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Synthesis and Characterization of Cobalt Homotrinuclear Biologically Active Compound

Abdullahi Mustapha* and Suleiman Musa Gani
Department Of Chemistry, Federal University Dutse, PMB 7156, Jigawa State
Email of the corresponding author: abmustapha2004@yahoo.com

Abstract

N_4O_3 tripodal Schiff-base ligand namely tris(5-Bromo-2-hydroxybenzylaminoethyl)amine (Tren5BrSal) have been prepared and characterized by various spectroscopic methods . It is derived from the condensation reactions of tris(2-aminoethyl)amine (Tren), with 3 equivalents of 5-bromo-2-hydroxybenzaldehyde (5BrSal). The Cobalt(III) complex of the resulting ligand was obtained from the reaction of Tren5BrSal with the salt of cobalt in absolute methanol. The antimicrobial screening was carried out against two bacterial species (*Escherichia coli* and *Streptococc.* Sp) and two fungal species (*Aspergillus niger* and *Fusarium* sp.). The complex is found to exhibit high antibacterial and anti fungal activity.

Keywords: Schiff- base, tris-(2-aminoethyl)amine, Tren5Brsal, Cobalt.

1. Introduction

A small number of complexes have been reported which demonstrate that multimetallic complexes can be formed by choice of appropriate ligand. Using TrMeSal, Ohta *et al.,* (2001) reported the synthesis of a trinuclear Ni(II) complex and its dinuclear analogue where each nickel atom is in approximately octahedral environment composed of three facially coordinated imine nitrogen atom and three phenolic oxygen atoms. Alternatively the latter can be considered to be two mononuclear Ni(II) complexes that were bonded together via strong hydrogen bonding. Chandrasekhar *et al.,* (2003) have also reported trinuclear metal(II) complexes of manganese, cobalt, nickel and zinc, using the phosphorus tripodal ligand (PsSal) (figure 1.). The compounds were reported to show intermolecular C-H----S=P contacts in the solid state which result in the formation of polymeric supramolecular architectures.

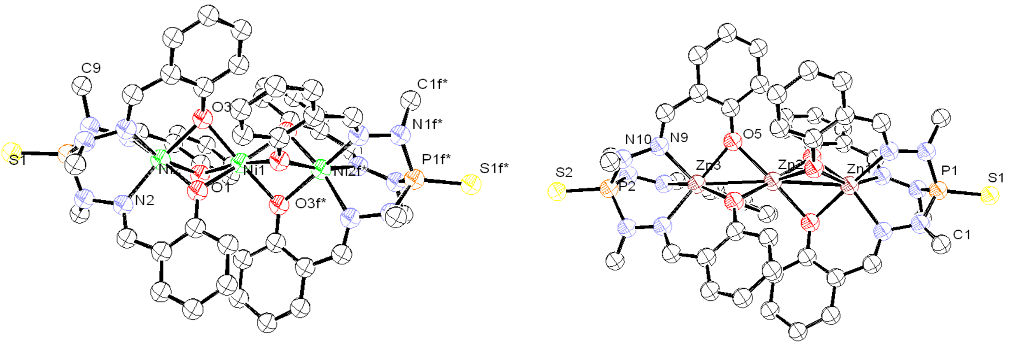

Figure 1: phosphorus trishydrazide trinuclear complexes (*left*=Ni_3, *right*=Zn_3) (Chandrasekhar *et al.,*2003)

The stability of this trimetallic motif is evident from the studies of Beissel *et al.,* (1996), who have also been successful in preparing a wide range of compounds including homotrimetallic, homobimetallic, heterobimetallic and mixed trimetallic complexes of transition metal and group 13 elements which adopt an isostructural motif. Prominent amongst these complexes is [$LNi^{III}Ni^{II}Ni^{III}L$] (where L = 1,4,7-tris(3,5-dimethyl-2-hydroxybenzyl)-1,4,7-triazacyclononane) which is isostructural with the trimetallic nickel complex [$PSal_2Ni_3$].

In the recent time (Kumar *et al.,*2009) metal complexes of Schiff bases have attracted more attention due to their remarkable antifungal, antibacterial and anti tumor activities. Alicylidene derivatives, neutral tetra-dentate ligand and metal-complexes show antibacterial activities against S. typhi, S. aureus, Kelbsiella pneumoniae, B. subtlis and S. flexneri. Organo-silicon (IV) complexes with bi-dentate Schiff base, and organo-silicon (IV) complexes and organo-lead (IV) complexes with nitrogen donor ligands possess antibacterial activities.

In here we report the synthesis of new potentially heptadentate Schiff-base ligand derived from condensation of 5-bromo-2-hydroxy benzaldehyde with tris-(2-aminoethyl)amine and complex it with Cobalt(II) metal salt, in the ratio of 2:3. The antimicrobial activity of the complex is also reported.

2. Experimental

All experiments were carried out using standard apparatus and the chemicals were of commercial grade and were used without further purification. The IR were measured on a broker FT-IR 8400s for the compound in the range 4500-500cm^{-1} and the UV-Vis was recorded in the range 280-750mm wavelength. The solubility test was determined in Ether, Ethanol, Nitro benzene, Chloroform, n-hexane, CCl_4, DMSO, Acetone and Distilled Water. The decomposition temperature was obtained using capillary tube and conductivity of 10^{-3}M in DMSO was determined at room temperature using conductometer. The resulting complex was tested against *Escherichia coli* and *Streptococcus.* Sp and two others *Aspergillus niger* and *Fusarium* sp. The procedure followed in the test is reported earlier (Mustapha and Suleiman, 2013).

2.1. Synthesis of Ligand (Tren5BrSal)

Tris(2-aminoethyl)amine (1.46, 10mmol) was added to a solution of 5-bromosalicylaldehyde (6.03g, 30mmole) in 100ml ethanol. The resulting solution was refluxed for 40 minutes. A yellow powdered solid was precipitated upon cooling for 24h. The product was filtered off, washed with ethanol and air dried. The yellow powdered solid was recrystallized by dissolving in ethanol/chloroform in the ratio 7:3 and was allowed to dry on water bath. Yield 88%. m/z; 691 Elemental analysis for [$C_{27}H_{27}O_3N_4Br_3$] : % Calculated C: 46.65; H: 3.91; N: 8.09, found C: 46.84; H: 3.97; N: 6.98

2.2. Synthesis of [Co_3(Tren5BrSal)$_2$]

Tren5BrSal (2.0g, 2.9mmol) was dissolved in ethanol (50ml) followed by addition of $CoCl_2.6H_2O$ (1.027g, 4.3mmol) in ethanol (20ml). The mixture was stirred after which few drops of triethylamine was added. The solution was refluxed for 60 minutes. A dark green solid was formed which was allowed to cool over night. The resulting Solid was filtered off, washed with ethanol and allowed to air-dry. Yield 71% m/z; 1589 Elemental analysis for [$Co_3C_{54}H_{54}N_8O_6Br_6$]: % Calculated C: 41.54; H: 3.10; N: 7.18, found C: 41.67; H: 3.14; N: 7.29

3. Results and Discussions

The CoTren5BrSal was obtained as Dark-green solid. The decomposition temperature of the complex was recorded and shown in table 1 below.

Table 1: Physical Measurements

Compound	Color	Molar weight	M.P/ Decomp Temp.(^oC)	Conductance (s/cm)
Tren5BrSal($C_{27}H_{27}O_3N_4Br_3$)	Yellow	695.24	145.7	0.002
[Co_3(Tren5BrSal)$_2$]	Dark-green	754.17	208.4	0.140

The high decomposition temperatures of the complexes showed stability as compared to melting point of the ligand. The low values of molar conductivity (Ω) indicate the absence of electrolytes in the complex [Cezar and Angela, 2000]. This is a good significance to indicate complete coordination of the ligand with the metal ion.

The solubility test of the synthesized complex indicates that the complex is insoluble in most of the solvents except in DMSO as shown in table 2. The ligand showed a clear variation as it dissolved in all the solvents except in diethyl ether and distilled water.

Table 2: Solubility Studies in different solvents

Compound	Ether	Ethanol	Nitro benzene	Chloroform	n-hexane	CCl_4	DMSO	Acetone	Distilled Water
($C_{27}H_{27}O_3N_4Br_3$)	Insoluble	Soluble	Soluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Insoluble
[Co_3(Tren5BrSal)$_2$]	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble	Insoluble	Insoluble

Table 3: Infrared Spectra Result of the Synthesized Complexes and the Schiff Base ligand

Compound	(C-OH)	(C=N)	(C-H)arom.	(C=C)aromatic	M-N	M-O
($C_{27}H_{27}O_3N_4Br_3$) Tren5BrSal	3412	1595	3062	1500	_	_
[Co_3(Tren5BrSal)$_2$]	_	1591	3051	1462	509	434

3.1. Infrared Spectral studies

The characteristic vibrations recorded on the infrared spectrophotometer and have been assigned to the Schiff base ligand and its complex with Co(III) are shown in Table 3.

The spectrum of the ligand exhibit strong band at 3412 cm^{-1} attributed to the stretching vibration of (OH) group attached to the benzene ring. The stretching vibration of the azomethine (C=N) in the ligand which is a characteristic feature of the Schiff base appears at 1595cm^{-1} which slightly drift down to 1591cm^{-1} in the spectra of the complex. The aromatic (C-H) stretching vibration appears in the range 3062 cm^{-1} to 3051 cm^{-1} while that of (C=C) appears in the range 1500 cm^{-1} to 1462 cm^{-1}. The disappearance of the broad (OH) band in the spectra of the metal complex indicates the coordination of phenolic oxygen with metal ions. The infrared of the complexes showed weak bands in the range 434cm^{-1} and 509cm^{-1} which is due to the stretching vibration of (M-O) and (M-N) respectively.

The structure of the cobalt compound is proposed below, as all the phenolic oxygen ware deprotonated and coordinated to the metal ion. The mass predicted for the complex is what is recorded in the mass spectral analysis *i.e.* m/z: 1589, while the elemental analysis recorded for the complex confirm the formation of the structure depicted below. The two side metal ions are sitting in the ligand pocket and are coordinated *via* three azomethine nitrogen atoms and three phenolic oxygen atoms which indicate an octahedral arrangement, the two monometallic complexes have one residual charge each which resulted from one of the phenolic oxygen. The two complexes coordinated to a third metal through three phenolic oxygen from each monometallic complex, making the coordinating environment octahedral through the six bridging oxygen. With this arrangement, the complex is neutral as it does not carry any charge

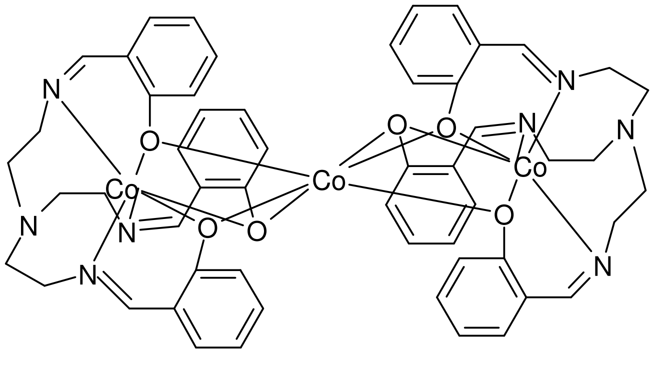

Figure 1: The proposed trimetallic [Co_3(TrenSal)$_2$] structure [Mustapha *et al.,* 2008]

3.2. The Electronic spectra

The spectrum of the free ligand shows a band at λ_{max} 420nm, which is attributed to ($\pi \rightarrow \pi^*$) transition. The Dark-green complex of Co(II) showed a strong band at λ_{max} 640nm which is also attributed to metal to ligand charge transfer.

3.3 The Biological studies of the Compound

The Antifungal activity of the ligand and metal complex was carried out using the pour plate technique as previously explained. (Buer *et al.,* 1966)The complexes and the ligand were tested against two fungal species, namely *Aspergillus niger* and *Fusarium sp*. The organisms were obtained at the microbiology Department, Umaru Musa 'Yar adua University. The result is shown in table 4, while sample result picture is shown in figure 2.

The antibacterial activity of the ligand and metal complex was also carried out using disc diffusion method as described by Bauer *et al.,* (1966). Both ligand and the complex were individually tested against two bacterial species, namely *Escherichia coli* and *Streptococcus* sp. The isolates were obtained and identified at the micro Biology Department, Umaru Musa 'Yar adua University. The zones of inhibition were measured at the end of the incubation period as shown in table 5

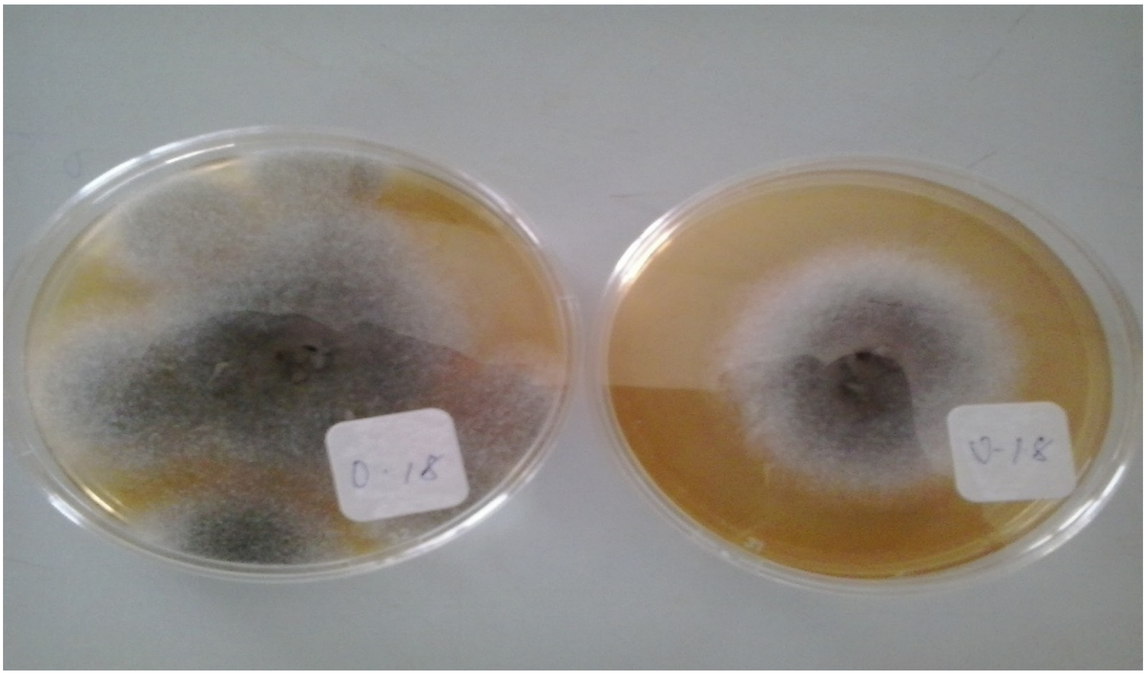

Figure 2: Samples from Disc diffusion result showing zone of inhibition

Table 4: The anti fungal activity of the Tren5BrSal and the complexes

COMPOUND	10 (mg/cm^3)		10^1 (mg/cm^3)		10^2 (mg/cm^3)	
	Fusarium sp.	*Aspergillus niger*	*Fusarium sp.*	*Aspergillus niger*	*Fusarium sp.*	*Aspergillus niger*
Tren5BrSal	_	_	_	_	_	_
$[Co_3(Tren5BrSal)_2]$	_	+	_	+	_	+

Table 5: The antibacterial activity of the Tren5BrSal and $[Co_3(Tren5BrSal)_2]$ complexes

	Concentrations in DMSO (mg/cm^3)						
	10		10^1		10^2		
COMPOUND	*E. coli*	*Strept.* sp.	*E. coli*	*Strept.* sp.	*E. coli*	*Strept.* sp.	
Tren5BrSal	16	18	0.6	12	0.6	0.6	Inhibition zone in diameter (cm)
$[Co_3(Tren5BrSal)_2]$	12	0.6	0.6	0.6	0.6	0.6	

Table 4 shows the results for the antifungal activity, it is shown that the ligand is not active against any of the fungal organism while the complex indicates high activity on *Aspergillus niger* at lower concentration which differ from its action against *Fusarium* sp. The study of the complex against bacteria indicated that the compound have high antibacterial activity, it is also indicative that at 10 mg/cm^3, the compound is very active against *Streptococcus. sp*., while at 100 mg/cm^3 the compound activity is higher on *Escherichia coli*.

4. Conclusion

In conclusion, we have successfully synthesized metal complex of cobalt using Tren5BrSal ligand. The metal was found to be trimetallic, their activity against two bacterial specie; *Escherichia coli* and *Streptococcus sp*. and two fungal specie; *Aspergillus niger* and *Fusarium sp.* reveals that the complex is active against *Streptococcus. sp*. and *Aspergillus niger* in either cases the compound is found active.

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