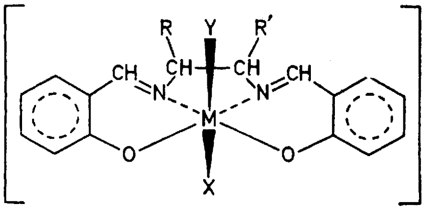
Optically Active Complexes of Schiff Bases. Part 4.[1] An Analysis of the Circular-dichroism Spectra of some Complexes of Different Co-ordination Numbers with Quadridentate Schiff Bases of Optically Active Diamines

By **Alessandro Pasini, Michele Gullotti,** and **Renato Ugo,*** Istituto di Chimica Generale, Via Venezian 21, 20133 Milano, Italy

The circular dichroism (c.d.) spectra of some transition-metal complexes of quadridentate Schiff bases derived from the condensation of 2 mol of salicylaldehyde with optically active (+)-(*S*)-propylene-1,2-diamine, (+)-(*SS*)-butane-2,3-diamine, *trans*-(+)-(*SS*)-cyclohexane-1,2-diamine, (+)-(*S*)-1-phenylethylenediamine, and (−)-(*SS*)-1,2-diphenylethylenediamine are reported. The conformational behaviour of the diamine chelate ring is discussed in relation to the co-ordination number of the metal ion ($M = V^{IV}$, Fe^{III}, Co^{II}, Co^{III}, Ni^{II}, or Cu^{II}). The assignment of the *SS* absolute configuration to (−)-1,2-diphenylethylenediamine has been confirmed. The anomalies in the c.d. spectra of metal complexes of Schiff bases containing this diamine are discussed.

METAL complexes of quadridentate Schiff bases derived from the condensation of 2 mol of salicylaldehyde with 1 mol of ethylenediamine (H_2salen) have been widely examined and studied even as possible models of biological significance.[1-3] In our and other laboratories ethylenediamines differently substituted at the carbon atoms (H_2saldiamine) have been synthesized and resolved and the conformational aspects of their Schiff-base complexes have been discussed in few cases.[4-12] The origin of some steric effects, observed in the reversible addition of oxygen to cobalt(II) Schiff-base complexes [13,14] or in the polarographic reduction and oxidation of the same cobalt(II) and the related iron(III) complexes,[15] can be attributed to the conformational properties of these complexes. Interestingly, even the stereoselective opening of the ring of propylene oxide in the presence of similar optically active Schiff-base complexes [16] of Co^{I} may have the same origin.

However, the conformational trends in the class of ligands studied in this paper have never been discussed in a general way. This work analyses the conformational behaviour of these Schiff bases in a number of metal complexes with different metal ions having different geometries and co-ordination numbers, and takes into account the effects of the co-ordination number, the co-ordination geometry, and the nature of the substituents of the diamine. The complexes described are summarized below, together with the abbreviations used throughout the paper. Some of the complexes have already been reported;[4-12] our circular-dichroism (c.d.) spectra agree with those reported or were their mirror images when a different enantiomer of the diamine was used. The absolute configuration of the diamines used in this work is *S* or *SS*. The absolute configuration of (—)-1,2-diphenylethylenediamine has been discussed,[17,18] and the original [19] assignment *SS* has been unambiguously confirmed [20] *via* a chemical correlation.



[ML(X)Y] $M = V^{IV}$, Fe^{III}, Co^{II}, Co^{III}, Ni^{II}, or Cu^{II}; X = O (for V^{IV}), Cl or N_3 (for Fe^{III}), pyridine(py) (for Co^{II}), I (for Co^{III}), or O_2 (for Co^{III}); Y = py (for Co^{III}, Fe^{III}, and Cu^{II})

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

Also L = 1,2-cyclohexylenebis(salicylideneiminate) (salchxn).

RESULTS AND DISCUSSION

The Free Schiff Bases.—The electronic and c.d. spectra of the free Schiff bases used in this work (H_2saldiamine) are presented in Figure 1. Some of the spectra have already been reported [4,9] and discussed.[4,21] The spectra consist mainly of a broad band centred at *ca.* 325 nm (with the same trend in the c.d. sign) probably due to the $\pi \rightarrow \pi^*$ transition, localized mainly on the azomethine chromophore,[4] and a positive–negative couplet centred at

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[1] Part 3, M. Gullotti, L. Casella, A. Pasini, and R. Ugo, preceding paper.

[2] F. Basolo, B. M. Hoffman, and J. A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

[3] D. G. Brown, *Progr. Inorg. Chem.*, 1973, **18**, 177.

[4] B. Bosnich, *J. Amer. Chem. Soc.*, 1968, **90**, 627.

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

[6] R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, 1969, **91**, 5977.

[7] R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, 1970, **92**, 5861.

[8] R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, 1970, **11**, 2562.

[9] M. Gullotti, A. Pasini, P. Fantucci, R. Ugo, and R. D. Gillard, *Gazzetta*, 1972, **102**, 855.

[10] A. Pasini, M. Gullotti, and E. Cesarotti, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3821.

[11] A. Pasini and M. Gullotti, *J. Co-ordination Chem.*, 1974, **3**, 319.

[12] M. Gullotti and A. Pasini, *Inorg. Chim. Acta*, 1975, **15**, 129.

[13] E. Cesarotti, M. Gullotti, A. Pasini, and R. Ugo, *J.C.S. Dalton*, 1977, in the press.

[14] C. Busetto, F. Cariti, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J.C.S. Dalton*, 1973, 754.

[15] G. Costa, personal communication.

[16] H. Aoi, M. Ishimori, S. Yoshikwa, and T. Tsuruta, *J. Organometallic Chem.*, 1975, **85**, 241.

[17] P. L. Fereday and S. F. Mason, *Chem. Comm.*, 1971, 1314; S. F. Mason and R. H. Seal, *J.C.S. Chem. Comm.*, 1973, 422.

[18] B. Bosnich and J. Mac B. Harrowfield, *J. Amer. Chem. Soc.*, 1972, **94**, 3425.

[19] R. D. Gillard, *Tetrahedron*, 1965, **21**, 503.

[20] R. Meric and J. P. Vigneron, *Tetrahedron Letters*, 1974, 2059, 2778.

[21] H. E. Smith, J. R. Neergaard, E. P. Burrows, and Fu-ming Chen, *J. Amer. Chem. Soc.*, 1974, **96**, 2908.

ca. 260 nm (with the positive band lying to lower energy) which could arise from exciton splitting of a transition involving mainly the π orbitals of the benzene rings of the salicylaldehyde groups.[21]

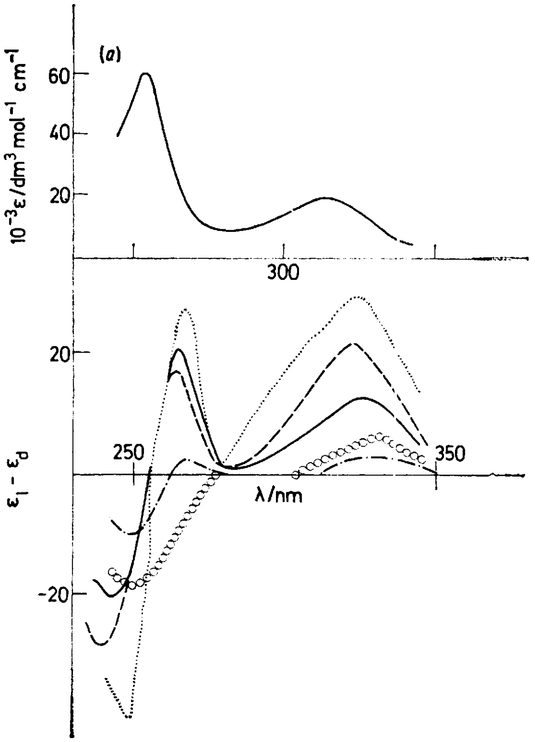

FIGURE 1 Electronic spectrum of (*a*) H_2sal(+)pn and c.d. spectra of (*S*)-H_2saldiamine: (——), H_2sal(+)pn; (— — —), H_2sal(+)bn; (· · · ·), H_2sal(+)chxn; (— · — · —), H_2sal(+)pen; (○), H_2sal(−)dpen

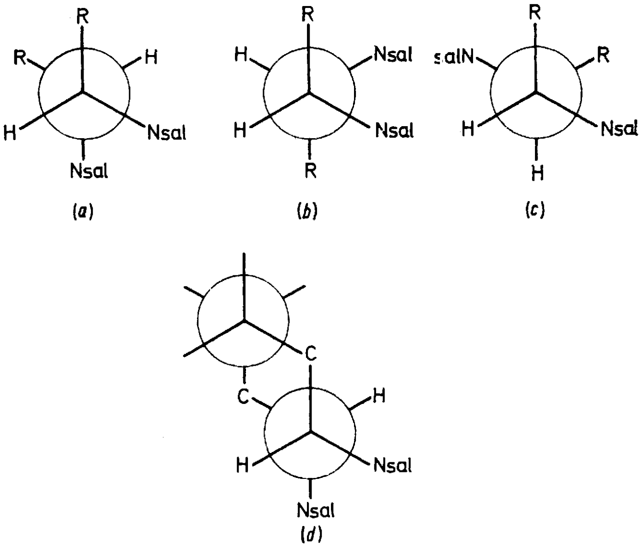

FIGURE 2 Conformations (*a*)—(*c*) of (*S*)-H_2saldiamine and the only possible conformation of (*SS*)-H_2salchxn (*d*)

The sign of the positive–negative couplet was the same throughout the series, with the exception of H_2(sal(−)-dpen where the 260 nm region is complicated by the absorption due to Cotton effects arising from coupling of the electronic transitions of the two phenyl rings of the diphenylethylenediamine moiety. The similarities of the spectra suggest the presence of the same predominant conformation in solution throughout the series. We have already discussed the molecular nature of these Schiff bases,[9] concluding that hydrogen bonding *does not* dictate the preferred conformation in solution. Of the three possible conformations in Figure 2, only (*a*) and (*b*) should give rise to strong optical activity since in (*c*) the two salicylaldehyde chromophores are *trans*-parallel in the first approximation, resulting in inactive coupling.

The strong Cotton effects do not arise solely from vicinal induction of the asymmetric carbon atoms of the diamines (which should give rise to small c.d.) but also from the intrinsic asymmetry of the conformers. Consequently, in (*a*) and (*b*), which are diastereoisomers, the two conformations dictate enantiomeric chiralities for the two azomethine chromophores, thus giving rise to Cotton effects which are nearly mirror images, as expected when the vicinal effect is irrelevant. Since the optical activity is high, we suggest that, in solution, one of the two conformations is much more stable than the other.

Since the patterns in the spectra of the sal(+)pn, sal(+)bn, sal(+)pen, and sal(−)dpen derivatives are the same as that of the sal(+)chxn derivative, which necessarily has conformation (*d*) [analogous to (*a*)] dictated by the rigidity of the ring, we conclude that (*a*) is always the most stable conformation in solution. It is also interesting to note that the size of the Cotton effect grows along the series sal(+)pn, sal(+)bn, sal(+)chxn, corresponding to increasing concentration of conformer (*a*) in solution. The low optical activity of the sal(+)pen and sal(−)dpen derivatives can be accounted for by: a larger amount of the conformers (*b*) or (*c*) in the equilibrium mixture in solution; or overlap of bands with different signs caused by effects of the new aromatic chromophores. It appears, as we shall see later, that the presence of phenyl groups easily alters the equilibrium composition of the conformers; however, only low-temperature experiments, which we hope to carry out in the future, can confirm this latter hypothesis.

Square-planar Complexes.—In this section the c.d. spectra of four-co-ordinate square-planar complexes of Cu^{II}, Co^{II}, and Ni^{II} in a non-donor solvent ($CHCl_3$) are described (Figures 3, 5, and 6, respectively). Some of these spectra have already been published.[4-8,14] In Figure 3 the spectra of the copper(II) derivatives are reported, together with a representative electronic spectrum. The main feature is that, on complex formation, the band at 325 nm of the free Schiff base is shifted to lower energy (350 nm), producing a splitting to give two components of different sign in the c.d. spectrum. As already pointed out by Bosnich,[4] in the case of [Zn{sal(−)pn}], such a splitting can be accounted for by assuming an exciton interaction of the $\pi\rightarrow\pi^*$ transitions of the two azomethine groups, which are now rigidly linked through the N–M–N bonds and constrained in a slightly tetrahedral arrangement (see Figure 4). In this way they form a dihedral angle which gives rise to non-zero components of the exciton interaction between the two $\pi\rightarrow\pi^*$ transitions of the azomethine. These transitions are, in the first approximation, polarized along the carbon–nitrogen bond or very near to its direction.[4] In other words, for an exciton interaction to occur, the molecular geometry of the complex must be such that the two azomethine groups do not lie on a plane, as in Figure 4(*a*), but produce a slight tetrahedral distortion as in Figure 4(*b*).

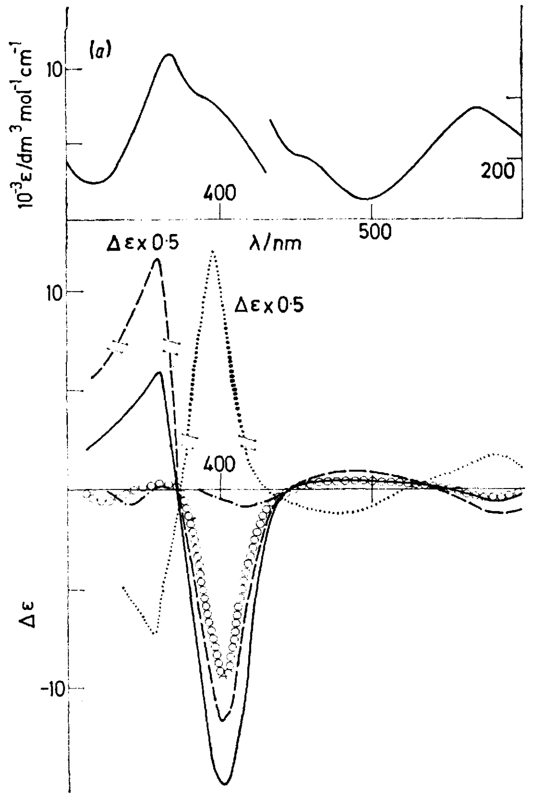

FIGURE 3 Electronic spectrum of (*a*) [Cu{sal(+)pn}] in chloroform solution and c.d. spectra of [Cu{(*S*)-saldiamine}]: (——), [Cu{sal(+)pn}]; (— — —), [Cu{sal(+)bn}]; (· · · ·), [Cu{sal(+)chxn}]; (— · — · —), [Cu{sal(+)pen}]; (O), [Cu{sal(−)dpen}]

In Figure 4(*c*), which is another representation of conformation 4(*b*), the substituents R of the ethylenediamine carbon atoms are clearly in axial positions with respect to the M–N–C–C–N ring in the half-chair conformation, as found by *X*-ray studies of copper(II) complexes and some related cobalt(II) complexes.[22,23] The origin of this arrangement lies in the steric repulsion between the substituents R and the hydrogen atoms of the azomethine as in Figure 4(*d*). In the case of the optically active *trans*-cyclohexanediamine, the only possible conformation is 4(*e*), which is another representation of conformation 4(*d*), because of the requirements of the two fused rings. The sign reversal[5,6] in the c.d. spectrum of [M{sal(+)chxn}] with respect to [M{sal(+)pn}] (Figure 3) is in agreement with this assumption.

The two conformations 4(*c*) and 4(*d*), which are enantiomeric, must be in equilibrium in solution (with the obvious exception of the chxn case). However, owing to the presence of the chiral carbon atoms in the bridge, the two conformations correspond to diastereoisomers; in the case of the cobalt complex of sal(+)bn, the energy difference between the isomers has been evaluated as *ca.* 5 kcal mol^{-1},[23] and consequently one of the isomers is predominant.* The intensities of the c.d. spectra in solution reflect this equilibrium, and are in agreement with the point that the chxn derivatives usually display the higher optical activity. According to I.U.P.A.C. nomenclature[24] the two conformations are Δλ [4(*b*) or 4(*c*)] and Λδ [4(*d*), 4(*e*), or 4(*f*)] where the lower-case symbols reflect the chirality (or conformation) of the ethylenediamine chelate ring and the upper-case symbols that of the tetrahedral distortion of the metal co-ordination (*i.e.* the configuration). In the case of four-coordinate pseudo-planar complexes of Cu^{II} we therefore have the following situations: (*i*) (*S*)Δλ for the sal(+)pn, sal(+)bn, sal(+)pen, and sal(−)dpen derivatives, which is essentially reflected by the negative–positive exciton couplet (with the negative component lying to lower

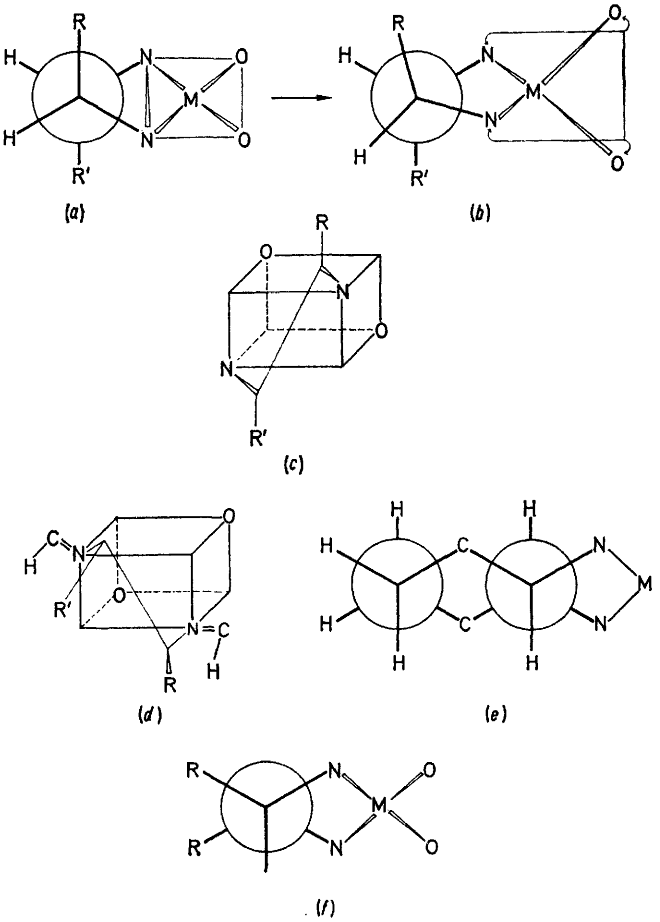

FIGURE 4 Tetrahedral distortion of the quadridentate ligand in complexes [M(saldiamine)] and the conformation of the diamine chelate ring: axial [(*a*)—(*c*)] and equatorial [(*d*)—(*f*)]

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* Throughout this paper: 1 cal = 4.184 J.

[22] F. J. Llewellyn and T. N. Waters, *J. Chem. Soc.*, 1960, 2639.

[23] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1973, 419.

[24] *Inorg. Chem.*, 1970, **9**, 1.

energy) in the 350 nm region; and (*ii*) (*S*)Λδ for the sal(+)chxn derivative with a concomitant inversion of the couplet, the negative component now lying to higher energy. Such behaviour is in agreement with the exciton-coupling theory.[4-8]

In Figure 5 the spectra of the analogous cobalt(II) complexes are reported. These spectra are usually more complicated than those of the corresponding complexes of Cu^{II}. An analysis was attempted in an earlier paper,[14] but for the purpose of the present paper it is sufficient to note that, although the 'exciton couplet' is complicated by the presence of a number of other bands, the conformation of the en chelate ring can still be inferred by careful inspection of the patterns in the c.d. spectra. Here again the sal(+)chxn derivative displays an almost mirror-image relation with the other complexes, and the same situation as in the copper complexes must be present, *i.e.* (*S*)Δλ for sal(+)pn, sal(+)pen, and sal(−)dpen and (*S*)Λδ for sal(+)chxn.

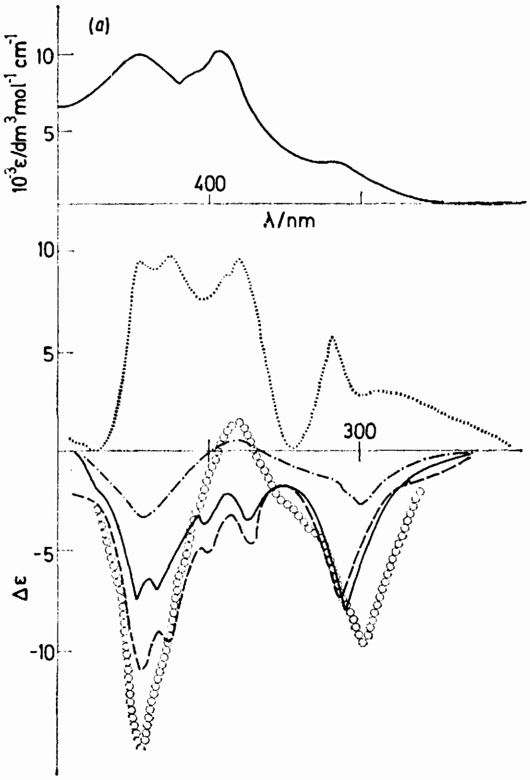

FIGURE 5 Electronic spectrum of (*a*) [Co{sal(+)pn}] and c.d. spectra of [Co{(*S*)-saldiamine}] in chloroform: (——), [Co{sal(+)pn}]; (— — —), [Co{sal(+)bn}]; (· · · ·), [Co{sal(+)chxn}]; (— · — · —), [Co{sal(+)pen}]; (O), [Co{sal(−)dpen}]

A few structures of cobalt(II) complexes have been resolved [23-25] and a comparison [25] has been made between some of them, namely [Co(salen)], [Co{sal(+)bn}], [Co(sal*meso*bn)], and [Co(sal*meso*chxn)]. While in [Co(salen)] the N–O–O–N geometry is almost planar (these four atoms being displaced from the best molecular plane by only 0.03 Å), in the other cases the tetrahedral distortion is quite high, the displacement of the four donor atoms from the plane reaching ±0.16 Å for [Co{sal(+)bn}]. {In [Co(sal*meso*bn)] the N–O–O–N chromophore is slightly more planar than in the corresponding optically active complex.} Two other interesting features of these structures [23-25] are of note. First the usual *X*-ray technique cannot discriminate between *R* and *S* configurations, but if one draws the structure starting from an (*SS*)-butanediamine and placing the substituents R in axial positions, as has been found, the configurations of the en chelate ring and of the N–O–O–N chromophore respectively are in agreement with the above discussion. Secondly, the azomethine groups are not collinear except in [Co(salen)]. This fact is rather important since Bosnich [4] used the structure of [Zn(salen)] (where the two azomethine groups are in the same plane [26]) for his calculations on [Zn{sal(−)pn}], being obliged to invoke mixing of the azomethine $\pi\rightarrow\pi^*$ transition with some transitions of the phenyl chromophore of the salicylaldehydes in order to explain the fact that the two transition vectors combine to give an exciton splitting. However, although some mixing of the excited states can occur, the resulting transition vectors do not combine in the free ligand (see previous section) for which we could not observe an exciton splitting. Therefore, the trends in the optical activity of the complexes in this region must

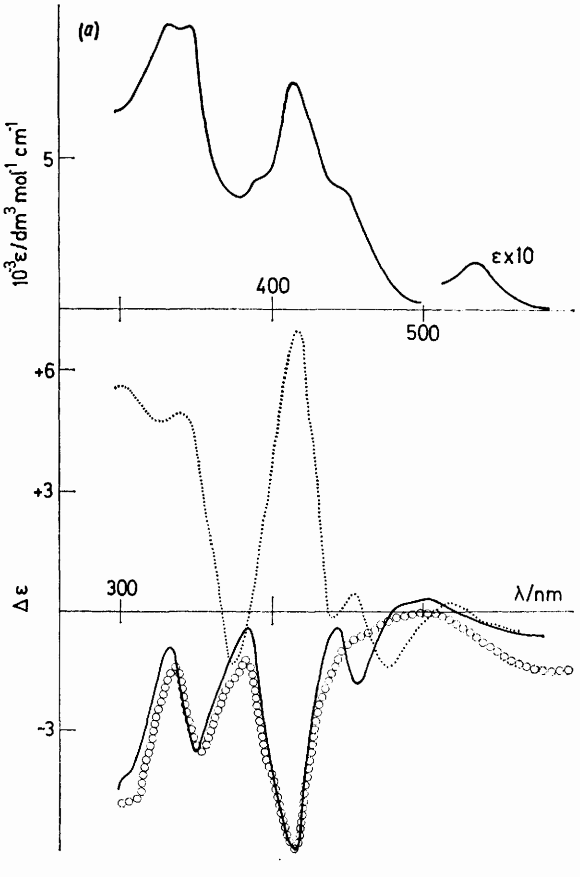

FIGURE 6 Electronic spectrum of (*a*) [Ni{sal(+)pn}] and c.d. spectra of [Ni{(*S*)-saldiamine}] in chloroform: (——), [Ni{sal(+)pn}]; (· · · ·), [Ni{sal(+)chxn}]; (—), [Ni{sal(−)dpen}]

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[25] N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 1606.

[26] D. Hall and F. H. Moore, *Proc. Chem. Soc.*, 1960, 256.

be the result of a tetrahedral distortion from the best molecular plane of the N–O–O–N chromophore.

The [Ni(saldiamine)] complexes (Figure 6) displayed the same pattern as the complexes of Cu^{II} and Co^{II} although, as already pointed out,[4,7] no exciton couplet was observed, either because one of its components is cancelled by the overlapping of some other bands or probably because the nickel(II) complexes are closer to planarity than the corresponding complexes of Co^{II} and Cu^{II}.[27] On comparison of the c.d. spectra of the series just described, a tentative correlation can be made between the signs of the Cotton effects of square-planar complexes and the absolute configurations of the diamines. Within this series, all the complexes derived from a diamine of the same absolute configuration show the same trend in the c.d. spectra, with the exception of cyclohexanediamine which displays opposite behaviour. The origin of this correlation resides only in conformational arguments.

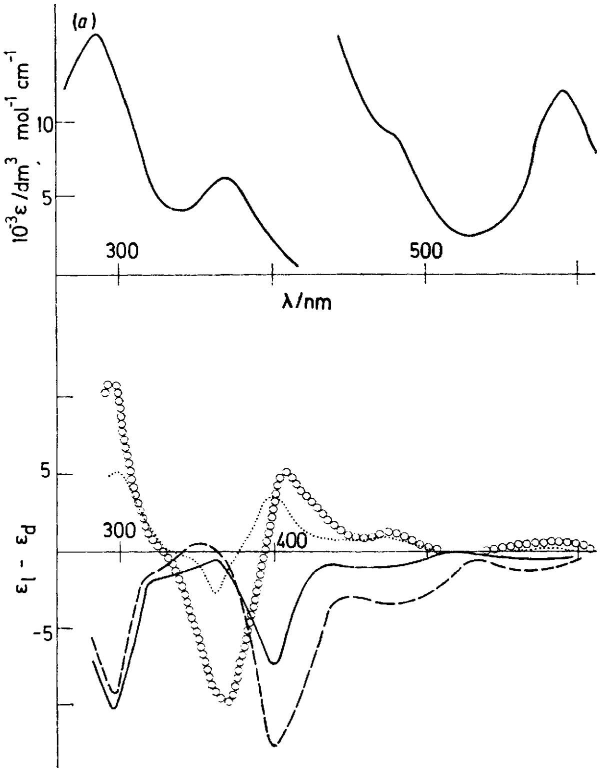

FIGURE 7 Electronic spectrum (*a*) of [VO{sal(+)pn}] and c.d. spectra of [VO{(*S*)-saldiamine}] in chloroform: (——), [VO{sal(+)pn}]; (— — —), [VO{sal(+)bn}]; (· · · ·), [VO{sal(+)-chxn}]; (○), [VO{sal(−)dpen}]

Five-co-ordinate Complexes.—In this section the c.d. spectra of the five-co-ordinate complexes of the types [VO(saldiamine)], [FeX(saldiamine)] (X = Cl or N_3), [CoI(saldiamine)], and [Co(py)(saldiamine)] are discussed. The c.d. spectra of [VO{(*S*)-saldiamine}], which have already been reported,[8-11] are shown in Figure 7. In general, the higher-energy components of the couplet of the $\pi \rightarrow \pi^*$ transition of the azomethines is nearly cancelled, presumably through overlap of other bands of different sign, but it is often sufficiently distinguishable to make a number of correlations.

The most important feature of these spectra is the inversion of sign in the case of the sal(−)dpen derivative. In fact, [VO{sal(−)dpen}] has a c.d. spectrum similar to that of [VO{sal(+)chxn}] and opposite to those of the sal(+)pn and sal(+)bn complexes. This fact has been explained [11] in that the steric interaction between X and R is very severe in the case of R = Ph (see Figure 8, X = O). This effect produces a change in conformation from 8(*b*) to 8(*c*) corresponding to a change from equatorial to axial phenyl groups. In order to check whether this inversion is really due to the presence of some new steric interaction or to a particular effect of the phenyl group on the whole conformation, we synthesized [VO{sal(+)pen}] (R = H, R′ = Ph) where less steric hindrance is expected, since in five-co-ordinate complexes the phenyl group (R′) is likely to be '*trans*' to X [Figure 8(*b*)]. The c.d. spectrum of this complex showed an extremely low optical activity, but of the same sign as [VO{sal(+)chxn}] and [VO{sal(−)dpen}], which seems to suggest that the equilibrium constant between the two conformations 8(*b*) and 8(*c*) is *ca.* 1, but with a very small dominance of 8(*c*). This peculiar behaviour of diamines with phenyl groups bound to the bridge is not restricted only to vanadyl complexes, and has been observed for practically all five-co-ordinate complexes in this paper.

In Figure 9 the spectra of the analogous $[FeX]^{2+}$ complexes (X = Cl or N_3) are reported. The sal(+)pen (R = H, R′ = Ph) derivative showed a reasonably high optical activity of the same sign as [FeCl{sal(+)chxn}] and [FeCl{sal(−)dpen}] and opposite to those of the corresponding sal(+)pn and sal(+)bn derivatives. The general trend in the spectra in Figure 9 is different from those of the corresponding $[VO]^{2+}$ derivatives; in particular it appears that in the sal(+)chxn case the bands in the region of the azomethine transitions are inverted with respect to the $[VO]^{2+}$ case. This, however, does not means a change in conformation because the chxn derivatives cannot change conformation, owing to the presence of two fused rings. It may be due to overlapping of other bands or to a change in the direction of polarization of the $\pi \rightarrow \pi^*$ transitions of the azomethine chromophore. Within the two series of complexes, the spectra, however, may be easily correlated.

The pattern in the spectra of the series [CoI(saldiamine)] (which are five-co-ordinate in $CHCl_3$ solution) (Figure 10) is not as clear, presumably because of large distortions due to the iodine atom or to some ionization of the iodine ligand, but in the spectra of pyridine solutions of [Co(saldiamine)], where the complexes are essentially five-co-ordinate,[13,14] the same trend is again observed (Figure 11). It appears that in the case of the five-co-ordinate complexes the diamines with phenyl groups in the ring invert their conformation with respect to that of the related square-planar complexes. The origin of this effect cannot be simply related to the steric repulsion produced by the ligand in the fifth position.

Unfortunately no crystal structures are available for five-co-ordinate complexes having R = Ph, and it is difficult to draw any conclusions as to the origin of the conformational behaviour of these complexes when five-co-ordinate. However, a few general points are worthy of discussion.

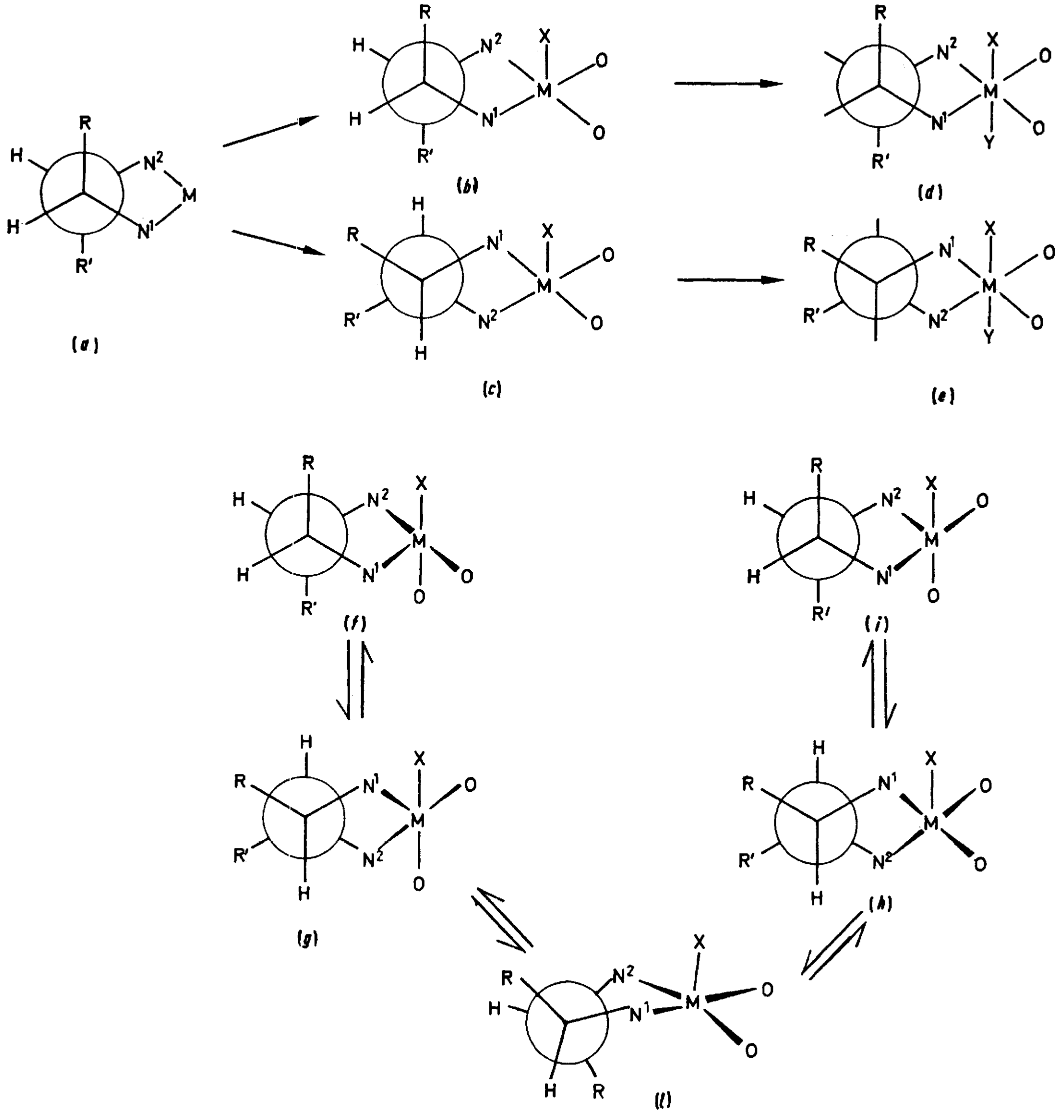

FIGURE 8 Axial [(*a*),(*b*), and (*d*)] and equatorial [(*c*) and (*e*)] conformations of the diamine chelate ring for various co-ordination numbers of the metal ion, and the axial [(*f*) and (*i*)]-equatorial [(*g*) and (*h*)] equilibrium in five-co-ordinate complexes together with the change from square-planar [(*h*) and (*l*)] to trigonal-bipyramidal [(*f*), (*g*), and (*i*)] geometry of [M(saldiamine)] complexes. In (*l*) the conformation of the diamine chelate ring is *cis*

Two structures of five-co-ordinate complexes of this type, namely [Co(py)(salen)] [28] and [Co(py){sal(+)bn}],[29] have been resolved. The former presents an ' inverted umbrella shape ' with the metal atom somewhat displaced from the plane of the chromophore towards the nitrogen atom of the pyridine and the two halves of the molecule folded to resemble an umbrella reversed by the wind. This structure seems quite common in five-co-ordinate [Co(salen)] complexes.[30,31] In crystals of [Co(py){sal(+)bn}] two crystallographically independent and non-equivalent molecules have been found in a 1 : 1 ratio; one molecule (A) has square-pyramidal geometry as in Figure 8(*b*) and 8(*c*) and the other (B) has nearly trigonal-bipyramidal geometry as in Figure 8(*f*)—8(*i*). Molecule (B) represents a larger distortion towards a reversed umbrella shape, associated with concomitant lengthening of the co-ordination bonds. However, the methyl groups of the butanediamine moiety (R and R' in Figure 8) are axial in both cases and

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[27] E. Larsen, *Proc. 11th Internat. Conf. Co-ordination Chem.*, Haifa, August, 1968, p. 193.

[28] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[29] N. Bresciani, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 498.

[30] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1974, 1903.

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

the en chelate ring has a half-chair conformation. In the case of [Co(py)(salen)] the en chelate ring no longer has a half-chair conformation, but has an envelope *cis* conformation.

It follows that in five-co-ordinate complexes we may easily induce not only inversions of the conformation of the chelated ring but also large deformations of the ligand from planarity; an increase in the co-ordination number usually brings about a deformation of the shape of the Schiff base from a pseudo-planar to a ' reversed-umbrella ' or ' stepped ' geometry.[31] The deformed geometry may have large effects on the conformation of the en chelate ring; for instance, in the reversed-umbrella geometry the en ring is no longer in a half-chair (*gauche*) conformation but in an ' envelope ' (*cis*) conformation [Figure 8(*l*)], the torsion angle in [Co(py)(salen)] being 0°.[28] This must be a limiting value due to the symmetry of the en moiety, and it will probably be highly altered by the introduction of an asymmetric carbon atom, as is clearly seen in the structure of molecule B of [Co(py)-{sal(+)bn}].

If we substitute methyl with phenyl groups we have a different situation; inspection of models (Figure 8) clearly shows that in the five-co-ordinate salpen derivatives (R = H, R′ = Ph) R′ interacts with one of the benzene groups of the aldehyde entity in 8(*i*), whereas in both 8(*f*) and 8(*g*) the molecule is unhindered. This effect stabilizes new conformers, because the conformation is no longer dictated only by the steric repulsion of the azomethine hydrogen and R or R′ groups [as for instance in the square-planar complexes in Figure 4(*b*)]. Now

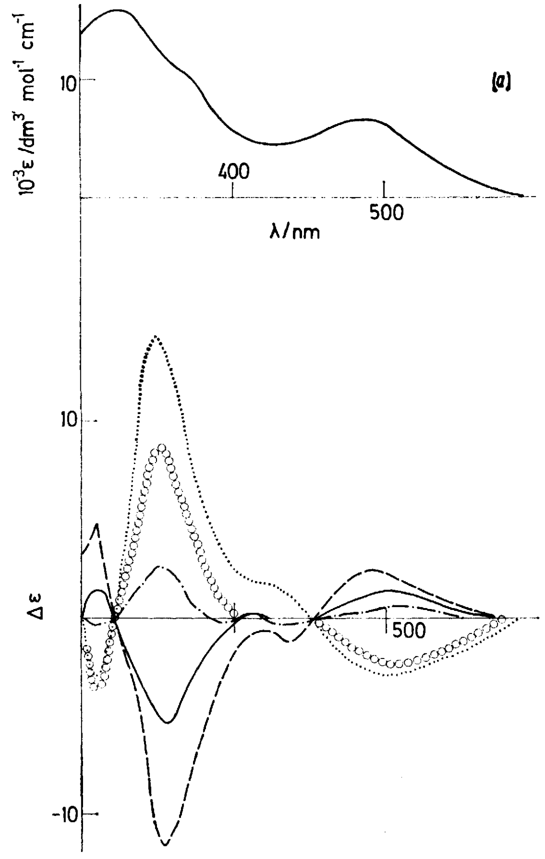

FIGURE 9(*a*).

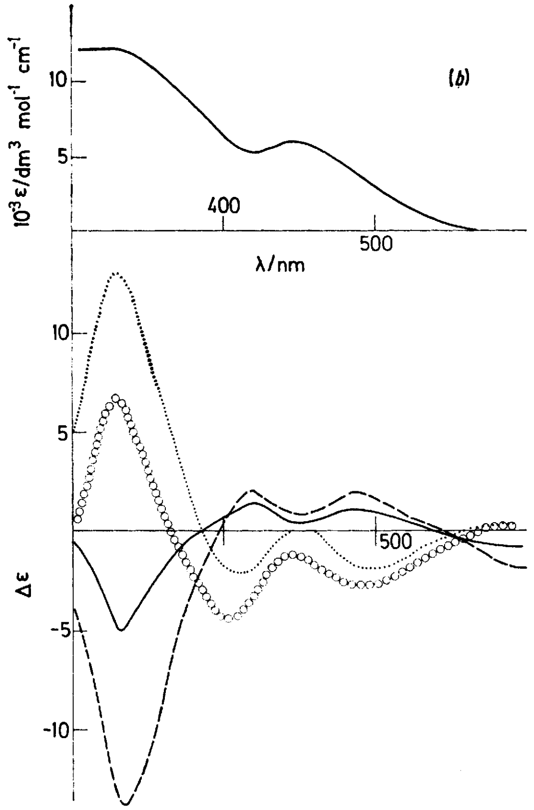

FIGURE 9 Electronic and c.d. spectra in chloroform solution of [FeCl{(*S*)-saldiamine}] (*a*) and of [Fe(N_3){(*S*)-saldiamine}] (*b*). The diamines are: (——), (+)pn; (— — —), (+)bn; (· · · ·), (+)chxn; (— · — · —), (+)pen; and (○), (−)dpen. The electronic spectra are those of the sal(+)pn derivatives

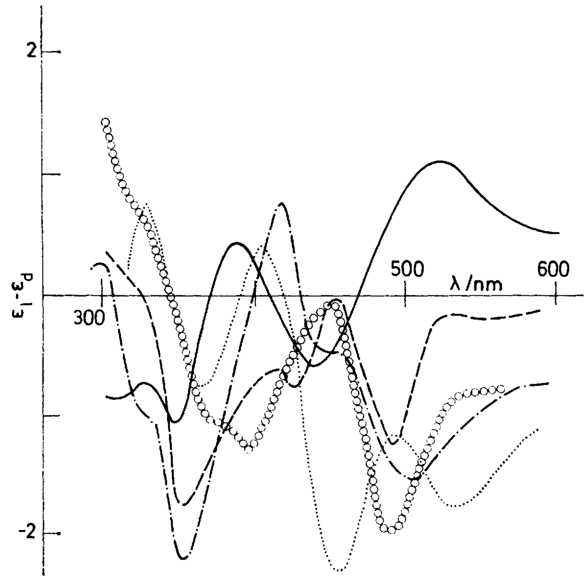

FIGURE 10 Circular-dichroism spectra of [CoI{(*S*)-saldiamine}] in chloroform solution: (——), [CoI{sal(+)pn}]; (— — —), [Co{sal(+)bn}I;]; (· · · ·), [CoI{sal(+)chxn}]; (— · — · —), [CoI{sal(+)pen}]; (○) [CoI{sal(−)dpen}]

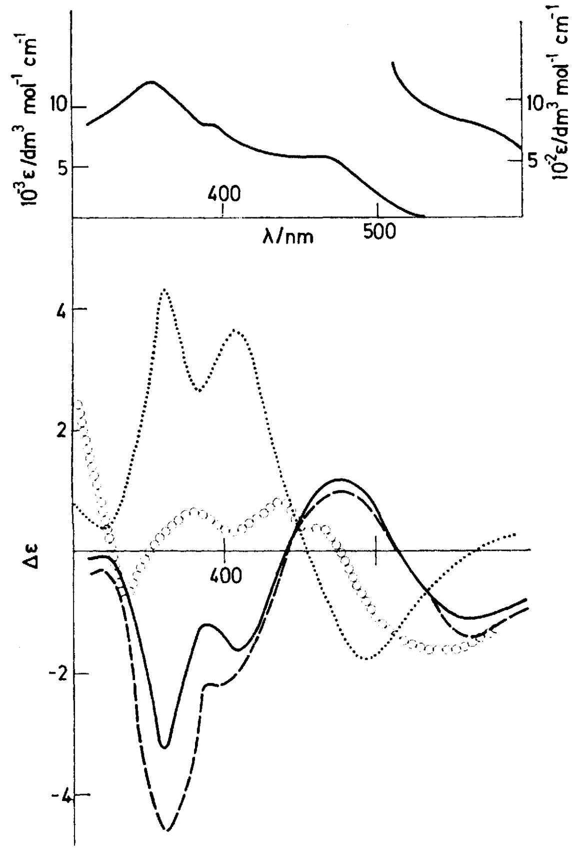

FIGURE 11 Electronic spectrum of [Co{sal(+)pn}] and c.d. spectra of [Co{(*S*)-saldiamine}] in pyridine solution: (——), [Co{sal(+)pn}]; (— — —), [Co{sal(+)bn}]; (· · · ·), [Co{sal(+)chxn}]; (O), [Co{sal(−)dpen}]

the van der Waals radius of a Me group is 2.0 Å compared with the half thickness of (1.70 Å) of a benzene ring.[32] This accounts for the fact that two phenyl groups can be accommodated in parallel equatorial positions, while this is very difficult in the case of Me groups which thus tend to stay away from each other and be *trans* diaxial.

Solvation also has an important role as can be inferred from Figure 12, where the c.d. spectra of [FeCl{sal(+)pen}] in a number of solvents are reported. Although the general pattern remains unchanged, large changes in intensity were observed. However, with the related iron complexes of other diamines such as sal(−)dpen and sal(+)chxn (Figure 2) the solvent effects were less pronounced suggesting that specific solvation must be present in the case of [FeCl{sal(+)pen}].

Six-co-ordinate Complexes.—In Figures 13 and 14 the electronic and c.d. spectra of pyridine solutions of [CoI(saldiamine)] and [FeX(saldiamine)] (X = Cl or N_3) are reported, together with the spectra of pyridine solutions of [Co(saldiamine)] saturated with oxygen. In each case, the complex is believed to be six-co-ordinate, with possibly a few exceptions; for instance, in the case of oxygenated pyridine solutions of [Co(saldiamine)] the fifth and sixth co-ordination positions are occupied by one molecule of pyridine and one of dioxygen respectively.[1,14] In the case of [CoI(saldiamine)] species, direct evidence for six-co-ordinate complexes has never been reported, but it is very probable that such species are formed in pure pyridine solution.

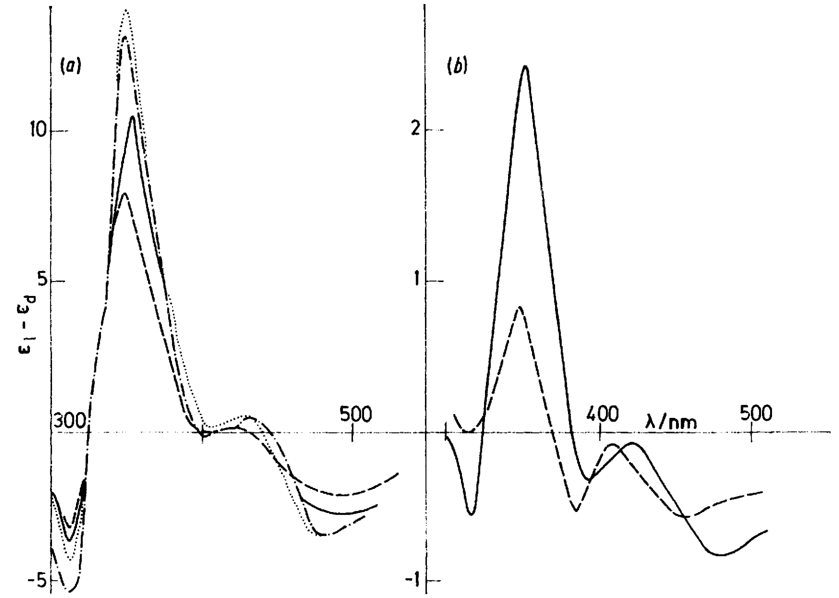

FIGURE 12 Circular-dichroism spectra of (*a*) [FeCl{sal(−)dpen}] in benzene (——) and in dioxan (– – – –) and of [FeCl{sal(+)chxn}] in benzene (— • — • —) and in dioxan (· · · ·) and (*b*)[FeCl{sal(+)pen}] in benzene (——) and in dioxan (— — —)

The same pattern was observed for all the iodocobalt(III) derivatives [Figure 13(*a*)]. The exciton couplet in these complexes is probably centred at *ca.* 390 nm (where there is maximum in the electronic spectrum); its lower-energy component is positive in sign as in the related complex [Cu{sal(+)chxn}] (see Figure 3). This feature is in accordance with a Λδ conformation for all these complexes, in agreement with the fact that the sal(+)chxn derivative must be locked

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[32] L. Pauling, ' The Chemical Bond,' Oxford University Press, 1967, p. 152.

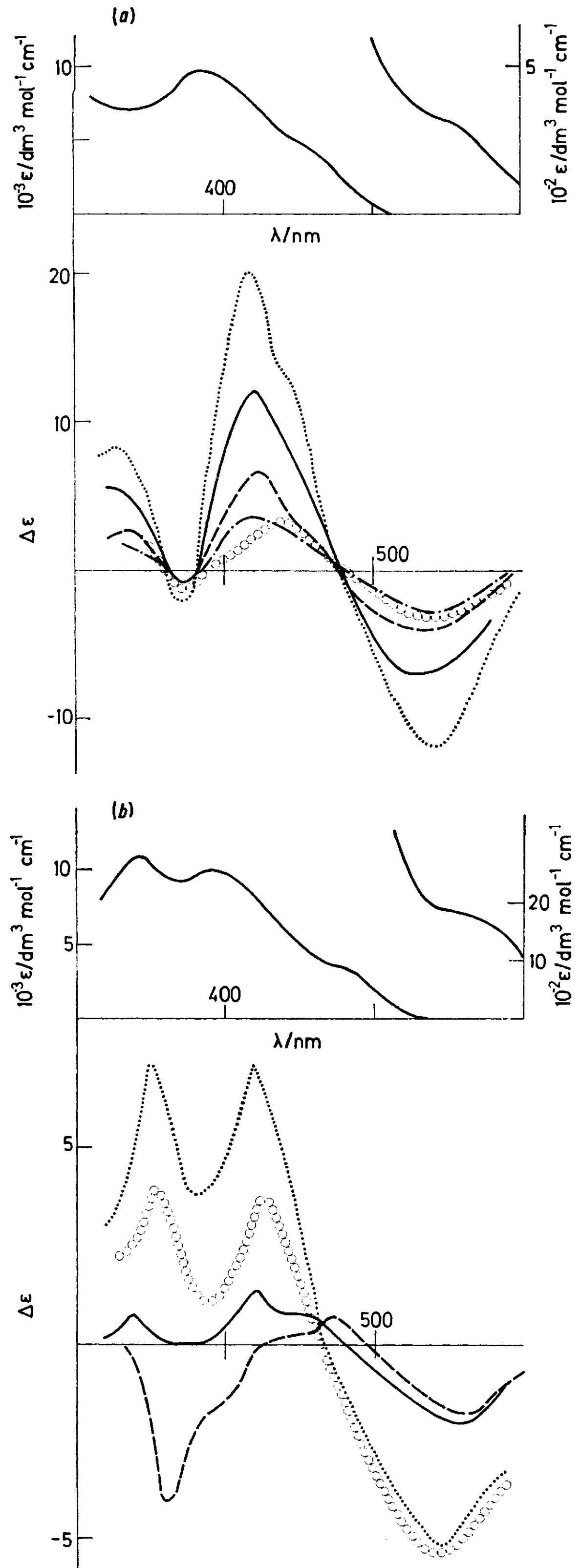

Figure 13 Electronic and c.d. spectra in pyridine solution of [CoI{(*S*)-saldiamine}] (*a*) and of oxygenated solutions of [Co{(*S*)-saldiamine}] (*b*). Other details as in Figure 9

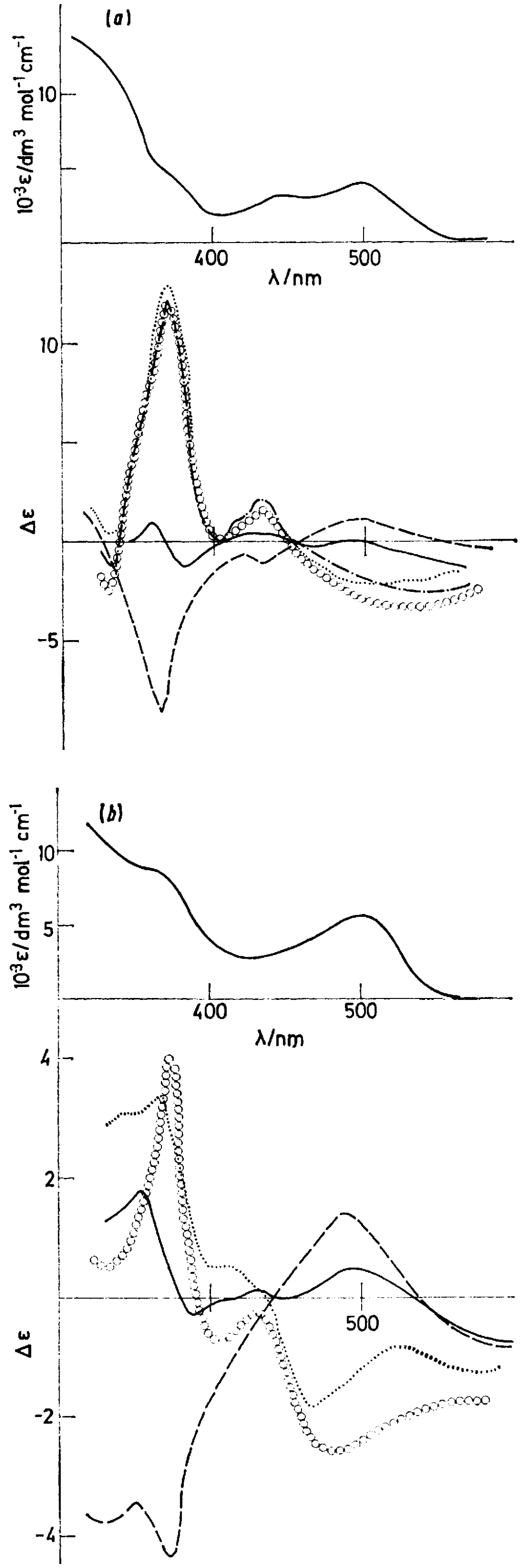

Figure 14 Electronic and c.d. spectra, in pyridine solution of [FeCl{(*S*)-diamine}] (*a*) and of [Fe(N_3){(*S*)-saldiamine}] (*b*). The diamines are: (——), (+)pn; (— — —), (+)bn; (· · · ·), (+)chxn (scale twice that shown); (— · — · —), (+)pen; and (○), (−)dpen. The electronic spectra are those of the sal(+)pn derivatives

in such a conformation. In support of this is the fact that the complex with the highest optical activity is that derived from sal(+)chxn, indicating the high rigidity of the en chelate ring as a consequence of the two fused rings. In the cases of the other complexes an equilibrium is probably present in solution, but clearly all the complexes of this series must have the $\Lambda\delta$ conformation (inverted with respect to that observed in related square-planar, and in the majority of five-co-ordinate, complexes) as the most stable. The origin of this inversion is presumably in the fact that in six-co-ordinate complexes of this kind the amount of interaction between the substituents R or R′ and the groups X or Y is so large that both R and R′ must be equatorial [Figure 8(*e*)]. Of interest is the fact that this change in conformation has also been observed in the case of butanediamine complexes. This is the only example in which this behaviour is observed with certainty in the case of butanediamine. Probably the bulkiness of the iodine atom exerts such a steric repulsion that only a conformation such as 8(*e*) is possible.

The spectra of the oxygenated pyridine solutions of [Co{(*S*)-saldiamine}] [Figure 13(*b*)] showed a similar trend, with the exception of the (+)-butanediamine case, and the same was observed for the six-co-ordinate iron(III) derivatives [Figure 14(*a*) and 14(*b*)] ($X = Cl$ or N_3). Comparison of Figure 13(*b*) with 10 and of Figure 14 with 9 shows very clearly the inversion of the spectrum of the sal(+)pn complexes in passing from co-ordination number five to six.

The anomalous behaviour of butanediamine is general; for instance in other six-co-ordinate Na[Fe(CN)$_2$(saldiamine)] complexes [33] the c.d. spectra of Na[Fe(CN)$_2$-{sal(+)bn}] is highly anomalous.

Conclusions.—The results obtained suggest the use of the general trends in the c.d. spectra of the Schiff-base complexes as a criterion of establishing the co-ordination number of the metal. This criterion is based on the comparison between the c.d. spectra of the derivatives containing salchxn, saldpen, and salpn which have the same absolute configuration. Thus the complexes are likely to be four-co-ordinated pseudo-planar if the spectra of the salpn and saldpen derivatives are similar but opposite to that of salchxn derivative, five-co-ordinate if the spectra of the saldpen and salchxn derivatives are similar but opposite to that of the salpn derivative, and six-co-ordinate if the spectra of all the three derivatives are similar. For instance, on the basis of the above criterion, the copper complexes can be described as five-co-ordinated in pyridine solution (Figure 15) because the couplet of the sal(—)dpen complex appears to be inverted with respect to that obtained in chloroform (see Figure 3). It is of interest that while the spectra of [Cu{sal(+)chxn}] are similar, not only in sign but also in magnitude in both the solvents, those of [Cu{sal(—)dpen}] in pyridine are not only inverted but also have a very low magnitude suggesting a low predominant concentration of the diequatorial conformer. The existence of these five-co-ordinate adducts in pyridine has already been suggested,[6] but never confirmed.

Such effects on the c.d. spectra arise from steric interactions which stabilize certain well defined conformations of the chelated ring of the diamine. These interactions are determined by the number and by the nature of the R groups bound to the chelate ring. Moreover the salen type of ligand is very flexible in terms of co-ordination geometry and conformation. This flexibility is related to the nature of the ethylenediamine moiety, and produces not only distortions of the N–O–O–N chromophore but also deformations of the conformation of the ligand towards a ' stepped ' or an ' umbrella ' shape. It is this flexibility which in some cases can produce an ambiguous pattern in a series of related c.d. spectra, as we have observed for six-co-ordinate dioxouranium [10] or in oxotitanium complexes.[12] The case of the derivatives containing butanediamine is another typical example.

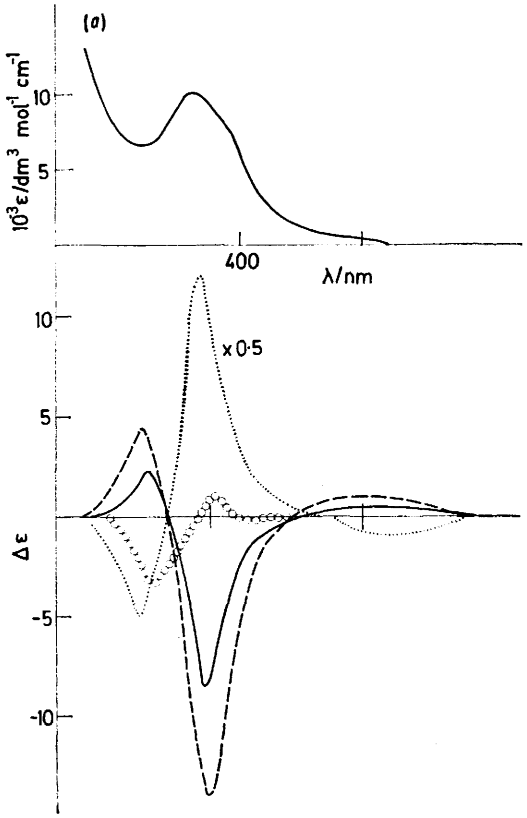

FIGURE 15 Electronic spectrum in pyridine solution of (*a*) [Cu{sal(+)pn}] and c.d. spectra of [Cu{(*S*)-saldiamine}] in the same solvent: (——), [Cu{sal(+)pn}]; (····), [Cu{sal(+)-chxn}]; and (○), [Cu{sal(—)dpen}]

Obviously the stabilization of one particular conformer can be induced, in some cases, by a very subtle balance of different steric interactions. For instance the strange behaviour of the butanediamine derivative in six-co-ordinate complexes can be related to the great tendency of the two Me groups to remain as far apart as possible in a diaxial conformation, even if other ligands produce

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[33] A. Pasini, M. Gullotti, L. Casella, and P. Romagnoli, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 705.

some repulsion. This repulsion is probably lowered by major distortions of the quadridentate ligand as a whole. Only in the free Schiff bases, where no steric interaction between the azomethine chromophores occurs, can a straightforward relation between the spectral pattern and the absolute configuration of the diamine be observed. In all the other cases one has to take into account a number of factors such as steric and ring requirements before making any generalization.

It is interesting that, although the results lead to the assignment of the absolute configuration of 1,2-diphenylethylenediamine, such an assignment can only be given when one has detailed knowledge of the conformational aspects of these molecules. In conclusion, great care must be taken in making generalizations from c.d. spectra of this class of complexes, particularly in the case of those of higher co-ordination number; some generalizations can be made within a well defined series of complexes.

EXPERIMENTAL

Analyses (see Table) were by the Microanalytical Laboratory of Milan University. Circular-dichroism spectra were recorded either on a Jouan II dichrographe or on a Jobin-Yvonne Mark III. The Schiff-base ligands were synthesized as described previously.[9] The preparations and characterizations of the following complexes have already been reported: [VO(saldiamine)];[11] [FeX(saldiamine)];[1] [Co(saldiamine)].[14] The complexes [Cu(saldiamine)] were obtained as reported by Downing and Urbach[6]; [Ni(saldiamine)] were prepared according to known methods,[4,7] as were [CoI(saldiamine)].[34]

Analytical data (%)

Complex	Found			Calc.		
	C	H	N	C	H	N
[Cu{sal(+)pn}]	58.6	4.3	8.6	58.3	4.2	8.5
[Cu{sal(+)bn}]	60.0	4.7	8.1	59.4	4.6	8.1
[Cu{sal(+)chxn}]	62.9	5.3	7.3	63.0	5.0	7.8
[Cu{sal(+)pen}]	65.8	4.4	6.8	65.1	4.4	6.9
[Cu{sal(−)dpen}]	70.1	4.3	5.7	70.0	4.6	5.8
[Ni{sal(+)pn}]	61.5	4.8	8.1	60.2	4.7	8.3
[Ni{sal(+)bn}]	60.0	5.6	7.4	61.2	5.1	7.9
[Ni{sal(+)chxn}]	63.5	5.4	7.5	63.4	5.3	7.4
[Ni{sal(−)dpen}]	70.1	4.5	5.8	70.5	4.6	5.9
[CoI{sal(+)pn}]	44.0	3.3	6.1	43.9	3.4	6.0
[CoI{sal(+)bn}]	44.8	3.9	5.6	45.0	3.8	5.8
[CoI{sal(+)chxn}]	47.2	3.6	5.4	47.4	3.9	5.5
[CoI{sal(+)pen}]	49.9	3.6	5.3	50.0	3.4	5.3
[CoI{sal(−)dpen}]	55.9	3.5	4.7	55.6	3.6	4.6

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[6/602 *Received*, *29th March*, 1976]

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[34] C. Floriani, M. Puppis, and F. Calderazzo, *J. Organometallic Chem.*, 1968, **12**, 209.