Polydentate Ligand Exchange *via* Formation of a Dimetallic Complex. Crystal Structures of [(thf)Fe(acen)MCl_2] (M = Fe or Zn), [ClFe(salphen)FeCl$(thf)_2$], [Ti(acen)$(thf)_2$][$CoCl_3$(thf)], and [Ti(acen)$(thf)_2$]$_2$[$Fe_3Cl_8(thf)_2$] [acen = *N,N'*-ethylenebis(acetylacetoneiminate), salphen = *N,N'*-*o*-phenylenebis(salicylideneiminate), and thf = tetrahydrofuran]†

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Complexation of metal halides $M'Cl_n$ by square-planar Schiff-base complexes, *i.e.* ML [M = Fe, Co, Ni, or Cu; L = acen = *N,N'*-ethylenebis(acetylacetoneiminate), salen = *N,N'*- ethylenebis-(salicylideneiminate), or salphen = *N,N'*-*o*-phenylenebis(salicylideneiminate)] led to adducts which are intermediates in the exchange of the quadridentate ligand between M and M′. Exchange occurs if M′ is in an higher oxidation state than M. Concomitant redox and ionization reactions are observed. Reaction of [Fe(acen)], (**1**) with MCl_2·*n*thf (M = Fe or Zn) led to the bimetallic adducts [(thf)Fe(acen)MCl_2] [M = Fe, (**2**); Zn, (**3**)] containing a square-pyramidal iron, while M has a tetrahedral co-ordination geometry. A complex analogous to (**2**), [ClFe(salphen)FeCl$(thf)_2$] (**4**) (thf = tetrahydrofuran), was obtained by treating $FeCl_2$·1.5 thf with H_2 salphen in a 2:1 molar ratio in the presence of Na(OMe). This reaction gave some insight into the ligand-exchange pathway. The reaction of [M(acen)] (M = Fe, Co, or Ni) complexes with $TiCl_4$·2thf in thf led to migration of the acen ligand to titanium and formation of [Ti(acen)Cl_2], (**7**) and the corresponding metal halide MCl_2·*n*thf. Related results have been obtained in the reaction of [M(acen)] and $TiCl_3$·3thf. When M = Ni or Cu complex (**7**) was obtained by exchange of the acen ligand and oxidation of titanium(III) by the corresponding metal halides. In the absence of a redox reaction, complexes of titanium(III) have been obtained: [Ti(acen)$(thf)_2$][$CoCl_3$(thf)], (**10**) and [Ti(acen)$(thf)_2$]$_2$[$Fe_3Cl_8(thf)_2$], (**11**), respectively. The structures of complexes (**2**)—(**4**), (**10**), and (**11**) have been determined by *X*-ray analysis: (**2**) space group $P\bar{1}$, a = 14.029(2), b = 9.854(1), c = 8.092(1) Å; α = 98.48(1), β = 90.96(1), γ = 107.44(1)°, Z = 2, and R = 0.065 for 1 360 observed reflections; (**3**), space group $P\bar{1}$, a = 14.006(3), b = 9.823(2), c = 8.077(2) Å, α = 98.49(1), β = 90.90(1), γ = 107.57(1)°, Z = 2, and R = 0.072 for 2 347 observed reflections; (**4**), space group $P2_1/c$, a = 12.882(2), b = 11.940(2), c = 21.701(3) Å, β = 95.40(1)°, Z = 4, R = 0.054 for 1991 observed reflections; (**10**), space group $P\bar{1}$, α = 12.735(3), b = 15.105(3), c = 8.935(2) Å, α = 95.30(2), β = 94.26(2), γ = 67.91(2)°, Z = 2, and R = 0.055 for 2 576 observed reflections; (**11**), space group $P\bar{1}$, α = 14.109(3), b = 14.713(3), c = 9.203(2) Å, α = 99.98(2), β = 104.76(2), γ = 63.08(2)°, Z = 1 for $C_{48}H_{84}Cl_8Fe_3N_4O_{10}Ti_2$ formula unit, and R = 0.050 for 2 685 observed reflections.

Ligand exchange between two metal ions is a common event in the case of unidentate ligands.[1] It is facilitated by a dimetallic unit bridged by the ligand.[1] Such exchange is rarer when polydentate geometrically rigid ligands are involved.[2] During our studies of the complexation of different inorganic or organic Lewis acids by quadridentate Schiff-base complexes[3] we observed the very easy migration of a quadridentate ligand from a metal ion in a lower oxidation state to a metal ion in a higher oxidation state. Such a migration involves the preliminary formation of a dimetallic complex in which the O ··· O′ bite of the Schiff-base complex acts as bidentate ligand for the Lewis acid. In particular, the reaction of [M(acen)] [M = Fe, Co, Ni, or Cu; acen = *N,N'*-ethylenebis(acetylacetoneiminate)] led to: (*a*) formation of dimetallic adducts in the case of reaction with $FeCl_2$·1.5thf and $ZnCl_2$·2thf (thf = tetrahydrofuran); (*b*) migration of the acen ligand in the reaction with $TiCl_4$·2thf and (*c*) migration of the ligand in the reaction with $TiCl_3$·3thf followed, in case of M = Cu and Ni, by the oxidation of titanium(III) to titanium(IV) and in case of M = Co or Fe by the ionization of Ti–Cl bonds.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Preparation of [M(acen)] (M = Fe,[4] Co,[5] Ni,[5] or Cu[5]) was carried out by published procedures, as was that of [Ti(acen)Cl(thf)],[6] $TiCl_3$·3thf,[7] and $TiCl_4$·2thf.[7] Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer. Magnetic susceptibilities were measured using a Faraday balance.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Reaction of [Fe(acen)] *with* $MCl_2 \cdot n$thf (M = Fe, *n* = 1.5; M = Zn, *n* = 2).—Solid crystalline $FeCl_2 \cdot 1.5$thf (2.10 g, 8.95 mmol) was added to a thf solution of [Fe(acen)] (2.49 g, 8.94 mmol). The suspension was stirred until complete solubilization of the white solid. The resulting red-brown solution was freed from some undissolved solid by filtration, then allowed to stand at room temperature for 48 h. A black crystalline solid formed, [(thf)Fe(acen)FeCl$_2$], (**2**) (56%) (Found: C, 40.10; H, 5.35; Cl, 14.95; N, 5.80. $C_{16}H_{26}Cl_2Fe_2N_2O_3$ requires C, 40.30; H, 5.45; Cl, 14.90; N, 5.85%), $\mu_{eff.}$ = 4.80 at 295 K. The zinc adduct, [(thf)Fe(acen)ZnCl$_2$], (**3**), was prepared by the same procedure (44.0%) (Found: C, 39.20; H, 5.20; Cl, 14.35; N, 5.60. $C_{16}H_{26}Cl_2FeN_2O_3Zn$ requires C, 39.50; H, 5.35; Cl, 14.60; N, 5.75%).

Synthesis of Complex (**4**).—A thf suspension (80 cm^3) of $FeCl_2 \cdot 1.5$thf (3.04 g, 12.93 mmol) was treated with H_2 salphen [salphen = *N,N′-o*-phenylenebis(salicylideneiminate)] (2.04 g, 6.46 mmol). The suspension was stirred until complete solubilization of the reagents. Then solid Na(OMe) (12.93 mmol) was added to the red solution. The NaCl formed was removed by filtration. On standing for 24 h the deep red solution gave a red-brown crystalline solid (*ca.* 51%) (Found: C, 52.30; H, 4.50; Cl, 11.00; N, 4.35. $C_{28}H_{30}Cl_2Fe_2N_2O_4$ requires C, 52.45; H, 4.85; Cl, 11.10; N, 4.40%), μ_{eff} = 5.14 at 295 K.

Reaction of [M(acen)] (M = Fe, Co, *or* Ni) *with* $TiCl_4$.—A thf solution of [Co(acen)] (1.50 g, 5.33 mmol) was treated with solid $TiCl_4 \cdot 2$thf (1.78 g, 5.33 mmol). The suspension was stirred until complete solubilization of the yellow solid. From the resulting brown solution a small amount of unidentified solid was removed by filtration. On standing for 24 h a crystalline blue solid separated, $CoCl_2 \cdot 1.5$thf (88.0%), which was removed by filtration. On cooling the solution at −20 °C [Ti(acen)Cl$_2$]^6 (**7**) crystallized (30%). The high solubility in thf of (**7**) is the reason for the relatively low yield. We did not try to recover the titanium complex quantitatively (Found: C, 42.00; H, 5.25; Cl, 20.80; N, 8.00. $C_{12}H_{18}Cl_2N_2O_2Ti$ requires C, 42.25; H, 5.30; Cl, 20.85; N, 8.20%). Reaction of iron, nickel, and copper acen complexes with $TiCl_4$ gave identical results. The difficult separation between the metal halides and [Ti(acen)Cl$_2$] is responsible for the low yield of the titanium complex, in all cases being no higher than 30%.

Reaction of [Ni(salen)] *and* [Ni(salphen)] *with* $TiCl_4 \cdot 2$thf.—A thf (70 cm^3) suspension of [Ni(salen)] [salen = *N,N′*-ethylenebis(salicylideneiminate)] (2.80 g, 8.61 mmol) was treated with solid $TiCl_4 \cdot 2$thf (2.87 g, 8.61 mmol). The suspension was stirred until the disappearance of the yellow solid. The resulting brown-violet solution was freed from some unsoluble material by filtration. On standing for 24 h, a microcrystalline solid formed, [Ti(salen)Cl$_2$] (60%) (Found: C, 49.50; H, 3.75; Cl, 18.20; N, 7.15. $C_{16}H_{14}Cl_2N_2O_2Ti$ requires C, 49.85; H, 3.65; Cl, 18.45; N, 7.25%). Similar results were obtained by carrying out the reaction between [Ni(salphen)] and $TiCl_4 \cdot 2$thf; [Ti(salphen)Cl$_2$] was isolated in 90% yield and compared with an authentic sample of it.

Reaction of [Ti(acen)Cl(thf)] *with* $TiCl_4 \cdot 2$thf.—$TiCl_4 \cdot 2$thf (0.78 g, 2.35 mmol) was added to a thf solution (50 cm^3) of [Ti(acen)Cl(thf)] (**8**) (0.89 g, 2.35 mmol). The suspension was stirred until complete solubilization of $TiCl_4 \cdot 2$thf. The resulting solution gave a small amount of a solid which was removed by filtration. On standing for 48 h microcrystalline compound (**7**) was isolated (45%).

Reaction of [M(acen)] (M = Cu *or* Ni) *with* $TiCl_3 \cdot 3$thf.—The compound $TiCl_3 \cdot 3$thf (2.60 g, 7.03 mmol) was added to a thf (70 cm^3) solution of [Cu(acen)] (2.01 g, 7.03 g), then the suspension was refluxed for 5 h. The resulting solution was cooled at room temperature and on standing for 24 h gave some brown-red solid which was removed by filtration. After 48 h the resulting solution gave [Ti(acen)Cl$_2$] (**7**), (43%). The same reaction carried out with [Ni(acen)] gave a very similar result and (**7**) was obtained in 41% yield.

Reaction of [M(acen)] (M = Co *or* Fe) *with* $TiCl_3 \cdot 3$thf.—The compound $TiCl_3 \cdot 3$thf (3.06 g, 8.26 mmol) was added to a thf (70 cm^3) solution of [Fe(acen)] (2.30 g, 8.26 g), then the suspension was stirred until $TiCl_3 \cdot 3$thf dissolved. The solution was freed from a very small amount of solid, then left to stand, giving a red crystalline solid, [Ti(acen)(thf)$_2$]$_2$[Fe$_3$Cl$_8$(thf)$_2$] (**11**) (42%) (Found: C, 40.10; H, 5.95; N, 3.85. $C_{48}H_{84}Cl_8Fe_3N_4O_{10}Ti_2$ requires C, 40.50; H, 5.90; N, 3.95%). The reaction between [Co(acen)] and $TiCl_3 \cdot 3$thf led to [Ti(acen)(thf)$_2$][CoCl$_3$(thf)] (**10**) (50%) (Found: C, 44.35; H, 6.50; Cl, 16.15; N, 4.15. $C_{24}H_{42}Cl_3CoN_2O_5Ti$ requires C, 44.25; H, 6.45; Cl, 16.30; N, 4.30%).

Complex (**10**) was equally well obtained by adding $CoCl_2 \cdot 1.5$thf (2.30 g, 9.53 mmol) to a thf (150 cm^3) solution of (**8**) (3.59 g. 9.51 mmol). The resulting deep red solution cooled at −5 °C gave (**10**) as a crystalline solid (70%).

Complex (**11**) was synthesized from (**8**) (3.03 g, 8.08 mmol) dissolved in thf (150 cm^3) reacted with $FeCl_2 \cdot 1.5$thf (2.85 g, 12.13 mmol). The solution formed gave, on cooling at −5 °C, (**11**) as a red crystalline solid (75%).

X-*Ray Structure Determinations.*—Compounds (**2**)—(**4**), (**10**), and (**11**) were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with the use of TRACER.^{8} Crystal data and details associated with data collection are given in Table 1. Data were collected at room temperature (295 K) on a single-crystal diffractometer. For intensities and background, individual profiles^9 were analyzed for (**2**) and (**3**) while the three-point technique was used for (**4**), (**10**), and (**11**). The structure amplitudes were obtained after the usual Lorentz and polarization corrections and the absolute scale was established by the Wilson method.^{10} The crystal quality was tested by ω scans showing that crystal absorption effects could be neglected for complex (**10**). Data for complexes (**2**), (**4**), and (**11**) were corrected for absorption according to ref. 11 and those for (**3**) were corrected using ABSORB.^{12} The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. A weighting scheme based on counting statistics was applied for (**10**) $\{w = 1.5907/[\sigma^2(F_0) + 0.000633\ F_0{}^2]\}$. Unit weights were used for complexes (**2**)—(**4**), and (**11**) since these gave a satisfactory analysis of variance.^{13} Anomalous scattering corrections were included in all structure-factor calculations.^{14b} Scattering factors for neutral atoms were taken from ref. 14*a* for non-hydrogen atoms and from ref. 15 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. All calculations were carried out on a GOULD 32/77 computer using SHELX 76.^{13}

Solution and refinement. Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Complexes (**2**) and (**3**) were found to be isostructural, so the structure of (**2**) was derived by refining the co-ordinates of (**3**). Refinement was first isotropic then anisotropic for non-H atoms, by full-matrix least squares. In the isostructural complexes (**2**) and (**3**) the C(14) and C(15) atoms of the thf molecule were found to be statistically distributed over two positions (A and B) which were isotropically refined as complementary atoms, *i.e.* the sum of their site occupation factors was fixed at 1.0 (Tables 2 and 3). All the hydrogen atoms excepting those of thf molecule, which were ignored, were located from Fourier

Table 1. Experimental data for the *X*-ray diffraction study of complexes (**2**)—(**4**), (**10**), and (**11**)

Complex	(**2**)	(**3**)	(**4**)	(**10**)	(**11**)
Formula	$C_{16}H_{26}Cl_2Fe_2N_2O_3$	$C_{16}H_{26}Cl_2FeN_2O_3Zn$	$C_{32}H_{38}Cl_2Fe_2N_2O_5$	$C_{24}H_{42}Cl_3CoN_2O_5Ti$	$C_{48}H_{84}Cl_8Fe_3N_4O_{10}Ti_2$
M	477.0	486.5	713.3	651.8	1 424.2
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Cell parameters[a]					
a/Å	14.029(2)	14.006(3)	12.882(2)	12.735(3)	14.109(3)
b/Å	9.854(1)	9.823(2)	11.940(2)	15.105(3)	14.713(3)
c/Å	8.092(1)	8.077(2)	21.701(3)	8.935(2)	9.203(2)
α/°	98.48(1)	98.49(1)	90	95.30(2)	99.98(2)
β/°	90.96(1)	90.90(1)	95.40(1)	94.26(2)	104.76(2)
γ/°	107.44(1)	107.57(1)	90	67.91(2)	63.08(2)
U/Å^3	1 053.4(2)	1 045.7(4)	3 323.0(9)	1 584.3(7)	1 643.5(7)
Z	2	2	4	2	1
D_c/g cm^{-1}	1.504	1.545	1.426	1.366	1.439
F(000)	492	500	1 480	680	738
Crystal size/mm	0.26 × 0.53 × 0.55	0.35 × 0.48 × 0.60	0.11 × 0.31 × 0.32	0.42 × 0.52 × 0.55	0.40 × 0.48 × 0.50
μ/cm^{-1}	16.5	95.9	10.7	10.6	12.5
Diffractometer	Philips PW1100	Siemens AED	Philips PW1100	Philips PW1100	Philips PW1100
Radiation	*b*	*c*	*b*	*b*	*b*
2θ range/°	6–46	6–130	5–47	6–48	6–50
Unique total data	2 939	3 530	4 925	4 945	5 689
Criterion for observed	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Unique obs. data	1 360	2 347	1 991	2 576	2 685
R[d]	0.065	0.072	0.054	0.055	0.050
R′[e]	—	—	—	0.060	—

[a] Obtained by least-squares analysis of the setting angles of 25—30 carefully centred reflections chosen from diverse regions of reciprocal space. [b] Graphite-monochromatized Mo-K_α (λ = 0.71069 Å). [c] Nickel-filtered Cu-K_α (λ = 1.54178 Å). [d] $\Sigma|\Delta F|/\Sigma|F_o|$. [e] $\Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$.

Table 2. Fractional atomic co-ordinates (× 10^4) for complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	2 577(2)	−941(2)	3 153(3)	C(6)	3 445(11)	−3 312(14)	2 720(21)
Fe(2)	2 635(2)	1 963(2)	2 042(3)	C(7)	3 439(12)	−2 854(15)	4 575(20)
Cl(1)	4 079(3)	3 157(5)	1 094(6)	C(8)	4 574(12)	−815(17)	7 508(19)
Cl(2)	1 348(4)	2 858(5)	2 335(7)	C(9)	3 910(12)	−439(19)	6 260(20)
O(1)	2 211(7)	−243(10)	1 109(12)	C(10)	3 896(12)	1 028(17)	6 564(19)
O(2)	2 946(7)	1 129(10)	4 134(11)	C(11)	3 463(11)	1 726(15)	5 621(18)
O(3)	1 097(8)	−1 921(11)	3 690(14)	C(12)	3 635(14)	3 359(17)	5 992(20)
N(1)	2 829(8)	−2 651(11)	1 793(15)	C(13)	670(14)	−3 451(18)	3 797(29)
N(2)	3 452(9)	−1 339(14)	4 958(15)	C(16)	263(14)	−1 392(21)	3 238(30)
C(1)	1 490(13)	−384(17)	−1 622(21)	C(14A)	−457(31)	−3 854(38)	3 320(65)
C(2)	1 987(11)	−1 014(15)	−423(18)	C(15A)	−682(29)	−2 503(38)	3 061(62)
C(3)	2 131(11)	−2 308(15)	−806(18)	C(14B)	−196(37)	−3 979(45)	2 441(78)
C(4)	2 646(10)	−3 038(13)	146(20)	C(15B)	−444(35)	−2 763(49)	2 111(77)
C(5)	2 913(12)	−4 269(16)	−794(21)				

The occupation factors for the disordered atoms C(14) and C(15) are 0.554 and 0.446 for sites A and B respectively.

difference maps and introduced in the final refinement as fixed atom contributions with isotropic *U* values fixed at 0.08 Å^2. For complex (**4**) the *X*-ray analysis revealed the presence of six peaks, in a region far from the complex molecules, which were interpreted as a disordered thf solvent molecule having the oxygen atom distributed over two pseudo-centrosymmetric positions in such a way as to simulate a six-membered ring. They were refined anisotropically with site occupation factors of 0.6 and 0.4 for O(5) and O(5′) respectively. Attempts to distinguish two positions for the carbon atoms failed and this accounts for the low accuracy of the parameters involved. The hydrogen atoms associated with this molecule were ignored while all the others (found from a difference map for salphen; put in geometrically calculated positions for the co-ordinated thf molecules) were introduced in the final refinement as fixed contributors (U = 0.08 Å^2). The benzene rings of the salphen ligand were refined as regular hexagons (C–C 1.39 Å). During the refinement of complexes (**10**) and (**11**) most of the carbon atoms of the thf molecules showed very high U_{ij} thermal parameters. The best fit was found by considering the C(20) carbon atoms for (**10**) and all the carbon atoms of the thf molecules bonded to titanium for (**11**) statistically distributed over two positions (A and B). They were anisotropically refined with site occupation factors treated as for the disordered carbons in complexes (**2**) and (**3**) (Tables 5 and 6). For both complexes only the hydrogen atoms associated with acen were located from difference maps while those of the non-disordered thf molecules were found from geometrical considerations. They were introduced in calculations as fixed contributors (U = 0.10 Å^2). The hydrogen atoms of the thf molecules affected by disorder were ignored. For all complexes the final difference maps showed no unusual feature, with no significant peak above the general background.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Zn	2 634(1)	1 939(1)	2 093(2)	C(6)	3 419(8)	−3 314(10)	2 755(14)
Fe	2 551(1)	−952(1)	3 218(2)	C(7)	3 453(8)	−2 811(11)	4 607(14)
Cl(1)	4 052(2)	3 140(3)	1 139(4)	C(8)	4 558(8)	−815(13)	7 513(14)
Cl(2)	1 363(2)	2 827(3)	2 351(5)	C(9)	3 915(7)	−409(11)	6 286(13)
O(1)	2 226(5)	−215(6)	1 157(8)	C(10)	3 884(7)	1 040(12)	6 565(13)
O(2)	2 910(5)	1 134(6)	4 165(8)	C(11)	3 465(7)	1 766(10)	5 588(14)
O(3)	1 050(5)	−1 909(7)	3 749(10)	C(12)	3 631(9)	3 345(12)	6 038(14)
N(1)	2 836(5)	−2 638(7)	1 823(11)	C(13)	659(10)	−3 430(14)	3 899(21)
N(2)	3 421(6)	−1 342(8)	5 008(11)	C(16)	246(10)	−1 405(14)	3 267(22)
C(1)	1 514(8)	−355(12)	−1 575(14)	C(14A)	−485(21)	−3 838(28)	3 336(43)
C(2)	1 984(7)	−1 018(9)	−341(12)	C(15A)	−697(22)	−2 462(30)	3 055(47)
C(3)	2 142(7)	−2 293(10)	−760(12)	C(14B)	−206(29)	−4 005(36)	2 556(58)
C(4)	2 627(7)	−3 038(9)	186(14)	C(15B)	−440(22)	−2 738(31)	2 182(46)
C(5)	2 938(8)	−4 254(11)	−751(14)				

The occupation factors for the disordered atoms C(14) and C(15) are 0.503 and 0.497 for sites A and B respectively.

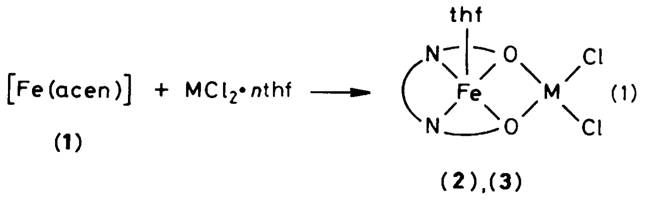
Table 4. Fractional atomic co-ordinates (× 10^4) for complex (**4**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	2 277(1)	3 937(1)	2 557(1)	C(15)	4 800(5)	4 112(5)	3 240(4)
Fe(2)	3 273(1)	5 170(1)	1 483(1)	C(16)	5 750(5)	4 233(5)	3 599(4)
Cl(1)	1 142(3)	4 985(3)	3 043(2)	C(17)	6 409(5)	5 124(5)	3 490(4)
Cl(2)	3 762(3)	6 216(3)	689(2)	C(18)	6 117(5)	5 893(5)	3 021(4)
O(1)	2 113(5)	4 033(7)	1 596(3)	C(19)	5 167(5)	5 772(5)	2 663(4)
O(2)	3 627(5)	4 792(7)	2 398(3)	C(20)	4 509(5)	4 881(5)	2 772(4)
N(1)	1 611(7)	2 329(7)	2 432(4)	O(3)	4 274(7)	3 789(8)	1 262(4)
N(2)	3 245(7)	2 938(8)	3 181(4)	C(21)	4 078(13)	3 187(14)	690(8)
C(1)	1 364(5)	3 566(6)	1 212(3)	C(22)	4 959(12)	2 461(14)	631(7)
C(2)	1 158(5)	4 037(6)	625(3)	C(23)	5 810(12)	2 905(17)	1 048(8)
C(3)	388(5)	3 577(6)	206(3)	C(24)	5 334(11)	3 722(16)	1 451(8)
C(4)	−176(5)	2 646(6)	373(3)	O(4)	2 290(7)	6 518(7)	1 776(4)
C(5)	30(5)	2 175(6)	960(3)	C(25)	2 556(12)	7 279(12)	2 280(6)
C(6)	800(5)	2 635(6)	1 380(3)	C(26)	1 614(20)	8 029(16)	2 264(11)
C(7)	1 003(9)	2 014(10)	1 961(5)	C(27)	1 099(16)	7 965(18)	1 646(12)
C(8)	1 828(5)	1 645(6)	2 962(3)	C(28)	1 366(12)	6 898(16)	1 398(8)
C(9)	1 224(5)	734(6)	3 115(3)	O(5)	3 156(14)	3 851(16)	4 719(8)
C(10)	1 491(5)	139(6)	3 660(3)	O(5′)	1 959(22)	5 630(21)	5 174(12)
C(11)	2 361(5)	455(6)	4 053(3)	C(31)	3 322(15)	4 960(17)	4 609(9)
C(12)	2 965(5)	1 366(6)	3 900(3)	C(32)	2 554(13)	5 806(15)	4 729(8)
C(13)	2 698(5)	1 961(6)	3 355(3)	C(33)	1 555(14)	4 755(18)	4 907(9)
C(14)	4 200(8)	3 151(10)	3 404(4)	C(34)	2 143(17)	3 812(17)	4 714(10)

The site occupation factors for the disordered atoms O(5) and O(5′) are 0.6 and 0.4 respectively.

Results and Discussion

Transition metal–Schiff base complexes act as bidentate oxygen-donor ligands towards transition-metal halides, giving adducts which do not undergo any transformation unless the affinity for the ligand is very different for the two metal ions involved in the adduct formation.[3] A thf solution of [Fe(acen)],[4] which is monomeric in solution, reacts both with $FeCl_2$·1.5 thf[4] and $ZnCl_2$·2thf giving the isostructural complexes (**2**) and (**3**) [equation (1)].



Complex (**1**) acts as a bidentate ligand complexing zinc(II) and iron(II) chloride. Both have pseudo-tetrahedral co-ordination, while iron in the acen complex is in a square-pyramidal geometry. We did not observe any evolution of adducts (**2**) and (**3**). A ligand-exchange reaction requires, probably, a stage in which the ligand is equally shared between the two metal ions. An indirect demonstration of this comes from the results of reaction (2). We treated $FeCl_2$·1.5thf with H_2 salphen in a 2:1 molar ratio in the presence of a base, Na(OMe). Reaction (2) led to the isolation of complex (**4**).

The pathway leading to (**4**), very probably, involves an intermediate (**A**) with a symmetric share of the quadridentate ligand. A complex structurally very similar to (**A**) was identified in the reaction between $FeCl_2$·1.5thf and dimethylglyoxime in the absence of any base.[16] Complex (**4**) apparently has a structure similar to that of (**2**), with the difference, however, that a chloride ion is still bonded to the iron–Schiff base moiety, the ligand exchange between the two iron atoms being incomplete. It should be considered as a di-iron(II) complex, formed between the $[Fe(salphen)Cl]^-$ anion and the $[FeCl(thf)_2]^+$ cation, rather than a mixed-valence iron(II, III) complex. The solid-state structure of (**4**) will be described later.

The next step was to explore the utilization of transition metal–Schiff base complexes as ligands for metal halides in

Table 5. Fractional atomic co-ordinates (× 10^4) for complex (**10**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Co	4 123(1)	3 350(1)	5 607(1)	C(8)	4 812(8)	398(7)	—2 596(13)
Ti	1 167(1)	1 547(1)	−1 234(1)	C(9)	3 585(7)	509(7)	−2 385(10)
Cl(1)	3 550(2)	2 295(2)	4 223(3)	C(10)	3 282(8)	−264(6)	−3 017(9)
Cl(2)	2 761(2)	4 482(1)	6 917(3)	C(11)	2 239(9)	−299(5)	−3 042(8)
Cl(3)	5 781(2)	2 689(2)	6 846(3)	C(12)	1 943(8)	−1 136(6)	−3 774(9)
O(1)	−326(4)	2 069(3)	−483(5)	C(13)	887(10)	3 038(8)	−3 695(12)
O(2)	1 368(4)	391(3)	−2 437(5)	C(14)	0(13)	3 510(8)	−4 871(12)
O(3)	495(4)	2 378(3)	−3 102(5)	C(15)	−791(11)	3 034(9)	−5 095(13)
O(4)	1 699(5)	707(3)	709(5)	C(16)	−575(11)	2 484(10)	−3 854(12)
O(5)	4 478(5)	4 078(4)	4 021(7)	C(17)	1 877(15)	1 049(9)	2 141(12)
N(1)	1 413(5)	2 731(4)	−31(6)	C(18)	1 978(14)	277(10)	3 143(13)
N(2)	2 883(5)	1 262(4)	−1 667(7)	C(19)	1 621(12)	−384(8)	2 339(12)
C(1)	−2 128(7)	2 983(6)	441(9)	C(20A)	1 008(70)	80(53)	848(48)
C(2)	−920(6)	2 875(5)	272(8)	C(20B)	1 984(43)	−347(13)	769(22)
C(3)	−476(7)	3 530(5)	808(8)	C(21)	5 319(9)	3 590(8)	2 964(16)
C(4)	664(8)	3 437(5)	694(8)	C(22)	4 932(11)	4 014(15)	1 573(16)
C(5)	949(8)	4 247(6)	1 536(10)	C(23)	3 978(12)	4 803(10)	1 771(14)
C(6)	2 586(8)	2 713(6)	−20(9)	C(24)	3 682(8)	4 905(6)	3 410(12)
C(7)	3 293(9)	2 016(8)	−1 042(15)				

The site occupation factors for the disordered carbon atoms are 0.377 and 0.623 for C(20A) and C(20B) respectively.

Table 6. Fractional atomic co-ordinates (× 10^4) for complex (**11**)

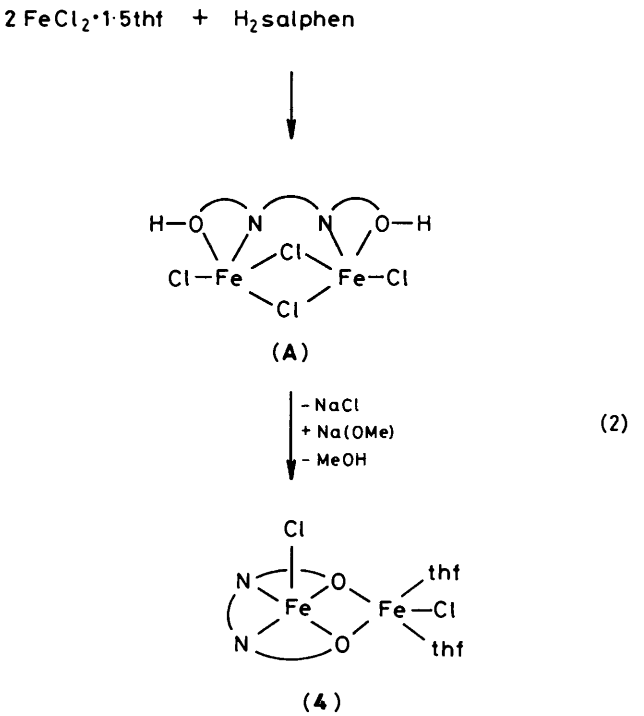
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	0(—)	0(—)	0(—)	C(6)	2 260(8)	2 610(8)	4 992(11)
Fe(2)	1 385(1)	1 258(1)	−814(1)	C(7)	1 752(8)	3 273(9)	6 221(13)
Cl(1)	1 895(1)	−179(2)	559(2)	C(8)	463(10)	4 962(10)	7 861(14)
Cl(2)	−466(2)	1 550(2)	−1 338(2)	C(9)	1 597(8)	4 841(9)	7 680(12)
Cl(3)	1 484(2)	2 681(2)	465(3)	C(10)	1 969(13)	5 576(8)	8 448(13)
Cl(4)	2 316(2)	679(2)	−2 694(3)	C(11)	2 963(13)	5 509(8)	8 536(11)
O(5)	−278(5)	949(5)	2 048(6)	C(12)	3 248(12)	6 338(9)	9 415(13)
C(21)	338(11)	1 494(14)	2 888(16)	C(13A)	3 922(18)	3 115(18)	9 977(23)
C(22)	−177(11)	2 134(10)	4 120(13)	C(14A)	4 690(45)	2 238(25)	11 035(30)
C(23)	−903(13)	1 755(13)	4 196(15)	C(15A)	5 098(36)	1 331(23)	10 082(39)
C(24)	−805(14)	1 000(12)	3 074(16)	C(16A)	5 135(25)	1 683(14)	8 676(23)
Ti	3 768(1)	3 577(1)	6 640(2)	C(13B)	5 413(31)	2 381(53)	9 353(59)
O(1)	5 172(4)	2 860(4)	6 169(6)	C(14B)	5 527(27)	1 800(48)	10 652(52)
O(2)	3 672(5)	4 775(4)	7 916(6)	C(15B)	4 503(50)	1 479(54)	10 256(64)
O(3)	4 351(4)	2 700(4)	8 561(6)	C(16B)	3 804(31)	2 161(41)	8 913(44)
O(4)	3 243(6)	4 486(5)	4 730(7)	C(17A)	2 255(19)	4 686(20)	3 594(24)
N(1)	3 423(5)	2 430(5)	5 216(7)	C(18A)	2 101(39)	5 565(46)	2 858(54)
N(2)	2 161(5)	4 028(6)	6 868(8)	C(19A)	3 276(48)	5 491(47)	3 068(42)
C(1)	6 832(8)	1 720(8)	5 496(12)	C(20A)	3 780(25)	5 083(22)	4 608(25)
C(2)	5 672(7)	2 000(7)	5 416(9)	C(17B)	3 519(44)	4 064(22)	3 259(30)
C(3)	5 172(8)	1 418(6)	4 606(9)	C(18B)	2 967(124)	4 949(41)	2 237(62)
C(4)	4 074(8)	1 648(6)	4 493(8)	C(19B)	2 448(77)	5 739(78)	2 792(111)
C(5)	3 681(9)	929(7)	3 458(11)	C(20B)	2 573(44)	5 545(25)	4 703(42)

The site occupation factors for the disordered thf carbon atoms are: 0.606 and 0.394 for C(13A)—C(16A) and C(13B)—C(16B) respectively; 0.658 and 0.342 for C(17A)—C(20A) and C(17B)—C(20B) respectively.

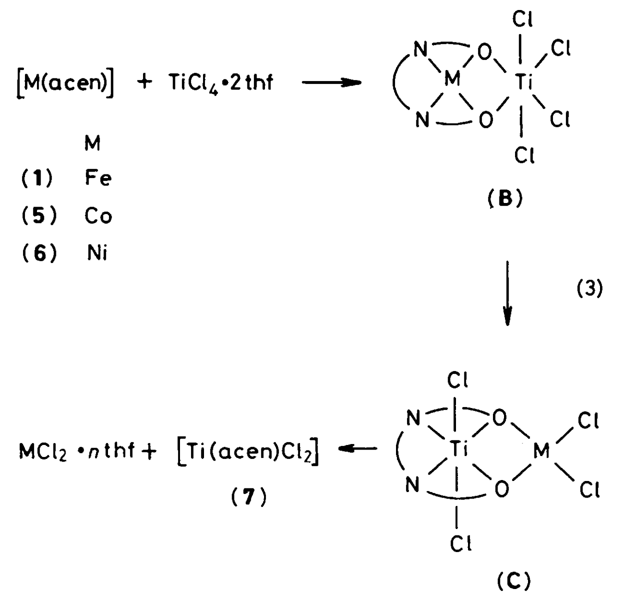
higher oxidation states.[3] In this context we chose $TiCl_4$ and $TiCl_3$, since the Schiff-base complexes derived from them are either known or recently synthesized by us.[6] Treatment of $TiCl_4$·2thf with a thf solution of [M(acen)] (M = Fe, Co, or Ni) [reaction (3)] resulted in a ligand-exchange reaction between M and titanium.

In reaction (3), independently of the transition metal, complex (**7**) is formed. Its formation very probably proceeds *via* the adduct (**B**) and exchange of the chloride and acen ligands [see complex (**4**)] between titanium and M. The resulting adduct (**C**) lacks stability because of the low basicity of the oxygens from (**7**),[6] so it decomposes to (**7**) and MCl_2·*n*thf. We never succeeded in forming adducts using complex (**7**). Such a migration is also independent of the quadridentate ligand. Thus [Ni(salen)] and [Ni(salphen)] reacted with $TiCl_4$·2thf equally well forming the corresponding complexes [Ti(salen)Cl_2][17a] and [Ti(salphen)Cl_2].[17b] The ligand migration from the lower to the higher oxidation state metal seems quite general, as a consequence of the higher stability for the same ligand associated with the metal ion having the higher oxidation state. Further support for this comes from reaction (4). The result of reaction (4) can be viewed either as acen exchange between Ti^{III} and Ti^{IV}, or an electron transfer between Ti^{III} and Ti^{IV} mediated by the bridging ligand acen.

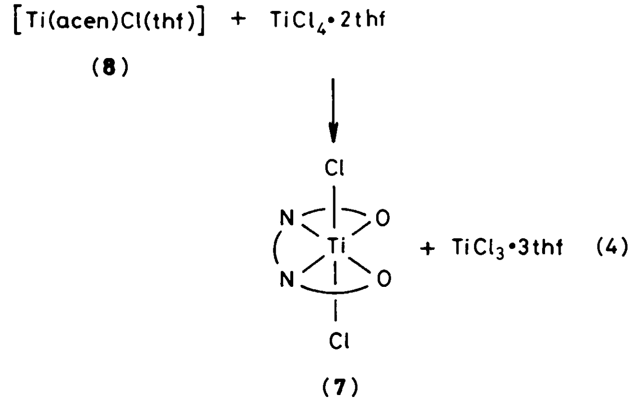
An electron-transfer reaction coupled with exchange of the polydentate ligand occurred between [Ni(acen)] (**6**) or [Cu(acen)] (**9**) and $TiCl_3$. The compound MCl_n is a reduced unidentified form of copper or nickel chloride. Reaction (5) is a classical electron transfer promoted by a bridging ligand.[1] By changing the nature of M we can suppress its reduction and the simple migration of the acen ligand is observed.



(2)



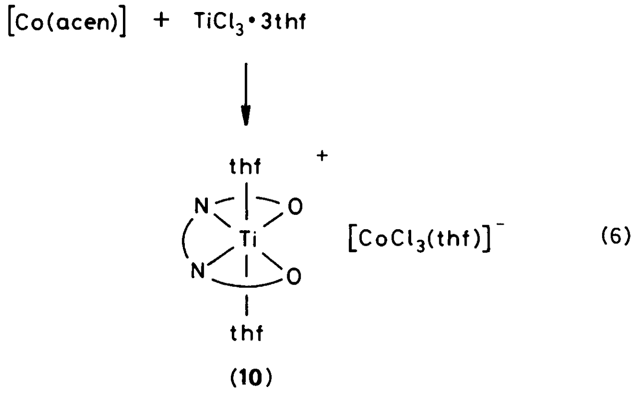
(3)



(4)

$$[M(acen)] + TiCl_3\cdot3thf \longrightarrow [Ti(acen)Cl_2] + MCl_n \quad (5)$$

M = Ni, (6); Cu, (9) (7)



(6)

$$3[Fe(acen)] + 3\,TiCl_3\cdot3thf \longrightarrow [Ti(acen)(thf)_2]_2[Fe_3Cl_8(thf)_2] + (8) \quad (7)$$

(11)

In the case of reactions (6) and (7) the migration of the acen ligand to titanium should produce an adduct analogous to (**C**), then (**8**) and the corresponding metal halide $MCl_2\cdot n$thf, as we observed in reaction (3). The formation of compounds (**10**) and (**11**) is due to ionization of the Ti-Cl bond in (**8**) by MCl_2. Thus $CoCl_2$ and $FeCl_2$ produce the counter anions $[CoCl_3(thf)]^-$ and $[Fe_3Cl_8(thf)_2]^{2-}$ respectively. In the latter case the stoicheiometry (7) requires the formation of (**8**) too. In a separate experiment we observed the formation of complexes (**10**) and (**11**) by treating (**8**) with $FeCl_2 1.5$thf and $CoCl_2\cdot1.5$thf. The structures of (**10**) and (**11**) are discussed below. The results reported so far show that adduct formation between the transition metal–Schiff base complexes and a metal ion precedes migration/exchange of ligands. Such a process occurs with the ligand moving from the lower to the higher oxidation state ion, and suggests how the relative stability of a complex formed from the same ligand and different metal ions in non-aqueous solvents may be qualitatively evaluated.

Description of the Structures.—Selected bond distances and angles are listed in Table 7 for complexes (**2**) and (**3**), Table 8 for (**4**) and Table 9 for (**10**) and (**11**). In complexes (**2**) and (**3**) a Fe(acen) unit acts as a bidentate oxygen-donor ligand toward iron and zinc chloride respectively, both being in a pseudo-tetrahedral geometry (Figure 1). The co-ordination geometry around iron is a square pyramid. Bond distances and angles within Fe(acen)(thf) in the two complexes (Table 7) are not significantly different and fall in the range of values generally observed.[4] The N_2O_2 core shows small but significant tetrahedral distortions ranging from −0.050(12) to 0.0624(13) Å for (**2**) and from −0.050(8) to 0.060(9) Å for (**3**). The Fe(1) atom deviates by 0.413(3) and 0.441(2) Å toward the O(3) oxygen atom in (**2**) and (**3**) respectively. The direction of the Fe(1)–O(3) bond is tilted with respect to the normal to the core plane by 7.8(4) and 6.7(3)° for (**2**) and (**3**) respectively. No isolated part of

Table 7. Selected bond distances (Å) and angles (°) for complexes (**2**) and (**3**). For (**3**), Fe(2) should be read Zn

	(**2**)	(**3**)		(**2**)	(**3**)
Fe(1)–O(1)	2.00(1)	2.008(7)	N(1)–C(4)	1.33(2)	1.324(13)
Fe(1)–O(2)	1.98(1)	1.985(5)	N(1)–C(6)	1.48(2)	1.459(14)
Fe(1)–O(3)	2.09(1)	2.107(7)	N(2)–C(7)	1.47(2)	1.446(13)
Fe(1)–N(1)	2.00(1)	2.009(7)	N(2)–C(9)	1.29(2)	1.303(11)
Fe(1)–N(2)	2.05(1)	2.028(9)	C(1)–C(2)	1.49(2)	1.510(16)
Fe(2)–Cl(1)	2.228(5)	2.198(3)	C(2)–C(3)	1.34(2)	1.333(14)
Fe(2)–Cl(2)	2.236(6)	2.206(3)	C(3)–C(4)	1.44(2)	1.426(15)
Fe(2)–O(1)	2.09(1)	2.039(5)	C(4)–C(5)	1.48(2)	1.499(15)
Fe(2)–O(2)	2.08(1)	2.032(7)	C(6)–C(7)	1.50(2)	1.499(15)
O(1)–C(2)	1.33(2)	1.321(10)	C(8)–C(9)	1.52(3)	1.503(17)
O(2)–C(11)	1.35(2)	1.334(11)	C(9)–C(10)	1.44(2)	1.422(16)
O(3)–C(13)	1.46(2)	1.452(14)	C(10)–C(11)	1.35(2)	1.371(16)
O(3)–C(16)	1.48(2)	1.430(17)	C(11)–C(12)	1.54(2)	1.485(14)
N(1)–Fe(1)–N(2)	83.5(5)	83.7(3)	Fe(1)–N(1)–C(4)	125.4(9)	125.4(6)
O(2)–Fe(1)–N(2)	91.6(5)	92.6(3)	C(4)–N(1)–C(6)	120.1(12)	121.2(8)
O(2)–Fe(1)–N(1)	153.5(5)	151.9(3)	Fe(1)–N(2)–C(9)	126.2(12)	126.1(7)
O(1)–Fe(1)–N(2)	159.3(5)	157.6(3)	Fe(1)–N(2)–C(7)	108.7(9)	109.3(7)
O(1)–Fe(1)–N(1)	92.2(4)	91.5(3)	C(7)–N(2)–C(9)	125.1(14)	125.1(4)
O(1)–Fe(1)–O(2)	83.2(4)	81.5(3)	O(1)–C(2)–C(1)	114.8(13)	113.9(8)
O(1)–Fe(2)–O(2)	78.6(4)	79.6(3)	C(1)–C(2)–C(3)	123.0(14)	122.1(9)
Cl(2)–Fe(2)–O(2)	112.9(3)	112.3(2)	O(1)–C(2)–C(3)	122.0(13)	124.1(9)
Cl(2)–Fe(2)–O(1)	113.8(3)	114.0(2)	C(2)–C(3)–C(4)	130.4(14)	129.9(9)
Cl(1)–Fe(2)–O(2)	108.5(3)	110.3(2)	N(1)–C(4)–C(3)	121.0(13)	121.5(9)
Cl(1)–Fe(2)–O(1)	112.0(3)	111.9(2)	C(3)–C(4)–C(5)	116.7(13)	117.6(9)
Cl(1)–Fe(2)–Cl(2)	122.5(2)	121.3(1)	N(1)–C(4)–C(5)	122.3(14)	120.9(9)
Fe(1)–O(1)–Fe(2)	98.7(4)	98.9(3)	N(1)–C(6)–C(7)	110.5(12)	111.3(9)
Fe(2)–O(1)–C(2)	133.9(9)	136.2(6)	N(2)–C(7)–C(6)	110.8(12)	112.8(9)
Fe(1)–O(1)–C(2)	125.8(9)	123.9(5)	N(2)–C(9)–C(8)	122.5(15)	121.3(9)
Fe(1)–O(2)–Fe(2)	99.5(4)	100.0(3)	C(8)–C(9)–C(10)	114.8(14)	117.1(9)
Fe(2)–O(2)–C(11)	133.6(9)	131.6(6)	N(2)–C(9)–C(10)	122.5(15)	121.6(9)
Fe(1)–O(2)–C(11)	125.2(9)	125.3(6)	C(9)–C(10)–C(11)	129.3(15)	130.6(10)
Fe(1)–O(3)–C(16)	122.6(10)	122.9(7)	O(2)–C(11)–C(10)	124.5(13)	123.3(9)
Fe(1)–O(3)–C(13)	124.7(10)	122.1(7)	C(10)–C(11)–C(12)	123.2(14)	121.3(10)
C(13)–O(3)–C(16)	107.3(13)	109.5(9)	O(2)–C(11)–C(12)	111.8(12)	115.3(9)
Fe(1)–N(1)–C(6)	113.4(9)	113.1(6)			

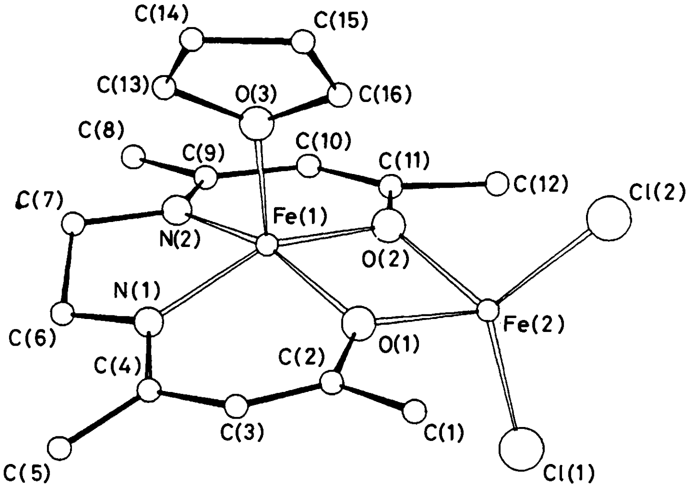


Figure 1. A view of complex (**2**). For the isostructural complex (**3**), Fe(2) should be replaced by Zn. For clarity only the A positions of the disordered atoms C(14) and C(15) are shown

the Fe(acen) unit is strictly planar as indicated by the parameters quoted in Table 10. Co-ordination of metal chlorides to acen oxygens causes a narrowing of the O(1)-Fe(1)-O(2) angle [83.2(4) for (**2**) and 81.5(3)° for (**3**)] with respect to the value of about 109° generally found in M(acen) units (Table 11), and the enlargement of the C(2)-C(3)-C(4) and C(9)-C(10)-C(11) angles

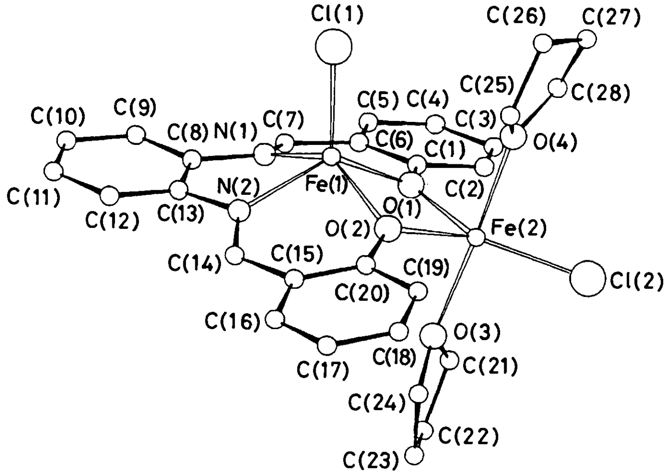


Figure 2. A view of complex (**4**)

which are significantly greater than 120° [130.4(14) and 129.3(15)° for (**2**), 129.9(9) and 130.6(10)° for (**3**)].[18]

Complex (**4**) is shown in Figure 2. The co-ordination around Fe(1) is square pyramidal involving the donor atoms of the salphen ligand in the basal plane and a chlorine atom in the axial position. The Fe(1) atom is 0.786(2) Å from the N_2O_2 core which shows significant tetrahedral distortions ranging from $-0.080(9)$ to 0.079(9) Å. The salphen ligand exhibits an umbrella conformation[18] as indicated by the dihedral angles the N_2O_2

Table 8. Selected bond distances (Å) and angles (°) for complex (**4**)

Fe(1)–Cl(1)	2.259(3)	O(2)–C(20)	1.336(9)
Fe(1)–O(1)	2.079(7)	N(1)–C(7)	1.284(13)
Fe(1)–O(2)	2.074(7)	N(1)–C(8)	1.417(10)
Fe(1)–N(1)	2.111(8)	N(2)–C(13)	1.432(11)
Fe(1)–N(2)	2.120(8)	N(2)–C(14)	1.303(13)
Fe(2)–Cl(2)	2.266(4)	O(3)–C(21)	1.44(2)
Fe(2)–O(1)	2.050(7)	O(3)–C(24)	1.39(2)
Fe(2)–O(2)	2.045(6)	O(4)–C(25)	1.44(2)
Fe(2)–O(3)	2.174(9)	O(4)–C(28)	1.45(2)
Fe(2)–O(4)	2.179(9)	C(6)–C(7)	1.466(13)
O(1)–C(1)	1.336(9)	C(14)–C(15)	1.446(13)
N(1)–Fe(1)–N(2)	77.2(3)	C(7)–N(1)–C(8)	122.5(9)
O(2)–Fe(1)–N(2)	86.0(3)	Fe(1)–N(2)–C(14)	127.2(8)
O(2)–Fe(1)–N(1)	139.8(3)	Fe(1)–N(2)–C(13)	110.6(6)
O(1)–Fe(1)–N(2)	132.0(3)	C(13)–N(2)–C(14)	122.1(9)
O(1)–Fe(1)–N(1)	85.4(3)	O(1)–C(1)–C(6)	122.3(6)
O(1)–Fe(1)–O(2)	79.2(3)	O(1)–C(1)–C(2)	117.7(6)
O(3)–Fe(2)–O(4)	175.8(3)	C(5)–C(6)–C(7)	114.9(7)
O(2)–Fe(2)–O(4)	87.8(3)	C(1)–C(6)–C(7)	124.9(7)
O(2)–Fe(2)–O(3)	88.0(3)	N(1)–C(7)–C(6)	125.7(10)
O(1)–Fe(2)–O(4)	90.2(3)	N(1)–C(8)–C(13)	115.2(6)
O(1)–Fe(2)–O(3)	88.8(3)	N(1)–C(8)–C(9)	124.8(6)
O(1)–Fe(2)–O(2)	80.6(3)	N(2)–C(13)–C(12)	123.4(7)
Cl(2)–Fe(2)–O(4)	91.4(3)	N(2)–C(13)–C(8)	116.5(6)
Cl(2)–Fe(2)–O(3)	92.1(3)	N(2)–C(14)–C(15)	124.8(9)
Cl(2)–Fe(2)–O(2)	143.9(2)	C(14)–C(15)–C(20)	126.0(7)
Cl(2)–Fe(2)–O(1)	135.6(2)	C(14)–C(15)–C(16)	114.0(7)
Fe(1)–O(1)–Fe(2)	98.7(3)	O(2)–C(20)–C(19)	116.9(7)
Fe(2)–O(1)–C(1)	133.9(5)	O(2)–C(20)–C(15)	123.0(7)
Fe(1)–O(1)–C(1)	126.9(5)	Fe(2)–O(3)–C(24)	124.4(9)
Fe(1)–O(2)–Fe(2)	99.0(3)	Fe(2)–O(3)–C(21)	120.7(9)
Fe(2)–O(2)–C(20)	132.1(5)	C(21)–O(3)–C(24)	108.3(11)
Fe(1)–O(2)–C(20)	128.1(6)	Fe(2)–O(4)–C(28)	122.3(9)
Fe(1)–N(1)–C(8)	111.9(6)	Fe(2)–O(4)–C(25)	125.8(8)
Fe(1)–N(1)–C(7)	125.4(8)	C(25)–O(4)–C(28)	110.8(11)

mean plane forms with the three nearly planar moieties of the molecule, *i.e.* C(8)–C(13),N(1),N(2); C(1)–C(7),N(1),O(1), and C(14)–C(20),N(2),O(2) which are 4.0(2), 5.6(2), and 15.0(2)°. The last two planes form a dihedral angle of 20.5(1)°. The [Fe(salphen)Cl]$^-$ anion acts as a bidentate oxygen-donor ligand towards a [FeCl(thf)$_2$]$^+$ cation. The co-ordination around Fe(2) can be described as a trigonal bipyramid with Fe(2), Cl(1), O(1), O(2) in the equatorial plane and the thf oxygen atoms at the apices. The main distortion from a regular polyhedron is due to the O(1) $\cdots$ O(2) bite, the O(1)–Fe(2)–O(2) angle being 80.6(3)°. This causes a remarkable enlargement of the angles in the equatorial plane [O(1)–Fe(2)–Cl(2) 135.6(2) and O(2)–Fe(2)–Cl(2) 143.9(2)°]. However the iron atoms lie exactly on the plane defined by O(1), O(2), Cl(2) which forms a dihedral angle of 14.0(2)° with the N_2O_2 core. The two Fe–Cl distances [Fe(1)–Cl(1) 2.259(3) and Fe(2)–Cl(2) 2.266(4) Å] are slightly longer than those found in complex (**2**) where the co-ordination is tetrahedral. These values along with the iron–oxygen and nitrogen distances within the Fe(salphen) moiety[19,20] suggest that complex (**4**) has to be considered as a di-iron(II) derivative.

The structure of complex (**10**) is built up by discrete [Ti(acen)(thf)$_2$]$^+$ cations and [CoCl$_3$(thf)]$^-$ separated by van der Waals contacts. Titanium exhibits a pseudo-octahedral co-ordination involving the donor atoms from the acen ligand in the equatorial plane and the oxygen atoms from two thf molecules in the axial positions (Figure 3). Table 11 lists the results of a few structure determinations of Ti(acen) derivatives. The Ti–O bond lengths observed in complexes (**10**) and (**11**) which contain the same cation [mean 1.908(4) and 1.906(5) Å] are in the middle of those in titanium-(IV) and -(III) complexes [1.878(7) and 1.930(8) Å respectively].[6] The complexes [Ti(acen)Cl$_2$] (**7**)[6] and [Ti(acen)Cl(thf)] (**8**)[6] are significant examples for evaluating the dependence of the Ti–O bond distances on the oxidation state of the metal. It is worthy of note that the Ti–O bond lengths in these complexes are at the extremes of the values quoted in Table 11 [1.861(7) and 1.941(4) Å respectively] and their difference of 0.08 Å could be accounted as due to the change in the oxidation state of the metal. The data in Table 11 do not show any variation in the Ti–N bond distances and in the N–Ti–N and O–Ti–O bond angles as a consequence of the difference in oxidation states or ligands. The distortion from planarity of the Ti(acen) moiety in the pseudo-octahedral [Ti(acen)(thf)$_2$]$^+$ cation is less important than in five-co-ordinated or unsymmetrical six-co-ordinated M(acen) units (Table 10). Titanium lies approximately in the plane of the N_2O_2 core, being displaced by 0.022(1) Å. The anion [CoCl$_3$(thf)]$^-$ [complex (**10**)] is shown in Figure 4. The repulsive interactions between chlorines enlarge the Cl–Co–Cl angles and narrow the Cl–Co–O ones with respect to an ideal tetrahedral geometry (Table 9).[21]

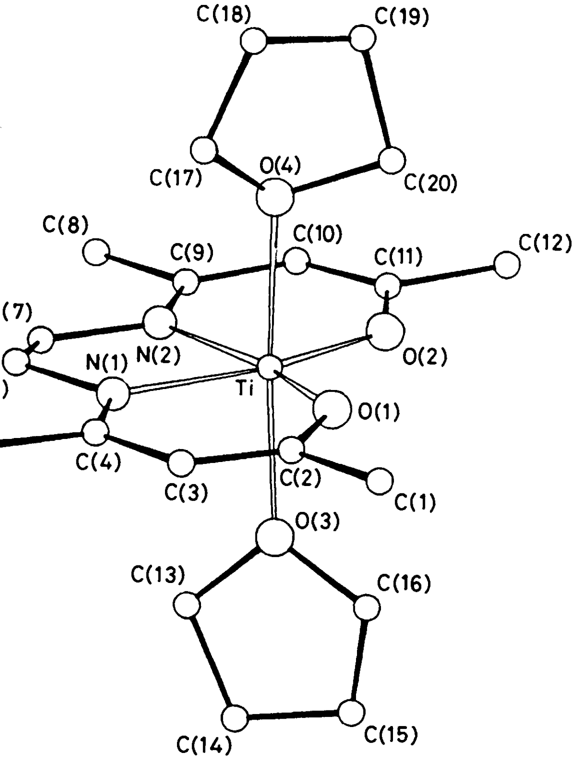


Figure 3. A view of the [Ti(acen)(thf)$_2$]$^+$ cation in complexes (**10**) and (**11**) (disorder not shown for clarity)

Complex (**11**) consists of [Ti(acen)(thf)$_2$]$^+$ cations and [Fe$_3$Cl$_8$(thf)$_2$]$^{2-}$ anions. The correct 2/1 molar ratio is provided by the presence of half an independent anion *vs.* one independent cation, the anion lying on a centre of symmetry. Except for some differences mainly related to the disorder affecting the co-ordinated thf molecules (see Experimental section), the geometry of the cation is the same as that found in complex (**10**) (Table 9), so only one view for both is given in Figure 3. The anion can be viewed as two [FeCl$_4$]$^{2-}$ anions symmetrically chelating a Fe^{2+} cation in a perfectly square-planar arrangement (Figure 5). The co-ordination around the central atom, *i.e.* flattened bipyramid, is completed by the oxygen atoms of two thf molecules. The terminal Fe–Cl bonds within a tetrahedron are considerably shorter than the bridging ones [mean 2.258(3)

Table 9. Selected bond distances (Å) and angles (°) for complexes (**10**) and (**11**)

	(**10**)	(**11**)		(**10**)	(**11**)
Ti–O(1)	1.911(4)	1.901(5)	N(2)–C(9)	1.300(9)	1.324(12)
Ti–O(2)	1.905(4)	1.911(5)	C(1)–C(2)	1.502(12)	1.481(15)
Ti–O(3)	2.112(4)	2.134(6)	C(2)–C(3)	1.349(12)	1.359(14)
Ti–O(4)	2.161(4)	2.163(7)	C(3)–C(4)	1.416(13)	1.406(15)
Ti–N(1)	2.114(7)	2.111(7)	C(4)–C(5)	1.523(13)	1.499(14)
Ti–N(2)	2.121(6)	2.111(7)	C(6)–C(7)	1.409(13)	1.464(14)
O(1)–C(2)	1.319(7)	1.309(9)	C(8)–C(9)	1.532(14)	1.577(20)
O(2)–C(11)	1.313(8)	1.261(13)	C(9)–C(10)	1.420(14)	1.416(20)
N(1)–C(4)	1.291(8)	1.303(9)	C(10)–C(11)	1.347(16)	1.343(26)
N(1)–C(6)	1.483(12)	1.503(13)	C(11)–C(12)	1.529(13)	1.497(20)
N(2)–C(7)	1.472(14)	1.448(16)			
Co–Cl(1)	2.231(3)		Fe(1)–Cl(1)		2.488(1)
Co–Cl(2)	2.237(2)		Fe(1)–Cl(2)		2.520(2)
Co–Cl(3)	2.225(2)		Fe(1)–O(5)		2.150(5)
Co–O(5)	2.043(7)		Fe(2)–Cl(1)		2.381(3)
O(5)–C(21)	1.419(13)		Fe(2)–Cl(2)		2.377(3)
O(5)–C(24)	1.405(9)		Fe(2)–Cl(3)		2.262(3)
			Fe(2)–Cl(4)		2.254(3)
			O(5)–C(21)		1.439(20)
			O(5)–C(24)		1.379(21)
N(1)–Ti–N(2)	78.9(3)	80.0(3)			
O(2)–Ti–N(2)	85.3(2)	84.9(3)	C(1)–C(2)–C(3)	124.4(7)	122.5(9)
O(2)–Ti–N(1)	164.3(3)	164.6(3)	O(1)–C(2)–C(3)	122.6(7)	123.2(9)
O(1)–Ti–N(2)	164.6(2)	164.8(3)	C(2)–C(3)–C(4)	125.6(7)	124.8(8)
O(1)–Ti–N(1)	85.8(2)	85.1(3)	N(1)–C(4)–C(3)	124.2(7)	123.6(8)
O(1)–Ti–O(2)	109.9(2)	110.2(3)	C(3)–C(4)–C(5)	113.8(8)	115.3(8)
O(3)–Ti–O(4)	174.8(3)	177.2(3)	N(1)–C(4)–C(5)	122.0(8)	121.0(9)
Ti–O(1)–C(2)	134.4(5)	135.2(6)	N(1)–C(6)–C(7)	114.4(9)	111.6(9)
Ti–O(2)–C(11)	134.9(6)	137.2(9)	N(2)–C(7)–C(6)	116.1(10)	114.0(10)
Ti–N(1)–C(6)	114.8(5)	113.1(5)	N(2)–C(9)–C(8)	121.5(8)	117.4(10)
Ti–N(1)–C(4)	126.9(6)	127.8(7)	C(8)–C(9)–C(10)	115.4(8)	118.3(11)
C(4)–N(1)–C(6)	118.4(7)	119.1(8)	N(2)–C(9)–C(10)	123.1(9)	124.2(13)
Ti–N(2)–C(9)	127.4(6)	125.7(8)	C(9)–C(10)–C(11)	125.7(8)	124.8(11)
Ti–N(2)–C(7)	114.1(6)	113.3(7)	O(2)–C(11)–C(10)	123.0(7)	123.0(10)
C(7)–N(2)–C(9)	118.5(8)	120.4(10)	C(10)–C(11)–C(12)	123.9(8)	118.7(13)
O(1)–C(2)–C(1)	112.9(6)	114.3(8)	O(2)–C(11)–C(12)	113.1(8)	118.3(13)
Cl(3)–Co–O(5)	103.6(2)		Cl(2)–Fe(1)–O(5)		89.5(2)
Cl(2)–Co–O(5)	104.0(2)		Cl(1)–Fe(1)–O(5)		89.8(2)
Cl(2)–Co–Cl(3)	115.9(1)		Cl(2′)–Fe(1)–O(5)		90.5(2)
Cl(1)–Co–O(5)	102.9(2)		Cl(1′)–Fe(1)–O(5)		90.2(2)
Cl(1)–Co–Cl(3)	113.8(1)		Cl(1)–Fe(1)–Cl(2)		85.3(1)
Cl(1)–Co–Cl(2)	114.4(1)		Cl(1′)–Fe(1)–Cl(2)		94.7(1)
Co–O(5)–C(24)	124.3(6)		Cl(3)–Fe(2)–Cl(4)		112.8(1)
Co–O(5)–C(21)	120.5(6)		Cl(2)–Fe(2)–Cl(4)		119.4(1)
C(21)–O(5)–C(24)	109.4(8)		Cl(2)–Fe(2)–Cl(3)		107.2(1)
			Fe(1)–Cl(1)–Fe(2)		92.2(1)
			Fe(1)–Cl(2)–Fe(2)		91.4(1)
			Fe(1)–O(5)–C(24)		130.1(8)
			Fe(1)–O(5)–C(21)		126.8(8)
			C(21)–O(5)–C(24)		101.3(9)

Primed atoms at $-x$, $-y$, $-z$.

Table 10. Comparison of structural parameters within the M(acen) unit for Complexes (**2**), (**3**), (**10**), and (**11**)

Complex	(**2**)	(**3**)	(**10**)	(**11**)
Folding* along the N(1) ··· O(1) line/°	11.2(6)	14.8(3)	5.4(2)	2.6(2)
Folding along the N(2) ··· O(2) line/°	6.8(5)	4.9(3)	5.4(2)	1.1(2)
Angle between M–N(1)–O(1) and M–N(2) – O(2) planes/°	34.5(4)	36.8(3)	2.1(2)	3.4(3)
Angle between the OC_3N planes/°	17.1(5)	18.0(3)	2.4(2)	4.2(3)
N(1)–C(6)–C(7)–N(2) torsion angle/°	−37.4(17)	−31.5(12)	−15.2(13)	32.1(13)
Distance of C(6) and C(7) from the M–N(1)–N(2) plane/Å	0.038(15) 0.520(16)	0.091(10) 0.484(11)	−0.094(8) 0.091(13)	0.161(10) −0.244(12)

* Defined as the dihedral angle between the MNO and OC_3N planes of a six-membered chelation ring.

Table 11. Bond distances (Å) and angles (°) found in Ti(acen) derivatives

Complex	Ti–O	Ti–N	O–Ti–O	N–Ti–N	Ref.
[Ti(acen)Cl_2]	1.861(7)	2.129(8)	109.3(3)	78.8(3)	6
[Ti{(acen)Cl}$_2$O]	1.908(3)	2.135(2)	110.3(1)	77.5(1)	6
[Ti(acen)Cl(thf)]	1.941(4)	2.123(5)	109.3(2)	78.1(2)	6
[Ti(acen)(NCS)(thf)]	1.922(4)	2.117(5)	109.9(2)	79.0(2)	Unpublished work
[Ti(acen)(thf)$_2$]$^+$ (**10**)	1.908(4)	2.118(7)	109.9(2)	78.9(3)	This work
[Ti(acen)(thf)$_2$]$^+$ (**11**)	1.906(5)	2.111(7)	110.2(3)	80.0(3)	This work

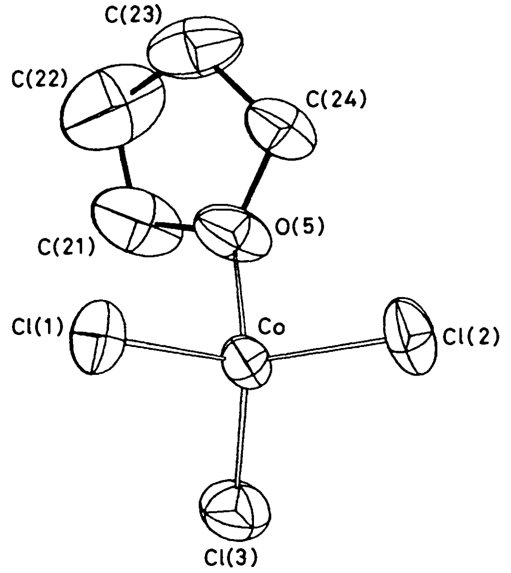


Figure 4. The [$CoCl_3$(thf)]$^-$ anion in complex (**10**)

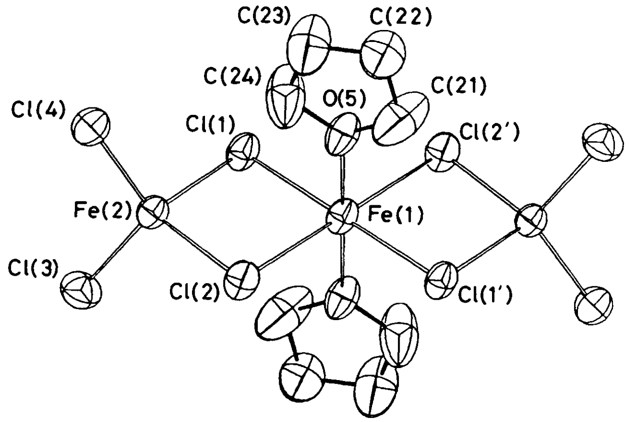


Figure 5. The [Fe_3Cl_8(thf)$_2$]$^{2-}$ anion in complex (**11**). The anion has a crystallographically imposed centre of symmetry. Primed atoms are at positions $\bar{x}, \bar{y}, \bar{z}$

vs. 2.379(3) Å]. All of them are very close to the corresponding values found in the dimeric [Fe_2Cl_6]$^{2-}$ ion for the complex [V_2Cl_3(thf)$_6$][Fe_2Cl_6][22] where the terminal and the bridging distances average 2.241(3) and 2.391(3) Å respectively. The terminal distances are however significantly shorter than those previously found in tetrahedral [$FeCl_4$]$^{2-}$ ions {*e.g.* 2.292(2) Å in [NMe_4]$_2$[$FeCl_4$][23]} and are close to those observed in complexes (**2**) and (**4**). The central Fe–Cl bonds are markedly longer than the others as a consequence of repulsive interactions between chlorines in the square array. To our knowledge this is the first structural characterization of such an anion.

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