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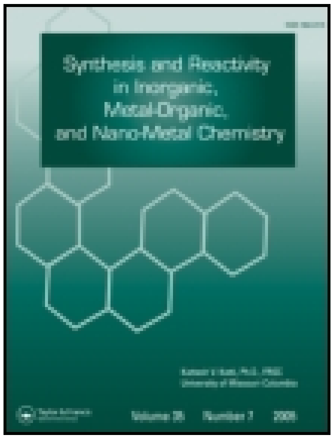

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Synthesis, Characterization, and Biocidal Studies of Some Transition Metal Complexes Containing Bidentate Monobasic Hydroxyaldehydes and a Neutral Bidentate Schiff Base

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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Synthesis, Characterization, and Biocidal Studies of Some Transition Metal Complexes Containing Bidentate Monobasic Hydroxyaldehydes and a Neutral Bidentate Schiff Base

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ABSTRACT

Complexes of the transition metals with salicylaldehyde (sa1H) or 5-bromosalicylaldehyde (Br-sa1H) 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 benzaldehyde in 1:1 molar ratio in alcoholic solution yields bis(benzylidene)ethylenediamine (benen). Further reaction of **(1)** or **(2)** with benen in alcohol yielded mixed-ligand complexes of the type$[M(sal)_2benen]$ or $[M(Br\text{-}sal)_2benen]$, respectively. All of these complexes are soluble in ethanol and methanol.

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They were characterized on the basis of elemental analyses, 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.

INTRODUCTION

An extensive amount of work on coordination compounds of transition elements with Schiff bases has been done.[1] Generally, Schiff bases are considered as a very important class of organic compounds. Mixed-ligand complexes are well known to play an important role in biological systems.[2] In continuation of earlier work,[3] we prepared new mixed-ligand complexes of the type$[M(sal)_2benen]\cdot H_2O$ and $[M(Br-sal)benen]\cdot H_2O$, where, M = Co(II), Ni(II), Cu(II), Mn(II), Zn(II) and Fe(II), Sal = salicylaldehyde anion, Br-sal = 5-bromosalicylaldehyde anion and benen = bis-(benzylidene)ethylenediamine and their physical properties were determined and discussed. The suggested structure of bis(benzylidene)ethylenediamine is shown in Figure 1.

EXPERIMENTAL

Materials

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

Preparation of Schiff Base

The ligand benen was synthesized by a published procedure.[5]

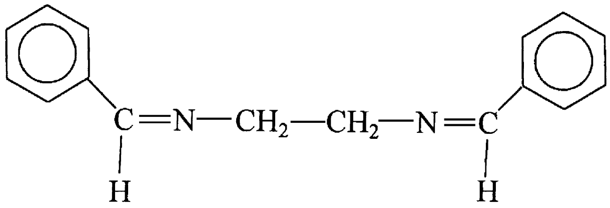


Figure 1. Bis(Benzylidene)ethylenediamine (benen).

Preparation of Complexes

Bis(salicylaldehydato)diaquoNi(II) and the similar complexes of Mn(II), Fe(II), Co(II), Cu(II), and Zn(II) were synthesized by published procedures.[6] The preparation of $[Ni(sal)_2benen]\cdot H_2O$ was carried out by refluxing an ethanolic solution (150 mL) of $[Ni(sal)_2(H_2O)_2]$ (0.02 mol, 0.734 g) with the Schiff base (0.02 mol, 0.472 g) for an hour. 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 Co(II), Cu(II), Mn(II), Zn(II) and Fe(II) were prepared similarly. The mixed-ligand complexes $[M(Br{-}sal)_2benen]\cdot H_2O$ [M = Co(II), Fe(II), Ni(II), Cu(II), Mn(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 appratus (Tempo Instruments Co. Mumbai). The magnetic moments have been obtained by a model 7300 vibrating sample magnetometer.

RESULTS AND DISCUSSION

Characterization of the Complexes

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

$$MCl_2 \cdot nH_2O + 2(salH) \xrightarrow{H_2O} [M(H_2O)_2(sal)_2] + 2HCl \qquad (1)$$

$$[M(H_2O)_2(sal)_2] + benen \xrightarrow[\text{1 hour}]{\text{EtOH, Reflux}} [M(sal)_2benen] + 2H_2O \qquad (2)$$

Table 1. Analytical data of the complexes.

Complex empirical formula	Mol wt.	Color	M. p. °C	Yield (%)	% Found (calc.)				μ_{eff} (B.M.)
					C	H	N	Metal	
benen[a]$C_{16}H_{18}N_2$	236.00	Light yellow	235	70.0	81.40 (81.42)	6.79 (6.83)	11.85 (11.88)	–	–
[Mn(sal)$_2$ benen]·H_2O $C_{30}H_{28}MnN_2O_5$	551.94	Brown	280	77.4	65.18 (65.22)	5.03 (5.07)	5.04 (5.07)	9.90 (9.95)	5.74
[Fe(sal)$_2$ benen]·H_2O $C_{30}H_{28}FeN_2O_5$	551.85	Brown	275	78.5	65.19 (65.23)	5.05 (5.07)	5.05 (5.07)	10.05 (10.12)	5.25
[Co(sal)$_2$ benen]·H_2O $C_{30}H_{28}CoN_2O_5$	554.93	Yellow	280	81.6	64.80 (64.87)	5.02 (5.04)	5.03 (5.04)	10.55 (10.61)	4.87
[Ni(sal)$_2$ benen]·H_2O $C_{30}H_{28}Ni\ N_2O_5$	554.71	Yellowish green	280	82.5	64.75 (64.89)	5.03 (5.04)	5.04 (5.04)	10.50 (10.58)	2.67
[Cu(sal)$_2$ benen]·H_2O $C_{30}H_{28}CuN_2O_5$	559.54	Green	275	83.4	64.25 (64.33)	4.85 (5.00)	5.05 (5.00)	11.25 (11.35)	1.71

[Zn(sal)$_2$ benen]·H_2O $C_{30}H_{28}ZnN_2O_5$	561.37	Light yellow	270	82.6	64.10 (64.12)	4.88 (4.98)	4.95 (5.00)	11.60 (11.64)	–
[Mn(Br–sal)$_2$ benen]·H_2O $C_{30}H_{26}Br_2MnN_2O_5$	709.94	Brown	275	78.8	50.63 (50.70)	3.70 (3.66)	3.89 (3.94)	7.66 (7.73)	5.75
[Fe(Br–sal)$_2$ benen]·H_2O $C_{30}H_{26}Br_2FeN_2O_5$	709.85	Brown	274	79.5	50.70 (50.71)	3.64 (3.66)	3.93 (3.92)	7.84 (7.86)	5.24
[Co(Br–sal)$_2$ benen]·H_2O $C_{30}H_{26}Br_2CoN_2O_5$	712.93	Yellow	280	76.5	50.43 (50.49)	3.59 (3.64)	3.85 (3.92)	8.20 (8.26)	4.75
[Ni(Br–sal)$_2$ benen]·H_2O $C_{30}H_{26}Br_2NiN_2O_5$	712.71	Yellowish green	290	81.6	50.63 (50.51)	3.55 (3.64)	3.99 (3.92)	8.22 (8.23)	2.72
[Cu(Br–sal)$_2$ benen]·H_2O $C_{30}H_{26}Br_2CuN_2O_5$	717.54	Green	292	82.3	50.20 (50.17)	3.59 (3.62)	3.90 (3.90)	8.80 (8.85)	1.84
[Zn(Br–sal)$_2$ benen]·H_2O $C_{30}H_{26}Br_2ZnN_2O_5$	719.37	Light yellow	290	81.8	50.02 (50.04)	3.50 (3.61)	3.85 (3.89)	9.05 (9.08)	–

[a] benen = bis(benzylidene)ethylenediamine.

$$\mathrm{MCl_2 \cdot nH_2O + 2(Br{-}salH) \xrightarrow{H_2O} [M(H_2O)_2(Br{-}sal)_2] + 2HCl} \qquad (3)$$

$$\mathrm{[M(H_2O)_2(Br{-}sal)_2] + benen \xrightarrow[\text{1 hour}]{\text{EtOH, Reflux}} [M(Br{-}sal)_2benen] + 2H_2O} \qquad (4)$$

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., consistent[7] with an octahedral structure. The magnetic moment values for the Co(II) complexes have been used as 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 4.7–5.2 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[8] an octahedral geometry. This deviation from the spin-only value (3.83 B.M.) may be 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[9] Ni(II) ions. The magnetic moment values of the Fe(II) complexes are 5.25 and 5.24 B.M. This value identifies it to be a high-spin complex in an octahedral geometry. 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 shows 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 three weak absorption bands for the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$ ($\sim 15{,}000$ cm^{-1}), ${}^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$ ($\sim 20{,}000$ cm^{-1}) and ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}({}^4G)$ ($\sim 25{,}000$ cm^{-1}) in accord with an octahedral geometry.[10] The electronic spectra of the Fe(II) complexes exhibit a band at about 11,500 cm^{-1}, assigned to the ${}^5T_{2g} \rightarrow {}^5E_g$ transition.[11] The electronic spectra of the Co(II) complexes exhibit three bands. The assignments of the spectral bands are ${}^4T_{1g}$-(F) $\rightarrow {}^4T_{2g}$ ($\upsilon_1 \sim 9{,}500$ cm^{-1}), ${}^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ ($\upsilon_2 \sim 18{,}000$ cm^{-1}) and ${}^4T_{1g}$(F) $\rightarrow {}^4T_{1g}$(P) ($\upsilon_3 \sim 19{,}000$ cm^{-1}). A strong charge transfer band is shown by the complex at $\sim 25{,}000$ cm^{-1}. König's method was used to

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

	Observed band (cm^{-1})							
Complexes	υ_1	υ_2	υ_3	υ_2/υ_1	B	β	β^0	$10D_q$
[Co(sal)$_2$ benen]·H_2O	9,434	18,000	19,047	1.907	715.84	0.737	26.27	10,558
[Ni(Br-sal]$_2$ benen]·H_2O	10,550	17,391	25,080	1.648	686.66	0.666	33.30	10,550
[Co(Br-sal)$_2$ benen]·H_2O	9,392	18,181	19,047	1.954	721.96	0.746	25.38	10,466
[Ni(sal)$_2$ benen]·H_2O	10,310	17,857	23,809	1.732	715.76	0.694	30.51	10,310

[a]benen = bis(benzylidene)ethylenediamine.

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) ($\upsilon_1 = 10{,}550$ cm^{-1}), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ($\upsilon_2 = 17{,}391$ cm^{-1}) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}$ (P) ($\upsilon_3 = 25{,}000$ cm^{-1}). The values of the electronic parameters such as the ligand field splitting energy (10 Dq), racah interelectronic repulsion parameter (B), nephelauxetic ratio (β) and the ratio are υ_2/υ_1 are represented in Table 2. All data are consistent with an octahedral geometry. The electronic spectra of the Cu(II) complexes[12] exhibit a band at $\sim 15{,}500$ cm^{-1} assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition which is in agreement with an octahedral

Table 3. Infrared spectral data of the complexes (cm − 1)[a].

Complexes	υ(C = O)	υ(C–O)	υ(C = N)	υ(M–O)	υ(M–N)
benen	–	–	1640 s	–	–
[Mn(sal)$_2$ benen]·H_2O	1620 s	1330 w	1615 s	410 w	480 w
[Fe(sal)$_2$ benen]·H_2O	1610 sh	1347 s	1610 s	410 w	490 m
[Co(sal)$_2$ benen]·H_2O	1615 s	1340 s	1615 s	415 m	480 w
[Ni(sal)$_2$ benen]·H_2O	1620 sh	1335 s	1610 s	420 w	495 sh
[Cu(sal)$_2$ benen]·H_2O	1622 sh	1347 s	1622 sh	410 m	490 w
[Zn(sal)$_2$ benen]·H_2O	1620 s	1340 s	1610 s	420 w	485 w
[Mn(Br–sal)$_2$ benen]·H_2O	1620 s	1330 sh	1620 s	415 m	480 w
[Fe(Br–sal)$_2$ benen]·H_2O	1620 s	1340 s	1610 s	420 w	475 m
[Co(Br–sal)$_2$ benen]·H_2O	1610 sh	1330 w	1610 sh	420 w	480 w
[Ni(Br–sal)$_2$ benen]·H_2O	1615 s	1340 s	1625 s	415 m	475 w
[Cu(Br–sal)$_2$ benen]·H_2O	1620 sh	1335 s	1620 sh	420 w	480 w
[Zn(Br–sal)$_2$ benen]·H_2O	1620 s	1340 w	1610 s	410 w	485 m

[a]b = broad, m = medium, s = strong, w = weak.

geometry. A strong charge transfer band is observed at 26,000 cm^{-1}. The ε values of all the complexes can not be find out as the concentration are not known.

Thermogravimetric Analyses

There are some remarkable features in the TGA curves. The decomposition temperatures of the complexes are higher than those of benen and sa1H or Br-sa1H, indicating that the complexes are more stable than the ligands. Thermal curves of the complexes clearly indicate that the weight loss between 35–105 °C corresponds to one water molecule for all complexes. Because of the low temperatures, this water molecule may be

Table 4. Antimicrobial activities of the complexes[a].

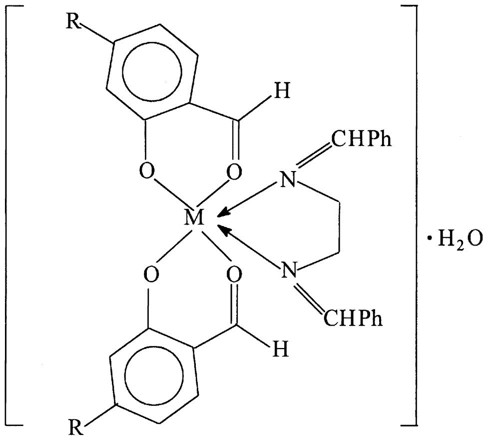
Compound	Percentage inhibition	
	S. typhi	*Seratia spp.*
salH	10	9
Br–salH	20	18
benen	20	18
$MnCl_2 \cdot 4H_2O$	22	18
$FeSO_4 \cdot 7H_2O$	20	18
$CoCl_2 \cdot 6H_2O$	15	9
$NiCl_2 \cdot 6H_2O$	11	9
$CuCl_2 \cdot 5H_2O$	22	9
$ZnCl_2$	10	9
$[Mn(sal)_2\ benen] \cdot H_2O$	30	27
$[Fe(sal)_2\ benen] \cdot H_2O$	30	27
$[Co(sal)_2\ benen] \cdot H_2O$	30	45
$[Ni(sal)_2\ benen] \cdot H_2O$	30	27
$[Cu(sal)_2\ benen] \cdot H_2O$	40	36
$[Zn(sal)_2\ benen] \cdot H_2O$	40	45
$[Mn(Br-sal)_2\ benen] \cdot H_2O$	30	27
$[Fe(Br-sal)_2\ benen] \cdot H_2O$	30	27
$[Co(Br-sal)_2\ benen] \cdot H_2O$	50	36
$[Ni(Br-sal)_2\ benen] \cdot H_2O$	30	27
$[Cu(Br-sal)_2\ benen] \cdot H_2O$	40	45
$[Zn(Br-sal)_2\ benen] \cdot H_2O$	40	45

[a] benen = bis(benzylidene)ethylenediamine.

considered as water of crystallization.[13] The TGA curve indicates that above 250 °C the compounds start to loose mass with partial evaporation of the Schiff base (benen) up to 320 °C. In the temperature range 320 to 500 °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 composition of the complexes.

IR Spectra

The infrared spectra of the complexes have been studied to characterize their structures. The important IR frequencies are given in Table 3. The infrared spectra of the complexes register the υ(C=O) band[14] at about 1600 cm^{-1} and υ(C–O)[15] at about 1340 cm^{-1}. The Schiff base (benen) shows the C=N stretching band at 1640 cm^{-1}. This band shifts to lower energy by 10–30 cm^{-1} in the chelates indicating coordination through the azomethine nitrogen.[16] The sharp bands in the ranges 750–780 and 1525–1535 cm^{-1} are due to aromatic υ(C–H)[15] and υ(C=C),[17] respectively. The frequencies in the range 410–420 and 475–495 cm^{-1} are attributed to υ(M–O)[18] and υ(M–N),[19] respectively.



M = Co(II), Ni(II), Cu(II), Mn(II), Fe(II) and Zn(II)

Figure 2. [M(sal)$_2$benen] or [M(Br–sal)$_2$benen], R = H or Br.

Antimicrobial Activity

In the present study, the ligands, the 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 *Seratia 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 versus controls. The percentage inhibition of various compounds is recorded in Table 4. 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, the metal salts and ligands. Hence, complexation increases the antimicrobial activity. The patterns of activity are complex and no clear trend can be ascertained.

A suggested structure of the mixed-ligand complexes is shown in Figure 2.

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