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THE CONFORMATION AND INTERCONVERSION OF SCHIFF BASE COMPLEXES OF NICKEL(II) AND COPPER(II)

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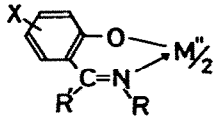
CONTENTS

A. INTRODUCTION

Metal(II) complexes with bidentate *N*-substituted salicylaldiminates (**I**) have various configurations, depending upon R and X [1,2]. In most cases, however, only one of the possible configurations has so far been isolated. In the present paper, we shall discuss attempts and possibilities to isolate various isomeric or associated species of the nickel(II) and copper(II) complexes of this series.



I: R'=H, II: R'=Ph

B. NICKEL(II) COMPLEXES

Bis(*N*-alkyl- or bis(*N*-aryl-salicylaldiminato) nickel(II) complexes are basically tetra-coordinate, square-planar in the solid state. In non-donor

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solvents, however, they exist as an equilibrium mixture of isomeric and associated species. Exhaustive studies [2–4] have revealed that the equilibria in solution are represented by

$$\text{Assoc.(paramag)} \rightleftharpoons \text{planar(diamag)} \rightleftharpoons \text{tetrahedr.(paramag)} \quad (1)$$

The equilibria are shifted toward right or left, depending upon the solvent, concentration and temperature. In the associated forms, the nickel(II) ion assumes six-coordination, except for the binuclear form, in which the nickel(II) ion is five-coordinate. In spite of strenuous efforts, isolation of isomeric pairs in the solid state has not been successfully accomplished. The complexes (**I** where R = Me; X = H, 5-Cl, 5-Br) were isolated in more than one form, one being diamagnetic, planar and the other paramagnetic, associated [5].

In view of the existence of an equilibrium mixture of various species in solution, further attempts at isolation of various isomers seemed to be promising. With R = t-butyl (t-Bu), the steric constraint is so enormous that the bis(Schiff base)nickel(II) complexes (**I**) have a pseudo-tetrahedral configuration distorted from the square-planar one, which is normally adopted by the corresponding n-alkyl complexes. The steric constraint in the case of α-branched alkyls is intermediate between t-butyl and n-alkyl, and the energy difference between the planar and tetrahedral forms may be comparatively small. We have thus initiated the examination with R = α-branched alkyls, cyclohexyl (ch), and cycloheptyl (cp) [1,6–8]. With R = diphenylmethyl, however, only the planar form has been isolated, in spite of considerable steric constraint, the planar configuration being retained in non-donor solvents [6].

The "conventional preparation methods" usually involve recrystallization of the "crude products" from hot organic solvents. By the "crude products" in this paper are meant substances obtained by reactions of bis(salicylaldehydato)nickel(II) with amines in solution. The heating method may also be useful for preparation, in case conversion from one configuration to another isomer takes place in the solid state as the temperature rises. For instance, the tetrahedral forms of some complexes are obtained by heating the planar forms at appropriate temperatures. Heating the tetrahedral forms, however, never yields the planar isomers. In most cases, species obtained by the heating methods are fairly stable e.g. for several months, except for only a few cases, which are so indicated in the text. For the purpose of finding proper heating temperatures, DTA measurements are very useful. The purity of the complexes obtained by the heating methods was checked with particular care and confirmed not only by elemental analyses but also by means of electronic spectra, IR spectra, magnetic properties, and powder X-ray diffraction patterns. The powder X-ray pattern is useful for seeing

whether the conversion of one configuration to the other is complete or not.

The configurations of the nickel(II) complexes may be inferred with reasonable certainty, mainly on the basis of electronic spectra and magnetic properties [1–3]. Results so far available have revealed that there are two cases, (A) and (B). Of the possible planar, tetrahedral and associated structures, in case (A) one species only can be isolated, or in case (B) more than one species can be isolated. When dissolved in non-donor solvents, however, even the complexes of type (A) exist as an equilibrium mixture consisting of such species as planar and tetrahedral. It should also be noted that complexes (**I**) (where R = n-alkyl), which are diamagnetic and planar in the solid state, do not undergo transformation into the tetrahedral form on raising the temperature, although the tetrahedral species occurs in solution at higher temperatures [3].

(i) Compounds in which R = isopropyl (i-Pr)

It was concluded that the conventional preparation methods yielded type (**I**) complexes in which R = i-Pr in either a planar or a tetrahedral form, depending upon X [3]. Succeeding studies have revealed that depending on the number of isomeric solid species isolated, nickel(II) complexes are classified into types: (A) and (B) [7].

(A-1). One tetrahedral species only can be isolated: X = H. No transformation into the planar form occurs as the temperature is raised.

(A-2). One planar species only can be isolated: X = 5-Br, 5-Cl, 5-NO_2, 3,5-Br_2. The tetrahedral form is not obtained by heating the planar form. DTA curves have only one endothermic peak at 482, 471, 541, and 461 K (for X = 5-Br, 5-Cl, 5-NO_2 and 3,5-Br_2), respectively, corresponding to the melting process.

(B). Both planar and tetrahedral species can be isolated: X = 3-CH_3O, 3-NO_2, 5,6-benzo.

The type (**I**) compound in which R = i-Pr; X = 3-CH_3O is obtained in two isomeric forms, one being olive-green and the other red-brown [7,8]. Red-brown crystals (form I) are isolated by the conventional recrystallization method, while olive-green crystals are obtained by spontaneous evaporation at room temperature of a solution of the crude product in ether/methanol or ether/chloroform. The red-brown and olive-green forms are paramagnetic (3.32 BM) and diamagnetic, respectively. Magnetic and spectral studies (Fig. 1) indicate that the red-brown and olive-green forms consist of pseudo-tetrahedral and planar complexes, respectively. According to X-ray studies [9], the pseudo-tetrahedral complex in the red-brown form has a dihedral angle of 79.1°. It should be noted that the Ni–O and Ni–N distances in the tetrahedral molecule are longer than in the isomeric planar molecule. Another

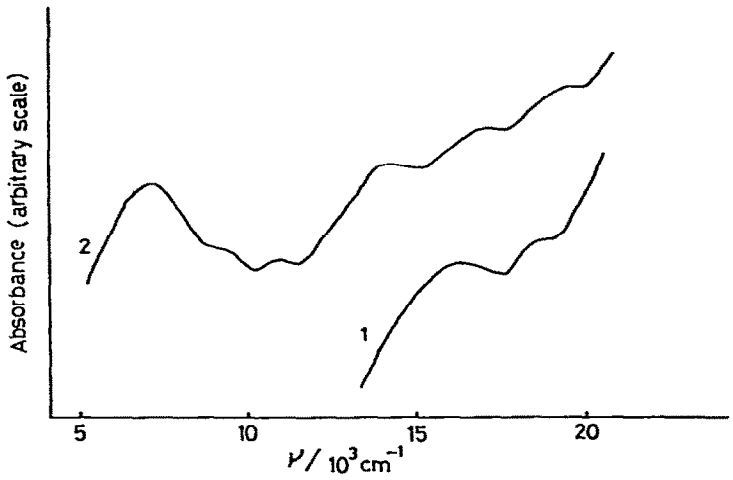


Fig. 1. Electronic absorption spectra of Ni(3-CH_3O-sal-*N*-i-Pr)$_2$ in Nujol. 1, green (planar) form; 2, brown (pseudotetrahedral) form.

red-brown form (form II) is obtained by heating the olive-green form at 150–165°C. Thermal studies indicate that the olive-green form is transformed at 431 K into the brown form II, which melts at 461 K [8]. The transition enthalpy was estimated to be 7.1 kJ mol^{-1} from DSC measurements. The brown form I is transformed at 448 K into the brown form II. The powder X-ray pattern of form II, which differs from that of the brown form I, is similar to those of the zinc(II) and cobalt(II) complexes having a tetrahedral configuration. Some phases at higher temperatures were detected and examined mainly on the basis of thermal measurements [10].

By conventional preparation methods, only the planar form of the type (**I**) complex in which R = i-Pr; X = 5,6-benzo is isolated as diamagnetic olive-green crystals [11]. The red-brown form was later isolated by heating a solution of the olive-green form in xylene/ethanol (about 1 : 10), until most of the ethanol had evaporated and brown crystals appeared in the hot solution [12]. The red-brown form is paramagnetic (3.32 BM) and shows an electronic spectrum typical of the tetrahedral nickel(II) complex. Its powder X-ray diffraction pattern closely resembles that of the corresponding zinc(II) complex having a tetrahedral configuration. The brown form is also obtained by heating the olive-green form at 205–215°C. According to DTA measurements, the green form in the solid state is transformed at 482 K into the brown tetrahedral form, which melts at 497 K. The transition enthalpy was estimated from DSC measurements [7] to be 21.8 kJ mol^{-1}.

Conventional methods yield only the planar form of the type (**I**) complex in which R = i-Pr; X = 3-NO_2. A tetrahedral form (red-brown) was later

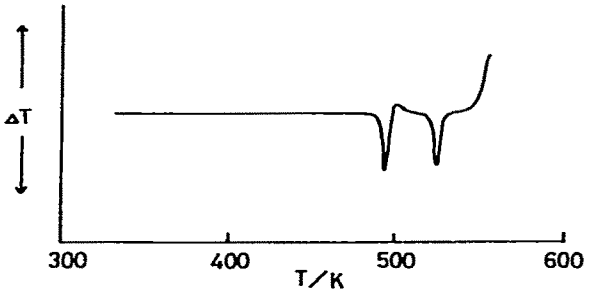


Fig. 2. DTA curve of the green (planar) form of Ni(3-NO_2-sal-*N*-i-Pr)$_2$

obtained by heating the planar form [7]. With the rise of temperature the planar form in the solid state is transformed at 489 K into the tetrahedral form (brown), which then melts at 521 K, as DTA measurements show (Fig. 2).

The results for R = i-Pr are summarized in Table 1. It is not easy at the moment to interpret the results in a consistent way simply in terms of the electronic effects due to the substituents at position X.

(ii) Compounds in which R = cyclohexyl (ch)

There are the following cases (A) and (B) [7].

(A). One planar form only can be isolated: X = H, 5,6-benzo. The conventional methods yield only the olive-green, planar form, which is diamagnetic. No transformation into the tetrahedral form occurs in the solid state on raising the temperature; DTA curves have one endothermic peak corresponding to the melting process.

TABLE 1

Species of type (I) nickel(II) complexes isolated

	X[a]						
R	H	5-Cl	5-Br	3-NO_2	3-CH_3O	5,6-benzo	3,5-Br_2
i-Pr	T	P	P	P,T	P,T	P,T	P
ch	P	P,T	P,T	P,T	P,T	P	T
cp	P,T	P	P,M	P,T	P	P	T

[a] The species underlined are not obtained by the conventional preparation methods. P, planar; T, pseudo-tetrahedral; M, multinuclear.

(B). Both the planar and tetrahedral forms can be isolated: X = 5-Br, 5-Cl, 3-NO_2, 3-CH_3O.

Olive-green crystals of the type (**I**) complex in which R = ch; X = 5-Br are obtained by recrystallization of the crude product from chloroform. They are diamagnetic, and show electronic spectra, with a *d–d* band maximum at 16.3×10^3 cm^{-1}, typical of the planar nickel(II) complex. Brown crystals are obtained by heating the olive-green form at 210–220°C for about 30 minutes [7]. DTA measurements show that the green planar form is transformed at 489 K into the brown form, which eventually melts at 525 K. The paramagnetic (3.23 BM) red-brown form shows electronic spectra typical of the tetrahedral nickel(II) complex. Its powder X-ray diffraction pattern is similar to that of the corresponding zinc(II) complex having a tetrahedral configuration. The transition enthalpy was estimated from DSC measurements to be 9.1 kJ mol^{-1}.

Both planar and tetrahedral isomers of the type (**I**) complex in which R = ch X = 5-Cl are obtained [7]. This pair is similar to the corresponding pair of the 5-bromo-complex. Recrystallization of the crude product from chloroform yields olive-green crystals, which are composed of planar nickel(II) complexes. The red-brown form, which is obtained by heating the planar form at 220–240°C, is paramagnetic (3.25 BM) and consists of tetrahedral nickel(II) complexes. The DTA curve of the olive-green planar form has two endothermic peaks, indicating that the planar form is transformed at 500 K into the red-brown tetrahedral form. The other peak at 521 K corresponds to the melting process of the tetrahedral form. The transition enthalpy was estimated to be 13.0 kJ mol^{-1}.

The type (**I**) complex in which R = ch; X = 3-NO_2 is obtained in planar and tetrahedral forms [7]. Recrystallization of the crude product from organic solvents yields brownish olive-green crystals, which consist of diamagnetic planar nickel(II) complexes. The brown tetrahedral form is obtained by heating the planar form at 210–220°C. The DTA curve of the olive-green planar form has two endothermic peaks at 490 and 550 K, showing that the planar form is transformed at 490 K into the red-brown tetrahedral form. The red-brown form shows only one endothermic peak at 550 K, which corresponds to the melting process.

Olive-green crystals of the type (**I**) complex where R = ch; X = 3-CH_3O are obtained by recrystallization of the crude product from ethanol or methanol [7]. The olive-green form, which is diamagnetic, shows an electronic spectrum typical of the planar nickel(II) complex, with a *d–d* band maximum at 15.8×10^3 cm^{-1}. Another form (red-brown) is obtained by heating the olive-green form. DTA measurements show that the olive-green form is transformed at 475 K into the red-brown form, which then melts at 483 K. When allowed to cool to room temperature, this red-brown form

again turns into the planar, olive-green form. This change proceeds so quickly that any spectral or magnetic measurements with this form have not been carried out. It is most likely that the red-brown form consists of tetrahedral molecules.

Exposure of the olive-green form to the vapour of chloroform or bromoform or recrystallization of the olive-green form from the haloforms yields red-brown crystals of the adducts, $Ni(SB)_2 \cdot 2CHX_3$, where SB stands for the salicylaldiminate ion. The electronic spectra show that the nickel(II) ion in these adducts assumes a four-coordinate pseudo-tetrahedral coordination. When left in the atmosphere, two molecules of CHX_3 are lost, yielding the olive-green, planar complex, $Ni(SB)_2$.

(iii) Compounds in which R = cycloheptyl (cp).

There are the following cases (A) and (B) [13].

(A-1). One planar form only can be isolated: X = 5-Cl, 3-CH_3O, 5,6-benzo.

(A-2). One tetrahedral form only can be isolated: X = 3,5-Br_2. The DTA curves of these complexes have one endothermic peak, which corresponds to the melting process, showing that no configurational change occurs in the solid state as the temperature is raised.

(B). More than one form can be isolated: X = H, 3-NO_2 (planar and tetrahedral), and X = 5-Br, 5-NO_2 (planar and multinuclear).

The type (**I**) compound in which R = cp; X = H is obtained in the planar and tetrahedral forms. The diamagnetic green form (G-**I**) is isolated by recrystallization of the crude product from chloroform and shows an electronic spectrum typical of the planar nickel(II) complex. Another olive-green form (G-**II**), which also consists of diamagnetic planar complexes, is obtained by heating the green form (G-**I**) above 463 K. The paramagnetic (3.32 BM) red-brown form is obtained by heating the green form (G-**II**) and consists of pseudo-tetrahedral nickel(II) complexes on the basis of spectral and magnetic data. The DTA curve of the green planar form (G-**II**) has two endothermic peaks at 439 and 461 K, indicating that the planar form (G-**II**) is transformed at 439 K into the paramagnetic red-brown tetrahedral form. The red-brown form shows only one endothermic peak at 461 K, which corresponds to the melting process.

The type (**I**) complex in which R = cp; X = 5-Br is isolated in two forms, one being planar and the other multinuclear. The olive-green planar form (diamagnetic) is obtained by heating the methanol adduct $Ni(SB)_2 \cdot 2MeOH$, which is prepared by evaporating a solution of the crude product in methanol at room temperature. This light green adduct contains nickel(II) ions in the six-coordinated environment, as spectral data indicate, and loses methanol molecules above 70°C, as revealed by TGA measurements. The

DTA curve of the methanol adduct has three endothermic peaks at 343, 448 and 508 K. Spectral and magnetic studies have shown that the species in the region between 343 and 448 K is the planar complex $Ni(SB)_2$, which above 448 K turns into the multinuclear form of the same composition having nickel(II) ions in the six-coordinate environment. The multinuclear form, which is paramagnetic (2.86 BM), is also isolated by evaporating a solution of the olive-green form in chloroform at room temperature. Heating the planar form does not yield the tetrahedral form. The hydrate $Ni(SB)_2 \cdot nH_2O$ $(2 > n > 1)$ exhibits similar behaviour to the methanol adduct.

Two forms of the type (**I**) complex having R = cp; X = 5-NO_2 are isolated, one being planar with four-coordinate nickel(II) and the other multinuclear with six-coordinate nickel(II) ions. Brownish green crystals, which are obtained by recrystallization of the crude product from organic solvents, are diamagnetic and consist of the planar complexes. No transformation into the tetrahedral form occurs as the temperature rises; the DTA curve has only one endothermic peak at 580 K, which corresponds to the melting process. Light green crystals of the same formula $Ni(SB)_2$, obtained by evaporating a solution of the crude product in chloroform/benzene mixture at about 10°C, are paramagnetic (2.88 BM) and show electronic spectra typical of the six-coordinate nickel(II) complex. It is thus very likely that they consist of multinuclear complexes. This multinuclear form is also obtained by heating the methanol adduct $Ni(SB)_2 \cdot 2MeOH$ at about 110°C, and is isolated as light green microcrystals by evaporation at about 10°C of a solution of the crude product in chloroform/methanol. The multinuclear form is transformed at 441 K into the planar form $Ni(SB)_2$, which finally melts at 580 K; the DTA curve has two peaks at these temperatures, the former being exothermic and the latter endothermic.

The isomeric and associated species of the nickel(II) complexes which have been isolated are set out in Table 1. Thermodynamic quantities, estimated by means of solution spectra at various temperatures, are shown in Table 2 [13], some data on the isopropyl and cyclohexyl derivatives being

TABLE 2

Free energies (kJ mol^{-1}) for the equilibria pl=td for the type (**I**) nickel (II) complexes having R=cp in chloroform

	X					
	H	5-Br	5-Cl	5-NO_2	3-NO_2	3-CH_3O
ΔG	2.2	1.8	1.5	2.7	−1.7	−1.8

TABLE 3

Enthalpies and temperatures of the transitions pl → td for type (I) nickel(II) complexes in the solid state

R	X	ΔH(kJ mol^{-1})	Trans. temp., T (K)
i-Pr	3-CH_3O	7.1	431
i-Pr	5,6-benzo	21.8	482
ch	5-Br	9.1	489
ch	5-Cl	13.0	496
ch	3-CH_3O	Small	475

given in Table 3 for comparison. It should be noted that even those complexes, which can be isolated only in one form in the solid state, exist as an equilibrium mixture among the planar, associated, and tetrahedral species in solution.

Inspection of Table 1 shows that the multinuclear species occur with the cycloheptyl complexes and not with the cyclohexyl or isopropyl complexes. It is also found that the tendency of the cycloheptyl complexes to have a tetrahedral configuration is lower than that of the isopropyl and cyclohexyl complexes. Thus the cycloheptyl group seems to exert less steric constraint than the cyclohexyl group. The difference in this respect between the cyclohexyl and isopropyl complexes is not very straightforward. A comprehensive interpretation of the results in terms of electronic and steric effects due to R and X may not be feasible at the moment.

(iv) Compounds in which R = aryl

Nickel(II) complexes of type (**I**) in which R = aryl have a higher tendency to form associated species than the alkyl derivatives, and most of the complexes have been isolated in either planar or multinuclear structures in the solid state. Even the type (**I**) complexes where R = 2,6-Y_2-Ph; Y = Me, Et, n-Pr, in which the steric constraint is comparatively high, are not tetrahedral but square-planar [1,14]. The first isolation of a tetrahedral species has been achieved with bis(*N*-4-methoxyphenyl-3-methoxysalicylaldiminato)nickel(II), which is obtained by the conventional method [15]. This complex is paramagnetic (3.34 BM), and its powder X-ray diffraction pattern is very similar to that of the corresponding cobalt(II) complex, which has a tetrahedral configuration. The tetrahedral configuration is retained in solution. The reason why the tetrahedral configuration occurs with this complex is not completely clear.

Type (**I**) compounds in which X = 3-CH_3O; R = 4-Cl-Ph, 4-Br-Ph are isolated in two forms, one being red-brown and the other light green [16]. Recrystallization of the crude product from chloroform yields the light green form, while the red-brown form is obtained by heating a solution of the crude product in a large amount of ethanol for several hours. Both the forms are paramagnetic with magnetic moments corresponding to two spin-free electrons. Spectral and magnetic measurements indicate that the green form has a multinuclear structure, in which the nickel(II) ions are six-coordinate. In a similar way, the red-brown form most probably consists of tetrahedral complexes, although a binuclear configuration was once proposed. The powder X-ray pattern of the brown form is similar to those of the corresponding zinc(II) and cobalt(II) complexes, which are tetrahedral.

The type (**I**) complex in which R = 4-CH_3O-Ph; X = 5-NO_2 is obtained in three kinds of species with different configurations [14b]. The conventional recrystallization methods yield two types of hydrate, one being $Ni(SB)_2 \cdot 3H_2O$ (brown) and the other $Ni(SB)_2 \cdot 1.5H_2O$ (light green) [17]. The former can be formulated as $[Ni(SB)_2(H_2O)_2] \cdot H_2O$, containing the six-coordinate complex, while the latter consists of binuclear complexes $[Ni_2(SB)_4H_2O]$, in which the two nickel(II) ions are six-coordinate, one H_2O and two phenolic oxygen atoms functioning as bridges.

The heating method starting from $Ni(SB)_2 \cdot 1.5H_2O$ yields various nickel(II) complexes of the same composition $Ni(SB)_2$ [14b], as shown in Scheme 1. As DTA curves show, forms **II**, **III** and **IV** occur in this order, as the temperature rises. Electronic spectra indicate that forms **III** and **IV** have square-planar and pseudo-tetrahedral configurations, respectively, the former being diamagnetic and the latter paramagnetic (3.35 BM).

$$\underset{\mathbf{I}}{[Ni_2(SB)_4H_2O] \cdot 2H_2O} \xrightarrow[190-200°C]{\Delta} \underset{\mathbf{II}\ (\text{multinucl})}{Ni(SB)_2\ (\text{light green})} \xrightarrow[225-235°C]{\Delta}$$

$$\underset{\mathbf{III}\ (\text{pl})}{Ni(SB)_2\ (\text{olive-green})} \xrightarrow[250-260°C]{\Delta} \underset{\mathbf{IV}\ (\text{ps-td})}{Ni(SB)_2\ (\text{brown})}$$

Scheme 1. $Ni(SB)_2$ denotes a type (**I**) complex in which R = 4-CH_3O-Ph and X = 5-NO_2. Pl, planar; ps-td, pseudo-tetrahedral; multinucl, multinuclear.

Form **II** is paramagnetic and shows an electronic spectrum typical of the six-coordinate nickel(II) complex, probably having a multinuclear structure with the nickel(II) ions in the six-coordinate environment. Form **III** (planar form) is also obtained by heating a solution of the complex **I** in n-butanol at its boiling point.

Powder X-ray diffraction patterns reveal that forms **I**, **III** and **IV** are

crystalline, while form **II** is not. Spontaneous evaporation at room temperature of form **II** in dichloromethane yields light green microcrystalline powder (form **II'**) of the composition $Ni(SB)_2$. There is a slight difference in the temperature dependence of magnetic susceptibilities between forms **II** and **II'**; both forms show nearly identical electronic spectra. Magnetic susceptibilities of form **II** obey the Curie–Weiss law from room temperature down to 4 K. On the contrary, susceptibilities of form **II'** obey the Curie–Weiss law from the room temperature to very low temperatures, where deviation occurs, showing the possible existence of superexchange interaction between nickel(II) ions [14c]. The difference between the two forms probably lies in the extent of structural disorder; the X-ray powder pattern of form **II'** shows it to be crystalline, in contrast to form **II**.

C. COPPER(II) COMPLEXES

The stereochemistry of Schiff base copper(II) complexes seems to be somewhat similar to, but is much more versatile than, that of the nickel(II) complexes [1–4,18]. For instance, the type (**I**) copper(II) complexes where R = n-Pr or n-Bu are planar, while the ethyl derivative crystallizes in two modifications, one of them (monoclinic) being composed of distorted tetrahedral complexes with a dihedral angle of 35.6° and the other (orthorhombic) containing two independent molecules which differ slightly in molecular geometry with dihedral angles of 7.4° and 11.4°, respectively [19]. The type (**I**) methyl derivative in which R = Me exhibits three different stereochemistries in its three crystalline forms. The α- and β-forms contain perfectly planar molecules, while the γ-form contains binuclear molecules with fivefold-coordination about the copper ion [20].

The type (**I**) complexes in which R = t-Bu are tetrahedral owing to the steric constraint arising from the bulky t-butyl. The present paper describes results of attempts to isolate isomeric species of copper(II) complexes with R = α-branched alkyls and cycloalkyls, where the steric constraint lies in between n-alkyl and t-butyl.

(i) Compounds in which R = α-branched alkyls

It was previously reported that by the conventional preparation methods the complexes of formula (**I**) in which R = i-Pr were obtained in either a planar or a tetrahedral form, but not both, the configuration of the isolated species depending upon X [3,21]. Subsequent studies have revealed that more than one isomeric or associated species for some copper(II) complexes of this series can be isolated in the solid state [7,22,23]. However, the configurations of isomeric pairs obtained are not similar to those of the corresponding

nickel(II) complexes. The difference in the configuration between isolated forms of the copper(II) complexes is not always as clear-cut as the nickel(II) complexes.

Two isomers of the type (I) complex in which R = i-Pr and X = 3-CH_3O have been isolated, both being distorted from the planar configuration [22–24]. The olive-green form is isolated by evaporating at 5–10°C a methanolic solution of the crude product and the red-brown form is obtained by the conventional recrystallization of the crude product from non-donor organic solvents. The brown form is also obtained by the heating method, and shows the same powder X-ray diffraction pattern as that of the brown form isolated from the solution.

According to X-ray studies, both forms are mononuclear and distorted from the planar configuration (Fig. 3) [24]. A remarkable difference between the two forms lies in the manner of the distortion. The fold angles between the Cu(N) (O) plane and O–C=C–CH=N and between the benzene ring and O–C=C–CH=N are 18.2 and 5.3° for the olive-green and 6.0 and 3.6° for the red-brown form, respectively. 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. DTA curves show that the olive-green form is transformed at 374 K into the brown form, which eventually melts at 397 K.

Brown crystals of the type (I) complex in which R = i-Pr; X = 5-Cl are obtained by reactions using an excessive amount of the amine, followed by recrystallization from chloroform. Green crystals were previously reported. Structural investigation is in progress.

The olive-green form of the type (I) complex having R = i-Pr; X = 5,6-benzo was previously prepared by conventional methods [21]. The brown form of the complex has recently been isolated by two different methods [7,22], i.e., (1) by heating a mixture of the olive-green crude product and an equimolar amount of isopropylamine in ethanol and (2) by heating the olive-green form at 105–110°C. Thermal studies show that the olive-green form is transformed at 375 K into the brown form, which melts at 463 K after undergoing another phase transition at 445 K. The brown form shows

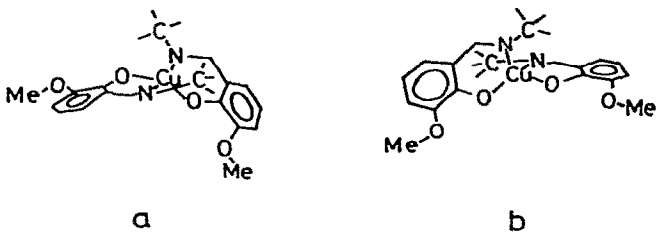


Fig. 3. Configurations of Cu(3-CH_3O–sal–*N*-i-Pr)$_2$: a, green form; b, brown form.

only one endothermic peak at 463 K. This pair of isomers is very similar, in many respects, to the isomers of the complex with X = 3-CH_3O. The electronic spectrum of the brown form has absorption bands or shoulders at 11.5, 15.3, and 20.5×10^3 cm^{-1}. The comparatively low frequencies of the *d–d* band maxima seem to indicate a configuration distorted from the planar. According to X-ray studies, the brown form consists of mononuclear tetrahedral complexes with a dihedral angle of 38.3° [24]. The olive-green form also seems to have a distorted-tetrahedral configuration, since its spectrum is very similar to that of the olive-green form of the type (**I**) complex in which R = i-Pr and X = 3-CH_3O, which is distorted-tetrahedral [24].

The red and green forms of the type (**II**) complex in which R = i-Bu; X = 5-Cl have been isolated in the solid state [25]. According to X-ray studies, the red form is *trans*-planar, while the green form is approximately *cis*-planar, slightly distorted from the planar configuration with a dihedral angle of 14.5°.

(ii) Compounds in which R = cycloalkyl

Two isomers of the type (**I**) complex where R = ch; X = H have been obtained from solution, one being red-brown and the other olive-green [22]. Recrystallization of the crude product from hot chloroform yields brown crystals, while the olive-green form is obtained by evaporation below 10°C of a solution of the crude product in chloroform. Heating the brown form at 165–175°C also yields the green form, which is identical with that obtained from solution. The green form shows one endothermic peak at 450 K in the DTA curve. The DTA measurements also show that the brown form is transformed at 439 K into the green form, which eventually melts at 450 K.

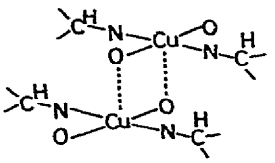
According to X-ray studies, the $Cu(N)_2(O)_2$ moiety in the brown form is perfectly *trans*-planar, while the olive-green form consists of binuclear complexes, in which copper(II) ions assume a distorted square-pyramidal configuration (Fig. 4) [26]. The brown planar form shows a *d–d* band at about 17×10^3 cm^{-1} with a shoulder at about 14.1×10^3 cm^{-1}, in addition to a more intense CT band beyond 20×10^3 cm^{-1}. The green binuclear form shows a comparatively broad band at about 17.4×10^3 cm^{-1}. The enthalpy of transition from the planar to binuclear form was estimated to be 11.3 kJ mol^{-1}.

More than two forms of the type (**I**) complex in which R = ch; X = 5-Br have been isolated [7,22]. Recrystallization of the crude product from hot chloroform yields the brown form (B-**I**), while the green form (G-**I**) is obtained by evaporating a chloroform solution of the crude product below 10°C. Another brown form (B-**II**) is obtained from the B-**I** form by the

heating method. DTA curves show that the B-I form is transformed at 478 K into the B-II form, which melts at 493 K. The form B-II, which readily undergoes configurational change of some sort when allowed to stand at room temperature, may most probably have a distorted-tetrahedral configuration. The green form shows one endothermic peak at 458 K, which corresponds to the melting process. Another green form (G-II) is obtained by rapid evaporation of a chloroform solution at 10–15°C. The G-II form, which shows only one endothermic peak at 485 K, obviously differs from the G-I form and may consist of complexes having a configuration different from that of the G-I form. Some of the DTA curves are shown in Fig. 5.

Electronic spectra of the green (G-I) and brown (B-I) forms of the 5-bromo-complex are very similar to those of the corresponding forms of the type (I) complex having R = ch; X = H, implying that the configurations of the two forms of the 5-bromo-complex are similar to those of the corresponding forms of the type (I) complex in which R = ch; X = H, respectively.

Two forms of the type (I) complex where R = ch; X = 5-Cl are obtained from solution [22]. In contrast to the 5-bromo-complex, the conventional recrystallization method from hot chloroform or ethanol yields the green



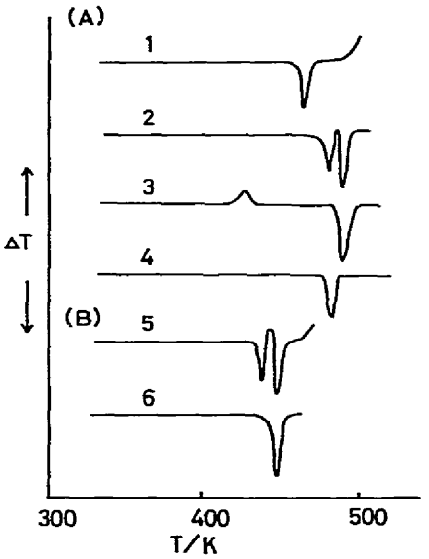


Fig. 4. Molecular structure of Cu(H–sal–*N*-ch)$_2$ in the green form.

Fig. 5. DTA curves of (A), Cu(5-Br–sal–*N*-ch)$_2$ and (B), Cu(H–sal–*N*-ch)$_2$: (A) 1, green (G-I) form; 2, brown (B-I) form; 3, brown (B-II) form; 4, green (G-II) form. (B) 5, brown form; 6, green form.

form (G-**I**, 1.97 BM), while the brown form (1.85 BM) is obtained by evaporating a solution of the green form in chloroform at about 5°C. Heating the brown form at 160–180°C yields a green form (G-**II**), which shows an endothermic doublet consisting of two peaks at 472 and 477 K. As DTA curves show, the brown form is transformed at 431 K into the green form (G-**II**), which melts at 473 K. The green form (G-**I**) is also transformed at 466 K into the green form (G-**II**).

The electronic absorption spectrum of the red-brown form closely resembles that of the brown form of the type (**I**) compound in which R = ch; X = H, implying that this form consists of mononuclear planar complexes. The powder X-ray pattern of the brown form is similar to that of the planar nickel(II) type (**I**) complex in which R = ch; X = 5-Cl. A close similarity in the electronic spectra also suggests that the olive-green form (G-**I**) has a similar configuration to that of the olive-green form of the parent type (**I**) complex having R = ch; X = H, namely a binuclear configuration. Spectral and DTA data combined seem to show that the green form (G-**II**) has a distorted-tetrahedral configuration, although a definitive conclusion about it must await further studies. The transition enthalpy from the red-brown to green form (G-**II**) was estimated to be 5.4 kJ mol^{-1}.

Two forms of the type (**I**) complex in which R = ch; X = 5,6-benzo can be isolated [22]. The olive-green form is obtained by recrystallization from methanol/chloroform, while the brown form is isolated by heating the green form at 200–215°C. Electronic spectra indicate that the olive-green form showing a main *d–d* band at a high frequency (16.5×10^3 cm^{-1}) consists of planar complexes, while the copper(II) complex in the red-brown form, which shows the main *d–d* band at about 14.5×10^3 cm^{-1}, is distorted from the square-planar configuration. The planar form (olive-green) is transformed at 490 K into the distorted-tetrahedral form (red-brown), which melts at 512 K.

The type (**I**) complex in which R = ch; X = 3-CH_3O is obtained in two forms. Recrystallization of the crude product from benzene or methanol/chloroform yields the olive-green form, which consists of planar copper(II) complexes [22]. The olive-green form is transformed at 450 K into the red-brown form, which reverts fairly rapidly to the olive-green planar form, when allowed to cool to room temperature [22]. The red-brown form most probably has a distorted-tetrahedral configuration.

The tetrahedral configuration seems to be stabilized in the red-brown adducts of the type $Cu(SB)_2 \cdot 2CHX_3$, X being Cl and Br, which are isolated in crystals by recrystallizing the parent complex from the haloforms. Electronic spectra indicate that the copper(II) complex in these adducts has a pseudo-tetrahedral configuration. When left to stand in the atmosphere, the adducts slowly lose the haloform molecules, turning again into the planar

olive-green form. The adducts may be kept in a glass tube at room temperature for a comparatively long period, e.g. a few months.

Similar results have been obtained with the type (**I**) cycloheptyl complex in which R = cp; X = 3-CH_3O [27]. Recrystallization from haloforms (X = Cl, Br) of the olive-green planar form, which is obtained by the conventional preparation methods, yields adducts of the composition $Cu(SB)_2 \cdot 2\,CHX_3$, in which the complex has pseudo-tetrahedral configuration. The brown tetrahedral form, obtained by heating the planar form, rapidly turns into the olive-green planar form, when allowed to cool to room temperature. By contrast, the haloform adducts lose the haloform molecules very slowly to turn into the planar olive-green form in the atmosphere at room temperature. As the temperature is raised, the chloroform adduct loses chloroform

TABLE 4

Species of type (**I**) copper(II) complexes isolated

R	X	Species isolated [a]	
i-Pr	3-CH_3O	Green (l.t.)	Brown(h.t.) [c]
		Ps-td [b]	Ps-td [b]
i-Pr	5,6-benzo	Green(l.t.)	Brown(h.t.) [c]
		Pl or td	Ps-td [b]
i-Pr	5-Cl	Green	Brown
		Pl or td	Ps-td
ch	H	Brown(l.t.)	Green(h.t.) [c]
		Trans-pl [b]	Binucl [b]
ch	5-Br	Brown **I**(l.t.)	Green **I**
		Pl	Binucl
		Brown **II**(h.t.)	Green **II**
		Ps-td (?)	Ps-td (?)
ch	5-Cl	Green **I**(l.t.)	Brown(l.t.) [c]
		Binucl	Pl
		Green **II**(h.t.)	
		Ps-td	
ch	5,6-benzo	Green(l.t.)	Brown(h.t.)
		Pl	Ps-td
ch	3-CH_3O	Green(l.t.)	Brown(h.t.)
		Pl	Ps-td
cp	3-CH_3O	Green(l.t.)	Brown(h.t.)
		Pl	Ps-td

[a] Pl, planar; ps-td, pseudo-tetrahedral; binucl, binuclear. The high temperature form (h.t.) is obtained by heating the low temperature form (l.t.) at an appropriate temperature.

[b] Determined by X-ray structure analysis.

[c] Isolated also from solution.

molecules at about 334 K, yielding the planar olive-green compound $Cu(SB)_2$, which is then transformed at 441 K into the brown pseudo-tetrahedral form, which eventually melts at 575 K.

The isolated species of the copper(II) complexes are set out in Table 4. Since the structures of the copper(II) complexes isolated are manifold, the copper(II) complexes of this series exhibit various types of isomeric and oligomeric pairs, which comprise *cis*- and *trans*-planar, tetrahedral with different degrees of distortion, and binuclear configurations. In solution there may occur various kinds of equilibria among several species having configurations with various types of distortion. It should also be noted that one can not always safely conclude the stereochemistries of the copper(II) complexes from their colours alone. Electronic spectra are useful to a limited extent for discussion of the configurations of the copper(II) complexes. Although a slight change in the distortion may give rise to some spectral change, this is however, often too inconsiderable and subtle to differentiate between the various degrees of minor distortion which often occur in copper(II) complexes of this series.

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