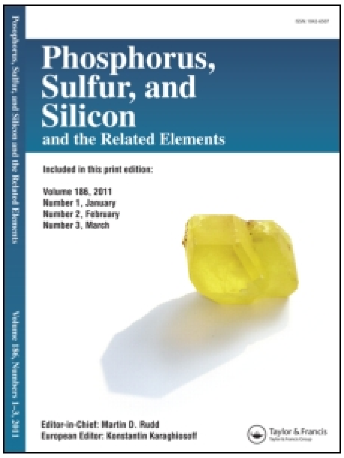


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Incorporation of Titanium(IV) into Sterically Hindered Schiff Bases of Heterocyclic β -Diketones Involving Ketooximes and Glycol as Coligands: Preparation and Structural Considerations

Shobhana Sharma[a]; Asha Jain[a]; Sanjiv Saxena[a]
[a] Department of Chemistry, University of Rajasthan, Jaipur, India

To cite this Article Sharma, Shobhana , Jain, Asha and Saxena, Sanjiv(2009) 'Incorporation of Titanium(IV) into Sterically Hindered Schiff Bases of Heterocyclic β -Diketones Involving Ketooximes and Glycol as Coligands: Preparation and Structural Considerations', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 7, 1676 — 1688

To link to this Article: DOI: 10.1080/10426500802176598

URL: http://dx.doi.org/10.1080/10426500802176598

Phosphorus, Sulfur, and Silicon, 184:1676–1688, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802176598

Taylor & Francis
Taylor & Francis Group

Incorporation of Titanium(IV) into Sterically Hindered Schiff Bases of Heterocyclic β-Diketones Involving Ketooximes and Glycol as Coligands: Preparation and Structural Considerations

Shobhana Sharma, Asha Jain, and Sanjiv Saxena
Department of Chemistry, University of Rajasthan, Jaipur, India

Titanium(IV) complexes of the general formula $TiL(OPr^i)_2$ *[where* $LH_2 = R\underline{CNH(C_6H_4)S}\overline{C:C(OH)N(C_6H_5)N:C}CH_3$ *where* $R = {-}C_6H_5, {-}C_6H_4Cl(p)$*] were prepared by the interaction of titanium isopropoxide with sterically hindered Schiff bases derived from heterocyclic β-diketones in 1:1 molar ratio in dry benzene. The complexes* $TiL(OPr^i)_2$ *were used as versatile precursors for the synthesis of other titanium(IV) complexes. Titanium(IV) complexes of the type* $TiLL'(OPr^i)$ *(where* $L'H{=}R^1R^2C{=}NOH$, $R^1 = R^2 = {-}CH_3$; $R^1 = {-}CH_3, R^2 = {-}C_6H_5$; $R^1 = {-}COC_6H_5$, $R^2 = {-}C_6H_5$*) were synthesized by the reaction of* $TiL(OPr^i)_2$ *with ketooximes (L'H) in equimolar ratio in dry benzene. Another type of titanium(IV) complexes having the general formula* $TiLGH(OPr^i)$ *(where* $GH_2{=}HO{-}G{-}OH$, $G = {-}CH_2{-}CH_2{-}$*) have been prepared by the reaction of* $TiL(OPr^i)_2$ *with glycol in 1:1 molar ratio in dry benzene. Plausible structures of these new titanium(IV) complexes have been proposed on the basis of analytical data, molecular weight measurements, and spectral studies.*

Keywords Glycol; ketooximes; Schiff bases; titanium isopropoxide

INTRODUCTION

In the field of chemistry, interest in titanium(IV) complexes of various organic ligands possessing nitrogen, oxygen, and/or sulfur atoms has experienced enormous growth.[1–10] The derivatives of titanium alkoxide continue to attract much attention because of their technological applications.[11–15] Lead-zirconium-titanate (PZT) is put to use in computer memories, whereas lead-titanate perovskite ($PbTiO_3$) is used in microelectronics. The reactivity and rate of hydrolysis of titanium alkoxide may be controlled by various modifiers. The rate of hydrolysis of titanium alkoxides plays an important role in material

Received 6 November 2007; accepted 2 May 2008.

Address correspondence to Sanjiv Saxena, Department of Chemistry, University of Rajasthan, Jaipur-302055, India. E-mail: saxenas348@rediffmail.com

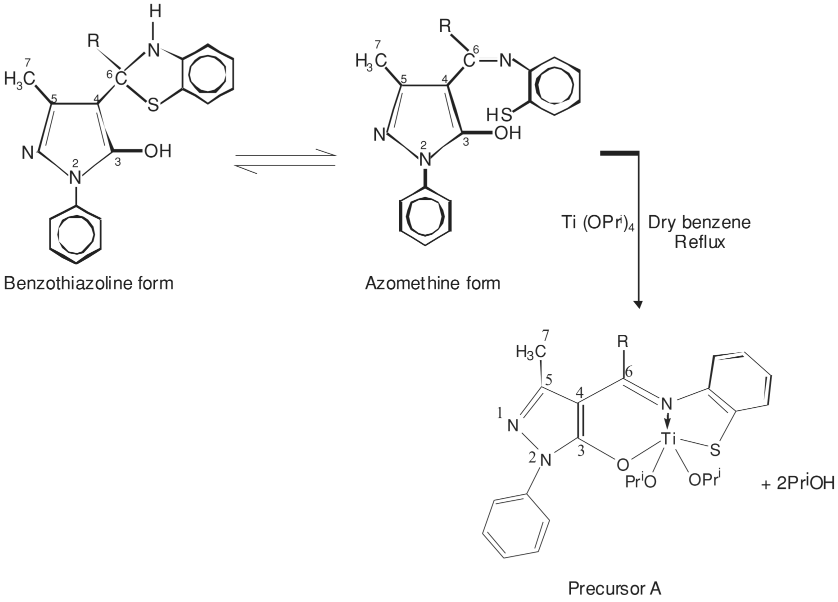
synthesis by sol-gel process.[15] Various organic ligands have been used as modifiers. Of the various potential modifiers, Schiff bases, oximes, and glycol, etc. are important. Schiff bases exhibit diversity in their structures[16]and possess biological applications. Oximes are important modifiers, as they possess hydrolytic stability, interesting structures, and are put to use as protecting groups.[17,18] It was considered relevant to modify the reactivity of titanium isopropoxide by reacting it with sterically hindered Schiff bases. The interaction of $Ti(OPr^i)_4$ with sterically hindered Schiff bases resulted in the formation of bis isopropoxy titanium (IV) complexes of the type $TiL(OPr^i)_2$, which were further treated with ketooximes and glycol. In the present article, we report the incorporation of titanium(IV) into sterically hindered Schiff bases derived from heterocyclic β-diketones involving ketooximes and glycol as coligands, which resulted in the formation of metallacyclic systems containing titanium surrounded by three heteroatoms—oxygen, nitrogen, and sulfur.

RESULTS AND DISCUSSION

The complexes of titanium(IV) derived from sterically hindered Schiff bases of heterocyclic β-diketones having the general formula $TiL(OPr^i)_2$ [where $LH_2 = R\overline{\underline{CNH(C_6H_4)SC}:C(OH)N(C_6H_5)N:C}CH_3$, R = $-C_6H_5$ and–$C_6H_4Cl(p)$] have been prepared by the interaction of $Ti(OPr^i)_4$ with sterically hindered Schiff bases of heterocyclic β-diketones in 1:1 molar ratio in dry benzene to afford precursor A. The preparations of these complexes are described in Scheme 1.

Attempts to prepare $Ti(L)_2$ by further reactions of precursor A′ and A″ with sterically hindered Schiff bases of heterocyclic β -diketones in 1:1 molar ratio were not successful. The most plausible explanation for this may be the steric factor.[19] It is quite interesting to study the steric profile of precursor A for further reactions. Ketooximes are comparatively less bulky organic ligands as compared to sterically hindered Schiff bases. The reactions of Precursor A′ and A″ with ketooximes were carried out in 1:1 molar ratio in dry benzene and are given in Scheme 2.

These reactions were completed in ∼ 10 hours of refluxing. However, reactions of precursor A with acetooxime in 1:2 molar ratio were not successful and resulted in the formation of only 1:1 product even after prolonged refluxing. This may be attributed to the steric crowding around the reaction site. The interaction of precursor A' and A" with glycol in 1:1 molar ratio were carried out in dry benzene, which afforded complexes of the type $TiLGH(OPr^i)$, and the preparation of these complexes are outlined in Scheme 3.



where

R = $-C_6H_5$	Precursor A'	Complex $[TiL_1(OPr^i)_2]$
R = $-C_6H_4Cl(p)$	Precursor A"	Complex $[TiL_2(OPr^i)_2]$

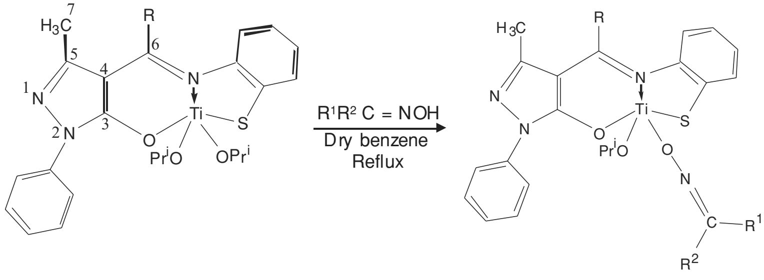
SCHEME 1

The progress of the reactions was monitored by estimating the liberated isopropanol in the azeotrope by oxidimetric method. The excess solvent was removed under reduced pressure, and yellowish brown colored solid products were obtained. These products were purified by recrystallization from benzene and pet.-ether mixture.

SPECTROSCOPIC STUDIES

IR Spectra

The IR spectra of the ligands and titanium(IV) complexes were recorded as KBr pellets in the range of 4000–400 cm^{-1}. A comparison of the IR spectra of titanium(IV) complexes of the types $TiL(OPr^i)_2$, $TiLL'(OPr^i)$, and $TiLGH(OPr^i)$ with their parent ligands provided important and



Precursor A Complex [TiLL'(OPr^i)]

where

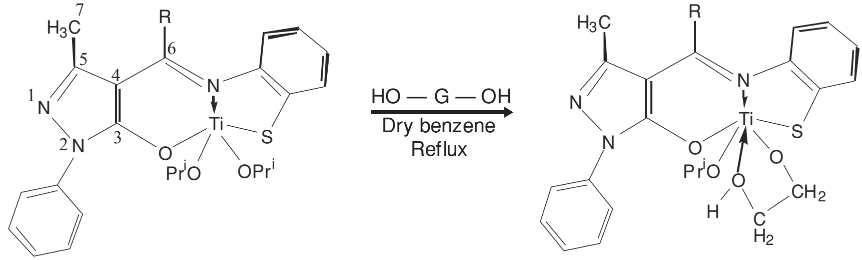
R = –C_6H_5 $R^1 = R^2 = –CH_3$ Complex [Ti$L_1L'_1$(OPr^i)]

R = –C_6H_5 $R^1 = –CH_3$, $R^2 = –C_6H_5$ Complex [Ti$L_1L'_2$(OPr^i)]

R = –C_6H_5 $R^1 = –COC_6H_5$, $R^2 = –C_6H_5$ Complex [Ti$L_1L'_3$(OPr^i)]

R = –C_6H_5Cl(p) $R^1 = R^2 = –CH_3$ Complex [Ti$L_2L'_1$(OPr^i)]

SCHEME 2



Precursor A Complex [TiLGH(OPr^i)]

where

R = –C_6H_5 G = -CH_2-CH_2- Complex [TiL_1GH(OPr^i)]

R = –C_6H_4Cl(p) G = -CH_2-CH_2- Complex [TiL_2GH(OPr^i)]

SCHEME 3

relevant information regarding mode of bonding in these complexes. In the IR spectra of the complexes $TiL(OPr^i)_2$, $TiLL'(OPr^i)$, and $TiLGH(OPr^i)$, two medium-intensity bands in the region 620–630 cm^{-1} and 515–520 cm^{-1} indicate the formation of Ti—O bond.[20] The band observed in the region 1085–1090 cm^{-1} may be attributed to Ti-O (isopropoxy) stretching.[9] A medium intensity band appearing in the region 470–480 cm^{-1} may be assigned to ν Ti ← N.[10] In the IR spectra of Schiff bases, broad bands appearing in the region 3400 cm^{-1} and 3300 cm^{-1} may be due to ν OH and ν NH, respectively.[21–22] These bands were absent in the corresponding titanium(IV) complexes. In titanium(IV) complexes, the band appearing in the region 1610–1625 cm^{-1} may be assigned to >C=N—, which suggests that the Schiff bases existing in benzothiazoline form in the free state rearrange to azomethine form during complex formation. In the IR spectra of free ketooximes, a strong band present at 920–930 cm^{-1} is due to N—O[23] and shows small shift towards lower wave numbers (910–915 cm^{-1}) in the corresponding titanium(IV) complexes. The weak band due to >C=N— of oximes appears in the region 1580–1600 cm^{-1} and shifts towards lower wave numbers (1560 cm^{-1}) in titanium(IV) complexes.[20]

^{1}H NMR Spectra

The ^{1}H NMR spectra of the complexes of the types $TiL(OPr^i)_2$, $TiLL'(OPr^i)$, and $TiLGH(OPr^i)$ and their parent ligands were recorded in $CDCl_3$ using TMS as an internal reference and are summarized in Table I. In the ^{1}H NMR spectra of the Schiff bases, the broad singlets appearing in the region δ 5.20–6.42 ppm may be assigned to >NH/–SH protons, which were absent in the corresponding titanium(IV) complexes indicating deprotonation of >NH/—SH protons. The ring $–C_6H_5$/terminal $–C_6H_5$/$–C_6H_4Cl$(p) and thiophenol ring protons are present in the region δ 6.22–8.08 ppm as a complex pattern in the ligands and complexes. The hydroxyl group of the ketooximes observed in the region δ 9.53–11.94 ppm as broad singlet was found to be absent in the complexes of the type $TiLL'(OPr^i)_2$, indicating the formation of another Ti—O bond through ketooximes. The disappearance of one of the hydroxyl protons of glycol in the complex $TiLGH(OPr^i)$ further supports the formation of Ti—O bonds through glycol. In the ^{1}H NMR spectra of the complexes $TiL(OPr^i)_2$, $TiLL'(OPr^i)$, and $TiLGH(OPr^i)$, the methyl and methine protons of the isopropoxy groups attached to titanium were observed in the region δ 1.16–1.26 ppm and δ 4.02–4.49 ppm, respectively. Other ^{1}H NMR signals of the ligands that exhibit no significant shift in titanium(IV) complexes are summarized in Table I.

TABLE I ^{1}H NMR Data of [TiL(OPr^i)$_2$], [TiLL'(OPr^i)] and [TiLGH(OPr^i)] Types of Complexes

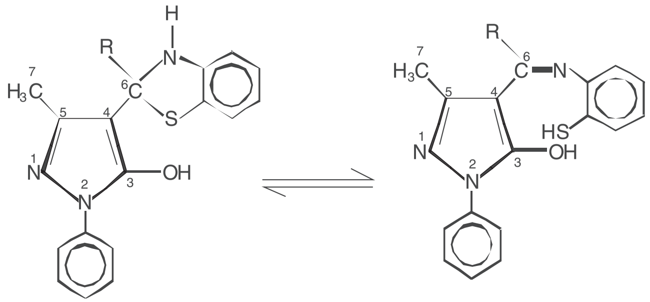
	$RCNH(C_6H_4)SC{:}C(OH)N(C_6H_5)N{:}CCH_3$, [$LH_2$]			$R^1R^2C{=}NOH$, [L'H]			$G(OH)_2$, [GH_2]		Isopropoxy	
Ligands and Complexes	NH/SH	Ring methyl	Ring Phenyl/Terminal phenyl/-C_6H_4Cl (p)/ thiophenol ring	$=$NOH	$-CH_3$	$-C_6H_5$	OH	CH_2	CH	CH_3
L_1H_2	5.20(bs)	1.92(s)	6.55–8.00 (m)							
$TiL_1(OPr^i)_2$	—	1.90 (s)	6.54–8.08 (m)						4.49 (sep.)$_{unr.}$	1.20 (d)
L'_1H				9.87 (bs)	1.90 (s) 1.91(s)					
$TiL_1L'_1(OPr^i)$	—	1.90(s)	6.55–7.45 (m)	—	*				4.33 (sep.)$_{unr.}$	1.20 (d)
L'_2H				9.53(bs)	2.31 (s)	7.37–7.64(m)				
$TiL_1L'_2(OPr^i)$	—	1.90 (s)	6.55–7.77 (m)	—	2.27 (s)	**			4.33 (sep.)$_{unr.}$	1.20 (d)
L_3H				11.94(bs)		7.30–8.00(m)				
$TiL_1L'_3(OPr^i)$	—	1.79(s)	6.56–8.01 (m)	—		**			4.34 (sep.)$_{unr.}$	1.21(d)
GH_2							5.22 (s)	3.75 (s)		
$TiL_1GH(OPr^i)$	—	1.95(s)	6.56–8.06 (m)				***	3.69(br)	4.33(sep.)$_{unr.}$	1.25(d)
L_2H_2	6.42 (bs)	2.10 (s)	6.54–7.86 (m)							
$TiL_2(OPr^i)_2$	—	1.93 (s)	6.46–7.97 (m)						4.26 (sep.)$_{unr.}$	1.16 (d)
$TiL_2L'_1(OPr^i)$	—	1.97 (s)	6.55–7.36 (m)	—	1.93 (s)				4.02 (sep.)$_{unr.}$	1.21 (d)
$TiL_2GH(OPr^i)$	—	1.74 (s)	6.22–8.02 (m)				***	3.70(br)	4.28 (sep.)$_{unr.}$	1.26 (d)

Note. where (bs) = broad singlet, (s) = singlet, (d) = doublet, (sep.) = septet, br = broad, unr. = unresolved, (m) = multiplet.

*overlap with ring methyl of Schiff bases of heterocyclic β-diketones

**overlap with phenyl region of Schiff bases of heterocyclic β-diketones

***overlap with methine proton of isopropoxy group.



Benzothiazoline form

Azomethine form

TABLE II ^{13}C NMR Data of [TiL(OPr^i)$_2$], [TiLL'(OPr^i)] and [TiLGH(OPr^i)] Types of Complexes

Ligands and Complexes	$RC\,NH(C_6H_4)SC{:}C(OH)N(C_6H_5)N{:}CCH_3$, [$LH_2$]						$R^1R^2C{=}NOH$, [L'H]			GH$_2$	Isopropoxy	
	C_3	C_4	C_5	C_6	C_7	Phenyl region	C=N	CH_3	Phenyl	CH_2	CH	CH_3
L_1H_2	161.15	104.18	137.28	191.80	15.75	115.21–148.58						
$TiL_1(OPr^i)_2$	163.10	107.01	136.72	189.29	16.12	115.21–148.64					64.27	25.04, 25.21
L'_1H							155.53 155.80	14.72, 15.01, 15.27, 21.32, 21.65, 21.97				
$TiL_1L'_1(OPr^i)$	163.57	107.49	136.71	191.28	16.11	115.24–148.65	155.18	14.87, 21.71			64.23	24.67, 25.22
L'_2H							156.02	12.42	126.05 128.53 129.27 136.47			
$TiL_1L'_2$ (OPr^i)	163.50	107.57	136.75	191.58	15.81	115.24–148.59	155.54	12.10	*		64.45	25.17, 25.23
L_2H_2	160.48	103.92	137.64	190.13	15.43	115.16–148.99						
$TiL_2(OPr^i)_2$	163.50	108.08	136.78	187.10	16.28	115.22–148.61					64.35	25.04, 25.31
$TiL_2L'_1(OPr^i)$	163.78	107.56	137.59	189.68	16.33	115.23–148.62	155.32	14.85 19.62 21.72			64.32	24.63, 25.27
GH_2										62.71		
$TiL_2GH(OPr^i)$	163.15	104.47	136.79	191.47	16.17	115.22–148.61				63.80 74.10	64.28	24.80

Note: *Overlap with phenyl region of Schiff bases of heterocyclic β-diketones.

TABLE III Physical and Analytical Data of [TiL(OPr^i)$_2$], [TiLL'(OPr^i)], and [TiLGH(OPr^i)] Types of Complexes

Complex Formula	Reactants in g (m mol)				Liberated Pr^{i}OH Found (Calc.)	–OPr^i % Found (Calc.)	Ti % Found (Calc.)	m.p. (°C)	Mol. wt. Found (Calc.)	Yield (in gms) Found (Calc.)
	Ti(OPr^i)$_4$/ TiL(OPr^i)$_2$	LH$_2$	L'H	GH$_2$						
TiL$_1$(OPr^i)$_2$ [$C_{29}H_{31}N_3O_3STi$]	Ti(OPr^i)$_4$ 0.64 g (2.2 mmol)	0.87 g (2.2 mmol)			0.26 (0.27)	20.80 (21.52)	8.6 (8.7)	110	555.10 (549.12)	1.00 (1.24)
TiL$_1$L'$_1$(OPr^i) [$C_{29}H_{30}N_4O_3STi$]	TiL$_1$(OPr^i)$_2$ 0.75 g (1.3 mmol)		0.09 g (1.3 mmol)		0.07 (0.08)	10..28 (10.51)	8.4 (8.5)	76	579.15 (562.12)	0.65 (0.76)
TiL$_1$L'$_2$(OPr^i) [$C_{34}H_{32}N_4O_3STi$]	TiL$_1$(OPr^i)$_2$ 1.02 g (1.8 mmol)		0.25 g (1.8 mmol)		0.10 (0.11)	9.19 (9.46)	7.5 (7.6)	90	636.08 (624.17)	0.96 (1.15)
TiL$_1$ L'$_3$(OPr^i) [$C_{40}H_{34}N_4O_4STi$]	TiL$_1$(OPr^i)$_2$ 1.05 g (1.9 mmol)		0.43 g (1.9 mmol)		0.10 (0.11)	8.16 (8.27)	6.6 (6.7)	84	720.14 (714.22)	1.10 (1.37)
TiL$_1$GH(OPr^i) [$C_{28}H_{29}N_3O_4STi$]	TiL$_1$(OPr^i)$_2$ 1.10 g (2.0 mmol)			0.13 g (2.0 mmol)	0.11 (0.12)	10.70 (10.72)	8.5 (8.6)	117	570.88 (551.10)	0.95 (1.10)
TiL$_2$(OPr^i)$_2$ [$C_{29}H_{30}N_3O_3STiCl$]	Ti(OPr^i)$_4$ 0.80 g (2.8 mmol)	1.18 g (2.8 mmol)			0.31 (0.33)	20.01 (20.24)	8.1 (8.2)	124	590.05 (583.62)	1.42 (1.65)
TiL$_2$L'$_1$(OPr^i) [$C_{29}H_{29}N_4O_3STiCl$]	TiL$_2$(OPr^i)$_2$ 1.54 g (2.6 mmol)		0.19 g (2.6 mmol)		0.14 (0.15)	9.68 (9.90)	7.9 (8.0)	130	610.20 (596.62)	1.35 (1.57)
TiL$_2$GH(OPr^i) [$C_{25}H_{20}N_3O_3STiCl$]	TiL$_2$(OPr^i)$_2$ 1.14 g (1.9 mmol)			0.12 g (1.9 mmol)	0.10 (0.11)	11.10 (11.24)	9.0 (9.1)	147	550.20 (525.58)	0.85 (1.02)

where

$LH_2 = RCNH(C_6H_4)SC{:}C(OH)N(C_6H_5)N{:}CCH_3$

$L_1H_2 = R = –C_6H_5$

$L_2H_2 = R = –C_6H_4Cl$ (p)

$L'H = R^1R^2C = NOH$

$L'_1H = R^1 = R^2 = –CH_3$

$L'_2H = R^1 = —CH_3, R^2 = –C_6H_5$

$L'_3H = R^1 = –COC_6H_5, R^2 = –C_6H_5$

$GH = HO—CH_2—CH_2—OH$

^{13}C NMR Spectra

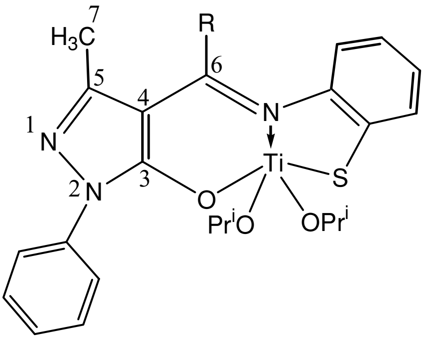
The ^{13}C NMR spectra of some representative titanium(IV) complexes of the types TiL(OPr^{i})$_2$,TiLL'(OPr^{i}), and TiLGH(OPr^{i}) and their parent ligands were recorded in $CDCl_3$ using TMS as an internal standard and are summarized in Table II. The ^{13}C NMR spectral study of the complexes and ligands provided important and useful information. This information was used in suggesting the mode of bonding and establishing plausible structures of these titanium(IV) complexes. The C_6 carbon signal appeared in the region δ 190.13–191.80 ppm in the ^{13}C NMR spectra of the free Schiff bases. There is some shift in the position of C_6 carbon signal in the ^{13}C NMR spectra of the complexes, which indicates the involvement of $>C_6{=}N$-in bonding. In the ^{13}C NMR spectra of the complexes TiL(OPr^{i})$_2$, TiLL'(OPr^{i}), and TiL$_2$GH(OPr^{i}), signals of methyl carbons, and methine carbon of isopropoxy groups attached to titanium appear at δ 24.67–25.31 ppm and δ 64.23–64.45 ppm, respectively. The signals of CH_2 carbons of ethylene glycol appear at δ 63.80 and δ 74.10 ppm in the ^{13}C NMR spectrum of the complex TiL$_2$GH (OPr^{i}).

CONCLUSION

Incorporation of titanium(IV) into sterically hindered Schiff bases of heterocyclic β -diketones involving ketooximes and glycol as coligands afforded titanium(IV) complexes of the types TiL(OPr^{i})$_2$, TiLL'(OPr^{i}), and TiLGH(OPr^{i}). These complexes are monomers. On the basis of physicochemical and spectral evidences, the following plausible structures may be proposed for these titanium(IV) complexes (see Figure 1).

In this complex (Precursor A), TiL(OPr^{i})$_2$, titanium is incorporated into sterically hindered Schiff bases. These complexes possess pentacoordinated titanium centers. These are metallacyclic complexes in which central titanium is surrounded by three heteroatoms—nitrogen, oxygen, and sulfur. Incorporation of titanium into sterically hindered Schiff bases results in the formation of a five- and a six-membered rings. The interesting feature of these complexes is the presence of a Ti← N bond, which is important for the possible biological activity of these complexes. The presence of two isopropoxy groups on titanium in these complexes provides reaction sites for further reactions, and because of this reason, these are used as versatile precursors for the synthesis of complexes of the types TiLL'(OPr^{i}) and TiLGH(OPr^{i}).

In the complexes of the type [TiLL'(OPr^{i})] (Figure 2), titanium is incorporated into sterically hindered Schiff bases and ketooximes. These complexes possess pentacoordinated titanium atoms. One isopropoxy



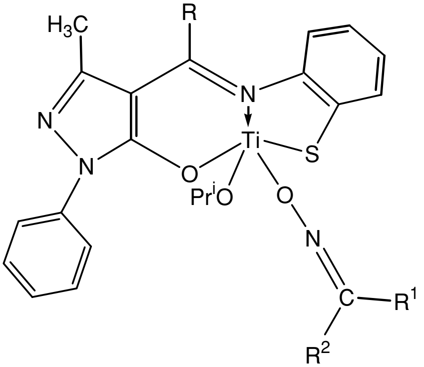
Where

R = $-C_6H_5$	Precursor A'	Complex $[TiL_1(OPr^i)_2]$
R = $-C_6H_4CL(p)$	Precursor A"	Complex $[TiL_2(OPr^i)_2]$

FIGURE 1 Proposed structure of Precursor A, complex $[TiL(OPr^i)_2]$.

group present over titanium atom could not be substituted by a second acetooxime molecule, probably due to steric reasons.

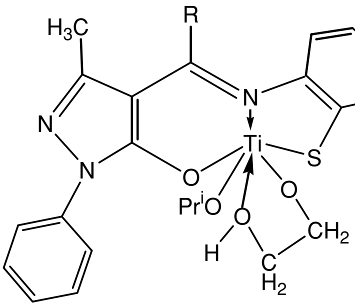
The metallacyclic complexes of the type $TiLGH(OPr^i)$ (Figure 3) possess an additional five-membered ring. The coordination number of titanium in these complexes is six.



Where

R = $-C_6H_5$	$R^1 = R^2 = -CH_3$	Complex $[TiL_1L'_1(OPr^i)]$
R = $-C_6H_5$	$R^1 = -CH_3, R^2 = -C_6H_5$	Complex $[TiL_1L'_2(OPr^i)]$
R = $-C_6H_5$	$R^1 = -COC_6H_5, R^2 = -C_6H_5$	Complex $[TiL_1L'_3(OPr^i)]$
R = $-C_6H_4Cl(p)$	$R^1 = R^2 = -CH_3$	Complex $[TiL_2L'_1(OPr^i)]$

FIGURE 2 Proposed structure of complex $[TiLL'(OPr^i)]$.



Where

R = $-C_6H_5$ Complex $[TiL_1GH(OPr^i)]$
R = $-C_6H_4Cl$ (p) Complex $[TiL_2GH(OPr^i)]$

FIGURE 3 Proposed structure of complex $[TiLGH(OPr^i)]$.

EXPERIMENTAL

Stringent precautions were taken to exclude atmospheric moisture during experimental work. The ligands, Schiff bases of sterically hindered heterocyclic β-diketones, were synthesized by reported method[21] and ketooximes were prepared by the standard methods. Glycol was commercially available and dried by standard method. The solvents used in the reactions were dried by standard methods. $Ti(OPr^i)_4$ was prepared by reported method.[24] Molecular weights of titanium(IV) complexes were determined cryoscopically in benzene solution by Beckmann's method. The liberated isopropanol in the azeotrope was estimated by oxidimetric method. Titanium was estimated gravimetrically as TiO_2.[25] IR (4000–400 cm^{-1}) spectra were recorded on SHIMADZU, FTIR-8400 spectrophotometer and samples were prepared as KBr pellets. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on JEOL FTAL 300 NMR spectrometer operating at 300 and 75.45 MHz, respectively.

Synthesis of Precursor A′,
$Ti(OPr^i)_2[C_6H_5\underline{\overline{C{:}N(C_6H_4)S}C}\overline{{:}C(O)N(C_6H_5)N{:}C}CH_3]$

To a benzene solution of $Ti(OPr^i)_4$ (0.64 g, 2.2 mmol) was added a benzene solution of the Schiff base, L_1H_2 (0.87 g, 2.2 mmol). The reaction contents were refluxed for ~ 10 h, and the progress of the reaction was monitored by estimating the liberated isopropanol in the azeotrope. After completion of the reaction, the excess solvent was removed under reduced pressure. A brown-colored solid was obtained, which was recrystallized from benzene and pet.-ether mixture. The physical and analytical data are summarized in Table III.

Synthesis of $Ti(OPr^i)[C_6H_5C{:}N(C_6H_4)SC{:}C(O)N(C_6H_5)N{:}CCH_3][(CH_3)_2C{=}NO]$

To a benzene solution of precursor A', $Ti(OPr^i)_2[C_6H_5C{:}N(C_6H_4)SC{:}C(O)N(C_6H_5)N{:}CCH_3]$ (0.75 g, 1.3 mmol) was added a benzene solution of acetooxime (0.09 g, 1.3 mmol). The reaction was completed in ~ 10 h of refluxing. The liberated alcohol in the azeotrope was estimated to monitor the progress of the reaction. After stripping off the excess solvent under reduced pressure, a brown-colored solid was isolated, which was purified by recrystallization from benzene and pet.-ether mixture. The physical and analytical data are summarized in Table III.

Synthesis of $Ti(OPr^i)[(p)ClC_6H_4C{:}N(C_6H_4)SC{:}C(O)N(C_6H_5)N{:}CCH_3][OCH_2CH_2OH]$

A benzene solution of ethylene glycol (0.12 g, 1.9 mmol) was added to a benzene solution of precursor A″ $Ti(OPr^i)_2[(p)ClC_6H_4C{:}N(C_6H_4)SC{:}C(O)N(C_6H_5)N{:}CCH_3]$ (1.14 g, 1.9 mmol). The reaction contents were refluxed for ~ 10 h, and isopropanol in the azeotrope was estimated by oxidimetric method. A yellowish brown-colored solid product was obtained after removing the excess solvent. This product was recrystallized from benzene and pet.-ether mixture. The physical and analytical data are summarized in Table III.

REFERENCES

[1] A. K. Saxena, S. Saxena, and A. K. Rai, *Synth. React. Inorg. Met.- Org. Chem.*, **20,** 21 (1990).

[2] G. J. Gainsford, T. Kemmitt, C. Lensink, and N. B. Milestone, *Inorg. Chem.*, **34,** 746 (1995).

[3] T. P. Vaid, J. M. Tanski, J. M. Pette, E. B. Lobkovsky, and P. T. Wolczanski, *Inorg. Chem.*, **38,** 3394 (1999).

[4] A. Singh and R. C. Mehrotra, *Coord. Chem. Rev.*, **248,** 101 (2004).

[5] A. L. Johnson, M. G. Davidson, M. D. Lunn, and M. F. Mahon, *Eur. J. Inorg. Chem.*, **2006,** 3088 (2006).

[6] K. V. Zaitsev, M. V. Bermeshev, S. S. Karlov, Y. F. Oprunenko, A. V. Churakov, J. A. K. Howard, and G. S. Zaitseva, *Inorg. Chim. Acta*, **360,** 2507 (2007).

[7] A. de Meijere, S. I. Kozhushkov, and A. I. Savchenko, *J. Organometall. Chem.*, **689,** 2033 (2004).

[8] T, J. Boyle, R. M. Sewell, L. A. M. Ottley, H. D. Pratt III, C. J. Quintana, and S. D. Bunge, *Inorg. Chem.*, **46,** 1825 (2007).
[9] M. Pathak, R. Bohra, R. C. Mehrotra, I.-P. Lorenz, and H. Piotrowski, *Trans. Met. Chem.*, **28,** 187 (2003).
[10] N. Sharma, V. Sharma, R. Bohra, V. S. Raju, I.-P. Lorenz, C. Krinninger, and P. Mayer, *Inorg. Chim. Acta*, **360,** 3002 (2007).
[11] Y. M. Rodionov, E. M. Slyusarenko, and V. V. Luninb, *Russ. Chem. Rev.*, **65,** 797 (1996).
[12] L. G. Zhen and L. R. Ze, *Mater. Sci. Eng. A.*, **280,** 25 (2000).
[13] K. A. Fleeting, P. O. Brien, D. J. Otway, A. J. P. White, D. J. Williams, and A. C. Jones, *Inorg. Chem.*, **38,** 1432 (1999).
[14] C. A. Zechmann, J. C. Huffman, K. Folting, and K. G. Caulton, *Inorg. Chem.*, **37,** 5856 (1998).
[15] U. Schubert, *J. Mater. Chem.*, **15,** 3701 (2005).
[16] J. Matijevic-Sosa, M. Vinkovic, and D. Vikic-Topic, *Croat. Chem. Acta*, **79,** 489 (2006).
[17] W. F. DeGrado and E. T. Kaiser, *J. Org. Chem.*, **45,** 1295 (1980).
[18] I. Cerny, V. Pouzar, M. Hill, H. Havlikova, and R. Hampl, *Steroids,* **71,** 120 (2006).
[19] P. G. Cozzi, *Chem. Soc. Rev.*, **33,** 410 (2004).
[20] A. Singh, A. K. Rai, and R. C. Mehrotra, *Ind. J. Chem.*, **12,** 512 (1974).
[21] S. Bhambhani, S. Saxena, and A. K. Rai, *Main Group Met. Chem.*, **21,** 747 (1998).
[22] S. Bhambhani, S. Saxena, and A. K. Rai, *Phosphorus, Sulfur, and Silicon*, **157,** 29 (2000).
[23] S. Sharma, A. Jain, and S. Saxena, *Main Group Met. Chem.*, **30,** 63 (2007).
[24] D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, *J. Chem. Soc.*, 2027 (1952).
[25] A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis* (Longmans, London, 1978).