ChemSearch Journal 5(1): 56 – 60, June, 2014
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 12052014 Accepted: 23062014

Synthesis and Characterization of Multimetallic Fe(II) and Mn(II) Using N4O3 Potentially Heptadentate Ligand

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ABSTRACT

Potentially heptadentate (N4O3) tripodal Schiff-base ligand, tris(5-Bromo-2-hydroxybenzylaminoethyl)amine has been prepared and characterized using various spectroscopic methods. It is derived from the condensation reactions of tris(2-aminoethyl)amine (tren), with 3 equivalents of 5-bromo-2-hydroxybenzaldehyde. Iron(II) and Manganese(II) complexes of the resulting ligand were obtained from its reactions with Fe(II) and Mn(II) salts in absolute methanol for the metal to ligand ratio 2:3. These complexes were characterized by Solubility, Conductivity, IR and UV-VIS spectrometry, elemental analysis and mass spectrometry.

Keywords: Iron, Manganese, Schiff- base, Tren5BrSal, tris-(2-aminoethyl)amine

INTRODUCTION

The structure of trensal motif of multidentate ligands has flexible and inflexible regions, and it also has the ability to change denticity (Mustapha *et al.,* 2009). Tris(2-aminoethyl)amine (Tren) condenses with salicylaldehyde and its substituted analogs in the mole ratio 1:3 to form schiff-bases which are potentially tribasic heptadentate ligands (Kanesato *et al.,* 2000; 2001; Mustapha *et al.,* 2008). There have been a number of studies of the coordination chemistry of the unsubstituted parent ligand $N[CH_2CH_2N{=}CH(2\text{-}OH–C_6H_4)]_3$ and its fully saturated analog $N[CH_2CH_2\text{-}NHCH_2(2\text{-}OH–C_6H_4)]_3$ including studies of their use as Tc-99 chelators in nuclear medicine (Essig *et al.,* 2001).

Studies on ligand flexibility is currently of interest, where researchers use series of multidentate Schiff base species derived from tris-(2-aminoethyl) amine and salicylaldehyde, which potentially offers seven donor atoms. Significantly this motif allows flexibility around the aminoethyl regions in conjunction with the rigidity of the salicylidene units. According to Mustapha *et al.* (2009) studies show that such ligands support the formation of multimetallic complexes. The strategy uses flexible, multidentate, salicylidene Schiff base ligands which have been chosen for their ability to encapsulate metal cations in such a manner that the three terminal phenoxide donors assemble into a secondary binding motif. When divalent metals (e.g., Ni, Zn, Pb) are used, a charge imbalance between the encapsulated cation and the ligand is created, which leaves a residual charge on the complex. This facilitates the binding of an additional metal center between pairs of complexes.

In the recent time metal complexes of Schiff bases have attracted more attention due to their remarkable antifungal, antibacterial and anti tumor activities. In particular Merck company has successfully developed an antibacterial drug Cilastatin using chiral copper(II) Schiff base complexes derived from salicylaldehydes and chiral amine (Hanna *et al.*, 2001; Chakravarty *et al*., 2002; Gao, and Zheng 2002). The synthesis of potentially heptadentate (N4O3) Schiff-base ligands and their complexes with nickel(II) and copper(II) has also been reported[Mustapha *et al.*, 2008]. 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 either Manganese(II) or Iron(II) metal salt, in the ratio of 2:3.

EXPERIMENTAL

All experiments were carried out using standard apparatus and the chemicals were of commercial quality and are used without further purification. The IR were measured on a broker FT-IR 8400s for the compound in the range 4500-400cm^{-1} and the UV-Vis was recorded in the range 280-750nm wavelength. The decomposition temperature was obtained using capillary tube and molar conductance of 10^{-3}M was determined at room temperature using (WTW) conductivity meter (model LBR). Elemental analysis and mass spectra were run at Al-azhar University Cairo Egypt.

Preparation of the Symmetric Schiff Base Ligand ($C_{27}H_{27}O_3N_4Br_3$)

2.235g (1M) of Tren [Tris(2-aminoethyl)amine] was dissolved in 50ml absolute methanol followed by 9.248g (3M) of salicylaldehyde. The mixture was stirred at room temperature and then refluxed for one hour. The solution was allowed to cool at room temperature. The resulting yellow powder was obtained, filtered and dried. .(Kanesato *et al.,* 2001; Alyea *et al.,*1989)

Synthesis of [Fe_3(Tren5BrSal)$_2$]

0.5679g of the ligand Tris-(2-hydroxybenzylaminoethyl) amine [Tren5BrSal] was dissolved in 50ml absolute ethanol followed by the addition of 0.2436g of $FeCl_2.4H_2O$ salt, 5 drops of NaOH was added to the mixture. The mixture was refluxed for 3 hours, after which the solution was allowed to cool and Dark-Purple solid filtered and air dried. Yield 68% (Mustapha *et al.,* 2008), m/z; 1558 Elemental analysis for [$Fe_3C_{54}H_{54}N_8O_6Br_6$] : % Calculated C: 41.63; H: 3.49; N: 7.19, found C: 41.31; H: 3.12; N: 7.49

Synthesis of [Mn_3(Tren5BrSal)$_2$]

0.5102g of the ligand (Tren5BrSal) was dissolved in 50ml absolute ethanol, followed by the addition of 0.21787g of $MnCl_2$. $4H_2O$ and 5 drops of NaOH to the mixture. The mixture was refluxed for 3 hours after which the solution was allowed to cool and a yellow solid filtered and air dried (Mustapha *et al.,* 2008). m/z; 1555, Yield 88%. Elemental analysis for [$Mn_3C_{54}H_{54}N_8O_6Br_6$]: % Calculated C: 41.70; H: 3.50; N: 7.20, found C: 41.43; H: 3.31; N: 7.38.

RESULTS AND DISCUSSION

The iron complex was obtained as dark purple powder while [Mn_3(Tren5BrSal)$_2$] was found to be of yellow color. Both complexes are highly stable with respect to heat as their decomposition temperature is above 250^0C, see Table 1.Table 1: Physical Measurements of the complexes

Table 1: Physical Measurements of the Complexes

Compounds	Colour	% Yield	M.P/ Decomp. Temp.(^{o}C)	Molar conductance (S/cm^{-1}) at 25^{0}C
($C_{27}H_{27}O_3N_4Br_3$)	Yellow	88	145.7	0.002
[Fe_3(Tren5BrSal)$_2$]	Dark-purple	68	309	0.03
[Mn_3(Tren5BrSal)$_2$]	Yellow	72	282	0.01

Table 2: Solubility Studies in Different Solvents

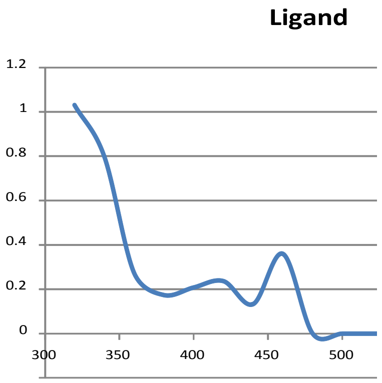
Compound	Ethanol	Chloroform	Benzene	Diethylether	n-hexane	Acetone	Distilled water
($C_{27}H_{27}O_3N_4Br_3$)	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble
[Fe_3(Tren5BrSal)$_2$]	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble
[Mn_3(Tren5BrSal)$_2$]	Soluble	Soluble	Soluble	Insoluble	Insoluble	Soluble	Insoluble

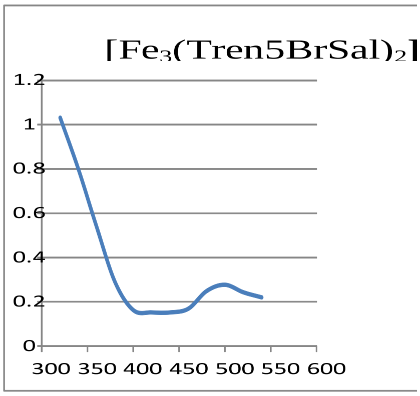
Conductance measurement on the complexes reveals low values. This low values of molar conductivity (Siemens) recorded indicate the absence of electrolytes in all the complexes and confirm the complexes neutrality. In addition, the compounds solubility in various organic solvents are shown in Table 2 and all the compounds are insoluble in distilled water, which indicates the covalent nature of the compounds.

The Electronic spectra

The spectrum of the free ligand show a band at λ_{max} 420nm and 460nm which is attributed to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transition.

The intense dark-purple color of [Fe_3(Tren5brSal)$_2$] complex, showed a band at λ_{max} 490nm which are attributed to charge transfer and electronic transition that took place as a result of complexation. However, the yellowish-brown [Mn_3(Tren5BrSal)$_2$] complex showed absorption band at 480nm which are also attributed to charge transfer and electronic transition in the complex formation.





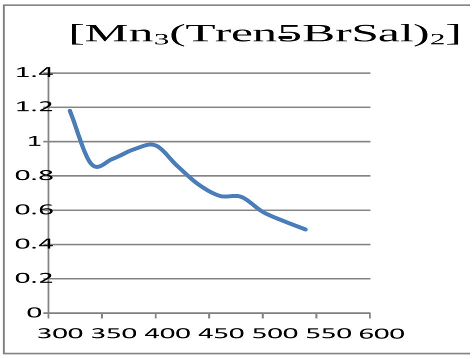


Figure 1c

Fig 1 a,b,c: UV-Visible Spectrum for ligand and the two complexes

Table 3: Characteristic Bands of Infrared Spectra of the Ligand and their Complexes

Compound	(C-OH)	(C=N)	(C-H)aromatic	(C=C)aromatic
($C_{27}H_{27}O_3N_4Br_3$)	3462	1600	3062	1500
[Fe_3(Tren5BrSal)$_2$]	_	1592	3053	1482
[Mn_3(Tren5BrSal)$_2$]	_	1594	3052	1482

Infrared Spectral studies

The characteristic vibrations and assignment of the Schiff base ligand and its complexes with Fe(II) and Mn(II) are described in Table 3.

The spectrum of the ligand exhibit broad band at 3462 cm^{-1} which was assigned to (OH) stretching vibration while the band that appear at 3062 cm^{-1} in the spectra is attributed to the C-H aromatic stretching vibration [Kanesato *et al.*, 2001]. The vibration bands for C=N stretching appears at 1600 cm^{-1} and C=C aromatic was observed at and 1500cm^{-1}. The observed value for (C=N) stretching shifted slightly to lower frequency 1594, and 1592 cm^{-1} for [Fe_3(Tren5brSal)$_2$] and [Mn_3(Tren5brSal)$_2$] complexes respectively, due to coordination with metal. The disappearing of band for (OH) vibration in the spectra of the complexes indicates the coordination of phenolic oxygen with metal ions.

The infrared of the complexes showed weak bands in the range (509-511) cm^{-1} and (425-430) cm^{-1} which was attributed to the stretching vibration of (M-N) and (M-O) respectively.

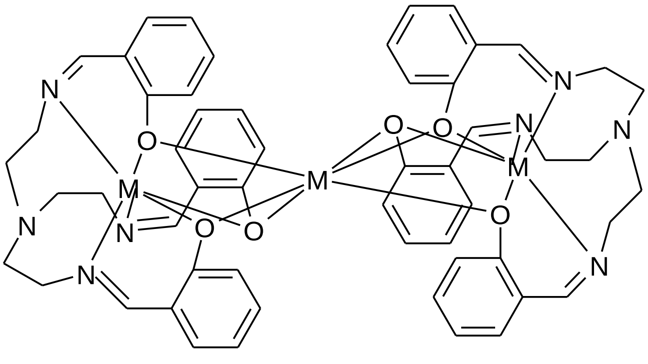


Figure 2: The proposed trimetallic structure of the metal complexes (M=Fe or Mn) [Mustapha *et al.*, 2008]

The mass spectra and elemental analysis recorded for the complexes confirm the formation of the structure depicted above. The two metal ions are sitting in the core center of the ligand which are coordinated *via* three azomethine nitrogen atoms and three phenolic oxygen atoms revealing an octahedral arrangement, while the two monometallic complexes having one residual charge, each complex is 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. This type of arrangement is previously reported by Mustapha *et al.*, 2008, where a trimetallic nickel assume the depicted structure above as it is characterized using x-ray crystallography analysis.

CONCLUSION

We have successfully synthesized trimetallic complexes using potentially (N4O3) heptadentate ligand. The complexes were neutral as revealed by the conductivity measurement. However, magnetic measurement was not conducted on the complexes, as such the measurement could unfold the potentiality of these complexes in the area of single molecule magnet (SMM).

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