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

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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.

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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 tetra dentate dibasic chelating agent with all metal ions under study.

Three bimetallic Cr(III), Co(II) and Fe(III) acyclic polydentate complexes $[M_2L_2Cl_2]Cl_4$, $M=Cr(III)$, Fe(III) and $[M_2L_2Cl_2]$, $M=Co(II)$ 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

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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]. Now days, 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-pyran-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 cations, 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-disc in the range 400-4000 cm^{-1} . Magnetic moments studies were carried out on magnet-Bruker balance MG. On Al-Nahrain university

Laboratories. The conductivity of solution of 10^{-3} M 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 Carolo 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].

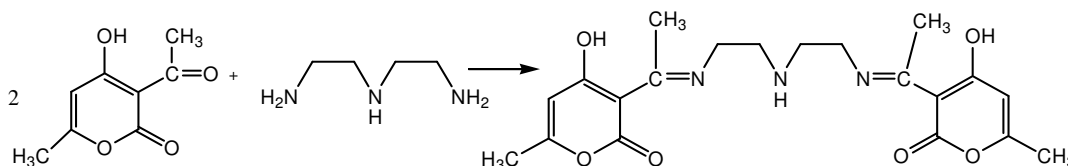
2.2 Reagents and Solvents

Dehydroacetic acid and diethylenetriamine (dien) obtained from Merk, was used as supplied, and the metal chloride hydrated $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6(\text{H}_2\text{O})$ 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'-azanediybis(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 (0.613,5.9 $\times 10^{-3}$ moles) of diethylenetriamine for about 9 hrs on water bath. The polydentate acyclic ligand (L), thus formed upon cooling the mixture to room temperature over night. m. p. 44-46 $^{\circ}\text{C}$. The yield was ca 60%.

Exact mass 403.17g/ml, of $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_6$ 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)

2.4 Synthesis of Metal Complexes

(0.65 g, 2 mole) of $(CrCl_3 \cdot 6H_2O)$ 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 under study. The stoichiometric 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 $\nu(\text{OH})$ and azomethane group $\nu(\text{C}=\text{N})$ [12]. As well as the work absorption at 1695cm^{-1} attributed to the $\nu(\text{C}=\text{O})$ of the pyrane group. The IR showed no bands around at 3571 and 3357cm^{-1} assigned to the $\nu_{\text{asy}}(\text{N-H})$ and $\nu_{\text{sy}}(\text{NH})$ respectively which indicate the absent of

$\nu_{\text{asy}}(\text{N-H})$ and $\nu_{\text{sy}}(\text{NH})$ [13]. The negative shift generally in $\nu(\text{C}=\text{N})$ further suggested the coordination to metal ions through nitrogen atom of $(-\text{C}=\text{N}-)$ Schiff's base [12] of the ligand.

The observations indicate the coordination of the ligand L through the carbonyl group stretching frequency decreases to $1650\text{-}1640\text{cm}^{-1}$ 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 group 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 31847cm^{-1} which are assigned to $\pi\text{-}\pi^*$ of benzenoid and E1, E2 and $n\text{-}\pi^*$ of $\text{C}=\text{N}$, and $\text{C}=\text{O}$ chromospheres [15]. The green solution of Cr (III) complex in DMF exhibits absorption in the range 22250 , 25666 and 37017cm^{-1} , which resemble these reported to be octahedral. Thus, assuming the effective symmetry to be D_{4h} , and the various bands can be assigned to ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{p})$, ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ respectively [15]. The Co(II) complex solution exhibit a well weak absorption in visible region at 25545cm^{-1} , 20955 , 19955cm^{-1} which can be assigned to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(\text{p})$ respectively [16]. The measurements of molar conductance in DMSO, Λ_m $90\text{ S.cm}^2\text{ ml}^{-1}$ for Co(II) showed that these are electrolytic and 115 , $125\text{ S.cm}^2\text{ ml}^{-1}$ for Cr(III) and Fe(III) respectively which showed electrolytic [10].

3.4 The Magnetic Measurement

The magnetic moment of Cr(III) ($\sim 3.35\text{BM}$) revealed the present of three unpaired electrons which agree with octahedral environments around Cr(III) ion, as well as the magnetic moment of Co(II), ($\sim 1.55\text{BM}$) [11]. The magnetic moment of Fe(III) ($\sim 3.34\text{BM}$) revealed which agree with octahedral environments around Fe(III) ion [17] Table (3).

3.5 The Proposed Structure

Based on various physicochemical studies like elemental analyses, conductivity 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 $\mu(\text{cm}^{-1})$	Molecule weigh	color	Calc. (Found)				
				C%	N%	H%	Cl%	M%
L	$\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_6$	403	Off white	58.98 (58.94)	10.97 (10.92)	5.76 (5.72)	-	-
C1	$[\text{Cr}_2\text{L}_2\text{Cl}_2]\text{Cl}_4$	1123	green	42.76 (42.71)	7.48 (7.45)	4.49 (4.44)	18.93 (18.90)	9.26 (9.23)
C2	$[\text{Co}_2\text{L}_2\text{Cl}_2]\text{Cl}_2$	1066	brown	45.05 (45.0)	7.88 (7.86)	4.73 (4.70)	13.30 (13.26)	11.05 (11.0)
C3	$[\text{Fe}_2\text{L}_2\text{Cl}_2]\text{Cl}_4$	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

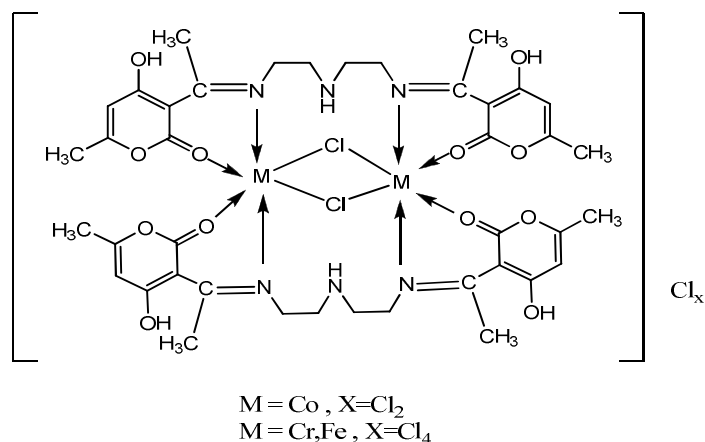
Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{H})$ aromatic, $\nu(\text{C}-\text{H})$ aliph.	$\nu \text{M}-\text{N}, \nu \text{M}-\text{O}$
L	1695(s)	3400(br)	1656	2990, 2920	-
C1	1640(m)	3399(br)	1606	2995, 2925	455, 535
C2	1650(m)	3401 (br)	1600	2985, 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 $\mu(\text{cm}^{-1})$	Assignment	Geometry	Magnetic moments $\mu \text{eff. (BM)}$	* $\text{Scm}^2\text{ml}^{-1}$
L	42735 37878 31847	INCT $\pi-\pi^*$ $n-\pi^*$	-	-	-
C1	37017 25666 22250	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{p})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	octahedral	3.35	115
C2	25545 20955 19955	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{p})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	octahedral	1.55	90
C3	23250 20530	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$	octahedral	3.34	125

INCT=Intra-ligand charge transfer, *Molar conductance measurement were carried out in 10^{-3} M solution of DMSO



Scheme 2. Proposed structure of metal complexes, M= Cr(III),Co(II) and Fe(III)

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.

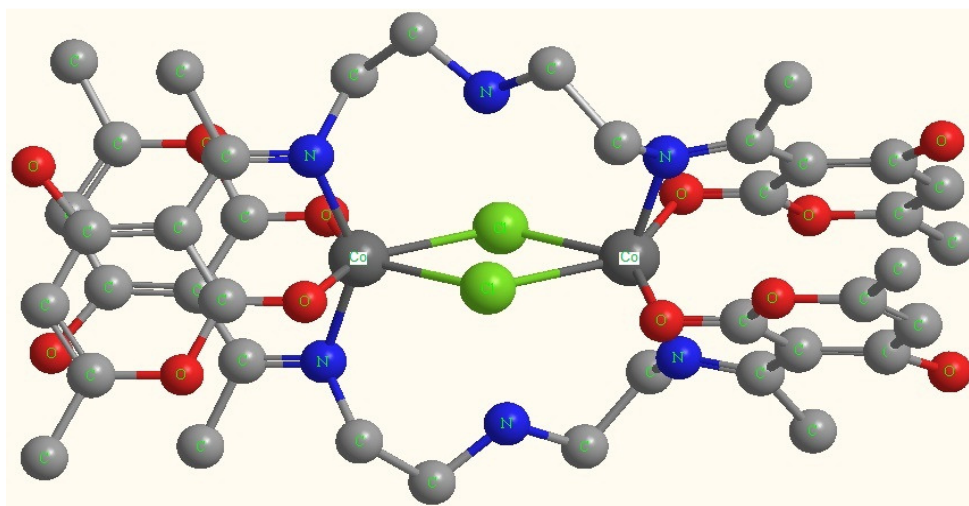


Fig. 1. The optimized structural geometry of Co(II) complex

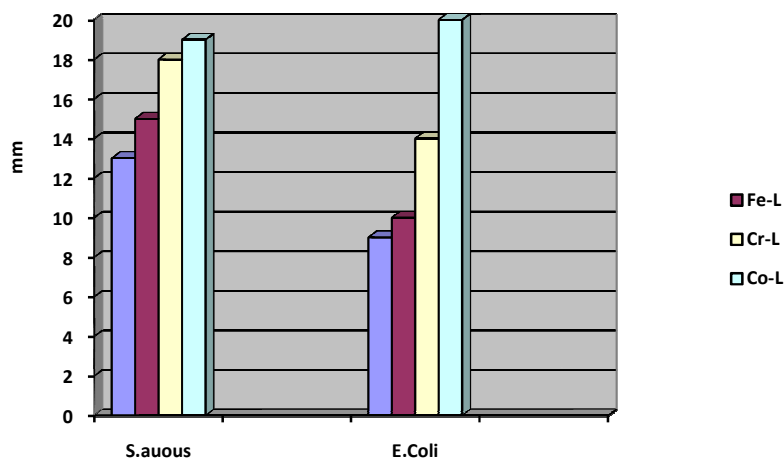


Fig. 2. The effect of ligand and their metal complexes toward bacteria

Table 4. Structural parameters, bond length (Å) and angles (°) of the $[\text{Co}_2\text{L}_2\text{Cl}_2]\text{Cl}_2$ complex

Parameters		Parameters		Parameters	
Bond lengths (Å)		Bond angles(°)		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)	120.4035	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)	120.0003	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)	90.0002
N(38)-Co(59)	1.8360	C(47)-C(43)-C(44)	118.4178	O(46)-Co(60)-N(32)	90.0004
N(38)-C(55)	3.1983	C(47)-C(43)-C(42)	85.1247	O(46)-Co(60)-O(27)	90.0001
N(32)-Co(60)	1.8360	C(44)-C(43)-C(42)	117.6004	O(46)-Co(60)-N(9)	89.9996
N(32)-C(47)	1.2600	C(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)	112.6989	O(27)-Co(60)-N(9)	89.9997
O(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(1)	
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.

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