Asian Journal of Chemistry; Vol. 23, No. 5 (2011), 2229-2230

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

NOTE

Synthesis, Characterization and Antibacterial Study of Co(II), Ni(II), Zn(II) and Cu(II) Complexes of Methyl 2-{1-[(Z)-3- methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl-idene]ethylamino}-3-phenylpropanoate

HUALING ZHU*, LUXIA BU, ZHEN WEI, LI LI, YINGCHAO WANG and XIAOPING XU

Department of Basic Science, Tianjin Agricultural College, Tianjin, P.R. China

*Corresponding author: +86 2223781295; E-mail: zhuhualing2004@126.com

(*Received*: 23 June 2010; *Accepted*: 30 January 2011) AJC-9534

Complexes of methyl 2-{1-[(Z)-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl-idene]ethylamino}-3-phenylpropanoate with Co(II), Ni(II), Zn(II) and Cu(II) have been prepared and characterized by elemental analysis, spectroscopic data (IR and UV) and ^{1}H NMR. From the analytical and spectral data, the stoichiometry of the complexes has been found to be 1:2 (metal:ligand). The antibacterial activity of the ligand and its metal complexes at different concentrations against *Bacillus coli* and *Bacillus subtilis* were performed by using disc diffusion method. The results indicate that almost all the compounds have the activity of inhibiting the growth of the two bacteria.

Key Words: Synthesis, Characterization, Complex, Antibacterial activity.

In recent years, the Schiff bases derived from 4-acyl-5-pyrazolones and their metal complexes have been studied widely for their high antibacterial activation[1,2]. Amino acid esters also possess good antibacterial and biological activations[3]. Keeping in mind above biological significance of Schiff base and in continuation of our earlier work[4,5], we report herein the preparation, characterization and antibacterial study of complexes of Co(II), Ni(II), Zn(II) and Cu(II) with Schiff base ligand methyl-2-{1-[(Z)-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl-idene]ethylamino}-3- phenylpropanoate.

1-Phenyl-3-methyl-4-acyl-pyrazolone-5 (HPMAP) were synthesized according to reported method[6]. Other chemicals obtained as reagent grade were used without further purification, IR spectra were recorded on Perkin-Elmer-1700 spectrophotometer using KBr disc. ^{1}H NMR spectrum were recorded on FT-AC-80 spectrophotometer using TMS as internal standard.

Preparation of the ligand: The ligand was synthesized by refluxing the mixture of HPMAP (15 mmol) and phenylalanine methyl ester (15 mmol) in ethanol (100 mL) over a steam bath for about 4 h, then the solution was cooled down to room temperature. After 4 days, pale yellow block was obtained. The block was separated, washed with ethanol and dried over $CaCl_2$ in vacuum.

Preparation of the complexes: The complexes of Co(II), Ni(II), Zn(II) and Cu(II) have been formed by reacting ethanolic solution of appropriate metal salts with ethanolic solution of ligand in the molar ratio 1:2. The resulting mixture was heated on water bath for about 4 h, then the mixture were cooled under room temperature and solid coloured complexes separated out which was filtered, washed with ethanol, dried over $CaCl_2$ in vacuum.

The IR spectra of the free ligand were compared with those of the complexes formed in order to confirm the coordination of ligand (Table-1). The spectra of the ligand exhibits

TABLE-1
IR DATA (cm^{-1}) OF LIGAND AND ITS METAL COMPLEXES

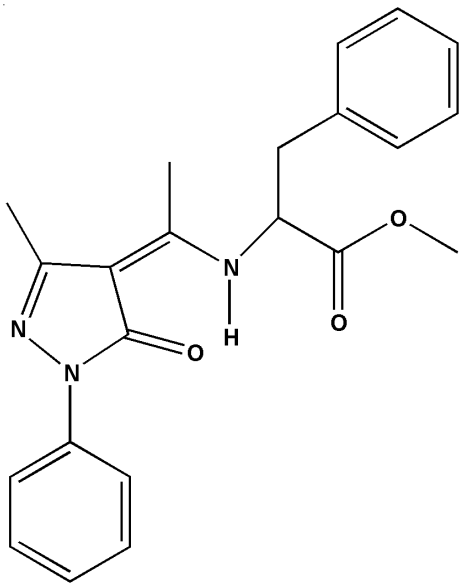
No.	ν(N-H)	ν(N-H)	ν(C=O)	ν(C=O(r))	ν(C=N)	ν(C-N)	ν(C-O)	ν(M-O)	ν(M-N)
L	3430.8	1540	1743	1634.8	–	1167	–	–	–
L-Cu	–	–	1678	1608	1516	–	1360	542	486
L-Co	–	–	1686	1606	1508	–	1368	544	480
L-Ni	–	–	1676	1605	1535	–	1376	538	476
L-Zn	–	–	1698	1611	1540	–	1366	540	498

TABLE-2
COLOUR, ELEMENTAL ANALYSIS AND ^{1}H NMR SPECTRAL DATA OF THE LIGAND AND COMPLEXES

No	Colour	Elemental analysis (%) found (calcd.)			Chemical shifts ($CDCl_3$, ppm)		
		C	H	N	N-H	Ar-H	CH_2/CH_3
L	Pale yellow	69.87 (69.95)	5.96 (6.09)	11.27 (11.13)	8.14	7.1-7.8	1.0-3.8
L-Cu	Green yellow	63.92 (64.63)	5.57 (5.39)	10.16 (10.28)	–	7.2-7.8	1.1-3.7
L-Co	Brown red	64.68 (65.02)	5.47 (5.42)	10.42 (10.34)	–	7.3-7.7	1.1-3.8
L-Ni	Green	64.89 (65.05)	5.51 (5.42)	10.24 (10.35)	–	7.3-7.8	1.2-3.9
L-Zn	Brown yellow	65.09 (64.53)	5.44 (5.38)	10.09 (10.27)	–	7.2-7.7	0.9-3.8

broad and weak band at about 3430 cm^{-1} assigned to ν(N-H), accordingly the band at 1540 cm^{-1} assigned to δ(N-H), there is also a band at 1167 cm^{-1} assigned to ν(N-C). All these bands suggest that the ligand exists in an enamine-keto form. These bands disappear in the metal complexes, which suggests that the nitrogen atom of the phenylalanine methyl ester moiety is a coordination atom. The linkage with nitrogen atom is confirmed by the appearance of band in the far IR region at 498-476 cm^{-1} assigned[1] to ν(M-N). The next IR spectrum of the ligand exhibits a strong and broad band at 1748 cm^{-1} assigned to ν(C=O), while this band suffered a downward shift by 45-77 cm^{-1} in the spectra of the complexes indicate coordination of the metal ion through carbonyl oxygen of phenylalanine methyl ester moiety. At the same time the band of C=O (ring) at 1634.8 cm^{-1} appearing obvious red shift in the complexes suggests that the oxygen atom of pyrazolone group is another coordination atom. Coordination through oxygen atom of phenylalanine methyl ester moiety as well as oxygen of pyrazolone group is supported by the presence of a far IR band at 544-538 cm^{-1} assigned to ν(M-O)[7].

The analytical data of all the synthesized metal complexes are given in Table-2. ^{1}H NMR spectra of the Schiff base and the complexes were recorded in the same solvent $CDCl_3$. The signals at 8.14 ppm in the ^{1}H NMR spectrum of the ligand due to the O=C-C=C-N-H and there is no other signals of -OH in lower fields, which shows that the ligand exists in an enamine-keto form. The signals disappear in complexes, probably because the enamine-keto form in the ligand turns to imine form of the complex. The possible structure of the ligand and the complexes are shown in Fig. 1.



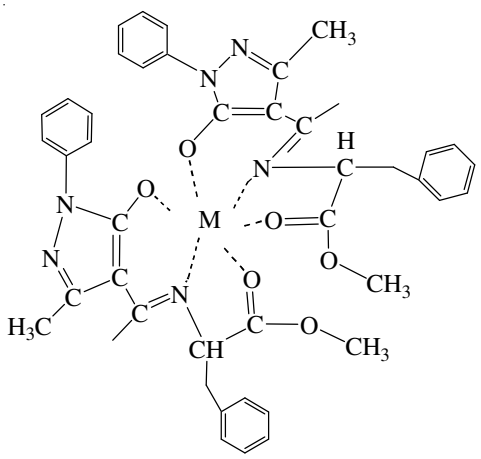


Fig. 1. Possible structure of the ligand and its metal complexes

The antibacterial activity tests of the ligand and its metal complexes at different concentrations against *Bacillus coli* and *Bacillus subtilis* were performed using disc diffusion method. The results indicate that almost all the compounds have the activity of inhibiting the growth of the two bacteria. The values reveal that the Schiff base became more pronounced when it is coordinated to the metal ions. The biological activity of the complexes follow the order: Zn(II) > Cu(II) > Co(II) = Ni(II). The data show that *E. coli* was inhibited to a greater degree by the Zn(II) complex.

Conclusion

The Zn(II) complex prepared with the new Schiff base could reasonably be used for the treatment of some common diseases caused by *E. coli*.

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Basic Science, Tianjin Agricultural College of China for providing available laboratory facilities. The authors are also grateful to the Science Development Commission of Tianjin Agricultural College [No: 2007029] and the Doctor Degree Fund Commission of Tianjin Agricultural College [No: 2007027] for financial supports.

REFERENCES

1. J.Z. Li, W.J. Yu and X.Y. Du, *Chin. J. Appl. Chem.*, **14**, 98 (1997).
2. J.Z. Li, L. Jiang and Y.M. An, *Chin. J. Appl. Chem.*, **21**, 150 (2004).
3. G.H. Xiong, Z.M. Yang and A.L. Guo, *Fine Chem.*, **6**, 1 (1993).
4. H.L. Zhu, J. Shi, Z. Wei, R.H. Dai and X. Zhang, *Acta Cryst.*, **E66**, o1352 (2010).
5. H.L. Zhu, X. Zhang, Y.J. Song, H.Z. Xu and M. Dong, *Acta Cryst.*, **E61**, o2387 (2005).
6. B.S. Jansen, *Acta Chem. Scand.*, **13**, 1668 (1959).
7. S.H. Baiu, M.M. El-Ajaily and N.M. El-Barasi, *Asian J. Chem.*, **21**, 1 (2009).