Preparations and Structures of *NN'*-Ethylenebis(salicylideneiminato)-titanium(III) Derivatives

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Reduction of [Ti(salen)Cl_2] [salen = *NN'*-ethylenebis(salicylideneiminate)] with zinc dust in tetrahydrofuran (thf) gives deep blue solutions from which dimeric [{Ti(salen)(thf)}$_2$][$ZnCl_4$] is obtained. The reduced paramagnetism ($\mu_{eff.}$ 0.96 B.M., 293 K) of this complex suggests a strong electronic interaction between two metal centres. The same solution, when treated with pyridine (py), leads to the very air-sensitive [Ti(salen)Cl(py)]·thf, whose magnetic moment ($\mu_{eff.}$ 1.79 B.M. at 293 K) corresponds to that expected for a d^1 system. *X*-Ray analysis of this complex confirms the pseudo-octahedral co-ordination around titanium, with the salen unit in the equatorial plane and Cl and py *trans* to each other in the axial positions. The crystal structure has been solved by the heavy-atom technique and refined by anisotropic least-squares methods to a final *R* of 0.066. The crystals are monoclinic, space group $P2_1/c$, with $a = 9.828(2)$, $b = 19.508(5)$, $c = 13.465(2)$ Å, $\beta = 109.5(4)°$, $U = 2\,440(2)$ Å^3, and $Z = 4$.

COMPLEXES of titanium in low oxidation states show very high reactivity in molecular activation since Ti^{II} and Ti^{III}, by virtue of their electronic configuration and co-ordination numbers, exhibit reactivities closely related to those of free radicals and carbenes.[1,2] The chemistry of titanium in low oxidation states concerns mainly η-cyclopentadienyl derivatives [3], with very few studies on titanium co-ordinated to polydentate or macrocyclic ligands, which stabilise low oxidation states of many transition metals.

Reactions between $TiCl_3$·3thf (thf = tetrahydrofuran) and the quadridentate ligand *NN'*-ethylenebis(salicylideneimine), H_2salen, do not afford the expected titanium(III) derivatives.[4] Such complexes were obtained by reducing dichloro[*NN'*-ethylenebis(salicylideneiminato)]titanium(IV),[5] [Ti(salen)Cl_2], with zinc dust in thf solution. On the other hand, reaction of [Ti(salen)Cl_2] with hydride-transfer agents, such as Li[BH_4], leads to the reduction of the Schiff-base ligand rather than the metal.[6] Zinc seems to be the only highly selective reductant for the preparation of titanium(III) derivatives.

EXPERIMENTAL

All the reactions described were carried out in an atmosphere of dry oxygen-free nitrogen and in carefully dried solvents. Dichloro[*NN'*-ethylenebis(salicylideneiminato)]titanium(IV), [Ti(salen)Cl_2], was prepared by the reported procedure.[5] Infrared spectra were recorded on a Perkin-Elmer 282 spectrophotometer. Magnetic-susceptibility measurements were carried out with a Faraday balance.

Preparations.— *Bis*{[NN'-*ethylenebis*(*salicylideneiminato*)](*tetrahydrofuran*)*titanium*(III)} *tetrachlorozincate*(II)–*tetrahydrofuran*, [{Ti(salen)(thf)}$_2$][$ZnCl_4$]·*n*thf (2). The complex [Ti(salen)Cl_2] (4.08 g, 10.6 mmol) and zinc dust (0.5 g, 7.6 mmol) were suspended in tetrahydrofuran (200 cm^3). A deep blue solution was obtained. After 4 h the excess of zinc dust was filtered off, the volume of the solution was reduced to 30 cm^3, and a deep blue crystalline solid precipitated (*ca.* 30%) (Found: C, 50.8; H, 4.9; Cl, 12.9; N, 4.9; Ti, 9.4; Zn, 6.5. Calc. for [{Ti(salen)(thf)}$_2$][$ZnCl_4$]·thf: C, 50.2; H, 4.9; Cl, 13.5; N, 5.3; Ti, 9.15; Zn, 6.20%). Thermal decomposition gave thf. The solid contains variable amounts of thf with a lower limit of Ti : thf = 1 : 1. $\mu_{eff.} = 0.96$ B.M.† at 293 K, ν(NC) (Nujol) at 1 630 cm^{-1}.

Chloro[NN'-*ethylenebis*(*salicylideneiminato*)](*pyridine*)-*titanium*(III)–*tetrahydrofuran*, [Ti(salen)Cl(py)]·thf (3). The complex [Ti(salen)Cl_2] (3.24 g, 8.41 mmol) and zinc dust (0.98 g, 15 mmol) were suspended in thf (150 cm^3) and stirred at room temperature. After 30 min a deep blue solution was obtained from which the excess of zinc dust was removed by filtration. On addition of absolutely dry pyridine (4 cm^3) the colour of the solution changed to deep green. On standing for 12 h the solution gave a deep green crystalline solid (*ca.* 70%) {Found: C, 59.6; H, 5.6; Cl, 7.1; N, 8.1. Calc. for [Ti(salen)Cl(py)]·thf: C, 59.9; H, 5.4; Cl, 7.1; N, 8.4%}. The i.r. spectrum in Nujol showed C=N bands at 1 625 cm^{-1}. $\mu_{eff.} = 1.79$ B.M. (293 K).

Selection and Reduction of Crystal Data.—An approximately laminar crystal of (3) having dimensions $0.30 \times 0.32 \times 0.03$ mm [3] was mounted in a Lindemann capillary under nitrogen. Unit-cell parameters were determined by the Weissenberg technique, using nickel-filtered Cu-K_α radiation. They were subsequently refined using a least-squares method and accurate positioning of 25 strong reflections by a Philips PW 1100 single-crystal automatic diffractometer, using graphite-monochromated Mo-K_α radiation. Integrated intensities for the reflections *hkl*, with $h,k > 0$ and $3 < \theta < 23°$, were measured by the same instrument, using a scan method, with a scan rate of 0.06° s^{-1}, scan width 1.1°, and background count of 7 s at the start and finish of each scan.

Crystal data. $C_{21}H_{19}ClN_3O_2Ti \cdot C_4H_8O$, $M = 428.76$ (+72.11), Monoclinic, $a = 9.828(2)$, $b = 19.508(5)$, $c = 13.465(2)$ Å, $\beta = 109.05°$ (4), $U = 2\,440(2)$ Å^3, $Z = 4$, $D_c = 1.363$ g cm^{-3}, $F(000) = 1\,044$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 3.73 cm^{-1}, space group $P2_1/c$.

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† Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

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[3] D. L. Kepert, 'The Early Transition Metals,' Academic Press, New York, 1972; P. C. Wailes, R. S. P. Coutts, and H. Weigold, 'Organometallic Chemistry of Titanium, Zirconium and Hafnium,' Academic Press, New York, 1974.

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[5] N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3847; F. Calderazzo, C. Floriani, M. Pasquali, M. Cesari, and G. Perego, *Gazzetta*, 1976, **106**, 127.

[6] G. Fachinetti, C. Floriani, M. Mellini, and S. Merlino, *J.C.S. Chem. Comm.*, 1976, 300.

Structure determination and refinement. Integrated intensities were corrected for Lorentz and polarisation effects but not for absorption in view of the very small size of the crystal. The positions of the titanium and chlorine atoms were determined by the Patterson method. All the non-hydrogen atoms around the titanium were located, from two successive Fourier maps, and two subsequent block-matrix least-squares cycles gave R 0.158. A difference-Fourier map showed five broad peaks arranged according to the geometry of a tetrahydrofuran molecule. After the introduction of five new atoms and two block-matrix and one full-matrix least-squares cycles, with isotropic thermal parameters for carbon atoms and anisotropic for the other atoms, R decreased to 0.112. A difference-Fourier map revealed the 14 hydrogen atoms of the salen group, while those of pyridine were located in calculated positions. We did not attempt to localise any hydrogen atoms of tetrahydrofuran owing to the low precision in the localisation of its heavy atoms. Two block-matrix least-squares cycles, in which the positions and anisotropic thermal parameters of the heavy atoms were allowed to vary, gave R 0.088. At this point, weighting schemes $[w^{\frac{1}{2}} = 1/(a + |F_o| + b|F_o|^2)]$ were introduced with $a = 90.0$ and $b = 0.04$. Two block-matrix and two full-matrix least-squares cycles in which the hydrogen parameters were not changed gave R 0.069. A successive full-matrix least-squares cycle was performed in which the parameters of the carbon atoms were held at their former values and those of the hydrogen atoms were allowed to vary. A final block-matrix least-squares cycle in which only the positions of the heavy atoms were allowed to vary reduced R to 0.066.

TABLE 1

Final atomic positional parameters (× 10^4) with estimated standard deviations in parentheses

	x	*y*	*z*
Ti	0.144 36(17)	0.194 18(8)	0.140 54(12)
Cl	0.201 4(3)	0.314 4(1)	0.134 7(2)
O(1)	0.209 0(6)	0.169 9(3)	0.026 9(4)
O(2)	−0.057 5(6)	0.213 6(3)	0.104 7(4)
O(3)	0.748 5(16)	0.053 9(9)	0.361 1(9)
N(1)	0.361 1(8)	0.171 3(4)	0.233 6(5)
N(2)	0.141 9(7)	0.201 0(4)	0.298 5(5)
N(3)	0.087 3(8)	0.081 6(4)	0.149 2(6)
C(1)	0.322 6(11)	0.143 9(5)	0.010 6(7)
C(2)	0.325 6(11)	0.130 5(5)	−0.090 8(8)
C(3)	0.447 3(13)	0.100 8(6)	−0.105 5(9)
C(4)	0.569 0(13)	0.084 0(7)	−0.020 1(10)
C(5)	0.569 3(12)	0.099 2(6)	0.076 3(10)
C(6)	0.449 7(11)	0.128 9(5)	0.097 8(8)
C(7)	0.463 9(10)	0.146 8(5)	0.203 5(8)
C(8)	0.397 8(10)	0.191 9(6)	0.345 0(8)
C(9)	0.271 9(10)	0.174 5(5)	0.379 9(7)
C(10)	0.038 6(10)	0.224 1(5)	0.330 8(7)
C(11)	−0.098 6(10)	0.247 2(5)	0.263 2(7)
C(12)	−0.194 4(12)	0.275 1(5)	0.308 7(8)
C(13)	−0.328 7(11)	0.295 1(5)	0.251 6(9)
C(14)	−0.373 6(10)	0.288 5(5)	0.144 2(9)
C(15)	−0.282 7(10)	0.261 6(5)	0.092 8(8)
C(16)	−0.143 1(10)	0.241 5(5)	0.153 2(8)
C(17)	−0.025 3(12)	0.064 7(6)	0.180 6(11)
C(18)	−0.061 7(14)	−0.003 0(8)	0.191 6(13)
C(19)	0.020 1(13)	−0.054 0(6)	0.172 0(11)
C(20)	0.136 8(15)	−0.036 7(6)	0.144 9(13)
C(21)	0.162 3(14)	0.030 3(6)	0.132 6(12)
C(22)	0.846 1(24)	0.093 3(13)	0.444 2(15)
C(23)	0.843 0(33)	0.064 1(15)	0.534 0(19)
C(24)	0.717 4(37)	0.026 9(16)	0.515 9(24)
C(25)	0.670 9(35)	0.001 0(13)	0.401 3(22)

Structure amplitudes and thermal parameters are available as Supplementary Publication No. SUP 22226 (11 pp).* The calculations were carried out on an I.B.M. 370/158 computer at C.N.U.C.E., Pisa. Atomic co-ordinates and molecular dimensions are given in Tables 1—4. Scattering

TABLE 2

Interatomic bond lengths (Å) with estimated standard deviations in parentheses

(*a*) Co-ordination polyhedron

Ti–Cl	2.418(4)	Ti–N(1)	2.137(7)
Ti–O(1)	1.899(8)	Ti–N(2)	2.139(9)
Ti–O(2)	1.920(6)	Ti–N(3)	2.279(9)

(*b*) Salen *

O(1)–C(1)	1.308(14)	O(2)–C(16)	1.338(14)	1.323
N(1)–C(7)	1.295(15)	N(2)–C(10)	1.308(15)	1.301
N(1)–C(8)	1.480(14)	N(2)–C(9)	1.479(11)	1.479
C(1)–C(2)	1.400(17)	C(15)–C(16)	1.403(14)	1.401
C(1)–C(6)	1.438(13)	C(11)–C(16)	1.406(14)	1.422
C(2)–C(3)	1.401(18)	C(14)–C(15)	1.399(18)	1.400
C(3)–C(4)	1.401(16)	C(13)–C(14)	1.373(17)	1.387
C(4)–C(5)	1.329(21)	C(12)–C(13)	1.351(15)	1.340
C(5)–C(6)	1.423(18)	C(11)–C(12)	1.390(18)	1.406
C(6)–C(7)	1.428(16)	C(10)–C(11)	1.432(13)	1.430
C(8)–C(9)	1.499(17)			

(*c*) Pyridine

N(3)–C(17)	1.348(18)	C(19)–C(20)	1.355(24)
C(17)–C(18)	1.389(20)	C(20)–C(21)	1.350(18)
C(18)–C(19)	1.358(21)	C(21)–N(3)	1.306(17)

* The values in the last column were obtained by averaging corresponding bond lengths in the two halves of the molecule.

TABLE 3

Angles (°) of the co-ordination polyhedron

Cl–Ti–O(1)	94.2(2)	O(1)–Ti–N(3)	87.3(3)
Cl–Ti–O(2)	91.8(2)	O(2)–Ti–N(1)	159.9(3)
Cl–Ti–N(1)	91.4(2)	O(2)–Ti–N(2)	83.8(3)
Cl–Ti–N(2)	92.8(2)	O(2)–Ti–N(3)	87.2(3)
Cl–Ti–N(3)	178.4(4)	N(1)–Ti–N(2)	76.3(3)
O(1)–Ti–O(2)	115.8(3)	N(1)–Ti–N(3)	89.0(3)
O(1)–Ti–N(1)	83.6(3)	N(2)–Ti–N(3)	85.8(3)
O(1)–Ti–N(2)	158.8(3)		

TABLE 4

Bond angles (salen) corresponding to (a) and (b), the two halves of the molecule

(a)			
Ti–O(1)–C(1)	139.4(6)	C(2)–C(3)–C(4)	121.3(12)
Ti–N(1)–C(7)	128.6(7)	C(3)–C(4)–C(5)	118.6(13)
Ti–N(1)–C(8)	113.8(7)	C(4)–C(5)–C(6)	123.4(10)
C(7)–N(1)–C(8)	117.4(8)	C(5)–C(6)–C(7)	118.9(9)
O(1)–C(1)–C(2)	121.8(8)	C(1)–C(6)–C(7)	122.7(10)
O(1)–C(1)–C(6)	120.2(9)	N(1)–C(7)–C(6)	124.6(8)
C(2)–C(1)–C(6)	118.0(10)	N(1)–C(8)–C(9)	107.6(8)
C(1)–C(2)–C(3)	120.0(4)		
(b)			
Ti–O(2)–C(16)	136.0(5)	C(13)–C(14)–C(15)	121.2(9)
Ti–N(2)–C(9)	115.3(7)	C(12)–C(13)–C(14)	119.4(12)
Ti–N(2)–C(10)	127.9(6)	C(11)–C(12)–C(13)	122.5(10)
C(9)–N(2)–C(10)	116.8(8)	C(10)–C(11)–C(12)	118.4(9)
O(2)–C(16)–C(15)	118.8(9)	C(10)–C(11)–C(16)	123.3(10)
O(2)–C(16)–C(11)	121.2(8)	N(2)–C(10)–C(11)	124.7(9)
C(11)–C(16)–C(15)	119.8(11)	N(2)–C(9)–C(8)	106.8(8)
C(14)–C(15)–C(16)	118.6(10)		
Pyridine			
N(3)–C(17)–C(18)	122.2(13)	C(19)–C(20)–C(21)	118.8(14)
C(17)–C(18)–C(19)	119.2(15)	C(20)–C(21)–N(3)	125.7(15)
C(18)–C(19)–C(20)	118.4(12)	C(17)–N(3)–C(21)	115.6(10)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

factors used in the structure-factor calculations were taken from ref. 7. The calculations were made by use of programs in the '*X*-Ray '70 ' system [8] and the ORTEP program.[9] The five atoms identifying the thf molecule are numbered O(3), C(22), C(23), C(24), and C(25).

RESULTS AND DISCUSSION

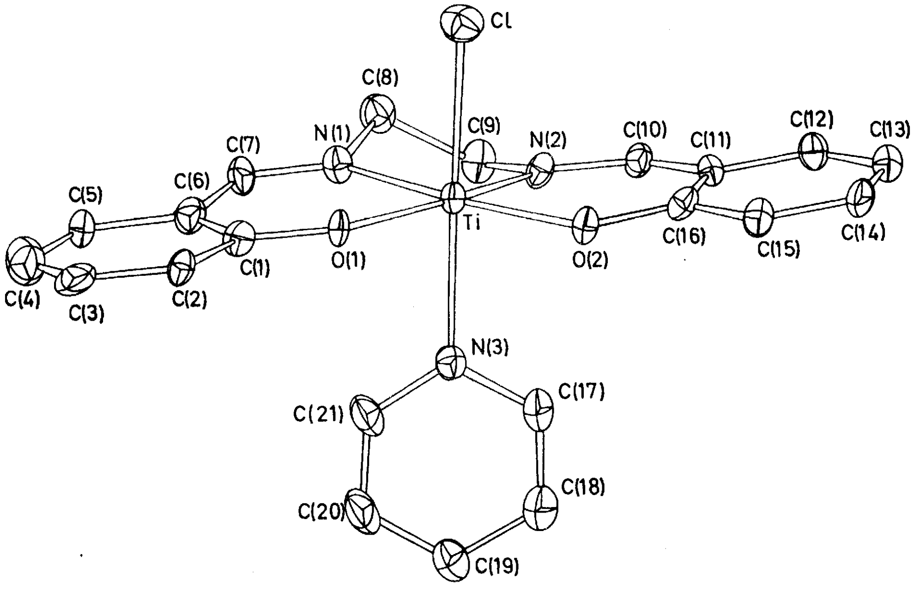
Chemical Studies.—Treatment of a thf suspension of [Ti(salen)Cl_2] (1) [5] with zinc dust gave a solution from which (2) could be recovered as a deep blue crystalline solid [equation (1)]. The high solubility of $ZnCl_2$ in

$$\underset{(1)}{2[\mathrm{Ti(salen)Cl_2}]} + \mathrm{Zn} \xrightarrow{\text{thf}} \underset{(2)}{[\{\mathrm{Ti(salen)(thf)}\}_2][\mathrm{ZnCl_4}]\cdot n\mathrm{thf}} \quad (1)$$

thf prevented its contaminating the solid. Addition of pyridine to the same solution induced the precipitation of (3) as deep green crystals [equation (2)]. The i.r.

$$\underset{(1)}{2[\mathrm{Ti(salen)Cl_2}]} + \mathrm{Zn} \xrightarrow[\text{thf}]{\text{py}} [\mathrm{ZnCl_2(py)}_n] + \underset{(3)}{2[\mathrm{Ti(salen)Cl(py)}]\cdot\mathrm{thf}} \quad (2)$$

spectra of (2) and (3) are not very informative, except to indicate the presence of the intact salen moiety.[4] The low solubility of (3) prevented a molecular-weight determination. Complex (3) is a very air-sensitive solid and it may contain variable quantities of thf depending on the crystallisation rate and drying conditions, but, normally, as for the example used in *X*-ray determination, it contains one thf molecule per titanium. Both (2) and (3) are fairly soluble in water. The resulting deep blue solutions are stable for some hours. Addition of Na[BPh_4] or Na[BF_4] to the solutions gave deep blue solids which can be recrystallised from acetone, but their nature is not yet well defined because of the variable amount of water they contain.



The molecular structure of [Ti(salen)Cl(py)] showing the atomic numbering scheme

Structures.—The results of the *X*-ray analysis show that crystals of (3) consist of discrete molecules of [Ti(salen)Cl(py)] with a distorted octahedral stereochemistry around the titanium atom. The salen ligand occupies the four equatorial positions, whereas the Cl and the pyridine molecule occupy the axial positions. A projection of the structure of (3) together with the numbering scheme is shown in the Figure. Titanium and the equatorial donor atoms are practically coplanar (Table 5), the metal atom being slightly displaced from plane (1) (0.074 Å) toward the Cl ligand. The titanium is practically equidistant from the planes defined by the two salen units. The two halves of the equatorial ligand are arranged in a stepped conformation, the angle between planes (3) and (4) being 1.6° (Table 5). The pyridine plane is nearly perpendicular to the equatorial plane (86.5°) and parallel to the N(1)–N(2) direction. The CH_2CH_2 bridge has a *gauche* conformation with a torsional angle around C–C of 48.1°.

Bond lengths and angles are in Tables 2—4. The values for the salen ligand are in agreement, within the experimental errors, with the mean values recently reported for a series of salen complexes.[10] Table 6 reports a comparison of the co-ordination sphere, C–O, and CH–N bond distances for different salen complexes. The more significant deviations from the mean values are observed for the Ti–N bond distances. A true

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[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] '*X*-Ray '70,' Technical Report, 1970, ed. J. M. Stewart, University of Maryland, Computer Science Centre.

[9] C. K. Johnson, 'ORTEP,' Report ORNL–3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

[10] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

comparison is restricted to [Ti(salen)Cl(py)]·thf and [Ti(salen)Cl_2]·thf.[11] The most significant difference between the last two complexes arises from the much longer Ti–Cl distance in (3) than in (1). This can be tentatively explained by the greater *trans* influence of py. This distance seems significantly longer than that found in other titanium(IV) chelate complexes,[12] while comparisons with titanium(III) systems are not possible.

TABLE 5

Least-squares planes

Plane	Atoms defining the plane and distances (Å) from the least-squares planes								Displacements (Å) of relevant atoms from the planes				Angles (°) between planes				
(1)	Ti	O(1)	O(2)	N(1)	N(2)				C(8)	C(9)	C(4)	C(14)	1	2	3	4	5
	0.074	−0.052	0.006	0.021	−0.049				0.328	−0.362	−0.728	0.659					
(2)	Ti	Cl	O(2)	N(1)	N(3)												
	−0.150	−0.112	0.207	0.184	−0.129								89.5				
(3)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)			Ti	C(7)	N(1)	O(1)					
	−0.017	0.010	0.007	−0.018	0.011	0.006			−0.161	0.116	0.066	−0.050	9.8	85.4			
(4)	C(11)	C(12)	C(13)	C(14)	C(15)	C(16)			Ti	C(10)	N(2)	O(2)					
	−0.010	0.004	0.002	−0.003	−0.002	0.009			0.289	−0.082	−0.016	−0.037	8.8	84.9	1.6		
(5)	N(3)	C(17)	C(18)	C(19)	C(20)	C(21)			O(1)	O(2)	N(1)	N(2)					
	−0.008	0.014	−0.002	−0.015	0.021	−0.009			−0.966	−0.830	1.723	1.842	86.5	40.2	85.1	84.6	
(6)	Ti	Cl	N(3)	C(17)	C(18)	C(19)	C(20)	C(21)	O(1)	O(2)	N(1)	N(2)					
	−0.022	0.047	−0.062	−0.017	0.018	0.030	0.042	−0.036	−1.099	−0.965	1.591	1.713	88.6	40.1	87.1	88.4	2.1

TABLE 6

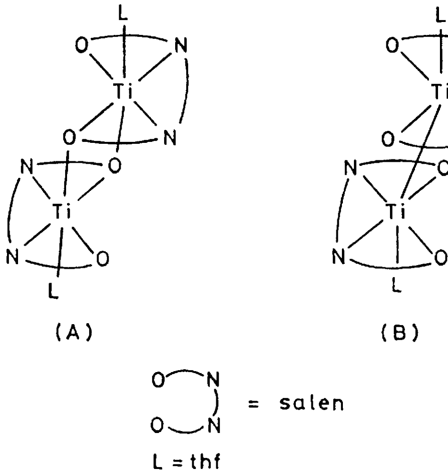
Comparison of the co-ordination polyhedron and CH–N and C–O bond distances (Å) in some salen complexes

Complex	M–N	M–O	M–Cl	C–O	C–N
[Ti(salen)Cl_2]·thf [a]	2.141 (5)	1.835 (5)	2.346 (2)	1.334 (9)	1.285 (10)
[Ti(salen)Cl(py)]·thf [b]	2.137 (7)	1.899 (8)	2.418 (4)	1.308 (14)	1.295 (15)
	2.139 (9)	1.920 (6)		1.338 (14)	1.308 (15)
	2.279 (9) [c]				
[{Fe(salen)Cl}$_2$] [d]	2.098 (9)	1.898 (7)	2.294 (3)	1.337 (12)	1.252 (13)
	2.091 (10)	1.978 (7)		1.352 (11)	1.314 (14)
[Fe(salen)Cl] [e]	2.099 (11)	1.879 (10)	2.238 (4)	1.329 (16)	1.317 (17)
	2.064 (10)	1.885 (11)		1.365 (16)	1.314 (17)
[Co(salen)(py)(CH=CH_2)]	1.860 (8)	1.878 (7)		1.32 (1)	1.27 (2)
	2.12 (1) [c]				
Weighted average [g]	1.912 (12)	1.904 (6)		1.321 (3)	1.291 (3)

[a] Ref. 11. [b] This work. [c] N is the nitrogen atom of pyridine. [d] M. Gerloch and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1967, 1900. [e] M. Gerloch and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1967, 1598. [f] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1972, 1433. [g] Ref. 10; mean value for many metal–salen complexes.

Reduction of (1) using zinc dust leads to Ti^{III} only, (2) and (3) being obtained from the solution in good yield. The structure of (2) can be discussed on the basis of its genesis and properties. The abnormal solubility of (3) in water seems to indicate the presence of an easily ionisable Ti–Cl bond in the basic structure Ti(salen)Cl. The starting deep blue thf solution is probably the result of the induced ionisation of the Ti–Cl bond caused by the Lewis acid $ZnCl_2$ formed during the reduction. This may give a cationic species such as $[Ti(salen)]^+$ (variously solvated) and $[ZnCl_4]^{2-}$. The function of pyridine in generating (3) from solutions of (2) can be understood from its action as Lewis base both for $ZnCl_2$ and Ti^{III}. In the reaction of pyridine with $[ZnCl_4]^{2-}$, chloride is released and both Cl^- and py are available for co-ordination to $[Ti(salen)]^+$.

Complex (2) was isolated with various amounts of thf of solvation, the lowest Ti : thf ratio being 1 : 1, which is not lost on drying. On the basis of the considerations outlined above, it is concluded that (2) can be represented as [{Ti(salen)(thf)}$_2$][$ZnCl_4$]·*n*thf. At room temperature, the magnetic moment of (2) is <1 B.M. per titanium (0.96 B.M., 293 K). This may be the consequence of a strong electronic interaction between two titanium(III) centres which can be transmitted either *via* bridging oxygens (A) or *via* direct interactions between the metals (B), or as a combination of both effects. We feel that $[ZnCl_4]^{2-}$ acts as an 'innocent' counter anion, its low stability in the solid state being



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enhanced by a large cation. Titanium(III) seems to prefer, as deduced from the *X*-ray analysis of (3), six-co-ordination as indicated in (A) or (B). The dimerisation process, strongly suggested by the reduced magnetic moment, is a quite general aspect of M(salen) chemistry. The geometry normally used for the dimerisation is that in (A).[10,13] Less frequently, a direct metal–metal interaction (B) is invoked in connection with macrocyclic or polydentate ligands containing an N_4 donor set.[14]

d^1 Systems have been the subject of many electronic studies, so that (2) and (3) can be considered as interesting examples in this context. Moreover, (3) could be a potential precursor of organotitanium(III) complexes.[15] Due to the high tendency for titanium to achieve the d^0 configuration, a free-radical-like reactivity is expected for (3),[16] similar to that observed for $[Co(CN)_5]^{3-}$ and [Co(salen)(py)].[17]

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