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Advancement in stereochemical aspects of Schiff base metal complexes

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Abstract

The object of the paper is to look back upon the development of coordination chemistry in the past several decades, during the career of the author, and possibly see how and through what accomplishments the present coordination chemistry has been built up. For the sake of space available, the paper will focus on the stereochemical aspects of Schiff base metal complexes. Those findings which are remarkable from a historical point of view are chosen and discussed. There is other work I would like to include, but must omit for lack of space. The paper is divided for convenience into the two parts dealing with Schiff base ligands of types (A) and (B): (A) Salen and multidentate ligands derived from Salen, and (B) bidentate N-substituted salicylidene-aminates. The main subjects to be discussed include: (A) non-planar Salen in metal complexes, effects of the polymethylene chain between the two imine nitrogen atoms on the structure of metal complexes, the first synthetic sexadentate metal chelates, possibility of trigonal-prismatic configuration for sexadentate chelates, dioxygen adducts of Co(Salen) and analogous complexes. (B) Anomalous solution paramagnetism of Ni(II) complexes, isomerism in the Ni(II) and Cu(II) complexes with Schiff base ligands and 5-coordination of Co(II) and Ni(II).

Keywords: Schiff bases; Dioxygen adducts; Trigonal-prismatic configuration; Steric requirements of Schiff base ligands

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1. Introduction

Firstly, I wish to thank the Organizing Committee for giving me this honourable opportunity. The object of the present paper, as the Committee intended, shall be to survey the advancement of coordination chemistry which has been proceeding, during my career, for several decades and thereby achieve the goal of retracing our roots with curiosity and historical awareness.

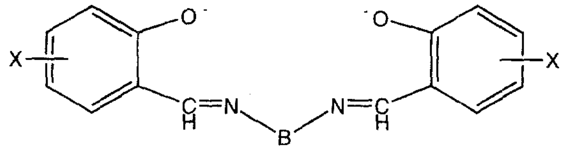
I entered upon a career as a coordination chemist more than 50 years ago with the research theme 'Polarized Crystal Spectra of Metal Complexes' under the guidance of Professor R. Tsuchida at Osaka University. The method for determination of polarized crystal spectra, developed in 1938 by R. Tsuchida and M. Kobayashi, lies in combining a microscope with a spectrograph. Some of the complexes dealt with included *trans*-$[Co(en)_2Cl_2]X$, $K_2[PtCl_4]$, and metal complexes involving interaction between metal ions, and so on.

In the late 1950s I also set out to research Schiff base metal complexes, which later on became one of our main research interests. It is a pleasure for me to present a paper related to this subject in Florence, where Professor H. Schiff was working at the University and reported on the first synthesis of Schiff base metal complexes as early as the 1860s [1].

The metal complexes with Schiff bases as ligands have been playing an important part in the development of coordination chemistry as a whole. However, it was not until the 1950s that concrete and rapid advances in this field became evident. In the early days the main efforts were directed toward synthesis and characterization of rather fundamental complexes, which do not look striking nowadays but were strongly needed in those days. Some of typical examples included metal complexes of the following types: M(II)(X-Sal-NR)$_2$, M(III)(X-Sal-NR)$_3$, and so on, where X-Sal-NR (formula II) denotes bidentate Schiff bases [2]. To cite another example, it was regarded as significant to synthesize complexes of the formula Co(X-Sal-NR)$_3$, R = *i*-Pr, where X = 5-Br and 5-NO$_2$ [3]; it had been believed that the formation of these complexes would be obstructed by the steric constraint due to the bulky *i*-Pr group. As the late Professor R.S. Nyholm used to say, "One type of excellent synthetic research accomplishments would be to prepare those compounds that have so far been believed, but not proven, to be non-existent."

Out of those distinguished pioneers who greatly contributed to the development of this area of Schiff base metal complexes, I wish to mention Professor B.O. West who has been engaged in active research from the early stage [2]. He has continued to work in this field up to the present day; in one of the more recent studies West and coworkers synthesized heteronuclear oxo-bridged compounds of the type (porphyrin)Cr–O–M(L) from the one-electron redox reactions of CrO(porphyrin) and Fe(II), Mn(II) or Mo(IV) complexes containing ligands such as salicylideneaminates and dithiocarbamates [4].

Nowadays, the research field dealing with Schiff base metal complexes has expanded enormously, and embraces very wide and diversified subjects comprising vast areas of organometallic compounds and various aspects of bioinorganic chemistry [5]. It is not possible to cover the whole area in the present paper. Therefore, I selected those achievements which are regarded as noticeable in the stereochemical aspects. There is more work that I would like to include, but must omit for lack of space. For convenience I will divide the contents of the present article into two parts: stereochemical aspects in metal complexes with the ligands of the following types (a) and (b): (a) Salen and multidentate ligands derived from it (Formula I) and (b) bidentate Schiff bases bearing bulky substituents on the imine nitrogen atom (Formula II).

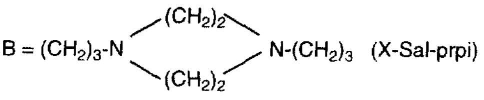


(I)

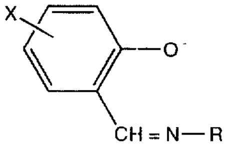
I a: $B = (CH_2)_x$. x = 2 (X-Salen), 3 (X-Saltn), 4 (X-Salbn), 5 (X-Sal-xmn)

I b: $B = -C_6H_4-$ (X-Salph)

I c: $B = (CH_2)_x-L-(CH_2)_y-L-(CH_2)_z$

I d:

$B = (CH_2)_3-N\langle{}^{(CH_2)_2}_{(CH_2)_2}\rangle N-(CH_2)_3$ (X-Sal-prpi)

I e: $B = (CH_2)_x-L-(CH_2)_y$



(II) X-Sal-NR

2. Steric requirements of Salen and related ligands and interaction of dioxygen with Co(Salen)

In 1938 Tsumaki discovered the oxygen-carrying property of Co(Salen) in the crystalline state [6a]. In the same year Tsuchida and Tsumaki reported on the electronic spectra of Co(Salen) and related compounds [6b]. Then, Tsumaki was a Professor of Chemistry at Osaka High School, my Alma Mater, and Tsuchida was a Professor of Chemistry at Osaka University. Because of the photographic plate available in those days, the measurements were limited to the wavelength region shorter than 550 nm. Much later, at the outset of our research on Schiff base metal complexes, more precise redetermination of the absorption spectrum of Co(Salen) in solution was undertaken, resulting in the discovery of the d–d band at about 8730 cm^{-1} with $\varepsilon = 20$ and half width of 1330 cm^{-1}, which is regarded as characteristic of the 4-coordinate planar Co(II) complex of a spin-free type [6c].

2.1. *Non-planar Salen in metal complexes*

The quadridentate ligand Salen normally demands planar 4-coordination in its metal complexes, such as Co(Salen), (Hpip)[Ln(Salen)$_2$] and so on, where Hpip denotes the piperidinium ion and Ln lanthanide(III) ions [7]. However, it turned out to be possible to synthesize metal complexes in which the Salen ligand has a strained non-planar conformation. These complexes with a non-planar Salen ligand may be classified into two types (a) and (b), as shown in Table 1. In complexes of type (a), the strained non-planar conformation of Salen is forced by a coexisting bidentate ligand, which occupies two *cis*-sites in the coordination sphere of the 6-coordinate metal complex [8,9]. The more rigidly planar quadridentate ligand Salph

Table 1
Non-planar Salen in metal complexes

(a) Presence of one bidentate ligand
    [Co(Salen)(bident)] bident = acac, bzac, tfac, etc.
    (1960s: M. Calligaris, G. Nardin, L. Randaccio et al.)

(b) Presence of two special unidentate ligands
    [MoO$_2$(QSB)] QSB = Salen, Saltn, Salbn
    (1974: K. Yamanouchi, S. Yamada)
    cis-[Ru(Salen)(CO)$_2$]
    (1978: J.R. Thornback, G. Wilkinson)

(**Ib**) is also distorted from the planar conformation in some Co(III) complexes containing β-diketonate as a coexisting ligand.

In complexes of type (b), the bonding nature of two coexisting unidentate ligands strongly demands *cis*-coordination, thereby forcing Salen into the non-planar conformation. Since dioxomolybdenum(VI), MoO_2^{2+}, demands a bent O–Mo–O structure, the quadridentate ligands in [MoO_2(Salen)], [MoO_2(Saltn)] and [MoO_2(Salbn)] have a non-planar conformation, as indicated by their PMR spectra [10a]. Single crystal X-ray diffraction studies of [MoO_2(Saltn)] confirmed the predicted structure [10b]. The two CO molecules in *cis*-[Ru(CO)$_2$(Salen)] tend to occupy *cis*- rather than *trans*-positions, probably by the bonding nature [10c].

Another unique type of non-planar Salen ligand has been found in the dinuclear complexes Co_2(3-CH_3O-Salen)$_2$·2Me_2SO·2H_2O (**1a**) and Pd_2(Salen)(2-Me-allyl)$_2$ (**1b**). In the crystal of **1a**, the two cobalt atoms are bridged by a 3-CH_3O-Salen ligand which acts as a bis-bidentate ligand occupying two *cis*-coordination positions of each cobalt atom [11a]. The octahedral coordination polyhedron of each metal atom is completed by a quadridentate 3-CH_3O-Salen ligand in a non-planar configuration. In the crystal of **1b**, one Salen ligand functions as a bridge in the dinuclear complex [11b].

2.2. *Polymethylene analogues of Ni(Salen) and Co(Salen)*

As the polymethylene chain between the two imine nitrogen atoms (**Ia**) is lengthened from 2 to larger numbers, how is the stereochemistry of their metal complexes affected? It has been reported that the molecule of [Rh(Salbn)Cl(py)] has the Cl and pyridine ligands 90° apart with Salbn twisted into a β-*cis*-conformation. The steric requirement by the tetramethylene chain favours non-planar conformation for Salbn in this rhodium(III) complex [12].

2.2.1. *Ni(II) complexes*

As the length x increases from 2, the ligand field produced becomes much weaker, as indicated by the shift of the main d–d band towards lower wavenumbers and by lowering of the capacity of Ni(II) to bind additional ligands, such as py, at the fifth and sixth coordination sites [13,14]. For instance, when dissolved in pyridine, [Ni(Salen)] maintains 4-coordinate planar configuration binding no additional pyridine molecules, while [Ni(Saltn)] binds two pyridine molecules to a form 6-coordinate bis(pyridine)nickel(II) complex. Crystals of the composition Ni(Salen)tu are obtained from an ethanolic solution of [Ni(Salen)] and thiourea (tu) [15]. However, single crystal X-ray analysis has revealed that in the crystal of the thiourea adduct no tu-Ni(II) bond is present, the tu molecule being held by hydrogen bonds between two N atoms of tu and the phenolic O atoms of Salen within the Ni(II) complex [16].

Hoyt and Everett [17] synthesized a series of [Ni(Sal-xmn)] complexes (**Ia**), where $x = 5-12$. The magnetic moments of these complexes range widely in the intermediate region between the values expected for spin-paired ($S = 0$) and spin-free type ($S = 1$), but the electronic spectra do not indicate the existence of tetrahedral species. The d–d band maxima of the complexes [Ni(Sal-xmn)], where $x = 5-12$, appear at about 16000 cm^{-1}, showing that the ligand field becomes weaker than that produced by Salen.

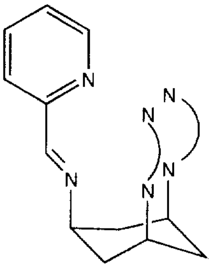
2.2.2. Co(II) complexes

In general, 4-coordinate Co(II) complexes have a higher tendency to assume a tetrahedral configuration than the corresponding 4-coordinate Ni(II) complexes. Although [Co(Salen)] is 4-coordinated spin-paired planar owing to the steric requirement by Salen, Co(II) complexes of the polymethylene analogues [Co(Sal-xmn)], where $x = 4-10$, are spin-free and exhibit electronic absorption spectra typical of tetrahedral Co(II) complexes, indicating that the steric requirement to demand the planar configuration is relieved more and more, as x increases [18]. The trimethylene analogue [Co(Saltn)], which is spin-free with a magnetic moment of 4.5 BM, was concluded to have a flattened tetrahedral configuration on the basis of the electronic spectrum.

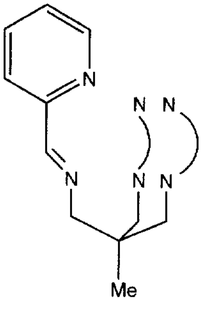
2.3. Sexadentate ligands and trigonal-prismatic complexes

When the polymethylene chain in X-Sal-xmn (**Ia**) bears two additional donor atoms at appropriate sites, sexadentate ligands would result. Dwyer and Lions reported on the first successful preparation of the synthetic sexadentate chelate compound 1,8-diamino-3,6-dithiaoctane (**Ic**, L = S; $x = y = z = 2$) and metal coordination compounds obtained from it [19]. For example, in the cobalt(III) complexes prepared, the chelate molecule occupies all six octahedrally disposed positions about the cobalt(III) ion. A little later, Bailar and coworkers prepared Co(III), Fe(III) and Al(III) complexes of the analogous ligand (**Ic**, L = NH; $x = y = z = 2$) [20].

Normally 6-coordinate metal complexes with such linear sexadentate Schiff bases as ligands have an octahedral configuration. However, attempts have been made to explore exceptional cases. Indeed, configurations distorted considerably from the trigonal antiprism (TAP) towards the trigonal-prism (TP) have been reported for 6-coordinate metal complexes with trifurcated sexadentate Schiff base ligands, which were especially designed so as to constrain the coordination [21]. Two systems (a) and (b) of an open-trifurcated type are shown below : (a) *cis*, *cis*-1,3,5-tris(pyridine-2-aldimino)cyclohexane(IIIa), for which the Zn(II) complex possesses nearly-trigonal-prismatic conformation (twist angle = 4.6°) [21a] and (b) 1,1,1-tris(pyridine-2-aldiminomethyl)ethane, for which the Zn(II), Ni(II) and Fe(II) complexes have conformations distorted from the octahedral one, the twist angle being 32, 28 and 17°, respectively [21b].



(III a)



(III b)

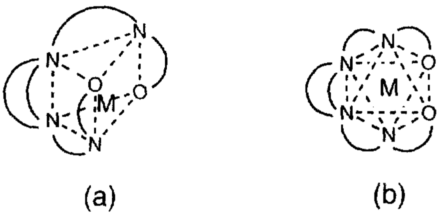


Fig. 1. Extreme configurations, TP(a) and ATP(b) of $[M(Sal\text{-}prpi)]^+$: (a) M = Fe(III); (b) M = Co(III).

More recently we have examined whether open-chain sexadentate ligands may form 3d metal complexes having configurations remarkably distorted from the TAP. The following metal(III) complexes have been synthesized and their structures determined by the single crystal X-ray method : $[M(Sal\text{-}prpi)]ClO_4$ (**Id**), where M(III) = Mn, Fe, Co [22]. The structure of the metal complex depends upon the metal ion involved. The structure of the Fe(III) complex is close to TP, while that of the Co(III) complex is close to TAP. The structure of the Mn(III) complex is intermediate between those of the Fe(III) and Co(III) analogues, being nearer to TP. Twist angles are 21, 14 and 56° for the Mn(III), Fe(III) and Co(III) complexes, respectively. We also prepared the Co(II) complex [Co(Sal-prpi)]. The X-ray study has revealed that the Co(II) complex has a nearly trigonal-prismatic configuration, with a twist angle of 6° [22]. The extreme configurations, TP(a) and ATP(b), of these complexes are schematically shown in Fig. 1.

The ligand rigidity of Sal-prpi, due to the presence of the piperazine part, seems to favour the trigonal-prismatic coordination of the metal complexes, the final configuration adopted also depending upon the metal ion, to a more or lesser extent.

2.4. *Interaction of dioxygen with Co(Salen) and related complexes*

The nature of bonding of the dioxygen molecule with Co(Salen) has been disputed for a long time [5,23]. It is known that the ligand field produced by Salen is so strong that Co(Salen) would have only weak bonding capacity at the fifth and sixth coordination sites. A small number of mononuclear 5-coordinate Co(II) complexes of the type [Co(Salen)B] have been reported, where B denotes ammonia and pyridine [24a]. They are spin-paired, and the bond distance between Co and N(py) in [Co(Salen)py] (2.10 Å) is much longer than the in-plane Co–N distance (1.90 Å).

2.4.1. *Definitely tervalent Co(III) Salen complexes*

In order to find a clue to the intrinsic oxidation state of Co in the dioxygen adducts of Co(Salen) and analogous complexes, eager efforts were made to prepare definitely tervalent Co(III) complexes with the Salen ligand. In the 1960s Co(III) complexes of the following types (A) and (B) were synthesized and characterized [25a]: (A) [Co(Salen)L_2]X (L = NH_3, $MeNH_2$, $EtNH_2$, py, H_2O; X = Br, Cl, ClO_4) and (B) K[Co(Salen)X_2] (X = NCS, CN, NO_2). They are all diamagnetic and have a *trans*-6-coordinate configuration. The corresponding Cr(III) complexes were also prepared [25b].

Costa and coworkers reported 6-coordinate Co(III) complexes of the type [RCo(Salen)B], where R = Me, Et and B = py, H_2O [26]. Salen-Co(III) complexes of another series have also been synthesized [27]: [Co(Salen)CH_2CN]CH_3OH (a), [Co(Salen)(OCH_3)py]CH_3OH (b) and [Co(Salen)(CH_3OH)(CH_2COCH_3)] (c). Compound (a) has a polynuclear structure with CH_2CN bridging two Co(III) ions. In compound (c) the CH_2COCH_3 group combines with Co(III) through the C atom.

2.4.2. *Dioxygen adducts of Co(Salen) and analogous complexes*

The compound Co(Salen) occurs in two different crystalline modifications, one being active and the other inactive as to absorption of the dioxygen molecule [23]. The active form consists of a mononuclear planar complex [Co(Salen)] and the inactive form is dinuclear, represented by [Co_2(Salen)$_2$], in which the two Co(II) ions are 5-coordinated [24b].

There has been a continuous interest in the dioxygen Salen-cobalt complexes. Extensive studies have revealed that the X–Salen–Co(II) complexes in non-aqueous solvents absorb the dioxygen molecule more readily in the presence of a nitrogenous base B [28,29]. The following equilibria may be assumed, where QSB denotes quadridentate Schiff bases:

$$[\mathrm{Co(QSB)B}] + \mathrm{O_2} \rightleftarrows [\mathrm{Co(QSB)B(O_2)}]$$

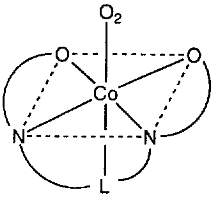
$$[\mathrm{Co(QSB)B(O_2)}] + [\mathrm{Co(QSB)B}] \rightleftarrows [\mathrm{B(QSB)Co{-}O_2{-}Co(QSB)B}]$$

In the late 1960s Floriani and Calderazzo [29] reported that reactions of dioxygen with Co(X-Salen) in various solvents, except for the complex with X = 3-CH_3O, yielded the diamagnetic peroxo-bridged species of the type [B(X-Salen)Co(III)–O_2–Co(III)(X-Salen)B], where B denotes a nitrogenous base, such as py, dmf and so on. The structure of [Co_2(Salen)$_2$(O_2)(dmf)$_2$] was determined by the X-ray method [29].

On the other hand, the 3-methoxy analogue in pyridine reacts with dioxygen to yield the mononuclear complex [Co(3-CH_3O-Salen)(py)O_2]. This was the first mononuclear 1:1 dioxygen complex to be isolated.

Similar mononuclear dioxygen cobalt complexes were obtained with H_2acacen and H_2bzacen [30]: [Co(acacen)B(O_2)] and [Co(bzacen)B(O_2)], where B = dmf, py and so forth. The structures of these complexes were determined by the X-ray method [31]. In the latter complex the angle Co–O–O is 125° and the O–O distance (1.20 Å) differs widely from that of the O_2^{2-} ion (1.49 Å in K_2O_2), consistent with the assumption that 1:1 cobalt dioxygen complexes should be formally described as Co(III)–O_2^- [30,32].

In addition to two types of dioxygen Co(III)-Salen complexes, [Co(X-Salen)B(O_2)] (a) and [B(X-Salen)Co–O_2–Co(X-Salen)] (b), described above, complexes of the type [B(X-Salen)Co–O_2–Co(X-Salen)B]$^+$ (c) are obtained by oxidation of type (b) complexes. Type (b) complexes are diamagnetic, while type (c) complexes are paramagnetic. An analogy to the dioxygen Co(III) complexes of type (a) suggests, quinquedentate ligands (**Ie**, Y = NCH_3, NH, S; $x = y = 3$) bearing an additional donor atom at an appropriate position also form dioxygen complexes(IV) [33].



(IV)

L = NCH_3, NH, S

The following ammine complexes (A and B) may be regarded as model complexes for μ-dioxygen dicobalt(III)bis(Salen) complexes: (A) $[(NH_3)_5Co{-}O_2{-}Co(NH_3)_5](NO_3)_4{\cdot}2H_2O$ and (B) $[(NH_3)_5Co{-}O_2{-}Co(NH_3)_5](NO_3)_5$. Werner termed the two types A and B the peroxodicobalt(III, III) and the peroxodicobalt(III, IV) complexes, respectively [34], which later became known as diamagnetic μ-peroxo- and paramagnetic μ-superoxo-dicobalt(III) complexes. In order to obtain fundamental information on the possible interaction between the two Co(III) ions through the dioxygen bridge in the dicobalt(III) complexes, polarized crystal spectra of complexes A and B were determined many years ago [35]. After this paper had been published, the crystal structure analysis of complex B was reported [36]. The absorption band at 15000 cm^{-1} is highly polarized; strong absorption is observed with electric vector parallel to the plane containing the Co–O–O–Co moiety, while no absorption is observed perpendicular to it.

Complex A shows a similar absorption band at 15200 cm^{-1}, which is also greatly polarized. The crystal structure of the complex has so far not been determined. However, judging from the considerably large ratio experimentally obtained, one may reasonably assume that the absorption ratio based upon the Co–O–O–Co moiety is very high, although the moiety in compound A may be slightly deviated from the planar conformation.

Taking into consideration that these distinctive absorption bands appear at unusually low wavenumbers and that their intensity is remarkably higher than that of normal d–d bands of Co(III) complexes, they may be regarded as related to a sort of interaction between the Co(III) ions through the peroxo- or the superoxo-bridge, characteristic of the μ-dioxygen complexes of this type including those with Salen and analogous ligands.

3. Steric effects on the structure of bidentate Schiff base metal complexes by bulky groups in the Schiff base ligands

It was at the 6th ICCC, Detroit in 1961 that I met Professor Luigi Sacconi for the first time. In 1964 I had the opportunity of spending a few months at his laboratory in Florence and of getting acquainted with a number of his excellent coworkers. There we often discussed current topics of significance, such as 5-coordinate Co(II) and Ni(II) complexes and the anomalous solution paramagnetism of Schiff base Ni(II) complexes. Bearing these problems in mind, we will now look back upon advances in the areas related to steric effects by bulky substituents at imine nitrogen atoms of the bidentate Schiff base ligands (II).

3.1. Compounds in which R = bulky alkyl groups: solution paramagnetism of the Ni(II) complexes and isomerism of the Ni(II) and Cu(II) complexes

Bis(*N*-alkyl- or bis(*N*-aryl-salicylideneaminato)nickel(II) complexes Ni(X-Sal-NR)$_2$ are basically 4-coordinate square-planar in the solid state. However, since Willis and Mellor found in 1947 that Ni(II) salicylideneaminato-complexes became partially paramagnetic in chloroform [37a], the origin of the anomalous paramagnetism in non-coordinating solvents attracted many coordination chemists, but remained puzzling for many years [37b]. Extensive and energetic studies, particularly by the groups of Sacconi and Holm, have independently revealed that the behaviour of the Ni(II) complexes in non-coordinating solvents is represented by the following equilibria [38]

$$\text{Associated (paramag)} \rightleftarrows \text{Pl (diamag)} \rightleftarrows \text{Td (paramag)}$$

The equilibria are shifted towards right or left, depending upon the solvent, concentration and temperature. In the associated form Ni(II) has 6-coordination, except for the dinuclear species in which Ni(II) ion is 5-coordinated.

In view of the existence of various species in equilibria, it is reasonable to assume that isolation of isomeric and associated species of one and the same Ni(II) complex may be quite within the boundary of possibility. In the late 1950s the Ni(II) complexes Ni(X-sal-NR)$_2$ in which R = Me; X = H, 5-Br, 5-Cl, were isolated in more than one form, one being diamagnetic planar and the other paramagnetic associated [39].

In the course of studies on the solution paramagnetism, it became evident that the structure of the Ni(II) complexes Ni(X-Sal-NR)$_2$ depends, in a remarkable way, upon the bulky substituent R on the imine nitrogen atom and to a lesser extent upon the ring-substituent X. When R = *t*-butyl, for example, the steric constraint is so large that the complexes Ni(X-Sal-NR)$_2$ have a tetrahedral configuration. The steric constraint due to R = α-branched alkyls is intermediate between *t*-Bu and *n*-alkyl groups. Thus, when R = *i*-Pr, the Ni(II) complex has been found to have a quasi-tetrahedral structure consisting of two planar salicylideneaminate groups making a dihedral angle of 82° [40].

In the 1960s and 1970s we extensively examined the complexes Ni(X-Sal-NR)$_2$, where R = α-branched alkyl and cyclohexyl(Ch) groups, and revealed that various configurations such as 4-coordinate planar, tetrahedral and oligomeric species occur in the solid state. It also turned out that isomeric pairs of some of the

Ni(II) complexes could be obtained as crystals. The main results of these studies, together with those of the Cu(II) complexes, were presented at the Symposium in honour of the 70th birthday of Professor Luigi Sacconi [41]. In the present paper, therefore, only a brief summary is given below.

As to the isolation of isomers, the complexes Ni(X-Sal-NR)$_2$, in which R = *i*-Pr and Ch, may be classified into the following types (A), (B) and (C) [41,42].

(A) One tetrahedral species can only be isolated: R = *i*-Pr, X = H; R = Ch, X = H, 5,6-benzo.

(B) One planar species can only be isolated: R = *i*-Pr, X = 5-Br, 5-Cl, 5-NO$_2$, 3,5-Br. The tetrahedral species is not obtained on heating the planar species.

(C) Both planar and tetrahedral species can be obtained: R = *i*-Pr, X = 3-CH$_3$O, 3-NO$_2$, 5,6-benzo; R = Ch, X = 5-Br, 5-Cl, 3-NO$_2$, 3-CH$_3$O. As the temperature rises the planar form is transformed into the tetrahedral form at the characteristic temperature.

In analogy to the Ni(II) complexes just discussed above, one might be tempted to assume the planar-tetrahedral isomerism for the corresponding Cu(II) complexes Cu(X-Sal-NR)$_2$, in which R = *i*-Pr and Ch. However, the stereochemistry of the Schiff base Cu(II) complexes, is much more versatile than that of the Ni(II) complexes [43,44]. An attempt was also made to interpret the conformation of the Schiff base Cu(II) complexes mainly in terms of electronic factors [44].

The Cu(II) complexes Cu(X-Sal-NR)$_2$, in which R = *n*-Pr or *n*-Bu, are 4-coordinate planar, while the ethyl derivative crystallizes in two modifications, one of them (monoclinic) being composed of distorted tetrahedral complexes with a dihedral angle of 35.7° and the other (orthorhombic) containing two independent molecules which differ slightly in molecular geometry with dihedral angles of 7.4 and 11.4°, respectively [45].

It was reported in the 1960s that the Cu(II) complexes Cu(X-Sal-NR)$_2$, in which R = *i*-Pr, could be obtained in either a planar or a tetrahedral form, but not both, the configuration of the isolated species depending upon the ring-substituent X [38]. Later, extensive studies have revealed that two isomeric or oligomeric pairs of some complexes of this series can be isolated as crystals [41,42]. The difference in the structure between the isolated species of the Cu(II) complexes is not always so succinct as in the case of the corresponding Ni(II) complexes.

One familiar type is the planar-tetrahedral isomerism. The olive-green and the red–brown form of the Cu(II) complex Cu(X-Sal-NR)$_2$ in which R = *i*-Pr; X = 5,6-benzo were obtained as crystals. The olive-green form was reported earlier [46]. The other red–brown form was isolated later by two different methods [41,42,47]. As the temperature is raised, the olive-green form is transformed at 375 K into the red–brown form. According to the single crystal X-ray study the red–brown form consists of pseudo-tetrahedral molecules with a dihedral angle of 38.3°. A similar isomeric pair of the complex Cu(X-Sal-NR)$_2$ in which R = Ch; X = 5,6-benzo were also isolated as crystals [41,42]. The olive-green planar form is transformed at 490 K into the red–brown tetrahedral form.

To our surprise, however, there are isomeric pairs that differ from the planar-tetrahedral pair. Such isomers were obtained in crystals for the complex Cu(X-Sal-

NR)$_2$ in which R = *i*-Pr; X = 3-CH$_3$O, one being olive-green and the other red–brown [41,42,47–49]. According to the X-ray studies both the forms are mononuclear and distinctly distorted from the planar configuration. A remarkable difference between the two forms lies in the manner of the distortion. The dihedral angles between the two Cu(N)(O) planes are 47.4° for the olive-green and 57.9° for the red–brown form. The olive-green form is transformed at 374 K into the brown form, which eventually melts at 397 K.

An isomeric pair of another type was obtained. Two forms of the complexes Cu(X-Sal-NR)$_2$, where R = Ch; X = H, have been isolated, one being red–brown and the other olive-green [41,42,50]. According to single crystal X-ray studies, the Cu(N)$_2$(O)$_2$ moiety in the red-brown form is perfectly planar, while the olive-green form consists of dinuclear molecules in which the Cu(II) ions assume a distorted square-pyramidal coordination.

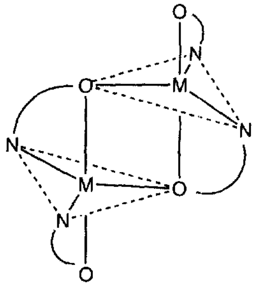
It has been found that the complexes Cu(X-Sal-NR)$_2$ in which R = *i*-Pr and Ch occur in various configurations such as pseudo-tetrahedral with different extents of distortion, in addition to square-planar and dinuclear forms. Therefore, in principle, one may expect to isolate more than two isomeric and oligomeric species of the complexes Cu(X-Sal-N)$_2$, aside from experimental difficulties. Recently, three isomeric forms (1, 2 and 3) of the complex Cu(X-Sal-NR)$_2$ in which R = Ph; X = 5-Cl have been isolated as crystals. The structures of the three forms, determined by the X-ray diffraction method, definitely differ from one another [51]. Form 1, which is red–brown, consists of perfectly *trans*-planar molecules. Form 2, which is olive-green, consists of dinuclear complexes with chloroform molecules in the interstice in the crystal lattice. The Cu(II) ions in the dinuclear complex are 5-coordinated in a distorted square-pyramidal configuration. Form 3, which is olive-green and has composition of Cu(5-Cl-Sal-NPh)$_2$·1/2CH$_2$Cl$_2$, consists of mononuclear 4-coordinate molecules which have a *cis*-planar configuration, though slightly distorted from perfect planarity, the dihedral angle being 38.6°. To our knowledge, this is the first *cis*-planar complex of the type Cu(X-Sal-NR)$_2$, the structure of which has been established by the X-ray method.

3.2. Compounds in which R = bulky aryl groups and 5-coordination

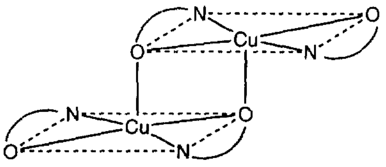
3.2.1. 5-Coordination of Ni(II) and Co(II)

In the 1950s the coordination number 5 of Ni(II) and Co(II) was not common and the exploration of 5-coordinate complexes was one of the research themes of importance, attracting many coordination chemists [52]. Indeed, in the 1960s various new 5-coordinate Co(II) and Ni(II) complexes with Schiff base ligands were reported. Above all, Sacconi and coworkers made great contributions to this area of research [53]. At the 10th ICCC in Nikko, Japan, 1967, Sacconi gave a splendid plenary lecture on ‘Five-coordination in 3d Metal Complexes’ [53a].

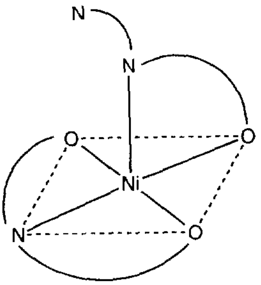
Representative types of 5-coordinate Co(II) and Ni(II) complexes with Schiff base ligands are shown below. Dinuclear complexes of the formula M(Sal-NMe)$_2$, M(II) being Mn, Co, Ni, Cu and Zn, have the metal ions in a trigonal-bipyramidal coordination geometry (Va) [54a]. Another dinuclear modification of $Cu_2(Sal\text{-}NMe)_2$ with Cu(II) ions in a square-pyramidal coordination was also reported (Vb) [54b].



(V a)

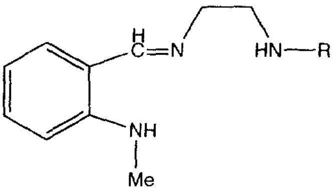


(V b)

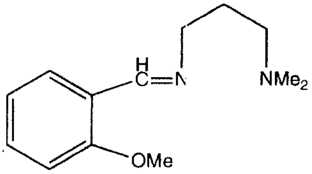


(VI)

Co(II) and Ni(II) complexes of the formula $[M(5\text{-}Cl\text{-}Sal\text{-}enEt)_2]$ are mononuclear 5-coordinate (VI). The diethylamino group on the imine nitrogen atom is so bulky that one of the Schiff base ligands functions as a tridentate and the other as a bidentate [55]. Co(II) complexes $Co(L)X_2$ have a mononuclear 5-coordinate configuration, where L denotes tridentate Schiff bases (VII) and X halide ions [56]. Similarly, complexes $Ni(L)X_2$ are mononuclear 5-coordinate, where L denotes a tridentate Schiff base (VIII) [57]. Quinquedentate Schiff bases (**Ie**, R = NH, NCH_3) form mononuclear 5-coordinate complexes of the formula [M(L)], where M(II) denotes all the metal ions from Mn to Zn [58].



(VII) R = Me, Et



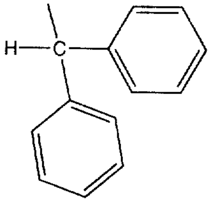
(VIII)

Later, the chemistry of 5-coordinate complexes of transition metals was greatly expanded by Sacconi and coworkers. Other chemists including E. Uhlig also discussed the electronic and steric factors influencing the structure of Schiff base metal complexes [59].

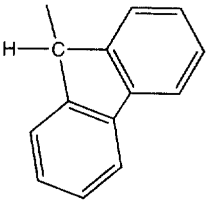
In the 1960s we also made eager efforts to obtain other types of 5-coordinate Co(II) and Ni(II) complexes with bidentate Schiff base ligands, using complexes of the type $M(X\text{-Sal-NR})_2$ in which R = bulky groups containing benzene ring(s). It was intended to isolate 5-coordinate mono(pyridine)-adducts of the Co(II) and Ni(II) Schiff base complexes. Another objective of this work was to compare the stereochemical effects of the bulky aryl groups with those of the α-branched alkyls. The main conclusions are briefly summarized in the next section.

3.2.2. Compounds in which R = diphenylmethyl (dpm) and fluorenyl (fl)

It is also interesting to compare, with respect to the stereochemical effects, dpm with fl as the substituent R. The complexes $Ni(X\text{-Sal-NR})_2$ in which R = dpm are diamagnetic and have a 4-coordinate square-planar $[Ni(N)_2(O)_2]$ configuration in the solid state and in non-donor solvents. They form 6-coordinate bis(pyridine)-adducts [60]. The complexes $Ni(X\text{-Sal-NR})_2$ in which R = fl are diamagnetic and have a square-planar configuration in the solid state and in non-donor solvents. The steric constraint due to dpm and fl opposing the planar configuration of the Ni(II) complexes is found to be less effective than the constraint due to α-branched alkyl groups.



(IX a)



(IX b)

In contrast to the corresponding dpm complexes, the complexes $Ni(X\text{-Sal-NR})_2$, in which R = fl, form 5-coordinate mono(pyridine)-adducts which can be readily isolated as diamagnetic red–brown crystals [61]. The steric constraint due to fl opposing the formation of the 6-coordinate bis(pyridine)-adduct is evidently higher than that due to dpm.

The Co(II) complexes Co(X-Sal-NR)$_2$, in which R = dpm, are tetrahedral and form 6-coordinate bis(pyridine)-adducts, which can be isolated as crystals [61]. On the contrary, the corresponding Co(II) complexes with R = fl have a tetrahedral configuration in the solid state and in non-donor solvents, but exist, when dissolved in pyridine, exclusively as 5-coordinate mono(pyridine)-adducts [61]. These mono(pyridine)-adducts, which are readily isolated as crystals, are either spin-paired or spin-free depending upon the ring-substituent X. The magnetic moments are 4.25 BM for X = 5-Br and 5-Cl and 2.5 BM for X = 5,6-benzo. Their 5-coordinate configuration is retained when dissolved in chloroform.

The results outlined above indicate that there is a marked difference in the steric constraint between dpm and fl. The steric requirement of the substituent R = fl is exceedingly suited to the formation of the 5-coordinate mono(pyridine)-adducts.

3.2.3. Compounds in which R = 2,6-dialkylphenyl (Y_2Ph)

Finally, we take up the Co(II) and Ni(II) complexes in which R = Y_2Ph. McKenzie and coworkers were also engaged in studies on these Ni(II) complexes. The complexes Ni(X-Sal-NR)$_2$ in which R = Me$_2$Ph and Et$_2$Ph are diamagnetic and square-planar [62–65]. When dissolved in pyridine these Ni(II) complexes exist as an equilibrium mixture consisting of 4-coordinate planar and 5-coordinate mono(pyridine)-species, except for the complexes with X = 5-NO$_2$ and 3-CH$_3$O, which exist entirely as 6-coordinate bis(pyridine)-adducts [64,65]. In any case, it is very difficult to obtain 5-coordinate mono(pyridine)-adducts as crystals.

The Ni(II) complexes Ni(X-Sal-NR)$_2$, in which R = *i*-Pr$_2$Ph, are also diamagnetic and 4-coordinate planar in the solid state and in non-donor solvents [64]. When dissolved in pyridine these Ni(II) complexes exist mainly as the 4-coordinate planar species in equilibrium with a minor proportion of the 5-coordinate mono(pyridine)-adduct, the proportion of the 5-coordinate adduct being much smaller than that of the corresponding dimethyl- and diethyl-phenyl analogues. Recrystallization from pyridine has yielded neither 5-coordinate mono(pyridine)-adducts nor 6-coordinate bis(pyridine)-adducts [64].

In contrast to the Ni(II) complexes, 5-coordinate mono(pyridine)-adducts of the corresponding Cu(II) complexes in which Y = Me, Et and *i*-Pr have been isolated without difficulty.

On the other hand, the Co(II) complexes Co(X-Sal-NR)$_2$ in which R = Me$_2$Ph and Et$_2$Ph have a tetrahedral configuration in the solid state and in non-donor solvents [62,66]. When dissolved in pyridine they exist mainly as a 5-coordinate mono(pyridine)-adduct in equilibrium with a small proportion of the tetrahedral parent complex and 6-coordinate bis(pyridine)-species [66,67]. We could manage to isolate crystals of the following 5-coordinate mono(pyridine)-adducts: R = Me$_2$Ph, X = H, 5,6-benzo; R = Et$_2$Ph, X = 5,6-benzo [66,67]. However, the isolation has not always been easily accomplished.

When Y = *i*-Pr, the steric constraint has proved to be more pronounced than when Y = Me and Et. When dissolved in pyridine the complexes Co(X-Sal-NR)$_2$ in which R = *i*-Pr$_2$Ph exist entirely as 5-coordinate mono(pyridine)-adducts, no 6-coordinate bis(pyridine)-adducts being present, as indicated by their electronic absorption spectra [68]. Recrystallization of the parent Co(II) complexes from pyridine readily gives brown–orange crystals of 5-coordinate mono(pyridine)-adducts of the formula Co(X-Sal-NR)$_2$(py), where R = *i*-Pr$_2$Ph; X = H, 5-Br, 5-Cl and 5-NO$_2$. They are spin-free with magnetic moments of 4.8–5.0 BM, and stable in the atmosphere near room temperature. The isolation of 5-coordinate mono(pyridine)-adducts is much more facile than when Y = Me and Et. In this respect, the Co(II) complexes differ remarkably from the Ni(II) complexes.

Single crystal X-ray analysis has revealed that Co(5-Br-Sal-NR)$_2$(py), where R = *i*-Pr$_2$Ph, consists of 5-coordinate molecules having a square-pyramidal configuration [69]. The corresponding mono(pyridine)zinc(II) complex was also shown, by the X-ray study, to consist of 5-coordinate molecules which are similar to that of the Co(II) complex.

The structures of the parent Co(II) complexes in which R = *i*-Pr$_2$Ph are rather extraordinary, showing the nature of the steric effect due to *i*-Pr$_2$Ph. Two types of magnetic moments have been observed for these Co(II) complexes: (i) 4.5 BM for X = H and (ii) 2.4–2.6 BM for X = 5-Br and 5-Cl. The magnetic moments, together with electronic spectra, indicate that the Co(II) complex (i) has a 4-coordinate tetrahedral configuration and that the complexes (ii) have a 4-coordinate planar configuration. To our knowledge, complexes (ii) are the first planar Co(II) complexes with bidentate *N*-aryl-salicylideneaminates as ligands to be isolated as crystals. The structure of the Co(II) complex in which R = *i*-Pr$_2$Ph; X = 5-Br has been determined by the X-ray diffraction method, which has revealed that the Co(II) complex consists of 4-coordinate trans-planar molecules [69].

The results outlined above indicate that the energy barrier between the planar and the tetrahedral configurations is remarkably low in these Co(II) complexes where R = *i*-Pr$_2$Ph. In chloroform these complexes (X = 5-Br, 5-Cl) have a 4-coordinate tetrahedral configuration, as clearly shown by their electronic spectra. The tetrahedral species of these Co(II) complexes, however, have not been isolated in crystal form as yet.

4. Concluding remarks

In the present paper we have been mainly concerned with mononuclear and dinuclear complexes. More complicated systems, such as those involving cooperative effects or interaction of various kinds between metal ions in polynuclear complexes have not been dealt with. The detailed accounts of these topics have already been reviewed elsewhere. For instance, alkoxo-bridged copper(II) complexes with Schiff base ligands (for example, **Ie**: L = C–OH), which involve the spin–spin interaction between Cu(II) ions, have been studied extensively [70]. Furthermore, in recent years more and more interest has been aroused by polynuclear systems, such as metal clusters and supramolecular complexes.

Looking back upon the achievements for the past 50 years, we are amazed at the tremendous progress. Now it would be interesting to dream of advancement anticipated for the next 50 years in the 21st century. It is hoped that the present article on the past will be of use for that purpose, and possibly for opening new, sometimes unexpected, ways to the future.

Acknowledgements

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Appendix Non-planar Salbn

[Rh(Salbn)Cl(py)]
(1974: B.M. Gatehouse, R.E. Reichert, B.O. West et al.)

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