	–	–	–	–
Griseofulvin	–	–	31	34	29	33	30	34

[a] 125 μg/disc; [b] 250 μg/disc

From the results in Table III, it can be concluded that the ligands and their metal complexes show significant antifungal activity at a concentration of 250 μg disc^{-1} against all the tested fungi. In addition, the activity decreased as the concentration decreased. The Cu(II)HL^2 complex exhibited a higher antifungal activity than the standard at a concentration of 250 μg disc^{-1}, while the Ni(II) and Co(II) complexes of HL^2 showed nearly same antifungal activity as the standard. The order of inhibition with respect to metal ions of HL^1 and HL^2 is Cu > Co > > Ni > Mn > Fe. It was found that these complexes show strong antifungal activity at lower concentration when compared to earlier reported literature.[17,24]

It was observed that the metal complexes show enhanced antimicrobial activity as compared to the ligands. The increased activity of the chelates can be explained on the basis of the overtone concept and the Tweedy chelation theory.[25] 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 metal ion is reduced to a greater extent due to overlap of the ligand orbital and partial sharing of its positive charge with the donor groups and also due to delocalization of the π-electrons over whole chelate ring, which enhances the penetration of the complexes into the lipid membranes and the blocking of the metal binding sites of the enzymes of the micro-organisms.

CONCLUSIONS

In the light of the above discussion, a distorted octahedral geometry for Cu(II), Mn(II) and Fe(III) complexes and an octahedral geometry for the Co(II) and Ni(II) complexes are proposed. The ligands behave as bidentate, coordinating through the phenolic oxygen and the acetyl carbonyl group of the dehydroacetic acid moiety. The complexes are biologically active and exhibit enhanced antifungal activities compared to their parent ligands. The Cu(II), Ni(II) and Co(II) complexes of ligand HL^2 show good antifungal activity, hence further study of these complexes in agriculture could lead to interesting results.

Acknowledgements. V. N. P. is grateful to the UGC (WRO) Pune, for the award of a Teacher fellowship under FIP in X$^{\text{th}}$ plan. The authors are also thankful to Dr. T. K. Chondekar, Dept of Chemistry, Dr. B. A. M. University, Aurangabad, for valuable suggestions.

ИЗВОД

ПРЕЛАЗНИ МЕТАЛНИ КОМПЛЕКСИ СА КИСЕОНИЧНИМ ДОНОРНИМ ЛИГАНДИМА: СИНТЕЗА И ТЕРМИЧКА, СПЕКТРАЛНА И АНТИМИКРОБНА ПРОУЧАВАЊА

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Добијени су прелазни метални комплекси халкона изведених кондезацијом 3-ацетил-6-метил-2*H*-пиран-2,4(3*H*)-диона (дехидросирћетне киселине) и *p*-метоксибензалдехида (HL^1) или *p*-нитробензалдехида (HL^2) и окарактерисани елементалном анализом, кондуктометријом, термичком анализом, магнетним, IR, ^{1}H-NMR, UV–Vis и проучавањем микробне активности. Из аналитичких и термичких података нађена је стехиометрија 1:2 (метал:лиганд). Подаци за моларну проводљивост потврдили су да су ови метални хелати неелектролити. Термичка стабилност комплекса проучавана је термогравиметријом и дате су схеме распада комплекса. Лиганди и њихови комплекси метала су тестирани на антибактеријску активност према *Staphylococcus aureus* и *Escherichia coli* и антигљивичну активност према *Aspergillus flavus*, *Curvularia lunata* и *Penicillium notatum*.

(Примљено 14. новембра 2007, ревидирано 6. јуна 2008)

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