ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2006, Vol. 51, No. 1, pp. 67-72. © Pleiades Publishing, Inc., 2006.

COORDINATION COMPOUNDS

Synthesis, Structural Characterization, and Antifungal Activity of Schiff Bases and Their Transition Metal Mixed-Ligand Complexes¹

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Received April 14, 2005

Abstract—Mixed-ligand complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) have been prepared with biologically active Schiff bases, viz. potassium salt of *o*-hydroxyacetophenoneglycine [KHL] and bis(ben-zylidene)ethylenediamine [A¹] or thiophene-*o*-carboxaldene-*p*-toluidine [A²]. The synthesized mixed-ligand complexes have been characterized on the basis of elemental analysis, thermogravimetric analysis, magnetic measurements, and electronic and infrared spectra. The mixed-ligand complexes show higher antifungal activity as compared to the free ligands, metal salts, and the control (dimethylsulfoxide) but moderate activity as compared to the standard fungicides (bavistin and emcarb).

DOI: 10.1134/S003602360601013X

INTRODUCTION

The field of Schiff base complexes was fast developing on account of the wide variety of possible structures for the ligands depending upon the aldehydes and amines. The mixed-ligand complexes containing N, O, and/or S donor atoms are important owing to their significant antifungal, antibacterial, and anticancer activity [1]. In view of the importance of the Schiff bases mixed-ligand complexes and in continuation of our earlier work [2], herein we describe the synthesis, characterization, and antifungal activity of transition metal mixed-ligand complexes with different Schiff bases. The structures of the Schiff bases are shown in Fig. 1.

EXPERIMENTAL

Reagents and Solvents

All the chemicals and solutions that were used were of analytical grade. The metal nitrates, *o*-gydroxyacetophenone, benzaldehyde, glycine, ethylenediamine, and *p*-toluidine were purchased from E. Meark Limited (Mumbai, India). The thiophene-*o*-carboxaldehyde was purchased from Lancaster, England. The organic solvents were purified by recommended methods [3].

Potassium salt of *o***-hydrosyacetophenoneglycine** (**KHL**). A solution of potassium hydroxide (10 mmol, 0.56 g) in 30 ml of pure alcohol was added to crystalline glycine (10 mmol, 0.75 g). The mixture was stirred until the added component completely dissolved in the ethanol and KOH solution. Then an ethanolic solution (100 ml) of *o*-hydroxyacetophenone (10 mmol, 1.36 g) was quickly added. The reaction was allowed to reach completion by stirring at 50°C for 1 hour. The product was crystallized by diffusion of excess absolute diethyl ether into the solution. The resulting product was fil-



Fig. 1. Structures of the Schiff bases.

¹ This text was submitted by the authors in English.







 $[M(L)(A^2)(H_2O)]$

Fig. 2. Suggested structures of the mixed-ligand complexes.

tered and dried in a vacuum desiccator. Yield: 1.602 g (62%), M.p. 262°C.

Bis(benzylidene)ethylenediamine (A¹)

The bis(benzylidene) ethylenediamine was synthesized by a published procedure [4].

Thiophene-o-carboxaldene-p-toluidine (A^2)

An ethanolic solution (100 ml) of thiophene-*o*-carboxaldehyde (10 mmol, 1.12 g) and an ethanolic solution (100 ml) of *p*-toluidine (10 mmol, 1.07 g) in a molar ratio of 1 : 1 were mixed with constant stirring. Refluxing was carried out for six hours. The solution was cooled overnight at room temperature. The yellow crystals that formed were collected and dried in air. Yield: 1.27 g (60%), M.p. >360°C.

Preparation of the Mixed-Ligand Complexes

The preparation of the mixed-ligand complexes was carried out by mixing an aqueous solution (100 ml) of metal nitrate (10 mmol) and a hot methanolic solution of potassium salt of *o*-hydroxyacetophenoneglycine (10 mmol, 2.31 g) and bis(benzylidene)ethylenediamine (10 mmol, 2.36 g) or thiophene-*o*-carboxaldene-*p*-toluidine (10 mmol, 2.01 g). The complexes were formed by heating the mixture on a water bath for two hours at 60°C. The mixture was kept overnight at room

temperature. Finally the colored crystals that were obtained were collected by filtration, washed with water and ethanol, and dried in air.

Physical Measurement

The metal content of the mixed-ligand complexes was analyzed by the EDTA titration [5] technique after decomposing the organic matter with a mixture of $HClO_4$, H_2SO_4 , and HNO_3 (1 : 1.5 : 2.5). The carbon, hydrogen, nitrogen, and sulfur were analyzed with a model 240 Perkin-Elmer elemental analyzer. The thermogravimetric analyses (TGA) were performed using a model 5000/2960 analyzer manufactured by T.A. Instruments, U.S.A. The reflectance spectra of the mixed-ligand complexes were recorded in the range 1700-350 nm (as MgO) on a Beckman DK-2A spectrophotometer. Infrared spectra were recorded on an FT-IR Nicolet 400D spectrophotometer. The magnetic moments were obtained by Gouy's method using mercury tetrathiocyanatocobaltate(II) as the calibrant (χ_{a} = 16.44×10^{-6} c.g.s. units at 20°C). Diamagnetic corrections were made using Pascal's constant.

RESULTS AND DISCUSSION

The following reaction describes the formation of the mixed-ligand complexes:

$$M(NO_3)_2 \cdot nH_2O + KHL + A \longrightarrow [M(L)(A)(H_2O)]$$

$$+ \text{KNO}_3 + \text{HNO}_3 + (n-1)\text{H}_2\text{O}$$

The elemental analysis data, the molecular weights, the colors, the percentage yields, the melting points, and the magnetic moment data are represented in Table 1. The results of the elemental analysis of the Schiff bases and their mixed-ligand complexes are in good agreement with those required by the proposed formula. All the mixed-ligand complexes are insoluble in methanol, diethyl ether, ethanol, and DMF but soluble in DMSO. The proposed structures of the mixedligand complexes are given in Fig. 2.

IR Spectra and Mode of Bonding

The coordinating sites involved in the bonding with the metal ion have been determined by carefully comparing the infrared spectra of the mixed-ligand complexes with those of the free ligands. The IR spectra of the ligand (KHL) shows a broad band at 3450 cm⁻¹, which can be attributed to the phenolic OH group. This band is absent in all the mixed-ligand complexes, thus, indicating coordination through the phenolic OH group [6]. The bands observed in the regions 3200–3300, 1280–1290, 880–850, and 730–700 cm⁻¹ are attributed to OH stretching, bending, rocking, and wagging vibrations, respectively, due to the presence of water molecules [7]. The band due to the azomethine (C=N) group

Compounds	Mol. Wt.	Color	% Found (Calcd.)					M.p.	V:-14 07
Empirical Formula			С	Н	N	S	metal	(°Ċ)	r iela, %
KHL	231.19	Yellow	51.92	4.35	6.07	_	_	262	62
C ₁₀ H ₁₀ KNO ₃			(51.94)	(4.32)	(6.05)				
A^1	236.16	Yellow	81.32	6.78	11.83	-	_	235	72
$C_{6}H_{18}N_{2}$			(81.36)	(6.77)	(11.85)				
A^2	201.20	Yellow	71.66	5.43	6.91	15.92	_	>360	58
$C_{12}H_{11}NS$			(71.63)	(5.46)	(6.95)	(15.94)			
$[Mn(L)(A^1)(H_2O)]$	500.20	Brown	62.47	5.35	8.32	_	10.98	>360	62
C ₂₆ H ₂₇ MnN ₃ O ₄			(62.42)	(5.39)	(8.39)		(10.98)		
$[\text{Co}(\text{L})(\text{A}^1)(\text{H}_2\text{O})]$	504.19	Brown	61.91	5.32	8.35	_	11.69	242	55
C ₂₆ H ₂₇ CoN ₃ O ₄			(61.93)	(5.35)	(8.33)		(11.68)		
$[Ni(L)(A^1)(H_2O)]$	503.95	Green	61.97	5.39	8.32	_	11.58	>360	58
C ₂₆ H ₂₇ NiN ₃ O ₄			(61.96)	(5.35)	(8.33)		(11.64)		
$[Cu(L)(A^1)(H_2O)]$	508.80	Green	61.39	5.30	8.31	_	12.43	229	63
C ₂₆ H ₂₇ CuN ₃ O ₄			(61.37)	(5.30)	(8.25)		(12.48)		
$[Zn(L)(A^1)(H_2O)]$	510.65	Yellow	61.17	5.28	8.23	_	12.84	261	60
C ₂₆ H ₂₇ ZnN ₃ O ₄			(61.14)	(5.28)	(8.22)		(12.80)		
$[Cd(L)(A^1)(H_2O)]$	557.67	Yellow	55.92	4.86	7.56	_	20.23	294	56
C ₂₆ H ₂₇ CdN ₃ O ₄			(55.99)	(4.84)	(7.53)		(20.15)		
$[Mn(L)(A^2)(H_2O)]$	465.22	Brown	56.76	4.74	6.04	6.87	11.73	>360	53
C ₂₂ H ₂₂ MnN ₂ O ₄ S			(56.79)	(4.72)	(6.01)	(6.89)	(11.80)		
$[\text{Co}(\text{L})(\text{A}^2)(\text{H}_2\text{O})]$	469.21	Brown	56.36	4.63	5.94	6.80	12.56	>360	57
C ₂₂ H ₂₂ CoN ₂ O ₄ S			(56.31)	(4.68)	(5.96)	(6.83)	(12.55)		
$[Ni(L)(A^2)(H_2O)]$	468.97	Green	56.35	4.71	5.95	6.86	12.50	>360	60
C ₂₂ H ₂₂ NiN ₂ O ₄ S			(56.34)	(4.69)	(5.97)	(6.83)	(12.51)		
$[Cu(L)(A^2)(H_2O)]$	473.82	Green	55.72	4.62	5.94	6.73	13.38	272	64
$C_{22}H_{22}CuN_2O_4S$			(55.76)	(4.64)	(5.90)	(6.76)	(13.41)		
$[Zn(L)(A^2)(H_2O)]$	475.67	Yellow	55.56	4.60	5.82	6.74	13.72	>360	56
$C_{22}H_{22}ZnN_2O_4S$			(55.54)	(4.62)	(5.88)	(6.73)	(13.74)		
$[Cd(L)(A^2)(H_2O)]$	522.69	Yellow	50.56	4.26	5.35	6.15	21.55	>360	59
$\mathrm{C}_{22}\mathrm{H}_{22}\mathrm{CdN}_{2}\mathrm{O}_{4}\mathrm{S}$			(50.55)	(4.20)	(5.35)	(6.13)	(21.50)		

Table 1. Analytical data of the mixed-ligand complexes^a

^a KHL = Potassium salt of *o*-hydroxyacetophenoneglycine.

 $A^1 = Bis(benzylidene)ethylenediamine.$

 A^2 = Thiophene-*o*-carboxaldene-*p*-toluidine.

in the free ligand is observed in the region 1625– 1635 cm⁻¹. This band is shifted to the lower frequency region upon complexation, thus, suggesting coordination via the azomethine group in all of the prepared complexes [8]. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1595 and 1400 cm⁻¹, respectively, in the potassium salt of *o*-hydroxyacetophenoneglycine, but, in the mixedligand complexes, they are shifted to lower frequency regions (~1580 and ~1385 cm⁻¹, respectively) [9]. The v(C–S) [10] band of the thiophene-*o*-carboxaldene-*p*toluidine observed at 765 cm⁻¹, which is shifted to a lower frequency of about 750 cm⁻¹ in the spectra of the mixed-ligand complexes, indicates the participation of

Complexes	Observed bands (cm ⁻¹)			V./V.	в	ß	ß°	10Da
	ν_1	v_2	ν ₃	•2/•1	Ъ	Ч	P	10D9
$[Co(L)(A^1)(H_2O)]$	9.125	17.990	19.060	1.97	737	0.76	24	10.247
$[\mathrm{Ni}(\mathrm{L})(\mathrm{A}^1)(\mathrm{H}_2\mathrm{O})]$	10.350	18.150	24.300	1.75	760	0.74	26	10.350
$[\text{Co}(\text{L})(\text{A}^2)(\text{H}_2\text{O})]$	9.180	18.050	19.000	1.96	729	0.75	25	10.300
$[\mathrm{Ni}(\mathrm{L})(\mathrm{A}^2)(\mathrm{H}_2\mathrm{O})]$	10.400	18.070	24.170	1.73	736	0.71	29	10.400

Table 2. Electronic parameters of the Co(II) and Ni(II) mixed-ligand complexes^a

^a KHL = Potassium salt of *o*-hydroxyacetophenoneglycine.

 $A^1 = Bis(benzylidene)ethylenediamine.$

 A^2 = Thiophene-*o*-carboxaldene-*p*-toluidine.

The ligand field splitting energy (10*Dq*), interelectronic repulsion parameter (B) and covalency factor (nephelauxetic ratio) (β) for the Co^{II} and Ni^{II} complexes have been calculated using the secular equations given by E. König [26].

For Co(II) complexes

For Ni(II) complexes

$$10Dq = 1/2[(2v_1 - v_3) + (v_3^2 + v_1v_3 - v_1^2)^{1/2}]$$
 $10Dq = v_1$ $15B = v_3 - 2v_1 + 10Dq$ $15B = (v_2 + v_3) - 3v_1$ $\beta = B/Bo$ [Bo(free ion) = 971] $\beta = B/Bo$ [Bo(free ion) = 1030] $\beta^\circ = (1 - \beta) \times 100$ $\beta^\circ = (1 - \beta) \times 100$

the sulfur atom of the thiophene ring in the coordination. The sharp bands in the range 750–780 and 1525– 1535 cm⁻¹ are due to aromatic v(C–H) and v(C=C), respectively. In the far IR spectra of all the mixedligand complexes, the band observed at the 520–540 cm⁻¹ region can be assigned to M–N stretching [11]. The bonding of oxygen to the metal ions is proved by the occurrence of the band at the 430– 440 cm⁻¹ region [12]. The bonding of sulfur to the metal ion is indicated by the occurrence of the band at the 410–425 cm⁻¹ region [13].

Thermogravimetric Analysis

The TGA curves were obtained in a nitrogen atmosphere between 50 and 800°C. The mixed-ligand complexes decompose in two steps. The first step is between 150–180°C and corresponds to the coordinated water molecule [14]. In the temperature range 180–800°C, the ligand molecules are lost. All the mixed-ligand complexes completely decompose to the corresponding metal oxides: MnO, Co₂O₃, NiO, CuO, ZnO, and CdO. These results are in good agreement with the composition of the mixed-ligand complexes.

Electronic Spectra

The electronic spectra of the Ni(II) complexes are consistent with the formation of an octahedral geometry with the appearance of three bands at ~24000, ~18000, and ~10500 cm⁻¹ corresponding to the following transitions [15]: ${}^{3}A_{2g} \longrightarrow {}^{3}T_{1g}(P)$, ${}^{3}A_{2g} \longrightarrow {}^{3}T_{1g}(F)$, and ${}^{3}A_{2g} \longrightarrow {}^{3}T_{2g}$. For the Co(II) mixed-ligand complexes, the electronic spectra show three bands of medium intensity at ~19000, ~18000, and ~9200 cm^{-1} , which are assigned, respectively, to the transitions ${}^{4}T_{1g}(F) \longrightarrow {}^{3}T_{1g}(P), {}^{4}T_{1g}(F) \longrightarrow {}^{4}A_{2g}(F), \text{ and} {}^{4}T_{1g}(F) \longrightarrow {}^{4}T_{2g}(F) \text{ of an octahedral geometry [16].}$ The electronic spectra of the Cu(II) mixed-ligand complexes show an absorption band at ~15500 cm⁻¹ attributed to the ${}^{2}E_{g} \longrightarrow {}^{2}T_{2g}$ transition, which are compatible with these complexes having an octahedral structure [17]. The ground state of the Mn(II) is ${}^{6}A_{1g}$. The Mn(II) mixed-ligand complexes in an octahedral [18] field should give three transitions corresponding to ${}^{6}A_{1g} \longrightarrow {}^{4}T_{1g}$ (v₁ ~ 14500 cm⁻¹), ${}^{6}A_{1g} \longrightarrow {}^{4}T_{2g}$ $(v_2 \sim 19800 \text{ cm}^{-1})$, and ${}^6A_{1g} \longrightarrow {}^4A_{1g} (v_3 \sim 24400 \text{ cm}^{-1})$ in increasing order of energy. The ligand field splitting energy (Da), the Racah interelectronic repulsion parameter (B), the nephelauxetic ratio (β), and the ratio v_2/v_1 for the Ni(II) and Co(II) mixed-ligand complexes are presented in Table 2.

Magnetic Measurements

The magnetic moments of the mixed-ligand complexes were measured at room temperature. In the present case, the magnetic moment values of the $[Mn(L)(A^1)(H_2O)]$ and $[Mn(L)(A^2)(H_2O)]$ are 6.01 and 6.04 μ_B , respectively, which are within the limit of the spin-free value (5.92 μ_B) for five unpaired electrons, thus, indicating that the complexes are high-spin



Fig. 3. Plot of antifungal activity.

 d^5 -systems with an octahedral geometry [19]. The magnetic moment values for the Co(II) mixed-ligand complexes have been used as criteria to determine the type of coordination around the metal ion. Due to the intrinsic orbital angular momentum in the ground state, there is consistently a considerable orbital contribution. The effective moment values magnetic of $[Co(L)(A^1)(H_2O)]$ and $[Co(L)(A^2)(H_2O)]$ are 4.06 and 4.09 $\mu_{\rm B}$, respectively, which are slightly greater than the spin only value (3.87 $\mu_{\rm B}$), which suggest an octahedral geometry for the Co(II) mixed-ligand complexes [20] in the high-spin state. The magnetic moment values of the $[Ni(L)(A^1)(H_2O)]$ and $[Ni(L)(A^2)(H_2O)]$ are 2.89 and 2.77 μ_B , respectively, which are within the range expected for similar hexacoordinated [21] Ni(II) ions. The magnetic moment values for the $[Cu(L)(A^1)(H_2O)]$ and $[Cu(L)(A^2)(H_2O)]$ are 1.89 and 1.76 μ_B , respectively, which are consistent with an octahedral structure [22]. The magnetic moment determinations show that the Zn(II) and Cd(II) mixed-ligand complexes are diamagnetic (as expected for the d^{10} system) and presumably octahedral.

ANTIFUNGAL ACTIVITY

Isolation of Fungi

The dilution plate method [23] was used for isolation of fungi. Selected and isolated fungi were maintained on potato dextrose agar plates at 4°C for further experimental work.

The antifungal activities of the ligands, mixedligand complexes, metal nitrates, fungicides (bavistin and emcarb), and the control (dimethylsulfoxide) were screened using the plate poison technique [24]. Sevenday-old cultures of Aspergillus niger, Fusarium oxysporum, and Aspergillus flavus were used as test organisms. A stock solution of 500 µg/ml was made by dissolving 50 mg of each compound in dimethylsulphoxide (100 ml). The sterilized medium with the added stock solution was poured into 90 mm sterile petri plates and allowed to solidify. They were inoculated with a 5 mm actively growing mycelial disc and incubated at 27°C for 72 h. After 72 h of inoculation, the percent reduction in the radial growth diameter over the control was calculated. The growth was compared with dimethylsulfoxide as the control. The results of the antifungal studies are given in Table 3 and Fig. 3.

The results show that the mixed-ligand complexes are more toxic than their parent ligands and metal nitrate against the same microorganisms. The increase in the antifungal activity of the mixed-ligand complexes may be due to the effect of the metal ion on the normal cell processes. A possible mode for the toxicity increase may be considered in light of Tweede's chelation theory [25]. Chelation considerably reduced the polarity of the metal ion because of the partial sharing of its positive charge with the donor groups and the π -electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane. Although there is a sufficient increase in the fun-

Compounds	Growth diameter in mm (% of inhibition)					
Compounds	A. niger	F. oxy- sporum	A. flavus			
DMSO (control)	29	46	39			
Bavistin	00(100)	00(100)	00(100)			
Emcarb	00(100)	00(100)	00(100)			
KHL	23(21)	33(28)	28(28)			
A^1	22(23)	34(27)	26(32)			
A^2	20(31)	31(32)	29(25)			
$Mn(NO_3)_2 \cdot 4H_2O$	18(38)	28(40)	29(25)			
$Co(NO_3)_2 \cdot 6H_2O$	20(31)	29(37)	27(30)			
$Ni(NO_3)_2 \cdot 6H_2O$	22(23)	31(32)	29(25)			
$Cu(NO_3)_2 \cdot 3H_2O$	19(34)	28(40)	28(28)			
$Zn(NO_3)_2 \cdot 6H_2O$	22(23)	30(35)	27(30)			
$Cd(NO_3)_2 \cdot 4H_2O$	20(31)	31(32)	27(30)			
$[Mn(L)(A^1)(H_2O)]$	13(55)	24(48)	21(46)			
$[\text{Co}(\text{L})(\text{A}^1)(\text{H}_2\text{O})]$	12(59)	28(40)	19(51)			
$[Ni(L)(A^1)(H_2O)]$	13(55)	27(41)	18(54)			
$[Cu(L)(A^1)(H_2O)]$	14(52)	24(48)	20(49)			
$[Zn(L)(A^1)(H_2O)]$	13(55)	23(50)	22(44)			
$[Cd(L)(A^1)(H_2O)]$	12(59)	22(52)	19(51)			
$[Mn(L)(A^2)(H_2O)]$	14(52)	24(48)	22(44)			
$[\text{Co}(\text{L})(\text{A}^2)(\text{H}_2\text{O})]$	13(55)	19(59)	23(41)			
$[Ni(L)(A^2)(H_2O)]$	14(52)	20(57)	22(44)			
$[Cu(L)(A^2)(H_2O)]$	13(55)	28(40)	23(41)			
$[Zn(L)(A^2)(H_2O)]$	14(52)	27(41)	24(38)			
$[Cd(L)(A^2)(H_2O)]$	13(55)	21(54)	21(46)			

Table 3. Antifungal activities of the compounds^a

^a KHL = Potassium salt of *o*-hydroxyacetophenoneglycine.

 $A^1 = Bis(benzylidene)ethylenediamine.$

 A^2 = Thiophene-*o*-carboxaldene-*p*-toluidine.

gicidal activity of the mixed-ligand complexes as compared to the free ligands (metal nitrate) and the control (dimethylsulfoxide), they cannot attain the effectiveness of the conventional fungicides (bavistin and emcarb).

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