

Template Synthesis of Oxozirconium(IV) Complexes with Tetraaza 16- and 18-Membered Macrocyclic Ligands

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The macrocyclic complexes of types $[\text{ZrO}(\text{mac})\text{H}_2\text{O}]\text{Cl}_2$ or $[\text{Zr}(\text{OH})_2(\text{mac})]\text{Cl}_2$ (where mac = macrocyclic ligands derived by condensation of diamines with β -diketones) have been synthesized by an *in situ* method where the metal cation acts as a template. The isolated complexes have been characterized on the basis of elemental analyses, electrical conductance and infrared spectral data. The oxozirconium(IV) complexes are six-coordinate. The tetraaza macrocyclic ligands are coordinated to the metal ion through four azomethine nitrogen atoms.

INTRODUCTION

Various metal cations have been used as template in the syntheses of complexes containing macrocyclic ligands with four nitrogen donor atoms¹⁻⁴. The study of such complexes where four nitrogen atoms are coordinated to the central metal ion in the planar fashion is of great importance because naturally occurring systems like heme, chlorophyll etc. have essentially tetraaza macrocyclic ligands around the central metal ion^{1,4}. However, the use of oxozirconium(IV) cation as template in the synthesis of tetraaza macrocyclic complexes is scarcely documented^{5,6}. Further, the zirconium(IV) complexes have been found to catalyse the reduction of unsaturated substrates by H_2 .^{7,8} Thus, keeping in view the above aspects, a new series of the complexes of oxozirconium(IV) with tetraaza macrocyclic ligands derived by condensation of 1,3-propanediamine or 1,4-butanediamine with different β -diketones, viz., acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane have been synthesized and characterized.

EXPERIMENTAL

1,3-Propanediamine was distilled before use whereas 1,4-butanediamine, obtained from Fluka, was used as supplied. All the solvents used were reagent grade B.D.H. products.

***In situ* Preparation of the Oxozirconium(IV) Complexes of Tetraaza Macrocyclic Ligands Derived by Condensation of Diamines with β -Diketones, $[\text{ZrO}(\text{mac})\text{H}_2\text{O}]\text{Cl}_2$**

A solution of 1,3-propanediamine or 1,4-butanediamine (0.02 mol) in 20 ml ethanol was mixed with an appropriate β -diketone (0.02 mol) in 20 ml ethanol. To this mixture, an aqueous solution (20 ml) of zirconylchloride (3.22 g, 0.01 mol) was added followed by addition of glacial acetic acid (5.0 ml) and a light brown precipitate was obtained. The reaction mixture was refluxed for 4 hrs when the colour of the reaction mixture intensified. The solvent was removed *in vacuo* and solid products were obtained. The complexes were thoroughly washed with ether and were crystallized from methanol (10 ml) (yield *ca.* 42–54%). The colour, decomposition temperature and analytical data of the complexes are given in Table 1.

TABLE 1
PHYSICAL AND ANALYTICAL DATA OF THE COMPLEXES

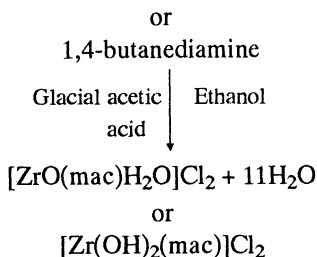
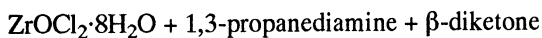
Complex	Decomp. temp. ($^{\circ}\text{C}$)	Calc. (Found)%			
		C	H	N	Zr
$[\text{ZrO}(\text{mac}^1)\text{H}_2\text{O}]\text{Cl}_2$ Brown ($\text{C}_{30}\text{H}_{30}\text{N}_4\text{O}_2\text{Cl}_2\text{Zr}$)	160	40.7 (40.5)	6.4 (6.3)	11.9 (11.8)	19.3 (19.3)
$[\text{ZrO}(\text{mac}^2)\text{H}_2\text{O}]\text{Cl}_2$ Brown ($\text{C}_{26}\text{H}_{34}\text{N}_4\text{O}_2\text{Cl}_2\text{Zr}$)	168	52.3 (52.2)	5.7 (5.6)	9.4 (9.3)	15.3 (15.1)
$[\text{ZrO}(\text{mac}^3)\text{H}_2\text{O}]\text{Cl}_2$ Reddish brown ($\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_2\text{Cl}_2\text{F}_6\text{S}_2\text{Zr}$)	178	36.9 (36.9)	3.4 (3.2)	7.8 (7.7)	12.7 (12.6)
$[\text{ZrO}(\text{mac}^4)\text{H}_2\text{O}]\text{Cl}_2$ Light brown ($\text{C}_{36}\text{H}_{38}\text{N}_4\text{O}_2\text{Cl}_2\text{Zr}$)	162	60.0 (59.8)	5.3 (5.1)	7.8 (7.6)	12.7 (12.7)
$[\text{ZrO}(\text{mac}^5)\text{H}_2\text{O}]\text{Cl}_2$ Brown ($\text{C}_{18}\text{H}_{34}\text{N}_4\text{O}_2\text{Cl}_2\text{Zr}$)	164	43.2 (43.0)	6.8 (6.8)	11.2 (11.0)	18.2 (18.0)
$[\text{ZrO}(\text{mac}^6)\text{H}_2\text{O}]\text{Cl}_2$ Brown ($\text{C}_{28}\text{H}_{38}\text{N}_4\text{O}_2\text{Cl}_2\text{Zr}$)	166	53.8 (53.7)	6.1 (6.0)	9.0 (8.9)	14.6 (14.6)
$[\text{ZrO}(\text{mac}^7)\text{H}_2\text{O}]\text{Cl}_2$ Dark Brown ($\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_2\text{Cl}_2\text{F}_6\text{S}_2\text{Zr}$)	180	38.7 (38.6)	3.8 (3.8)	7.5 (7.4)	12.3 (12.2)
$[\text{ZrO}(\text{mac}^8)\text{H}_2\text{O}]\text{Cl}_2$ Brown ($\text{C}_{38}\text{H}_{42}\text{N}_4\text{O}_2\text{Cl}_2\text{Zr}$)	156	60.9 (60.8)	5.6 (5.5)	7.5 (7.5)	12.9 (12.9)

where mac^1 to mac^4 are 16-membered macrocyclic ligands derived by condensation of 1,3-propanediamine with acetylacetone or benzoylacetone or thenoyltrifluoroacetone or dibenzoylmethane and mac^5 to mac^8 are 18-membered macrocyclic ligands derived by condensation of 1, 4-butanediamine with the same β -diketones respectively.

RESULTS AND DISCUSSION

The macrocyclic complexes of oxozirconium(IV) were synthesized using an *in situ* method by refluxing the reaction mixture containing zirconyl chloride,

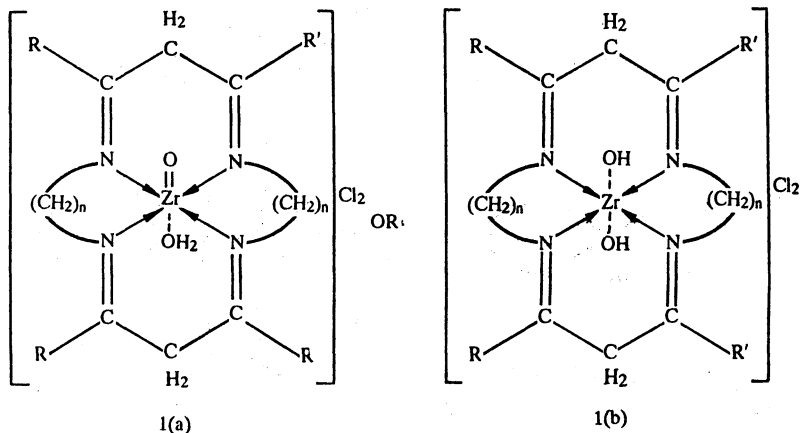
diamine, β -diketone in 1 : 2 : 2 molar ratio in aqueous ethanol in the presence of glacial acetic acid. The reactions appear to proceed according to the following equation:



where mac = tetraaza macrocyclic ligands derived from condensation of 1,3-propanediamine or 1,4-butanediamine with different β -diketones. The elemental analyses (Table 1) of the complexes show 1 : 1 metal to ligand stoichiometry. The conductance measurement for oxozirconium(IV) complexes in methanol show an electrolytic nature.

The macrocyclic complexes of oxozirconium(IV) exhibit the $>\text{C}=\text{N}$ absorption around $1620\text{--}1610\text{ cm}^{-1}$, which normally appears at 1660 cm^{-1} in the free ligands⁹⁻¹¹. The lowering of this band in the complexes indicates the coordination of the nitrogen atoms of the azomethine groups to the zirconium⁹⁻¹¹. The presence of band at around $400\text{--}410\text{ cm}^{-1}$ may be assigned to the $\nu(\text{Zr-N})$ vibration¹². The appearance of the $>\text{C}=\text{N}$ band and the absence of the $>\text{C}=\text{O}$ band at around 1700 cm^{-1} is conclusive evidence for the condensation of the diamines with the β -diketones¹¹. A large number of bands also arise due to phenyl rings and different alkyl groups, but definite assignments of these bands are not possible due to the complexity of the spectrum arising out of the overlap of the these absorptions. The oxozirconium(IV) complexes show bands at *ca.* 3480 cm^{-1} which are assigned to the $\nu(\text{OH})$ vibration¹³ of the coordinated water molecule. Further, a weak band at *ca.* 820 cm^{-1} is assigned to the $\nu(\text{Zr}=\text{O})$ vibration¹². However, there is no reliable evidence for the existence of the $(\text{Zr}=\text{O})$ moiety in oxozirconium(IV) complexes. The X-ray structure determination of ' $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ' by Clearfield and Vaughan¹⁴ was a great step forward, since it showed that this salt contained $[\text{Zr}(\text{OH})_2]^{2+}$ or $[\text{Zr}(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ ions in aqueous solution. Hence, the exact composition of the macrocyclic products *i.e.*, whether they are oxozirconium aqua complexes or dihydroxo species can only be ascertained with the help of X-ray studies.

Thus, on the basis of the above studies, the following tentative structure Ia or Ib may be proposed for 16- and 18-membered macrocyclic complexes of oxozirconium(IV).



where $n = 3$ for 16-membered macrocyclic ligands, i.e., mac^1 , mac^2 , mac^3 and mac^4 .
 $n = 4$ for 18-membered macrocyclic ligands, i.e., mac^5 , mac^6 , mac^7 and mac^8 .

and	R	R'	β -diketones	Macrocylic ligands
	CH ₃	CH ₃	acetylaceton	(mac^1), (mac^5)
	C ₆ H ₅	CH ₃	benzoylaceton	(mac^2), (mac^6)
	C ₄ H ₃ S	CF ₃	thenoyltrifluoroacetone	(mac^3), (mac^7)
	C ₆ H ₅	C ₆ H ₅	dibenzoylmethane	(mac^4), (mac^8)

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