American Journal of Chemistry 2014, 4(3): 97-100
DOI: 10.5923/j.chemistry.20140403.02

N_4O_3 Potentially Heptadentate Schiff Base Ligand in the Synthesis of d/f Trimetallic Metal Complexes

Abdullahi Mustapha[1,*], **Suleiman Musa Gani**[2], **Muhammad Saleh Salga**[2]

[1]Department Of Chemistry, Federal University Dutse, PMB 7156, Jigawa State
[2]Department of Pure and Industrial Chemistry, Umaru Musa Yar'adua University Katsina

Abstract Potentially heptadentate (N_4O_3) tripodal Schiff-base ligand: tris(5-Bromo-2-hydroxybenzylaminoethyl)amine (TrenSal) 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. Three new heteronuclear trimetallic complexes ware prepared by complexing monometallic (Mn^{II}), (Fe^{II}), and (Co^{II}) with lanthanum (La^{III}) metal ion to produce complexes the following complexes $[LaCo_2(Tren5BrSal)_2]Cl$, $[LaMn_2(Tren5BrSal)_2]Cl$ and $[LaFe_2(Tren5BrSal)_2]Cl$.

Keywords Trimetallic, Schiff base, Heptadentate, Lanthanum

1. Introduction

Several studies showed that the presence of a lone pair of electrons in the Sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance [1, 2]. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents [2, 4, 5, 6] especially when a functional group like –OH or –SH is present close to the azomethine group so as to form a five or six membered ring with the metal ion. Versatility of Schiff base ligands and biological, analytical and industrial applications of their complexes make further investigations in this area highly desirable [7].

Multidentate salicylidene Schiff base (N_4O_3) ligands have been chosen for study, due to the ligand ability to encapsulate metal cations in such a manner that the three terminal phenoxide donors assemble into a secondary binding motif to form six ring coordinating size. 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 [8].

Recently, the scope of this research was extended to the construction of oligometallic lanthanide complexes and mixed lanthanide/transition metal ion arrays. In this latter work the coaggregation of nickel (Ni^{II}) and lanthanide (Ln^{III}) metal ions in the presence of a tripodal amine phenol ligand, H^{3-}tam [1,1,1-tris (((2`-hydroxybenzyl) amino) methyl) ethane], provided a series of $LnNi_2$ trinuclear complexes that were characterized in terms of their crystal structures and magnetic properties [9]. The synthesis and physical characterization of a series of lanthanide (Ln^{III}) and nickel (Ni^{II}) mixed trimetallic complexes with the heptadentate (N_4O_3) ([tris(2`-hydroxybenzylaminoethyl)amine]) amine phenol ligand has been accomplished [10].

Investigations concerning the structural and chemical properties of polynuclear transition-metal compounds are receiving increasing interest. The area has important implications for topics such as the nature of orbital interaction, electron transfer in redox reaction processes, and biological electron-transport chains. Trinuclear copper clusters have been found at the active sites of multicopper blue oxidases such as ascorbate oxidase, laccase and ceruloplasmin [11].

In this paper we report the synthesis of 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) or Cobalt (II) and Lanthanum(III) metal salt, in the ratio of 2:2:1.

2. Experimental

All experiments were carried out using standard apparatus and the chemicals were of commercial quality and were used without further purification. The IR was measured on a Bruker 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 decomposition temperature

---

* Corresponding author:
abmustapha2004@yahoo.com (Abdullahi Mustapha)

was obtained using capillary tube and molar conductance of 10^{-3}M was determined at room temperature. Elemental analysis and mass spectra were run at Al-azhar University Cairo Egypt.

Preparation of Tren5BrSal

Tris(2-aminoethyl)amine (1.46g, 10mmol) was added to a solution of 5-bromosalicylaldehyde (6.03g, 30mmol) in 100ml ethanol. The resulting solution was refluxed for 40mins. A yellow powdered solid was precipitated upon cooling for 24h. The product was filtered off, washed with ethanol, and allowed to air dried. Yield 77.7% [8].

Synthesis of [Co2(Tren5BrSal)2La]Cl

Tren5BrSal (1.0g, 1.4mmol) was dissolved in ethanol (50ml) followed by addition of $CoCl_2.6H_2O$ (0.342g, 1.4mmol) in ethanol (10ml). The mixture was stirred after which few drops of triethylamine was added. $LaCl_3.7H_2O$ (0.267g, 0.7mmol) in ethanol (10ml) was also added. The solution was refluxed 60 minutes. A shiny dark green solid was obtained from the filtrate when allowed to air dry. Yield 63%, [12].

Synthesis of [Fe2(Tren5BrSal)2La]Cl

Tren5BrSal (1.0g, 1.4mmol) was dissolved in ethanol (50ml) followed by addition of $FeCl_3.6H_2O$ (0.389g, 1.4mmol) in ethanol (10ml). The mixture was stirred after which few drops of triethylamine were added followed by addition of $LaCl_3.7H_2O$ (0.267g, 0.7mmol) in 10ml ethanol. The solution was refluxed for 60 minutes and was allowed to cool over night. The dark purple Solid was filtered off and allowed to air-dry. Yield 71%.

Synthesis of [Mn2(TrenSal)2La]Cl

Trensal (1.0g, 1.4mmol) was dissolved in ethanol (50ml) followed by addition of $MnCl_2.4H_2O$ (0.285g, 1.4mmol) in 10ml ethanol. The mixture was stirred after which few drops of triethylamine was added. $LaCl_3.7H_2O$ (0.267g, 0.7mmol) in 10ml ethanol was also added. The solution was refluxed for 60 minutes. The resulting solution was allowed to cool over night. The grey-yellow Solid was filtered off and allowed to air-dry. Yield 52%.

3. Results and Discussion

The cobolt-lantanum complex was obtained as dark green solid, $[LaFe_2(Trensal)_2]^+$ was obtained as dark purple solid while $[LaMn_2(TrenSal)_2]^+$ was found to be of grey-yellow color. All the complexes showed certain level of stability with respect to heat as their decomposition temperature is above 200℃, see table 1.

Conductance measurement on the complexes revealed low values. This low values of molar conductivity (Ω) 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 and soluble in some organic solvents which indicates the covalent nature of the compounds.

The Electronic spectra

The spectrum of the free ligand show a band at λ_{max} 380nm and 420nm which is attributed to ($\pi \longrightarrow \pi^*$) and ($n \longrightarrow \pi$) transition

The intense greenish-black color of $[Co_2(TrenSal)_2La]^+$ complex, showed a strong band at λ_{max} 610nm and another band with low intensity at λ_{max} 580nm which are attributed to charge transfer and electronic transition that took place as a result of complexation. The dark purple $[Fe_2(TrenSal)_2La]^+$ complex shows an absorption band at λ_{max} 530nm. However, the grey-yellow $[Mn_2(Tren5BrSal)_2La]^+$ complex showed a strong absorption band at 540nm and another band at λ_{max} 360nm which are also attributed to charge transfer and electronic transition in the complex formation.

Infrared Spectral studies

The characteristic vibrations and assignment of the Schiff base ligand and its complexes with La-Co, La-Fe and La-Mn are described in table 3.

The spectrum of the ligand exhibit broad band at 3400 cm^{-1} which was assigned to (OH) stretching vibration while the band that appear in the range (3057-3053) cm^{-1} in the spectra is attributed to the C-H aromatic stretching vibration [13]. The vibration bands for C=N stretching appears in the range (1632-1591) cm^{-1} and C=C aromatic was observed at (1464-1452) cm^{-1}. The observed value for (C=N) stretching shifted slightly to lower frequency 1628, 1593, and 1591 cm^{-1} for $[Mn_2(Tren5BrSal)_2La]$, $[Fe_2(Tren5BrSal)_2La]$ and $[Co_2(Tren5BrSal)_2La]$ complexes respectively, due to coordination with the metal ion. The disappearance of the broad band for (OH) vibration in the spectra of the complexes indicates the coordination of phenolic oxygen with metal ions [8].

The infrared of the complexes also 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 which are absent in the ligand.

Table 1. Physical Measurements

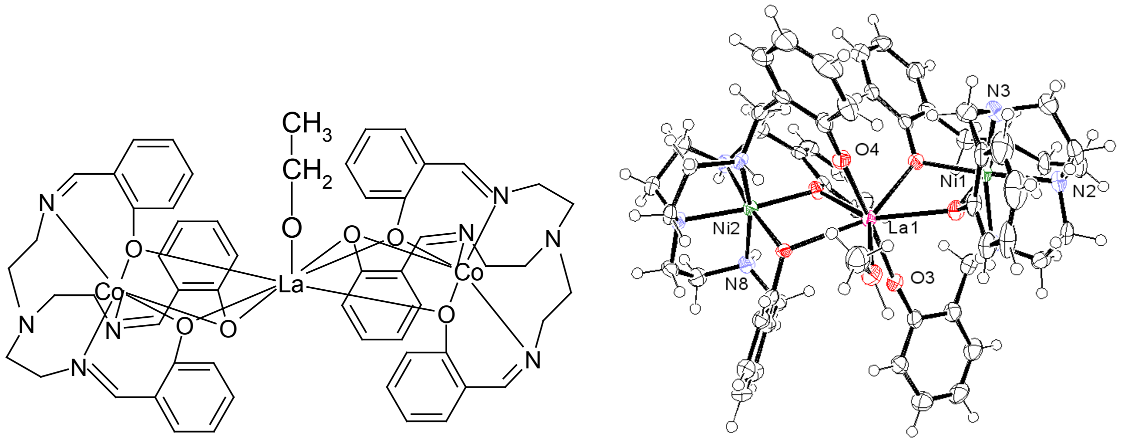
Compounds	Colour	Molar weight	M.P/ Decomp Temp.(°C)	Conductance (S/cm)
Tren5BrSal ($C_{27}H_{27}O_3N_4Br_3$)	Yellow	695.24	144.3	0.002
$[LaCo_2(Tren5BrSal)_2]Cl$	Greenish-black	1641.22	224	0.208
$[LaFe_2(Tren5BrSal)_2]Cl$	Dark purple	1635.04	227	0.140
$[LaMn_2(Tren5BrSal)_2]Cl$	Grey-yellow	1633.22	218.7	0.132

Table 2. Showing elemental analysis and mass spectra results

Compound	%C cal. (found)	%H cal. (found)	%N cal. (found)	m/z
$C_{27}H_{27}O_3N_4Br_3$	46.65 (46.84)	3.91 (3.97)	8.09 (6.98)	691 (100%)
$LaCo_2C_{54}H_{48}O_9N_9Br_6Cl$	37.30 (37.64)	2.78 (2.91)	7.25 (7.08)	1703 (31%)
$LaFe_2C_{54}H_{48}O_9N_9Br_6Cl$	37.44 (37.11)	2.79 (3.02)	7.28 (6.98)	1697 (20%)
$LaMn_2C_{54}H_{48}O_9N_9Br_6Cl$	37.48 (37.84)	2.80 (3.01)	7.28 (7.33)	1695 (11%)

Table 3. The Characteristic bands of Infrared Spectra of the ligand and its Complexes

Compound	(C-OH)	(C=N)	(C-H)aromatic	(C=C)aromatic
($C_{27}H_{27}O_3N_4Br_3$)	3400	1632	3054	1464
[$LaCo_2$(Tren5Brsal)$_2$]	_	1591	3057	1452
[$LaFe_2$(Tren5BrSal)$_2$]	_	1593	3053	1460
[$LaMn_2$(Tren5BrSal)$_2$]		1628	3054	1463



a. b.

Figure 1. The proposed mixed trimetallic structure of the [$LaCo_2$(Tren5BrSal)$_2$] [b. 10]

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 (Lanthanum) through three phenolic oxygen from each monometallic complex, a third oxygen came from the solvent [10] making the coordinating environment heptacoordinate on the lanthanum, while on the transition metal it is octahedral. This arrangement revealed that the two adjacent transition metal ions are M^{II} while the lanthanum is M^{III}. With this arrangement, the complex carries +1 charge which is counter balanced by chloride ion ([$La^{III}M_2^{II}$(Tren5BrSal)$_2$]Cl). This type of arrangement is previously reported by Simon *et al.,* 2003, where a mixed trimetallic Ni/Ln assumed the depicted structure above as it is characterized using x-ray crystallography analysis.

4. Conclusions

We have successfully synthesized mixed trimetallic complexes using potentially (N4O3) heptadentate ligand. The complexes could not dominate the mass spectra (100%) due to its larger size, as such it is not the dominant peak. Further study on the complexes would be look into with regards to its magnetic property.

REFERENCES

[1] Elmali, A. Kabak, M. and Elerman, Y. (2000): Schiff Base compounds and Their Biological Application. *Journal of Molecular Structure.* 151: 447.

[2] Patel, P. R., Thaker, B. T. and Zele, S. (1999): Medicinal Chemistry of Schiff Base Complexes. *Indian Journal of Chemistry.* 38A: 563.

[3] Patel, S. (1970): The Chemistry of the Carbon-Nitrogen Double Bond", *Journal of Wiley & Sons*. London.

[4] Jungreis, E. and Thabet, S. S. (1969): Analytical Applications of Schiff bases. *Marcell Dekker*. New York.

[5] Metzler, C. M., Cahill, A. and Metzler D. E. (1980): *Journal of American Chemical Society*. 102: 6075.

[6] Dudek, G. O. and Dudek, E. P. (1965): Chemistry of Schiff Bases. *Chemistry Communi*cation. 464.

[7] Ashraf, M.A., Mahmood, K., and Wajid A. (2011): Synthesis, Characterization and Biological Activity of Schiff Bases. *International Conference on Chemistry and Chemical Process*. 10: 1-7.

[8] Mustapha, A., Busch, K., Patykiewicz, M., Apedaile, A., Reglinski, J., Kennedy, A.R., and Prior, T.J. (2008): Multidentate ligands for the synthesis of multi-metallic complexes. *Polyhedron* 27: 868–8.

[9] Simon, R.B., Xu, Z., Patrick, B.O., Rettig, S.J., Pink, M., Thompson, R.C., and Orvig, C. (2003): Different Complexes with Uniform Coordination Geometry, Structural and Magnetic Properties of an $LnNi_2$ Core Supported by a Heptadentate Amine Phenol Ligand. *Inorganic Chem*istry 42: 1576-1583.

[10] Mustapha, A., Reglinski, J., and Kennedy, A.R. (2009): The use of hydrogenated Schiff base ligands in the synthesis of multi-metallic compounds. *Inorganica Chimica Acta* 362: 1267–1274.

[11] Bailey, N.A., Fenton, D.E., He, Q., Terry, N., Haase, W. and Werner R. (1995): Linear Trinuclear Copper (II) Complexes derived from Acyclic Hexadentate Schiff Base Ligangs. *Inorganic Chimica Acta.* 273-279.

[12] Mustapha, A., Busche, C., Reglinski, J., and Kennedy, A.R. (2011): The Use of Hydrogenated Schiff Base Ligands in the Synthesis of Multi-metallic Compounds II. *Polyhedron.* 30: 1530-153.

[13] Kanesato M., Ngassapa F. N., and Yokoyama T., (2000) Crystal Structure of Tris(((5- chlorosalicylidene) amino)ethyl) amine *Analytical Sciences*, 16(7), 781.