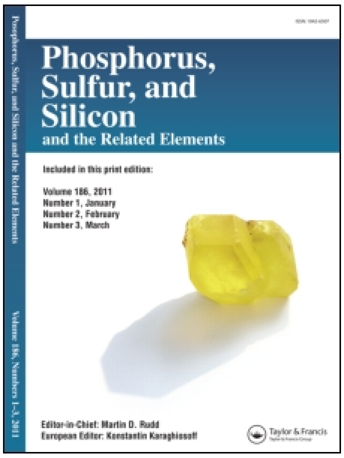

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

TITANIUM(IV) COMPLEXES OF CHELATING 2-(SALICYLIDENEAMINO) BENZENETHIOL

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To cite this Article Singh, M. S. , Narayan, Prem and Singh, A. K.(1999) 'TITANIUM(IV) COMPLEXES OF CHELATING 2-(SALICYLIDENEAMINO) BENZENETHIOL', Phosphorus, Sulfur, and Silicon and the Related Elements, 155: 1, 245 — 252

To link to this Article: DOI: 10.1080/10426509908044986

URL: http://dx.doi.org/10.1080/10426509908044986

Phosphorus, Sulfur, and Silicon, 1999, Vol. 155, pp. 245-252
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TITANIUM(IV) COMPLEXES OF CHELATING 2-(SALICYLIDENEAMINO) BENZENETHIOL

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(Received March 23, 1999; In final form May 20, 1999)

This paper describes the synthesis and structural features of titanium(IV) complexes of biologically active 2-(salicylideneamino) benzenethiol. The complexes have been synthesized by the reaction of $TiCl_4$ with the sodium salt of the ligand (prepared *in situ*) in different stoichiometric ratios and are characterized by elemental analyses, molecular weights, and spectral (IR, ^1H and ^{13}C NMR) studies.

Keywords: 2-(Salicylideneamino) benzenethiol; titanium tetrachloride; monodentate and bidentate; coordination number; spectral studies

Studies of sulfur containing complexes of various transition metals have been reported in the literature.[1-5] The chemistry of stable organotitanium complexes have attracted the attention of chemists in the past few years as evidenced by a number of monographs[6–10] and reviews.[11,12] The titanium derivatives are becoming more and more important for industrial applications,[13,14] and many organic syntheses have been improved by the use of them.[15,16] Titanium(IV) complexes have been cited as Lewis acid promotors in Diels-Alder reactions.[17] However, two recent reviews[5,18] related to the subject as well as sulfur and nitrogen donor ligands indicated that very little work has so far been done on the titanium(IV) complexes of such ligands. Sulfur containing ligands are known for their anticarcinogenic,[19] antibacterial,[20] tuberculostatic[21] and antifungal activities,[22] probably due to their ability to chelate with trace metals. The copper complex of 2-(sali-

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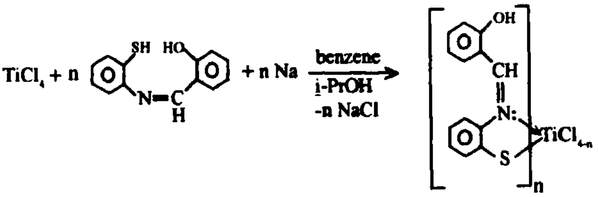
cylideneamino)benzenethiol with trigonal bipyramidal geometry around copper atoms has been discussed.[23] In view of this, and in continuation of our studies on titanium(IV) derivatives,[24] we report the synthesis and characterization of some new titanium(IV) complexes.

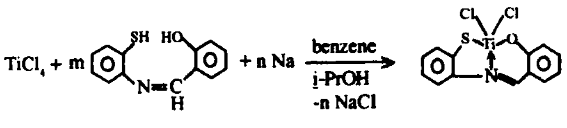
RESULTS AND DISCUSSION

Titanium(IV) derivatives of 2-(salicylideneamino)benzenethiol with the general formulae L_nTiCl_{4-n}, have been synthesized by the reaction of $TiCl_4$ with the sodium salt of the ligand (prepared *in situ*) in different molar ratios, as shown by the following reaction:



1. n = 1
2. n = 2
3. n = 3
4. n = 4

Similarly, the disodium salt of the ligand reacted with $TiCl_4$ in a 1:1 and 2:1 molar ratios to give nine membered titanacyclic complexes.[27] (Table I).



5. m = 1, n = 2
6. m = 2, n = 4

Intermolecular nucleophilic substitution with elimination of chloride ions leads to the formation of products. The resulting complexes are coloured solids, which are further purified by crystallization from CH_2Cl_2-n-hexane mixture. All complexes are nearly soluble in most of the common organic solvents. The solubility increases when the polarity of the solvent increases. Molecular weight determinations in $CHCl_3$ solution show monomeric nature of these complexes.

TABLE I Synthetic and Analytical data of the complexes

Compd. No.	Reactants in (g, mmol)			Molar ratio	Yield in g, (%)	Analyses % found(calcd.)			
	$TiCl_4$	Ligand	Sodium			N	S	Ti	Cl
(1)	1.29 (6.8)	1.56 (6.8)	0.16 (6.8)	1:1:1	2.02 (78)	3.42 (3.66)	8.53 (8.37)	12.78 (12.55)	27.47 (27.84)
(2)	0.46 (2.4)	1.10 (4.8)	0.11 (4.8)	1:2:2	0.99 (72)	4.53 (4.87)	10.87 (11.13)	8.62 (8.35)	12.70 (12.35)
(3)	0.28 (1.5)	1.02 (4.5)	0.10 (4.5)	1:3:3	0.96 (85)	5.83 (5.47)	12.87 (12.51)	6.63 (6.25)	4.91 (4.63)
(4)	0.26 (1.4)	1.24 (5.4)	0.12 (5.4)	1:4:4	0.96 (73)	5.98 (5.80)	13.19 (13.33)	5.17 (5.00)	—
(5)	0.63 (3.3)	0.76 (3.3)	0.16 (6.8)	1:1:2	0.98 (87)	4.45 (4.05)	9.52 (9.25)	13.67 (13.84)	20.94 (20.52)
(6)	0.44 (2.3)	1.05 (4.6)	0.22 (9.2)	1:2:4	1.00 (86)	5.82 (5.58)	12.48 (12.75)	9.87 (9.54)	—

IR spectra

Important absorption bands in the IR spectra of the titanium(IV) complexes are summarized in Table 2. The IR spectrum of the free ligand shows a band in the region 3185–3110 cm^{-1} due to the ν(OH) of the intramolecularly hydrogen bonded[26] phenolic OH. The complexes do not show this band indicating the loss of a hydrogen bond and deprotonation. The spectra of the complexes (1-4) exhibit a broad band within the range 3525–3210 cm^{-1}attributable to ν(OH) of the phenolic group which did not take part in complexation. The Schiff bases exhibit a band at ~2500 cm^{-1} due to ν(S-H). This band disappears in the spectra of all complexes, indicating deprotonation and consequent coordination of the sulfur atom to titanium. This fact is further supported by the appearance of a new band in the region 335–320 cm^{-1}, which is ascribed to a Ti-S stretching mode.[28,29] The disappearance of ν(OH) in the complexes **5** and **6** (Table II) indicates deprotonation of phenolic-OH and consequent bonding of phenolic oxygen to the titanium, which is further strengthen by the appearance of a new band around 435 cm^{-1}, ascribable to Ti-O stretching mode.[29] A strong band at 1590 cm^{-1} assignable to ν(C=N) in the free ligand, is shifted to a higher frequency by 20–30 cm^{-1} in the spectra of the complexes, indicating participation of the azomethine nitrogen in coordination[27] which is further confirmed by the appearance of Ti-N band at ~ 540 cm^{-1}.

^{1}H NMR spectra

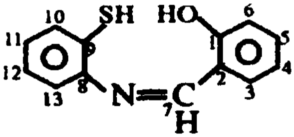
A comparison of the ^{1}H NMR spectral data of the ligand and titanium(IV) complexes provides interesting results given in Table II. The chemical shifts of -SH and -OH protons are concentration dependent and are shifted to lower δ values in dilute solutions. The -SH signal is absent in the spectra of all the complexes, confirming deprotonation and its subsequent involvement in coordination. The -OH signal observed at ~ δ 13.10 in compounds **1–4** also disappeared in compounds **5** and **6**, indicating deprotonation and involvement in coordination. The azomethine proton suffers deshielding and appears at ~ δ 8.30, indicating coordination of azomethine nitrogen to titanium. The resonance due to phenyl moiety remains almost unaffected in all the complexes.

TABLE II Physical and spectral data of the complexes

Compd.	Mol.Formula / Mol.Wt.F(C)	M.P. (°C)/ Colour	*IR* ν(cm^{-1})				*NMR* δ *(ppm)*				
								^{13}C			
			(C=N)	*(OH)*	*(Ti-S)*	*(Ti-O)*	^{1}H	*C-1*	*C-2*	*C-7*	*C-9*
(1)	$C_{13}H_{10}NOSTiCl_3$ 406 (382.5)	180 Yellow	1615	3500–3210	330	—	6.78–7.22 (m, 8H, arom); 8.26 (s, 1H, CH=N); 13.15 (s, 1H, OH).	157.2	118.3	187.4	171.3
(2)	$C_{26}H_{20}N_2O_2S_2TiCl_2$ 594 (575)	201 Yellow	1620	3520–3200	335	—	6.82–7.34 (m, 16H, arom); 8.32 (s, 2H, CH=N); 13.10 (s, 2H,OH).	157.9	118.5	187.7	170.8
(3)	$C_{39}H_{30}N_3O_3S_3TiCl$ 782 (767.5)	189 Yellow	1610	3500–3220	325	—	6.75–7.25 (m, 24H, arom); 8.28 (s, 3H, CH=N); 12.98 (s, 3H,OH).	156.8	118.7	187.5	171.1
(4)	$C_{52}H_{40}N_4O_4S_4Ti$ 985 (960)	102 Brown	1625	3525–3225	320	—	6.68–7.32 (m, 32H, arom); 8 20 (s, 4H, CH=N); 13.05 (s, 4H,OH).	157.6	118.9	187.3	170.9
(5)	$C_{13}H_9NOSTiCl_2$ 391 (346)	174 Orange	1605	—	335	430	6.80–7.25 (m, 8H, arom); 7.64 (s, 1H, CH=N).	167.4	118.1	187.8	170.7
(6)	$C_{26}H_{18}N_2O_2S_2Ti$ 533 (502)	194 Yellow	1615	—	330	435	6.72–7.30 (m, 16H, arom); 7.80 (s, 2H, CH=N).	167.9	118.6	187.9	171.4

^{13}C NMR spectra

^{13}C NMR spectrum of free ligand indicates signals at δ 156.8, 117.8, 127.5, 118.2, 129.5, 115.4, 175.44 and 158.64 ppm, which could be assigned to C-1, C-2, C-3 (13), C-4 (12), C-5 (11), C-6 (10), C-7 and C-9, respectively.



A perusal of spectra of the complexes indicates that the ^{13}C NMR spectra have the expected number of signals. The shifts of the carbons attached to N, O, and S indicate their coordination with the titanium atom.[27]

Although the actual structure can be elucidated only after X-ray crystal structural study of at least one of the products, yet on the basis of above studies a coordination numbers of five, six, seven and eight may be assumed around titanium(IV).

EXPERIMENTAL

All manipulations were carried out under strictly anhydrous conditions. Chemicals and solvents used were dried and purified by standard methods.[25] $TiCl_4$(b.p 134°C, Aldrich) was freshly distilled before use. The ligand 2-(salicylideneamino) benzenethiol was prepared by the literature method.[26] All the melting points are uncorrected. Titanium(IV) was estimated gravimetrically as TiO_2 and chlorine and sulfur were estimated gravimetrically as AgCl and $BaSO_4$, respectively.[25] Nitrogen was determined by the Kjeldahl's method.[25] IR spectra were recorded on a Perkin-Elmer model 577 spectrometer in the range 4000–200 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz spectrometer in $CDCl_3$ using TMS as an internal reference. Molecular weights were determined by a Knauer Vapour Pressure Osmometer in dilute $CHCl_3$ solution at 45°C.

Reaction between titanium(IV) chloride and the sodium salt of 2-(salicylideneamino) benzenethiol in a 1:1 molar ratio

To a clear cold solution of sodium isopropoxide [prepared *in situ* by dissolution of sodium (0.16 g, 6.8 mmol) in isopropanol (25 ml)] was added 2-(salicylideneamino)benzenethiol) (1.56 g, 6.8 mmol) slowly, and the contents were refluxed for 4 hours. After cooling, 1.29 g (6.8 mmol) of $TiCl_4$ in 15 ml of dry benzene was added dropwise, and the mixture was further refluxed for 2 hours to ensure the completion of the reaction. After filtering off the precipitated NaCl, the desired product (2.02 g, 78%) was isolated by evaporation of the solvents under reduced pressure. The product was further purified by crystallization using dichloromethane-*n*-hexane mixture. All other titanium(IV) derivatives of 2-(salicylideneamino)benzenethiol were synthesized analogously. The pertinent data for this and other derivatives are listed in Table I.

Acknowledgements

The authors are highly grateful to Dr. Ganesh Pandey from National Chemical Laboratory, Pune for valuable academic guidance and spectral help.

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