

Synthesis and antimicrobial studies of binuclear complexes of Cu^{II} and Ni^{II} metal chelates of Schiff base *N,N'*-ethylenebis(2-hydroxyacetophenonimine) with some organic derivatives of alkaline earth metals

D. Prakash*, Kushwaha Kant, Birendra Kumar and S. Prakash

Department of Chemistry, Patna University, Patna-800 005, Bihar, India

Manuscript received 5 May 2009, revised 8 February 2010, accepted 29 March 2010

Abstract : A series of new Cu^{II} and Ni^{II} binuclear complexes of Schiff base *N,N'*-ethylenebis(2-hydroxyacetophenonimine) (EA) with some organic derivatives of alkaline earth metals of general formula M_aEA.M_bL₂, where M_a = Cu or Ni; M_b = Mg, Ca, Sr or Ba; L = deprotonated *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N) have been synthesized. The nature of bonding and stereochemistry of the complexes have been deduced by elemental analysis, infrared spectra, electronic spectra, magnetic susceptibility and conductivity measurements. The compounds are tested against Gram +ve bacteria (*S. aureus*), Gram -ve bacteria (*E. coli*) and fungi (*C. albicans*).

Keywords : Binuclear complexes, Schiff base, electronic spectra, antimicrobial studies.

Introduction

Schiff bases have the ability to act as coordinating ligands and the polynuclear complexes derived from Schiff bases find variety of applications in analytical and biological systems¹⁻⁸. Schiff base complexes of transition metals are of great interest and have extensively been studied over past few decades⁹⁻¹³. Keeping in view the importance of Schiff base complexes of transition metal, the present work was undertaken to study the binuclear complexes of Cu^{II} and Ni^{II} ions with bioactive ligands. In the present paper, we report a series of new Cu^{II} and Ni^{II} binuclear complexes of Schiff base *N,N'*-ethylenebis(2-hydroxyacetophenonimine) (EA) with some organic derivatives of alkaline earth metals of general formula M_aEA.M_bL₂, where M_a = Cu or Ni; M_b = Mg, Ca, Sr or Ba; L = deprotonated *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP), 1-nitroso-2-naphthol (1N2N).

Results and discussion

The physical properties and analytical data of the metal chelates and their alkaline earth metal adducts are listed in Table 1. From the results, it is evident that the adducts have characteristic colour and show high decomposition temperature indicating greater stability. The molar conductivities of the compounds were measured in DMSO at 30 °C at a concentration of 10⁻³ M. The compounds

show low values (3.5–9.5 Ω⁻¹ cm² mol⁻¹) of molar conductivity which indicate their non-electrolytic nature.

The infrared spectra of metal chelate CuEA, NiEA and their binuclear alkaline earth metal complexes were recorded. Selected infrared spectral bands of the compounds are given in Table 2. Study reveals that when transition metal complex acts as ligand, the spectra of binuclear complexes recorded are similar independent of the fact whether the second metal involved in the binuclear complex is a transition metal or a non-transition metal¹⁴⁻¹⁸. The metal complex ligands CuEA and NiEA exhibit ν_{C-O} str. (phenolic) at 1531 and 1530 cm⁻¹ respectively. When CuEA and NiEA undergo complex formation with alkaline earth metal salt of organic acids, there is shifting in ν_{C-O} str. (phenolic) frequency by ~2–43 cm⁻¹. There is also splitting of ν_{C-O} str. (phenolic) band in few cases. The shifting of ν_{C-O} str. (phenolic) band towards higher energy side indicates coordination through the phenolic oxygen. Also the major shift in the frequency upto ~43 cm⁻¹ suggests presence of phenoxo bridge. The bands in the far infrared region i.e. 505–588 and 471–499 cm⁻¹ in the binuclear complexes are tentatively assigned to ν_{M-O} str. and ν_{M-N} str. modes¹⁹ respectively. These bands are not present in the ligand, *N,N'*-ethylenebis(2-hydroxyacetophenonimine) while in the neutral transition metal chelate CuEA and NiEA they occur in the region 518–588 and 490–495 cm⁻¹.

Table 1. Colour, decomposition temperature, molar conductance, magnetic moment and elemental analysis of the complexes

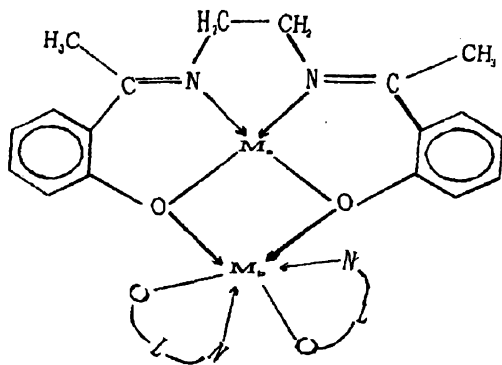
Compd.	Colour	Dec. temp. (°C)	Molar cond.		Analysis (%) : Found (Calcd.)				
			($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	(μ_{eff}) (B.M.)	C	H	N	M _a	M _b
CuEA.Ca(ONP) ₂	Pale green	212	5.5	1.75	58.53 (58.67)	4.15 (4.23)	9.02 (9.12)	9.28 (9.43)	5.82 (5.94)
CuEA.Sr(ONP) ₂	Light brown	180	4.6	1.80	49.85 (49.91)	3.52 (3.60)	7.61 (7.76)	8.69 (8.81)	12.02 (12.15)
CuEA.Mg(DNP) ₂	Pink	248	7.0	1.90	48.02 (48.14)	3.15 (3.21)	11.06 (11.23)	8.29 (8.49)	3.10 (3.25)
CuEA.Ca(DNP) ₂	Sand stone	255	7.5	1.78	47.03 (47.15)	3.05 (3.14)	10.89 (11.00)	8.15 (8.32)	5.13 (5.24)
CuEA.Sr(TNP) ₂	Leaf brown	272	4.5	2.05	39.86 (39.95)	2.35 (2.40)	12.28 (12.43)	6.86 (7.05)	9.56 (9.72)
CuEA.Ba(TNP) ₂	Pale green	270	6.3	1.76	37.72 (37.86)	2.25 (2.31)	11.62 (11.78)	6.58 (6.68)	14.28 (14.44)
CuEA.Sr(1N2N) ₂	Dark green	220	7.5	1.81	58.12 (58.27)	3.87 (3.98)	6.78 (6.97)	7.75 (7.91)	10.79 (10.91)
NiEA.Mg(ONP) ₂	Almond	260	6.0	Dia.	54.25 (54.32)	3.85 (3.92)	8.21 (8.45)	8.75 (8.86)	3.49 (3.66)
NiEA.Sr(ONP) ₂	Orange yellow	230	6.5	Dia.	50.15 (50.25)	3.56 (3.63)	7.71 (7.82)	8.05 (8.19)	12.11 (12.23)
NiEA.Ca(DNP) ₂	Almond	290	8.5	Dia.	47.35 (47.45)	3.05 (3.16)	10.89 (11.07)	7.65 (7.74)	5.03 (5.27)
NiEA.Ba(DNP) ₂	Brownish yellow	283	6.5	Dia.	41.95 (42.06)	2.76 (2.80)	8.75 (9.81)	6.72 (6.86)	15.89 (16.04)
NiEA.Sr(TNP) ₂	Yellowish orange	270	3.5	Dia.	40.02 (40.17)	2.39 (2.45)	12.35 (12.49)	6.38 (6.55)	9.65 (9.77)

Table 2. IR and electronic absorption bands of CuEA, NiEA and their complexes

Compd.	IR absorption bands (cm^{-1})		Diffuse reflectance (nm)
	$\nu_{\text{C-O}}$	$\nu_{\text{M-O/M-N}}$	
CuEA	1531	588, 521, 490	370
CuEA.Ca(ONP) ₂	1536	566, 528, 471	358, 409, 555
CuEA.Sr(ONP) ₂	1536, 1505	566, 530, 471	358, 391, 427, 434, 474
CuEA.Mg(DNP) ₂	1533	588, 522	326, 362, 391, 412, 427, 558
CuEA.Ca(DNP) ₂	1564, 1532	584, 526, 505, 481	362, 369, 391, 423, 550
CuEA.Sr(TNP) ₂	1535, 1516	583, 490	319, 355, 391, 430, 552
CuEA.Ba(TNP) ₂	1536	580, 523, 472	348, 362, 391, 495
CuEA.Sr(1N2N) ₂	1537	521	348, 398, 559
NiEA	1530	570, 518, 495	316, 390
NiEA.Mg(ONP) ₂	1568, 1521	520, 490	358, 405, 555
NiEA.Sr(ONP) ₂	1563, 1519	519	362, 427, 772
NiEA.Ca(DNP) ₂	1534	521	362, 430, 776
NiEA.Ba(DNP) ₂	1559, 1533	524, 499	358, 391, 416, 423, 772
NiEA.Sr(TNP) ₂	1539	522	362, 416
NiEA.Ba(TNP) ₂	1573, 1538	522, 499	362, 427, 550
NiEA.Mg(1N2N) ₂	1540	519	370

Electronic absorption bands for CuEA and NiEA observed at 370 nm and in the region 316–390 nm respectively arises due to $\pi \rightarrow \pi^*$ transition and charge transfer. Electronic spectra in all the binuclear complexes of CuEA with alkaline earth metal salts of organic acids are found at 316, 390 and 550–558 nm suggestive of square planar geometry of the complexes and also indicate charge transfer and *d-d* transitions. Similar types of bands are recorded in the binuclear complexes of NiEA. Absorption in the region 362–405 nm suggests for square planar structure for Cu^{II} and Ni^{II} in the binuclear adducts with coordination number 4. The magnetic moment around ~1.75 to 2.05 B.M. for the adducts of CuEA suggests square planar geometry with coordination number 4. The adducts of NiEA are found to be diamagnetic.

On the basis of elemental analysis, molecular formula of binuclear alkaline earth metal complexes with CuEA and NiEA have been suggested as $M_aEA.M_bL_2$. The infrared spectra, electronic spectral studies and magnetic properties of the adducts suggest the bonding between *N,N'*-ethylenebis(2-hydroxyacetophenonimine)metal(II) complex (M_aEA) and the alkaline earth metal is most likely to occur by dative bonding via two phenolic oxygen atoms of the ligand. The structure and bonding of the newly prepared compounds are shown in Fig. 1.



where, $M_a = \text{Cu}^{\text{II}}$ or Ni^{II} ; $M_b = \text{Mg}$, Ca or Ba ; $L =$ deprotonated *o*-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol or 1-nitroso-2-naphthol

Fig. 1

Experimental

All the chemicals used were of A.R. grade. IR spectra were recorded on FTIR spectrophotometer, Shimadzu model 8201PC. UV-Vis spectra were recorded on Perkin-

Elmer-Lambda 15 UVB Vis spectrophotometer. Magnetic measurements were done on Vibrating Sample Magnetometer (VSM) model-150 AEG and G. Parc. Faraday Magnetic Susceptibility balance. Molar conductivities were measured with the help of Systronic digital direct conductivity meter 306. The C, H, N were analyzed micro analytically. Cu^{II}, Ni^{II} and Mg^{II} ions have been estimated by complexometric EDTA titrations; estimation of alkaline earth metals Ca, Sr and Ba were carried on Systronic Flame Photometer 128.

Synthetic procedures :

The Schiff base of *o*-hydroxyacetophenone and ethylenediamine were prepared by refluxing the ketone and diamine in 2 : 1 molar ratio in ethanol for 10 min. The yellow coloured Schiff base precipitated out. It was filtered off, washed thoroughly with ice-cold ethanol and recrystallised (m.p. 194 °C). A solution of copper(II) acetate hydrate (2.0 g) or nickel(II) acetate tetrahydrate (2.5 g) in ethanol (15 ml) was added slowly with stirring to a hot solution of the Schiff base (2.96 g). The mixture was refluxed with constant stirring with the help of magnetic stirrer for 40 min. The solution upon cooling deposited purple coloured copper complex or the brownish-orange coloured nickel complex. These were filtered off, washed thoroughly with ethanol and dried. For the preparation of heterobinuclear complexes, *N,N'*-ethylenebis(2-hydroxyacetophenoniminato)copper(II) (CuEA) or *N,N'*-ethylenebis(2-hydroxyacetophenoniminato)nickel(II) (NiEA) was taken in absolute alcohol in a conical flask and alkaline earth metal salts of *o*-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol or 1-nitroso-2-naphthol were added to it in 1 : 1 molar proportion. The mixture was refluxed on a hot plate at 75–80 °C with constant stirring for 1–1½ h. The characteristic coloured adducts were precipitated which was filtered, washed thoroughly with absolute ethanol and dried in electric oven at 80 °C.

Microbiological studies :

The Schiff base heterobinuclear complexes were examined for their antimicrobial activity against bacteria viz. *E. coli*, *S. aureus* and fungus viz. *C. albicans* by serial dilution method²⁰ in DMF. The Minimum Inhibitory Concentration (MIC) value of some of the complexes

is shown in Table 3. The results of antibacterial activity evaluation revealed that the Schiff base binuclear complexes were relatively better potential inhibitor than the

Table 3. Antibacterial and antifungal activity of the complexes

Compd.	Minimum inhibitory conc. ($\mu\text{g ml}^{-1}$)		
	<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>
CuEA.Ca(ONP) ₂	20	40	20
CuEA.Mg(DNP) ₂	20	40	20
CuEA.Sr(1N2N) ₂	20	40	20
NiEA.Mg(ONP) ₂	40	20	40
NiEA.Ca(DNP) ₂	40	20	40
NiEA.Ba(TNP) ₂	40	20	40
Streptomycin	20	80	-
Chlometrizol	-	-	100

standard streptomycin against the growth of the test bacteria *S. aureus*. The binuclear complexes of CuEA showed similar activity as the standard streptomycin against the bacteria *E. coli* whereas the binuclear complexes of NiEA showed lower activity. All the binuclear Schiff base complexes showed higher antifungal activity than the standard chlometrizol.

Acknowledgement

We are thankful to the CSIR, New Delhi for providing financial assistance as one of the author (KK) is getting CSIR fellowship.

References

- L. Mishra and R. Sinha, *Indian J. Chem., Sect. A*, 2000, **29**, 1131.
- U. Mukhopadhyay and D. Ray, *Indian J. Chem., Sect. A*, 2001, **40**, 228.
- K. Krishnankutty and M. B. Ummathur, *J. Indian Chem. Soc.*, 2006, **83**, 633.
- R. K. Dubey, *J. Indian Chem. Soc.*, 2006, **83**, 1087.
- P. Saritha, B. S. Reddy and Jayatyagaraju, *J. Indian Chem. Soc.*, 2006, **83**, 1204.
- M. Gulloli, L. Casella, A. Pasini and R. Ugo, *J. Chem. Soc., Dalton Trans.*, 1977, 339.
- L. Muslim, W. Roth and H. H. Eriemeyer, *Acta Chem. Helv.*, 1983, **36**, 36.
- R. R. Vyas and R. N. Mehata, *J. Indian Chem. Soc.*, 1991, **68**, 294.
- S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.
- S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1805.
- S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem. Lett.*, 1968, **4**, 107.
- G. Fachinetti, C. Floriani, P. F. Zanzzi and A. R. Zanzari, *Inorg. Chem.*, 1979, **18**, 3469.
- A. K. Banerjee, D. Prakash and S. K. Roy, *J. Indian Chem. Soc.*, 1982, **59**, 1303.
- K. Ueno and A. E. Martell, *J. Am. Chem. Soc.*, 1956, **60**, 1270.
- P. L. Teyessie and J. J. Charette, *Spectrochim. Acta*, 1963, **19**, 1407.
- B. Das and J. C. Bailer (Jr.), *J. Am. Chem. Soc.*, 1955, **77**, 5476.
- G. E. Batley and D. P. Graddon, *Aust. J. Chem.*, 1967, **20**, 877.
- P. L. Orioli, M. Divaira and L. Sacconi, *Inorg. Chem.*, 1966, **5**, 400.
- S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.
- R. Cruickshank, J. P. Marmion and R. H. A. Swain, *Medical Microbiology*, 1975, **2**, 190.