

Schiff Base Complexes of Oxocations. Part III*. Oxotitanium(IV) Complexes with Tetradentate Optically Active Schiff Bases

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The synthesis and properties of oxotitanium(IV) complexes with tetradentate Schiff bases produced by the condensation of two moles of salicylaldehyde with one mole of optically active 1,2-diamine, namely (–)propylenediamine, (–) and meso-butanediamine, (–)cyclohexanediamine and (+)stilbenediamine, are described. One to one adducts of these complexes with protonic acids have also been isolated. The structures of the metal complexes are discussed on the basis of infrared, circular dichroism and electronic spectra and ionic conductivities in solution.

Introduction

We have recently undertaken a study on complexes of oxocations with optically active tetradentate Schiff bases derived from salicylaldehyde and C-substituted ethylenediamines (saldiamineH₂)^{1,2}, with the hope of elucidating the conformational behaviour of these ligands in complexes with coordination number higher than four. Moreover we have compared their conformational properties with those of related cobalt dioxygen adducts which are under investigation in our laboratory³. So far we have studied two series of compounds derived from the species UO₂²⁺ and VO²⁺ respectively. In the former case we have observed that the conformation of the ligands does not follow any predictable pattern, it being dependent on the overall coordination number (six or seven), on the diamine and on the solvent¹.

More general results² were obtained with penta-coordinate oxovanadium(IV) complexes for which the circular dichroism spectra showed that the substituents of the carbon atoms of the diamine chelate ring are axial in the case of propylenediamine and butanediamine, but equatorial in the case of cyclohexanediamine and stilbenediamine. Both electronic and circular dichroism spectra of oxovanadium(IV) compounds

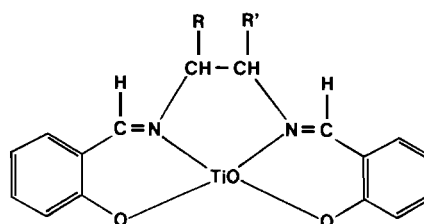


Figure 1. Compounds and abbreviations in parentheses R = R' = H, ethylenediamine (en); R = H, R' = CH₃, propylenediamine (pn); R = R' = CH₃, butanediamine (bn); R = R' = C₆H₅, stilbenediamine (stien); R = R' = 1/2(CH₂)₄, cyclohexanediamine (chxn).

contained bands due to the presence of an odd *d* electron. In order to make the system of the oxo-transition metal complexes electronically more comparable to that of UO₂²⁺, we decided to synthesize and study a series of compounds derived from the species oxotitanium(IV), which does not contain any *d* electron, its electronic spectrum being due only to charge transfer and/or intraligand bands.

To the best of our knowledge, only one example of oxotitanium(IV) complexes with tetradentate Schiff bases⁴ has been described, although Pfeiffer⁵ reported some titanium(IV) complexes which he formulated as [Ti(salen)]²⁺(OH⁻)(X⁻) where X⁻ is Cl⁻, ClO₄⁻, NO₃⁻ etc. Here we report some oxotitanium(IV) complexes with tetradentate optically active Schiff bases derived from salicylaldehyde and a variety of *R*, or *R,R* optically active diamines^{6,7,8}, which are summarized in Figure 1, together with the abbreviations used.

Experimental

Analyses (see Table I) were performed by the microanalytical laboratory of the University of Milan; infrared spectra were recorded on Perkin-Elmer 137 and 621 instruments. Conductivity measurements and titrations with NaOH and AgNO₃ were performed

* Part II. A. Pasini and M. Gullotti, *J. Coord. Chem.*, 3, 319 (1974).

TABLE I. Elemental Analyses.

Compound	Calc.			Found		
	C	H	N	C	H	N
TiO(salen) · HClO ₄ ^a	44.6	3.5	6.5	45.5	3.5	6.6
TiO(salen) · HClO ₄ ^b	44.6	3.5	6.5	44.4	3.5	6.7
TiO(salen) · HCl ^{c,d}	52.5	4.1	7.7	53.0	3.9	7.8
TiO(salen) · HClO ₄ ^c	44.6	3.5	6.5	44.4	3.7	6.4
TiO(salen) · HClO ₄ ^e	44.6	3.5	6.5	44.0	3.5	6.0
TiO(salen)1/2H ₂ C ₂ O ₄	54.4	4.0	7.5	54.0	4.3	7.6
TiO(sal- <i>o</i> -phen) · HClO ₄ ^a	50.2	3.1	5.9	50.0	2.9	6.0
TiO(sal- <i>o</i> -phen) · HClO ₄ ^b	50.2	3.1	5.9	51.0	3.0	6.1
TiO(sal(-)pn) · 3/2HClO ₄ ^a	41.2	3.5	5.6	41.3	3.5	5.6
TiO(sal(-)pn) · HClO ₄ ^b	45.9	3.8	6.3	45.2	3.7	6.2
TiO(salmesobn) · HClO ₄ ^a	47.1	4.1	7.0	47.1	4.0	6.4
TiO(salmesobn) · HClO ₄ · 1/2py ^b	49.4	4.1	7.0	49.5	3.8	6.9
TiO(salen) · 1/2CH ₃ OH	57.2	4.6	8.1	57.8	4.1	8.0
TiO(sal(-)pn) · CH ₃ OH	57.4	5.3	7.4	57.2	5.4	7.6
TiO(sal(-)bn) · 2CH ₃ OH	56.9	6.1	6.6	55.9	5.8	6.4
TiO(salmesobn) · CH ₃ OH	58.5	5.6	7.2	58.2	5.3	7.2
TiO(sal(-)chxn) · CH ₃ OH	60.0	5.7	6.7	59.5	5.1	6.7
TiO(sal(+)stien) · CH ₃ OH	67.7	5.0	5.5	68.0	4.7	5.6
TiO(sal- <i>o</i> -phen) · CH ₃ OH	61.5	4.4	6.8	61.4	4.4	6.3

^a Crystallized from methanol. ^b Crystallized from pyridine. ^c Pfeiffer's compounds⁵. ^d Cl calc. 9.69, found 9.83.

^e Obtained treating the corresponding complex of class B with aqueous perchloric acid.

on a Philips conductimeter PR 9500. Electronic spectra were obtained on a Beckman DK-2A spectrophotometer, circular dichroism (C.D.) spectra on a Jouan dichrograph II.

The Schiff bases were prepared as described elsewhere⁸.

TiO(salicylaldimine) · HClO₄ Species

These were prepared by the following method. Titanil perchlorate⁹ was dissolved in methanol with an equimolar amount of the appropriate Schiff base and the solution was refluxed for a couple of hours. The red-brown precipitate was filtered, washed with aqueous methanol and dried *in vacuo*. Upon treatment with pyridine (py) or dimethylformamide (DMF) the compound turned yellow. Both compounds analyzed for TiO(salicylaldimine) · HClO₄.

TiO(salen) · HCl

This was prepared, following Pfeiffer⁵, by treating in wet pyridine TiCl₄ with an equimolar amount of the Schiff base. This red material can be transformed into the perchlorate derivative by treating it with aqueous perchloric acid (70%).

TiO(salen) · 1/2H₂C₂O₄

This was prepared in a similar way from titanil oxalate¹⁰. Since TiO(C₂O₄) is very insoluble in methanol, the reaction required three days.

TiO(salicylaldimine) Species

Titanil acetylacetonate was suspended in methanol together with the appropriate Schiff base and refluxed for one day giving a yellow solution from which a yellow microcrystalline compound insoluble in most common organic solvents precipitated. Upon treatment with aqueous hydrochloric or perchloric acid, these compounds transformed into the adducts with HCl and HClO₄ respectively.

Results and Discussion

Preparation and Characterization of the Compounds

Two classes of compounds were obtained: compounds A, with one equivalent of acid per mole of complex and compounds B which did not contain any acid (see Table I).

Compounds of type B were obtained by an exchange reaction between the Schiff base and bis(acetylacetonate)oxotitanium(IV) (TiO(acac)₂) whilst by direct reaction of the Schiff bases with TiO(CIO₄)₂, TiO(C₂O₄) or TiCl₄ (in non completely anhydrous solvents) we obtained complexes which contain one equivalent of the corresponding acid per mole of complex (type A compounds). In the case of perchloric acid, the acid adducts crystallized in two different forms, according to the solvent used: a red form from methanol and a yellow one from pyridine or DMF.

The two forms are interchangeable, it being sufficient to treat the solid material with the appropriate solvent.

The infrared spectra suggest that in the red form the perchloric acid is weakly interacting with the metal complex whilst it changes to an essentially ionic perchlorate in the yellow form. In particular a complex series of bands at about 1100–1000 and 930 cm^{-1} can be detected in the infrared spectrum of the red form, while in the yellow form one strong band at 1100 cm^{-1} and one at 620 cm^{-1} indicate the presence of an ionic perchlorate¹¹. However it must be said that in the 1100 cm^{-1} region there are a number of bands of the ligands, thus making any correct assignment of the bands very difficult. As a consequence our arguments are based more on the shape than on the number of bands, particularly in the case of the red form. Only in the case of $\text{TiO}(\text{salmesobn})$ two clear and very different patterns were obtained (Figures 2b and 2c).

The presence of an anion in the yellow form poses the problem of the protonation of the complex which can occur in either of the two positions: the oxygen atoms of the Schiff base or that of the oxotitanium moiety. The difficulty of assigning with certainty the $\text{Ti}=\text{O}$ stretching frequencies in both series of compounds (see later) does not allow the exact definition of the site of protonation. In the infrared spectra usually two bands appear in the OH stretching region at about 3400 and 3200 cm^{-1} which could reflect different sites of protonation. For instance in the case of

$\text{TiO}(\text{salmesobn})\cdot\text{HClO}_4$ (Figure 2b), two clear bands at 3450 and 3230 cm^{-1} appear in the spectrum of the material crystallized from methanol, whereas in that of the material obtained from pyridine, there is a broad band at about 3500 cm^{-1} and a rather intense and narrow band at 3260 cm^{-1} (Figure 2c). This variations are concomitant with those of the shape and number of the perchlorate bands at about 1100 cm^{-1} ; very likely they reflect the equilibrium between the undissociated HClO_4 and the ionic perchlorate ion in the two crystalline forms.

The perchlorate and chloride derivatives dissociate in solution giving 1 : 1 electrolytes as shown by values of their conductivities (Table II) compared with those given in the literature for 1 : 1 electrolytes¹². The low conductivity in pyridine can be due to a variety of factors as its low dielectric constant and good donor properties which can alter the conductivity of complexes in this solvent¹². Water slurries of type A compounds react acid to litmus paper and conductimetric titrations of the anion with NaOH (and with AgNO_3 in the case of the chloride) give values in accordance with the presence of one mole of acid per mole of complex.

Class A compounds are very stable and we were unable to obtain the corresponding class B compounds, removing the acid either by heating the compounds *in vacuo* or by treatment with bases such as aqueous sodium carbonate. Coordinated oxalic acid can of

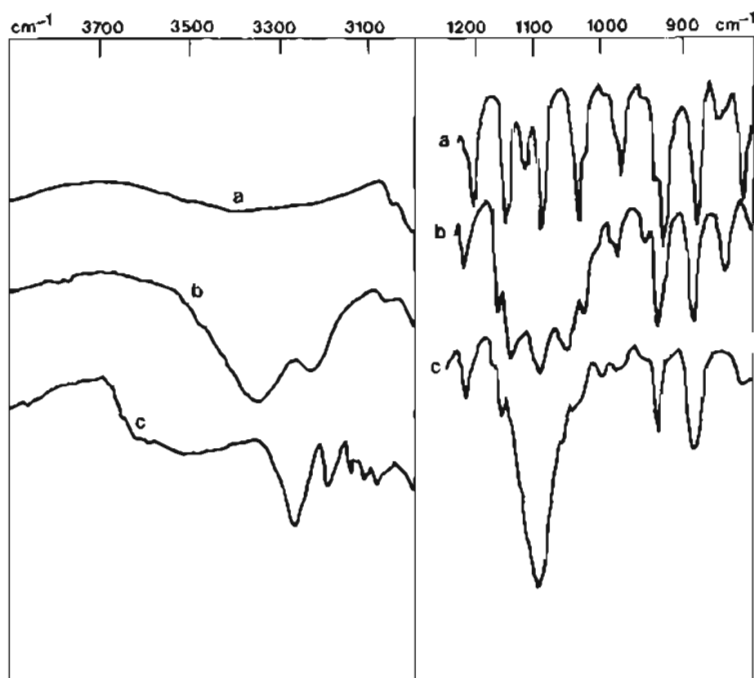


Figure 2. Infrared spectra in the 3500 cm^{-1} and in the 1000 cm^{-1} regions of $\text{TiO}(\text{salmesobn})$ (a); $\text{TiO}(\text{salmesobn})\cdot\text{HClO}_4$ crystallized from methanol (b) and from pyridine (c).

TABLE II. Conductivity Measurements in Several Solvents at 25° C, Concentration 10⁻³ M.

Compound	Solvent	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)
TiO(salen)·HCl	H ₂ O	181.5
TiO(salen)·HCl	CH ₃ OH	75.8
TiO(salen)·HCl	DMF	66.1
TiO(salen)·HCl	py	8.5
TiO(salen)·HClO ₄	H ₂ O	184.1
TiO(salen)·HClO ₄	CH ₃ OH	86.3
TiO(salen)·HClO ₄	DMF	66.0
TiO(salen)·HClO ₄	py	42.6

course be oxidised by dilute aqueous permanganate, but with concomitant destruction of the complex.

On the contrary all class B compounds can be easily transformed to class A compounds by treatment with an aqueous solution of the appropriate acid. This fact is quite surprising since, on treating the related compounds of oxovanadium or dioxouranium with acids the complexes are usually destroyed¹³.

Class A compounds have been already reported in the literature, although with different formulations^{4,5}.

For instance some workers⁴, by reacting TiO(ClO₄)₂ with bis-salicylidene-*ortho*-phenylenediamine (sal-*o*-phenH₂) obtained a compound which they claimed to be TiO(sal-*o*-phen), but which was not too well characterized (only nitrogen and titanium analyses were given). We have repeated their synthesis and obtained a compound which analyses as TiO(sal-*o*-phen)·HClO₄ (Table I). The infrared band at 1090 cm⁻¹ is due to the ionic ClO₄⁻ species and not to the Ti=O bond as proposed by these authors⁴.

Also Pfeiffer⁵, in his classical work on complexes of Schiff bases, reacted TiCl₄ with salenH₂ in non-anhydrous pyridine obtaining a compound to which he assigned the formula [Ti(salen)]²⁺(OH⁻)(Cl⁻). We repeated this synthesis obtaining a compound which behaves as a 1:1 electrolyte (Table II) thus ruling out Pfeiffer's formulation.

We suggest the formulation TiO(salen)·HCl (which has the same analysis as Pfeiffer's compound) since the same material can also be obtained from TiO(salen) (class B compound) upon treatment with aqueous hydrochloric acid; moreover conductimetric titrations are perfectly in agreement with this assumption.

Class B compounds crystallized with different amounts of solvent molecules (see Table I). They are very insoluble in practically every solvent or dissolve with great difficulty in basic solvents. We believe that they are polymeric species with Ti-O-Ti-O chains both because of their low solubility and because we did not observe any infrared band in the 1100-900 cm⁻¹ region where the monomeric Ti=O species are expected to absorb^{14,17}.

The infrared evidence would suggest that these chains are not broken also in class A compounds. In fact the infrared spectrum of TiO(salen) is almost superimposable with that of the corresponding type A compounds apart the bands due to the anions and those in the OH region (see Figure 2).

The position of the titanyl stretching frequency is difficult to define with certainty. Only few compounds containing a monomeric Ti=O moiety have been reported: TiO(β -diketone)₂¹⁵, TiO(phthalocyanine)¹⁶ and TiO(porphyrine)¹⁷. They present a band in the 1040-970 cm⁻¹ region. This is surely not the case of our compounds, since as already stated, we could not observe any typical band in that region.

However, upon comparison of the spectra of our compounds with those of the free ligands and those of their complexes with other metals, it appears that the only band which can be possibly assigned to a Ti-O vibration is one of medium intensity at about 820-810 cm⁻¹ (class A) and at about 810-800 cm⁻¹ (class B). These values would suggest a polymeric structure by comparison with known polymeric oxotitanium compounds such as, for instance, TiOSO₄·H₂O,¹⁸ [TiO(OCOCF₃)₂]_n¹⁹ and K₂[TiO(C₂O₄)₂]¹⁵, which are known to possess (TiO)_n chains and show a band at about 800 cm⁻¹.

It must be said, however, that polymeric oxotitanium species usually give broad bands, in contrast to what found in our complexes where the band at about 810 cm⁻¹ is a sharp one.

Sharp bands at 825 cm⁻¹ were reported for some sulphoxide complexes of oxotitanium(IV); they have

been attributed to dimeric di- μ -oxo Ti species²⁰.



As a matter of fact similar species are not uncommon in oxotitanium compounds²¹. In this arrangement, however, the two halves of the Schiff base should fold to a large extent because of the geometry of the dimeric species. For this reason, although some irregularities of the patterns of the circular dichroism spectra (see later) could support the di- μ -oxo hypothesis, we tend to believe that all the compounds here described possess both in solution and in the solid state the Ti-O moiety either as monomer (in solution of basic solvents) or as a part of a polymeric Ti-O-Ti-O chain (in the solid state and presumably also in solution of some particular solvents). This belief is also supported by the fact that both type A and B compounds can be prepared from compounds which contain both the Ti=O and the Ti-O-Ti-O entities, as shown by the infrared spectrum of TiO(acac)₂¹⁵.

Circular Dichroism Spectra

In Figure 3 the electronic spectra (in a variety of solvents) of an example compound, namely TiO(sal

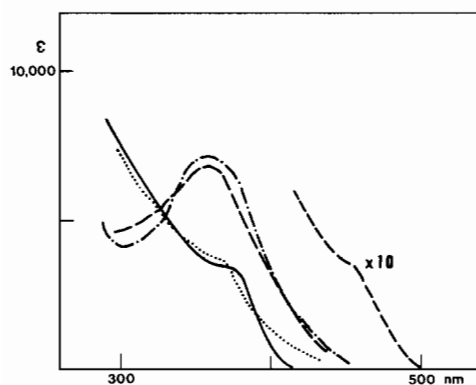


Figure 3. Electronic absorption spectra of $\text{TiO}(\text{sal}(-)\text{pn}) \cdot \text{HClO}_4$ (class A) in methanol (—) and in dimethylformamide (---) and of $\text{TiO}(\text{sal}(-)\text{pn})$ (class B) in dimethylformamide (- · -) and in pyridine (....)

(-) pn) and its perchloric acid derivative are reported. They mainly consist of a band at about 380 nm which has been assigned to the $\pi \rightarrow \pi^*$ transition of the azomethine groups²², shifted to lower energy than in the free ligand⁸, as is usually the case of this type of complexes^{2,22}. Another weak shoulder at about 450 nm appears in the DMF and pyridine solution spectra of the perchloric acid adduct. Apart from this band no charge transfer band can be detected.

Interestingly the methanol solution of the type A derivative produces the same spectrum of the corresponding type B. The differences observed in the

spectra of the perchloric acid derivatives carried out in basic solvents or in methanol probably reflect the differences of the structures of the yellow and red forms which are respectively present in these solvents and from which crystallize.

Since from pyridine or DMF the form with an anionic perchlorate is obtained, the weak shoulder at 450 nm is probably related with the direct protonation of the complex. In Figure 4 the circular dichroism spectra in methanol solution of a series of perchloric acid (type A) adducts are reported.

They consist of a simple positive-negative couplet centered at about 380 nm (*i.e.* where the isotropic absorption lies), which should arise from the exciton splitting of the $\pi \rightarrow \pi^*$ transitions of the two azomethine groups²² in a tetrahedral distortion of the essentially planar structure of the Schiff base. As expected for this kind of complexes^{2,7,23} the (-) chxn derivative displays a pattern which is opposite to those of the (-) pn and (-) bn derivatives because of the different conformation of the chelate ring in the two cases. In fact it is known^{2,7} that the conformation of the diamine chelate ring in pentacoordinate complexes is such that the substituents R of the diamine (Figure 5) are axial in the case of (-) pn and (-) bn , but opposite (R equatorial) for the cyclohexanediamine of the same absolute configuration (that is (-) chxn).

The circular dichroism spectra in methanol solution of type B compounds have been found to be similar, in agreement with the trends of electronic spectra. These results would support that both A and B type compounds produce in methanol solution the same

TABLE III. Circular Dichroism Spectra.

Compound	Solvent	λ (nm); $\epsilon_1 - \epsilon_d$ (in parentheses)
$\text{TiO}(\text{sal}(-)\text{pn}) \cdot \text{HClO}_4$	CH_3OH	395 (+1.25); 332 (-3.10)
	DMF	422 (+0.41)sh; 353 (-1.20); 312 (+2.90)
	py	390 (+1.61); 342 (-1.60)
$\text{TiO}(\text{sal}(-)\text{bn}) \cdot \text{HClO}_4$	CH_3OH	410 (+2.39); 345 (-1.59); 322 (+0.25)sh
	DMF	452 (+0.89); 360 (-3.28); 315 (+8.10)
	py	344 (+0.42); 396 (-1.71); 360 (+1.83); 341 (+0.87)
$\text{TiO}(\text{sal}(-)\text{chxn}) \cdot \text{HClO}_4$	CH_3OH	420 (-0.76); 345 (+4.88); 310 (+0.75)sh
	DMF	405 (+2.21); 379 (+1.58); 355 (+2.57); 328 (-1.68)
	py	396 (-3.35); 351 (+6.08); 335 (+5.30); 327 (+5.55)
$\text{TiO}(\text{sal}(+)\text{stien}) \cdot \text{HClO}_4$	CH_3OH	373 (+3.65); 325 (-1.26); 300 (+3.58)
	DMF	428 (+2.02); 400 (+0.85)sh; 346 (-0.9); 315 (+7.83)
	py	430 (+2.08); 386 (-1.12); 371 (-0.77); 342 (-2.92)
$\text{TiO}(\text{sal}(-)\text{pn})$	CH_3OH	395 (+2.42); 320 (-0.4)
	DMF	382 (+2.35); 350 (-0.2)sh; 330 (-1.08)
	py	382 (+5.25); 335 (-1.35)
$\text{TiO}(\text{sal}(-)\text{bn})$	DMF	395 (-2.00); 350 (+2.25)
	py	395 (-5.00); 375 (+7.30)
$\text{TiO}(\text{sal}(-)\text{chxn})$	DMF	382 (-22.60); 345 (+12.45); 315 (+8.85)
	py	392 (-20.80); 345 (+10.35)
$\text{TiO}(\text{sal}(+)\text{stien})$	DMF	398 (-15.75); 355 (+22.35)
	py	390 (-17.75); 355 (+23.40)

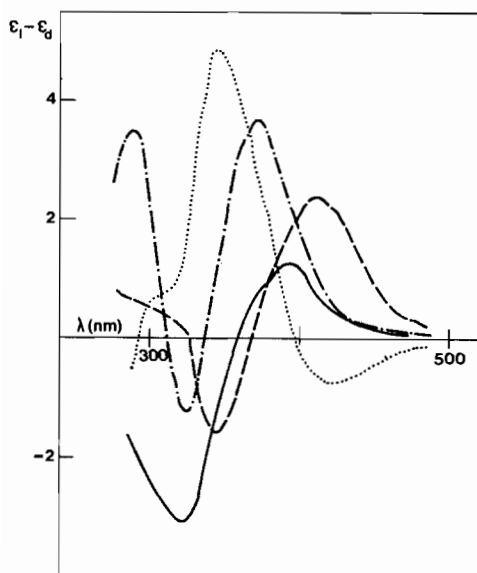


Figure 4. Circular dichroism spectra of $\text{TiO}(\text{sal-}R\text{-diamine})\cdot\text{HClO}_4$ in methanol solution; — $(-)\text{pn}$, ---- $(-)\text{bn}$,, $(-)\text{chxn}$, -.- $(+)\text{stien}$.

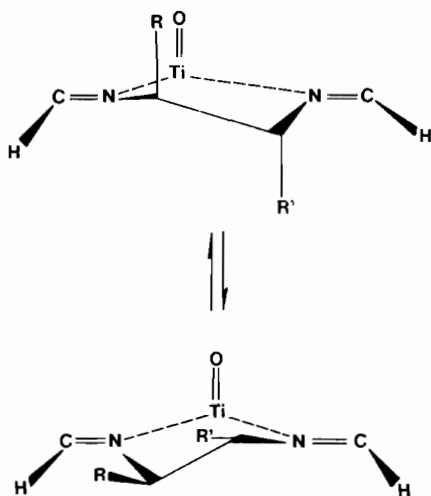


Figure 5. The equatorial-axial equilibrium, with the concomitant λ - δ inversion, of the conformation of the chelate ring.

oxotitanium species which is probably pentacoordinated.

However on the ground of this geometry, one would expect the circular dichroism spectrum of $\text{TiO}(\text{sal}(+)\text{stien})$ to be similar to that of the related complexes of $(-)\text{chxn}$, in line with what found for oxovanadium² and other pentacoordinated complexes⁷. For this reason the case of the complex of $(+)\text{stilbenediamine}$ is, at the moment, difficult to rationalise. The similarity

of circular dichroism spectra of $(-)\text{pn}$, $(-)\text{bn}$, and $(+)\text{stien}$ Schiff base complexes has been observed only in the case of square planar complexes⁷, but this coordination seems unlikely in the case of oxotitanium compounds. Hexacoordination around the metal in a polymeric chain structure, or with the perchloric acid or methanol interacting in *trans* position to the oxygen atom of the TiO group should also be ruled out.

In this case steric repulsions between the R groups and the two apical ligands would require the substituents R to be equatorial in nearly all cases²⁴.

From models it appears that, in the case of $R(-)$ propylenediamine the axial position of the methyl group requires a δ conformation²⁵ of the diamine chelate ring and a concomitant λ tetrahedral distortion of the Schiff base²³.

The positive-negative couplet centered at about 380 nm (with the positive band lying at lower energy) is in agreement with this conformation^{22,23}.

In more basic solvents (e.g. DMF or pyridine) type B compounds show a similar pattern of C.D. spectra (Figure 6) Only the $(-)\text{pn}$ derivative shows in both solvents an opposite trend of the spectrum.

The circular dichroism spectra of these complexes seem to reflect a λ and Δ configuration of the chelate

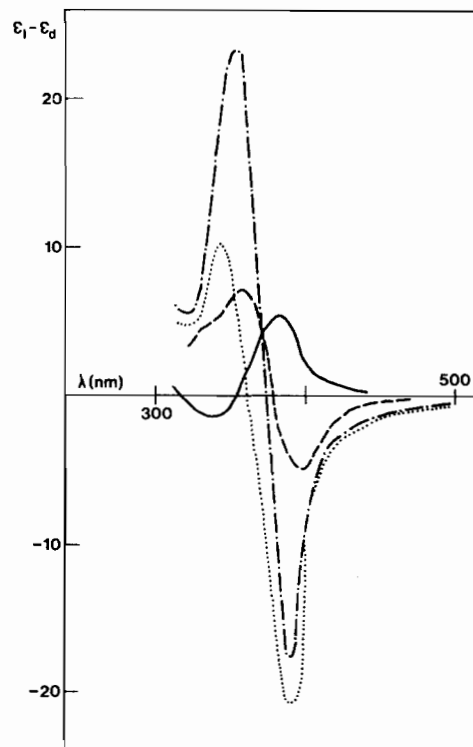


Figure 6. Circular dichroism spectra of $\text{TiO}(\text{sal-}R\text{-diamine})$ in pyridine; — $(-)\text{pn}$, ---- $(-)\text{bn}$, $(-)\text{chxn}$, -.- $(+)\text{stien}$.

ring and of the N_2O_2 chromophore respectively. This would correspond to the stabilization of the equatorial position of substituents (Figure 5), which would suggest an hexacoordination of the titanium atom²⁴.

Strangely enough this is not the case of $TiO(sal(-)pn)$. However it is likely that these compounds can be highly distorted, thus making general correlations very difficult in the absence of any sure structural data.

The perchloric acid derivatives show in DMF more complicated spectra (Figure 7). In particular a new band at about 450 nm, positive in all cases, is clearly detectable in correspondence with the shoulder observed in the isotropic electronic spectra (Figure 3). Another interesting feature is the inversion of signs of the dominant couplet, with respect to the spectra of the methanol solution (Figure 4). The inversion of sign, also in the case of cyclohexanediamine, is not in agreement with an inversion of conformation of the chelate ring, because this ring, in the case of the cyclohexanediamine derivative, must always be locked in a *trans* diaxial conformation. The change of sign of the C.D. could reflect the presence of a site of direct protonation of the Schiff base ligand (for instance the oxygen atoms) which could reverse the directions of polarization of the two coupled $\pi \rightarrow \pi^*$ transitions of the azomethines thus inverting the sign of the exciton coupling.

Moreover the cyclohexanediamine compound has a C.D. spectrum opposite to that of type B cyclohexanediamine compound in the same solvent, a result in agreement with the previous assumption.

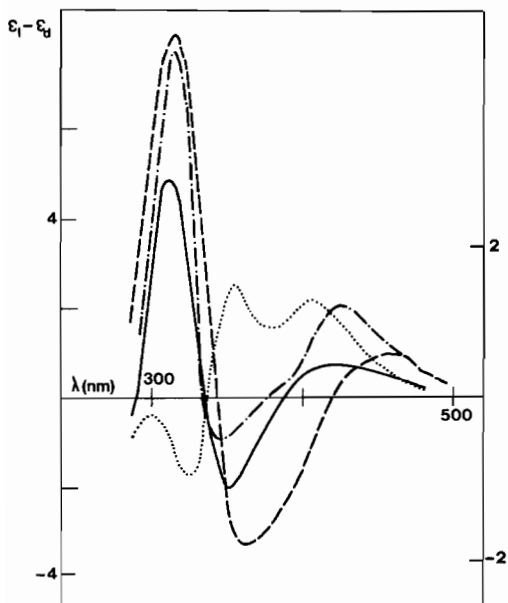


Figure 7. Circular dichroism spectra of $TiO(sal-R-diamine) \cdot HClO_4$ in dimethylformamide; — ($-$)pn (scale on the right hand side), ---- ($-$)bn, ($-$)chxn, - · - ($+$)stien.

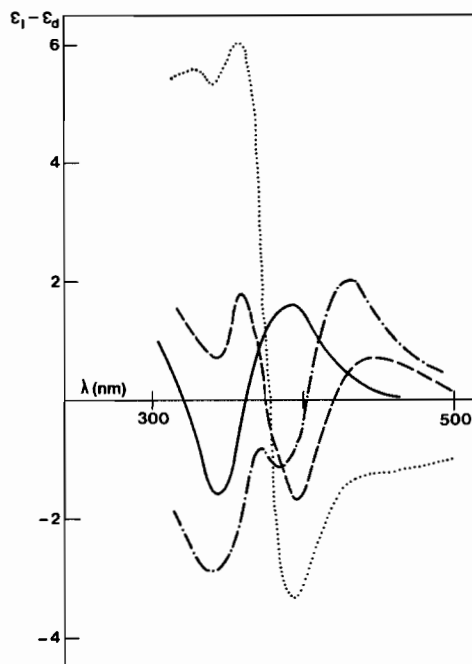


Figure 8. Circular dichroism spectra of $TiO(sal-R-diamine) \cdot HClO_4$ in pyridine; — ($-$)pn, ---- ($-$)bn, ($-$)chxn, - · - ($+$)stien.

In the case of pyridine solutions (Figure 8), the patterns are no longer easily explicable in general terms; presumably, in this solvent the coordination of a solvent molecule to the metal plays an important role, producing equilibria between species with different coordination geometries and consequently conformations of the chelated ligand.

Finally it is known that a $\lambda \rightleftharpoons \delta$ equilibrium is likely to be operative²⁶ in solution and the stabilization of one of the two conformations depends on too many factors, like the solvation, the possibility of forming adducts, the bulkiness of the R group, and the size of the titanium ion. Consequently it could be difficult to rationalise the possible distortion of the N_2O_2 chromophore of the Schiff bases in general terms.

It must be remembered that in some instances $Ti(IV)$ has been found to be heptacoordinated²⁷ even in polynuclear oxo species²⁸ and some irregularities of the C.D. spectra could probably be interpreted by invoking such a coordination number (with the coordination of some solvent molecules) or the formation of μ -oxo or $di\mu$ -oxo bridges.

In these complicated geometries the steric interactions between the substituents of the ethylenediamine chelate ring and the other ligands should be very severe. In order to minimize these interactions, the two halves of the Schiff base should fold to a different extent according to the bulkiness of the substit-

uents of the diamine chelate ring thus making any simple correlation very difficult.

Of course in the absence of structural data these remain only hypotheses.

Conclusions

Salicylaldimine compounds of oxotitanium(IV) probably possess, in the solid state, polymeric Ti—O—Ti—O chains as is suggested by their extremely low solubility and the low lying stretching of the TiO band. They behave as bases, reacting with aqueous solutions of mineral acids to give one to one adducts which, in donor solvents, are 1 : 1 electrolytes and must be described as (TiOsaldiamine·H)⁺X⁻ (X = Cl, ClO₄) as suggested by titrations of the anions.

The site of protonation probably varies with the solvent and cannot be defined in the absence of X-ray data. The conformational behaviour of the ligand as reflected by the C.D. spectra depends on the solvent and on the presence of the equivalent of acid. It cannot always be easily interpreted as in the case of the similar vanadyl compounds².

In some instances the conformation of the chelate ring is comparable with that of the VO²⁺ compounds², as in the case of the (-)pn derivatives, but usually they are more complicated, thus stressing the importance of a detailed knowledge of factors such as the true molecular coordination number, the size of the metal ion and the subsequent amount of distortion of the ligand, before any discussion on conformations can be proposed.

As a matter of fact a similar conclusion has been reached in the case of similar uranyl complexes, thus suggesting a conformational behaviour of these titanil complexes between that of the related vanadyl and uranyl compounds.

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