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Titanium(IV) and Zirconium(IV) Derivatives of Tetradentate Schiff Bases

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Summary

Titanium and zirconium isopropoxides react with the tetradentate Schiff bases, bis-salicylaldehyde-*o*-phenylenediimine (SBH_2) and bis-salicylaldehyde-*p*-phenylenediimine ($S'B'H_2$) in anhydrous benzene in 1 : 1 and 1 : 2 molar ratios to give almost quantitative yields of $M(OPr\text{-}i)_2(SB)$ and $M(OPr\text{-}i)_2(SB)(SBH)$, where M = Ti or Zr and $[SB]^{2-}$ is the anion of the corresponding Schiff base, SBH_2. The i.r. spectra of the complexes have been recorded and tentative assignments for C=N and C–O stretching frequencies made.

Introduction

The complexes of titanium tetrachloride and zirconium chloride with a few tetradentate Schiff bases have been reported$^{(1-6)}$. The $Ti(SB)Cl_2$ complex has been prepared by reacting $TiCl_4$ or $TiCl_3 \cdot 3$ THF with $SBH_2$$^{(1, 7)}$, whereas $Zr(SB)Cl_2$ has been prepared by refluxing zirconium chloride with SBH_2 in methanol$^{(6)}$. Tandon *et al.*$^{(8-12)}$ have reacted titanium and zirconium isopropoxides with certain tridentate and tetradentate Schiff bases and reported some interesting properties of the products. However, the reactions of titanium and zirconium alkoxides with the Schiff bases bis-salicylaldehyde-*o*-phenylenediimine (SBH_2) and bis-salicylaldehyde-*p*-phenylenediimine ($S'B'H_2$) do not seem to have been investigated hitherto. In continuation of our work on complexes of metal alkoxides$^{(13-15)}$ with Schiff bases, we report the complexes of titanium and zirconium isopropoxides with Schiff bases, SBH_2 and $S'B'H_2$.

Experimental

Titanium and zirconium isopropoxides were prepared according to the literature methods$^{(16, 17)}$. Benzene (BDH) was dried over sodium wire followed by azeotropic fractionation in presence of EtOH. i-PrOH (BDH) was dried over sodium and then fractionated over $Al(OPr\text{-}i)_3$. The Schiff bases, prepared by the usual methods, were recrystallized from EtOH : $CHCl_3$ mixtures. All reactions were carried out under anhydrous conditions.

Titanium and zirconium were estimated as their dioxides, while nitrogen was determined by the Kjeldahl method. i-PrOH was estimated by an oxidimetric method$^{(18)}$ using M $K_2Cr_2O_7$ in 12.5% H_2SO_4. I.r. spectra were recorded on a Perkin-Elmer 621 spectrometer using KBr pellets.

Reaction of zirconium isopropoxide with bis-salicylaldehyde-p-phenylenediimine (Molar ratio 1 : 1)

Zirconium isopropoxide (1.20 g) and bis-salicylaldehyde-*p*-phenylenediimine (0.98 g) were mixed in C_6H_6 (40 cm^3) and refluxed for 10 h, during which time the C_6H_6 : i-PrOH azeotrope was removed. The remaining C_6H_6 was removed under reduced pressure and a yellow solid was obtained which was washed with hot C_6H_6 (3 × 5 cm^3). Finally, the product was dried at 40°/0.5 mm for 3 h and analysed (Found: N, 5.2; Zr, 17.4. $C_{26}H_{30}O_4Zr$ calcd.: N, 5.4; Zr, 17.4%. i-PrOH in azeotrope: Found: 0.55 g; calcd.: 0.56 g).

All the reactions of titanium and zirconium isopropoxides with tetradentate Schiff bases in 1 : 1 and 1 : 2 molar ratios were carried out using above technique. The synthetic details and analytical data are summarized in Table 1.

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Table 1. Reactions of titanium and zirconium isopropoxide with tetradentate Schiff bases

Reactants Alkoxide (g)	Schiff base	Molar ratio	Reflux time (h)	Product	Characteristics	Amount of i-PrOH (g) in azeotrope. Found (calcd.)	Found (Calcd.)%	
							M	N
$Ti(OPr\text{-}i)_4$ 1.19	SBH_2[a] 1.32	1 : 1	10	$Ti(OPr\text{-}i)_2(SB)$	Brown solid, sparingly soluble in benzene	0.48 (0.50)	10.2 (10.0)	5.6 (5.8)
$Ti(OPr\text{-}i)_4$ 0.73	SBH_2 1.62	1 : 2	12	$Ti(OPr\text{-}i)(SB)(SBH)$	Brown solid, insoluble in benzene	0.43 (0.46)	6.4 (6.5)	7.4 (7.6)
$Ti(OPr\text{-}i)_4$ 1.00	$S'B'H_2$[b] 1.11	1 : 1	10	$Ti(OPr\text{-}i)_2(S'B')$	Light yellow solid, insoluble in benzene	0.42 (0.43)	9.9 (10.0)	5.7 (5.8)
$Ti(OPr\text{-}i)_4$ 0.80	$S'B'H_2$ 1.78	1 : 2	12	$Ti(OPr\text{-}i)(S'B')(S'B'H)$	Yellowish red solid, insoluble in benzene	0.50 (0.51)	6.5 (6.5)	7.5 (7.6)
$Zr(OPr\text{-}i)_4$ i-PrOH 0.87	(SBH_2) 0.71	1 : 1	12	$Zr(OPr\text{-}i)_2(SB)$	Pale-yellow solid, sparingly soluble in benzene	0.39 (0.40)	17.7 (17.4)	5.3 (5.4)
$Zr(OPr\text{-}i)_4$ i-PrOH 0.75	(SBH_2) 1.22	1 : 2	18	$Zr(OPr\text{-}i)(SB)(SBH)$	Yellow Solid, insoluble in benzene	0.43 (0.46)	11.9 (11.7)	7.0 (7.2)
$Zr(OPr\text{-}i)_4$ i-PrOH 1.20	$(S'B'H_2)$ 0.98	1 : 1	10	$Zr(OPr\text{-}i)_2(S'B')$	Yellow solid, insoluble in benzene	0.55 (0.56)	17.6 (17.4)	5.2 (5.4)
$Zr(OPr\text{-}i)_4$ i-PrOH 1.04	$(S'B'H_2)$ 1.70	1 : 2	20	$Zr(OPr\text{-}i)(S'B')(S'B'H)$	Yellow solid, insoluble in benzene	0.62 (0.64)	12.0 (11.7)	7.0 (7.2)

[a] SBH_2 = bis-salicylaldehyde-*o*-phenylenediimine; [b] $S'B'H_2$ = bis-salicylaldehyde-*p*-phenylenediimine.

Results and Discussion

Titanium and zirconium isopropoxides reacts with tetradentate Schiff bases in a 1 : 1 molar ratio as follows:

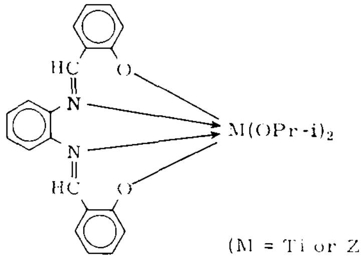
$$Ti(OPr\text{-}i)_4 + SBH_2 \rightarrow Ti(OPr\text{-}i)_2(SB) + 2\ i\text{-}PrOH$$
$$Zr(OPr\text{-}i)_4\ i\text{-}PrOH + SBH_2 \rightarrow Zr(OPr\text{-}i)_2(SB) + 3\ i\text{-}PrOH$$

{$[SB]^{2-}$ represents the anion of the Schiff base, bis-salicylaldehyde-*o*-phenylenediimine, SBH_2}

The reactions were also carried out in 1 : 2 molar ratios, the resulting derivatives being of the type $M(OPr\text{-}i)(SB)(SBH)$ where M = Ti or Zr. With a view to preparing compounds of the type $M(SB)_2$, reactions were also carried out in the presence of an excess of Schiff base or by using *p*-toluenesulphonic acid as catalyst. Both methods were unsuccessful.

The complexes are yellow to brown solids, insoluble or sparingly soluble in benzene. They are susceptible to hydrolysis and decompose upon attempted distillation under reduced pressure.

On the basis of analytical data and i.r. spectra the following structure is suggested for the monomeric $M(OPr\text{-}i)_2(SB)$ complexes (M = Ti or Zr).



(M = Ti or Zr)

Table 2. I.r. frequencies (cm^{-1}) of Schiff bases and the titanium(IV) and zirconium(IV) complexes

Compound	ν(C=N)	ν(C–O)
(SBH_2)[a]	1611s	1280s
$Ti(OPr\text{-}i)_2(SB)$	1608s	1310s
$Zr(OPr\text{-}i)_2(SB)$	1607s	1311s
$Zr(OPr\text{-}i)(SB)(SBH)$	1605s	1310s
$(S'B'H_2)$[b]	1610s	1281s
$Ti(OPr\text{-}i)_2(S'B')$	1607s	1313s
$Zr(OPr\text{-}i)_2(S'B')$	1605s	1310s
$Zr(OPr\text{-}i)(S'B')(S'B'H)$	1600s	1315s

[a] SBH_2 = bis-salicylaldehyde-*o*-phenylenediimine;
[b] $S'B'H_2$ = bis-salicylaldehyde-*p*-phenylenediimine.

A similar structure was suggested by other workers for diisopropoxytitanium(IV) bis-benzoylacetone ethylenediimine$^{(8)}$. The coordination number of zirconium in $Zr(SB)Cl_2$ has been shown to be six and a monomeric structure has been reported$^{(6)}$. Unfortunately, the limited solubility of the $M(OPr\text{-}i)_2(SB)$ complexes (M = Ti or Zr) in organic solvents did not permit determination of the molecular weights.

Infrared spectra

The tentative assignments of the C=N and C–O stretching frequencies for the titanium(IV) and zirconium(IV) Schiff base complexes are listed in Table 2.

A strong band is observed at *ca.* 1610 cm^{-1} in the spectra of the Schiff bases, which is characteristic of the azomethine (>C=N–) group. Coordination of nitrogen to the metal atom would, however, be expected to reduce the

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electron density in the azomethine link and thus lower the ν(C=N) frequency. In the complexes, this band is very slightly shifted to the lower side in our studies (Table 2). Similar observations have been made also by other workers(14, 15, 19).

A strong band at *ca.* 1280 cm^{-1} in the Schiff bases can be assigned to the phenolic C–O stretch(1, 6). In the complexes, the C–O stretching vibration appears at 1315–1310 cm^{-1}. This shift to higher frequency indicates bonding of ligand to the metal through oxygen. These observations are similar to those of previous workers(1, 3, 6, 13). Complex formation is supported further by the absence of absorptions in the $M(OPr\text{-}i)_2(SB)$ and $M(OPr\text{-}i)_2(S'B')$ complexes in the 2800–2600 cm^{-1} region where weak and broad absorptions are observed in the spectra of the Schiff bases.

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Transition Metal Nitrosyl Compounds, Part XXV[1]. Studies of some Nitrosyl Complexes of Molybdenum and Tungsten

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Summary

On u.v. irradiation, the dinitrosyldithiocarbamato $M(NO)_2(S_2CNR_2)_2$ (M = Mo or W) complexes are converted quantitatively into the mononitrosyl $M(NO)(S_2CNR_2)_3$ complexes. The tungsten complex exhibits nonrigid behaviour at high temperatures; the activation energy for this process has been determined and compared to that of the molybdenum analogue. The $M(NO)_2(MeCOCHCOMe)_2$ and $M(NO)_2[(O)SCNR_2]_2$ compounds have been prepared; these undergo conversion into uncharacterized nitrosyl derivatives upon irradiation. Cationic complexes of the type $[M(NO)_2(MeCN)_4]^{2+}$, $[M(NO)_2(MeCN)_3X]^{+}$ and $[M(NO)_2(MeCN)_2(MeCOCHCOMe)]^{+}$ have been prepared and their exchange with CD_3CN studied. Exchange occurs *via* a dissociative process and is stereospecific for $[M(NO)_2(MeCN)_4]^{2+}$ (M = Mo or W) and $[M(NO)_2(MeCN)_3X]^{+}$ (M = Mo, X = Cl; M = W, X = Br).

Introduction

This work is concerned with the relatively high barrier to polytopal rearrangement exhibit by penta- and heptacoordinate nitrosyl complexes. Our interest in this work follows from our previous studies(2) of $Mo(NO)(S_2CNR_2)_3$ (R = Me, Et or n-Bu) complexes and the reactions of $[M(NO)_2(PPh_3)_2]^{n+}$ (M = Fe, Ru or Os, n = 0; M = Co, Rh or Ir, n = 1) with carbon monoxide which apparently

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