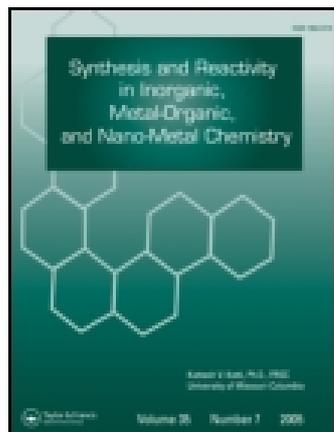


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Synthesis, Spectral, and Biocidal Studies of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) Mixed-Ligand Complexes

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Synthesis, Spectral, and Biocidal Studies of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) Mixed-Ligand Complexes

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ABSTRACT

Complexes of transition metals with salicylaldehyde (salH) or 5-bromo-salicylaldehyde (Br-salH) in 1:2 molar ratio, have the compositions $[M(H_2O)_2(sal)_2] \cdot H_2O$ (1) or $[M(H_2O)_2(Br-sal)_2] \cdot H_2O$ (2), respectively. The Schiff base derived from ethylenediamine and acetophenone in 1:1 molar ratio in alcoholic solution yields *bis*(acetophenone)ethylenediamine (acphen). Further reaction of (1) or (2) with acphen in alcohol yielded mixed-ligand complexes of the type $[M(sal)_2acphen]$ or $[M(Br-sal)_2acphen]$, respectively. All of these complexes are soluble in ethanol and methanol. They were characterized on the basis of elemental analyses,

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magnetic measurements, infrared spectra, electronic spectra, and thermogravimetric analyses. All of these complexes have been screened for their antimicrobial activity against bacterial strands using the agar diffusion method.

Key Words: Elemental analyses; Magnetic measurements; Schiff base; Mixed-ligand complexes.

INTRODUCTION

Schiff bases and their metal complexes play a key role in our understanding of transition metal ions. The complexes containing O,N donor atoms are very important owing to their significant antibacterial and anticancer activity.^[1] It is well known that some drugs have increased activity when administered as metal complexes than as free organic compounds.^[2] A large number of reports are available on the chemistry and the biocidal activities of transition metal complexes containing O,N donor atoms. As a continuation of our earlier work,^[3] in this article, we describe the synthesis and characterizations of bidentate Schiff base ligands and their metal complexes. The structure of *bis*(acetophenone)ethylenediamine (acphen) is shown in Fig. 1.

EXPERIMENTAL

Materials

The chemicals used in the synthesis were of A. R. grade. Stock solutions of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) chlorides were prepared and standardized by complexometric titration.^[4]

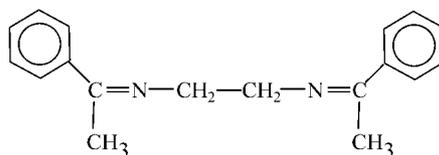


Figure 1. *bis*(Acetophenone)ethylenediamine (acphen).



Preparation of Schiff Base

The acphen ligand was synthesized by mixing ethylenediamine (10 mmol, 0.06 g) and acetophenone (20 mmol, 0.528 g) in an ethanolic solution (100 mL). The reaction mixture was heated in a water bath at 50 °C for 3–4 hr. The reaction mixture on ice-cooling overnight gave the Schiff base in the form of yellow crystals. The product was filtered and dried in air. It was recrystallized from ethanol to give 0.441 g (75%) of the ligand; m.p. = 260 °C.

Preparation of Complexes

bis(Salicylaldehydato)diaquonickel(II) and the analogous complexes of Mn(II), Co(II), Cu(II), and Zn(II) were synthesized by published procedures.^[5] The preparation of [Ni(sal)₂acphen]·H₂O was carried out by refluxing an ethanolic solution (150 mL) of [Ni(sal)₂(H₂O)₂] (20 mmol, 0.734 g) with the Schiff base (20 mmol, 0.528 g) for 1 hr. The solution was then concentrated to 15 mL, and cooled in a refrigerator overnight at 6 °C. The formed crystals were collected and recrystallized from chloroform and dried in air. The mixed-ligand complexes of Mn(II), Co(II), Cu(II), and Zn(II) were prepared similarly. The mixed-ligand complexes [M(Br-sal)₂acphen]·H₂O [M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)] were prepared by the same method.

Analytical Procedures

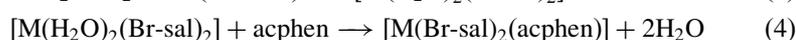
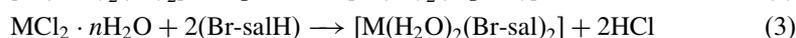
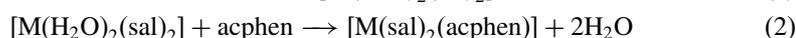
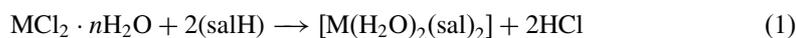
Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a model 240 Perkin–Elmer elemental analyzer. Metal contents were determined by EDTA titration. The infrared spectra were measured on a FT-IR Nicolet 400 D spectrophotometer as KBr pellets. The electronic spectra of the complexes were recorded on a Beckman DK-2A spectrophotometer using MgO as the reference in the solid state. The melting points of the ligands and complexes were recorded in open capillaries in a capillary melting point apparatus (Tempo Instruments Co., Mumbai). The magnetic moments were obtained by a model 7304 vibrating sample magnetometer.



RESULTS AND DISCUSSION

Characterization of the Complexes

The given formulas (Table 1) are based on analytical data. The formation of the complexes may be represented by the following equations.



Magnetic Measurements

The magnetic moment data of the complexes are presented in Table 1. The magnetic moment values for the Cu(II) complexes are 1.71 and 1.84 B.M., which is consistent^[6] with an octahedral structure. The magnetic moment values for the Co(II) complexes have been used as a criterion 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 and the effective magnetic moment lies between 4.7 and 5.2 B.M. at room temperature. In the present case, the magnetic moment values of the Co(II) complexes are 4.87 and 4.75 B.M., suggesting^[7] an octahedral geometry. This deviation from the spin-only value (3.83 B.M.) maybe ascribed to spin-orbit coupling. The magnetic moment values of the Ni(II) complexes are 2.67 and 2.72 B.M., which are usual for the range expected for similar hexa-coordinated^[8] Ni(II) ions. The magnetic moment values of the Mn(II) complexes are 5.74 and 5.75 B.M., due to a high-spin d^5 -system with octahedral geometry. The magnetic moment determinations show that the Zn(II) complexes are diamagnetic.

Electronic Spectra

The electronic spectra of the complexes were recorded in the solid state. The electronic spectra of the Mn(II) complexes exhibit 3 weak absorption bands for the transitions ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}({}^4\text{G})$ ($\sim 15,000 \text{ cm}^{-1}$), ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}({}^4\text{G})$ ($\sim 20,000 \text{ cm}^{-1}$), and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g, {}^4\text{A}_{1g}({}^4\text{G})$ ($\sim 25,000 \text{ cm}^{-1}$), in accord with an octahedral geometry.^[9] The electronic spectra of the Co(II) complexes



Mixed-Ligand Complexes

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

Complex empirical formula	Mol wt.	Color	Yield (%)	% Found (calcd.)				M.p. (°C)	μ_{eff} (B.M.)
				C	H	N	Metal		
acphen C ₁₈ H ₂₀ N ₂	264	Yellow	75.0	81.79 (81.81)	7.60 (7.57)	10.54 (10.60)	—	260	—
[Mn(sal) ₂ acphen] · H ₂ O	579.94	Brown	77.4	66.25 (66.21)	5.53 (5.51)	4.84 (4.82)	9.62 (9.64)	280	6.05
[Co(sal) ₂ acphen] · H ₂ O	582.93	Yellow	81.8	65.85 (65.87)	5.47 (5.48)	4.84 (4.80)	10.15 (10.10)	290	4.82
[Ni(sal) ₂ acphen] · H ₂ O	582.71	Yellowish green	81.5	65.90 (65.89)	5.46 (5.49)	4.83 (4.80)	10.11 (10.07)	275	2.95
[Cu(sal) ₂ acphen] · H ₂ O	587.54	Green	82.5	65.37 (65.35)	5.45 (5.44)	4.80 (4.76)	10.85 (10.80)	290	1.71
[Zn(sal) ₂ acphen] · H ₂ O	589.37	Light yellow	83.5	65.18 (65.15)	5.45 (5.42)	4.73 (4.75)	11.13 (11.09)	292	—
[Mn(Brsal) ₂ acphen] · H ₂ O	737.94	Brown	78.8	52.03 (52.03)	4.05 (4.06)	3.79 (3.79)	7.58 (7.58)	290	6.13
[Co(Brsal) ₂ acphen] · H ₂ O	740.93	Yellow	76.5	51.81 (51.82)	4.02 (4.04)	3.76 (3.77)	7.95 (7.95)	285	4.74
[Ni(Brsal) ₂ acphen] · H ₂ O	740.71	Yellowish green	82.5	51.80 (51.84)	4.05 (4.05)	3.78 (3.78)	7.90 (7.92)	280	2.72
[Cu(Brsal) ₂ acphen] · H ₂ O	745.54	Green	81.5	51.50 (51.50)	4.02 (4.02)	3.71 (3.75)	8.52 (8.52)	285	1.70
[Zn(Brsal) ₂ acphen] · H ₂ O	747.37	Light yellow	83.6	51.38 (51.38)	4.00 (4.01)	3.72 (3.74)	8.71 (8.74)	290	—

^aacphen = bis(acetophenone)ethylenediamine.

exhibit three bands. The assignments of the spectral bands are ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ ($\nu_1 \sim 9500 \text{ cm}^{-1}$), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ($\nu_2 \sim 18,000 \text{ cm}^{-1}$), and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ($\nu_3 \sim 19,000 \text{ cm}^{-1}$). A strong charge transfer band is shown by the complex at $\sim 25,000 \text{ cm}^{-1}$. König's method^[10] was used to ascertain the correct position of the bands. The Ni(II) complexes also exhibit three d–d transition bands at ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ($\nu_1 \sim 10,550 \text{ cm}^{-1}$), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ($\nu_2 \sim 17,400 \text{ cm}^{-1}$), and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ($\nu_3 \sim 25,000 \text{ cm}^{-1}$). The values of the electronic parameters such as the ligand field splitting energy ($10Dq$), Racah interelectronic repulsion parameter (B), nephelauxetic ratio (β), and the ratio ν_2/ν_1 are presented in Table 2. All data are consistent with an octahedral geometry.^[11] The electronic spectra of the Cu(II) complexes^[12] exhibit a band at $\sim 15,500 \text{ cm}^{-1}$ assigned to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition, which is in agreement with an octahedral geometry. A strong charge transfer band is observed at $26,000 \text{ cm}^{-1}$. The ϵ values of the complexes were not determined.

Thermogravimetric Analyses

There are some remarkable features in the TGA curves. The decomposition temperatures of the complexes are higher than those of acphen and salH or Br-salH, indicating that the complexes are more stable than the ligands. Thermal curves of the complexes clearly indicate that the weight loss between 35 and 105°C corresponds to one water molecule for all complexes. Because of the low temperatures, this water molecule may be considered as water of crystallization.^[13] The TGA curve indicates that above 250°C the compounds start to lose mass with partial evaporation of the Schiff base (acphen) up to 320°C . In the temperature range $320\text{--}500^\circ\text{C}$ the remaining organic ligand molecules are lost. In all cases the final products are metal oxides. These results are in good agreement with the proposed composition of the complexes.

IR Spectra

The infrared spectra of the complexes have been studied to characterize their structures. The infrared spectra of the complexes register the $\nu(\text{C}=\text{O})$ ^[14] band at about 1600 cm^{-1} and $\nu(\text{C}-\text{O})$ ^[15] at about 1340 cm^{-1} . The Schiff base (acphen) shows the $\nu(\text{C}=\text{N})$ stretching band at 1640 cm^{-1} . This band shifts to lower energy by $10\text{--}30 \text{ cm}^{-1}$ in the chelates indicating coordination through the azomethine nitrogen.^[16] The sharp bands in the ranges $750\text{--}780$ and $1525\text{--}1535 \text{ cm}^{-1}$ are due to aromatic $\nu(\text{C}-\text{H})$ ^[15] and $\nu(\text{C}=\text{C})$,^[17] respectively. The absorptions in the range $410\text{--}420$ and $475\text{--}495 \text{ cm}^{-1}$ are attributed to $\nu(\text{M}-\text{O})$ ^[18] and $\nu(\text{M}-\text{N})$,^[19] respectively.



Table 2. Electronic spectral data of the Co(II) and Ni(II) complexes.^a

Complexes	Observed band (cm ⁻¹)						β	β^0	10 Dq
	ν_1	ν_2	ν_3	ν_2/ν_1	B	β			
[Co(sal) ₂ acphen] · H ₂ O	9,302	18,180	18,940	1.950	717.03	0.738	26.20	10,419	
[Ni(Br-sal) ₂ acphen] · H ₂ O	10,540	17,391	25,000	1.650	718.07	0.697	30.28	10,540	
[Co(Br-sal) ₂ acphen] · H ₂ O	9,030	18,200	19,047	2.010	742.55	0.765	23.50	10,151	
[Ni(sal) ₂ acphen] · H ₂ O	10,525	16,930	25,000	1.600	690.33	0.670	32.97	10,525	

^aacphen = bis(acetophenone)ethylenediamine.

Table 3. Antimicrobial activities of the complexes.^a

Compound	<i>S. typhi</i>		<i>setatia spp.</i>	
	Zone of Inhi (mm)	% Inhi	Zone of Inhi (mm)	% Inhi
Control (methanol)	10	—	11	—
SalH	11	10	12	09
acphen	12	20	12	09
BrsalH	12	20	13	18
MnCl ₂ · 4H ₂ O	12	22	13	18
CoCl ₂ · 6H ₂ O	11	15	13	18
NiCl ₂ · 6H ₂ O	11	11	12	09
CuCl ₂ · 5H ₂ O	12	22	12	09
ZnCl ₂	11	10	12	09
[Mn(sal) ₂ acphen] · H ₂ O	13	30	14	27
[Co(sal) ₂ acphen] · H ₂ O	13	50	16	45
[Ni(sal) ₂ acphen] · H ₂ O	14	30	14	27
[Cu(sal) ₂ acphen] · H ₂ O	13	40	14	27
[Zn(sal) ₂ acphen] · H ₂ O	13	40	14	27
[Mn(Brsal) ₂ acphen] · H ₂ O	13	30	14	27
[Co(Brsal) ₂ acphen] · H ₂ O	14	40	16	45
[Ni(Brsal) ₂ acphen] · H ₂ O	14	40	16	45
[Cu(Brsal) ₂ acphen] · H ₂ O	13	30	15	36
[Zn(Brsal) ₂ acphen] · H ₂ O	13	30	14	27

^aacphen = *bis*(acetophenone)ethylenediamine.

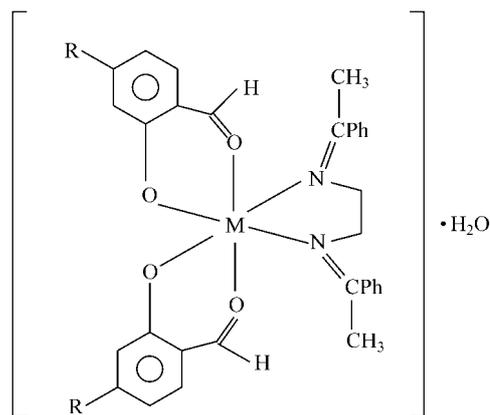


Figure 2. [M(sal)₂acphen] or [M(Br-sal)₂acphen] R = H or Br, M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II).



Antimicrobial Activity

In the present study, the ligands, metal salts, and complexes have been tested for their effects on the growth of microbial cultures and were studied for their interaction with *S. typhi* and *Serratia* spp. using the agar diffusion method.^[20,21] All compounds have significant antibacterial activity at 1×10^{-4} g mL⁻¹ against bacteria. The growth was compared with a control (blank) and is expressed as percentage inhibition vs. control. The percentage inhibition of various compounds are recorded in Table 3. The data represent the values of five replicates. From the data, it is observed that the complexes show higher activity against bacteria as compared to the control, metal salts, and ligands. Hence, complexation increased the antimicrobial activity. The patterns of activity are complex and no clear trend can be ascertained. However, a suggested structure of the mixed-ligand complexes is shown in Fig. 2.

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