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ZIRCONIUM (IV) COMPLEXES WITH SOME POLYMETHYLENEDIIMINES

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ABSTRACT
The syntheses of zirconium (IV) complexes have been carried out by the reaction of oxozirconium (IV) chloride with the appropriate diimines (Schiff bases). The complexes were isolated as yellow solids which are stable to heat. The complexes were found to be insoluble in most solvents. The infrared spectra, elemental analysis and other properties suggest that the complexes are six coordinate. The schiff bases were isolated as yellow crystals with sharp melting points on refluxing 2 – hydroxyl -1- benzaldehyde and the appropriate diamines in methanol.

Keywords: Complexes, crystals, decomposition, characterization and condensation.

INTRODUCTION

Schiff bases (diimines) are compounds formed by condensation of primary amines with carbonyl compounds. The bases usually act as ligands because of the presence of – N and – O donor atoms. Schiff base complexes are useful in biochemistry (Ayodele *et al.*, 2005), drugs (Hodnett and Mooney, 1970) and as catalyst in many biological processes (Bello, 2008). Metal Schiff base complexes have been known for decades from the work of Ettling in 1840 and pfiffer in 1933 (kolawole, 1979 and Bello, 2008). Many researches have been conducted on Schiff base complexes (Claudio and shaqif, 2006; Alev *et al.*, 2004). Most of these complexes were found to be biologically active.

As there has been considerable interest in the study of first row transition metal schiff base complexes however, relatively less work has appeared on the complexes of 2nd and 3rd rows transition metal ions. There is not much information on zirconium (IV) complexes from the available literature, therefore this paper reports the synthesis and partial characterization of zirconium (IV) complexes of Schiff bases (polymethylenediimines) derived from salicylaldehydes and diamines.

MATERIALS AND METHODS

All the chemicals and solvents which were of analytical grade were obtained from Aldrich and were used directly without further purification. However, the 2-hydroxy-1-benzaldehyde (Salicylaldehyde) was distilled under reduced pressure (Vogel, 1961).

Preparation of the Schiff Bases (POLYMETHYLENEDIIMINES)

The Schiff base ligands were prepared by refluxing 2-hydroxy-1-benzaldehyde (0.2 mol) and the corresponding aliphatic diamine (0.1 mol) in about 60 cm^3 methanol for 15 minutes. The diamines used include ethylenediamine, tetramethylenediamine and hexamethylenediamine respectively. The Schiff bases (polymethylenediimines) separated as yellow needles on cooling the reaction mixture. The crystals were recrystallized from methanol. The crystals were filtered, dried in a desiccator over phosphorus(v) oxide and yield recorded. The melting points of the ligands were determined using Gallenkamp melting apparatus and are found to within the range 72 - 125^oC.

Preparation of Zirconium Complexes

The complexes were prepared by treating oxozirconium (IV) chloride (0.003 mol) in methanol with the corresponding polymethylenediimine (ligand) (0,003 mol) in the same solvent. The mixture was refluxed for three hours on a water bath after which the crystals of the complex separate out on cooling and where there was no crystallization; the mixture was concentrated on a steam bath until about one-third of the solution remained. The concentrated solution was cooled after which the crystal were filtered, washed with methanol and then dried in vacuum. The complexes were analysed for zirconium (Mendham *et al.,* 2000) and chlorine (Vishnoi, 1979). The yield, decomposition temperature and solubility test in various solvent were determined for each of the complex. Also the infrared analyses of the complexes were carried out using potassium bromide pellets.

RESULTS AND DISCUSSION

The polymethylenediimines were obtained as yellow crystals with sharp melting points (Table 1) and soluble in most solvents except water (Table 3). The colour is associated with the presence of chromophoric group, - C = N. The yellow colour is retained in the complexes due to the presence of the same groups bound to zirconium ion. The complexes decomposed without melting and the temperature decreases with increase in the methylene chain length (Table 2) as a result of steric factor. The insolubility of the complexes (Table 4) might be associated with the structure of the complexes and on the nature of the solvents.

The infrared bands of the ligands (Table 5) showed 1630 – 1640 cm^{-1} and were assigned to C = N and also at 1250 - 1305 cm^{-1} assigned to C – O.

However, the position of C – N band of the Schiff base is very little changed on coordination of the metal to the nitrogen, (Table 6). The assignment is similar to the value of 1615 cm^{-1} assigned to C = N in N, N-bis(salicylidene) -1- (Dimethyl)ethylenediamine as reported by Patel and Blair (Patel and Blair, 1974). The broad band 2600 to 2720 cm^{-1} assigned to OH in the ligands (Table 5) which is absent in the spectra of the complexes (Table 6) indicates complexation has taken place between the ligands and zirconium ion. The shift in the C – O band from 1250 – 1305 cm^{-1} region to 1300 to 1330 cm^{-1} in the complexes also indicates that hydroxyl groups of the ligands are involved in the bond formation as established by Nakamato *et al* (Nakamoto *et al.,* 1970).

CONCLUSION

The synthesis of polymethylene complexes of zirconium (IV} was achieved from the characterization and qualitative analysis data of the complexes. Therefore the catalytic, antifungal, antibacterial activities of the complexes could be studied.

Table 1: Yield, colour and melting point of the ligands

Ligand	Colour	Melting point(^oC)	Yield(%)
H_2Sal_2-en	Yellow	125	73.65
H_2Sal_2-tm	Yellow	91	68.73
H_2Sal_2-hxm	Yellow	72	79.83

Table 2: Yield, colour and decomposition temperature of the complexes

Complexes	Colour	Melting point(^oC)	Yield(%)
$[Zr(Sal_2\text{-en})]Cl_2$	Yellow	235	50.85
$[Zr(Sal_2\text{-tm})]Cl_2$	Yellow	210	95.3
$[Zr(Sal_2\text{-hxm})]Cl_2$	Yellow	203	81.88

Table 3: solubility of the ligands

Solvent	H_2Sal_2-en	H_2Sal_2-tm	H_2Sal_2-hxm
Water	IS	IS	IS
Methanol	SH	SH	SH
Ethanol	SH	S	S
Carbon tetrachloride	SH	S	S
Trichloromethane	S	S	S
Dichloromethane	S	S	S
Dimethylformamide	S	S	S
Dimethylsulfoxide	S	SH	SH
Nitrobenzene	S	S	S
Acetonitrile	S	S	S
Ether	SH	SH	S

S: Soluble SH: Soluble on heating IS: Insoluble

Table 4: solubility of the complexes

Solvent	$[Zr(Sal_2\text{-en})]Cl_2$	$[Zr(Sal_2\text{-tm})]Cl_2$	$[Zr(Sal_2\text{-hxm})]Cl_2$
Water	IS	IS	IS
Methanol	SSH	SSH	SSH
Ethanol	SH	S	S
Carbon tetrachloride	IS	IS	IS
Trichloromethane	IS	IS	IS
Dichloromethane	IS	IS	IS
Dimethylformamide	IS	IS	IS
Dimethylsulfoxide	SSH	SSH	SSH
Nitrobenzene	IS	IS	IS
Acetonitrile	IS	IS	IS
Ether	IS	IS	IS

SSH: Slightly soluble on heating IS: Insoluble

Table 5: Infrared spectra of ligands

Ligand	v(C – H)/cm^3	v(OH.....N) /cm^{-1}	v(C = N) /cm^{-1}	v(C – O) /cm^{-1}
H_2Sal_2-en	2966	2600	1630	1250
H_2Sal_2-tm	2960	2670	1630	1305
H_2Sal_2-hxm	2960	2720	1640	1275

Table 6: Infrared spectra of complexes

Complex	v(C – H) /cm^{-1}	v(OH.....N) /cm^{-1}	v(C = N) /cm^{-1}	v(C – O) /cm^{-1}
$[ZrSal_2\text{-en}]Cl_2$	2956	-	1615	1330
$[ZrSal_2\text{-tm}]Cl_2$	2960	-	1610	1330
$[ZrSal_2\text{-hxm}]Cl_2$	2980	-	1630	1300

REFERENCES

Alev, D., Iffect, S. and Esma, K. (2004). Potentiometric studies on some ɑ – amino acid Schiff bases and their manganese (II) complexes. J of soln. chem. 33(12): 1539 – 1547.

Bello I. (2008). Synthesis and characterization of Cu(II) complexes with some Schiff bases.Unpublished M. Sc. dissertation, Department of Pure and Industrial Chemistry, Bayero University, Kano.

Claudio, C. H. and Shafiq, Z. (2006). Invivo antibacterial and antifungal agents; Metal based synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes with amino acid – derivrd compound. App. Organo metal chem.. 21:294 – 302.

Cotton, F. A. and Wilkinson G. (1994). Advanced inorganic chemistry. Interscience. New York third edition Pp 624.

Hodnett, E. M. and Mooney, P. D. (1970). Biological activity of complexes. J. of medicinal chem.. 13: 786.

Nakamoto, N., Udovinch, C. and Takamato, N. (1970). Metal isotope effect on metal – Ligand vibrations of metal complexes of acetylacetone. J. Am. Chem. Soc. 92: 3973 – 3976.

Patel, K. S. and Blair, J. C. (1974). Infrared spectra of N,N-bis(Salicylidene)-1,1-(Dimethyl)ethylenediamine and its metal complexes. J. Inorg. Nucl. Chem. 34:1547.

Vishnoi, N. K. (1979). Advanced practical organic chemistry.Vikas pub. House India Pp 421.

Vogel, A. L.(1961). Textbook of quantitative inorganic analysis, 3rd edition, Longmans, London. Pp 546-548.

Mendaham, J., Denney, R. C., Barnes, J. D. and Thomas, M. J. K. (2000). Vogel's Textbook of quantitative chemical analysis, 6th edition, Pearson Education, Pp 494 - 501