Asian Journal of Chemistry Vol. 21, No. 1 (2009), 5-10

Antibacterial Activity of Schiff Base Chelates of Divalent Metal Ions

S.H. BAIU†, M.M. EL-AJAILY* and N.M. EL-BARASI
Chemistry Department, Faculty of Science, Garyounis University, Benghazi, Libya
E-mail: melagaily@yahoo.com

Some new chelates of Mn(II), Co(II), Cu(II) and Cr(III) ions with Schiff base derived from salicylaldehyde and thiourea have been synthesized and investigated by elemental analysis, molar conductance measurements, infrared and electronic spectra. The elemental analysis data exhibited the formation of 1:1 [M:L] ratio. The obtained molar conductance values revealed that all the chelates are non-electrolytic in nature. The infrared spectral data showed the chelateation behaviour, which is through to the nitrogen and oxygen atoms of the ligand. The electronic absorption spectral data displayed the existence of π-π*, n-π* (HC=N) transitions and the expected geometrical structures. By testing the effects of these Schiff base ligands on five species of bacteria (*S. aureus, K. pneumoniae, E. coli, P. aeruginosa* and *P. mirabilis*) *in vitro*, it has been found that Mn(II) chelate was very effective, Co(II) chelate had moderate effect and no effect of Cu(II) chelate was found on these bacteria. The effects of Mn(II) and Co(II) chelates increased with higher concentrations.

Key Words: Schiff base complexes, Metal(II) ions, Antibacterial activity.

INTRODUCTION

Recent interest in the synthesis and investigation of Schiff base chelates[1-3] has been prompted that the systematic investigation of these chelates may shed light on the nature of the free ligand environment. Boghaei *et al.*[4] synthesized and characterized non-symmetrical Ni(II) and Cu(II) ions tetradentate Schiff base chelates with N_2O_2 and N_2O donor sites. The series of N-salicylidenglutamatocopper(II) chelate of the formulae Cu(sal-glu)X, where sal-glu represents Schiff base derived from salicylaldehyde and L-glutamic acid (DL-glutamic acid) and X = pyridine, 2-methylpyridine, 3-methylpyridine were prepared and characterized. On the basis of crystal structures of N-salicylidenglutamatocopper(II) chelate containing pyridine and 4-methylpyridine using the results of electronic spectra, the stereo-

---

†Botany Department, Faculty of Science, Garyounis University, Benghazi, Libya.

chemical arrangement of individual components in chelates under investigation is discussed. The prepared chelates were supported to possess square pyramidal geometry and were found to exhibit antimicrobial activity against bacteria; *Staphylococcus aureus*, *Escherichia coli* and fungi *Candida albicans*[5]. El-Ajaily *et al.*[6] studied the antibacterial activities of the Schiff base derived from the salicylaldehyde and histidine and its Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) chelates on some pathogenic bacteria. The results showed a better activity of Cd(II) chelate against *Escherichia coli, Pseudomonas aeruginosa, Proteus* spp. and *Staphylococcus aureus*. In constrant, no activities were recorded against *Klebsiella pneumoniae*. However, Cu(II) chelate exhibited pronounced effect only against *Escherichia coli*. No effect of other chelates tested observed against all bacterial used. Therefore, the use of Cd(II) chelate can be recorded as an antibacterial agent after further investigation on its toxicity.

The aim of this paper is to elucidate the chemical structures of the synthesized chelates and to study their antibacterial activities on some pathogenic bacteria.

EXPERIMENTAL

All chemicals used in this work were laboratory pure (BDH or Aldrich) including salicylaldehyde, thiourea, $CrCl_3\cdot6H_2O$, $MnCl_2\cdot4H_2O$, $CoCl_2\cdot6H_2O$, $CuCl_2\cdot2H_2O$, NaOH, C_2H_5OH, DMF and double distilled water. Five species of pathogenic bacteria were tested namely: *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Escherichia coli*, *Pseudomonas aerugthosa* and *Proteus mirabilis*. These bacterial species were isolated and identified as uropathogens in Ibn-Sina polyclinic in the city of Benghazi, Libya.

Synthesis of Schiff base: Schiff base was synthesized by condensation of salicylaldehyde (0.0l mol, 1.22 g) in 25 mL of ethanol and (0.01 mol, 0.76 g) of thiourea in the same solvent. The mixture was stirred magnetically at ambient temperature in the presence of NaOH solution. When the mixture was refluxed for 2 h, it was evaporated to 25 % of its original volume. yellow crystals were appeared and recrystallized from hot ethanol. The crystals were dried at ambient temperature with 80 % yield and its purity was confirmed by TLC technique.

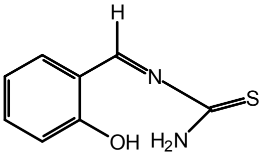
Synthesis of chelates: The Schiff base chelates under investigation were synthesized by mixing the Schiff base (0.01 mol; 1.80 g) in 25 mL of ethanolic solution with 25 mL of ethanolic solution of the metal salts; $CrCl_3\cdot6H_2O$ (2.66 g), $MnCl_2\cdot4H_2O$ (1.98 g), $CoCl_2\cdot6H_2O$ (2.38 g), $CuCl_2\cdot2H_2O$ (1.70 g). The mixtures were refluxed for 3 h and their volumes were reduced to 75 % of its original volume and the residues were left to stand overnight and then filtered by suction. The products were recrystallized from methanol/ethanol (1:1) mixture. Their yields range from 40-80 %.

The five species of bacteria were streaked on nutrient agar (Oxoid, England) plates, so that the streaking covered the surface of the plate. The chelates were applied on the streaked nutrient agar plate as a powder (5, 10 and 15 mg), taking an area not more than 6 mm (size of an antibiotic paper disc) and leaving enough distances between them. The plates were then inverted and incubated at 37 ºC for 24 h. The inhibition zones were then increased in millimeters and recorded.

The chemical analyses (C, H, N and S) were performed in advanced laboratory of chemical analysis, Cairo University, Egypt. The molar conductance measurements carried out in DMF solvent using conductivity meter model CMD 650 digital meter. Infrared spectra were recorder using KBr disc technique on IFS-25 DPUS/IR spectrometer (Bruker). The electronic spectra were measured by using a Perkin-Elmer lambda 4β spectrophotometer.

RESULTS AND DISCUSSION

The reaction of salicylaldehyde and thiourea yields Schiff base compound (**I**).



Structure of Schiff base compound (**I**)

The elemental analyses (C, H, N and S) of the Schiff base and their chelates are listed in Table-1. The empirical formulae of the chelates indicate the formation of a 1:1 [M:L] ratio. Furthermore, the calculated elemental analyses are in good agreement with the found values. The molar conductance values of the chelates under study were determined using 1×10^{-3} M DMF solvent, as shown in Table-1 and suggest the existence of a non-electrolytic nature[7].

The infrared band assignments of the Schiff base and its chelates are listed in Table-2. The infrared spectrum of the Schiff base exhibits a band at 1617 cm^{-1} attributed to ν(C=N) of the azomethine, the shifting of this band to higher frequencies indicates its involvement in complexation with the metal ions under investigation[8]. The infrared spectral data of the synthesized Schiff base chelates show a band in the range of 1275-1214 cm^{-1} suggesting the existence of C-O of the C-OH group in the salicylaldehyde ring. The change in its position compared to its original position in the free ligand which is 1244 cm^{-1} indicates the involvement of this group in chelation with the metal ions through the oxygen atom[9]. The spectral data for

TABLE-1
SOME PHYSICAL PROSPERITIES OF SCHIFF BASE CHELATES

Chelates	m.w. / (m.p. °C)	Elemental analysis %: Calcd. (Found)				μ_{eff} (BM)/ (Λ_m)
		C	H	N	S	
($C_8H_8N_2OS$)L	180	53.30	4.40	15.50	17.70	–
	(170-173)	(53.10)	(4.35)	(14.95)	(17.00)	(–)
[CoL(OH)(H_2O)$_2$]7H_2O	415	23.14	6.26	6.74	7.72	4.18
	(>300)	(22.80)	(6.10)	(6.88)	(6.00)	(0.00)
[CuL(OH)]H_2O	276	34.81	3.63	10.15	11.62	1.42
	(>300)	(34.07)	(3.29)	(9.95)	(11.55)	(0.00)
[MnL (OH)]H_2O	267	36.00	3.72	10.10	13.52	4.34
	(>300)	(37.00)	(4.00)	(9.85)	(13.10)	(0.00)
[CrL(OH)$_2$(H_2O)]11H_2O	320	30.00	4.68	8.75	11.13	4.30
	(>300)	(29.25)	(4.50)	(8.16)	(11.30)	(0.00)

Λ_m = ohm^{-1} cm^2 mol^{-1}

$[CoL^1(OH)_2(H_2O)_2]\cdot 7H_2O$, $[CuL^1(OH)]\cdot H_2O$, $[MnL^1(OH)]\cdot H_2O$ and $[CrL^1(OH)_2(H_2O)]\cdot 11H_2O$ chelates exhibit a broad band in the range 3554-3383 cm^{-1} which is attributed to the presence of water molecules during the chelates formation[10]. The spectra of the chelates display the disappearance of δ(OH) and ν(C-OH) of bands at 1350 and 850 cm^{-1}, respectively and the appearance of new bands at the range of 505-446 and 667-613 cm^{-1} that attributed to ν(M-N) and ν(M-O) vibrations[7], supporting the involvement of the nitrogen and oxygen atoms in coordination with metal ions. There is no band due to ν(NH_2) vibration[11]. The absence of this band indicates that NH_2 group is not involved in chelation. The disappearance of ν(C=S) band (1083 cm^{-1}) suggest that one of the chelation sites is through sulfur atom of the thiourea compound[12].

The electronic spectra of the Schiff base and its chelates were recorded in DMF solvent and their band assignments as shown in Table-2. The Schiff base spectrum shows a band at 289 nm (346021 cm^{-1}) due to π-π* and n-π* (C= N) transitions[13]. The absorption bands at 293 nm (34130 cm^{-1}) and 372 nm (26881 cm^{-1}) in the spectrum of the Co(II) chelate is attributed to $^4T_{1g} \rightarrow {}^4T_{2g}$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transitions. The intensity of these bands indicates an octahedral geometry[14]. The electronic spectrum of Cu(II) chelate of the type $[CuL^1 (OH)]H_2O$ shows two bands at 294 nm (34014 cm^{-1}) and 363 nm (27548 cm^{-1}), due to $^2E_g \rightarrow {}^2T_{2g}$ transitions. These data suggest the presence of square planar geometry[15]. The electronic absorption spectral data of Mn(II) chelate exhibit two bands at 291 nm (34483 cm^{-1}) and 375 nm (26667 cm^{-1}) assigned to charge transfer transition. The intensity of these bands supports a tetrahedral structure[16]. The spectral data of Cr(III) Schiff base chelate show two bands at 288 nm (34722 cm^{-1}) and 403 nm (24814 cm^{-1}) due to $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F) and $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P) transitions. An octahedral geometry was proposed[17]. The magnetic moment values (Table-2) reveal the presence of a paramagnetic character for all chelates.

TABLE-2
INFRARED BAND ASSIGNMENTS (cm^{-1}) AND ELECTRONIC SPECTRAL DATA OF THE SCHIFF BASE CHELATES

Chelates	Bands (cm^{-1})						nm (cm^{-1})
	ν(OH) (H_2O)	ν(C=N)	ν(C-O)	ν(C=S)	ν(M-O)	ν(M-N)	
$(C_8H_8N_2OS)L$	3379	1617	1244	1083	–	–	283 (34662)
$[C_oL(OH)(H_2O)_2]7H_2O$	3554	1628	1214	–	631	484	372 (26881), 293 (43129), 277 (36101)
$[CuL(OH)]H_2O$	3365	1621	1221	–	613	446	363 (27548), 294 (34013), 251 (39761)
$[MnL(OH)]H_2O$	3389	1614	1268	–	643	449	375 (26666.6), 290 (34482.7)
$[CrL(OH)_2(H_2O)]11H_2O$	3383	1618	1275	–	667	505	42 (24876), 287 (34483)

The antibacterial activities showed that Mn(II) chelate is effective on all pathogenic bacterial species tested. This antibacterial effect increased by increasing the concentration of these compounds, especially on *S. aureus* and *K. pneumoniae* (Table-3). The same effect was observed with Co(II) chelate, especially on *S. aureus*, *K. pneumoniae* and *P. mirabilis* (Table-4). Cu(II) chelate did not have any effect on all bacterial species tested.

TABLE-3
EFFECT OF Mn(II) CHELATE ON THE BACTERIAL spp. (Inhibition zones in mm)

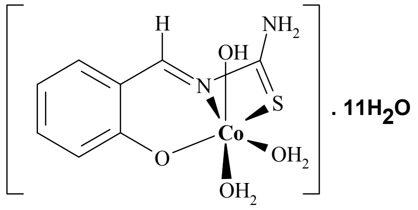
Bact. sp conc. (mg)	*Staphylococcus aureus*	*Klebsiella pneumoniae*	*Escherichia coli*	*Pseudomonas aeruginosa*	*Proteus mirabilis*
5	22	23	20	22	19
10	32	27	25	23	22
15	37	38	28	28	28

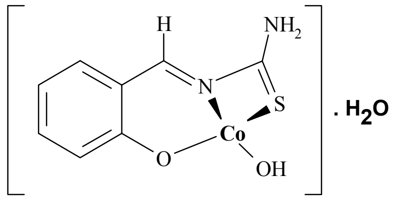
TABLE-4
EFFECT OF Co(II) CHELATE ON THE BACTERIAL spp. (Inhibition zones in mm)

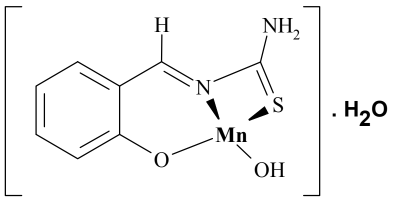
Bact. sp conc. (mg)	*Staphylococcus aureus*	*Klebsiella pneumoniae*	*Escherichia coli*	*Pseudomonas aeruginosa*	*Proteus mirabilis*
5	20	15	10	13	15
10	23	20	15	15	20
15	25	25	20	20	25

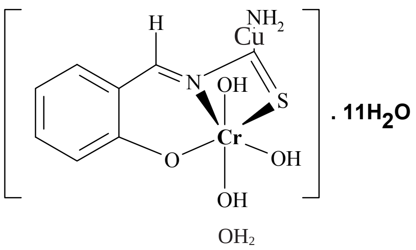
Conclusion

From the chemical analyses, one can suggest the following chemical structures:









REFERENCES

1. Y.S. Sharma, H.N. Pandey and P. Mathur, *Polyhedron*, **13**, 3111 (1994).
2. M. Kwiathowski and G. Bandoli, *J. Chem. Soc., Dalton Trans.*, 379 (1992).
3. J.P. Costes and M.I.E. Fernandez-Garcia, *Inorg. Chim. Acta*, **237**, 57 (1995).
4. D.M. Boghaei and S. Mohebi, *J. Chem. Res.*, **5**, 72 (2002).
5. H. Keypour, S. Salehzadeh and R.V. Parish, *Molecules*, **7**, 140 (2002).
6. M.M. El-Ajaily, S.F. Ben-Gweirif, A.A. Maihub and A.N. El-Tajoury, First Symposium of Chemistry, Science Faculty, Garyounis University, pp. 197-210 (2005).
7. D.M. Boghaei and N. Lashanizadegan, *Synth. React. Inorg. Met. Org. Chem.*, **30**, 1393 (2000).
8. N. Raman, Y.P. Raja and A. Kulandaisary, *Indian Acad. Sci.*, **113**, 183 (2001).
9. W. Qui, Y.M. Song, R. Wendeng and Z.N. Chen, *Chem. Papers*, **53**, 210 (1999).
10. L.J. Bellamy, Infrared Spectra of Chelate Molecules, Chapman and Hall Lt, London (1975).
11. A.K. Jain, R.N. Goyal and D.D. Agarwal, *J. Inorg. Nucl. Chem.*, **43**, 2005 (1981).
12. M.D. Boghaei, S.J. Sabounchei and S. Rayati, *Synth. React. Inorg. Met. Org. Chem.*, **30**, 1535 (2000).
13. S.M. Ben Saber, A.A. Maihub, S.S. Hudere and M.M. El-Ajaily, *Am. Microchem. J.*, **81**, 191 (2005).
14. M.M. Osman and M. Amer, *Egypt. J. Chem.*, **26**, 99 (1983).
15. B.N. Figgs, Introduction to Ligand Field Theory, Inter Science New York, p. 31 (1967).
16. A.D. Leihr, *J. Phys. Chem.*, **67**, 1314 (1963).
17. A. Saxena, J.P. Tandon, K.C. Molloy and J. Zuckerman, *J. Inorg. Chim. Acta*, **63**, 71 (1982).

(*Received*: 13 December 2006; *Accepted*: 1 August 2008) AJC-6734