

SYNTHESIS AND STUDY OF SOME TRANSITION METAL COMPLEXES WITH MANNICH BASE DERIVED FROM 2-HYDROXY 1, 3, 4-TRIAZOLE-5-THIONE

Taghrid M. Al-Deen, Hawra Q.H, Amjjad G. Aliwi and Al-Ameen B. O.

Abstract

A new Mannich base N,N-di{4-(2-hydroxy-1,3,4-triazole-5-thione)-Methyl}.

Amino benzothiazole (HL) have been prepared by condensation reaction of formaldehyde, 2-aminobenzothiazole & 2-hydroxy-1,3,4-triazole-5-thione.

The new ligand has been characterized by spectroscopic techniques (F.T.I.R, UV-Visible), micro, analytical (C.H.N).

The new base have been used as ligand to prepare a number of complexes with Ni(II), Cu(II), Pd(II), Zn(II), Cd(II) and Hg(II) ions. The new metals complexes have been fully characterized by physical properties, melting point, molar conductance in 10^{-3} M of (D.M.S.O).

Measurements of magnetic moments μ_{eff} (B.M), as well as the spectroscopic measurements (F.T.I.R and UV-Visible).

Moreover the anti-bacterial activity of the complexes were estimated and compared with that of free ligand by using diffusion method.

Introduction

A triazoline derivatives, contain a ring up of than are kind of atom, it contains in addition to carbon, other kinds of atoms commonly nitrogen, may seem most interesting wide spectrum in biological activity⁽¹⁻⁵⁾.

The triazole ring is associated with centrifugal, hypoglycemia, analgesic and antimicrobial properties.

The presence of nitrogen and sulfur atoms provide more than one donor atoms, for complexation with metal ions (8-10), this may lead to synergistic effect in biological activities as well as synthetic models in studying the effect of metal ion on some structural related enzyme activities.

The present work focuses the attention on one of these compounds, it is N, N-di [4-(2-hydroxy-1, 3, 4-triazole-5-thione) methyl] amino benzothiazole (HL).

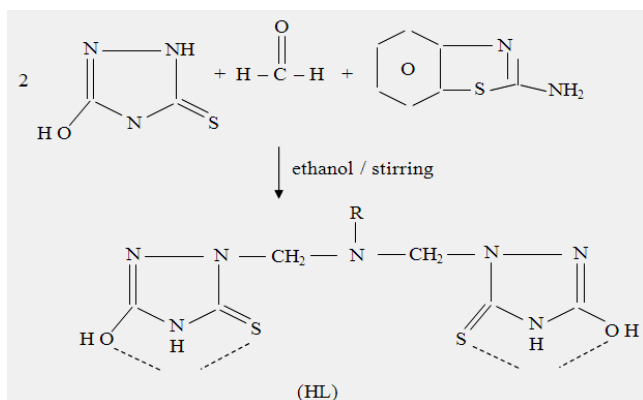
Experimental

All the chemicals used were of highest purity available. Melting points were recorded on Gallen Kamp M. F. 600 visual melting point apparatus. I. R. spectra were obtained using FT-IR-shimadzu 3600 Spectrophotometer.

Micro analytical data (C.H.N) were obtained using C.H.N Elementary Analyzer of Perkin-Elmer. 240B; Flame atomic absorption data were done using Shimadzu AA-670. Electronic spectra of ligand and complexes solution (UV-Vis.) were recorded using Shimadzu UV-160A for the range (800-200) nm, magnetic susceptibility measurements were carried out using Bruker magnet BM6, conductivity measurements were obtained using Corning-conductivity meter 220.

Preparation of the Mannich Base (HL)

The new ligand was prepared by mixing (50 ml) of ethanolic solution of (2-hydroxy-1,3,4-triazole-5-thione) 0.02 mole and (0.030 mole) formaldehyde (30%), then the mixture was treated with (0.01 mole, 1.5g) of 2-amino benzothiazole, under stirred with slow addition. The mixture was stirring for 2hrs, and let overnight in air. The white-yellow solid was obtained, was filtered, washed with distilled water, then dried under vacuum for 3hours. The physical properties of ligand are shown in Table (1).



where R = 2-benzothiazolyl ring

Scheme (1): Preparation of Mannich base(HL).

Synthesis of Mannich Metal Complex

(0.001 mole, 0.36g) of (HL) ligand dissolved in 25ml of absolute ethanol was added dropwise to 0.002 mole of 0.24g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.27 g ZnCl_2 , 0.50g HgCl_2 , 0.49g CdCl_2 or 0.42 g $\text{Na}_2 \text{Pd Cl}_4$ in 15ml of distilled water. The pH of the solution was raised up to 7.5 by adding 5 ml of 20% sodium solution. The reaction mixture was refluxed for half hour. Coloured compounds separated in each case, filtered under section and washed successively with water, ethanol and Pet. ether to remove unreacted ligands and dried over anhydrous CaCl_2 , Tables (1).

Table (1)

Physical properties and elemental analysis of the ligand and its metal complexes.

Formula	Symbol of compound	M.P° Colour	Elemental analysis %calc. (found)			
			C%	H%	N%	M%*
$\text{C}_{13}\text{H}_{10}\text{N}_7\text{O}_2\text{S}_2$	HL	180-182, White-yellow	43.33 (42.50)	2.77 (2.30)	27.22 (26.61)	-
$\{\text{Ni}(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2\}$	C_1	Orange 245-247	28.57 (27.77)	2.93 (2.83)	17.94 (17.99)	21.24 (20.88)
$\{\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2\}$	C_2	Brown 275 ^d	(28.00) (27.33)	2.51 (2.44)	17.54 (17.71)	22.80 (22.01)
$\{\text{Pd}_2(\text{L})\text{Cl}_4\}$	C_3	Red 295 ^d	21.19 (20.81)	2.01 (1.99)	13.31 (13.61)	25.81 (25.11)
$\{\text{Zn}_2\text{L}(\text{H}_2\text{O})_2\text{Cl}_2\}$	C_4	Yellow 298 ^d	(20.11) (20.00)	2.11 (1.90)	10.81 (9.91)	(30.12) (30.29)
$\{\text{Cd}_2\text{L}(\text{H}_2\text{O})_2\text{Cl}_2\}$	C_5	Yellow 315 ^d	18.50 (17.71)	1.90 (1.30)	8.94 (8.11)	40.80 (39.9)
$\{\text{Hg}_2\text{L}(\text{H}_2\text{O})_2\text{Cl}_2\}$	C_6	Dark Yellow 210 ^d	16.91 (15.81)	1.50 (1.00)	7.89 (7.99)	45.71 (44.81)

* =percents of metal were evaluated via flame atomic absorption using standard addition method,

d = decomposed.

Table (2)
Infrared spectra of the Mannich base (HL) and its metal complexes.

Compound	Absorption peak (cm ⁻¹)					
	O-H,C-O	C=S,S-H	C=N,C-N	M-O	M-S	Other perk
HL	3430(br) 1010(s)	1020, 2500(w)	1600(s),905	-	-	-
C ₁	- 1005(s)	650	1595, 895	415(w)	389(w)	3360(br) H ₂ O, 250 (Ni-Cl)
C ₂	- 995(w)	930	1600,900	420	375(w)	3540(br) 325(Cu-Cl)
C ₃	- 990	945	1590,880	430	405(w)	240-260(w) (Pd-Cl)
C ₄	- 1000	935	1590,913	418	398(w)	3590(br)
C ₅	- 985	930	1610(s) 910	432	410(br)	3500, (b) 1615(δ -OH)
C ₆	- 990(w)	915(w)	1593(s) 907	430	400m	3390(br), 1590(δ -OH)

s = strong, w = weak, br = broad, m = medium, a = asymmetric vibration of water molecules bonded to metal ion, b = rocking vibration of O-H for water molecules.

Table (3)
Electronics spectral data, conductance (in DMSO) and magnetic moments (B.M) of metal complexes.

Compound	UV-Visible $\lambda_{\max}(\epsilon_{\max})$	Assignment	ohm ⁻¹ cm ² mol ⁻¹	Magnetic Moment (B.M)
HL	240, 305	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
C ₁	260, 380 (19500), 525	C.T, $A_{1g} \rightarrow A_{2g}^2$	35	0
C ₂	280, 360, 700(90), 895(120)	$\pi_2 \rightarrow \pi^*$, $B_{1g} \rightarrow B_{2g}$ $B_{2g} \rightarrow E_{2g}$	40	1.5
C ₃	250, 592(80), 415(100)	$\pi \rightarrow \pi^*$ $A_{1g}^1 \rightarrow A_{2g}^2$ $A_{1g}^1 \rightarrow B_{1g}^2$	180	0.80
C ₄	240, 370(30.000)	$\pi \rightarrow \pi^*$ C.T(M \rightarrow L)	50	0
C ₅	218, 310, 350(20.000)	$\pi \rightarrow \pi^*$ C.T(M \rightarrow L)	30	0
C ₆	240, 295(50.000)	$\pi \rightarrow \pi^*$ C.T(M \rightarrow L)	40	0

C.T = charge transfer transitions.

Results and Discussion

Micro analytical, and other physical properties of Mannich base and its metal complexes are given in Table (1).

The stoichiometries of the ligand and its complexes were confirmed by either elemental analyses. The molar conductance measured in DMSO of 10^{-3} M solutions of these complexes fall in the range (30-50) $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating their non-electrolytic behavior, except for pd(II) complex which exhibits electrolytic properties in 2:1 ratio⁽¹¹⁾.

The observed magnetic moment of Cu(II) complex was 1.5BM this value suggested square planar stereochemistry of the complex. The observed magnetic moment of pd(II) complex was 0.80 BM, this agrees with the suggested square planar configuration.

IR Spectra:

The broad band that appeared in the I.R spectrum of the Mannich base (HL) at 3430 cm^{-1} is assigned to the stretching vibration of the intermolecular hydrogen bonded O-H in the molecule⁽¹³⁾. This band disappeared in the IR spectra of the complexes. The disappearance of this band in all the complexes suggests the coordination of oxygen atom of O-H in the 2-position of triazole ring after deprotonation. The broad band accruing around $3360\text{-}3390\text{ cm}^{-1}$ may be attributed to the OH vibration of water moleaules in the complexes⁽¹⁴⁾. However the medium absorption at 1020 cm^{-1} in the I.R spectrum of the base, was shifted to lower frequency ($950\text{-}915\text{ cm}^{-1}$) due to coordination of sulfur atom of thione group to the metal ion. This evidence of the bonding is also shown by the observation that new band in the spectra of the metal complexes appear at $375\text{-}410\text{ cm}^{-1}$ and $415\text{-}432\text{ cm}^{-1}$ assigned to (M-S) and (M-O) stretching vibrations that are not observed in the specter of the free ligand.⁽¹⁵⁻¹⁶⁾ Moreover the weak absorptions in the range ($250\text{-}380\text{ cm}^{-1}$) were assigned to M-Cl⁽¹⁷⁾.

Electronic spectra:

Bands of maximum absorption related to the three ligand nad metal complexes are shown in Table (3). The ligand solution in ethanol shows two peaks at 240 and 305nm assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions⁽¹⁸⁾ respectively. The Ni(II) complex in (DMSO) solution exhibits two spin allowed transitions in the region (380-515) nm which may be attributed to $A_{1g}^1 \rightarrow A_{2g}^2$ and $A_{1g}^1 \rightarrow B_{2g}^2$ respectively⁽¹⁹⁾, this supports the square planar geometry around metal ion.

The brown complex of Cu(II) gave orange colour in DMSO, this refers to the presence of vacant site on the metal ion. The electronic spectra in Dmso gave abroad band splited at 700 and 592 nm which were assigned to $B_{1g}^2 \rightarrow B_{2g}^2$ and $B_{1g}^2 \rightarrow E_g^2$ transitions⁽¹⁹⁾ of square planar complex.

The red palladium complex show two absorption bands which were observed at 415 and 592nm. The spectrum was typical of square planar pd(II) complexes⁽²⁰⁾. The bands were assignees to $A_{1g}^1 \rightarrow B_{1g}^1$ ($10D_h$) and $A_{1g}^1 \rightarrow E_{1g}^1$ transitions respechrely. However the Zn(II), Cd(II) and Hg(II) complexes are dark colored and diamagnetic expected for d^{10} ions. The UV-vis. Spectra of the complexes show relative change in the bands absorption compared to that of ligand.

Bactericidal Activity:

The antibacterial activities of the ligand and its metal complexes were carried out by using agar techniques⁽²¹⁾ against growth cultures of Escherichia coli and Bocillus respectively at the concentration of 1000mg/ml of the compound.

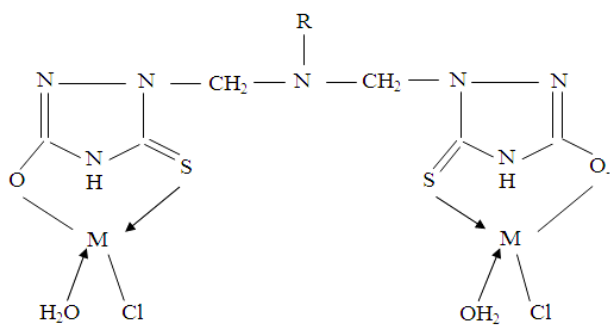
The ligand was found to be active while Zn(II) and Hg(II) complexes found to be inactive. In contrast Ni(II), Cu(II) and Pd(II) complexes showed growth inhibition against the two bacteria, this result can be attributed to the synergic effect⁽²²⁾ between the metal ion and ligand. Table (4).

Table (4)
Anti bacterial activity of Manusich base (HL) and its metal complexes (mg/ml).

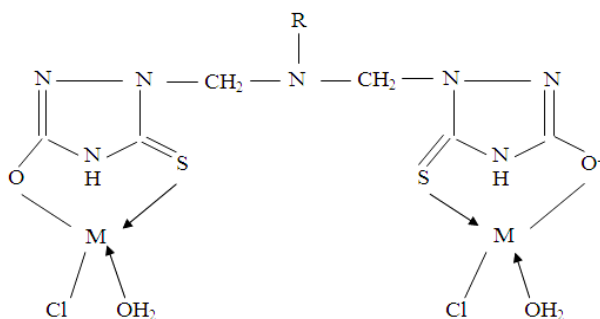
Compound	Bacillus	E. coli
HL	20(++)	5(+)
C ₁	22(++)	30(+++)
C ₂	18(++)	15(++)
C ₃	21(+++)	10(++)
C ₄	(-)	(-)
C ₅	(-)	(-)
C ₆	(-)	(-)

Suggested stereo chemical structures:

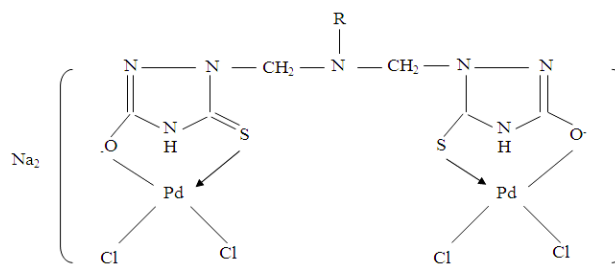
According to the results obtained from elemental and spectral analyses, the structures of the above mentioned complexes can be illustrated as follows:



M = Ni(II) and Cu(II)
 Square planar geometry of Ni(II) and Cu(II) complex.



M = Zn(II), Cd(II) and Hg(II)
 Tetrahedral geometry of Zn(II), Cd(II) and Hg(II), complexes.



Square planer geometry of pd(II) complex.

References

- [1] G. Weiber, M. C. Aversa and F. Bucchen, *Ann. Chem. (Rome)*, 10, 59, 912 (1969).
- [2] H. Single. L. D. S. Yadar and S. B. S. Mishar; *J. Inorg. Nucl. Chem.* 43, (1981).
- [3] B. N. Goswami, J. C. Katakya and J. N. Baruah, *J. Heterocyclic Chem.* 21, 205 (1984).
- [4] Vishuj. J. and J. Arnold, *J. Hetcroyclic Chem.* 25, 253 (1988).
- [5] Y. Okada, *Japan Med. J. Chem.*, P. 7024 (C1. 16E 391.2) 982.
- [6] V. J. Babar, D. V. Khasnis and V. M. Shind, *J. Indian Chem. Soc.* 18, 970 (1981).
- [7] N. N. Orlova, V. A. Aksevova and G. N. Pershin, *Russ. Pharm Toxic* 384 (1990).
- [8] C. W. Johnson, J. W. Joyner and R. {Antibiotics Chemotherapy}2, 636 (1993).
- [9] D. J. Bauer, L. S. Vinscent and A. W. Downe, *J. Heterocyclic Chem.* 39, 215 (1999).
- [10] A. I. Vogel *"Text Book of Quantitative Analysis"* Longmans Green, London, , 497, 529 (1962).
- [11] C. B. Maeto and R. P. Singh, *J. Inorg. Chem.* 42, 286 (1980).
- [12] K. Nakamoto *"Infrared Spectra of Inorganic and Coordination Compounds"* Wiley New York (1967).
- [13] K. Nakamoto *"Infrared Spectra of Inorganic and Coordination Compound"* 4th Ed. Wiely, Interscinee, New York (1986).
- [14] G. A. A. Al. Safar, *M. Sc. Thesis*, Baghdad University (1998).

- [15] N. N. Green Wood, and A. Eamshaw "Chemistry of the Elements" Pergamon Press (1986).
- [16] J. C. Bailor, H. J. Emeleus and R. Nypholm "Comprehensive Inorganic Chemistry" Progamon Press (1973).
- [17] K.Nekamoto "Infrared and Raman spectra of Inorganic compounds" pp.130-132 (1976).
- [18] N. Rama, and M. C. Ganorkar, J. Indian Chem. Soc. 27A (1), 53 (1988).
- [19] R. C. Saxena, C. L. Jain, R. B. Enjomin and S. K. Sangal, J. Indian Chem. Soc. LXIII, 435 (1986).
- [20] B. N. Figgis "Introduction to Ligand Field", Interscience, New York (1966).
- [21] A. B. P. Lever, "Inorganic Electronic Spectroscopy", Amsterdam-London-New York (1968).
- [22] A.M. Ra, S. Sexan Jones and Mc. Rao, *Indian J. Chem. Soc.* 52, 130 (1998).
- [23] D. Sutton "Electronic Spectra of Transition Metal Complexes", 1st. Ed., New York (1968).
- [24] F. A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry" 4th Ed. Wiley Interscience (1980).
- [25] G. A. Washington "Laboratory Procedures in Clinical Micro. Biology" New York (1981), P.299.
- [26] R. A. Rai, U. Agarwala and Eak Shmi, *Indian J. Chem.*, 18A, 426 (1979).

تحليل العنصر (C.H.N.M)، طيف الأشعة تحت الحمراء، الأطياف الالكترونية، قياس العزم المغناطيسي المؤثر بطريقة فارادي - التوصيلية المولارية لمحاليل المعقدات في 10^{-3} مولاري في مذيب ثنائي مثيل سلفوكسيد. كما قيست النسبة المولية (فلز، لكيند) في المحلول و أعطت نتائج متقاربة مع تلك التي تم الحصول عليها في الحالة الصلبة. تم اقتراح التركيب المحتملة للمعقدات المدصرة كما تم تعيين الفعالية المضادة للبكتريا ومقارنتها مع فعالية الليكند بواسطة استخدام طريقة الانتشار.

الخلاصة

جرى تحضير قاعدة مانخ الجديدة N-N- ثنائي

[4]- (2- هيدروكسي - 3، 1، 4- ترايبازول -5

ثايون) مثيل] أمينو بنزو ثايازول (HL).

استخدمت القاعدة كليند مخلي لتدضير عدد من

المعقدات الجديدة مع ايونات العنصر [النيكل (II)

- النحاس (II) - البلاتيوم (II) - الزنك (II) - الكاديوم (II)

- الكاديوم (II) الزئبق (II)] وشخصت ودرست

تركيب المعقدات الجديدة بالحالة الصلبة باستخدام