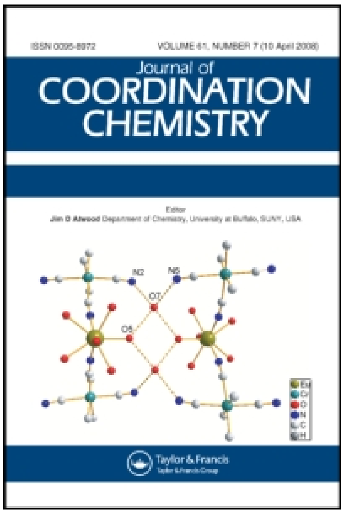

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SYNTHESIS AND CHARACTERIZATION OF TITANIUM(IV) SCHIFF BASE COMPLEXES. I. TITANIUM(IV) COMPLEXES OF SALICYLALDEHYDE-2-MERCAPTOANIL[1]

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The synthesis of new Schiff base complexes of titanium(IV) of the type $TiX_2(SSP)$, where X = SSP/2, OEt, OPr^i, OBu^t, and $(h^5-C_5H_5)Cl/2$, and SSP is the dianion of the tridentate ONS donor ligand salicylaldehyde-2-mercaptoanil, is reported. Electronic, infrared, nmr, and mass spectral data indicate that the colorless ligand exists in the heterocyclic benzthiazoline form but rearranges to the chelating Schiff base from in the titanium complexes. The titanium(IV) atom is six-coordinate in the monomeric $Ti(SSP)_2$ and dimeric $Ti(OR)_2(SSP)$ (R = Et, Pr^i) complexes and five-coordinate in the monomeric $Ti(OBu^t)_2(SSP)$ and $(h^5-C_5H_5)TiCl(SSP)$ compounds.

INTRODUCTION

In contrast to the extensive studies of the complexes of the late first-row transition-metal ions with chelating Schiff base ligands, relatively little information is available on such complexes of the early transition metals.[2–5] Interest in the anomalous magnetic properties of dinuclear oxovanadium(IV) complexes has stimulated the preparation of various vanadyl Schiff base complexes.[6,7] Titanium(IV) derivatives of different types of Schiff bases are known but, in general, structural information is not available.[2,5,8] However, recent X-ray crystal structures have established octahedral geometry for the titanium atom in tetrakis-(*N*-ethylsalicylaldiminato)titanium(IV)[9] and in dichloro-*N*,*N*′-ethylenebis(salicylideneiminato)titanium(IV).[10] In continuing our studies of titanium(IV) compounds having uncommon coordination numbers for titanium[11,12] we are presently engaged in investigations involving various Schiff base ligands. In this paper we report the synthesis and characterization of compounds of the type $TiX_2(SSP)$, where X = SSP/2, OEt, OPr^i, OBu^t, and $(h^5-C_5H_5)Cl/2$, and SSP is the dianion of the tridentate ONS Schiff Base ligand salicylaldehyde-2-mercaptonil.

EXPERIMENTAL

Chemicals

Salicylaldehyde was obtained from Fisher Scientific Company or J. T. Baker Chemical Company and *o*-aminothiophenol from Eastman Organic Chemicals. $TiCl_4$, $Ti(OEt)_4$, and $Ti(OPr^i)_4$ were obtained from Alfa Inorganics, Inc; the chloride was distilled at 136° from copper turnings and subsequently handled *via* the syringe technique. $(h^5-C_5H_5)TiCl_3$ was prepared by previously described methods.[13,14] Solvents were purified and dried following standard procedures; all were stored and transferred under dry dinitrogen. Tertiary-butanol was fractionally distilled and used as the benzene azeotrope.

Physical Measurements

Titanium was determined gravimetrically by hydrolysis with aqueous ammonia and ignition to the oxide. Carbon, hydrogen, and nitrogen analyses were performed in this department by Mr S. McKinnon and by M-H-W Laboratories, Garden City, Mich. Infrared spectra were obtained in the region 4000–200 cm^{-1} using a Beckman IR-12 spectrophotometer. Solid state spectra were recorded as Nujol mulls between KBr plates or polythene discs. Electronic spectral data were collected using matched solution cells on a Unicam SP800 recording spectrophotometer. Mass spectra were recorded with a Varian Mat-7 mass spectrometer at an ionizing energy of 70 eV by Miss L. MacDonald. Proton nmr spectra were obtained with a Varian A-60A spectrometer using deuterochloroform, dimethylsulfoxide-d_6 or dichloromethane solutions with TMS as the internal standard. Molecular weight determinations were made cryoscopically in benzene using fluorene as the calibrant. Conductivity measurements were obtained for nitrobenzene solutions with Beckman Instruments, Inc. Model RC-16B2 conductivity bridge and a conductivity cell with platinum electrodes.

Preparation of the Complexes

Since titanium compounds are readily hydrolyzed, all operations involved in synthesis, purification, and subsequent handling of these compounds were conducted under a dry dinitrogen atmosphere. Glassware with ground-glass joints in conjunction with a manifold providing access to either dry dinitrogen or vacuum allowed most procedures to be carried out on the bench top.[15] Samples and solutions for physical measurements were prepared in a Labconco glove box. The preparative details for the ligand and the complexes are outlined below.

H_2SSP

The ligand was prepared by the addition of 12.5 g (0.10 mol) of o-aminothiophenol dissolved in 10 ml of absolute ethanol to a stirred solution of salicylaldehyde (12.2 g, 0.10 mol) in 100 ml absolute ethanol. Both solutions were precooled in ice baths and the resulting solution was stirred briefly before allowing it to stand overnight under a dinitrogen atmosphere. The solid which had formed was isolated by filtration, washed with cooled absolute ethanol, and dried under reduced pressure. The colorless crystals had a melting point of 140–141° (lit.[16] 136–137°). *Anal.* Calcd. for $C_{13}H_{11}ONS$: C, 68.1; H, 4.8; N, 6.1. Found: C, 67.9; H, 4.8; N, 6.0.

$Ti(SSP)_2$

$Ti(OEt)_4$(0.78 g, 3.4 mmol) dissolved in 40 ml of benzene was added to the solid ligand H_2SSP(1.56 g, 6.8 mmol). The resulting dark brown solution was refluxed for 3 hr. The dark brown solid remaining after removing the solvent under reduced pressure was dissolved in 10 ml dichloromethane; the solution was filtered, and the product reprecipitated by adding n-hexane. The yellowish brown solid was filtered off and dried under vacuum; m.p. > 154° (gradually chars). *Anal.* Calcd. for $Ti(C_{13}H_9ONS)_2$: Ti, 9.6; C, 62.2; H, 3.6; N, 5.6. Found: Ti, 9.6; C, 62.6; H, 4.9; N, 5.2.

$Ti(OEt)_2(SSP)$

To $Ti(OEt)_4$(3.31 g, 14.5 mmol) dissolved in 50 ml of benzene was added 3.32 g (14.5 mmol) of the ligand H_2SSP. The resulting dark red solution was refluxed for 3 hr. A gummy product remained after removing the solvent under reduced pressure. It was dissolved in dichloromethane and the solution was filtered. A red solid product was precipitated from this solution by adding n-hexane. The red solid was collected on a frit and then dried at 100° *in vacuo* overnight; m.p. > 128°. *Anal.* Calcd. for $Ti(OC_2H_5)_2(C_{13}H_9ONS)$: Ti, 13.2; C, 55.9; H, 5.2; N, 3.8. Found: Ti, 13.0; C, 55.6; H, 5.3; N, 4.1.

$Ti(OPr^i)_2(SSP)$

$Ti(OPr^i)_4$(1.84 g, 6.3 mmol) in 20 ml of benzene was added to solid H_2SSP(1.48 g, 6.3 mmol), giving immediately a red solution. After refluxing the solution for 3 hr, the solvent was removed and the viscous oil remaining placed under vacuum overnight. The product was then dissolved in dichloromethane and the solution filtered. Pentane was added to the filtrate and subsequent reduction of the volume gave an orange solid product, which was dried *in vacuo*; m.p. 105–109°. *Anal.* Calcd. for $Ti(OC_3H_7)_2(C_{13}H_9ONS)$: Ti, 12.2; C, 58.0; H, 5.9; N, 3.3. Found: Ti, 11.9; C, 57.8; H, 5.7; N, 3.6.

$Ti(OBu^t)_2(SSP)$

$Ti(OEt)_4$(1.17 g, 5.2 mmol) in 50 ml benzene was added to solid H_2SSP(1.17 g, 5.2 mmol). The resultant dark red solution was refluxed for 3 hr, then the benzene was removed under reduced pressure. To the product was added t-butanol-benzene azeotrope (50 ml) and the solution was stirred overnight. Evaporation of the solvent to dryness gave a yellow solid product. This was dissolved in dichloromethane and the solution filtered. Removal of the dichloromethane under vacuum reprecipitated the yellow solid, which was dried *in vacuo* overnight; m.p. 109–112°. *Anal.* Calcd. for $Ti(OC_4H_9)_2(C_{13}H_9ONS)$: Ti, 11.4; C, 59.9; H, 6.5; N, 3.3. Found: Ti, 11.3; C, 59.5; H, 6.2; N, 3.5.

$(h^5\text{-}C_5H_5)TiCl(SSP)$

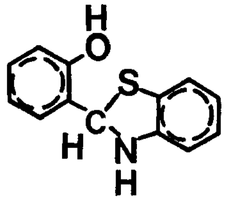
To a mixture of $(h^5\text{-}C_5H_5)TiCl_3$(0.75 g, 3.4 mmol) and triethylamine (1.0 ml, 7.2 mmol) in benzene was added 0.79 g (3.4 mmol) of solid H_2SSP. The dark brown mixture was stirred and warmed for 1 hr.

Filtration removed a tan powder; addition of hexane to the filtrate gave a fine brown precipitate. The product was collected on a frit, washed with hexane, and dried in vacuo overnight at *ca.* 100°; m.p. > 125° (gradually chars). *Anal.* Calcd. for $(h^5\text{–}C_5H_5)$-$TiCl(C_{13}H_9ONS)$: C, 57.5; H, 3.7; N, 3.7. Found: C, 57.8; H, 4.0; N, 3.7.

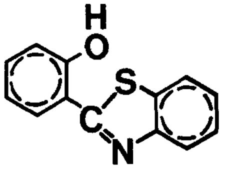
RESULTS AND DISCUSSION

Structure of the Ligand

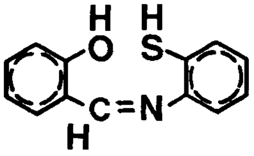
The condensation products of salicylaldehyde and σ-aminothiophenol have been variously described as the thiazoline,[16] thiazole,[17] and anil (or Schiff base form).[18] The three proposed structures are represented in Figure 1. On the basis of chemical and spectral evidence, Charles and Freiser[16] assigned the thiazoline structure to the yellowish crystals they isolated in a neat reaction. These authors also demonstrated the oxidation of their product to the previously reported deep yellow thiazole form.[17] The absence of an infrared band near 2500 cm^{-1} due to ν(S–H) and the presence of an infrared band at 3210 cm^{-1} assignable to ν(N–H) supported their assignment. However, Muto[18] later isolated colorless crystals from a cooled reaction in ethanol and claimed the structure to be the anil form. In a modification of Muto's method we have isolated colorless crystals and shown them to have the thiazoline structure in the solid state, in several solvents, and in the vapor state. The results of the spectroscopic investigation of the condensation product isolated in this work are summarized in Table I.



THIAZOLINE



THIAZOLE



SALICYLALDEHYDE-2-MERCAPTOANIL

FIGURE 1 Three proposed structures of the ligand H_2SSP

In their previous differentiation of the thiazoline and thiazole forms by electronic spectroscopy, Charles and Freiser[16] reported that the thiazoline form gave absorption maxima in 95% ethanol at 262 nm and 298 nm of equal intensity (ϵ_M of 4.8 x 10^3 calculated from their data). The discrepancy with our results (Table I) can be explained if some of the thiazole form was present as an impurity

TABLE I
Electronic, infrared and nmr data for salicylaldehyde-2-mercaptoanil

Electronic (nm)			Infrared (cm^{-1})		Nmr (δppm)			
Nujol	95%EtOH	$CHCl_3$	Halocarbon	DMSO	C_6D_6	$CDCl_3$	Acetone-d_6	DMSO-d_6
280	279(5.61)[a]	283(5.81)[a]	3400–2800 w,br	3500 s,br	8.60[b]	8.75[b]	8.85[b]	9.81[b]
310	311(4.74)[a]	300(4.74)[a]	3275 s	3270 s,br	5.82[c]	6.53[c]	5.93[b]	6.57[c]
			1630 m	1625 s	6.0–	6.4–	6.5–	6.4–
			1594 s	1590 m	7.3[d]	7.3[d]	7.7[d]	7.6[d]

[a] 10^{-3} ϵ_M (molar extinction coefficients) in parenthesis.
[b] Peak vanishes after the addition of D_2O.
[c] Peak integrates for one hydrogen and no exchange was observed with deuterium.
[d] Phenyl absorption region.

in the crystals isolated in the earlier work. This contention is supported by the yellowish color, elemental analysis and lower melting point reported by Charles and Freiser for their condensation product. In our work the constancy of position of the two absorption maxima in the solid state and in solution indicates that the same structure is found in both states. This conclusion is supported by the similarity of the infrared spectral bands in both a halocarbon mull and in dimethylsulfoxide solution. That the structure is the cyclic thiazoline form is indicated by the presence of a strong band near 3500 cm^{-1} (broadened to 2800 cm^{-1} in the solid state) attributable to ν (O–H), the presence of a strong band at 3270 cm^{-1} due to ν(N–H), and the absence of a ν(S–H) band near 2500 cm^{-1}. The bands at 1625 cm^{-1} and 1590 cm^{-1} can be assigned to the expected phenyl skeletal modes; these bands shift appreciably when conjugated with the C=N linkage in the anil form of the ligand (*vide infra*). That the thiazoline form also exists in the vapour state is indicated by the observance of the molecular peak at m/e 229 as the base peak. The presence of an intense peak at m/e 136, attributable to the fragment ion $[C_7H_6NS]^+$, reflects the stability of the thiazoline ring. The ready loss of the C_6H_4OH radical from the molecular ion in a one-step process is confirmed by the occurrence of the metastable ion at m/e 80.5.

The broad singlet at 8.60δ or greater in the nmr spectrum of the ligand corresponds to the hydrogen atom of the hydroxyl group and shifts to lower field as the degree of hydrogen-bonding increases with the polarity of the solvent (see Table I). It was also possible, with acetone-d_6 as solvent, to identify the resonance peak at 5.93δ as due to the presence of an NH group because the peak disappeared after the addition of D_2O. Integration of the broad phenyl resonance peaks before and after the addition of D_2O indicated that the NH resonance peak was hidden in this region with the solvents other than acetone-d_6. It was not possible to definitely assign a resonance peak to the hydrogen atom of the CHN linkage of the thiazoline form but a single proton resonance on the high field edge of the phenyl resonance region (5.82δ in C_6D_6 but *ca.* 6.5δ in the other solvents used) disappears in the nmr spectra of the titanium(IV) complexes, as expected for conversion of the ligand to the coordinated anil form. Evidence for the ligand rearrangement to the chelating form is presented in the following discussion of the titanium complexes.

TABLE II
Molecular weight and conductance data

Compound	Molecular Weight		Conductance	
	Calcd.[a]	Found[b]	Concentration (10^3M)	Λ[c]
$Ti(SSP)_2$	502	562 (502)	2.03	0.20
$Ti(OEt)_2(SSP)$	365	744 (730)	3.58	0.81
$Ti(OPr^i)_2(SSP)$	393	711 (499)	1.27	0.23
$Ti(OBu^t)_2(SSP)$	421	438 (421)	2.20	0.15
$(h^5\text{-}C_5H_5)TiCl(SSP)$	375	-- (375)	0.48	<0.20

[a] Monomeric value.
[b] Determined cryoscopically in benzene at *ca.* 10^{-2} M. Highest observed m/e peak in parenthesis.
[c] Molar conductance in nitrobenzene (ohm^{-1} cm^2 mole^{-1}). $\Lambda \approx$ 30 for a 1:1 electrolyte (19).

Titanium(IV) Complexes

Five new titanium(IV) complexes having the empirical formulae $Ti(SSP)_2$, $Ti(OEt)_2(SSP)$, $Ti(Opr^i)_2(SSP)$, $Ti(OBu^t)_2(SSP)$, and $(h^5-C_5H_5)$-TiCl(SSP) have been prepared in this investigation. The dianion (SSP) of the Schiff base salicylaldehyde-2-mercaptoanil acts as a binegative tridentate ligand in these complexes. The new isolated complexes are moderately sensitive toward air as well as moisture and thus were handled under a dinitrogen atmosphere. All of the complexes, which range in color from yellowish brown to dark red, are reasonably solub in dichloromethane and benzene but are insoluble in hexane.

The results of cryoscopic molecular weight determinations in benzene and conductivity measurements in nitrobenzene are summarized in Table II. Further, mass spectra of the complexes indicate that the same degree of molecularity exists in the gas phase as in solution. The highest m/e peak observed for $Ti(SSP)_2$, $Ti(OBu^t)_2(SSP)$ and $(h^5-C_5H_5)TiCl(SSP)$ (Table II) corresponds to the monomeric parent ion. The highest m/e peak observed for $Ti(OEt)_2(SSP)$ corresponds to the dimeric molecular ion species. Interesting among the m/e fragments in the mass spectrum of $Ti(OEt)_2(SSP)$ at 200° is the presence of a high intensity peak at m/e 502, corresponding to $[Ti(SSP)_2]^+$. Nevertheless, the mass spectra of $Ti(OEt)_2(SSP)$ revealed several fragment ions of m/e between 365 and 730 that are not observed in the mass spectrum of $Ti(SSP)_2$ itself. Evidence for the dimeric structure of $Ti(OPr^i)_2(SSP)$ was also found through its mass spectral data. The m/e peaks observed between 391 and 499 (m/e 471 is the most intense in this region) can be attributed to fragments of the dimeric species. All of the complexes are essentially nonelectrolytes in nitrobenzene and therefore the coordination number of the titanium atom must be five for $Ti(OBu^t)_2(SSP)$ and $(h^5-C_5H_5)TiCl(SSP)$ and six for $Ti(SSP)_2$, $Ti(OEt)_2(SSP)$, and $Ti(OPr^i)_2(SSP)$ assuming a tridentate chelating base ligand.

Evidence that the ONS donor ligand is a tridentate chelate comes from the infrared and nmr spectra of the isolated titanium complexes. Their infrared spectra do not show the N–H and O–H stretching frequencies characteristic of the thiazoline form of the ligand (Table I). Also, several new bands appear in the 200–600 cm^{-1} region in the infrared spectra. These new bands are within the region where ν(Ti–O), ν(Ti–N), and ν(Ti–S) frequencies occur.[20] The 1500–1700 cm^{-1} region of the infrared spectra of the complexes are compared to the spectrum of the uncoordinated ligand in Figure 2. The lowering of stretching frequency of these bands, which can reasonably be associated with C=N stretching modes,[21] suggests coordination of the central nitrogen atom in each titanium complex. Similarly, the nmr data for the complexes (Table III) are com-

TABLE III
Proton nmr data for the $TiX_2(SSP)$ complexes[a]

Compound	Solvent	Azomethine Region	Phenyl Region	Other Resonance Peaks
$Ti(SSP)_2$	CH_2Cl_2	8.87	6.7-8.0	
	$CDCl_3$	8.80	6.2-7.7	
$Ti(OEt)_2(SSP)$	$CDCl_3$	8.85	6.5-7.7	1.23(triplet), 4.46(quartet)
	DMSO-d_6	8.79	6.2-7.5	1.06(triplet), 4.36(quartet)
$Ti(OPr^i)_2(SSP)$	$CDCl_3$	8.97	6.6-8.0	1.24(doublet), 4.59(septet)
	CH_2Cl_2	8.77[b]	6.6-8.0	1.20(doublet), 4.60(septet)
$Ti(OBu^t)_2(SSP)$	$CDCl_3$	8.85	6.7-7.7	1.28(singlet)
	CH_2Cl_2	8.87	6.7-7.7	1.18(singlet)
$Ti(C_5H_5)Cl(SSP)$	$CDCl_3$	9.08	7.0-8.0	6.21(singlet)

[a] Chemical shift (δ) downfield from TMS as internal standard.
[b] In DMSO-d_6.

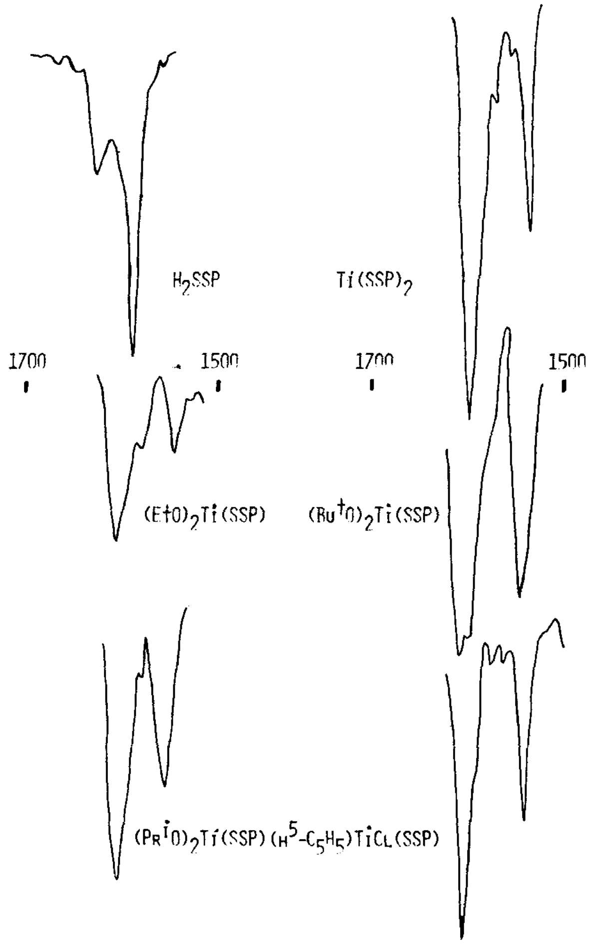


FIGURE 2 Infrared spectra of H_2SSP and the titanium(IV) complexes in the 1500–1700 m^{-1} region.

patible with rearrangement of the thiazoline form of the ligand to the tautomeric Schiff base form. In particular, the chemical shift of the azomethine proton is shifted considerably downfield relative to its resonance position in the free H_2SSP ligand and is in the region found for analogous coordinated Schiff base ligands.[21,22]

The results are most conveniently discussed according to the structural types that are found for these Ti(IV)–SSP complexes.

Monomeric Octahedral Complex

Compounds of the type $Ti(SB)_2$, where SB is the dianion of a dibasic tridentate Schiff base ligand, are expected to contain a six-coordinate titanium atom in view of the propensity of Ti(IV) for this coordination number.[5,23] Previous workers[24] showed that complexes of this type, where the Schiff bases are salicylaldehyde-2-hydroxyanil(H_2SAP) and acetylacetone-mono-(2-hydroxyanil)(H_2AAP), can be prepared in high yield from the reaction of $Ti(OPr^i)_4$ with a 1:2 molar ratio of the appropriate tridentate ligand. The displaced isopropanol is removed azeotropically with benzene. We have prepared a number of $Ti(SB)_2$ complexes in order to establish spectral criteria for the tridentate coordinating ability of this type of Schiff base toward titanium(IV).[1,22] The yellowish brown complex $Ti(SSP)_2$ was accordingly isolated by refluxing $Ti(OEt)_4$ with salicylaldehyde-2-mercaptoanil in benzene, followed by removal of the ethanol-benzene azeotrope and recrystallization of the product from dichloromethane-hexane solution.

Since both reactants are colorless, the immediate development of a dark brown solution when the tetraethoxide is added to the ligand suggests that ligand rearrangement from the thiazoline to the anil form occurs. Confirmatory evidence was obtained from the nmr and infrared spectral shifts. The nmr resonance peaks that are characteristic of the cyclic thiazoline form (*vide supra*) are absent in the nmr spectrum of $Ti(SSP)_2$ whereas the new resonance peak (Table III) is at the expected position for an azomethine proton for coordinated Schiff base ligands derived from salicylaldehyde and N-aryl amines.[21] It is relevant that the azomethine proton signal for the analogous ligand, salicylaldehyde-2-hydroxyanil(H_2SAP), shifts from $\delta 9.0$ ppm in the free anil form to $\delta 9.1$ ppm in the bis-derivative $Ti(SAP)_2$.[22]

The shift in the infrared spectral bands in the 1700–1500 cm^{-1} region between the uncomplexed H_2SSP ligand (Table I) and the bis-derivative (Figure 2) is also indicative of ligand rearrangement to the complexed anil form. The intense bands observed for $Ti(SSP)_2$ [1605 vs, 1578 w, 1560 w, 1544 s] are doubtless associated with $\nu(C{=}N)$ in view of their similarity to the bands assigned recently for a wide range of N-aryl salicylaldimine complexes by Percy and Thornton[21] on the basis of ^{15}N-labelling and metal ion substitution studies. For example, the bands attributable to $\nu(C{=}N)$ in uncoordinated N-phenyl salicylaldimine at 1625 cm^{-1} and 1579 cm^{-1} shift to 1609 cm^{-1} and 1589 cm^{-1} in the Zn(II) complex.[21] Extensive vibrational coupling likely occurs between the $\nu(C{=}N)$ and $\nu(C{=}C)$ frequencies in all of the titanium-SSP complexes; nevertheless, the similarity of the band profile in the

1700–1500 cm^{-1} region of all the complexes is consistent with the presence of tridentate SSP in each case.

$Ti(SSP)_2$ is monomeric in benzene and the highest peak in the mass spectrum (m/e 502) corresponds to the molecular ion of the monomer. Since the compound is also a non-electrolyte, the coordination number of the titanium(IV) atom is six and the geometry is presumably octahedral.

Dimeric Octahedral Complexes

Cryoscopic molecular weight determinations over a concentration range in benzene indicate that both the orange solid of formula $Ti(OPr^i)_2(SSP)$ and the red solid of formula $Ti(OEt)_2(SSP)$ are dimers. The mass spectra of both complexes indicated that association persists in the vapor state, since several fragments, including the dimeric molecular ion of the ethoxide, occur above the monomeric molecular ions observed at m/e 365 (ethoxide) and m/e 393 (isopropoxide). These fragments are most reasonably derived from the dimeric molecular ions since they do not occur in the mass spectrum of $Ti(SSP)_2$. The disproportionation of these dimeric compounds in the mass spectrometer is evidenced by the occurrence of the m/e 502 $[Ti(SSP)_2]^+$ peak in the ethoxide spectrum and by the presence of strong m/e peaks for $[(RO)_4Ti]^+$, $[(RO)_3Ti]^+$, and $\{[(RO)_4Ti]^+{-}CH_3\}$ in both spectra. The latter peaks, which are the three most intense m/e peaks in the mass spectrum of the pure $Ti(OR)_4$ compounds,[25] would arise by the formation of $Ti(OR)_4(R{=}Et, Pr^i)$ under the conditions employed to observe the mass spectra. We are currently studying other dimeric complexes of the type $(RO)_2Ti(SB)$ in which attempted sublimation *in vacuo* leads to the isolation of $Ti(OR)_4$ and $Ti(SB)_2$ products that are readily identified by their nmr and infrared spectra.[22]

Both $(EtO)_2Ti(SSP)$ and $(Pr^iO)_2Ti(SSP)$ show strong infrared bands in the 800–1200 cm^{-1} region which can be assigned to ν(C–O) modes.[20,26] Furthermore, the positions of these alkoxy-bands are compatible with the presence of bridging alkoxy-groups, e.g. 1035 cm^{-1} and 890 cm^{-1} for the ethoxide. The equivalence of the bridging and terminal alkoxy-groups on the nmr time-scale at room temperature (Table III) is not surprising though as rapid exchange is expected with titanium alkoxides.[20] As illustrated in Figure 2, the infrared bands associated with the ν(C=N) modes in the $(RO)_2Ti(SSP)(R{=}Et, Pr^i)$ compounds are almost identical with those observed for $Ti(SSP)_2$. Hence, both dimeric compounds apparently contain tridentate SSP ligands and bridging alkoxy-groups, thereby satisfying the tendency of titanium to be six-coordinate.

Monomeric Pentacoordinate Complexes

Previous work in our laboratory involving trisalkoxytitanium(IV) complexes of the type $(RO)_3TiL$, where L is a uninegative bidentate ligand, showed that increased bulkiness of the alkoxy-group allowed the titanium atom to attain pentacoordination.[11] Accordingly, we have prepared the yellow solid of formula $(Bu^tO)_2Ti(SSP)$ to determine whether steric hindrance is an important factor in the adoption of five-coordination for titanium(IV) in compounds of the type $(RO)_2Ti(SB)$. The synthetic method employed the $(EtO)_2Ti(SSP)$ compound as an intermediate, replacement of the ethoxy-groups being readily effected with an excess of the tertiary–butanol–benzene azeotrope.

The tertiary–butoxide is quite soluble in dichloromethane and benzene and is a monomer in the latter solvent (Table II). Furthermore, the compound can be sublimed at *ca.* 130°/2μ without the disproportionation which occurs with the dimeric compounds of the type $(RO)_2Ti(SB)(R{=}Et, Pr^i)$.[22] The highest m/e peak (421) in the mass spectrum corresponds to the monomeric molecular ion. No fragments were observed corresponding to the formation of $Ti(SSP)_2$ and $Ti(OBu^t)_4$ in the mass spectrometer.

As with the other SSP complexes, the ν(O–H) and ν(N–H) bands observed for the free ligand (Table I) are absent in the infrared spectrum of $(Bu^tO)_2Ti(SSP)$. The bands associated with the ν(C=C) and ν(C=N) modes occur at 1612(vs), 1575(sh), and 1548(s) cm^{-1}. The intense broad bands centered at 1185 cm^{-1} and 1010 cm^{-1} are doubtless due to C–O stretching modes,[20,26] whereas the 605 cm^{-1} band (not present in the spectrum of $Ti(SSP)_2$) can be attributed to the Ti–O stretching vibration of the $Ti{-}OBu^t$ bond.

The observance of a singlet for the resonance peak of the tertiary-butoxy-protons does not provide any structural information because alkoxy-exchange is rapid on the nmr time-scale.[20] However, the occurrence of a peak at *ca.* δ8.8 ppm assignable to the azomethine proton[21,22] corroborates the infrared spectra that indicates tridentate chelating behaviour by the Schiff base ligand. Since the tertiary-butoxide derivative is also a non-electrolyte, we conclude that the coordination number of titanium(IV) has been restricted to five by the bulkiness of the alkoxy-group.

Preliminary attempts to prepare compounds of stoichiometry $(h^5-C_5H_5)_2Ti(SB)$ from the reaction of $(h^5-C_5H_5)_2TiCl_2$ and several dibasic potentially tridentate Schiff bases in the presence of triethylamine as the hydrogen chloride acceptor led to the isolation of compounds of the type $(h^5-C_5H_5)TiCl(SB)$. Displacement of one cyclopentadienyl group was not entirely surprising because complexes of formula $(h^5-C_5H_5)TiClL_2$ (HL=8-hydroxyquinoline,[27] acetylacetone[28]) have recently been reported using similar reaction conditions. In this paper we report the synthesis of $(h^5-C_5H_5)TiCl(SSP)$ as a brown solid obtained in good yield by employing $(h^5-C_5H_5)TiCl_3$ as the starting material. Filtration of the brown reaction mixture removed most of the triethylamine hydrochloride by-product; its complete removal was effected by heating the product to *ca.* 100° *in vacuo.*

The monocyclopentadienyl derivative is a non-electrolyte in nitrobenzene and the highest m/e peak in the mass spectrum (at a temperature of 200° for the direct insertion probe and at 70 eV ionizing energy) corresponds to the monomeric molecular ion (Table II). The fragmentation pattern changes at higher temperatures, though prominent m/e peaks at 65, 66 and 227 still attest to the ready loss of C_5H_5 and SSP. This evidence for decomposition of the complex at higher probe temperatures is in agreement with our observation that attempted sublimation *in vacuo* results in decomposition. Redistribution reactions in the mass spectrometer were also reported for the $(h^5-C_5H_5)TiClL_2$ compounds mentioned above.[27]

The nmr spectra of $(h^5-C_5H_5)TiCl(SSP)$, in deuterochloroform solution, exhibits two singlet peaks at δ9.1 ppm and δ6.2 ppm in addition to a broad multiplet in the phenyl region. Integration and comparison with the spectra of related compounds[21,28] allows the assignment of these resonances to the azomethine proton and the cyclopentadienyl group, respectively. The position of the δ(CH=N) resonance, together with the positions of the 1604 cm^{-1} and 1542 cm^{-1} infrared bands associated with ν(C=N), is good evidence for a tridentate chelate (SSP) ligand (*vide supra*). The resonance of the C_5H_5 group is in the range for h^5-bonded species, and, as would be predicted, the protons are more shielded than in $(h^5-C_5H_5)TiCl_3$ (δ7.07 ppm)[22] or $(h^5-C_5H_5)TiCl(acac)_2$ (δ6.60 ppm).[28] The infrared spectrum of $(h^5-C_5H_5)TiCl(SSP)$ provides more conclusive evidence for a π-bonded or pentahaptocyclopentadienyl group through absorption bands at 3100 cm^{-1} (CH stretching) and at 1025 cm^{-1} (CH in-plane wagging).[29] An attempt to assign infrared bands near 400 cm^{-1} to Ti-ring and Ti–Cl modes, by comparison with the recent assignments for $(h^5-C_5H_5)TiX_3$[30] and $(h^5-C_5H_5)TiXL_2$.[27,28] will be postponed until spectral data will be available for a whole series of $(h^5-C_5H_5)TiX(SB)$ and $TiX_2(SB)$ compounds (X=Cl, Br).[22] Whilst $(h^5-C_5H_5)TiCl(SSP)$ and $(Bu^tO)_2Ti(SSP)$ are both presumably pentacoordinate titanium(IV) complexes, knowledge of the coordination geometry must await the results of further structural characterization currently in progress.

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