Optically Active Complexes of Schiff Bases. Part 3.[1] Complexes of Iron(III) with Quadridentate Schiff Bases derived from Salicylaldehyde

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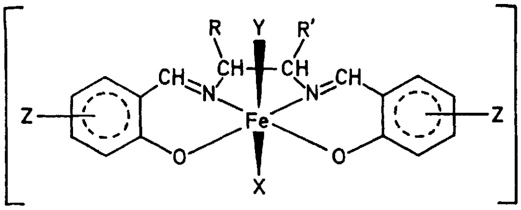
Five-co-ordinate complexes of iron(III) have been prepared with quadridentate Schiff-base ligands obtained by the condensation of 2 mol of salicylaldehyde with 1 mol of a C-substituted diamine. They are neutral high-spin iron(III) species which in some cases can crystallize as dimers, depending on the solvent of crystallization and the natures of the apical anionic ligand, the substituents in the benzene ring of the salicylaldehyde, and the diamine. A new criterion of distinguishing between mono- and di-meric structures, based on i.r. spectroscopy, is presented. In only one case, with the cyanide ligand, have anionic low-spin species been obtained. The factors favouring the addition of a base to five-co-ordinate complexes to form six-co-ordinate adducts are discussed, together with the conformational aspects of the quadridentate Schiff-base ligand.

THE chemistry of metal complexes with multidentate ligands having delocalized π orbitals like Schiff bases or porphyrins has recently gained much attention because of their use as models of biological systems, such as some respiratory pigments or the coenzyme of vitamin B_{12}. In the case of Schiff-base complexes most of the work has been done on cobalt(II) complexes, considered as reversible oxygen carriers [1-3] or as models of the coenzyme B_{12},[4] and comparatively little work has been done on similar iron(II) or iron(III) complexes,[5,6] despite the interest in iron which is often present in living systems.

In this paper we have extended our investigations of steric and conformational effects in metal complexes with optically active Schiff bases, of the type alkylenebis(salicylideneiminate), to the case of Fe^{III}. Preliminary observations of these effects have been already reported in the case of Co^{II},[1] and will be extended in Parts 4 and 5 of this series.[2,7] The complexes described (Tables 1 and 2) are summarized below, together with the abbreviations used throughout this paper. As already stated, the optically active diamines used all have the same absolute configuration (S or SS);[8] butane-2,3-diamine, cyclohexane-1,2-diamine, and 1,2-diphenylethylenediamine have also been used in the *meso* form.



[FeL(X)Y] X = Cl, N_3, NCS, or CN; Y = pyridine (py) or CN (when X = CN); Z = Cl, OMe, or NO_2

L	R	R'
salen	H	H
salpn	Me	H
salbn	Me	Me
salpen	Ph	H
saldpen	Ph	Ph

Also L = *o*-phenylenebis(salicylideneiminate) (salpd), 1,2-cyclo(hexylenebis(salicylideneiminate) (salchxn), or ethylenebis-1-phenylbutane-1,3-dionate) (pbden)

RESULTS AND DISCUSSION

It is known [7,9] that [FeCl(salen)] can be obtained either as a monomer or as a dimer according to the solvent from which it is crystallized. It has also been reported that the two forms can be distinguished by their magnetic moments at room temperature (*ca.* 5.7—6.0 B.M. for the monomer and 5.1—5.4 B.M.† for the dimer), although more recently [10] a value of 5.5 B.M. for a monomeric derivative (structure confirmed by Mössbauer spectroscopy) has been reported. The only information available for the assignment of structure to these crystalline complexes seems to be the variation of the magnetic

TABLE 1

Magnetic moments and i.r. data in the 800—900 cm^{-1} region of the complexes [FeX(Z-salen)]

Complex	Solvent of crystallization	Magnetic moment (μ/(B.M.)) 295	85 K	$\bar{\nu}/cm^{-1}$		
[FeCl(salen)]	EtOH	6.04			865	
	$MeNO_2$	5.90			865	
	Me_2CO	5.45	3.93 *	890	865	850
[FeCl(salen)]·2py	Pyridine	5.66			865	
[Fe(N_3)(salen)]	EtOH	5.36	3.86	890	870	850
[Fe(NCS)(salen)]	EtOH	5.31	3.83	890	870	850
[FeI(salen)]	EtOH	5.40		890	865	850
[FeCl(5Cl-salen)]	EtOH	5.15	3.63	890	870	850
[FeCl(5NO_2-salen)]	EtOH	5.32		900	870	855
	Me_2CO	5.13		900	870	855
[FeCl(3OMe-salen)]	EtOH	6.20			860	
	Me_2CO	5.13		890	870	850
[FeCl(5OMe-salen)]	EtOH	4.66		890	850	830
	Me_2CO	5.13		890	850	830
[FeCl(salpd)]	EtOH	5.71	5.65 *		875	860
[Fe(N_3)(salpd)]	EtOH	5.53	4.09		870	850
[FeCl(pbden)]	EtOH	5.76	5.82		855	
[Fe(N_3)(pbden)]	EtOH	5.81			855	

* Taken from ref. 6.

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

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[5] A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1968, 1048; F. Calderazzo and C. Floriani, *Chem. Comm.*, 1968, 417; C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1971, 3665; J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, 1973, **95**, 5757.

[6] M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (*A*), 1968, 112.

[7] Part 4, A. Pasini, M. Gullotti, and R. Ugo, following paper.

[8] M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazzetta*, 1972, **102**, 855; A. Pasini, paper in preparation.

[9] M. Gerloch, J. Lewis, F. E. Mabbs, and A. Richards, *Nature*, 1966, **212**, 809; M. Gerloch and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1967, 1598.

[10] G. M. Bancroft, A. G. Maddock, and R. D. Randl, *J. Chem. Soc.* (*A*), 1968, 2939.

TABLE 2

Magnetic moments and i.r. data in the 800—900 cm^{-1} region of the complexes [FeX(saldiamine)] crystallized from ethanol

Complex	Magnetic moment (μ/B.M.) 295	85 K	$\tilde{\nu}/cm^{-1}$		
[FeCl{sal(+)pn}]	5.88	5.82		865	
$[Fe(N_3)\{sal(+)pn\}]$	5.11		890	865	850
[Fe(NCS){sal(+)pn}]	5.62	3.92	890	875	860
[FeCl{sal(+)bn}]	5.93			855	
$[Fe(N_3)\{sal(+)bn\}]$	5.99			855	
[Fe(NCS){sal(+)bn}]	5.83			860	
[FeCl(sal*meso*bn)]	5.10	3.70	890	865	855
$[Fe(N_3)$(sal*meso*bn)]	5.50	3.84	890	865	850
[FeCl{sal(+)chxn}]	5.82			855	
$[Fe(N_3)\{sal(+)chxn\}]$	5.27		885	865	855
[FeCl(sal*meso*chxn)]	5.10		880	865	850
$[Fe(N_3)$(sal*meso*chxn)]	5.03		880	865	855 (sh)
[FeCl{sal(+)pen}]	5.15		875	865	850
[FeCl{sal(−)dpen}]	5.95	5.87		860	
$[Fe(N_3)\{sal(-)dpen\}]$	5.90	5.88		860	
[FeCl(sal*meso*dpen)]	5.01		890	865	855
$[Fe(N_3)$(sal*meso*dpen)]	5.18		890	870	860 (sh)

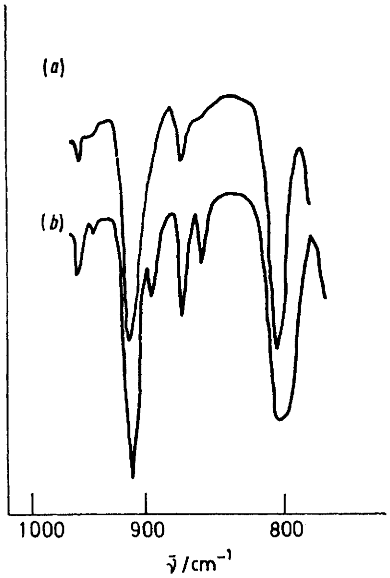

FIGURE 1 Infrared spectra (Nujol mulls) of (*a*) [FeCl(salen)] and (*b*) $[\{FeCl(salen)\}_2]$ in the 800—1 000 cm^{-1} region

moment with temperature; the moment decreases to *ca.* 3.8 B.M. at low temperature (*ca.* 100 K) in the case of the dimers, through the antiferromagnetic coupling of the two high-spin iron atoms.[6]

A careful comparison of i.r. spectra in the 800—900 cm^{-1} region of the present series of complexes, for which the structures were assigned through the variation of the magnetic moment with temperature, led us to find another (simpler) criterion for distinguishing between the mono- and the di-meric forms. In the case of monomers only one band at *ca.* 865 cm^{-1} is present in the spectra, whereas for the dimers three bands were always found at 890, *ca.* 865, and *ca.* 855 cm^{-1} (Tables 1 and 2 and Figure 1). It is clear that very little is known about the factors which control the dimerisation in the solid state, and we therefore examined two of these factors: steric and electronic effects.

Steric effects were analyzed by synthesising a number of complexes derived from C-substituted diamines, electronic effects by preparing either some complexes of the type [FeX(saldiamine)] (X = I, NCS, or N_3) *via* a metathesis reaction or other complexes derived from 5- or 3-substituted salicylaldehydes, *i.e.* [FeX(Z-salen)] ($Z = NO_2$, Cl, *etc.*). The physical properties of these complexes are summarized in Tables 1 (electronic effects) and 2 (steric effects). All of the complexes have high-spin ground states at room temperature. The formation of a dimeric structure is essentially driven by the electronic influence of the ligands, both in the plane (substituents on the salicylaldehyde ring) and in the apical positions (with softer anionic ligands, like $[N_3]^-$ and $[NCS]^-$, the dimeric structure is favoured). The influence of the solvent of crystallization is not as relevant as in the case of the related H_2salen derivatives, like [FeCl(salen)].[9] Thus, in contrast to the behaviour of [FeCl(salen)], the complexes $[Fe(N_3)(salen)]$ and [Fe(NCS)(salen)] are dimers in the solid state even when crystallized from ethanol.

The effect of the 'in-plane' ligand is complicated: electron-withdrawing groups on the salicylaldehyde ring favour the dimeric structures (Table 1), but, in the case of the methoxy-group, the position of substitution also seems to be important. The complex [FeCl(3OMe-salen)] crystallizes as a monomer from ethanol, whereas the 5-methoxy-analogue precipitates as a dimer from the same solvent; both the complexes are dimers when crystallized from acetone. The flatter quadridentate ligand derived from *o*-phenylenediamine (salpd) behaves similarly to salen. Obviously from these preliminary observations, it appears that not only the electronic nature of the apical ligand or that of the in-plane quadridentate ligand, but also the flatness and probably the conformation of the whole molecule are important.

In the case of C-substituted diamines (Table 2) the complexes with less steric hindrance (*e.g.* [FeX{sal(+)-pn}] and [FeX{sal(+)chxn}]) behave as the salen derivatives. With the other diamines, the complexes crystallized from ethanol and are monomers when an optically active diamine is used but dimers with the *meso*-diamine. The explanation of this complicated behaviour is not very clear at the moment. If the quadridentate ligand remains nearly planar, as in Figure 2, we should expect that dimerisation of the optically active complexes would require an equatorial arrangement of both the substituents R and R′ of the chelate diamine ring, which is a rather unfavourable situation in the case of butane-2,3-diamine.[7] In the case of the *meso*-diamine compounds, one face of the iron complex may have a lower amount of steric interaction if the axial substituent points towards the apical X ligand (Figure 2), a situation which becomes more favourable if the chelated ligand is particularly distorted from planarity.[2,7] Only *X*-ray investigations, which we hope to undertake very soon, can settle these points.

The structures of both the mono- and the di-meric forms of [FeCl(salen)] have been resolved by *X*-ray crystallography.[9,11] For the dimer the bridges between the two iron atoms are the oxygen atoms of the Schiff base [Figure 3(*d*)]. It is likely that this is the case for all the complexes described in this paper, even when X = N_3 or NCS. In fact a bridging N_3 ligand should result in an increase of *ca.* 50 cm^{-1} in its stretching frequency,[12,13] as with the NCS ligand [13] (bridging N_3 and NCS groups occur at *ca.* 2 100 and 2 150 cm^{-1} respectively [13]). The values of the stretching frequencies of the N_3 and NCS groups in our complexes are summarized in Table 3; they are all in agreement with the presence of terminal groups, and the NCS ligand is bound through the nitrogen atom.[13] The values of $\nu(N_3)$ increase by *ca.* 20 cm^{-1} on going from di- to mono-meric structures, in agreement with a change in the co-ordination sphere from five- to a weak six-co-ordination.

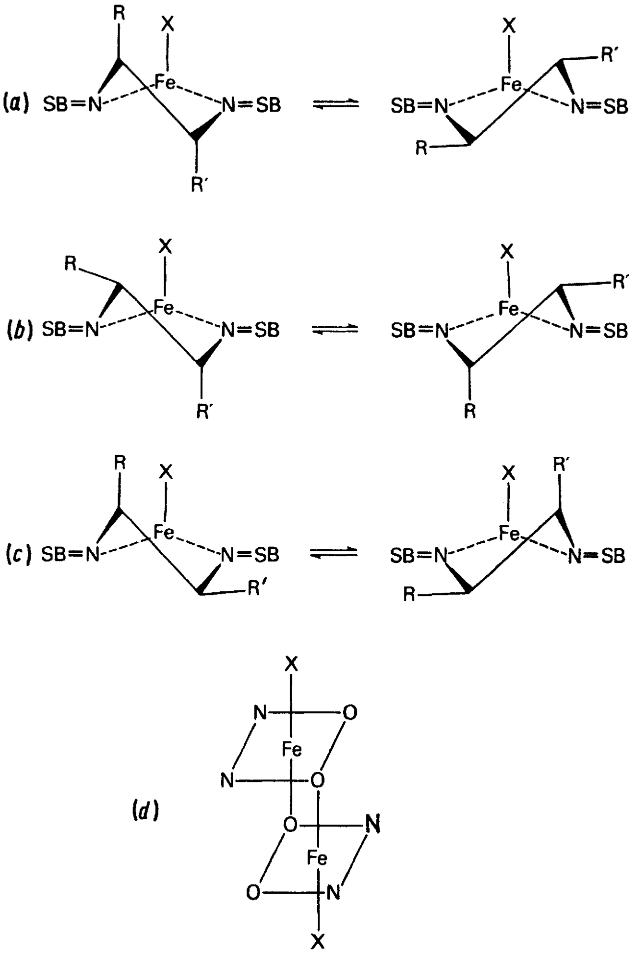

FIGURE 2 Schematic structures of the complexes derived from optically active diamines [(*a*)], *meso*-diamines [(*b*) and (*c*)], and of the dimers found in ref.11. SB = Schiff base

It is possible that the dimeric structures can be maintained in non-donor solvents. We determined by the Evans method [14] some magnetic moments of the complexes in solutions of $CHCl_3$–CH_2Cl_2 (1 : 1) (Table 4). All the complexes investigated, which are dimers in the solid state, showed a magnetic moment >6 B.M. over the range 313—173 K, indicative of the presence of monomeric species. In conclusion, dimer formation is essentially a solid-state phenomenon, controlled by both steric and electronic factors. By changing the nature of the apical ligand X we have also been able to characterize one type of monomeric low-spin complex: by reaction of [FeCl(saldiamine)] with Na[CN], six-co-ordinate complexes of the general formula Na[Fe(CN)$_2$(saldiamine)] (μ 2.21 B.M.) have been obtained.[15] These are the first cases of iron(III) low-spin complexes with this kind of ligand, although the well known [16] μ-oxo-dimers [{Fe(saldiamine)}$_2$O] are also low-spin (μ 1.87 B.M.), but this results from a strong antiferromagnetic interaction of the two $S = \frac{5}{2}$ high-spin iron centres.[16,17]

TABLE 3

Stretching frequencies of N_3 and NCS groups

Complex	$\tilde{\nu}$/cm^{-1}
[Fe(N_3)(salen)]	2 046 (d)
[Fe(N_3){sal(+)pn}]	2 045 (d)
[Fe(N_3){sal(+)bn}]	2 062 (m)
[Fe(N_3)(sal*meso*bn)]	2 045 (d)
[Fe(N_3){sal(+)chxn}]	2 045 (d)
[Fe(N_3)(sal*meso*chxn)]	2 050 (d)
[Fe(N_3){sal(−)dpen}]	2 072 (m)
[Fe(N_3)(sal*meso*dpen)]	2 050 (d)
[Fe(NCS)(salen)]	2 048 (d)
[Fe(NCS){sal(+)pn}]	2 040 (d)
[Fe(NCS){sal(+)bn}]	2 038 (m)

d = Dimer, m = monomer.

TABLE 4

Magnetic moments* in $CHCl_3$–CH_2Cl_2 (1 : 1)

	μ/B.M.	
Complex	313	173 K
[Fe(N_3){sal(+)pn}]	6.08	7.13
[FeCl(sal*meso*bn)]	6.12	7.47
[Fe(N_3)(sal*meso*bn)]	6.22	7.04
[Fe(N_3){sal(+)chxn}]	6.07	6.88

* Calculated by the Evans [14] method with 2% $SiMe_4$ as reference. The concentration of the complexes was 10—15 mg cm^{-3}. The values are uncorrected for the changes in solvent density, and are consequently higher than they should be.

In the case of the dicyanide derivatives, the ionic complexes are monomeric; [15] consequently they are true low-spin six-co-ordinate iron(III) complexes both in solution and in the solid state. The tendency to form six-co-ordinate species is not limited to cyanide; in donor solvents, the electronic spectra of the five-co-ordinate complexes [FeX(saldiamine)] changed with respect to the spectra in non-donor solvents (Figures 3 and 4), in agreement with the formation of six-co-ordinate adducts in these basic solvents. The stability of the six-co-ordinate adducts is obviously dependent on the strength of the

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[12] W. Beck, P. Kreutzer, and K. Werner, *Berichte*, 1971, **104**, 528.

[13] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley–Interscience, New York, 1971.

[14] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

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[16] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (*A*), 1967, 1014.

[17] W. M. Reiff, W. A. Baker, jun., and N. E. Erickson, *J. Amer. Chem. Soc.*, 1968, **90**, 4794; H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *ibid.*, 1972, **94**, 2683.

base, being lower in methanol than in pyridine (Figure 3). One complex, when crystallized from pyridine, analyzed as [FeCl(salen)]·2py where presumably one molecule of pyridine is co-ordinated to the metal atom and the other is clathrated. The formation of six-co-ordinate complexes has already been reported in the case of the μ-oxo-derivative [{Fe(salen)}$_2$O]·2py.[18] It is also likely that the tendency to form six-co-ordinate complexes increases with the π-acceptor properties of the apical ligands. This trend is also found in the solid state where the N_3 derivatives form dimers more easily than the Cl derivatives; the formation of dimers in the solid state must be regarded as six-co-ordination of the iron atom[11] (Figure 2). In agreement with this point, when the apical ligand is CN the only stable structure is six-co-ordinate; in this case, even a relatively weak base such as a second [CN]$^-$ group can co-ordinate yielding a *trans*-dicyano-complex.[15] The resulting anionic complex, however, is stable only in the presence of an excess of cyanide ion; in its absence, and in the presence of water, a fast hydrolysis takes place and the μ-oxo-dimer is quickly obtained. This is an equilibrium situation because the μ-oxo-dimer reforms in the presence of excess of cyanide, the six-co-ordinate dicyano-anion.[15] The hydrolysis reaction is a more useful route to the μ-oxo-derivatives, since we have observed that the traditional method [16] of hydrolysis of [FeCl(saldiamine)] species with alcoholic K[OH] often leads to extensive decomposition of the Schiff-base ligand.

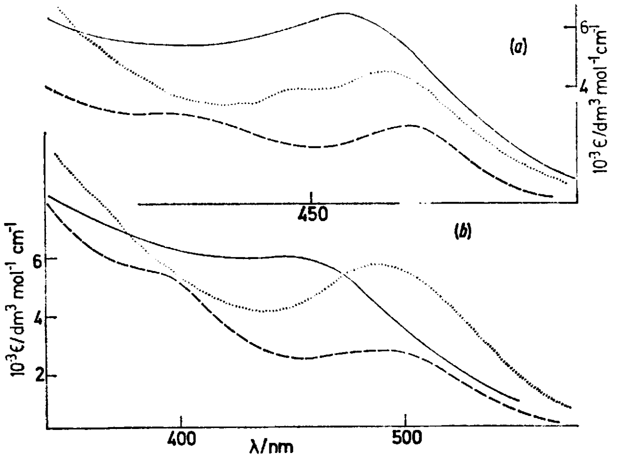

FIGURE 3 Electronic spectra of (*a*) [FeCl{sal(+)pn}] and (*b*) [Fe(N_3){sal(+)pn}] in chloroform (——), methanol (– – – –), and pyridine (· · · ·)

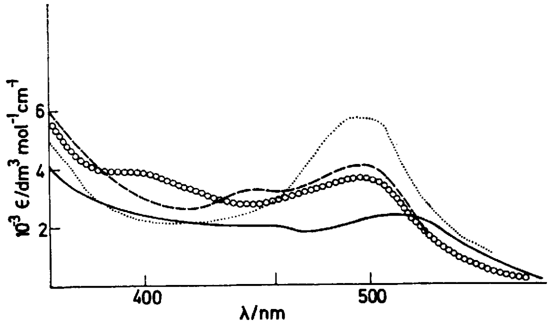

FIGURE 4 Electronic spectra of [FeI(salen)] (——), [Fe(NCS)(salen)] (○), [FeCl(salen)] (– – – –), and [Fe(N_3)(salen)] (· · · ·) in pyridine solution

The five-co-ordinate species [FeX(saldiamine)] dissolve easily in boiling water, producing 1 : 1 electrolytes (see Experimental section), which can sometimes be isolated as fluoroborates, *e.g.* [Fe(salen)][BF_4]·H_2O. Interestingly, pyridine solutions of the same complexes do not show evidence of electrolytic dissociation of the apical ligand X. In the case of aqueous solutions, electronic and circular-dichroism (c.d.) spectra (Figure 5) suggest the existence of a five-co-ordinate cation of the type [Fe(salen)(OH_2)]$^+$. The electronic spectrum in water is more similar to that in chloroform (one band at *ca.* 500 nm) than to that in pyridine (where a second band at 425 nm is present). The c.d. evidence will be discussed later.

In order to obtain a better insight into the ligand conformation, which should play an important role in the definition of the solid-state structure (*e.g.* stabilization of dimers *versus* monomers), we also investigated the conformational behaviour of these complexes in different solvents (*e.g.* donors and non-donors). In Figures 6 and 7 are shown the c.d. spectra in chloroform and pyridine of the derivatives of the optically active diamines having the same absolute configuration. In chloroform the main feature is the almost mirror image of the spectra of the

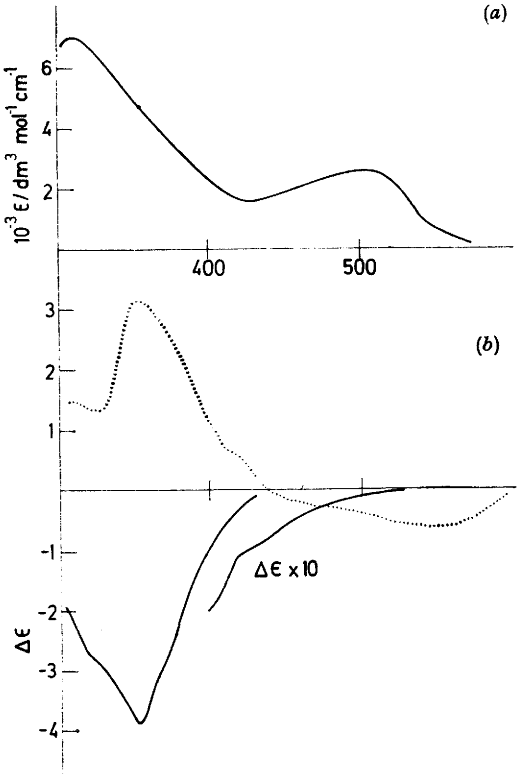

FIGURE 5 Electronic spectrum of an aqueous solution of [FeCl(salen)] (*a*) and c.d. spectra (*b*) of [FeCl{sal(+)pn}] (——) and [FeCl{sal(+)chxn}] (· · · ·) in water

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[18] M. Gerloch, E. D. McKenzie, and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1969, 2850.

sal(+)pn and sal(+)bn derivatives with respect to those of the sal(+)chxn and sal(−)dpen derivatives. In pyridine solution this is no longer true and only the sal(+)bn derivative displayed a spectrum which is opposite to those of sal(+)chxn and sal(−)dpen complexes. It is known that these spectra reflect the different conformations of the five-membered chelate ring C–N–M–N–C.[7] In the case of cyclohexane-1,2-diamine the cyclohexane moiety must always be arranged in such a way as to be *trans*-diequatorial with respect to the five-membered chelate ring C–N–M–N–C because of the requirements of the two fused rings.[7,19]

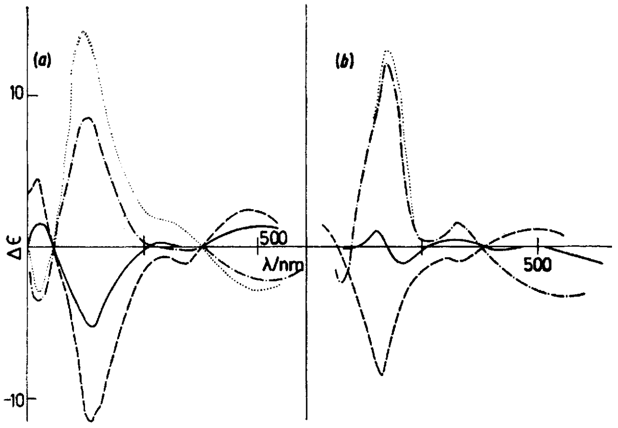
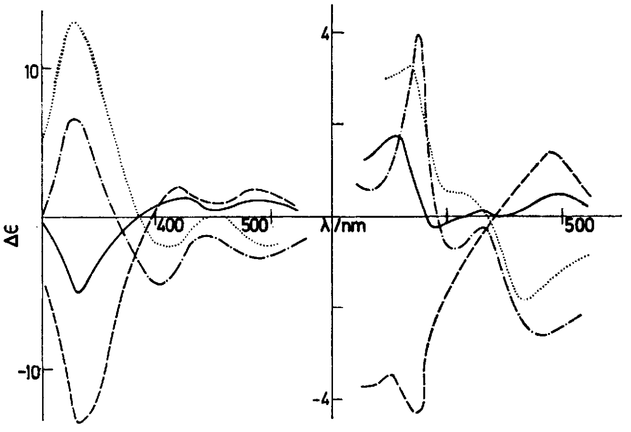


FIGURE 6 Circular-dichroism spectra of [FeCl(saldiamine)] in chloroform (*a*) and pyridine (*b*). The diamines are (+)pn (——), (+)bn (– – –), (+) chxn (· · · ·), and (−)dpen (— · — · —)



(*a*) (*b*)

FIGURE 7 Circular-dichroism spectra of $[Fe(N_3)(saldiamine)]$ in chloroform (*a*) and pyridine (*b*). The diamines are (+)pn (——), (+)bn (– – – –), (+)chxn (· · · ·), and (−)dpen (— · — · —)

By simple inspection of the c.d. spectra in Figures 6 and 7 one can infer that, in chloroform solution, the conformation of the chelate ring in the case of [FeX{sal(+)pn}] and [FeX{sal(+)bn}] must be opposite to that in the case of [FeX{sal(+)chxn}] and [FeX{sal(−)dpen}]. In pyridine all the complexes tend to have the same conformation with the exception of the sal(+)bn derivative. The behaviour, in chloroform solution, seems to be quite typical of five-co-ordinate derivatives and that in pyridine solution of six-co-ordinate derivatives, on the basis of a more general analysis.[7]

In accordance with this approach, the species which are present in an aqueous solution of [FeX(saldiamine)] are likely to be five-co-ordinate since the spectra of the sal(+)pn and sal(+)chxn derivatives show an opposite pattern. However, four-co-ordinate Schiff-base complexes also show an opposite pattern to the sal(+)pn and sal(+)chxn derivatives; for a definite assignment of the co-ordination number the spectrum of the sal(−)dpen derivative is also required,[7] but unfortunately this complex was practically insoluble in water.

Although the conformations of these complexes will be discussed in detail in the following paper,[7] it is interesting to point out here that, since these kinds of conformational arguments can be used to deduce the co-ordination number, it also appears (Figures 6 and 7) that the tendency to form six-co-ordinate complexes is greater in the case of the azide than in that of the chloride ligand. For instance the spectrum of [FeCl{sal(+)pn}] in pyridine is complicated, suggestive of an equilibrium between five- and six-co-ordinate species; on the other hand the spectrum of $[Fe(N_3)\{sal(+)pn\}]$ in pyridine is similar to that of the sal(+)chxn complex, in agreement with a larger amount of the six-co-ordinate species.

Conclusions.—The results have shown that there is a very delicate balance of electronic and conformational aspects in the stabilization of mono- and di-meric structures in crystals of complexes of the type [FeX(saldiamine)]. It seems that soft X groups (N_3 or NCS) stabilize the dimeric structure in which the iron atom is formally six-co-ordinate. This has been confirmed by the c.d. spectra in pyridine, which show that there is a higher tendency to form six-co-ordinate adducts when X = N_3 than Cl.

Conformational aspects are very important because the complexes derived from *meso*-diamines form dimeric structures more easily than those derived from the corresponding optically active diamines. It is rather difficult at the moment to rationalize such an effect in the absence of a complete *X*-ray investigation; however, it appears that when the ligand is very flat or very flexible the dimeric structure is favoured.

We have also observed that by introducing different X groups or by changing the electronic and conformational properties of the Schiff base the iron(III) always remains in a high-spin ground state over a large range of temperature; we have not detected the presence of any low-lying low-spin excited state. However, when X = CN the ground state becomes low spin over a wide range of temperature, and the tendency to form six-co-ordinate complexes increases.[15]

This latter point is an interesting observation. It is known that in iron(III) heme compounds the stabilization of the low-spin electronic configuration increases with increasing π-acceptor properties of the axial anionic

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[19] R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, 1968, **90**, 5344.

TABLE 5

Elemental analyses (%)

Complex	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
[FeCl(salen)]	53.6	4.1	7.9	53.7	4.0	7.8
[FeCl(salen)]·0.5MeNO$_2$	51.1	3.9	9.1	51.2	4.0	9.1
[{Fe(salen)}$_2$O]	58.1	4.1	8.1	58.2	4.3	8.5
[Fe(N$_3$)(salen)]	52.4	3.6	19.0	53.0	4.0	19.3
[Fe(NCS)(salen)]	53.9	3.7	11.0	53.7	3.7	11.1
[FeI(salen)]	43.1	3.3	6.6	42.7	3.1	6.2
[FeCl(salen)]·2py	60.5	4.6	10.7	60.6	4.7	10.9
[FeCl(5Cl-salen)]	45.1	2.7	6.5	45.0	2.8	6.6
[FeCl(5NO$_2$-salen)]	43.0	2.8	12.6	42.9	2.7	12.5
[FeCl(3OMe-salen)]·H$_2$O	49.2	4.6	6.7	49.6	4.6	6.4
[FeCl(5OMe-salen)]	51.4	4.5	6.9	51.8	4.3	6.7
[FeCl(salpd)]	58.8	3.3	6.7	59.2	3.5	6.9
[Fe(N$_3$)(salpd)]	58.5	3.3	16.9	58.3	3.4	17.0
[FeCl(pbden)]	59.9	5.4	6.8	60.6	5.0	6.4
[FeCl{sal(+)pn}]	55.5	4.1	7.5	55.0	4.3	7.5
[Fe(N$_3$){sal(+)pn}]	53.7	4.0	18.6	54.0	4.2	18.6
[Fe(NCS){sal(+)pn}]	54.0	3.9	10.1	54.7	4.1	10.7
[FeCl{sal(+)bn}]	55.8	4.4	7.0	56.1	4.7	7.3
[Fe(N$_3$){sal(+)bn}]	55.8	4.7	16.7	55.1	4.6	17.8
[Fe(NCS){sal(+)bn}]	55.2	4.4	10.1	55.9	4.4	10.3
[FeCl(sal*meso*bn)]	56.2	4.6	7.3	56.1	4.7	7.3
[Fe(N$_3$)(sal*meso*bn)]	55.3	4.6	16.6	55.1	4.6	17.8
[FeCl{sal(+)chxn}]·0.5EtOH	58.2	5.2	6.5	58.0	5.3	6.5
[Fe(N$_3$){sal(+)chxn}]	57.2	4.9	17.0	57.4	4.8	16.7
[FeCl(sal*meso*chxn)]	57.9	4.7	7.0	58.3	4.9	6.8
[Fe(N$_3$)(sal*meso*chxn)]	57.5	4.5	16.9	57.4	4.8	16.7
[FeCl{sal(+)pen}]	61.0	3.9	6.4	61.0	4.1	6.5
[Fe(N$_3$){sal(+)pen}]	59.8	4.0	16.0	60.0	4.1	15.9
[FeCl{sal(−)dpen}]	64.9	4.4	5.3	65.9	4.3	5.5
[Fe(N$_3$){sal(−)dpen}]	64.6	4.1	13.7	65.1	4.3	13.6
[FeCl(sal*meso*dpen)]	66.2	4.1	5.5	65.9	4.3	5.5
[Fe(N$_3$)(sal*meso*dpen)]	64.8	4.2	13.5	65.1	4.3	13.6
Na[Fe(CN)$_2$(salen)]·NaCl	47.4	3.0	12.3	47.5	3.1	12.3
[AsPh$_4$][Fe(CN)$_2$(salen)]·NaCl	62.5	4.6	7.0	61.8	4.2	6.9
Na[Fe(CN)$_2${sal(+)pn}]·1.5NaCl	45.2	3.2	11.0	45.7	3.2	11.2
[AsPh$_4$][Fe(CN)$_2${sal(+)pn}]·NaCl	62.3	4.6	6.3	62.2	4.3	6.7
Na[Fe(CN)$_2${sal(+)bn}]	50.1	4.4	13.5	50.8	4.2	13.8
Na[Fe(CN)$_2$(sal*meso*bn)]	51.2	4.1	13.5	50.8	4.2	13.8
[AsPh$_4$][Fe(CN)$_2$(sal*meso*bn)]·NaCl	62.2	4.8	6.6	62.6	4.5	6.6
Na[Fe(CN)$_2${sal(+)chxn}]	58.4	4.6	12.2	58.5	4.4	12.4
Na[Fe(CN)$_2${sal(−)dpen}]·2NaCl	52.8	3.6	7.5	51.3	3.4	8.0
[Fe(salen)][BF$_4$]·H$_2$O	45.4	4.0	6.8	45.0	3.7	6.6

Unless stated otherwise, the complexes did not contain molecules of crystallization.

TABLE 6

Variation with absolute temperature of atomic susceptibilities (χ/c.g.s. units) and magnetic moments (μ/B.M.)

[Fe(N$_3$)(salen)]								
T/K	293	277	238	200	174	143	110	86
$10^6\chi$	12.163	12.571	14.167	15.784	17.044	18.804	20.607	21.548
μ	5.36	5.30	5.21	5.05	4.90	4.66	4.26	3.86
[Fe(NCS)(salen)]								
T/K	293	270	247	211	180	143	110	85
$10^6\chi$	11.959	12.787	13.631	15.231	16.645	18.807	20.503	21.404
μ	5.31	5.28	5.21	5.08	4.92	4.66	4.26	3.83
[Fe(N$_3$)(salpd)]								
T/K	291	252	218	192	160	134	110	84
$10^6\chi$	13.044	14.656	16.245	17.685	19.723	21.546	23.101	24.677
μ	5.53	5.45	5.34	5.23	5.04	4.82	4.52	4.09
[FeCl(pbden)]								
T/K	291	259	220	193	166	130	111	
$10^6\chi$	14.130	15.967	18.919	21.571	25.255	32.431	37.907	
μ	5.76	5.77	5.79	5.79	5.81	5.83	5.82	
[FeCl(sal*meso*bn)]								
T/K	290	254	221	192	160	132	110	84
$10^6\chi$	11.112	12.357	13.664	14.862	16.525	18.017	19.174	20.270
μ	5.10	5.03	4.93	4.80	4.62	4.38	4.12	3.70
[Fe(N$_3$){sal(−)dpen}]								
T/K	293	265	217	195	158	131	100	86
$10^6\chi$	14.715	16.392	20.261	22.433	20.014	33.693	43.598	49.950
μ	5.90	5.92	5.94	5.94	5.97	5.96	5.93	5.88

ligand (*e.g.* CN $>$ N_3 $>$ Cl $>$ OH).[20] In our case we have a drastic change from high spin (as in the six-co-ordinate pyridine adducts of the azide complexes) to low spin (as in the six-co-ordinate dicyano-anions) without evidence in both cases, and over a wide range of temperatures, of a low spin–high spin equilibrium. The behaviour of iron in our complexes is therefore more similar to that of Fe^{III} in the met-form of the respiratory pigments than to that of Fe^{III} in the catalases [21] in which there is a continuous change from high to low spin on increasing the π-acceptor properties of the anionic axial ligand (*e.g.* when X = CN, at room temperature, there is still a mixture of low- and high-spin forms).

EXPERIMENTAL

Analyses were by the Microanalytical Laboratory of the University of Milan and are reported in Table 5. Infrared and electronic spectra were recorded on Perkin-Elmer models 137 and 621 and on a Beckman DK-2A spectrophotometer, respectively. Circular dichroism curves were obtained on a Roussel-Jouan dichrograph. Magnetic moments were measured by both the Gouy and the Faraday methods (Table 6). Conductivity measurements were made on a Philips PR 9500 conductimeter at room temperature. Magnetic moments in solution (Table 4) were measured by the Evans method [14] with a Varian 60 spectrometer on solutions (10—15 mg cm^{-3}) of the complexes in $CHCl_3$–CH_2Cl_2 (1 : 1) and are uncorrected for the variation of the density of the solvent with temperature; consequently the moments appear higher than they should be.[14]

The Schiff-base ligands were obtained as described earlier.[8]

Preparation of Complexes.—[FeCl(saldiamine)]. These complexes were prepared, following Gerloch *et al.*,[6] by treating in ethanol and at room temperature the appropriate Schiff base with an equimolar amount of $FeCl_3$. The brown complexes were filtered off after 1 h, washed with ethanol–water, and dried *in vacuo*.

[FeX(saldiamine)] (X = I, N_3, *or* NCS). These complexes were obtained by stirring in ethanol [FeCl(saldiamine)] with a slight excess of NaX. Brown-black precipitates were obtained after 2—6 h. All the complexes could be crystallized from ethanol, acetone, acetonitrile, or chloroform.

$Na[Fe(CN)_2(saldiamine)]\cdot nNaCl$ (n = 0—2). These species were obtained as green powders by reaction of [FeCl(saldiamine)] with an excess of Na[CN] in aqueous ethanol (2—3% water).[15]

$[AsPh_4][Fe(CN)_2(saldiamine)]$. These species were obtained as solids on treating a saturated aqueous solution of $[AsPh_4]Br$ with the dicyano-derivatives.

$[\{Fe(saldiamine)\}_2O]$. Three different methods can be employed: (*i*) reaction of $Fe[OH]_3$ with the appropriate Schiff base;[16] (*ii*) hydrolysis of the [FeX(saldiamine)] with alcoholic K[OH];[16] (*iii*) hydrolysis of $Na[Fe(CN)_2(saldiamine)]$.[15] When the cyanide derivatives were dissolved in water, the solutions slowly changed from green to brown and the μ-oxo-derivatives precipitated. This reaction is reversible and the green dicyano-complexes could be obtained by treating slurries of $[\{Fe(saldiamine)\}_2O]$ in water with an excess of Na[CN].

$[Fe(saldiamine)][BF_4]\cdot H_2O$. When a suspension of [FeCl(saldiamine)] in water was warmed, the complex slowly dissolved giving a red-purple solution. Each subsequent operation must be made rapidly because a red precipitate (shown to be $[\{Fe(saldiamine)\}_2O]$ by i.r. spectroscopy) separated after *ca.* 1 h. Spectroscopic data for these solutions are given in Figure 5. The molar conductivity of an aqueous solution of the salen derivative was Λ = 190 S cm^2 mol^{-1}. When these aqueous solutions were treated, in the cold, with $Ag[BF_4]$ and then concentrated, after the removal of AgCl, brown crystalline products were obtained, which analysed as $[Fe(saldiamine)][BF_4]\cdot H_2O$ and which showed intense and broad bands at 1 080 cm^{-1} in the i.r. spectrum.

[FeCl(salen)]·2py. This complex was obtained by slow evaporation under dry nitrogen (20 d) at room temperature of a concentrated solution in pyridine. When moisture was not carefully avoided, $[\{Fe(salen\}_2O]$ was obtained.

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