

## METAL-SULPHUR, METAL-NITROGEN AND METAL-OXYGEN BONDED COORDINATION COMPOUNDS OF TITANIUM(IV) AND ZIRCONIUM(IV) WITH SULPHUR DONOR KETAMINES AND ALDIMINES

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### ABSTRACT

Reactions of sulphur donor bifunctional tridentate ketamines  $\text{CH}_3\text{COCHCCH}_3\text{NHCH}_2\text{CH}_2\text{SH}$  and  $\text{OC}_6\text{H}_4\text{CCH}_2\text{NHCH}_2\text{CH}_2\text{SH}$  and aldimine  $\text{HOC}_6\text{H}_4\text{CH} : \text{NCH}_2\text{CH}_2\text{SH}$  with Ti(IV) and Zr(IV) isopropoxides in 1 : 1 and 1 : 2 molar ratios have led to products of the types  $\text{M}(\text{OPr}^i)_2(\text{L})$  and  $\text{M}(\text{L})_2$  (where  $\text{M} = \text{Ti(IV)}$  or  $\text{Zr(IV)}$  and  $\text{LH}_2 = \text{ligand molecule}$ ). The labile nature of the isopropoxy groups in the 1 : 1 derivatives has been shown by exchange reactions with 2-methylpentane-2,4-diol ( $\text{C}_6\text{H}_{14}\text{O}_2$ ) in 1 : 1 molar ratio leading to the formation of  $\text{M}(\text{C}_6\text{H}_{14}\text{O}_2)(\text{L})$ . The resulting new derivatives have been characterized on the basis of elemental analyses, molecular weight determinations, conductance measurements and infrared and proton magnetic resonance spectral studies.

### INTRODUCTION

A SURVEY of literature revealed that in the past several years, there has been a growing interest in the study of the various coordination compounds of titanium and zirconium and especially with nitrogen donor ligands including Schiff bases<sup>1-4</sup>. However, similar reactions with sulphur containing ketamines and aldimines are lacking. In view of this, reactions of titanium isopropoxide and zirconium isopropoxide with sulphur donor bifunctional tridentate ketamines and aldimines derived by the condensation of pentane-2,4-dione, 2-hydroxyacetophenone or salicylaldehyde with cystamine have been attempted and the results of these studies are discussed in the present paper.

### EXPERIMENTAL

Adequate precautions were taken to exclude moisture at all stages of the reactions and all glass apparatus fitted with standard quickfit interchangeable joints was used.

#### Materials

Titanium and zirconium isopropoxides were prepared by the ammonia method<sup>5</sup>. Ligands were synthesized by the condensation of ketone/aldehyde with cystamine and purified by distillation under vacuum before use. The analytical data for carbon, hydrogen and nitrogen agreed with the calculated values within the limits of experimental errors.

1. 4-(2-Mercaptoethyl)amino-3-pentene-2-one ( $\text{C}_7\text{H}_{13}\text{NSO}$ ), yellow liquid, B.P.  $95^\circ\text{C}/0.5\text{ mm}$ .
2. N-(2-Mercaptoethyl)-2-hydroxyacetophenonimine ( $\text{C}_{10}\text{H}_{13}\text{NSO}$ ), yellow solid, B.P.  $132-134^\circ\text{C}/0.01\text{ mm}$ .
3. N-(2-Mercaptoethyl)salicylaldimine ( $\text{C}_9\text{H}_{11}\text{NSO}$ ), yellow viscous liquid, B.P.  $69^\circ\text{C}/3.6\text{ mm}$ .

#### Preparation of the Complexes

For the preparation of metal Schiff base complexes, a weighed amount of  $\text{Ti}(\text{OPr}^i)_4$  or  $\text{Zr}(\text{OPr}^i)_4 \cdot \text{Pr}^i\text{OH}$  was taken in anhydrous benzene and the calculated

amount of the ligand added. The mixture was refluxed on a fractionating column and the progress of the reaction was ascertained by the estimation of isopropanol periodically in the azeotrope. The products were dried under reduced pressure and characterised on the basis of elemental analyses.

#### Exchange Reactions

Diisopropoxy metal complexes  $\text{M}(\text{OPr}^i)_2(\text{L})$  were made to react with 2-methylpentane-2,4-diol in 1 : 1 molar ratio in anhydrous benzene and refluxed. In the azeotrope collected during the reaction process, the isopropanol was estimated oxidimetrically. The resulting complexes,  $\text{M}(\text{C}_6\text{H}_{14}\text{O}_2)(\text{L})$ , were dried under reduced pressure and analysed.

#### Physical Measurements

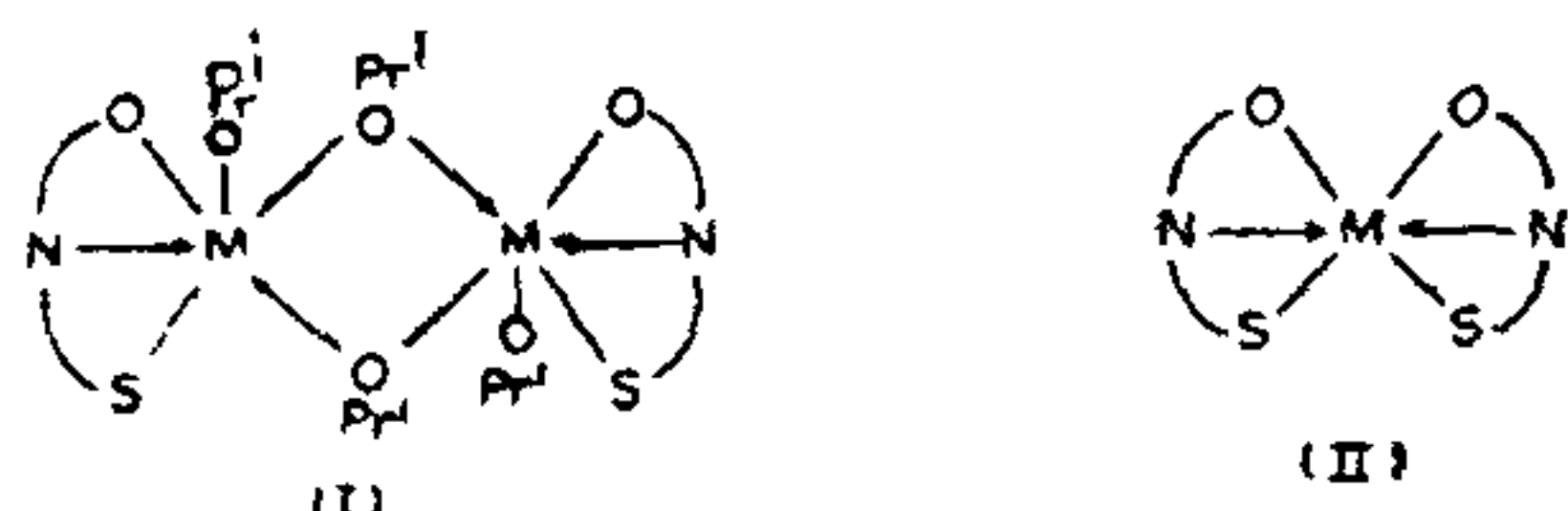
Molecular weights were determined in chloroform with the help of a semi-micro ebulliometer (Gallenkamp) using thermistor sensing. Infrared spectra were recorded as Nujol mulls using a Perkin-Elmer 577 Grating I.R. Spectrophotometer in the range,  $4000-200\text{ cm}^{-1}$  and proton magnetic resonance spectra on a Perkin-Elmer RB-12 Spectrometer in  $\text{CDCl}_3$  using TMS as the internal standard.

Titanium and zirconium were estimated as their oxides, nitrogen by the Kjeldahl's method, sulphur by Messenger's method and isopropanol by oxidimetric method using normal  $\text{K}_2\text{Cr}_2\text{O}_7$  in 12.5% sulphuric acid. The carbon and hydrogen analyses were performed by the micro-analytical laboratory of the Department.

### RESULTS AND DISCUSSION

Several new derivatives of the types  $\text{M}(\text{OPr}^i)_2(\text{L})$  and  $\text{M}(\text{L})_2$  have been synthesized during the present investigations. These are yellow to brown solids, soluble in DMF, DMSO and chloroform and are non-electrolytes in DMF. Compounds containing the isopropoxy groups are highly hydrolysable in the open

atmosphere and decompose on keeping probably due to the weaker M-S bonding as compared to M-O bonding. The molecular weights of these complexes (Table I) in boiling chloroform indicate them to be monomeric (1:2 products) and dimeric (1:1 products). Thus in the resulting derivatives the central metal atoms appear to be in the hexa-coordination state (I and II) as shown below:



(Where M = Ti(IV) or Zr(IV) and  $\text{O} \text{---} \text{N} \text{---} \text{S}$  represents the anion of ligand molecule)

TABLE I  
Molecular weight data of titanium(IV) and zirconium(IV) complexes

Sl. No.	Compound	Molecular Weight	
		Found	Calcd.
1.	Ti(OPr <sup>t</sup> ) <sub>2</sub> (C <sub>7</sub> H <sub>11</sub> ONS)	672.2	323.2
2.	Ti(C <sub>7</sub> H <sub>11</sub> ONS) <sub>2</sub>	374.4	362.5
3.	Ti(OPr <sup>t</sup> ) <sub>2</sub> (C <sub>10</sub> H <sub>11</sub> ONS)	719.2	359.2
4.	Ti(C <sub>10</sub> H <sub>11</sub> ONS) <sub>2</sub>	440.1	434.5
5.	Ti(OPr <sup>t</sup> ) (C <sub>9</sub> H <sub>9</sub> ONS)	720.2	345.1
6.	Ti(C <sub>9</sub> H <sub>9</sub> ONS) <sub>2</sub>	422.0	406.3
7.	Zr(OPr <sup>t</sup> ) <sub>2</sub> (C <sub>7</sub> H <sub>11</sub> ONS)	705.4	366.5
8.	Zr(C <sub>7</sub> H <sub>11</sub> ONS) <sub>2</sub>	415.4	405.8
9.	Zr(OPr <sup>t</sup> ) <sub>2</sub> (C <sub>10</sub> H <sub>11</sub> ONS)	825.3	402.5
10.	Zr(C <sub>10</sub> H <sub>11</sub> ONS) <sub>2</sub>	489.2	477.8
11.	Zr(OPr <sup>t</sup> ) (C <sub>9</sub> H <sub>9</sub> ONS)	790.3	388.4
12.	Zr(C <sub>9</sub> H <sub>9</sub> ONS) <sub>2</sub>	440.3	449.6
13.	Ti(C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> ) (C <sub>7</sub> H <sub>11</sub> ONS)	330.4	321.1
14.	Ti(C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> ) (C <sub>10</sub> H <sub>11</sub> ONS)	349.8	357.2
15.	Ti(C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> ) (C <sub>9</sub> H <sub>9</sub> ONS)	360.3	343.2
16.	Zr(C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> ) (C <sub>7</sub> H <sub>11</sub> ONS)	385.0	364.4
17.	Zr(C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> ) (C <sub>10</sub> H <sub>11</sub> ONS)	390.3	400.5
18.	Zr(C <sub>6</sub> H <sub>12</sub> O <sub>2</sub> ) (C <sub>9</sub> H <sub>9</sub> ONS)	374.9	386.5

The exchange products with 2-methylpentane-2,4-diol are also yellow to brown solids and monomeric in boiling chloroform. These are stable at room temperature in the open atmosphere due to the absence of the isopropoxy groups.

#### Conductance Measurements

Very low molar conductance values for these complexes in dimethylformamide show their non-electrolytic nature,

#### IR Spectra

In the IR spectra of the Schiff bases, broad absorption bands in the region, 3400–3100 cm<sup>-1</sup> are observed and these are due to the hydrogen bonded OH. However, in the spectra of the complexes, these bands disappear indicating the bonding of oxygen to the metal atoms. Further a weak band in ligands in the region, 2580–2540 cm<sup>-1</sup> is observed and this may be assigned to νSH. The disappearance of this band in the titanium and zirconium complexes shows the coordination of sulphur to the metal atoms.

All the three ligands show a medium intensity band at about 1620 cm<sup>-1</sup> and assigned to the νC=N vibrations. In the titanium and zirconium complexes, this band appears at around 1600 cm<sup>-1</sup> and the shift of this band to the lower frequency indicates that the nitrogen of the azomethine linkage gets coordinated to titanium and zirconium atoms.

Several new bands of medium to strong intensity in the regions, 620–580, 550–510 and 360–320 cm<sup>-1</sup> may be assigned to ν(M-O), ν(M-N) and ν(M-S) respectively in view of the previous assignments<sup>6-8</sup>.

#### PMR Spectra

Further, to confirm the bonding in these complexes, the proton magnetic resonance spectra of 4-(2-mercaptoethyl)amino-3-pentane-2-one and its 1:2 titanium complex have been recorded in CDCl<sub>3</sub>. The bonding from the thiolic sulphur of the ligand moiety in the compound is substantiated by the disappearance of the SH proton signal, which is observed in the ligand at δ 2.90 ppm.

The δ 12.33 ppm peak due to hydrogen bonded NH proton of the ligand disappears in the corresponding titanium complex showing the bonding of oxygen as well as nitrogen of the ligand moiety to the central titanium atom.

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