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N,N'-ETHYLENEBIS(SALICYLIDENEIMINATO) TRANSITION METAL ION CHELATES

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CONTENTS

A. INTRODUCTION

The prodigous growth of the published literature on Schiff-base complexes dictates certain limitations in the scope and depth of this review. It aims to present the salient developments in the chemistry of transition metal ion complexes of the type M(salen), where M(salen) = *N,N'*-ethylenebis(salicylideneiminato)metal(II) (Fig. 1). Where necessary other redox states of the metal ion will be considered.

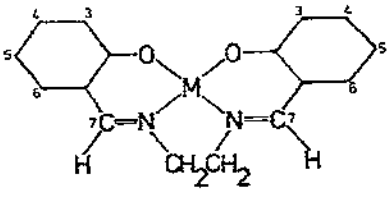

Fig. 1. Schematic representation of M(salen).

Metal Schiff-base complexes have been known since the mid-nineteenth century[1], and even before the general preparation of Schiff-base ligands themselves[2]. However, there was no comprehensive, systematic study until the preparative work of Pfeiffer and associates[3–15].

This work still serves as a source of chemical and preparative detail for the contemporary chemist and its importance may be gauged by the relatively large number of citations of these papers in the modern literature. Since Pfeiffer's initial contributions, the interest in Schiff-base complexes has increased significantly. Only over the last two decades, however, with the advent of suitable techniques, have structural, electronic, and magnetic properties, etc., been measured and explained in some depth. For convenience, the review has been divided into sections, each dealing with a certain group of metal complexes. A comprehensive review[16] covers much of the Schiff-base chemistry known up to 1966. Since that time there has been rapid progress in this area and the present survey concentrates on developments since the earlier review.

B. TITANIUM, ZIRCONIUM, HAFNIUM

Schiff-base complexes of the early members of the transition metal series have, in general, received less attention than those of the later members. $Ti(H_2salen)Cl_4$, $Ti(salen)Cl_2$ and Ti(salen)(OH)Cl have been isolated from the reaction of titanium tetrachloride and the Schiff-base ligand[17–20] H_2(salen). Ti(salen)(OH)Cl may be converted to the corresponding nitrate or perchlorate when reacted with nitric or perchloric acids, the hydroxyl group remaining intact. On the other hand, an acetic acid–acetic anhydride mixture converts it to the monoacetate $Ti(salen)(OCOCH_3)Cl$. Conductivity measurements on $Ti(salen)Cl_2$ indicate that this complex behaves as a bivalent electrolyte in solution[19]. The analogous bis-isopropoxy derivative $Ti(salen)(Pr^iO)_2$ (where Pr^iO = isopropoxy group) is produced by the reaction of titanium isopropoxide with the ligand (H_2(salen))[21]. Zirconium and hafnium complexes of tetradentate Schiff-base ligands have not been investigated.

C. VANADIUM, NIOBIUM, TANTALUM

The complex VO(salen), first isolated by Pfeiffer et al.[6], has been shown to possess magnetic properties that conform to the Curie law over the temperature range 77–300°K, with a magnetic moment of 1.72 B.M.[22]. In contrast, the methanol adduct $VO(salen)CH_3OH$ possesses an effective magnetic moment of 1.95 B.M., which is lowered to 1.72 B.M. in chloroform solution[23].

The solution electronic and ESR spectroscopic properties have been reported for VO(salen) and other similar vanadyl quadridentate complexes. These have been found to be relatively independent of both donor and non-donor solvents[24], unlike their β-diketone analogues[25]. It is suggested that the solvent independence is a consequence of either steric hindrance to complex–base interactions, or distortion of the complex from the anticipated square pyramidal geometry. Circular dichroism and electronic spectroscopic studies have led to tentative assignments of electronic absorption bands for tetradentate vanadyl Schiff-base complexes[24,26,27]. The low-energy regions (10,000–22,000 cm^{-1}) of the absorption spectra of complexes studied by Farmer and Urbach[27] contain three bands, viz. at approximately 13,000 cm^{-1}, 17,000 cm^{-1}, and 21,000 cm^{-1}. These absorptions, with the aid of circular dichroism, are tentatively assigned to the $d_{xy} \rightarrow (d_{xz}, d_{yz})$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{z^2}$ transitions.

The structural determination of VO(salen) has not been reported, but the structures of other aliphatic[28,29] and aromatic[30] tetradentate complexes are presumably basically similar. The propylene-bridged analogue of VO(salen) possesses interesting stereochemical and spectral properties[30]. The vanadyl oxygen of one molecule occupies the sixth position about the vanadium in the adjacent molecule, forming a polymeric chain (Fig. 2). The complex is yellow-orange in colour, unlike the usual characteristic blue or green colour of vanadyl complexes, and possesses the vanadium–oxygen infrared stretching frequency at 854 cm^{-1}, outside the normal range of 910–1010 cm^{-1} (cf. 989 cm^{-1} for VO(salen) itself). The magnetic moment of the complex has been reported[31] to be 1.78 B.M. at 295°K.

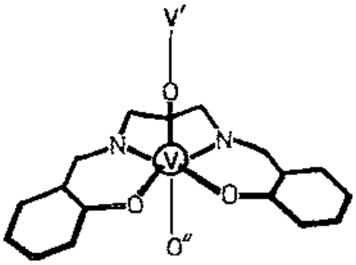

Fig. 2. Structure of VO(salpn), the propylene-bridged analogue of VO(salen).

Binuclear adduct complexes involving VO(salen) and copper and zinc halides, and also a trinuclear adduct with copper perchlorate, have been isolated[23]. In these adducts the metal Schiff base is thought to act as a neutral bidentate ligand forming donor bonds through the phenolic oxygen atoms, in the same manner as found for other metal salen compounds[32]. Reduced magnetic moments in the copper halide adducts indicate antiferromagnetic interactions of the type found for Cu(salen) adducts (see Sect. I). Increases in the proposed carbon–oxygen stretching infrared frequency are also consistent with this mode of adduct formation[32]. Evidence for the formation of a vanadium(III)(salen)–oxygen adduct has been outlined by Swinehart[33].

Niobium and tantalum salen complexes have been isolated and formulated as [M(salen)Cl] Cl_2 from their solution conductivities (M = Nb, Ta)[18,19]. A neutral adduct of the form H_2(salen)$NbCl_4$ has also been reported[34].

D. CHROMIUM, MOLYBDENUM, TUNGSTEN

Despite the ease with which Schiff-base ligands coordinate to transition metal ions, there are relatively few reports of chromium Schiff-base complexes. The oxidation by air of aqueous solutions of chromium(II) chloride in the presence of the ligand H_2(salen) is the best method[35] of preparing [Cr(salen)$(H_2O)_2$] Cl. The nature of the product is consistent with the observation that the oxidation in air of chromium(II) solutions leads to the formation of hydroxo or aquo species and not oxo complexes, as appears to be the case in, for example, the aqueous Fe(salen) system. The ionic nature of the chloride in aqueous solutions is demonstrated by conductivity measurements and the rapid precipitation of the tetraphenyl-borate and hexafluorophosphate salts, and in the solid by an X-ray structural determination.

Crystallographic data[35] for $[Cr(salen)(H_2O)_2]Cl$ indicate that the four Schiff-base hetero-atoms and the water molecules surround the chromium in a slightly distorted octahedral geometry with angles subtended at the central metal in the range 81.6–95.7°. The chromium ion is displaced by 0.077 Å out of the mean plane through the four hetero-atoms. In common with other Schiff-base complexes of the salen type, there is slight distortion from the planar ligand geometry towards a tetrahedral arrangement (Fig. 3).

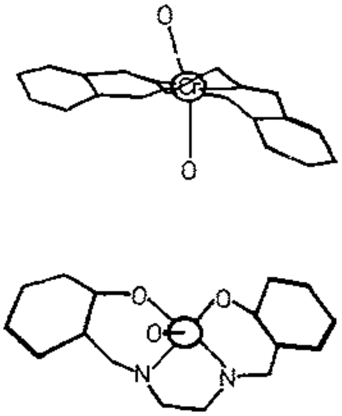

Fig. 3. Structure of the $[Cr(salen)(H_2O)_2]^+$ anion.

The low-intensity absorptions observed in the 20,000–25,000 cm^{-1} region for this complex are attributable to transitions to the split components of the $^4T_{2g}(O_h)$ and the $^4T_{1g}(F)(O_h)$ terms.

Other complexes of the type $[Cr(salen)L_2]X$ have been isolated by Yamada et al.[36] (where $L = H_2O$, NH_3 or aliphatic amine, or CN^-, $X = Cl^-$; or for $L = CN^-$, $X = K^+$). An earlier attempt to prepare chromium(III)(salen) complexes by reaction of tris(salicylaldehydato)chromium(III) with ethylenediamine did not lead to the required product[37].

There is very little published work on molybdenum tetradentate Schiff-base complexes. Recently the synthesis of a range of molybdenum Schiff-base complexes which included the complex $Mo^{IV}(salen)Cl_2$ was reported[38]. The complexes were prepared by treating $MoCl_4(MeCN)_2$ with the appropriate ligand. The diamagnetic complex $[MoO(salen)]_2O$ was also prepared by reaction of molybdenum hexacarbonyl with $H_2(salen)$ in dimethylformamide solution.

There are no reported tetradentate complexes of tungsten.

E. MANGANESE, TECHNETIUM, RHENIUM

Manganese complexes of the Schiff base salen were originally isolated by Pfeiffer et al.[4]. In the solid state Mn(salen) is air-stable, but in solution this complex rapidly oxidises to give manganese(III) derivatives. The magnetic properties of Mn(salen) have been the subject of a number of investigations[39—41], all of which indicate the presence of antiferromagnetic exchange interactions. The discontinuity in the magnetic susceptibility curve at 85–107°K, originally reported as due to a structural change[40], was not confirmed by subsequent work[39,41]. The variation of magnetic susceptibility with temperature can be accounted for by the assumption of a binuclear structure involving antiferromagnetic exchange interactions. The exchange integral J and spectroscopic splitting factor g have been estimated as $J = -6.5\ \text{cm}^{-1}$ (ref. 41) and $-6.3\ \text{cm}^{-1}$ (ref. 39) with $g = 2.00$ and 1.96 respectively. In the former case agreement between calculated and experimental values of susceptibility were not very good at high temperatures, but were improved by increasing the value of J to $-7.0\ \text{cm}^{-1}$ over the higher temperature range[41]. Further evidence for the binuclear nature of Mn(salen) was obtained by comparing the X-ray diffraction powder data of this complex[40] with those of Cu(salen); the latter is known to be dimeric[42,43]. Similar manganese(II) Schiff-base complexes with substituent groups in the phenyl rings are assumed to possess a binuclear or linear chain structure[41].

The manganese(III) halide complexes Mn(salen)X (X = I, Br) have been prepared by the addition of a potassium halide or tetraethylammonium halide salt to an alcoholic solution of manganese(III) acetate and the Schiff-base ligand. These complexes are soluble in water and methanol to give solutions with molar conductance values approaching those expected for 1:1 electrolytes, but they are insoluble in nitromethane. This is in contrast to the behaviour of the Fe(salen)X analogues; the latter do not ionise in nitromethane solution and are practically insoluble in methanol and water[45]. Furthermore, facile conversion of manganese(III) tetradentate complexes into oxy-bridged compounds by the addition of base, as in the iron(III) analogues, does not occur.

Studies of the magnetic behaviour of the Mn(salen)X complexes reveal small deviations from the Curie law[44]. It was suggested that spin exchange occurs and J was estimated to be between -1 and $-3\ \text{cm}^{-1}$, with the value of g close to 2.0. Similarly, weak exchange interactions have been put forward to explain the small θ (Weiss constant) value observed for the corresponding manganese Schiff-base acetate. The magnetic properties of the Mn(salen)X complexes outlined above differ from those found by other workers[46] who report magnetic moments close to the spin-only value for Mn(salen)X and also for the monohydrate Mn(salen)Cl(H_2O).

The magnetic properties of the aerobic oxidation product isolated from solutions of Mn(salen), formulated as Mn(salen)(OH), have been reported[39] to correspond to high-spin manganese(III). However, Lewis et al.[41] isolated two forms of oxidation product, one of which showed anti-ferromagnetic behaviour suggested as arising from an oxy-bridged structure of the form [Mn(salen)]$_2$O(H_2O). More recently it has been reported that three types of oxidation product can be obtained from solutions of manganese(II) Schiff-base complexes[47]. In this case the products are as follows: (salen)Mn–O_2–Mn(salen), the effective magnetic moment of this compound (2.79 B.M.) corresponding to two unpaired electrons and formally involving spin pairing between manganese(III) and the O_2^{2-} ion; $[Mn(salen)O]_n$ (effective magnetic moment 1.97 B.M.), which may be regarded as a polymeric complex, and MnO[3-MeO(salen)].1.5 CH_3OH, the effective magnetic moment of this compound (3.68 B.M.) indicating high-spin manganese(IV). The complex may be considered as an intermediate in the formation of polymeric complexes of the type found for the corresponding salen system, $[Mn(salen)O]_n$.

Nitric oxide reacts with manganese(II) acetate and the salen ligand to form Mn(salen)($OCOCH_3$). This compound possesses magnetic properties indicative of antiferromagnetic interactions[39]. The electronic spectrum[48] of Mn(salen)($OCOCH_3$) is similar to the spectra of the Mn(salen)X complexes[44]. The absorption bands observed at 17,000 cm^{-1}, 20,800 cm^{-1} in Mn(salen)($OCOCH_3$) are possibly due to the $^5T_{1g} \leftarrow {}^5E_g$ transition. The band splitting is most likely due to the Jahn–Teller effect[44].

The tetradentate Schiff-base complex *N,N'*-trimethylenebis(salicylideneiminato)-manganese(II) is claimed to undergo adduct formation with molecular oxygen, nitrogen and carbon monoxide[49]. Subsequent work has failed to substantiate molecular nitrogen addition but has confirmed an uptake of oxygen[50], though this is more likely due to irreversible oxidation of the type already described, rather than molecular adduct formation.

The formation and properties of rhenium and technetium salen Schiff-base complexes have not been reported.

F. IRON, RUTHENIUM, OSMIUM

Octahedral high-spin complexes of iron(II) are expected to possess effective magnetic moments of about 5.5 B.M., but increasing electron delocalisation and distortion from cubic symmetry cause the magnetic moments to approach the spin-only value and to vary little with temperature. Magnetic measurements on Fe(salen) and its ring-substituted derivatives suggest that these compounds have a highly distorted, if not planar, structure with considerable delocalisation[39]. The observed magnetic moment of Fe(salen) (4.77 B.M.) is below the spin-only value of 4.9 B.M. However, this may be due to contamination by the binuclear oxy-bridged iron(III) species. Alternatively, the low moment may result from antiferromagnetic interactions of the type found for Mn(salen), suggesting a dimeric arrangement. This is supported by the fact that the monopyridine adduct Fe(salen)py shows magnetic properties that are, within experimental error, consistent with normal high-spin iron(II)[50].

The importance of obtaining iron(II) compounds free of contamination by oxidation products is highlighted by the interpretation of the Mössbauer spectrum of Fe(salen). The spectra of the iron(II) complexes of salicylaldoxime, salicylaldehyde and salen were reported to yield values of isomer shifts and quadrupole splitting significantly different from those observed for other high-spin iron(II) compounds[51]. It was suggested that a large lattice contribution to the electron field gradient and back-donation were responsible for the anomalies. However, the work of De Vries et al.[52] shows that normal iron(II) spectra can be obtained if oxygen-free conditions are maintained during the preparation of the samples and subsequent measurement of the Mössbauer spectra.

Some apparently pentacoordinate mononitrosyls of Fe(salen) and its derivatives have been reported[53]. The compounds are prepared by reacting nitric oxide with the Schiff-base complex. The effective magnetic moments indicate that the products contain three unpaired electrons. The magnetic susceptibility of the Fe(salen) nitrosyl derivative decreases sharply with temperature at about 180°K to a value corresponding to one unpaired electron. The infrared spectrum of this complex in the $S = 3/2$ state indicates that the formal oxidation states of the iron and the nitrosyl group could be regarded as on the borderline between iron(I) and NO^+ and iron(III) and NO^-, i.e. iron(II) and NO. However, the Mössbauer isomer shift is more compatible with the complex containing iron(III) and NO^-.

Fe(salen) readily reacts with oxygen and undergoes irreversible oxidation to form the oxy-bridged complex $[Fe(salen)]_2O$. The magnetic properties of this compound, originally studied by Klemm and Raddatz[54] and Michaelis and Granick[55], have been analysed using a dipolar coupling mechanism and interpreted in terms of interaction between two ions with $S = 3/2$ or with $S = 5/2$ in their ground states[56]. The observed comparatively strong interaction, as determined from the exchange integral (J) value of $-95\ cm^{-1}$ with $g = 2.00$, contrasts with those observed[45,57,58] for weakly coupled systems such as $[Fe(salen)Cl]_2$, and has been interpreted in terms of a linear Fe—O—Fe system. Similar magnetic behaviour was observed by others[58,59], who concluded that overall magnetic and Mössbauer data were most consistent with $S = 5/2$ for each iron.

The suggested oxy-bridge linkage has been confirmed by X-ray diffraction structural studies on both $[Fe(salen)]_2$.0.2 py (ref. 60) and $[Fe(salen)]_2O.CH_2Cl_2$ (ref. 56). In the former compound the iron atoms, linked by an oxygen atom, are five-coordinate with a distorted square-pyramidal geometry (Fig. 4). The average Fe—O(bridge) bond length is 1.80 Å with the Fe—O—Fe bridge angle at 139°. This compares with the angle of 142.2° found in the methylene chloride solvate[61]. These angles are more acute than those observed in other oxygen-bridged iron systems. This is thought to be due to steric effects[61]. The

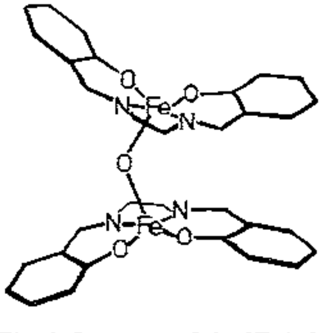

Fig. 4. Structure of the $[Fe(salen)]_2O$ unit.

$[Fe(salen)]_2O$ units in both the pyridine and methylene chloride solvates are very similar.

The temperature variation in the magnetic susceptibilities for compounds of the type $[Fe(salen)]_2O$ are usually interpreted in terms of the dipolar coupling approach and assuming isotropic exchange, a formal spin state for each iron, a spectroscopic g value, and also temperature-independent paramagnetism, all of which may be adjusted to give the best fit to the data. Yet very little work has been done to test these assumptions by measuring the anisotropy in either the magnetic susceptibility or the g values. The average magnetic susceptibility for $[Fe(salen\text{-})]_2O.CH_2Cl_2$ has been interpreted[64] on the basis of an isotropic spin exchange interaction with $J = -87$ cm^{-1} and $g = 2.00$. The observed anisotropies for this complex[61] may be accounted for by retaining the isotropic exchange integral and allowing the g values to be anisotropic with $g_x = 1.98$, $g_z = 2.00$ and $g_y = 2.02$. Within the accuracy of the anisotropic determination it appears from these values that the assumptions of isotropic exchange and of $g = 2.00$ are reasonable within this system.

The temperature dependence of the Knight shifts of the pyrrole protons in binuclear μ-oxo-iron(III) porphyrins has been used as a direct measure of the isotropic exchange parameters[62] and similar studies have been carried out on some oxygen-bridged iron(III) Schiff-base complexes[63].

An infrared absorption attributable to the Fe—O—Fe linkage[64] is expected in the range 800—1000 cm^{-1}. The absorption at 825 cm^{-1} in $[Fe(salen)]_2O$ has been assigned to the asymmetric metal—oxygen stretching vibration[50]. This is supported by a variable-temperature infrared study that assigns an absorption at 807 cm^{-1} (room temperature) to this vibration[58]. Since there is only one absorption in this immediate region, both groups of authors are presumably referring to the same band. Other authors have failed to distinguish between systems involving directly bonded Fe—O—Fe groups and those with weak iron—oxygen interactions[64].

Binuclear complexes have been found for Fe(salen)X compounds (X = halide). Magnetic data supplied the initial evidence[54] of a dimeric species for Fe(salen)Cl, and more recent studies confirm these results[45,57,58]. For a magnetically dilute octahedral spin-free iron(III) complex the ground state is $^6A_{1g}$ with an associated magnetic moment of 5.92 B.M. independent of temperature. Antiferromagnetic exchange interactions between iron atoms result in departures from Curie law behaviour. Such is observed in Fe(salen)X (X = Cl, Br) and other related Schiff-base compounds[45,58]. Using the dipolar coupling approach Gerloch et al.[45] have fitted the temperature-dependent susceptibilities of these compounds to a binuclear spin-free iron(III) model, with exchange integral (J) values of approximately -7.5 cm^{-1} and -7.0 cm^{-1} for the chloride and bromide respectively. These results have been confirmed by other magnetic measurements over a greater temperature range[58].

The dimeric nature of Fe(salen)Cl has been unequivocally determined by X-ray diffraction techniques[65,66]. The binuclear units involve intermolecular interactions between phenolic oxygen atoms of the Schiff base and metal ions to give an asymmetric bridging arrangement similar to those found in other salen systems[42,45,67,68] (Fig. 5). The Mössbauer spectra for a number of iron(III) salen derivatives have been reported[58,59,64,71].

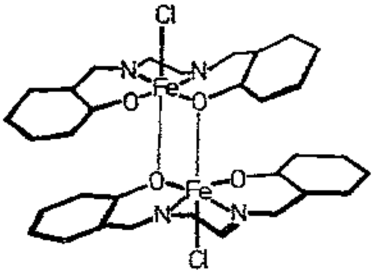

Fig. 5. Structure of $[Fe(salen)Cl]_2$.

The temperature-dependent asymmetry observed in the Mössbauer spectrum of dimeric Fe(salen)Cl has been explained in terms of a combination of spin–spin relaxation effects and the Karyagin effect[71,72]. Monomeric units of Fe(salen)X compounds are formed as solvates, as indicated by Mössbauer and magnetic measurements[45,64]. The structure of the nitromethane solvate of Fe(salen)Cl reveals[69] a monomeric metal Schiff-base unit with the metal involved in five-coordination.

The iron Schiff-base complexes discussed up to this point may be categorised into three groups according to their magnetic properties[65]. These are: spin-free paramagnetic compounds with magnetic moments approximately equal to those expected for the orbitally non-degenerate ground term (5.92 B.M.), e.g. monomeric Fe(salen)Cl; weakly coupled antiferromagnetic systems with exchange coupling integrals in the range -5 to -10 cm^{-1}, e.g. $[Fe(salen)Cl]_2$; and medium-coupled systems with J approximately -100 cm^{-1}, e.g. $[Fe(salen)]_2O$.

The preparation of Fe(salen)R (R = Ph, CH_2Ph) has been reported[70]. Magnetic susceptibility measurements show that the compounds are high-spin. Their preparation involved a prior reduction of Fe(salen) with stoichiometric quantities of sodium sand in tetrahydrofuran. The temperature dependence of the magnetic susceptibility of the resulting Fe(salen)$^-$ anion behaves essentially as a normal d^7 system, as expected on the simple assumption of one-electron addition to the high-spin Fe(salen) with a belief (based on good solubility in tetrahydrofuran) that the anion is monomeric. Fe(salen) was shown to undergo an addition reaction with cyclohexylisocyanide to form a 1:1 adduct, which contrasts with the failure to obtain an adduct with carbon monoxide. This confirms that isocyanides are in general poorer π-acceptors and better σ-donors than carbon monoxide.

Fe(salen) can also be oxidised by iodine to give the monoiodoiron Schiff-base complex[70] Fe(salen)I.

Very little is known about the Schiff-base chemistry of ruthenium and osmium. Dodecacarbonyltriruthenium reacts with the salen ligand to produce a compound formulated as $[Ru(salen)CO]_2$, although a dicarbonyl monomer formulation is also possible[50].

G. COBALT, RHODIUM, IRIDIUM

The preparation of Co(salen) was first reported by Pfeiffer et al.[4] in 1933. Since then this compound has received a great deal of attention owing to its ability to undergo reversible adduct formation with molecular oxygen. The oxygenation ability of Co(salen) was first recognised as such by Tsumaki[73] in 1938, but only during recent years, with the advent of modern physical techniques, has an understanding of the oxygenation process emerged.

The first extensive studies of this property were by Calvin, Diehl, and associates[74–91]. It was found that different crystalline and solvate forms existed, each with differing capacity for oxygenation, including one completely inactive form. The variation in oxygenation activity in the solid state has been related to the presence of voids in the crystal lattice, sufficient in size to allow the passage of oxygen[92]. This suggestion is supported by two independent structural determinations[67,68] of the inactive form of Co(salen). The structure consists of dimeric units, $[Co(salen)]_2$, rather than monomeric layered units as previously suggested[92]. Dimerisation is accomplished by the presence of interactions between the cobalt atoms and phenolic oxygen atoms of adjacent pairs of molecules. Similar situations have been found in other salen compounds[42,43,65,66] (Fig. 6). In this manner the cobalt becomes five-coordinated in a distorted rectangular-based pyramid. The intermolecular cobalt–oxygen distance is 2.25 Å. The close stacking of the dimeric units prevents the formation of voids in the lattice and possibly explains the compound's oxygenation inactivity. The structure of the active monochloroform adduct of Co(salen) has also been determined and reveals a planar arrangement of the metal Schiff base with the chloroform molecules weakly hydrogen-bonded to the phenolic oxygen atoms[93], not axially bonded as previously thought[94]. The complex contains pairs of Co(salen) units centrosymmetrically arranged at the van der Waals distance apart (3.5 Å). The easy loss of chloroform from the adduct can be achieved via passageways that extend throughout the crystal. These passageways contain the loosely bound chloroform molecules and provide a means by which they may diffuse out of the crystal, enabling reaction between oxygen and Co(salen) to take place, and explaining the observed oxygenation activity of this complex. The active forms of Co(salen) are presumed to contain dimeric $[Co(salen)]_2$ units but with an open lattice packing relative to the inactive form[67]. The importance of solid-state packing effects in determining oxygenation ability is further indicated by kinetic studies of oxygen

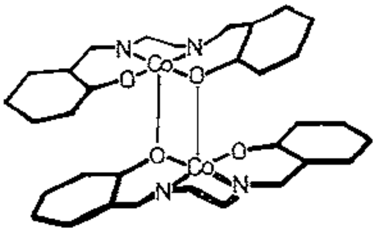

Fig. 6. Structure of $[Co(salen)]_2$.

absorption at the Co(salen) crystal surface[95]. Measurements involving different temperature and pressure conditions show that, following the induction period and after the attainment of equilibrium, the kinetics of absorption of oxygen at the crystal surface are no longer important and oxygenation is controlled exclusively by the diffusion of oxygen into the crystal.

Oxygen adducts of cobalt complexes containing both 1:1 and 1:2 oxygen to cobalt ratios have been isolated[96,97]. It was suggested that adducts of the form $[Co(salen)]_2O_2L_2$ (where L is a σ-donor ligand) contain a peroxo bridge between the metal ions with the ligand (L) acting as a stabiliser for the $Co-O_2-Co$ bonding system. An X-ray diffraction analysis of the structure of the complex $[Co(salen)]_2O_2(DMF)_2$ (where DMF = dimethylformamide) reveals two cobalt ions joined by an oxygen–oxygen bridge; the non-planarity of the bridge system (Co–O–O angle is 120.3°) and the diamagnetism of the adduct are consistent with the suggested peroxo type of bonding[96], but the oxygen–oxygen bond length (1.339 Å) is reminiscent of a superoxo group (Fig. 7). The reason why the situation found in this complex differs from the normal superoxo or peroxo system is suggested as being due to partial transfer of electrons from cobalt to O_2, in such a way that irreversible oxidation does not take place[98]. Moreover, the reversibility of oxygenation is thought to be related to the difficulty in oxidising cobalt, due to delocalisation of electron density within the molecular orbitals of the equatorial ligand. The delocalisation of electron density from cobalt to the ligand in Co(salen) generates the need for an axial σ-donor ligand before oxygenation can take place[86,98]. This activation towards oxygenation is not only necessary in solutions of cobalt(II) complexes but also in the solid state; hence the suggestion that the active form of Co(salen) is dimeric in the solid state with pentacoordinate cobalt[67].

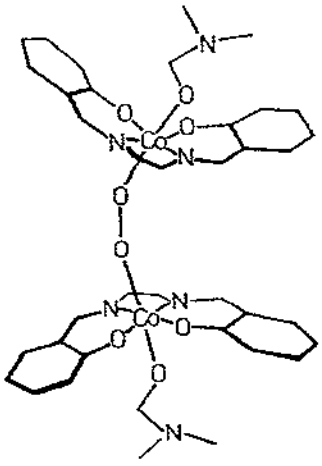

Fig. 7. Structure of $[Co(salen)]_2O_2(DMF)_2$.

The structure of the 1:1 adduct of Co(salen) with the σ-donor ligand pyridine reveals a pyramidal coordination about cobalt[99], the apical position being occupied by the nitrogen atom of the pyridine molecule. According to the preceding suggestions this complex should be activated towards oxygenation by the σ-donor ligand. In actual fact the adduct is inactive in the solid state, presumably due to packing effects, but when moistened with solvent readily undergoes oxygenation[80]. Ligands bound axially to the cobalt in such complexes do influence the electron distribution within the equatorial ligand to some extent, at least for certain cobalt(III) derivatives, as seen by changes in their PMR spectra with variations in the axial group[100]. The steric effects of axial σ-bonded groups on Co(salen) derivatives have also been noted[101,102]. The effects of such groups on the charge donation from both equatorial and axial ligands in cobalt chelates, and the subsequent change of the ability of the metal to vary its oxidation state, have been shown by polarographic studies[103,104]. From these indications it is clear that, although packing effects are very likely a major factor in determining oxygenation activity in the solid, electronic effects, determined to some extent by the groups present, are also significant[105].

Oxygen adducts of 1:1 stoichiometry were originally suggested to involve the oxygen in an excited singlet state, resembling ethylene, and π-bonded to the metal[96]. But, as pointed out by Calligaris et al.[98], a more likely structure would involve a superoxo type of bonding. Although few 1:1 adducts of this general class have been isolated[96,97], there exists extensive evidence that such complexes are common in solution. Originally 1:1 adduct formation was proposed by Harle and Calvin[79]. More recently electrochemical studies have revealed their existence in solution for both aliphatic and aromatic cobalt Schiff-base complexes[99]. Solution ESR studies of bisdimethylglyoximatocobalt–oxygen adducts[106], aliphatic[107] and aromatic[108] cobalt Schiff-base–oxygen adducts, vitamin B_{12r} (refs. 109, 110) and cobalt mesoporphyrin IX dimethylester–oxygen adducts[111], and other studies[112], are all consistent in suggesting that the complexes are best formulated as superoxo-cobalt(III) compounds with O_2^- acting as a ligand. ESR studies have also provided an insight into the mechanism of oxygenation in solution for certain complexes of the Co(salen) type; Busetto et al.[108] propose the following scheme based on ESR evidence.

$$\mathrm{LCo^{II} + O_2 \rightleftharpoons LCo^{III}{-}O{-}O^{\bullet}} \tag{a}$$

$$\mathrm{LCo^{III}{-}O{-}O^{\bullet} + LCo^{II} \rightleftharpoons LCo^{III}{-}O{-}O{-}Co^{III}L} \tag{b}$$

$$\mathrm{LCo^{III}{-}O{-}O{-}Co^{III}L + O_2 \rightleftharpoons 2\ LCo^{III}O_2} \tag{c}$$

(L represents the σ-donor ligand present in the system.)

Two forms of 1:1 adduct are generated in the oxygenation process; the transition from one to the other proceeds via the 1:2 adduct. The mechanism is general for the several complexes studied, including Co(salen). Manometric measurements have also been used to provide evidence of 1:1 oxygenation products in solution[113]. The process of oxygenation in general has been reviewed[114,115].

Adduct formation with gaseous molecules is not restricted to oxygen alone. Co(salen) and related derivatives irreversibly complex with nitric oxide to form 1:1 adducts that are essentially diamagnetic and very likely involve pentacoordinate cobalt[116]. The adducts were originally thought to contain Co^I and NO^-; however, the authors now favour the Co^{III}, NO^+ formalism[53]. The latter is more compatible with the oxidising properties of nitric oxide[117,118] and the relative ease with which Co(salen) and related compounds are oxidised (e.g. by oxygen and iodine)[119]. Certain aliphatic cobalt Schiff-base complexes react in the same way with nitric oxide[120]; however, the corresponding nickel and palladium analogues form oxime-type compounds[121].

Until recently the Schiff base salen was thought to maintain, without exception, an approximately planar configuration in its metal complexes. In most situations the four bonding atoms of the salen ligand are found in a planar arrangement that is slightly tetrahedrally distorted. However, the structure determination[122,123] of the complex Co(salen)(acac).0.7 H_2O (where acac = acetylacetone anion) provides unequivocal evidence for the existence of non-planar salen complexes. The structure of this compound reveals discrete units involving distorted octahedral coordination about the metal with the acac oxygen atoms occupying *cis* positions; the angles around the cobalt range from 83° to 97° (Fig. 8). The water molecules form hydrogen bonds to the phenolic oxygen atoms of the Schiff base. Presumably, similar compounds also involve salen in this conformation[126]. The unusual occurrence of the salen ligand in non-planar form has been suggested for some R_2Sn^{IV}(salen) complexes (where R = Me or Ph)[124]. However, recent structural determinations have shown that the two methyl groups are actually *trans*-bonded[123].

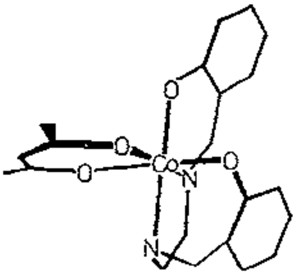

Fig. 8. Structure of the Co(salen)(acac) unit.

The crystal and molecular structure of benzoylacetonato[*N,N'*-ethylenebis(salicylideneiminato)] cobalt(III).1.5 H_2O has also been reported[125]. Here the cobalt(III) molecule has a normal octahedral coordination with a bidentate β-diketonate ligand and a strained non-planar configuration of the quadridentate ligand. The water molecules form a hydrogen-bonded chain of four water molecules linking phenolate oxygens of two different molecules across a crystallographic centre of symmetry. Bond lengths are normal though molecular strain manifests itself by significant distortion of bond angles of the ligand and cobalt(III) coordination polyhedron.

The preparation of the mixed Schiff-base β-diketone of cobalt(III) has been critically assessed and the available structural data augmented by a study of the infrared, NMR and mass spectra[127].

Other mixed-ligand complexes incorporating salen and rare earth elements have also been isolated[128]. The complexes are of the form $LnA_2(salen)_{1/2}$ (where Ln = lanthanide metal ion, A = anion of acetylacetone or propionylacetone) and LnB(salen) (where B = anion of benzoylacetone or dibenzoylmethane). The proposed structure of the former contains the salen ligand in a non-planar conformation bridging the two lanthanide metals. In this way, it serves as a bidentate ligand with respect to each metal. The latter class of complexes are thought to involve salen in an analogous conformation to that found in Co(salen)(acac)H_2O. It is proposed that compounds with the stoichiometry $Ln_2(salen)_3$ incorporate the salen unit in each of the above conformations[128,129]. The existence of bridging quadridentate Schiff-base ligands of the salen type has been shown by the structure determination[130] of $[Co_2(3\text{-}MeO(salen))_3.2H_2O.2DMSO]$ (3-MeO(salen) = *N,N'*-ethylenebis(3-methoxysalicylideneiminato) dianion, DMSO = dimethylsulphoxide; the water and DMSO contents are not stoichiometric). The $[Co_2(3\text{-}MeO(salen))_3]$ unit possesses the steric arrangement suggested for the $[Ln_2(salen)_3]$ complexes and the two cobalt ions are bridged by the Schiff-base ligand, which acts as a bis-bidentate ligand occupying two *cis* coordination sites around each cobalt. The octahedral coordination polyhedron of each metal is completed by the quadridentate Schiff-base ligand in a non-planar conformation (Fig. 9).

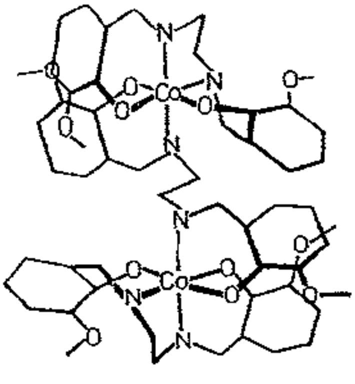

Fig. 9. Structure of the $[Co_2(3\text{-}MeO(salen))_3]$ unit.

The structural investigations reported so far have eliminated the possibility of the occurrence of carbon bonding in the cobalt(salen) β-diketone complexes. However, in a number of other circumstances their existence has been firmly characterised, and when malononitrile reacts with the oxidised Co(salen) under the same conditions used to prepare the β-diketone compounds, a complex containing a cobalt—carbon bond is formed[131].

Co(salen) can be reduced to a monoanion using sodium metal as the reducing agent. This was first reported by Calderazzo et al.[132] and later confirmed by others[133]. The reduced form of Co(salen), formulated as Na[Co(salen)], reacts with organic halides to form alkyl and aryl cobalt(III) derivatives of the Schiff-base complex (III) that contain stable cobalt—carbon bonds. Alternative methods of preparation of complexes of the general type

RCo(salen)L have since been reported (R = alkyl, aryl, acyl; L = H_2O, pyridine, etc.)[119,120], with related systems providing similar results[135–137]. Stable cobalt–carbon bonds have some biochemical significance in that a coenzyme of vitamin B_{12} contains such a bond[138], and simpler systems, in particular cobaloximes, have been regarded as chemical models for the more complicated natural systems[139].

The crystal and molecular structure of the complex Co(salen)C_2H_5 has been determined[140]. The crystals are built up of centrosymmetric dimeric units, dimerisation being achieved by the coordination of the cobalt atoms with the oxygen atom of an adjacent Co(salen)C_2H_5 molecule.

The stability of the cobalt–carbon bond in the Schiff-base complexes has been explained in terms of a stereochemical arrangement of the ligand and a delocalisation of cobalt electron density within that ligand[134]. Similar considerations were invoked to explain the reversibility of oxygen adduct formation[98]. Other factors involved in the stabilisation of the cobalt–carbon σ-bond have been discussed previously[141]. However, more recently what has become the conventional wisdom concerning the stability of transition metal to carbon bonds has been questioned. It is argued that the transition metal to carbon bond is no weaker than the bonds between carbon and other metallic elements and that the main purpose of additional ligands in stabilising compounds with metal to carbon σ-bonds is merely the blocking of the coordination sites required for decomposition reactions to proceed[142,143].

The reactivity of the cobalt–carbon bond towards sulphur dioxide has been investigated[144]. Insertion into the bond occurs for alkyl derivatives, yielding the corresponding sulphinato-cobalt(III) Schiff-base compounds.

Electron transfer reactions involving alkyl group transfer between the cobalt ions bonded to quadridentate Schiff-base complexes have been studied[145].

Cobalt(III) complexes of the type $[Co^{III}(chel)(OH)(H_2O)]$, where chel is a tetradentate conjugated ligand which includes salen, have been found to react with carbon monoxide yielding[146], in the pH range 4–13, $Co^{II}(chel)$. It was assumed that formation of $[Co^{III}(chel)(COOH)(H_2O)]$ occurs by nucleophilic attack of hydroxyl ion on the intermediate $[Co^{III}(chel)(CO)(OH)]$. The carboxy derivative undergoes an elimination process giving carbon dioxide and $Co^{I}(chel)^-$, which in turn produces $Co^{II}(chel)$ by different reaction paths, depending on the pH of the solution. In alkaline solution (pH 13) the carbonyl derivative $Co^{I}(chel)(CO)$ can be isolated, while in methanol carbon monoxide is taken up to form a methoxyl carbonyl derivative $[Co(chel)(COOCH_3)(CH_3OH)]$. Mono- and di-organometallic derivatives can be prepared by the reduction of the cobalt complexes in the presence of organic halides.

The electronic spectra of planar cobalt(II) complexes are in general diagnostic of this particular stereochemistry. The first systematic study of cobalt(II) Schiff-base complexes of the planar tetradentate type[147,148] revealed an absorption in the near infrared of the visible range characteristic of the planar configuration. Similar results were obtained in other studies where solution magnetic properties were also consistent with a planar stereochemistry[149,150]. The electronic spectra of other cobalt(II) tetradentate complexes involving polymethylene bridging groups have been reported[149–151], but only Co(salen) was assigned a planar configuration about the metal on the basis of its electronic spectrum. The diffuse reflectance spectrum[149] of Co(salen) differs from the solution spectrum in that the near-infrared absorption shows a positive shift of 3100 cm^{-1} on going from the solution to the solid. Electronic and circular dichroism spectra have been measured for several optically active cobalt(II) tetradentate complexes of the type *N,N'*-(–)propylenebis(7-X-salicylideneiminato)cobalt(II) (X = CH_3–, C_6H_5–, etc.)[152]. There are ten spin-allowed *d–d* absorptions expected for one-electron transitions in planar *cis*-N_2O_2 complexes with C_{2v} symmetry, one group with seven components is expected in the visible region and a second group with three components in the near-infrared region. Although the absorption spectra in the near-infrared region contains only one asymmetric band, the circular dichroism in this region shows that the band possesses at least three components. The visible absorption spectra of these complexes possess very intense metal-to-ligand charge transfer bands starting at ca. 20,000 cm^{-1}, and these prevent the complete location and assignment of the *d–d* bands expected in this region. However, circular dichroism distinguishes some of these bands from the overlapping charge transfer absorptions.

Thus the lowest-lying visible region Co absorption at 15,500 cm^{-1} can be assigned to the $d_{xy} \to d_{x^2-y^2}$ transition. In those cases where the *d–d* bands could be clearly observed, the second band at about 17,500 cm^{-1}, which appeared to have the weakest circular dichroism, is assigned to the low-energy component of the $d_{z^2} \to d_{x^2-y^2}$ transition. The highest-energy *d–d* band observed (about 19,000 cm^{-1}) is assigned to the lower-energy component of the $d_{xz} \pm d_{yz} \to d_{x^2-y^2}$ transition. The remaining bands in the visible region are either charge transfer or intraligand in origin.

Low-spin planar cobalt(II) complexes with normal magnetic properties exhibit room temperature magnetic moments[153] in the range 2.1–2.9 B.M. No authenticated high-spin planar cobalt(II) compounds are known. Co(salen) itself, as the active form, possesses an effective magnetic moment reported as 2.24 B.M. at 300°K (ref. 154), 2.52 B.M. at 298°K (ref. 77) and 2.72 B.M. at 297°K (ref. 155). The reciprocal susceptibility of Co(salen) follows Curie–Weiss variation with temperature, and θ (Weiss constant) is reported as 20° (ref. 155) and 25° (ref. 154). A small curvature in the temperature–susceptibility plot at higher temperatures is due to the effect of a small temperature-independent paramagnetism contribution to the susceptibility. No relationship between the detailed magnetic properties of Co(salen) and its oxygenation ability has emerged.

Tetradentate Schiff-base complexes of rhodium and iridium have only recently been investigated and very little is known about their chemistry. Complexes of the form $[(CO)_2M]_2$(salen) (where M = rhodium and iridum) and $(Cod.Rh)_2$(salen) have been isolated (Cod = 1,5-cyclooctadiene)[156,157]. The geometry about the metal in these complexes is presumably planar with the salen moiety in the unusual bridging bidentate configuration.

The preparation and reduction of rhodium(III) salen complexes and the synthesis of organo-rhodium(III) derivatives of these complexes has been described. These investigations describe the preparation of the complexes Rh^{III}(salen)(Cl)(py), [py.H] [Rh^{III}(salen)Cl_2]

and the $\mathrm{Rh^{II}}$–$\mathrm{Rh^{II}}$-bonded dimer $[\mathrm{Rh(salen)py}]_2$ and their reactivities and probable structures are outlined[158]. Reduction of $\mathrm{Rh^{III}(salen)(Cl)(py)}$ with 0.2% sodium amalgam or sodium borohydride/palladium(II) chloride leads to the formation of solutions containing mono- and disodium derivatives. The disodium derivative reacts with a number of organic halides[159] to yield a series of organometallic derivatives, R–Rh(salen)py.

H. NICKEL, PALLADIUM, PLATINUM

A great deal of confusion arose in the early development of the area of chemistry concerned with nickel Schiff-base complexes, owing to the ability of the compounds, particularly bidentate complexes, to aggregate to various degrees, both in the solid state and in solution, to undergo conformational change in solution, and to coordinate additional solvent molecules. The electronic and steric factors governing the ability of nickel to increase its coordination above four have been discussed[160], and most of the work in this area has been reviewed[16,148]

Ni(salen), first reported by Dubsky and Sokol[161], and later by Pfeiffer et al.[4], has been shown to exist as centrosymmetric dimers in the solid state[162], incorporating approximately planar Ni(salen) units. The structure is unique in that of the structural analyses involving complexes of the salen ligand determined to date, this is the only example of a dimeric structure formed by direct metal–metal interactions. The nickel–nickel distance is 3.21 Å and this results in only a weak interaction, hence the diamagnetism of the complex, typical of planar nickel compounds, is retained[77,163]. The diamagnetism of Ni(salen) is also maintained in solutions of coordinating and non-coordinating solvents[164,165]

The electronic absorption spectra of planar nickel Schiff-base complexes have been the subject of several studies[166–171]. With the aid of circular dichroism, where greater resolution of bands associated with electron transitions is achieved, assignments to the observed transitions have been made[172,173]. Depending on the symmetry of the complex three or four transitions are expected within the *d*-orbital manifold of the metal ion. For optically active Schiff-base complexes of the tetradentate salen type three circular dichroism *d*–*d* bands are observed – these correspond to a single shoulder in the absorption spectra. Bands occurring in the approximate region 17,000–22,000 $\mathrm{cm^{-1}}$ have been assigned to the $d_{x^2-y^2} \leftarrow d_{xy} ({}^1B_2 \leftarrow {}^1A_1)$, $d_{z^2} \leftarrow d_{xy} ({}^1B_2 \leftarrow {}^1A_1)$, and $d_{xz} \leftarrow d_{xy} ({}^1A_1 \leftarrow {}^1A_1)$ plus $d_{yz} \leftarrow d_{xy} ({}^1B_1 \leftarrow {}^1A_1)$ transitions. The latter two transitions are observed as one band since the d_{xz} and d_{yz} orbitals are not expected to differ much in energy in these compounds[173]. For purposes of general characterisation planar complexes of nickel can be distinguished from octahedral and tetrahedral symmetries by the lack of electronic absorptions below 10,000 $\mathrm{cm^{-1}}$, a consequence of the large crystal field splitting[174].

Clarke and Odell[169] have reported the solution absorption spectrum of Ni(salen) in coordinating solvents and found both temperature-variable solid and solution magnetic properties consistent with a planar arrangement[165]. The lack of solvent coordination is thought to be due to the large ligand field[167]. The increased solvating ability found on increasing the number of bridging methylene units in the Schiff-base ligand is presumably due to a corresponding weakening of the ligand field[167]. A similar effect was noted for copper compounds, where a decline in intermolecular interactions resulted from increased ligand field strength caused by adduct formation.

Ni(salen) has been used as a neutral bidentate ligand to form binuclear and trinuclear adducts with metal halides and perchlorates respectively[32,175]. In these complexes the planarity about the nickel within the Schiff base is retained. Adducts of this type are discussed in greater detail in the following section.

Salen complexes of other metals of the nickel group have not been studied in any significant detail, although Pd(salen) has been isolated[176a], and more recently a π-allyl organometallic derivative of Pd(salen) has been prepared[176b].

The preparation of palladium(II) and platinum(II) complexes with bidentate Schiff-base ligands has been reported[177–179].

I. COPPER, SILVER, GOLD

The interest in copper Schiff-base complexes has centred around their spectral, magnetic and structural properties. The structure of Cu(salen) has been determined by X-ray diffraction methods[42,48]. These reveal a dimeric situation involving intermolecular copper–oxygen bonding interactions. The resulting stereochemistry about the copper is approximately square-pyramidal with an intermolecular copper–oxygen distance of 2.41 Å (cf. 2.25 Å in the inactive Co(salen) dimer[67,68]). A basically similar structure is found for the propylene-bridged analogue; however, in this case the apical position is occupied by an aquo oxygen atom, the copper–aquo oxygen distance[180] being 2.53 Å.

The colour isomerism of copper(II)–Schiff-base complexes has been related to the coordination number of the metal ion by Waters et al.[181,182], who proposed that the green-coloured copper(II) complexes possess an effective coordination number exceeding four, due either to intermolecular association or adduct formation with Lewis bases, whereas brown or violet complexes contain four-coordinate copper. If the deficiencies of using merely colours as opposed to assigned absorption spectra are recognised, this observation points the way to structural considerations. In practice the green complexes absorb less in the 500 mμ region and more in the 700 mμ region than do the violet or brown complexes. The rule applies in a substantial number of cases but there are a few exceptions[183,184].

The acetic acid and phenol adducts of Cu(salen), isolated by Tanaka[185], are violet in colour. This led Baker et al.[186] to suspect a mode of attachment of the acetic acid or phenol molecule by a means other than direct bonding to the metal. A structural investigation of the red *p*-nitrophenol adduct of Cu(salen) reveals a hydrogen bonding association between the phenolic and metal Schiff-base oxygen atoms[186]. This adduct is monomeric, unlike Cu(salen) itself, and essentially planar about the metal. The monomeric nature of the *p*-nitrophenol adduct contrasts with that of the analogous chloroform adduct, where weak dimeric interactions of the type found in Cu(salen) are still detectable[182]. In this adduct the intermolecular copper–oxygen distance is 2.79 Å and the chloroform molecule is also associated by means of hydrogen bonding interactions. There is no dimerisation in the comparable Co(salen) chloroform adduct[93], though other examples of hydrogen bonding to the oxygen atoms of copper complexes are known[187,188].

The reason why copper complexes such as Cu(salen) are able to engage in intermolecular interactions in various degrees, as reflected by the appropriate copper–oxygen distance (e.g. compare Cu(salen) 2.46 Å, Cu(salen)$CHCl_3$ 2.76 Å, and Cu(salen)*p*-nitrophenol ca. 3.5 Å) is thought to be related to the ligand field strength generated by the donor atoms[182,186,189]. The decline in the coordination about copper in the above complexes results from increased ligand field strengths on adduct formation, hence as the hydrogen bonding interactions increase in strength (Cu(salen)*p*-nitrophenol greater than Cu(salen)$CHCl_3$) a corresponding decrease is observed in the intermolecular interactions. Ligand field strengths have also been found to influence the ability of nickel Schiff-base complexes to engage in aggregation or solvent interactions[160]. Presumably this is quite a general phenomenon.

The structure of di-*μ*-*N,N'*-*m*-phenylenetetrakis(salicylideneiminato)dicopper(II) reveals an interesting bridging situation[190] – the Schiff-base ligand bridges two adjacent copper ions, acting as a bidentate ligand with respect to each copper. (A similar bis-bidentate bridging arrangement was found in the $[Co_2(3\text{-MeOsalen})_3]$ complex previously discussed.) This copper complex also contains chloroform molecules that are probably hydrogen bonded to the Schiff-base phenolic oxygens, but the interactions are so weak that an alternative packing argument is equally applicable in explaining their presence.

The donor bonding properties of the phenolic oxygen atoms in Cu(salen) have been extensively studied by Gruber, Harris, Sinn, and others[32,175,191–199]. The metal Schiff-base complex has been found to act as a neutral bidentate ligand towards metal halides and perchlorates, forming both homo- and hetero-binuclear and trinuclear adducts. These complexes are represented as Cu(salen)MX_2 (X = halide) and $[Cu(salen)]_2M(ClO_4)_2$ (where M may be copper or another metal). The Schiff-base complex is not restricted to Cu(salen), but may also be the nickel or vanadyl complex[23,175] or alternatively, the Schiff-base ligand itself may be varied[32]. When both metals in the adduct system are paramagnetic, interesting magnetic properties arise due to antiferromagnetic interactions between the metals. Adduct formation occurs via donor bonds from the Schiff-base oxygens to the metal halide or perchlorate. The Cu(salen) adducts with copper halides are binuclear and as such their temperature-dependent susceptibilities follow the Bleaney–Bowers expression for pair-wise antiferromagnetic interactions[32,175,192,195]. The exchange integral (J) and the average g values for adducts of copper Schiff bases and copper halides have been determined using this expression and are found to vary over the range $-49\ cm^{-1}$ to $-255\ cm^{-1}$ and 2.05 to 2.36 for J and g respectively[32]. Similarly, antiferromagnetic interactions have been observed in the trinuclear complexes involving copper Schiff bases and paramagnetic perchlorates. The magnetic properties of these complexes have been interpreted by positioning the metals at the corners of an isosceles triangle. Exchange interactions occur only through the central metal in accordance with the direction of bonding from the Schiff-base complexes[32,175].

The electronic spectral properties of the copper Schiff-base complexes and their adducts reveal that as the environment about the copper ion is increasingly distorted from planar to tetrahedral, a corresponding decrease to lower energies is observed in the main ligand field absorption band[32,175]. For example, the adduct Cu(salen)CuCl$_2$ possesses absorptions characteristic of both planar (18,700 cm^{-1}) and approximately tetrahedral (10,700 cm^{-1}) copper environments.

The basic structures proposed for the binuclear adducts Cu(salen)CuCl$_2$ and Cu(salpn)CuCl$_2$ (Cu(salpn) = *N,N'*-propylenebis(salicylideneiminato)copper(II)), on the basis of their spectral and magnetic properties, have been confirmed by recent structural determinations[200]. The copper Schiff-base compounds act as neutral bidentate ligands towards the copper chloride acceptor, utilising donor bonds through the phenolic oxygen atoms (Fig. 10). The Cu(salen)CuCl$_2$ complex was predicted to possess a pseudo-tetrahedral environment about the acceptor copper ion[192]. In fact, the situation is closer to a square-pyramidal arrangement owing to a bonding interaction with one of the chlorides on an adjacent molecule. This produces a polymeric arrangement involving chloride bridges between copper ions. The suggestion that adduct formation of this type results in a more planar arrangement about the copper ion within the Schiff base is also verified by the structure determination[200]. Halide bridging is not present in the analogous Cu(salpn) adduct.

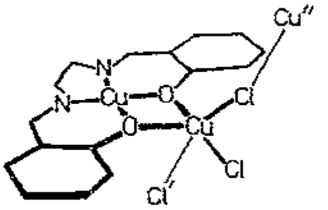

Fig. 10. Structure of Cu(salen)CuCl$_2$.

The structure of the adduct [Cu(salen)]$_2$NaClO$_4$(C$_8$H$_8$) (C$_8$H$_8$ = *p*-xylene)[201] reveals an arrangement of the type suggested for the trinuclear adducts, involving planar Schiff-base complexes as neutral ligands[175]. The sodium ion is surrounded approximately octahedrally by oxygen atoms, two from the chelating perchlorate ion (sodium–oxygen distance 2.6 Å), and four from two chelating Cu(salen) units acting as bidentate ligands (sodium–oxygen distance 2.3 Å) (Fig. 11). Other examples of planar copper Schiff-base complexes acting as neutral ligands are known[199].

Other investigations of the Lewis base properties of transition metal ion Schiff-base complexes have shown that M^{II}–salen complexes where the metal ion is cobalt(II), nickel(II) or copper(II) react with the halides SnX$_4$ and SnX$_2$ (where X = Cl or Br) to form 1:1 adducts. Characterisation of these adducts using magnetic data and diffuse reflectance and infra-red spectroscopy indicated a retention of planarity about the transition metal ion and that adduct formation involves *cis*-addition to SnX$_4$. In polar solvents the cobalt(II)-(salen)SnX$_4$ adduct was found to undergo an exchange reaction[202] to produce Sn(salen)X$_2$

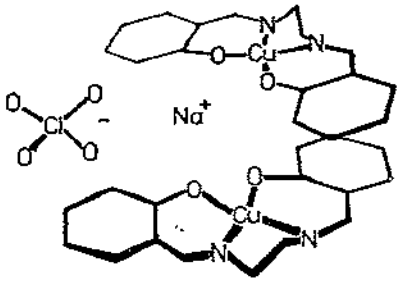

Fig. 11. Structure of $[Cu(salen)]_2NaClO_4$.

Reaction of $SbCl_3$, $SbBr_3$ and $SbCl_5$ with M(salen) complexes, where M is cobalt(II), nickel(II) or copper(II), also leads to the formation of adducts in which the planarity about the transition metal is retained. To clarify the question of local symmetry about the acceptor metal in such adducts, substitution products of the form Ni(salen)M′$(CO)_4$ (where M′ = Mo, W), Ni(salen)Mn$(CO)_3$X (X = Cl, Br), and Ni(amben)Mn$(CO)_3$X (Ni(amben) = *N,N′*-ethylenebis(*o*-aminobenzylideneiminato)nickel(II) were isolated. The infra-red spectra of these compounds over the carbonyl region were used to assign structures to these complexes[203]. M(salen) complexes where the metal ion is cobalt(II), nickel(II) or copper(II) react with the halides InX_3 (where X = Cl or Br) to form 1:1 adducts. The reaction of Ni(salen) with the halides GaX_3 (where X = Cl or Br) results in the formation of a 1:1 adduct whose structure, it is proposed, is best represented as $GaX_2\ [Ni^{II}(salen)]_2{}^+GaCl_4{}^-$. It was found that the reaction of indium(III) and gallium(III) halides with $Fe^{III}(salen)_2O$ leads, in the majority of cases, to products arising from halide exchange reactions. However, in the reaction of $InBr_3$ with $Fe^{III}(salen)_2O$, a product formulated as $Fe^{III}(salen)OInBr_2$ has been isolated[204].

Reaction of phosphorus trichloride and arsenic trichloride with M(salen) complexes, where M = cobalt(II), nickel(II) or copper(II), yields cyclic products. These systems have been characterised by magnetic measurements, ultra-violet and infra-red spectroscopy. The reaction products involve tetrahedral cobalt and copper(II) and octahedral nickel environments. The $Cu^{II}(salen)PCl_3$ adduct exhibits a non-linear variation of reciprocal susceptibility with temperature attributed to the presence of an antiferromagnetic spin-quenching mechanism. Good agreement between observed and calculated susceptibilities was obtained[205] using a linear chain model, i.e. chains of copper(II) ions interacting equally with neighbouring copper(II) ions throughout the lattice with $g = 2.11$ and $J = -55\ cm^{-1}$.

The temperature variation in the reciprocal susceptibility of Cu(salen) is reported to obey the Curie–Weiss law[192,206] and to indicate the absence of antiferromagnetic interactions between the metal centres despite the known dimeric nature of this compound[42,48]. This is suggested to result from the copper–oxygen bond lengths and angles involved. The magnetic properties determined by these workers, viz. magnetic moments of 1.84 B.M.[206] and 1.90 B.M.[183] with $\theta = 4°$ and $-13.5°$ respectively, differ from those of other workers who report magnetic moments close to 2.0 B.M.[77,207]. The solution ESR spectrum of this complex indicates appreciable dissociation of the dimeric units, as determined from the relative intensities of the doublet spectrum arising from the monomeric form, and the triplet spectrum from the dimeric species. The observation of ESR signals attributable to transitions within the triplet state in both the solution and solid (as the pure and doped powders) indicates the presence of magnetic exchange. The exchange present is so weak, however, that the exchange integral is thought to be quite low[207] and possibly[208] less than $-10\ \text{cm}^{-1}$.

In a recent electron spin resonance study of the dimeric form of some tetradentate copper(II) Schiff-base complexes, the observation of low-field lines at 77°K was attributed to $\Delta M = \pm 2$ transitions arising from the triplet state due to magnetic dipole–dipole interactions occurring between copper(II) ions in dimeric forms of these complexes which exist in frozen solution[209]. The salient features of the spectra were accounted for by a set of magnetic parameters obtained by consideration of a spin Hamiltonian which involves the angular dependence of the zero-field splitting term. The results obtained for the internuclear separation of the copper(II) ions agree well with that obtained from crystallographic data. The ESR spectra of copper(II) and oxo-vanadium(IV) complexes with quadridentate Schiff bases in nematic glasses have been studied[210]. The anisotropic ESR parameters obtained compare favourably with published values obtained by single-crystal procedures.

The electronic spectra of Cu(salen) and similar tetradentate Schiff-base complexes have been the subject of a number of investigations[168,175,181,206,211–219]. Comparison of tetradentate *trans*-planar and *cis*-planar systems reveals spectra similar in appearance but differing in intensities. *Trans* complexes possess absorptions with intensities approximately an order of magnitude less than the *cis* complexes. The greater intensity of absorptions of the latter are thought to reflect the electronic contribution to the now electronically allowed transition[213]. For copper(II) ions, theory predicts that three or four transitions should occur within the 3*d* orbital manifold, depending on the symmetry involved[213,219]. In most cases the spectra of planar copper(II) complexes possess only a single broad band, making assignment of individual electronic transitions difficult. Circular dichroism spectra of optically active tetradentate copper complexes have been applied to the problem of assigning transitions[219]. Circular dichroism indicates the presence of three transitions. These have been assigned to $d_{z^2} \leftarrow d_{xy}$, $d_{x^2-y^2} \leftarrow d_{xy}$, and tentatively $d_{xz} \leftarrow d_{xy}$, in order of increasing energy and under C_2 symmetry. The variation in the energy of the ligand field absorption band observed on changing a planar environment about copper to an approximately tetrahedral arrangement has already been discussed.

Silver and gold Schiff-base complexes have received very little attention, although gold compounds of the form [Au(salen)] AuCl_2 and similar complexes have been reported[220,221].

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The fully occupied *d*-orbital levels in the zinc group Schiff-base complexes result in simplified physical and chemical properties for these compounds. This has been used in electronic spectral assignment studies where the absence of electronic transitions within the metal orbitals has allowed the detection of absorptions due to ligand and charge-transfer transitions[156,168,172]. The near ultra-violet absorption spectrum and the associated circular dichroism of *N,N'*-(–)propylenebis(salicylideneiminato)zinc(II), and that of the ligand itself, have been used in the assignment of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in this region[172].

The $\pi \rightarrow \pi^*$ transition in the zinc complex (ca. 28.7 kK) contains two components. The nearly equal magnitudes of the positive and negative circular dichroism of this transition suggest the presence of exciton interactions..

The solid-state structure of Zn(salen), as the monohydrate, reveals a typical, almost planar, ligand arrangement with square-pyramidal stereochemistry about the metal. The water molecule occupies the apical position[222]. The complex Cd(salen) also appears to possess a planar arrangement, as determined from X-ray diffraction powder studies[176], whereas a tetrahedral stereochemistry about the metal is thought likely for Hg(salen), although polymeric aggregation cannot be ruled out[223].

REFERENCES

1 C. Ettling, *Ann. Chem. Pharm.*, 35 (1840) 241.
2 H. Schiff, *Ann. Chem. Pharm., Suppl.*, 3 (1864) 343.
3 P. Pfeiffer, E. Bucholz and O. Bauer, *J. Prakt. Chem.*, 129 (1931) 163.
4 P. Pfeiffer, E. Breith, E. Lübbe and T. Tsumaki, *Justus Liebigs Ann. Chem.*, 503 (1933) 84.
5 P. Pfeiffer and H. Pfitzinger, *J. Prakt. Chem.*, 145 (1936) 243.
6 P. Pfeiffer, T. Hesse, H. Pfitzinger, W. Scholl and T. Thielert, *J. Prakt. Chem.*, 149 (1937) 217.
7 P. Pfeiffer and H. Thielert, *Ber. Deut. Chem. Ges. B*, (1938) 119.
8 P. Pfeiffer, W. Christeleit, T. Hesse, H. Pfitzinger and H. Thielert, *J. Prakt. Chem.*, 150 (1938) 261.
9 H. Thielert and P. Pfeiffer, *Ber. Deut. Chem. Ges. B*, 71 (1938) 1399.
10 P. Pfeiffer, H. Thielert and H. Glaser, *J. Prakt. Chem.*, 152 (1939) 145.
11 P. Pfeiffer and H. Glaser, *J. Prakt. Chem.*, 153 (1939) 265.
12 P. Pfeiffer and H. Krebs, *J. Prakt. Chem.*, 155 (1940) 77.
13 P. Pfeiffer, *Angew. Chem.*, 53 (1940) 93.
14 P. Pfeiffer and S. Saure, *Ber. Deut. Chem. Ges. B*, 74 (1941) 935.
15 P. Pfeiffer, W. Offermann and H. Werner, *J. Prakt. Chem*, 159 (1942) 313.
16 R.H. Holm, G.W. Everett, Jr. and A. Chakravarty, *Progr. Inorg. Chem.*, 7 (1966) 83.
17 N.S. Biradar and V.H. Kulkarni, *Rev. Roum. Chim.*, 15 (1970) 1993.
18 Y.-W. Chuang, I.A. Savich, A.V. Lapitskii, V.R. Samorukou and L.G. Titov, *Vestn. Mosk. Univ., Khim.*, 15 (1960) 40.
19 A.V. Lapitskii, Y.-W. Chuang and I.A. Savich, *Russ. J. Inorg. Chem.*, 6 (1961) 333.
20 N.S. Biradar and V.H. Kulkarni, *J. Inorg. Nucl. Chem.*, 23 (1971) 3847.
21 S.R. Gupta and J.P. Tandon, *Z. Naturforsch. B*, 25 (1970) 1231.
22 E. Bayer, H.J. Bielig and K.H. Hausser, *Justus Liebigs Ann. Chem.*, 584 (1953) 116.
23 J. Selbin and L. Ganguly, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 815.
24 L.J. Boucher and T.F. Yen, *Inorg. Chem.*, 8 (1969) 689.
25 J. Selbin, *Chem. Rev.*, 65 (1965) 153.
26 R.L. Dutta and G.P. Sengupta, *J. Indian Chem. Soc.*, 48 (1971) 33.
27 R.L. Farmer and F.L. Urbach, *Inorg. Chem.*, 9 (1970) 2562.
28 L.J. Boucher, D.E. Bruins, T.F. Yen and D.L. Weaver, *J. Chem. Soc. D*, (1969) 363.
29 D. Bruins and D.L. Weaver, *Inorg. Chem.*, 9 (1970) 130.
30 M. Mathew, A.J. Carty and G.J. Palenik, *J. Amer. Chem. Soc.*, 92 (1970) 3197.
31 D.M.L. Goodgame and S.U. Wagget, *Inorg. Chim. Acta*, 5 (1971) 155.
32 E. Sinn and C.M. Harris, *Coord. Chem. Rev.*, 4 (1969) 391.

33 J.H. Swinehart, *Chem. Commun.*, (1971) 1443.
34 D.J. Machin and J.F. Sullivan, *J. Less-Common Metals*, 19 (1969) 413.
35 P. Coggon, A.T. McPhail, F.E. Mabbs, A. Richards and A.S. Thornley, *J. Chem. Soc. A*, (1970) 3296.
36 S. Yamada and K. Iwasaki, *Bull. Chem. Soc. Jap.*, 42 (1969) 1463; *Inorg. Chim. Acta*, 5 (1971) 3.
37 M.J. O'Connor and B.O. West, *Aust. J. Chem.*, 21 (1968) 369.
38 A. van den Bergen, K.S. Murray and B.O. West, *Aust. J. Chem.*, 25 (1972) 705.
39 A. Earnshaw, E.A. King and L.F. Larkworthy, *J. Chem. Soc. A*, (1968) 1048.
40 R.W. Asmussen and H. Soling, *Acta Chem. Scand.*, 11 (1957) 1331.
41 J. Lewis, F.E. Mabbs and H. Weigold, *J. Chem. Soc. A*, (1968) 1699.
42 D. Hall and T.N. Waters, *J. Chem. Soc., London*, (1960) 2644.
43 K. Pachler and M.V. Stackleberg, *Z. Anorg. Allg. Chem.*, 305 (1960) 286.
44 A. van den Bergen, K.S. Murray, M.J. O'Connor and B.O. West, *Aust. J. Chem.*, 22 (1969) 39.
45 M. Gerloch, J. Lewis, F.E. Mabbs and A. Richards, *J. Chem. Soc. A*, (1968) 112.
46 C.C. Patel and C.P. Prabhakaran, *J. Inorg. Nucl. Chem.*, 31 (1969) 3316.
47 T. Yarino, T. Matsushita, I. Masuda and K. Shinra, *J. Chem. Soc. D*, (1970) 1317.
48 R. Dingle, *Acta Chem. Scand.*, 20 (1966) 33.
49 G.L. Johnson and W.D. Beveridge, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 323.
50 F. Calderazzo, C. Floriani, R. Hengi and F. l'Eplattenier, *J. Chem. Soc. A*, (1969) 1378.
51 E. Fluck, in V.I. Gol'danskii and R.H. Herber (Eds.), *Chemical Applications of Mössbauer Spectra*, Academic Press, New York, 1968, Chap. 4, p. 286.
52 J.L.K.F. De Vries, J.M. Trooster and E. De Boer, *J. Chem. Soc. D*, (1970) 605.
53 A. Earnshaw, E.A. King and L.F. Larkworthy, *J. Chem. Soc. A*, (1969) 2459.
54 W. Klemm and K.H. Raddatz, *Z. Anorg. Chem.*, 250 (1942) 207.
55 L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, 65 (1943) 481.
56 J. Lewis, F.E. Mabbs and A. Richards, *J. Chem. Soc. A*, (1967) 1014.
57 J. Lewis, F.E. Mabbs and A. Richards, *Nature*, 207 (1965) 855.
58 W.M. Reiff, G.J. Long and W.A. Baker, Jr., *J. Amer. Chem. Soc.*, 90 (1968) 6347.
59 W.M. Reiff, W.A. Baker, Jr. and W.E. Erickson, *J. Amer. Chem. Soc.*, 90 (1968) 4794.
60 M. Gerloch, E.D. McKenzie and A.D.C. Towl, *J. Chem. Soc. A*, (1969) 2850.
61 P. Coggon, A.T. McPhail, F.E. Mabbs and V.N. McLachlan, *J. Chem. Soc. A*, (1971) 1014.
62 P.D.W. Boyd and T.D. Smith, *Inorg. Chem.*, 10 (1971) 2041.
63 P.D.W. Boyd and K.S. Murray, *J. Chem. Soc. A*, (1971) 2711.
64 G.M. Bancroft, A.G. Maddock and R.P. Randl, *J. Chem. Soc. A*, (1968) 2939.
65 M. Gerloch and F.E. Mabbs, *J. Chem. Soc. A*, (1967) 1900.
66 M. Gerloch, J. Lewis, F.E. Mabbs and A. Richards, *Nature*, 212 (1966) 809.
67 S. Bruckner, M. Calligaris, G. Nardin and L. Randaccio, *Acta Crystallogr., Sect. B*, 25 (1969) 1671.
68 R. De Isasi, S.L. Holt and B. Post, *Inorg. Chem.*, 10 (1971) 1498.
69 M. Gerloch and F.E. Mabbs, *J. Chem. Soc. A*, (1967) 1598.
70 F. Calderazzo and C. Floriani, *Chem. Commun.*, (1968) 417; *J. Chem. Soc. A*, (1971) 3665.
71 A. van den Bergen, K.S. Murray, B.O. West and A.N. Buckley, *J. Chem. Soc. A*, (1969) 2051.
72 A.N. Buckley, K.S. Murray and G.V.H. Wilson, *Solid State Commun.*, 7 (1969) 471.
73 T. Tsumaki, *Bull. Chem. Soc. Jap.*, 13 (1938) 252.
74 M. Calvin, R.H. Bailes and W.K. Wilmarth, *J. Amer. Chem. Soc.*, 68 (1946) 2254.
75 C.H. Barkelew and M. Calvin, *J. Amer. Chem. Soc.*, (1946) 2257.
76 W.K. Wilmarth, S. Aranoff and M. Calvin, *J. Amer. Chem. Soc.*, 68 (1946) 2263.
77 M. Calvin and C.H. Barkelew, *J. Amer. Chem. Soc.*, 68 (1946) 2257.
78 E.W. Hughes, W.K. Wilmarth and M. Calvin, *J. Amer. Chem. Soc.*, 68 (1946) 2273.
79 O.L. Harle and M. Calvin, *J. Amer. Chem. Soc.*, 68 (1946) 2612.
80 R.H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 69 (1947) 1886.
81 H. Diehl, *Iowa State Coll. J. Sci.*, 21 (1947) 271.
82 H. Diehl, R.J. Brouns, G.C. Harrison and L.M. Liggett, *Iowa State Coll. J. Sci.*, 21 (1947) 335.
83 H. Diehl, C.C. Hach, G.C. Harrison and L.M. Liggett, *Iowa State Coll. J. Sci.*, 21 (1947) 278.
84 H. Diehl, C.C. Hach, G.C. Harrison and L.M. Liggett, *Iowa State Coll. J. Sci.*, 21 (1947) 287.
85 H. Diehl and L.M. Liggett, *Iowa State Coll. J. Sci.*, 21 (1947) 326.

86 H. Diehl, L.M. Liggett, G.C. Harrison, C.C. Hach and R. Curtis, *Iowa State Coll. J. Sci.*, 22 (1947) 91.

87 H. Diehl, L.M. Liggett, C.C. Hach, G.C. Harrison, L. Henselmeier, R. Schwandt and J. Mathews, Jr., *Iowa State Coll. J. Sci.*, 22 (1947) 110.

88 H. Diehl and T.S. Chao, *Iowa State Coll. J. Sci.*, 22 (1947) 126.

89 H. Diehl, R.J. Brouns, G.C. Harrison and L.M. Liggett, *Iowa State Coll. J. Sci.*, 22 (1948) 129.

90 H. Diehl, C.C. Hach, G.C. Harrison, L.M. Liggett and R.J. Brouns, *Iowa State Coll. J. Sci.*, 22 (1948) 150.

91 H. Diehl and J. Henn, *Iowa State Coll. J. Sci.*, 23 (1949) 273.

92 A.E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, Englewood Cliffs, N.J., U.S.A., 1952.

93 W.P. Schaefer and R.E. Marsh, *Acta Crystallogr., Sect. B*, 25 (1969) 1675.

94 S. Katagari and J. Endo, *J. Chem. Soc. Jap.*, 84 (1963) 197.

95 L. Rampazzo, P. Silvestroni and A. Trazz, *Ric. Sci.*, 37 (1967) 648.

96 C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, (1969) 946; F. Calderazzo, C. Floriani and J.-J. Salzmann, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 379.

97 A.L. Crumbliss and F. Basolo, *Science*, 164 (1969) 1168; *J. Amer. Chem. Soc.*, 92 (1970) 55.

98 M. Calligaris, G. Nardin, L. Randaccio and A. Ripamonti, *J. Chem. Soc. A*, (1970) 1069; M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc. D*, (1969) 763.

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

100 H.A.O. Hill, K.G. Morallee, G. Pellizer, G. Mestroni and G. Costa, *J. Organometal. Chem.*, 11 (1968) 167; H.A.O. Hill, K.G. Morallee and G. Pellizer, *J. Chem. Soc. A*, (1969) 2096.

101 M. Cesari, C. Neri, G. Perego, E. Perrotti and A. Zazzetta, *J. Chem. Soc. D*, (1970) 276.

102 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Acta Rev.*, 4 (1970) 41.

103 G. Costa, G. Mestroni, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc. A*, (1970) 2870.

104 G. Costa, A. Puxeddu and E. Reisenhofer, *Collect. Czech. Chem. Commun.*, 36 (1971) 1065.

105 G. Costa, A. Puxeddu and L. Stefani, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 191.

106 G.N. Schrauzer and L.P. Lee, *J. Amer. Chem. Soc.*, 92 (1970) 1551.

107 B.R. Hoffman, D.L. Diemente and F. Basolo, *J. Amer. Chem. Soc.*, 92 (1970) 61.

108 C. Busetto, C. Neri, N. Palladino and E. Perrotti, *Inorg. Chim. Acta*, 5 (1971) 129.

109 S.A. Cockle, H.A.O. Hill, J.M. Pratt and R.J.P. Williams, *Biochim. Biophys. Acta*, 177 (1969) 686.

110 J.H. Bayston, N.K. King, F.O. Looney and M.E. Winfield, *J. Amer. Chem. Soc.*, 91 (1969) 2775.

111 S.A. Cockle, H.A.O. Hill and R.J.P. Williams, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 131.

112 A. Misono, S. Koda and Y. Uchida, *Bull. Chem. Soc. Jap.*, 42 (1969) 3470; A. Misono and S. Koda, *Bull. Chem. Soc. Jap.*, 42 (1969) 3048.

113 M. Green and D. Mettrick, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 149.

114 L.H. Vogt, H.M. Faigenbaum and S.E. Wiberly, *Chem. Rev.*, 63 (1963) 269.

115 E. Bayer and P. Schretzmann, *Struct. Bonding (Berlin)*, 2 (1967) 181.

116 A. Earnshaw, P.C. Hewlett and L.F. Larkworthy, *J. Chem. Soc., London*, (1965) 4718.

117 A. Earnshaw, E.A. King and L.F. Larkworthy, *J. Chem. Soc., London*, (1968) 1048.

118 G.M. Bancroft, M.J. Mays and B.E. Prater, *J. Chem. Soc. D*, (1969) 39.

119 C. Floriani, M. Puppis and F. Calderazzo, *J. Organometal. Chem.*, 12 (1968) 209.

120 M. Tamaki, I. Masuda and K. Shinra, *Bull. Chem. Soc. Jap.*, 42 (1969) 2858.

121 M. Tamaki, I. Masuda and K. Shinra, *Bull. Chem. Soc. Jap.*, 42 (1969) 157.

122 M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc. D*, (1969) 1248.

123 M. Calligaris, G. Mangini, G. Nardin and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, (1972) 543.

124 A. van den Bergen, R.J. Cozens and K.S. Murray, *J. Chem. Soc. A*, (1970) 3060.

125 N.A. Bailey, B.M. Higson and E.D. McKenzie, *J. Chem. Soc., Dalton Trans.*, (1972) 503.

126 S.N. Poddar and D.K. Biswas, *J. Inorg. Nucl. Chem.*, 31 (1969) 565.

127 R.J. Cozens and K.S. Murray, *Aust. J. Chem.*, 25 (1972) 911.

128 N.K. Dutt and K. Nag, *J. Inorg. Nucl. Chem.*, 30 (1968) 2493, 2779.

129 A recent communication reports the isolation of compounds of the type $[Ln_2(salen)_3]$ with physical properties differing from those previously reported[117]. See S. Yamada, K. Youmanochi and H. Kuma, *Bull. Chem. Soc. Jap.*, 44 (1971) 1448.

130 M. Calligaris, G. Nardin and L. Randaccio, *J. Chem. Soc. D*, (1970) 1079.
131 N.A. Bailey, B.M. Higson and E.D. McKenzie, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 591.
132 F. Calderazzo and C. Floriani, *J. Chem. Soc. D*, (1967) 139.
133 G. Costa and G. Mestroni, *Tetrahedron Lett.*, (1967) 1783.
134 G. Costa, G. Mestroni and L. Stefani, *J. Organometal. Chem.*, 7 (1967) 943.
135 G.N. Schrauzer and J. Kohale, *Chem. Ber.*, 97 (1964) 3056.
136 G. Costa, G. Mestroni, G. Tauzher and L. Stefani, *J. Organometal. Chem.*, 6 (1966) 181.
137 A. van den Bergen, K.S. Murray and B.O. West, *J. Organometal. Chem.*, 33 (1971) 89.
138 D. Crowfoot-Hodgkin, *Proc. Roy. Soc., Ser. A*, 288 (1965) 294.
139 G.N. Schrauzer, *Accounts Chem. Res.*, 1 (1968) 97.
140 M. Calligaris, D. Minichelli, G. Nardin and L. Randaccio, *J. Chem. Soc. A*, (1971) 2720.
141 M. Green, J. Smith and P.A. Tasker, *Discuss. Faraday Soc.*, 47 (1969) 172.
142 W. Mowat, A. Shortland, G. Yagupsky, N.J. Hill, M. Yagupsky and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1972) 533.
143 P.S. Braterman and R.J. Cross, *J. Chem. Soc., Dalton Trans.*, (1972) 657.
144 R.J. Cozens, G.B. Deacon, P.W. Felder, K.S. Murray and B.O. West, *Aust. J. Chem.*, 23 (1970) 481.
145 A. van den Bergen and B.O. West, *Chem. Commun.*, (1971) 52.
146 G. Costa, G. Mestroni and G. Tauzher, *J. Chem. Soc., Dalton Trans.*, (1972) 450.
147 H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jap.*, 37 (1964) 8.
148 S. Yamada, *Coord. Chem. Rev.*, 1 (1966) 415.
149 H. Weigold and B.O. West, *J. Chem. Soc. A*, (1967) 1310.
150 J. Manassen, *Inorg. Chem.*, 9 (1970) 966.
151 M. Hariharan and F.L. Urbach, *Inorg. Chem.*, 8 (1969) 556.
152 C.J. Hipp and W.A. Baker, Jr., *J. Amer. Chem. Soc.*, 92 (1970) 792.
153 E. Kent Barefield, D.H. Busch and S M. Nelson, *Quart. Rev., Chem. Soc.*, 22 (1968) 457.
154 B.N. Figgis and R.S. Nyholm, *J. Chem. Soc., London*, (1959) 338.
155 A. Earnshaw, P.C. Hewlett, E.A. King and L.F. Larkworthy, *J. Chem. Soc. A*, (1968) 241.
156 R.J. Cozens, K.S. Murray and B.O. West, *Aust. J. Chem.*, 23 (1970) 683.
157 R.J. Cozens, K.S. Murray and B.O. West, *J. Organometal. Chem.*, 27 (1971) 399.
158 R.J. Cozens, K.S. Murray and B.O. West, *J. Organometal. Chem.*, (1972) in press.
159 R.J. Cozens, K.S. Murray and B.O. West, *Chem. Commun.*, (1970) 1262.
160 S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, K. Yamanouchi and K. Iwasaki, *Coord. Chem. Rev.*, 3 (1968) 247.
161 J.V. Dubsky and A. Sokol, *Collect. Czech. Chem. Commun.*, 3 (1931) 548.
162 L.M. Shkol'nikova, E.M. Yumal', E.A. Shugam and V.A. Voblikova, *J. Struct. Chem. (USSR)*, 11 (1970) 819.
163 D.P. Mellor and D.P. Craig, *J. Proc. Roy. Soc. N.S.W.*, 74 (1940) 475.
164 J.P. Willis and D.P. Mellor, *J. Amer. Chem. Soc.*, 69 (1947) 1237.
165 H.C. Clark and A.L. Odell, *J. Chem. Soc., London*, (1955) 3431.
166 G. Maki, *J. Chem. Phys.*, 28 (1958) 651; *J. Chem. Phys.*, 29 (1958) 1129.
167 R.H. Holm, *J. Amer. Chem. Soc.*, 82 (1960) 5632.
168 S.M. Crawford, *Spectrochim. Acta*, 19 (1963) 255.
169 H.C. Clark and A.L. Odell, *J. Chem. Soc., London*, (1956) 520.
170 R.L. Belford and T.S. Piper, *Mol. Phys.*, 5 (1962) 251.
171 J. Ferguson, *J. Chem. Phys.*, 34 (1961) 611.
172 B. Bosnich, *J. Amer. Chem. Soc.*, 90 (1968) 627.
173 R.S. Downing and F.L. Urbach, *J. Amer. Chem. Soc.*, 92 (1970) 5861.
174 A.B.P. Lever, in M.F. Lappert (Ed.), *Inorganic Electronic Spectroscopy*, Monogr. 1, Elsevier, Amsterdam, 1968.
175 S.J. Gruber, C.M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, 30 (1968) 1805.
176 (a) L.M. Shkol'nikova, E.A. Shugam and L.G. Makarevich, *Zh. Strukt. Khim.*, 4 (1963) 927.
(b) B.E. Reichert and B.O. West, *J. Organometal. Chem.*, 36 (1972) C29.
177 S. Yamada, H. Nishikawa and K. Yamasaki, *Bull. Chem. Soc. Jap.*, 36 (1963) 483.
178 S. Yamada and E. Yoshida, *Bull. Chem. Soc. Jap.*, 38 (1965) 2179.

179 S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Jap.*, 42 (1969) 2543.
180 F.J. Llewellyn and T.N. Waters, *J. Chem. Soc., London*, (1960) 2639.
181 T.N. Waters and D. Hall, *J. Chem. Soc., London*, (1959) 1200, 1203.
182 E.N. Baker, D. Hall and T.N. Waters, *J. Chem. Soc. A*, (1970) 406.
183 J.M. Stewart and E.C. Lingafelter, *Acta Crystallogr.*, 12 (1959) 842.
184 D. Hall, A.D. Rae and T.N. Waters, *Proc. Chem. Soc., London*, (1962) 143; *J. Chem. Soc., London*, (1963) 5897.
185 T. Tanaka, *Bull. Chem. Soc. Jap.*, 29 (1956) 93.
186 E.N. Baker, D. Hall and T.N. Waters, *J. Chem. Soc. A*, (1970) 400.
187 C.A. Bear, J.M. Waters and T.N. Waters, *J. Chem. Soc. A*, (1970) 2494; G.R. Clark, D. Hall and T.N. Waters, *J. Chem. Soc. A*, (1968) 223; E.N. Baker, D. Hall and T.N. Waters, *J. Chem. Soc. A*, (1970) 396.
188 E. Sinn, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 811.
189 H.C. Freeman, in J. Peisach, P. Aisen and W.E. Blumberg (Eds.), *The Biochemistry of Copper*, Academic Press, New York, 1966.
190 C.A. Bear, J.M. Waters and T.N. Waters, *J. Chem. Soc. A*, (1970) 2494.
191 S.J. Gruber, C.M. Harris and E. Sinn, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 495.
192 S.J. Gruber, C.M. Harris and E. Sinn, *Inorg. Chem.*, 7 (1968) 268.
193 C.M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, 30 (1968) 2725.
194 C.M. Harris, J.M. James, P.J. Milham and E. Sinn, *Inorg. Chim. Acta*, 3 (1969) 81.
195 R.B. Coles, C.M. Harris and E. Sinn, *Inorg. Chem.*, 8 (1969) 2607.
196 S.J. Gruber, C.M. Harris and E. Sinn, *J. Chem. Phys.*, 49 (1968) 2183.
197 S.J. Gruber, C.M. Harris and E. Sinn, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 107.
198 R.B. Coles, C.M. Harris and E. Sinn, *Aust. J. Chem.*, 23 (1970) 243.
199 M. Kato, Y. Muto, H.B. Jonassen, K. Imai and T. Tokii, *Bull. Chem. Soc. Jap.*, 43 (1970) 1066.
200 C.H. Bear, J.M. Waters and T.N. Waters, *J. Chem. Soc. D*, (1971) 703.
201 G.H.W. Milburn, M.R. Truter and B.L. Vickery, *J. Chem. Soc. D*, (1968) 1188.
202 M.D. Hobday and T.D. Smith, *J. Chem. Soc. A*, (1971) 1453.
203 M.D. Hobday and T.D. Smith, *J. Chem. Soc. A*, (1971) 3424.
204 M.D. Hobday and T.D. Smith, *J. Chem. Soc., Dalton Trans.*, (1972), in press.
205 M.D. Hobday and T.D. Smith, *J. Chem. Soc. A*, (1970) 1085.
206 J. Lewis and R.A. Walton, *J. Chem. Soc. A*, (1966) 1559.
207 G.O. Carlisle and W.E. Halfield, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 633.
208 E. Sinn, *Inorg. Chem.*, 9 (1970) 2376.
209 T.D. Smith, P.D.W. Boyd, A.D. Toy, M.D. Hobday and J.R. Pilbrow, *J. Chem. Soc., Dalton Trans.*, (1972), in press.
210 J.P. Fackler, J.D. Levy and J.A. Smith, *J. Amer. Chem. Soc.*, 94 (1972) 2436.
211 J. Ferguson, *J. Chem. Phys.*, (1961) 2206.
212 R.L. Belford and T.S. Piper, *Mol. Phys.*, 5 (1962) 251.
213 R.L. Belford and W.A. Yeramos, *Mol. Phys.*, 6 (1963) 121.
214 T. Tsumaki, *Bull. Chem. Soc. Jap.*, 13 (1938) 583.
215 R.S. Downing and F.L Urbach, *J. Amer. Chem. Soc.*, 90 (1968) 5344.
216 J.M. Waters and T.N. Waters, *J. Chem. Soc.*, (1964) 2489.
217 J. Stankowski, S. Hoffmann and I. Stronski, *Acta Phys. Pol. A*, 37 (1970) 855.
218 R.H. Holm, *J. Amer. Chem. Soc.*, 82 (1960) 5632.
219 R.S. Downing and F.L. Urbach, *J. Amer. Chem. Soc.*, 91 (1969) 5977.
220 T. Inazu, *Bull. Chem. Soc. Jap.*, 39 (1966) 1065.
221 S. Yamada and K. Yamanouchi, *Bull. Chem. Soc. Jap.*, 43 (1970) 1744.
222 D. Hall and F.H. Moore, *J. Chem. Soc. A*, (1966) 1822.
223 S.N. Poddar and K. Day, *J. Indian Chem. Soc.*, 47 (1970) 909.