Synthesis and Theoretical Evaluation of New Binuclear Cr(III), Co(II) and Fe(III) Metal Complexes of Tetradeutate Schiff Base and Its Biological Activity

Omar Hamad Al-Obaidi1*

1Chemistry Department, Women Education College, Al-Anbar University, Iraq.

Author’s contribution

The study was designed, analyzed and discussed by the author. The author takes full responsibility for the whole study including data collation, manuscript drafting and editing.

Article Information

DOI: 10.9734/IJBcRR/2015/7866

Editors:
(1) Carmen Lúcia de Oliveira Petkowicz, Federal University of Parana, Curitiba, Parana, Brazil.
(2) Francisco Torrens, Institut Universitari de Ciència Molecular, Universitat de València, Edifici d’Instituts de Paterna, València, Spain.

Reviewers:
(1) Anonymous, Yildiz Technical University, Istanbul, Turkey.
(2) Saira Shahzadi, Department of Chemistry, GC University, Faisalabad 38000, Pakistan.

Complete Peer review History: http://www.sciencedomain.org/review-history.php?id=652&iid=3&aid=6152

Original Research Article

Received 14th November 2013
Accepted 21st March 2014
Published 19th September 2014

ABSTRACT

The new acyclic Schiff base [L] ligand: 3,3’-(1E,1’E)-1,1’-(2,2’-azanediylbis(ethane-2,1-diyl))bis(azan-1-yl-1-ylidene))bis(ethan-1-yl-1-ylidene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) derived from condensation of one mole diethylene diamine triamine (dien) with two moles of dehydroacetic acid have behaved tetradeutate dibasic chelating agent with all metal ions under study. Three bimetallic Cr(III), Co(II) and Fe(III) acyclic polydentate complexes [M2L2Cl2]Cl4, M=Cr(III), Fe(III) and [M2L2Cl2], M=Co(II) have been prepared and fully characterized by UV-Vis., FTIR, micro-elemental analysis, as well as the magnetic moments of solid complexes and the measurements of molar conductance in DMSO solution helped us in investigate the chemical structure of bimetallic models. From the results obtained by different techniques, it was found that the proposed structures of the prepared complexes have octahedral structure. A theoretical treatment of the formation of complexes in the gas phase was studied, this was done...
using the HYPERCHEM-6 program in general. The synthesized compounds were tested for antimicrobial activity by cup plate diffusion method. The results indicate the enhanced activity of metal complexes over the parent ligands.

Keywords: Synthesis; spectral study; binuclear complexes; pyrane-2-one.

1. INTRODUCTION

The binuclear metal complexes possessing heterocyclic rings are one of the most widely used as antibiotics, antifungal and semiconductor sensors [1-4]. Nowadays, there exists interest in the development of new and more effective antifungal compounds [5], urged infection by the increasing importance of opportunistic provoked by factors that depress or destroy the immune system, like chemotherapy of cancer, the use of drugs to avoid organ rejection in transplanted patients and discussed like AIDS [6]. According to that, the development of new systemic fungicides is of prime importance in modern medicinal chemistry. 3-acetyl-6-methyl-2H-pyr-2,4(3H)-dione [I] a commercially available compound usually obtained through the on to condensation of ethyl acetate [7] has been shown to possess modest antifungal properties [8]. Also, it has been shown that the complexes of dehydroacetic acid with zinc and several transition metal cat ions, are fungi static [9]. This has motivated our study on the synthesis and structural characterization of new bimetallic complexes of Cr(III), Co(II) and Fe(III) with new acyclic Schiff base [L] derived from condensation of diethylenetriamine with dehydroacetic acid.

2. MATERIALS AND METHODS

2.1 Physical Measurements

Electronic spectra of the new ligand and its metal complexes were recorded in the region 800-200nm on Shimadzu 670 spectrophotometer. IR-spectra were recorded on PC, Shim adz FT-IR spectrophotometric—Japan model as KBr and CsI-dsic in the range 400-4000cm⁻¹. Magnetic moments studies were carried out on magnet-Bruker balance MG. On Al-Nahrain university Laboratories. The conductivity of solution of 10⁻³M complexes in DMSO were done on digital conductivity meter (HPG system, G-3001).

As well as the micro analysis, of C.H.N, were recorded at Carlo Erba 1108 elemental Vario in Laboratories of chemistry Depart in Al-Mustanisrya University. As well as %M in solid complexes were estimated using standard methods [10].

2.2 Reagents and Solvents

Dehydroacetic acid and diethylenetriamine (dien) obtained from Merk, was used as supplied, and the metal chloride hydrated CrCl₃.6H₂O, CoCl₂.6H₂O and FeCl₃.6(H₂O) of An. grade, were used for synthesis of complexes without any purification.

2.3 Synthesis of Ligand 3,3′-(1E,1′E)-1,1′-(2,2′-azanediylbis(ethane-2,1-diyl)bis(azan-1-yl-1-ylidene))bis(ethan-1-yl-1-ylidene)bis(4-hydroxy-6-methyl-2H-pyran-2-one) (L)

The ligand (L), was prepared by refluxing (2g,0.011moles) of dehydro acetic acid in 30ml absolute ethanol with (0.613,5.9x10⁻³moles) of diethylenetriamine for about 9hrs on water bath. The polydentate acyclic ligand (L) thus formed upon cooling the mixture to room temperature over night. m. p. 44-46°C. The yield was ca 60%.

Exact mass 403.17g/ml, of C₂₀H₂₅N₂O₄ formula with good solubility in methanol and ethanol, DMF and DMSO, to give clear off white solutions. The micro elemental analysis %calc (found) %C 59.54 (58.69), %H 6.25 (5.81), %N 10.42(11.61) as shown in scheme (1).

![Scheme 1. Synthesis of ligand(L)](image)
2.4 Synthesis of Metal Complexes

(0.65 g, 2 mole) of (CrCl,
3H2O) in (20mL)
methanol was added to
(0.5g, 1mol) of [L] ligand
dissolved in methanolic
solution of potassium
hydroxide(5%) to keep the
pH of the solution
for(=8). The resulting mixture was refluxed under
nitrogen atmosphere for 3 hrs. until its solution
has become green in color, then cooled to room
temperature, a green precipitate formed, filtered
off, washed several times with 15ml of diethyl
ether , and dried under vacuum to afford (0.51g,
61%) yield, scheme(2),

A similar method was used to prepare Co(II), and
Fe(III) complexes Scheme(2), Table (1) shows
some physical properties and reactant amount of
the prepared complexes.

2.5 Study of Biological Activity for
Ligands and Their Metal Complexes

The biological activity of the ligands and their
metal complexes were studied against two
selected type of bacteria which included
Escherichia coli, as gram negative (-Ve) and
Staphylococcus aureus as gram positive (+Ve)
to be cultivated and as control for the disc
sensitivity test [11]. This method involves the
exposure of the zone of inhibition toward the
diffusion of microorganism on agar plate. The
plates were incubated for 24 hours at 37°C, the
zone of inhibition of bacteria growth around the
disc was observed.

3. RESULTS AND DISCUSSION

The new acyclic Schiff base [L] ligand derived
from condensation of one mole
diethylenetriamine with two moles of
dehydroacetic acid have behaved tetra dentate
dibasic chelating agent with all metal ions
understudy. The stochiometric of the ligand and
its complexes were confirmed by their elemental
analysis. Table (1).

3.1 Infrared Spectra

The IR spectrum of the (L) ligand shows bands in
the region at 3400cm
-1
and 1656cm
-1
which assignable to ν(–OH) and azomethane group ν
(C=N) [12]. As well as the work absorption at
1695cm
-1
attributed to ν(N=O) of the pyrane
group. The IR showed no bands around at 3571
and 3357cm
-1
assigned to the ν asym (N-H) and ν asym
(NH) respectively which indicate the absent of
υ asym (N-H) and υ asym (NH) [13]. The negative shift
generally in υ(C=N) further suggested the
coordination to metal ions through nitrogen atom of
(C=N−) Schiff’s base [12] of the ligand.

The observations indicate the coordination of the
ligand L through the carbonyl group stretching
frequency decreases to 1650-1640cm
-1
compared to the free ligand at 1695cm
-1
, due to
the charge transfer from the ligand to the metal
[13]. The band assigned to the phenolic OH
in the same wave number comparing with
that of the free ligand, proving it’s not involve
coordination. [12] (Table 2). New bands which
appeared at low frequencies in the spectra of the
prepared complexes were probably due to
(metal- nitrogen), and (metal- oxygen), [14]
(Table 2).

3.3 Electronic Spectra and Conductivity
Measurements

The free ligand (L) in methanol spectral exhibits
three distinct absorptions in the range 42735,
37878 and 31847 cm
-1
which are assigned to π-π*
of benzenoid and E1, E2 and n-π* of C=N, and
C=O chromospheres [15]. The green solution of
Cr (III) complex in DMF exhibits absorption in the
range 22250, 25666 and 37017 cm
-1
, which
resemble these reported to be octahedral. Thus,
assuming the effective symmetry to be Duh, and
the various bands can be assigned to
4A2g(F)+→2T1g(p), 4T1g(F)+→1T1g(P) respectively
[15]. The Co(II) complex solution exhibit a well
weak absorption in visible region at 25545cm
-1
, 20955, 19955 cm
-1
which can be assigned to
4T1g(F)+→2T1g and 4T1g→1T1g(p) respectively
[16]. The measurements of molar conductance
in DMSO , A m 90 S.cm
-1
2 mol
-1
for Co(II) showed
that these are electrolytic and 115, 125 S.cm
-1
1 mol
-1
for Cr(III) and Fe(III)respectively which showed
electrolytic [10].

3.4 The Magnetic Measurement

The magnetic moment of Cr(III)(BM) revealed the
presence of three unpaired electrons which agree with octahedral environments
around Cr(III) ion, as well as the magnetic
moment of Co(II) (BM) [11]. The magnetic moment of Fe(III) (BM) revealed
which agree with octahedral environments
around Fe(III) ion [17] Table (3).
3.5 The Proposed Structure

Based on various physiochemical studier like elemental analyses, conductively measurements, magnetic moments, UV-Visible, and IR spectral studies, a distorted octahedral geometry may be proposed for Cr(III),Co(II) and Fe(III) complexes, as shown in scheme (2).

**Table 1. Analytical data and physical properties for ligand and their complexes**

| Compound | Formula | Molecule weigh | color   | Calc. | Found |
|----------|---------|----------------|--------|-------|-------|
| L        | C_{20}H_{25}N_{3}O_{6} | 403          | Off white | 58.98 (58.94) | 10.97 (10.92) | 5.76 (5.72) |
| C1       | [Cr_{2}L_{2}Cl_{4}]Cl_{2} | 1123         | green   | 42.76 (42.71) | 7.48 (7.45) | 4.49 (4.44) | 18.93 (18.90) | 9.26 (9.23) |
| C2       | [Co_{2}L_{2}Cl_{4}]Cl_{2} | 1066         | brown   | 45.05 (45.0) | 7.88 (7.86) | 4.73 (4.70) | 13.30 (13.26) | 11.0 (11.0) |
| C3       | [Fe_{2}L_{2}Cl_{4}]Cl_{2} | 1131         | brown   | 42.47 (42.45) | 7.43 (7.39) | 4.45 (4.42) | 18.80 (18.76) | 9.87 (9.83) |

*Analysis of metal percentage via F.A.A.S*

**Table 2. IR spectrum data for ligand and their complexes**

| Compound | u(C=O) | u(OH) | u (C=N) | u (C-H) aromatic, u (C-H)alaph. | u M-N | u M-O |
|----------|--------|-------|---------|----------------------------------|-------|-------|
| L        | 1655(s) | 3400(br) | 1656    | 2990, 2920                     |       |       |
| C1       | 1640(m) | 3399(br) | 1606    | 2995, 2925                     | 455,535 |
| C2       | 1650(m) | 3401(br) | 1600    | 2985, 2925                     | 478, 529 |
| C3       | 1645(s) | 3400(br) | 1605    | 2995, 2920                     | 475,545 |

Br=Broad, S=strong, m=medium, and w=weak

**Table 3. (UV-Vis) spectra data for ligand and their complexes, magnetic moment and molar conductivity measurement for the prepared complexes**

| Compound | Absorption | Assignment | Geometry | Magnetic moments | µ eff. (BM) | * Scm²ml⁻¹* |
|----------|------------|------------|----------|------------------|-------------|-------------|
| L        | 42735      | INCT       | -        | -                | -           | -           |
| C1       | 37878      | n-π*       | -        | 37017            | 23250       | 115         |
|          | 31847      | π-π*       | -        | 25666            | 20530       | 105         |
| C2       | 37017      | n-π*       | -        | 25545            | 1131        | 115         |
|          | 25666      | n-π*       | -        | 20955            | 20530       | 105         |
|          | 22250      | n-π*       | -        | 19955            | 20530       | 105         |

INCT=Intra-ligand charge transfer, *Molar conductance measurement were carried out in 10⁻⁴ M solution of DMSO
3.6 Theoretical Study

The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in Fig. 1 Table 4. As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds.

3.7 Biological Activity

The antibacterial activity of the Schiff bases and its complexes were tested on Gram positive bacteria, Staphylococcus aureus and Gram negative, E. coli. The antibacterial activities of the samples were evaluated by measuring the inhibition zone observed around the tested materials as shown in Fig. 2.

The improved activity of metal complexes can be explained on the basis of chelation theory [18]. The cobalt complex showed the highest value of inhibition against all types of micro organisms, this indicates that the chelation tends to make the ligand act as more powerful and potent antimicrobial agents, thus, inhibiting the growth of bacteria and fungi more than the parent ligand. The structural changes have marked effect on the sensitivity and sensitivity varies with organisms.
Fig. 2. The effect of ligand and their metal complexes toward bacteria

Table 4. Structural parameters, bond length (Å) and angles (°) of the [Co₂L₂Cl₂]Cl₂ complex

| Parameters | Bond lengths (Å) | Bond angles(°) | Parameters | Bond angles(°) |
|------------|------------------|----------------|------------|----------------|
| Cl(62)-Co(60) | 2.1500 | H(98)-N(35)-C(36) | 120.4029 | Cl(62)-Co(60)-Cl(61) | 0.0000 |
| Cl(61)-Co(60) | 2.1500 | H(98)-N(35)-C(34) | 120.4055 | Cl(62)-Co(60)-O(46) | 141.3880 |
| Cl(62)-Co(59) | 2.1500 | C(36)-N(35)-C(34) | 119.1935 | Cl(62)-Co(60)-N(32) | 89.9999 |
| Cl(61)-Co(59) | 2.1500 | H(97)-C(34)-H(96) | 109.5000 | Cl(62)-Co(60)-O(27) | 51.3879 |
| C(53)-C(48) | 1.3370 | N(32)-C(47)-C(31) | 129.9443 | Cl(62)-Co(60)-N(9) | 90.0002 |
| C(48)-C(49) | 1.3510 | H(104)-O(45)-C(44) | 120.0001 | Cl(61)-Co(60)-O(46) | 141.3880 |
| O(46)-Co(60) | 0.6000 | O(45)-C(44)-C(43) | 120.0002 | Cl(61)-Co(60)-N(32) | 89.9999 |
| O(45)-H(104) | 0.9720 | O(45)-C(44)-C(39) | 120.0033 | Cl(61)-Co(60)-O(27) | 51.3879 |
| C(39)-C(40) | 1.3787 | O(41)-C(40)-C(39) | 123.0011 | Cl(61)-Co(60)-N(9) | 90.0000 |
| N(38)-Co(59) | 1.8560 | O(47)-C(43)-C(44) | 118.4178 | O(46)-Co(60)-N(32) | 90.0004 |
| N(38)-C(55) | 3.1983 | O(47)-C(43)-C(42) | 85.1247 | O(46)-Co(60)-O(27) | 90.0001 |
| N(32)-Co(60) | 1.8360 | O(44)-C(43)-C(42) | 117.6004 | O(46)-Co(60)-N(9) | 89.9996 |
| N(32)-C(47) | 1.2600 | O(42)-O(41)-C(40) | 112.0000 | N(32)-Co(60)-O(27) | 90.0004 |
| N(32)-C(33) | 1.4700 | O(46)-C(42)-C(43) | 123.0004 | N(32)-Co(60)-N(9) | 179.9999 |
| C(28)-H(82) | 1.1130 | O(46)-C(42)-O(41) | 112.6898 | O(27)-Co(60)-N(9) | 89.9997 |
| C(27)-Co(60) | 0.6000 | C(43)-C(42)-O(41) | 124.2984 | C(19)-C(26)-N(9) | 103.9373 |
| O(25)-H(81) | 0.9720 | O(21)-C(20)-C(19) | 124.2988 | C(19)-C(26)-C(11) | 90.0000 |
| C(24)-O(25) | 1.3550 | Co(60)-O(46)-C(42) | 179.9993 | 128.0312 |
| O(17)-Co(59) | 0.6000 | Co(60)-N(32)-C(47) | 120.0002 | O(56)-C(49)-C(48) | 123.0000 |
| O(16)-H(79) | 0.9720 | Co(60)-N(32)-C(33) | 120.0003 | O(50)-C(49)-C(48) | 124.2987 |
| C(15)-O(16) | 1.3550 | C(47)-N(32)-C(33) | 107.9998 | Co(60)-Cl(62)-Co(59) | 90.0000 |
| C(14)-C(18) | 1.3370 | Co(60)-O(27)-C(20) | 179.9994 | Co(60)-Cl(61)-Co(59) | 90.0000 |
| C(14)-C(15) | 1.3370 | Cl(62)-Co(59)-Cl(61) | 0.0000 | Co(59)-O(56)-C(49) | 179.9996 |
| C(13)-O(17) | 1.9625 | Cl(62)-Co(59)-O(56) | 90.5730 | Co(59)-N(38)-C(55) | 72.0407 |
| N(9)-Co(60) | 1.8360 | Cl(62)-Co(59)-N(38) | 90.0000 | Co(59)-N(38)-C(37) | 120.0000 |
| N(9)-C(26) | 1.9830 | Cl(62)-Co(59)-O(17) | 90.0000 | C(55)-N(38)-C(37) | 107.9999 |
| N(3)-Co(59) | 1.8360 | Cl(62)-Co(59)-N(3) | 90.0000 | Co(59)-O(17)-C(13) | 146.3428 |
| N(3)-C(18) | 1.2600 | Cl(61)-Co(59)-O(56) | 90.5730 | H(84)-C(28)-H(83) | 109.5199 |

4. CONCLUSION

Prepared type of Schiff base ligand derived from pyrane-2-one and their complexes. The synthetic and structural study of above new type of octahedral complexes have bidentate ligands. The study of biological activity of the ligands and their metal complexes against two selected type
of bacteria which included Escherichia coli, as gram negative (-Ve) and Staphylococcus aureus as gram positive (+Ve) to be cultivated and as control for the disc sensitivity test shows that different activity of inhibition on growth of the bacteria.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Constable EC. Coordination Chemistry of Macrocyclic compounds. Oxford university press, oxford; 1999.
2. Singh DP, Kumur R, Malik V, Tyagi P. Synthesis and characterization of complexes of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with macrocycle 3,4,11,12-tetraoxo-1,2,5,6,9,10,13,14-octaaza-cyclohexadeca-6,8,14,16-tetraene and their biological screening. Transition Met. Chem. 2007;32:1051-1055.
3. Wason AD, Rockladge SM. Macrocyclic and Acyclic Ligands in Therapy and Diagnostics in Higgins CB ed., NY; 1992.
4. Mane P, Sangir SM, More BS, World. Eur. J of Chem. 2011;8(51):245-252.
5. Mnude As, Jagdale AN, Jadhar SM, Chondhaker TK, J. Korean Chem. Soc. 2004;53:407.
6. Mnude A, Jagdale AN, Jadhavsm, Chandhekar TK, J. Serb. Chem. Soc. 2010;75:349.
7. Zucolotto M, Danicl CJ, Javior AE, Castellana EE. Inorg. Chim. Acta. 2002;328:45.
8. Arndt F, Org. Synth. Coll. Ill. 1955;231.
9. Rao DS, Garonkar MC, DLS, John VT, Nat. Acad. Sci. Let. 1978;1:402.
10. Chandra S, Sharma D, Chromium(III), manganese(II), nickel(II), copper(II) and palladium(II) complexes of a 12-membered tetraaza [N4] macrocyclic ligand Transition-Met. Chem. 2002;27:732-735.
11. Vandpitte J, et al. Basic laboratory procedures in clinical bacteriology, WHO, Genevap. Johnson. 1991;78-110.
12. Raman N, SR, Sukthicevel A. Transition metal complexes with Schiff-base ligands: 4-aminoantipyrine based derivatives—a review J. Coord. Chem. 2009;62:691.
13. Silverstein R, Webster F. Spectra photometric Identification of Organic Compound” 6th ed.; 1998.
14. Nakamato K. Infrared and Raman spectra of Inorganic and coordination Compounds. 4th ed., Wiley, New York; 1986.
15. Rena VB, Singh DP, et al. Transition met. chem. 1981;6:36.
16. Lever AB. Electronic spectra of dn ions Inorganic Electronic Spectroscopy, 2nd ed., Elsevier; 1984.
17. Chandra S, Kumar R, Transition Met. Chem. 1999;29:337.
18. Negm NA, Zaki MF. Structural and biological behaviors of some nonionic Schiff-base amphiphiles and their Cu(II) and Fe(III) metal complexes. Colloid Surface B. Biointerfaces. 2008;64:179–83.

© 2015 Al-Obaidi; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=652&id=3&aid=6152