Coordination Chemistry Reviews, 47 (1982) 239–261
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

STRUCTURAL ISOMERISM OF COPPER(II) COMPOUNDS

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(Received 12 February 1982)

CONTENTS

ABBREVIATIONS

α-ala	α-alaninate
5,6-benzo-salim-ch	*N*-cyclohexyl-5,6-benzosalicylideneaminate
5,6-benzo-salim-i-C_3H_7	*n*-isopropyl-5,6-benzosalicylideneaminate
bipy	2,2′-bipyridine
$BH(N_2C_3H_3)_3$	hydrotris(pyrazol-1-yl)borate
5-Br-salim-ch	*N*-cyclohexyl-5-bromosalicylideneaminate
5Brsal	5-Bromosalicylate
3-CH_3O-salim-ch	*N*-cyclohexyl-3-methoxysalicylideneaminate
2-CH_3pyNO	2-methylpyridine-*N*-oxide
$C_{14}H_{12}N_4O_2$	*N,N′*-ethylenedi-2-pyridinecarboxyamide
citr	citrate
5Clsal	5-chlorosalicylate
dea	$(C_2H_5)_2NH_2$
dieten	*N,N*-diethylethylenediamine
dm	6,7-dihydroxo-5,8-dimethyl-dibenzo[b, j][1,10]phenanthroline
dmaep	2-(2-dimethylaminoethyl)pyridine
DMF	dimethylformamide
dppa	phenyl-di-2-pyridylamine
EIA	7-hydroxy-4-methyl-5-aza-hept-4-en-2-one
en	ethylenediamine
Et_5dien	1,1,4,7,7-pentaethyldiethylenetriamine
i-Bu-cbp	*N*-isobutyl-(5-chloro-α-phenyl-2-hydroxybenzylidene)aminate

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im	imidazole
ipa	$(CH_3)_2CHNH_3$
ipsalim	*N*-isopropylsalicylaldiminate
2,9-me-phen	2,9-dimethyl-1,10-phenanthroline
4-mepy	4-methylpyridine
ω-nap	ω-nitroacetophenonate
N-ch-salim	*N*-cyclohexylsalicylideneaminate
nct	nicotinate
nic	nicotine
nmpH	*N*-methylphenethylammonium
$OPph_3$	triphenylphosphine oxide
pbsa	1-phenylbiquanide-*p*-sulfonic acid anion
pfb	pentafluorobenzoate
1,10-phen	1,10-phenanthroline
2-pic	2-picoline
pz	pyrazole
py	pyridine
sal-pr-$N(CH_3)_2$	*N*-(3-hydroxypropyl)salicylideneamine
tbpa	*N*-thiobenzoyl-*N*-phenylhydroxylamine
teen	*N*,*N*,*N'*,*N'*-tetraethylethylenediamine
tppo	tri(2-pyridyl)phosphine oxide
tren	2,2',2''-triaminotriethyl
tripyam	tri(2-pyridyl)amine
urt	urotropine

A. INTRODUCTION

Systematic studies in the field of stereoselectivity of coordination compounds in the last two decades have rapidly found a wide interest and several reviews have already appeared [1–5]. It is noteworthy that the problem of stereoselectivity in coordination compounds is very often related to the well-known stereochemical specificity of biological systems, catalysis and the stereochemical effect in technical processes, etc.

One can define diastereoselectivity as the formation of diastereoisomers in a non-statistical ratio in any chemical transformation [5]. Such a definition concerns equilibrium as well as non-reversible reactions.

One of the various types of structural isomerism is stereoisomerism. Stereoisomerism [6–9], in turn, is subdivided into geometric isomerism and optical isomerism. Although the two types of isomerism are encountered among coordination compounds which involve the relatively kinetically stable central atoms (Pt(II), Co(III), etc.) such isomers also exist (although not so frequently), when the central atom is a kinetically labile copper(II) atom. It seems that in the case of copper(II) compounds distortion isomers prevail [10].

In this review we present the types of isomer observed in copper(II) compounds. Despite the considerable literature on isomers of copper(II) compounds, no such review exists.

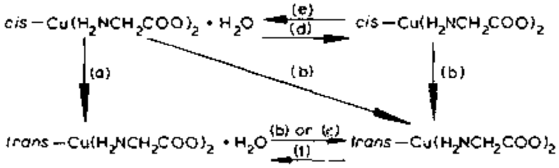
The aim of following presentation is to discuss the factors which may lead to a better understanding of the stereochemical interactions in the coordination sphere of copper(II) compounds and to discuss some cooperative effects between the isomeric types.

B. *CIS–TRANS* ISOMERISM

The first example of *cis–trans* isomerism in compounds of the kinetically labile copper(II) atom was bis(glycinato)copper(II). The compound that led Ley [11] to formulate his concept of inner complexes was first discovered in 1841 by Baussingault [12]. Mauthner and Suida [13] discovered that the compound occurred in two isomeric forms, pale blue needles and bluish violet glistening scales. Ley and Wiegner [14] and later Grinberg and Globraith [15] have studied these two isomeric forms and they proposed geometrical isomerism, the more stable *trans* and less stable *cis* isomer. In 1961 Tomita [16,17] confirmed this supposition by X-ray diffraction (*cis*) and by infrared spectroscopy (*trans*).

The crystal structure of *cis*-bis(glycinato)copper(II) monohydrate was determined by Tomita and Nitra [17] and the refinement by Freeman et al. [18] is essentially the same as reported by Tomita and Nitra [17], but the standard deviations of the distances have been reduced to a third of their previous values. Crystals of the *cis*-compound crystallize in the orthorhombic system in space group $P2_12_12_1$ with 4 molecules per unit cell ($Z = 4$). Two glycine molecules are chelated to the copper(II) atom, forming an almost planar *cis* configuration, where Cu–O distances are 1.957 and 1.946 Å and Cu–N distances are 1.984 and 2.021 Å, respectively. The irregular octahedral coordination is completed by two oxygen atoms: one belonging to a water molecule (Cu–O = 2.405 Å) and the other a "free" carboxyl oxygen atom of an adjacent asymmetric unit (Cu–O = 2.742 Å). Crystals of the *trans*-$Cu(H_2NCH_2COO)_2 \cdot H_2O$ crystallizes in the monoclinic system with 4 molecules per unit cell ($Z = 4$) [19]. Two glycine molecules are chelated to the copper(II) atom, forming an almost planar *trans* configuration. The octahedral coordination is completed by two oxygen atoms belonging to a carboxyl group of an adjacent asymmetric unit (Cu–O = ca. 2.8 Å). The water molecule is not present in the coordination sphere of the copper(II) atom but is situated in the channels between the copper(II) glycine molecules.

The thermal decomposition of the two isomeric forms follows different courses [20,21]. The initial temperature of decomposition is 353 K for *trans*-$Cu(H_2NCH_2COO)_2 \cdot H_2O$ and 418 K for the *cis* isomer. They both lose the water molecule in one step. The anhydrous forms of $Cu(H_2NCH_2COO)_2$ show differences in their Debye-grams [20]. Ablov et al. [20] found thermal interconversion in geometrical isomers of copper(II) glycinate, as can be seen in Scheme 1.



Scheme 1

(a) Refluxing with a small amount of water for several hours; (b) at 473 K; (c) at 378 K for 60 min; (d) at 413 K for 25 min; (e) standing in desiccator over water for 7 days; (f) standing in desiccator over water for 28 days.

The IR spectra [16,22–30] of both the monohydrate and anhydrous isomers are different. The greatest differences occur in the $\nu_{(Cu-N)}$ and $\nu_{(Cu-O)}$ frequencies [30]. The metal–nitrogen stretching frequencies are attributed to lines at 477 cm^{-1} in the *trans* form and at 471 and 454 cm^{-1} in the *cis* form. The metal–oxygen stretching frequencies for these isomers are assigned at 334 cm^{-1} for the former, and at 330 and 277 cm^{-1} for the latter.

The electronic spectra of the monohydrate isomers in the solid state are different [31]. The spectrum of the *cis* isomer has a peak at a longer wavelength and is more intense than that of the *trans* isomer and has an accompanying shoulder on the longer wavelength side. Moreover, the isomers give identical spectra in aqueous solution, which are similar to that of the *trans* isomer in the solid state. This is a consequence of the rapid rearrangement of the ligands in the *cis* isomer. The EPR spectra of the isomers are also different [20,30,32].

The bis(α-alaninato)copper(II) also exists in two geometric isomeric forms [33]. In the crystal structure of *trans*-$Cu(\alpha\text{-ala})_2$ [34], the copper(II) atom is surrounded by two nitrogen and two oxygen atoms in the *trans* position and distorted octahedral coordination is completed by two carboxylate oxygen atoms of neighbouring molecules (Fig. 1a). These six atoms are at the corners of a distorted octahedron. While the crystals of *trans*-$Cu(\alpha\text{-ala})_2$ are pale blue in colour and crystallize in the space group $P2_1$ of the monoclinic system [34], the *cis*-$Cu(\alpha\text{-ala})_2$ are deep blue in colour and crystallize in the space group $P2_12_12_1$ of the orthorhombic system [35,36]. The stereochemistry of the deep blue isomer is shown in the Fig. 1b. The inner coordination sphere around the copper(II) atom is square-pyramidal, the two bidentate amino acids rings are *cis* and form the basal plane of the pyramid, the apex being occupied by a carboxylate oxygen atom from a neighbouring molecule at a distance of 2.390(7) Å. The sixth position of what would constitute

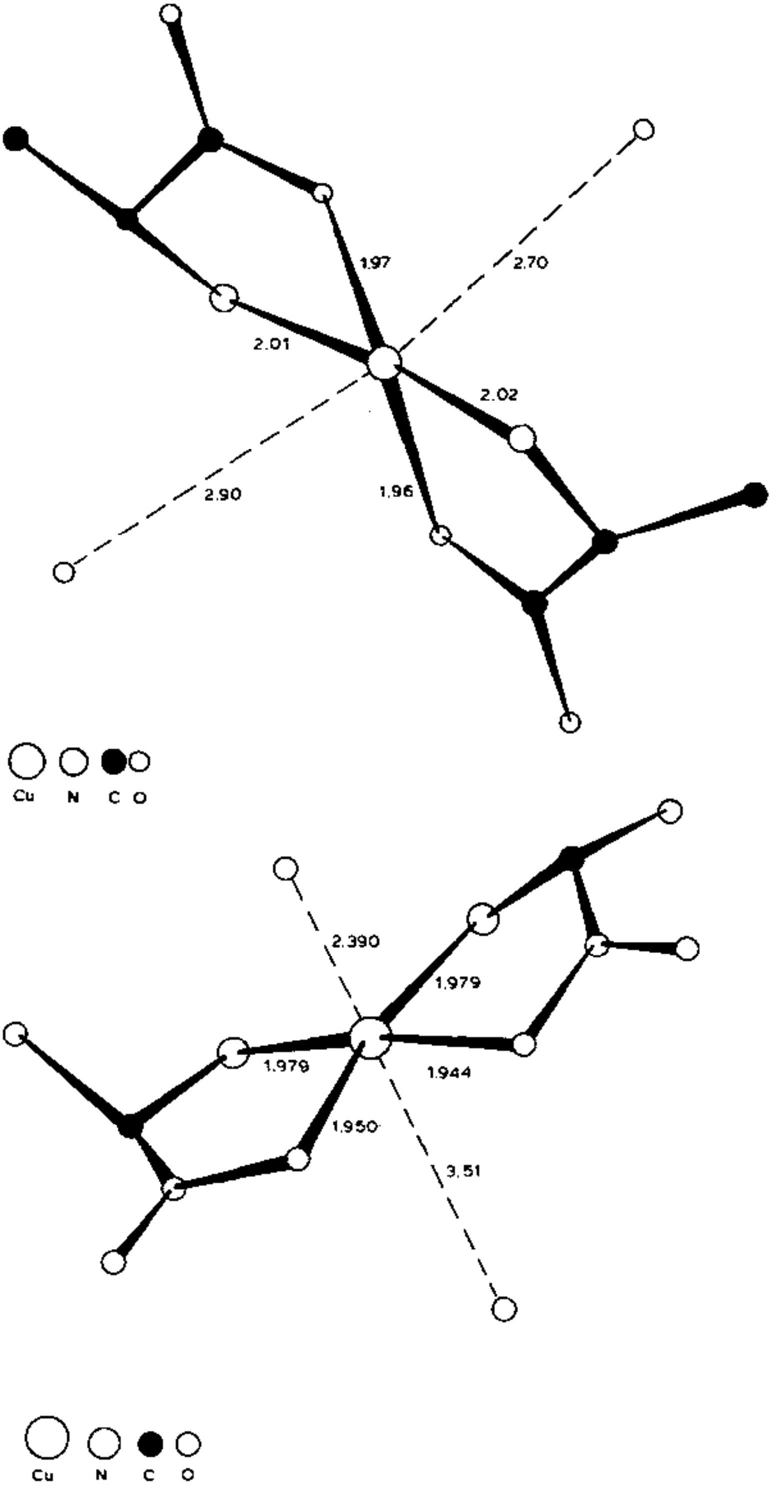


Fig. 1. A schematic view of the crystal structure of (a) *trans*- [34] and (b) *cis*-copper(II) α-alaninate [36].

octahedral coordination of the copper is filled by a methyl group of a neighbouring molecule at a distance (Cu–C(H_3)) of 3.51(1) Å. The molecular structure is built up from parallel chains of molecules. The geometrical isomers of Cu(α-ala)$_2$ differ in their IR spectra [37,38] and are very similar to those of the copper(II) glycinate isomers.

The blue and blue-violet isomers of Cu(DL-phenyl-alaninato)$_2$ display differences in their electronic, EPR and IR spectra [37,39], attributed to the existence of a *trans* configuration for the blue isomer, while the blue violet adopts a *cis* configuration.

The compound Cu(tyrosinato)$_2$ exists in two isomeric forms, the dark blue *trans*(L) and the blue violet *cis*(DL) isomer [40,41]. Kauffman et al. [42] studied the separation by thin-layer chromatography on silica gel of Cu(tyrosinato)$_2$ isomers as well as of a number of square-planar geometric isomers of Pt(II), Pd(II), Ni(II), etc. They found, with only a few exceptions, the *trans* isomer is more mobile than the *cis* isomer, i.e. R_F *trans* > R_F *cis*.

It is interesting to note that *cis*-Cu(aminoacido)$_2$ has so far been isolated only from a saturated solution of the *trans* compound [20,38]. The reason that it is possible to isolate the metastable *trans* isomer must be kinetic rather than thermodynamic. It may well be that formation of suitable nuclei is much more difficult for the *cis* than for the *trans* crystal. It is probable that the main cause of the molecule adopting this geometrical isomer in the solid state is the strong apical bond, and that the distortions observed in the geometry of the chelate rings, compared to those of the free ligand, may result from crystal packing considerations [36].

Attanasio et al. [43] prepared two isomers of Cu(ω-nap)$_2$py$_2$, one green and the other yellow. The electronic spectra of both isomers display three absorption bands appearing at about 0.91, 1.43 and 2.15 μm^{-1} (green), and at about 0.70, 1.30 and 2.13 μm^{-1} (yellow). Magnetic data have been completed only for the green-isomer, the effective magnetic moment of which equals 1.97 B.M. at room temperature. The unit cell data and electronic spectra indicate for both isomers a pseudo-octahedral structure, in which the green has the *cis* and yellow the *trans* configuration [43]. Hall et al. [44] prepared Cu(2,9-me-phen)(NO_3)$_2$ and studied its spectral behaviour. From the EPR spectrum of the compound at 120 K it was deduced [45] that the compound exists at that temperature in two isomeric forms as *cis*- and *trans*-Cu(2,9-me-phen)(NO_3)$_2$.

The red and green forms of Cu(pbsa)$_2$ have been prepared by Ray et al. [46–48]. They suggested that these could be *cis* and *trans* isomers. But Catron et al. [49] on the basis of spectral data concluded that the red and green form of Cu(pbsa)$_2$ are not *cis* and *trans* isomers. They formulated the red isomer as a zwitterion (II) and the green as a neutral compound.

Investigations of [Cu(bipy)$_2$(H_2O)$_2$]$^{2+}$ have been concerned with the

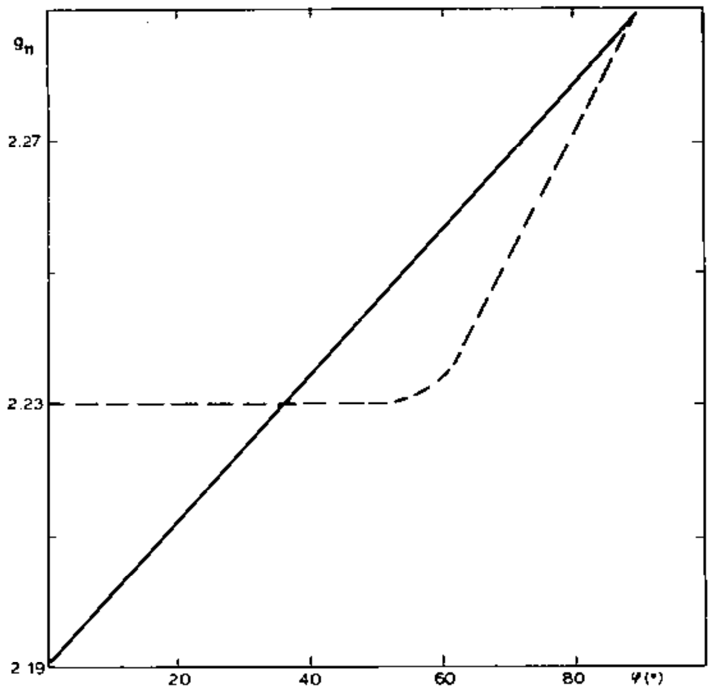


Fig. 2. The plot of $g_{\parallel}$ against the φ angle values of *cis* (———) and *trans* (------) compounds [55].

existence of the two geometrical isomers at 77 K; one in which the two water molecules are *cis* to each other and the other in which they are *trans* [50–52]. The EPR data presented by Walker and Sigel [53] have been attributed to the presence of disproportionation species and not to the presence of *cis* and *trans* isomers of $[Cu(bipy)_2(H_2O)_2]^{2+}$.

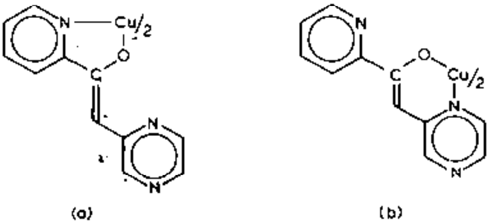
Rehorek et al. [54] studied the spectroscopic properties of planar $Cu(tbpa)_2$ and found that the compound exists as both *cis* and *trans* isomers.

Larin et al. [55] have studied the EPR spectra of some Schiff bases of Cu(II) some of which have a *cis* and some a *trans* configuration. They found a correlation between the $g_{\parallel}$ value and the value of angle (φ) between two metalocycles. In Fig. 2 we can see that the $g_{\parallel}$ value in the compounds which have a *cis* configuration are dependent more on the value of φ than in the case of the *trans* configuration.

C. LINKAGE ISOMERISM

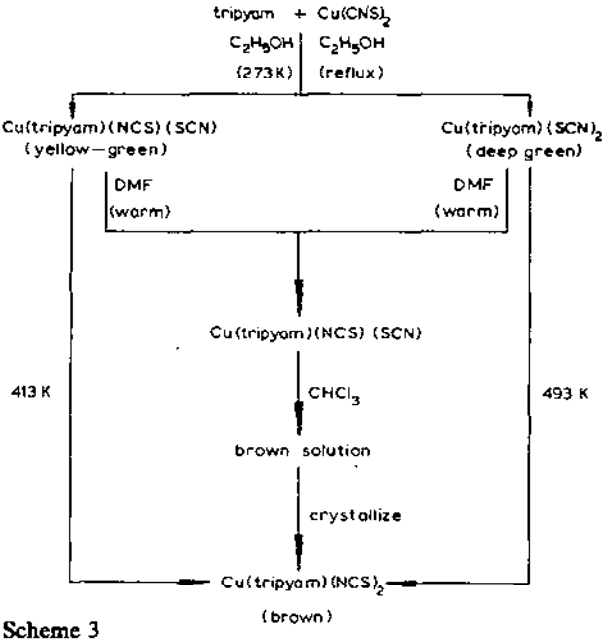
Coordination compounds which exist in at least two forms having the same molecular formula and differ only in the bonding modes of the same ligand to the metal atom are said to be linkage isomers [56,57]. In spite of the fact that the first linkage isomeric pair of metal compounds, the isoxantho and xantho compounds of Co(III), was isolated more than 100 years ago [58] linkage isomers with copper(II) were found only in 1962 [59].

Naqvi et al. [59] studied two linkage isomeric forms of Cu(2-pyridyl pyrazylmethyl ketone)$_2$ and found that two types of chelates were formed with copper(II) and the 2-pyridyl pyrazylmethyl ketone; as can be seen in Scheme 2. We can see (a) chelation with the pyridine nitrogen and the carbonyl oxygen forming a five-membered chelate ring and (b) chelation with the pyrazine nitrogen and the carbonyl oxygen forming a six-membered chelate ring.



Scheme 2

Three isomeric forms of copper(II) thiocyanate with tri-(2-pyridyl)amine were prepared [60]. The preparations of the isomers are summarized in Scheme 3.

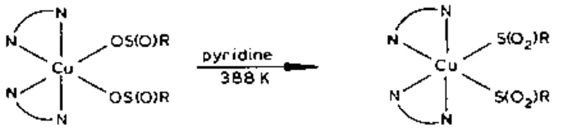


Scheme 3

The isomers were characterized mainly by IR and diffuse reflectance spectra [60]. The spectral data of the isomeric compounds are significantly different, but all are typical of copper(II) atoms in an unsymmetrical planar environment, built up by a bidentate tri-(2-pyridyl)amine and by two monodentate thiocyanate anions.

Kulasingam and McWhinnie [61] prepared another three linkage isomeric forms of copper(II) thiocyanate with phenyl-di-2-pyridylamine (dppa). The isomers Cu(dppa)$(NCS)_2$ (brown), Cu(dppa)(SCN)(NCS) (yellow-green) and Cu(dppa)$(SCN)_2$ (deep green) were characterized mainly by IR and electronic diffuse reflectance spectra. On the basis of spectral data it was proposed [61] that the isomers have structures similar to those of copper(II) isomers with tri-(2-pyridyl)amine [60].

Two linkage isomeric forms of bis(*p*-toluensulfinato-O)-2,2′-bipyridylcopper(II), one deep green (O-isomer) and the other blue (S-isomer), were prepared and characterized by spectral and magnetochemical investigations [62]. Both isomers are reported to possess a pseudo-octahedral environment. Lindner et al. [62] found that in pyridine at 388 K the O-isomer is converted irreversibly into the S-isomer (Scheme 4).



R = p-$CH_3C_6H_4$

Scheme 4

The only known examples of copper(II) cyanato solid linkage isomers are the pairs of isomers of $Cu(NCO)_2$(2,4-lutidine)$_2$ [63] and $Cu(NCO)_2$(2-ethylbenzimidazole)$_2$ [64]. The isomers have been studied by X-ray powder diffraction patterns, IR, electronic and EPR spectroscopy, and by variable-temperature magnetic susceptibility measurements. On the basis of experimental data a pseudo-octahedral coordination was proposed [63] for the isomers, in which are axially coordinated NCO groups, in one case through nitrogen and in the other through oxygen atoms.

Tomlinson and Hathaway [65] studied $Cu(NO_2)_2(NH_3)_2$ and found that the compound exists in a green form at 338 K containing N-coordinated NO_2 groups and in a purple form below 308 K containing O-chelated NO_2 groups.

Similar observation has been made by Mori et al. [66] for $[CuX_n(NO_2)_{2-n}(NH_3)_2]$ where X is Cl or Br. These compounds exist in a purple form at low temperatures and in a green form at high temperature. The temperature of the transition becomes lower as the chloride or bromide ion content increases. IR spectroscopy, as well as a preliminary X-ray study [66], have shown that the purple form contains an N-coordinated NO_2 group, whereas the green form has an O-chelated O_2N group.

D. COORDINATION NUMBER ISOMERISM

This type of isomerism denotes compounds containing the same empirical formula but with different coordination number. Kauffman [67] found Werner's unpublished paper in Zürich, where Werner cited $[Cr(en)_2Cl_2]Cl \cdot H_2O$ and $[Cr(en)_2(H_2O)Cl_3]$ as isomers with coordination number six for the first [68] and eight for the second. The compound formulated by Werner has been tentatively identified as octahedral 1,2,3-$[Cr(en) \cdot (enH)Cl_3]OH$, in which one molecule of ethylenediamine is bidentate but the protonated en group is monodentate [69]; the compounds do not exemplify Werner's proposed type of coordination number isomerism but rather ionization isomerism [70].

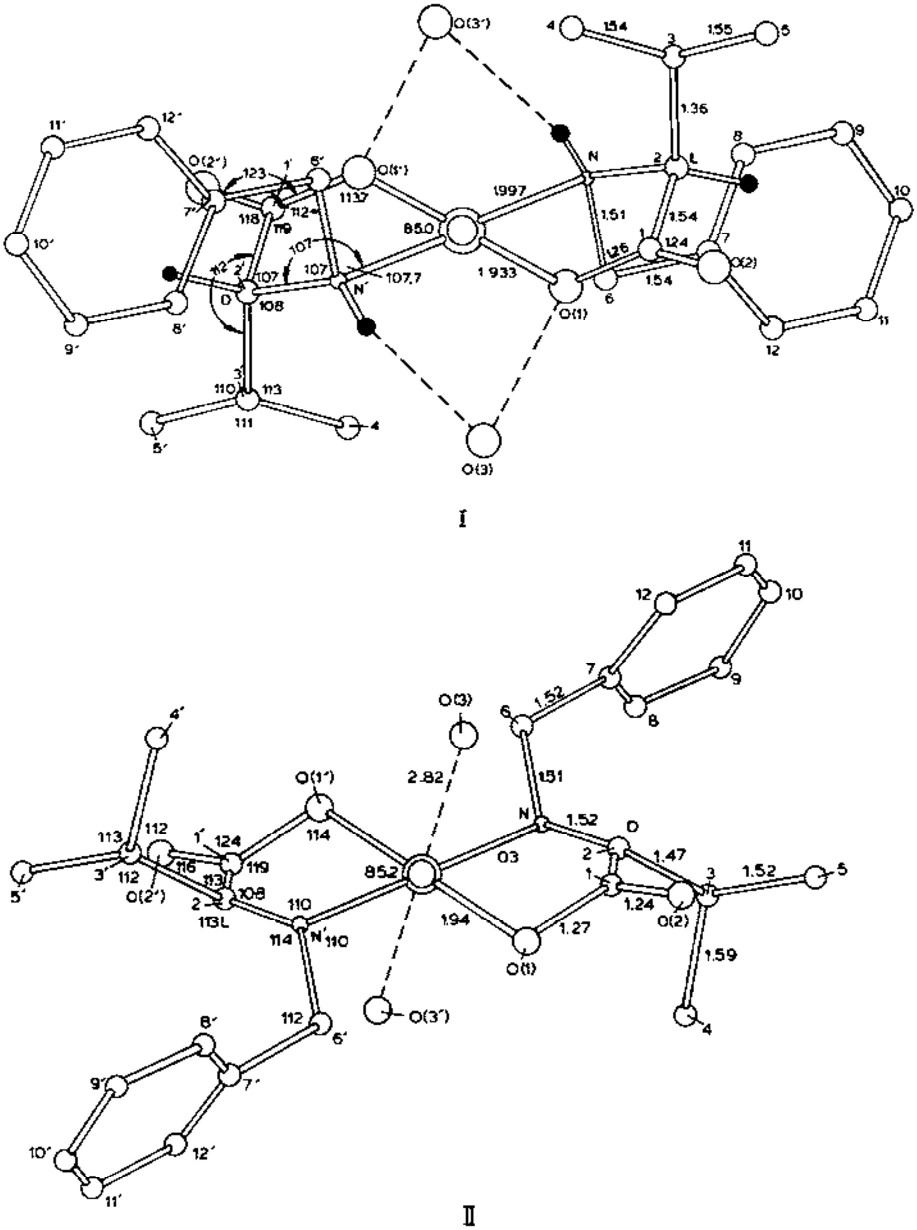
The structures of the red and blue isomers of (*N*-benzyl-L-valinato)(*N*-benzyl-D-valinato)copper(II) dihydrate have been determined [71]. Red crystals are monoclinic in space group $P2_1/C$ with two molecules per unit cell ($Z = 2$). Two amino acid molecules are chelated to the copper(II) atom maintaining a square planar *trans* configuration, (Fig. 3a) where Cu–O (2 ×) is 1.933 Å and Cu–N (2 ×) is 1.997 Å, respectively. The blue crystals are triclinic in space group *P1* and $Z = 1$. The copper(II) atom has a pseudo-octahedral configuration. The equatorial plane is formed as in the red isomer by two amino acid molecules in a *trans* configuration (Cu–O (2 ×) = 1.94 Å and Cu–N (2 ×) = 2.03 Å). In the axial positions are coordinated water molecules ($Cu{-}OH_2$ (2 ×) = 2.82 Å) (Fig. 3b).

X-ray analysis data of the three isomeric forms of Cu(*N*-methyl-2-hydroxy-1-naphthaldiminato)$_2$ showed that the γ-isomer is a dimer with tetragonal pyramidal, 4 + 1 coordination to the copper(II) atom [72]. This contrasts with the distorted octahedral, 4 + 2 geometry found in the β-isomer [73] and planar, 4-coordination of the δ-form [74].

Two isomeric forms of Cu(6,7-dihydro-5,8-dibenzo-1,10-phenanthroline)$(NO_3)_2$ were prepared [75]. For the brown α-form coordination number six was proposed and for the green β-form seven [75].

Bullock et al. [76] have prepared two isomeric forms of Cu(4-formyl-2-methoxyphenolato)(*N*,*N*,*N′*,*N′*-tetramethylethylenediamine)$_2$, bluish-black and red in colour. X-ray analysis of the red-isomer showed [77] the stereochemistry is distorted compressed octahedral with twofold symmetry, the N-atoms in the CuN_2O_4 chromophore being both in-plane and *cis* with $Cu{-}O_{(axial)} < CuO_{(in\text{-}plane)}$. On the basis of spectroscopic data for the bluish-black-isomer, a distorted square planar stereochemistry was proposed [76].

Investigation of α- and β-$[Cu(dmaep)OH]_2(ClO_4)_2$ showed [78,79] that they differ in having different structures, and spectral and magnetic behaviour. α-$[Cu(dmaep)OH]_2(ClO_4)_2$ crystallizes in the triclinic space group *P1* with one dimeric molecule in the cell. The pairs of copper(II) atoms are



I

II

Fig. 3. A schematic view of the crystal structure of the red isomer (I) and blue isomer (II) of (*N*-benzyl-L-valinato)(*N*-benzyl-D-valinato) copper(II) dihydrate [71].

linked by two hydroxo bridges and two intramoleuclar bidentate perchlorate groups. The geometry at each copper(II) atom is distorted octahedral. β-[Cu(dmaep)OH]$_2$(ClO$_4$)$_2$ crystallizes in the monoclinic space group $P2_1/C$

with two dimeric units in a cell. The coordination geometry at each copper(II) atoms is tetragonal pyramidal where the perchlorate ion is unidentate. The experimentally determined [80] magnetic exchange interaction ($2J$) is only $-4.8\ \text{cm}^{-1}$ for the α-isomer, but $-200\ \text{cm}^{-1}$ for the β-isomer [79].

The red-violet and green isomers of Cu(sal-pr-N$(CH_3)_2$)Cl were prepared and characterized by spectral and magnetic data [81]. The red-violet isomer showed the usual magnetic behaviour expected for a mononuclear copper(II) compound, whereas the green one exhibited the antiferromagnetic behaviour typical of binuclear copper(II) compounds. On the basis of experimental data a mononuclear structure with a pseudo-tetrahedral geometry around the copper(II) atom was proposed for the red-violet isomer, [81]. For the green isomer a phenolic oxygen-bridged binuclear structure with trigonal-bipyramidal copper(II) coordination was proposed.

It seems possible, that some cyanato-copper(II) compounds, e.g. α- and β-$Cu(NCO)_2$(urt) [82], α- and γ-$Cu(NCO)_2(\text{urt}) \cdot 2H_2O$ [82], α- and β-Cu(3,4,5-trimethylpyrazole $\cdot$ $NCO)_2$ [83] as well as α- and β-Cu(3,5-dimethylpyrazole $\cdot$ $NCO)_2$ [84] represent further examples of coordination number isomers and not distortion isomers as was proposed [82–84].

E. POLYMERIZATION ISOMERISM

Werner [85] used this term to denote compounds with the same empirical formula but with formula weights that are different multiples of same formula weight. As would be expected from the great differences in structure among such compounds, their physical and chemical properties differ widely.

Merz and Haase [86] have studied the crystal structures and magnetic behaviour of two isomers of isocyanato(2-dipropylaminoethanolato)-copper(II). While the A-isomer (Fig. 4a) crystallizes as monoclinic crystals of space group $P2_1/n$, the β-isomer crystallizes (Fig. 4b) as orthorhombic space group *Pnna*. The first complex is built up from discrete centrosymmetric oxygen-bridged dimeric molecules and the second consists of oxygen-bridged cubane-type tetramers. The different structural features are responsible for the different magnetic properties. Whereas the dimeric compound shows strong antiferromagnetic interaction, the tetrameric compound has a normal magnetic moment at room temperature.

Salicylamide has been reported [87] to form three isomeric compounds with copper(II): $Cu(\text{salicylamide})_2$ A, B and C. According to their spectral and magnetic behaviour the structure of the isomers are different [88]. The electronic reflectance spectra of the A-isomer exhibits three ligand field bands at 1.33, 1.60 and 1.74 μm^{-1}, the B-isomer has only two bands at 1.28 and 1.33 μm^{-1}, and the C-isomer also exhibits three bands at 1.40, 1.47 and 1.75 μm^{-1}, respectively. For the B-isomer the variation of μ_{eff} with tempera-

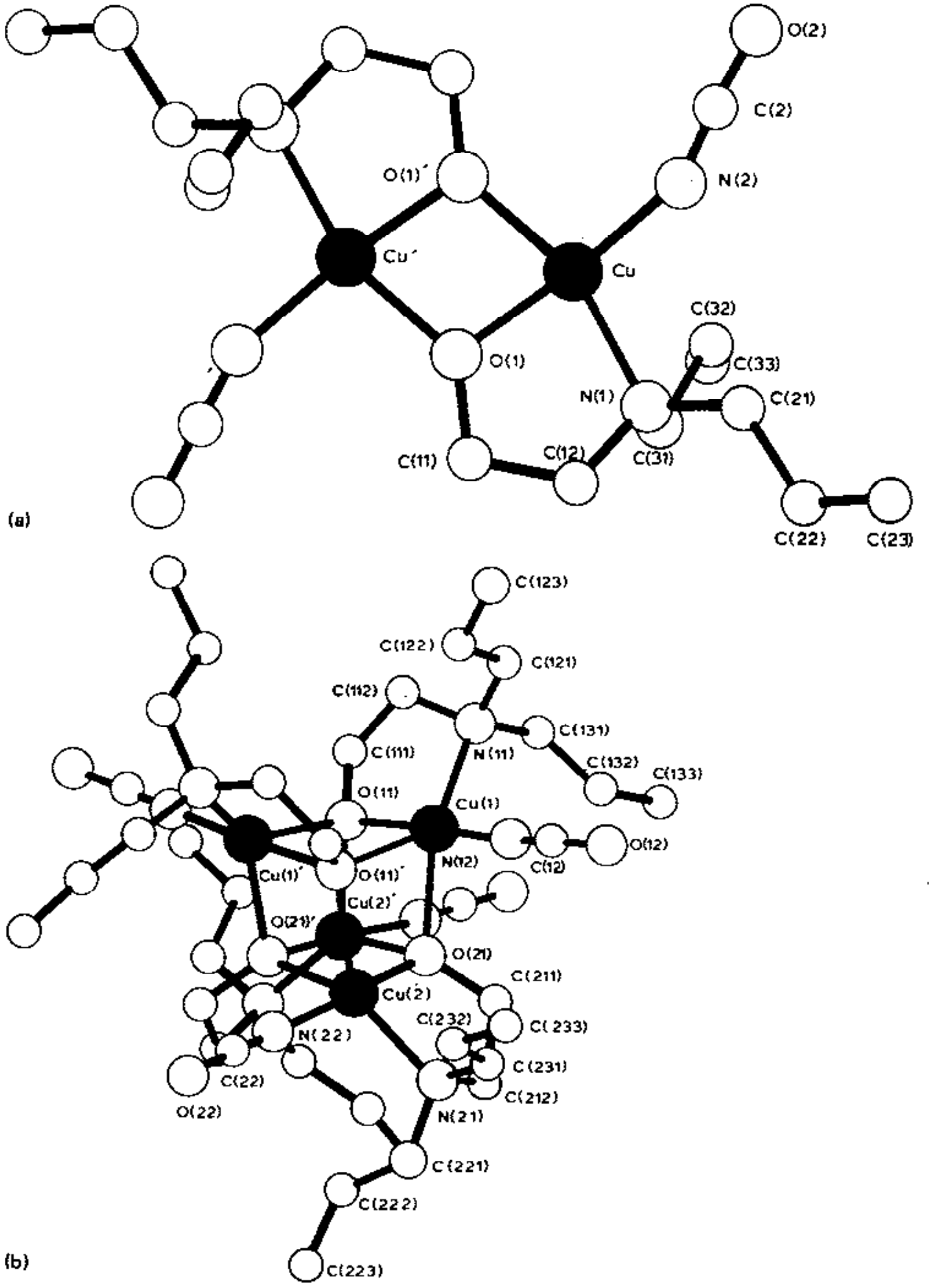


Fig. 4. A schematic view of the crystal structure of (a) dimeric and (b) tetrameric isocyanato(2-dipropylaminoethanolato)copper(II) [86].

ture is in accord with the reported antiferromagnetic character and consequent binuclear nature [89]. The temperature paramagnetic susceptibility data of the A- and C-isomers obey the Curie–Weiss law with different Curie–Weiss constants. The IR spectra [88] of the isomers are different. On the basis of spectral and magnetic data a mononuclear structure with square-coplanar stereochemistry has been assigned for the A-isomer; for the B-isomer a binuclear structure similar to those of copper(II) acetate monohydrate has been proposed [89] and for C-isomer a polynuclear structure. In spite of the fact that the authors [87,88] do not specify the type of isomerism, it seems to us that it is a typical example of polymerization isomerism of copper(II).

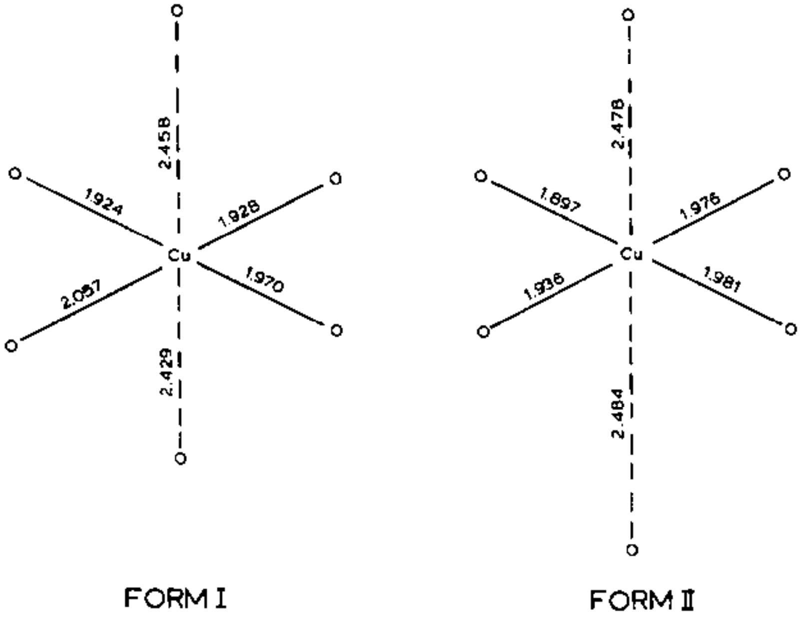
Three isomers of copper(II) salicylate tetrahydrate were prepared, the turquoise blue α-, blue-green β- [90,91] and green γ-isomer [92]. X-ray analysis of the α-$Cu(C_6H_4OHCOO)_2 \cdot 4H_2O$ showed [90] an elongated tetragonal bipyramid around copper(II). The magnetic data [91,92] are consistent with the results of the X-ray analysis. The spectral and magnetic behaviours of the β-isomer [92,93] is similar to that of copper(II) acetate monohydrate [89] and the familiar binuclear structure can be proposed. The magnetic and spectral properties of the γ-isomer [92] are typical for copper(II) compounds which possess a tetranuclear structure. These results show that the isomers of $Cu(C_6H_4OHCOO)_2 \cdot 4H_2O$ are another example of polymerization isomerism.

An analogous case of such isomerism occurs [94–96] with [Cu(2-dibutylaminoethanolato)Br], where one of the three forms is binuclear [95,96], the other tetranuclear [97,98] and for the third a polynuclear structure can be proposed.

F. DISTORTION ISOMERISM

Distortion isomerism involves two or more equilibrium arrangements of ligands differing in the distortion of the coordination polyhedron of the metal [99,100]. This isomerism is reviewed in ref. 101. Detailed theoretical discussions of this phenomenon have been given [10]. In this section some additional examples of distortion isomers are presented.

Chia et al. [102] prepared red and green isomers of $Cu(i\text{-}Bu\text{-}cbp)_2$. X-ray analysis of the isomers showed [102] that the copper(II) atoms are four coordinated. The red isomer contains two crystallographically independent molecules, which are nearly planar, having the dihedral angle $\tau = 0.8$ and 3.4° for molecules 1 and 2, respectively, and each having the isobutyl groups *trans*. The structure of the green isomer with the isobutyl group *cis* shows a greater tetrahedral distortion ($\tau = 14.5°$) than the related red isomer. The isomers also differ in their spectral and magnetic behaviour [102].



FORM I FORM II

Fig. 5. A schematic representation of the coordination sphere around Cu(II) of dinitratobis(antipyrine)copper(II) isomers [103,104].

The two isomers of dinitratobis(antipyrine)copper(II) exhibit very similar structures [103,104]. The coordination polyhedron is a distorted octahedron (Fig. 5). The greatest differences in the interatomic distances were observed in the Cu–O bonds to the oxygen atoms of the nitrate groups in the axial positions. This distance is 2.443(13) Å for form I and 2.480(21) Å for form II. In form II the antipyrine molecules are enantiomorphous.

The structure of α- and β-$[Cu(teen)OH]_2(ClO_4)_2$ [105,106] consists of dimeric $[Cu(teen)OH]_2^{2+}$ cations where the copper(II) atom has a planar coordination and discrete ClO_4 anions. The geometry around the copper atoms in both cases is slightly distorted from planarity, with distortion slightly greater in the case of α-isomer. Both isomers display antiferromagnetic interactions, somewhat bigger in the case of β-isomer; $2J = -410\ cm^{-1}$ in the α-isomer [107] and $-469\ cm^{-1}$ in the β-isomer [106].

Investigation of the two isomers of $(Cu(EIA))_4$ showed that they differ in their structures and magnetic properties [108–110]. X-ray data for α-$(Cu(EIA))_4$ [109] show that the isomer has a cubane-type tetramer structure. A similar structure was proposed for β-$(Cu(EIA))_4$ on the basis of the X-ray analysis of β-$(Cu(EIA))_4 \cdot 2C_6H_6$ [110].

Crystallographic analysis of $Cu[BH(N_2C_3H_3)_3]_2$ indicates the presence of two independent molecules with the copper(II) atoms at centres of symmetry

[111]. The two independent CuN_6 chromophores have significantly different Cu–N bond lengths which yield tetragonalities (R_e/R_a; R_e in-plane bond lengths and R_a the out-of-plane bond lengths) of 0.792 and 0.866, respectively [111]. These results indicate the presence of two distortion isomers of copper(II) in molecules of $Cu[BH(N_2C_3H_3)_3]_2$ with no indication of the reason for the difference in tetragonality observed.

Similar observation has been made by Chapman et al. [112] for $[Cu(C_{14}H_{12}N_4O_2)(H_2O)] \cdot H_2O$. The crystal contains two distinct distortion isomers. In each the ligand acts as an approximately planar N_4 quadridentate ligand with a water molecule occupying the apex of a distorted square pyramid, with a Cu–O distance of 2.361(8) Å in one case and 2.317(8) Å in the other.

The room-temperature crystal structure of $Cu(NH_3)_2(NO_3)_2$ consists of two crystallographically independent $Cu(NH_3)_4(NO_3)_2$ units [113]. The space group is probably *Pnnm* with eight molecules in the unit cell. In each of these units, the copper(II) atom is surrounded by four ammonia molecules in a near square planar arrangement and by two oxygen atoms (of the nitrate ion) at the apex. The two independent CuN_4O_2 chromophores differ mostly in their Cu–O bond lengths on the long coordinates, which yield tetragonalities of 0.793 and 0.767, respectively. Evidently there are two octahedral distortion isomers for the $Cu(NH_3)_4(NO_3)_2$ units. The symmetry of the crystal at 77 K involves a simple shear of the room temperature cell, becoming monoclinic with space group $P2_1/n$.

The green and blue isomers of $[Cu_2(Et_5dien)_2(C_2O_4)](BPh_4)_2$, prepared from aqueous or acetonitrile solutions display differences in their spectral and magnetic behaviour [114]. X-ray analysis [114] of the green isomer has shown that it consists of discrete $[Cu_2(Et_5dien)_2C_2O_4]^{2+}$ and BPh_4^- units. The dimeric cation consists of two Cu(II) atoms, separated by 5.41 Å and bridged by a bis-bidentate oxalate ion at each Cu(II) ion; an Et_5dien ligand forms two five-membered chelate rings and, apparently, enforces a distorted trigonal bipyramidal geometry. On the basis of spectral and magnetic properties of both isomers, an essentially identical structure with that of the green isomer was proposed for the blue isomer.

$[Cu_2(tren)_2(NCO)_2](BPh_4)_2$ was prepared in two isomeric forms [115]. X-ray analysis of form I shows that it consists of discrete $[Cu_2(tren)_2(NCO)_2]^{2+}$ and BPh_4^- units [116]. In the dimeric cation the Cu–Cu distance is 6.537(3) Å and each copper(II) atom is trigonal-bipyramidally coordinated with tren occupying four sites and with an axially bonded NCO group through nitrogen. A similar dimeric structure can be proposed for form II on the basis of spectral and magnetic behaviour [116].

In the isomers of the orthorhombic (green) and monoclinic (brown) $Cu(ipsalim)_2$ [117,118], the copper(II) atoms are coordinated by two nitrogen atoms and by two oxygen atoms from two chelate rings of ipsalim. The two isomers differ in the degree of tetrahedral distortion. The green isomer is transformed at 374 K into the brown isomer [117].

In addition to the isomers above numerous pairs of distortion isomers of copper(II) have been prepared and studied, e.g. $Cu(2\text{-}ClC_6H_4OCH_2COO)_2 \cdot 4H_2O$ [119], $Cu(2\text{-}OHC_6H_4COO)_2(2\text{-}CH_3pyNO)_2$ [120], $CuFe(CN)_5NO$ [121], $Cu(tppO)_2(ClO_4)_2$ [122], $Cu(im)_2$ [123], $Cu(dm)(NO_3)_2$ [124], Cu(5,6-benzo-salim-i-C_3H_7)$_2$ [118,125], Cu(3-CH_3O-salim-ch)$_2$ [118], Cu(*N*-ch-salim)$_2$ [126,127], $Cu_2(citr)_2 \cdot 2\ H_2O$ [128], $Cu(pfb)_2$ [129], $Cu(1,10\text{-}phen)_3(ClO_4)_2$ [130,131], $Cu(NCO)_2(2\text{-}pic)_2$ [132,133], $Cu(NCO)_2(pz)_2$ [133], $Cu(4\text{-}FC_6H_4COO)_2nic_2$ [134], $Cu(5Clsal)_2py_2$ [135], $Cu(OPph_3)_2Cl_2$ [136], $Cu(5Brsal)_2py_2$ [137,138], $Cupy_2Cl_2$ [139], $CuCl_2(4\text{-}mepy)_2$ [139], $Cu(nct)_2py_2$ [140].

The plasticity of the coordination sphere of copper(II) compounds [10] is a reason why the polyhedron distortion is influenced by factors such as temperature and pressure. Crystal structures of the green (at 298 K) and yellow (at 353 K) $[(nmpH)_2CuCl_4]$ [141] show that in the green isomer the copper(II) atom is situated on a crystallographic centre of symmetry with nearly square planar coordination of the chlorine atoms, but in the yellow isomer the copper(II) is located on a twofold axis with the chlorine atoms coordinated to form an irregular flattened tetrahedron.

In the crystals of the red-brown $[(nmpH)CuCl_3]$ coordination about the copper(II) atom at 298 K is that of a distorted trigonal bipyramid [142]. The electronic spectra of $[(nmpH)CuCl_3]$ recorded at 298 K and at 77 K indicate at low temperature a change of geometry about Cu(II) in the compound, to one intermediate between trigonal bipyramidal and square pyramidal [141].

X-ray analysis of $(ipa)_2CuCl_4$ at room temperature shows that one-third of the $CuCl_4^{2-}$ have a planar geometry while the other two-thirds have a significant tetrahedral distortion configuration [143]. Willett et al. [144] have studied the influence of high temperature and high pressure on $[(ipa)_2CuCl_4]$ and found that the high-temperature phase contains only distorted tetrahedral $CuCl_4^{2-}$ anions, while the high-pressure phase has only a planar configuration.

In $(dea)_2CuCl_2$ spectroscopic evidence indicates that the low-temperature phase contains nearly square planar $CuCl_4^{2-}$ anions, while the high temperature phase contains distorted tetrahedral $CuCl_4^{2-}$ [145].

Compounds of the composition CuX_2, where X is 5,6-benzo-salim-i-C_3H_7, 5,6-benzo-salim-ch, 3-CH_3O-salim-ch or 5-Br-salim-ch have a planar structure which is transformed to tetrahedral by the action of high temperature [118].

Some copper(II) coordination compounds change colour by the action of temperature. Such thermochromism is usually associated with temperature dependent changes in the stereochemistry of the chromophore and depends on the nature of both the central metal atom and the ligands. Grenthe et al. [146] reported the results of structure determination of thermochromic Cu(dieten)$_2$(ClO$_4$)$_2$. At 298 K this compound exists as a red form which is triclinic and at 333 K as a monoclinic form which is blue-violet in colour. In both forms the copper(II) atom has a square planar geometry. Although there is no significant difference in the Cu–N bond distances, the configuration of the dieten is different.

Pressure and thermal studies in the electronic and IR spectra of Cu(dieten)$_2$X$_2$; where X is NO_3^-, ClO_4^- or BF_4^-, have been reported by Fabrizzi and co-workers [147,148]. They found a red shift in the spectra of the compounds with an increase in temperature as well as at high external pressures. A few factors are involved in determining these differences such as steric effects, nature of anions, basicity of the ligand, etc. The dominant factor appears to be the distortion of the tetragonal copper(II) atom environment and axial interaction between the anions and the CuN$_4$ plane [148,149].

G. CONCLUSIONS

It is clear (Section B) that copper(II) *cis* and *trans* isomers can only arise with chelate ligands. From the stability point of view *trans* isomers are more stable than *cis*. Spectroscopy can be used to discriminate between *cis* and *trans* isomeric forms. Usually, in the electronic spectra the *d–d* band of the *cis* isomer has a peak at a longer wavelength than that of the *trans* isomer. Also the maximum absorption of the former is more intense than that of the latter. There is a difference in the symmetry of the chelate rings of geometrical isomers. This can be used for their characterization by IR spectra. In the *trans* compounds the chelate rings possess a centre of symmetry and only the metal–ligand antisymmetric stretching vibration is IR active. In the *cis* isomer there is no centre of symmetry and an additional absorption band due to the metal-ligand symmetric stretching vibration should appear.

As was noted in Section C, linkage isomers differ in the bonding modes of the same ligand to the metal atom. Such isomers can be transformed from one isomeric form to the other by the influence of temperature. The data (Section C) indicate that there are signficant differences in behaviour of the linkage isomers of copper(II) compounds especially in their spectroscopic behaviour.

Great differences in the structures of polymerization isomers of copper(II) mean that their physical and chemical behaviour also differ widely.

Distortion isomers [101] of copper(II) compounds are more common than other types. In our recent paper [10] we have described in detail relationships between the plasticity of the coordination sphere and the distortion isomers of copper(II), as well as of the differences in properties, interconversion, etc.

It must be noted, that for some isomers of copper(II) compounds, no precise conclusion regarding the nature of the isomeric type can be drawn; for example: Cu(*N*-methyl-2-hydroxy-1-naphthaldiminato)$_2$ and Cu(sal-pr-N$(CH_3)_2$)Cl, can also be classified as polymerization isomers; Cu(salicylamide)$_2$ as coordination number isomers, etc. Some overlap exists between the isomerism given in the Sections D, E and F.

APPENDIX

Very recently [83,133,150] another type of copper(II) isomer, coligand, has been isolated and studied. A few pairs of such isomers were prepared, with the composition $Cu(NCO)_2L_2$ and $Cu(L \cdot NCO)_2$ where L is pyrazole, 3,5-dimethylpyrazole, 3,4,5-trimethylpyrazole, 4-iodopyrazole, or indazole. In $Cu(NCO)_2L_2$, the NCO^- groups and L molecules are coordinated to the copper(II) atom separately, yet in $Cu(L \cdot NCO)_2$ chelate type ligands of 1-carbamoylpyrazole are observed. A detailed discussion of this phenomenon has been given previously [83].

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