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THE CONFORMATION OF SCHIFF-BASE COMPLEXES OF COPPER(II): A STEREO-ELECTRONIC VIEW

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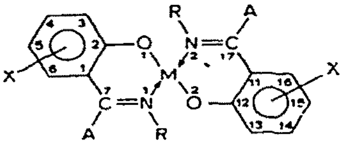
A. INTRODUCTION

The prominent place held in coordination chemistry by metal complexes of Schiff-base ligands has been attested over many years by the large number of publications and by the comprehensive reviews [1—3], particularly the extensive surveys of Holm and his co-authors [4,5] which are to be found in the literature. The reasons for this sustained interest in these compounds are undoubtedly many, but important among them must be their general ease of preparation, their diverse properties and their use as biological models.

We intend in this present survey to reconsider some of the properties of a restricted number of Schiff-base complexes, especially their stereochemistry, with the aim of proposing a new explanation for the experimental observations. This interpretation will be mainly in electronic terms and will therefore differ from the steric view now current [5]. It will not be suggested that steric arguments are thus superseded but that they are not adequate for the observational demands now made on them and should, for the Schiff-base complexes at least, be complemented by an appreciation of electronic states. We shall consider compounds of the salicylaldimine type, mainly those of copper (II), in putting forward what might, unimaginatively, be termed a stereo-electronic view.

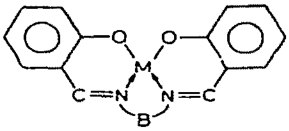
Discussion will centre on molecules (1), derived from bis(salicylaldiminato)-M(II) in which X = A = R = hydrogen. The substituents can vary widely with



(1)

those at A being most restricted and we shall confine attention to derivatives of the salicylaldimines (A = H) or the *o*-hydroxyacetophenoneimines (A = CH_3). A cupric complex in which X = 3-ethyl and R = methyl will be systematically named bis(*N*-methyl, 3-ethylsalicylaldiminato)copper(II) and abbreviated Cu-(*N*-Me, 3-Etsalim)$_2$. The abbreviation hapim is used for the body of the ligand when A = methyl.

Quadridentate ligands are also well known. These are formed when the two nitrogen donors of a bis-chelate are linked by a group B as in (2). Common



(2)

nomenclature is based on two patterns which can be exemplified by the cupric complex in which B = $-CH_2 \cdot CH_2-$. It is either *N*,*N'*-bis(salicylidene)-1,2-ethanediaminocopper(II) or *N*,*N'*-dimethylenebis(salicylaldiminato)copper-(II), with the relaxation that 1,2-diaminoethane is usually termed ethylenediamine. Hence the common abbreviation Cu(salen) which will be formalised to Cu(*N*,*N'*$-CH_2 \cdot CH_2-$salim$_2$).

Early observations established the diverse properties of these salicylaldimine complexes, some of the more striking being the range of colours in the solid state and in solution [6—18], the variation in dipole moments [19—22] and, perhaps most stimulating at the time, the variation in magnetic moments found in nickel complexes [23—29]. These magnetic anomalies focussed attention on molecular structures [30—34] as well as on electronic states [35—40]. The present position has been assessed and stated, with extensive references, by Holm and his co-workers [4,5] and is summarised here as necessary background. It can be stated that the explanation for many of the puzzling features of the chemistry of the salicylaldimine compounds has been found in their structures. This is particularly true of complexes of divalent nickel and copper. Structures reflect variations in coordination number brought about by polymerisation or solvation and variations in stereochemistry resulting from changes between planar and tetrahedral donor arrangements. Details have been revealed by X-ray crystallography and other physical methods showing that structures often deviate markedly from "ideal" geometries. Thus many compounds have a "pseudo-tetrahedral" stereochemistry, and many are "distorted" in the sense of having one or two metal—donor bonds which are longer than the remainder. In addition a "deviation from planarity" is often found in four-coordinate complexes which should be, at least at first sight, perfectly planar.

The tetrahedrality can be defined, after Holm [5], in terms of the dihedral angle, θ, between the metal—donor (M,N,O), i.e. coordination, planes of each chelate moiety and it can be noted that the "pseudo-tetrahedral" geometry so expressed differs from a "flattened" tetrahedral geometry in which θ would remain at 90° with the chelate "bite" angle, β, at the metal being the value which decreases. Normally in the salicylaldimine complexes β is fixed at ca. 90° by the geometry of the chelate ring and is not 109° even in a complex regarded as unequivocally tetrahedral; i.e. one in which θ approaches 90°.

Deviations from planarity are usually described as being manifest as a "fold" in a chelate ring along a line through the oxygen and nitrogen donor atoms. The dihedral angle then present is defined as ϕ and for a salicylaldimine complex is the angle between the plane through metal, nitrogen and oxygen (the coordination plane) and the plane through the ligand skeleton variously defined. This feature can also be described in terms of a "half step", σ, the distance of the metal atom from the plane through a ligand (Fig. 1a). If the folding or stepping is in the same rotatory sense for a bis-chelate complex, i.e. one group up, the other down, for a molecule viewed edge-on (Fig. 1b), the molecule is said to be "stepped" and the step distance is defined by Holm as S. In terms of the half-steps of two separate ligands, $S = \sigma_1 + \sigma_2$; discussion in terms of σ is retained here since a distinction between chelate groups is discernable in some instances. Molecules in which the folding is in the contrary sense are also known and have been less elegantly termed "umbrella-shaped".

These structural variations are those currently recognised and regarded as being responsible for the observed properties of Schiff base complexes. Thus Ni(N-Me,salim)$_2$ is paramagnetic in some solid state modifications and in some inert solvents because molecular association alters the coordination geometry from the expected *trans*-planar to high-spin five- or six-coordinate arrangements [25]. Ni(N-i-propyl,salim)$_2$, however, is paramagnetic in the solid state and inert solvents because the adoption of a tetrahedral geometry also pro-

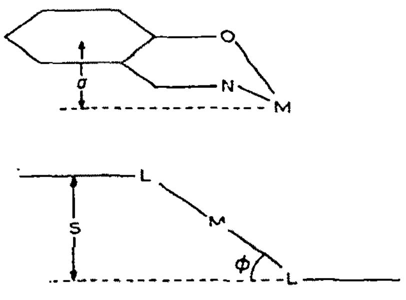


Fig. 1. Molecular folding and stepping.

duces a triplet ground state [41]. Similar structural changes are observed in copper(II) compounds.

The observed correlation between properties and molecular geometry led on to a consideration of the structural variations themselves and their causes. The extensive and detailed investigations of the Florence group in Italy and, in the U.S.A., of Lingafelter, Holm and their respective co-workers eventually laid the basis for the current view that the raison d'être for the molecular structures of complexes of the salicylaldimine type is largely steric in origin. Thus a recent review [5] reports: "The (benzene) ring substituent may also be varied but these changes have decidedly secondary effects on stereochemistry compared to alterations in (the nitrogen substituent) R"; and later, " . . . . steric interference between R and the opposite chelate ring decreases the energy of the tetrahedral stereoisomer relative to the planar one".

We propose below a somewhat contrary view in which the conformation of a molecule is closely related to the electron density maintained in the atoms of the chelate rings by substituents on the aromatic portion of the ligand, as well as on N and C(7). This density will be especially manifest at the two donors, because of their electronegativity, with conformational consequences.

The very examples which, after Lingafelter's detailed studies, did much to consolidate the steric arguments just quoted can be used to propose an alternative solution. Hitherto, structural studies of Ni(*N*-*i*-propylsalim)$_2$ and its 3-ethyl and 3-methyl derivatives have been interpreted as illustrating the point that the bulkiness of the substituent, R, is the important destabilising force leading to a pseudo-tetrahedral geometry. Thus Ni(*N*-*i*-propyl,salim)$_2$ [41] and Ni(*N*-*i*-propyl,3-ethylsalim)$_2$ [42] both have dihedral angles, θ, between the coordination planes Ni,O(1),N(1) and Ni,O(2),N(2), which at 81.3° and 85.3° respectively, approach the tetrahedral value. That this configuration does move a bulky nitrogen substituent away from the neighbouring ligand, especially its oxygen donor, was clearly demonstrated by the study [43] of Ni(*N*-*i*-propyl,3-methylsalim)$_2$ which retains a planar configuration about the metal at the expense of severe steric interactions between the *i*-propyl groups and the oxygens.

The question which remains, of course, concerns the planar nature of this 3-methyl derivative since this geometry must be as sterically unacceptable as in Ni(*N*-*i*-propyl,salim)$_2$ itself, and as demanding of a tetrahedral configuration. Other awkward difficulties can be raised when the corollary is considered, namely that straight-chain, and therefore non-bulky, substituents favour planar molecules. Again there is an unhappy exception in that all the crystalline modifications of Cu(*N*-Et,salim)$_2$ are pseudo-tetrahedral [44—46], with θ being as much as 35.9° in one polymorph, instead of being planar as are the *N*-Me [47—49], *N*-*n*-propyl [50] and *N*-*n*-butyl [51] analogues. The conventional answer to these objections is to invoke "crystal packing forces" the existence of which cannot be denied and the importance of which cannot be easily assessed. Many of the difficulties disappear, however, if the electronic state of these molecules, as evidenced by X-ray structural data, is also considered. We do this below in a general way, and then in more detail for specific structural categories, in illustration of our proposal.

B. GENERAL BACKGROUND TO AN ELECTRONIC VIEW

The complex Cu(*N*-Et,salim)$_2$ has been investigated by a number of workers and its configurations have been determined four times, twice in the orthorhombic α-form [46] which has two molecules in the asymmetric unit and twice, by different workers, in the monoclinic β-form [44,45]. These molecular structures are labelled 1—4 in Table 1 and all are pseudotetrahedral, 3 and 4 markedly so. A further feature is that each has abnormal bond lengths within one ethyl substituent. Thus whereas an N—C length of 1.475(10) Å is typical of an N—C single bond [52], an N—C$_\alpha$ bond of 1.50 Å is present in each molecule with an accompanying C$_\alpha$—C$_\beta$ distance of 1.50 Å, shorter than the expected 1.54 Å. (Standard deviations in bond lengths and angles are given in this and succeeding Tables. Omissions mean that they are not available.) Furthermore, in molecules 1 and 2 hydrogen atoms were located and those associated with the shorter C$_\alpha$—C$_\beta$ bonds found to be nearly eclipsed. When seen against the normal N(sp^2)—C(sp^3) and C(sp^3)—C(sp^3) single bond lengths the weight of evidence provided by the four measurements cannot be dismissed and we regard it as a manifestation of an electronic interaction between the ethyl substituents and the chelate ring through induction and a process which seems akin to hyperconjugation [53—58]. Such an interpretation is not without criticism. A continuing difficulty is the credence to be placed on the "reality" of bond and angle changes. Often we find them to be of the order of one or two standard deviations so that individual values provide little foundation for our deductions. Some are, however, statistically very significant but, in any event, it is the totality and consistency of the overall picture which we regard as being persuasive. A further difficulty that must be faced, nevertheless, is that many of the effects we quote are seen in side-chains where enhanced thermal vibrations — as with the *N*-ethyl substituents just discussed — could be accounted responsible for apparent bond shortening [59,60]. The effect can be appreciable if the atomic motions are assumed, incorrectly we

TABLE 1

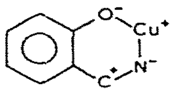
Structural details for Cu(*N*-Et,salim)$_2$

Cu(*N*-R,salim)$_2$	θ (deg.)	N—C$_\alpha$ (Å)	C$_\alpha$—C$_\beta$ (Å)	Ref.
1	9.4	1.48(2), 1.50(2)	1.52(2), 1.46(2)	46
2	12.8	1.46(2), 1.48(2)	1.47(2), 1.50(2)	46
3	35.5	1.50(1), 1.48(1)	1.49(2), 1.52(2)	44
4	35.9	1.53(1), 1.48(2)	1.50(2), 1.51(2)	45

believe [61], to be independent [62] and makes the interpretation of individual bond lengths controversial. Assumption of a "riding" motion, although giving a much smaller correction, seems similarly invalid and likely to overestimate the effect [61,63]. Where thermal motion has been measured over a temperature range [64—67] or through a full vibrational analysis [63—68] it is not found to affect bond lengths of the type under discussion by more than ca. 0.01 Å. Of importance, also, is the evidence presented by complexes such as Cu(*N*-2-phenylethyl,hapim)$_2$ [69] where the C_α—C_β bond contraction of 0.050(5) Å occurs between atoms with thermal parameters much less than those further along the side-chain where bond changes are not so dramatic. Further observational evidence will be presented later but the consequences of, and the mechanisms for, electron feed from the substituents (which evidently do not need to be conjugated) into the π-system of a complex is now considered.

Our view has three features. The first is that the electron flow has an overall effect on stereochemistry, the second is that the extent of the electron input is related to hyperconjugation with substituents and the third recognises that the electron redistribution implied by electron shifts is also manifest in small geometrical changes throughout a molecule.

Any enhanced electron density appearing in the π-system will be found especially at the electronegative donor atoms, O and N, and since the basic skeleton of all the complexes under discussion can be regarded as a heterocycle, (3), a density alternation [70] will be established by the metal atom and the two donors. It is our contention that this electron loading at oxygen



(3)

and nitrogen is then associated with electronic and structural consequences. One is that the oxygen atom becomes increasingly "tetrahedral" in its bonding geometry, i.e. increasingly sp^3 hybridised, with associated conformational shifts being apparent. Another is that the metal, under the influence of enhanced electron density on the donors, particularly the nitrogens, begins to take up a tetrahedral bonding geometry. With copper(II) this latter change could be regarded as a partial reduction and a favouring of the tetrahedral cuprous stereochemistry but since the observations apply, at least partly, to nickel(II) as well, and since the configurational changes are gradual, we visualise it as a consequence of changing orbital interactions, perhaps resulting in the destablising of the $e_g(\pi^*)$ and $b_{2g}(\pi^*)$ orbitals appropriate for planar bonding and the need to stabilise, for nickel(II) and copper(II), the $b_{1g}(\sigma^*)$ orbital which would accept the increased electronic charge.

This hypothesis relies on the conjugated nature of the salicylaldiminato ligands which will constitute, when complexed, a modified naphthalene system if there are 10 π-electrons available. These can be formally obtained without involving the metal if the oxygen donor supplies two electrons and is in an sp^2

hybridised state with its p_z orbital as part of the π-system. This formalism is in accord with, although not necessarily proved by, the M—O—C angle which in many copper complexes is ca. 130°. This same formalism can be invoked in furan where the electron donation from oxygen occurs to an extent which gives this molecule a dipole of 0.71 D, much less than the value of 1.68 D for tetrahydrofuran [70]. Interestingly, it has been claimed that in furan the oxygen is the positive end of the dipole [70] although this assertion is disputed [71]. It is not unreasonable to suggest, therefore, that the oxygen donor is probably slightly electron deficient, relative to its uncomplexed $—O^-$ state, a situation which is likely to promote Cu(d_{xz})—O(p_z) back bonding* with some metal electrons also in the π-system. On the other hand, increased density at oxygen could be thought to favour O(p_z)—Cu($4p_z$) forward bonding, or, as we shall later demonstrate, O(sp^3)—Cu($4p_z$) and/or O(sp^3)—Cu($d_z{}^2$) and O(sp^3)—Cu(d_{xz}) bonding. We do not intend that this formalism be regarded rigidly; we include it as our "visualisation" of some of the bond changes. Evidence for these alterations will be offered through a detailed study of molecular conformation but general support for the contention that increasing sp^3 hybridisation is present is provided by the o-hydroxyacetophenone-iminato complexes in which enhanced electron density on the donor atoms should result from the presence of the methyl group on C(7), through induction or hyperconjugation, as well as from substituent input through the nitrogen. The C(7)—C(methyl) length is listed in Table 2 as is also the marked effect on

TABLE 2

Some geometric details for ligands in Cu(N-R, hapim)$_2$

R	C(7) —C(methyl) C(17)—C(methyl) (Å)	Cu—O(1)—C(2) Cu—O(2)—C(12) (deg.)	Ref.
—H[a]	1.515(8)	128.5(2)	103
—H	1.512(7), 1.506(7)	128.0(2), 127.9(2)	103
$—CH_3$[a]	1.498(6)	121.1(2)	69
$—CH_3$	1.505(8), 1.511(7)	120.8(3), 119.2(2)	69
$—CH_2Ph$	1.513(6), 1.511(5)	122.8(2), 122.3(2)	69
$—CH_2CH_2Ph$[b]	1.522(4)	125.4(2)	69
—i-butyl[a]	1.514(4)	118.4(2)	90
—n-octyl[a]	1.508(3)	114.8(2)	69

[a] Centrosymmetric molecule.
[b] Molecule with 2-fold symmetry.

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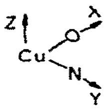
* The axes are defined as:



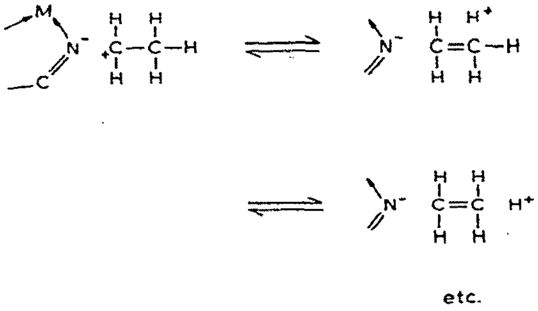


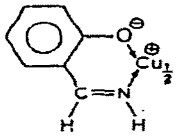
Fig. 2. Charge stabilisation on substituents.

the Cu—O(1)—C(2) angle in planar complexes in which it falls to 115° from the value of ca. 130° in *n*-alkyl substituted salicylaldiminato compounds. It must be noted, however, that there is some evidence that the decrease in bond angle can be given a "mechanical" explanation [69].

The processes leading to the electron drift into the chelate ring are seen as involving hyperconjugation. Thus the ability of a nitrogen substituent, R, to sustain an electron feed into the chelate ring will be enhanced by its ability to stabilise a positive centre on its carbon, C_α, attached to the donor. Hyperconjugation, by redistributing the charge, provides such a mechanism and will be particularly effective when methyl groups are attached to C_α [55,58] as demonstrated by Fig. 2.

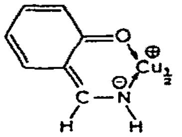
This phenomenon is not, in our view, restricted to the nitrogen substituents since we believe it can be demonstrated for the methyl substituent on C(7) and for groups attached to the benzene ring. Its effects are apparent not only in the consequences of the electron loading at the donor atoms but, as already intimated, in small geometrical changes elsewhere in these molecules. Many occur as deviations from "expected" bond lengths and can be expressed in terms of the increased significance of particular canonical contributors to the bonding state. A molecular orbital approach is naturally preferable but unfortunately does not allow, without a semi-quantitative treatment, a simple pictorial view to be taken. It is particularly valuable, however, in providing the conceptual basis for hyperconjugative interactions free from the "no-bond", "σ—π overlap" terminology necessary in a valence bond treatment. Nevertheless in what follows we draw valence bond canonical structures for their pictorial usefulness.

The main canonical form of the simple complex Cu(*N*-H,salim)$_2$ is likely to be (4) with the charge separation acknowledging the formal ionisation

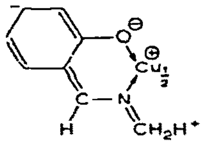


(4)

of the atoms. However, a consideration of the bond lengths in the chelate ring shows that the alternative, (5) is also a significant contributor and the


(5)

implied conjugation is unlikely to be disputed. It must be noted that the situation is undoubtedly more complex than these two structures imply since it is often found that the benzene ring has three consecutive short bonds (C(3) to C(6)) and three long bonds (C(6) to C(3)). We will suggest that certain substituents increase the importance of these, or other, canonical structures, and that the electron shifts so implied are reflected in changes in the molecular geometry. Thus with the simple nitrogen-substituted complex, Cu(*N*-Me,salim)$_2$, we believe that the structures (6) and (7) should be included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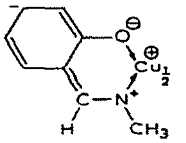
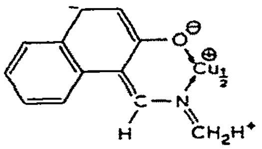

(7)

even though the N(sp^2)—C(sp^3) bond lengths are not noticeably shorter than the 1.47 Å expected [52]. However, it is now possible to deduce that if a compound which reinforces this bonding pattern is prepared then a decrease in the N—C distance may become apparent. It can be seen that a naphthalene system with its α-position at (1)* will have this effect. In quantum mechanical terms the α-position has the higher "free valence" [72,73] in practical terms α-naphthol is a stronger acid than β-naphthol; both are observations suggesting significance for contributor (8).


(8)

The four independent measurements made of the N—C(methyl) distance in three polymorphs are 1.44(1) [74], 1.44(2) and 1.42(2) [75], 1.45(1) Å [76].

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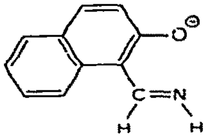
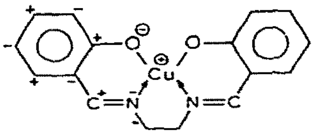
* This ligand, napim, is:



Another convenient way of viewing electronic changes is in terms of the alternation of electron density over atomic sites. This is shown in (9) for a portion of the quadridentate molecule $\mathrm{Cu}[N,N'\text{-CH}_2\cdot\mathrm{CH}_2\text{-(salim)}_2]$ which has, in a number of derivatives, an unusually short C—C bond in the dimethylene link. In the present context the diagram is a synthesis of the charge distributions to be found in the dominant canonical structures of the valence bond description. Its virtue, like that of the old "law of alternating polarities" [77—79], lies in its visually descriptive capacity although, as shortly indicated, it can also be used in a qualitative sense to predict how the contributions of the significant canonical forms could be further enhanced. Thus the shortening of the C—C bond in the dimethylene link can be regarded as a partial oxidation due to the presence of two juxtaposed "positive", i.e. lowered density, centres, (10), and the increased significance of the canonical forms



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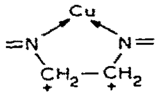

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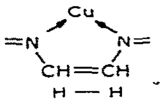

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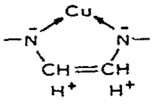


(12)

(11) and (12) in the bond description. An alternative description can be given in terms of second-order hyperconjugation [54,55], for which (11) is a valence-bond diagram. Our point for the moment, however, is to use the description to postulate that the bond shortening will be enhanced by substituents which reinforce the positive charges at the dimethylene carbons, e.g. by an hydroxyl group at the "positive" C(4) position. Thus $\mathrm{Cu}[N,N'\text{-CH}_2\cdot\mathrm{CH}_2\text{-(4-OH,salim)}_2]$ has a C—C bond length of 1.47(3) Å as well as evidence for increased electron loading at the donor atoms.

It can additionally be postulated that the presence of a positive centre near an oxygen donor, rather than suitable substitution elsewhere, will also reinforce the electron density alternation, but it seems necessary to distinguish between the consequences of the two effects. Hydrogen bonding can be though of as increasing the apparent electronegativity of the oxygen atom and its role as an electron sink, whereas a substituent participates in a redistribution of density throughout the system which enhances other atoms as well as oxygen. Appropriate substitution can thus be redescribed as providing an electron surfeit to the donor atoms, nitrogen and oxygen, leading, in the simple view already mentioned, to a partial reduction of the copper centre. Hydrogen bonding to an oxygen atom will, on the other hand, have an opposite effect on the metal. The consequence can be experimentally seen to be an increase in the overall planarity of the molecule [81,82], a feature which has been ascribed to in-

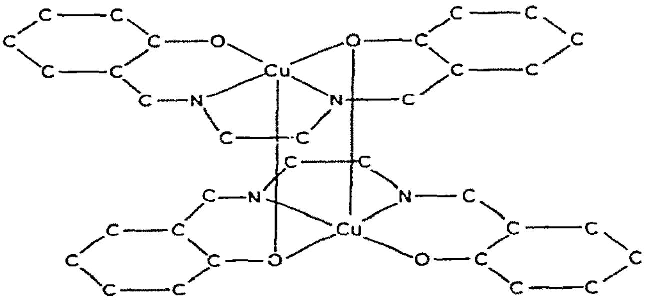
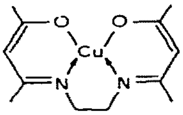


Fig. 3. The dimeric complex $\{Cu[N,N'—CH_2 \cdot CH_2—(salim)_2]\}_2$.

creased conjugation in the chelate ring and back-bonding from the metal [83]. In terms of the orbital changes at oxygen it must be also associated with a return to an $sp^2 + p_z$ orbital description and, indeed, in crystals of the methylammonium perchlorate adduct of $Cu[N,N'—CH_2 \cdot CH_2—(acacim)_2]$, i.e. the adduct of the N,N'-linked acetylacetoneiminato complex, (13), the complex



(13)

has full crystallographic mirror symmetry with the hydrogen bond between the oxygen donor and the methylammonium cation also lying in this plane [84] as expected for trigonal hybridisation.

A further consequence of hydrogen bonding is the weakening of the "dimeric" bonds in $\{Cu[N,N'—CH_2 \cdot CH_2—(salim)_2]_2\}$ which complete a tetragonal pyramidal stereochemistry about each copper atom by interaction with a donor oxygen of a parallel complex as illustrated by Fig. 3. The initial Cu—O′ bond lengths of 2.41 Å [85] increase to 2.79 Å in the hydrogen bonded chloroform adduct [83] and are absent in the p-nitrophenol adduct [82]. An explanation for this behaviour must take cognisance of the fact that the o-hydroxyacetophenoneiminato analogue $Cu[N,N'—CH_2 \cdot CH_2—(hapim)_2]$ is monomeric [86] even in the absence of hydrogen-bonding adducts and will lead to a brief consideration of five-coordinate complexes of copper(II) during the more detailed examination of the crystalline state which is now made in the light of the foregoing introductory explanation.

C. CHANGES AT THE COORDINATION SPHERE

(i) Planar complexes

Commonly listed "deviations from planarity" seem to imply that many complexes of the type under discussion should, in ideal circumstances, be perfectly planar. This assumption first needs examination.

The dimensions of the salicylaldimine ligand and its planarity have been established experimentally for 5-chlorosalicylaldoxime [87], 2-chloro-*N*-salicylideneaniline [88] and *N*-5-chlorosalicylideneaniline [89]. The "bite" of these ligands is 2.45 Å and if they and a coordinated metal ion are to remain coplanar and define a bond angle of 90° the metal atom must lie on a semicircle with the two donors, oxygen and nitrogen, as diameter. It can readily be shown that some, or all, of the remaining bond angles and bond lengths must then take non-ideal values. Conversely, if standard lengths and angles are required, the interior angle sum of the chelate ring will be approximately 690—700° instead of the 720° demanded of a planar ring. Deviations from planarity may therefore need no other explanation and the "stepping" phenomenon may simply result from normal bond requirements. In this event the one structure which does need discussion is that of α-Cu(*N*-Me,salim)$_2$ in which molecules lie in crystallographic mirror planes [47].

As has been demonstrated by Holm [5], however, and others [69], "step heights" vary over a wide range (see Table 3) and these require comment. These variations are developed for bis-chelate salicylaldimine complexes of copper(II) in Table 4 and Fig. 4 which describe displacements from the plane defined by Cu,N(1) and C(7). (Since all listed molecules are centrosymmetric only one ligand need be considered.) The bis-chelate *o*-hydroxyacetophenoneiminato complexes are similarly tabulated and displayed in Table 4 and Fig. 5. Except for α-Cu(*N*-Me,salim)$_2$ all compounds show deviations of chelate ring atoms from the defined plane, that of *O*(1) usually being particularly marked with C(2) and C(1) being seemingly dragged in its wake. This non-planarity can, of course, be illustrated with respect to other defined portions of the molecule —

TABLE 3

Values of half-step, σ, for centrosymmetric molecules

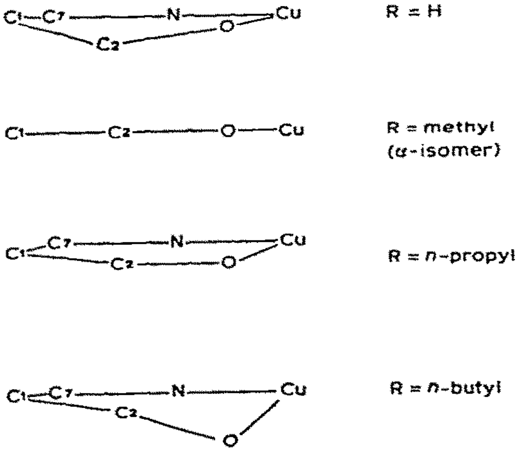
Cu(*N*-R,salim)$_2$			Cu(*N*-R,hapim)$_2$		
R	σ (Å)	Ref.	R	σ (Å)	Ref.
—H	0.15	91	—H	0.24	103
—Me(α)	0	47	—Me	0.96	69
—Me adduct	0.38	124			
—*n*-propyl	0.13	50	—*i*-butyl	1.12	90
—*n*-butyl	0.37	51	—*n*-octyl	1.33	69
—phenyl	0.45	125			
			Cu(*N*-R,napim)$_2$		
			R	σ (Å)	Ref.
			—Me(β)	0.63	76
			—Me(δ)	0.19	74

TABLE 4

Atom displacements from the plane defined by Cu, N(1), C(7) in Cu(N-R,salim)$_2$ and Cu(N-R,hapim)$_2$. (All molecules are centrosymmetric)

Cu(N-R,salim)$_2$	O(1)	C(2)	C(1)	Cu(N-R,hapim)$_2$	O(1)	C(2)	C(1)
R	(Å)	(Å)	(Å)	R	(Å)	(Å)	(Å)
—H	0.11	0.09	—0.01	—H	0.10	—0.02	—0.05
—Me	0	0	0	—Me	0.99	0.65	0.13
—*n*-propyl	0.26	0.30	0.10	—*i*-butyl	1.03	0.62	0.05
—*n*-butyl	0.39	0.19	0.02	—*n*-octyl	1.30	0.93	0.20

the benzene ring is an obvious group for the purpose. The choice made here makes it immediately apparent, however, that a π-decoupling of substantial proportions must be occurring, especially between the copper and oxygen atoms. This can also be seen from Fig. 6 which shows rotations about the bond axes in the chelate rings of a number of complexes which arise if an initially planar ring be thought to distort to the observed conformation and testifies (see, for example, Cu(N-n-octyl,hapim)$_2$) [69], to the resulting break in O(p_z)—Cu($4p_z$) (or Cu(d_{xz})) conjugation. The C(1)—C(7) bond distance (Table 5) cannot be used to support this contention since other factors affect



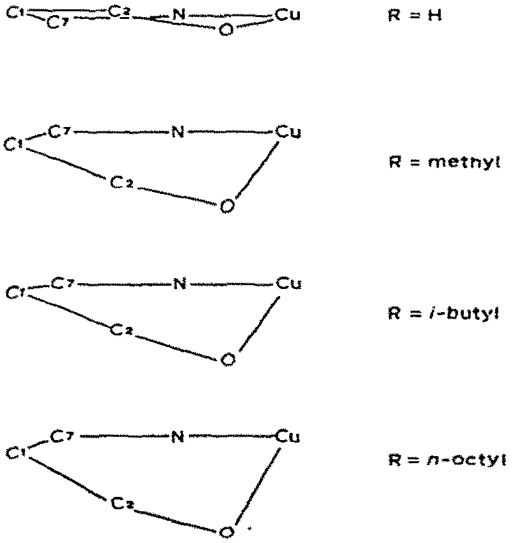


Fig. 4. Deviations from the plane defined by Cu,N(1) and C(7) in the complexes Cu(N-R,salim)$_2$.

Fig. 5. Deviations from the plane defined by Cu,N(1) and C(7) in the complexes Cu(N-R,hapim)$_2$.

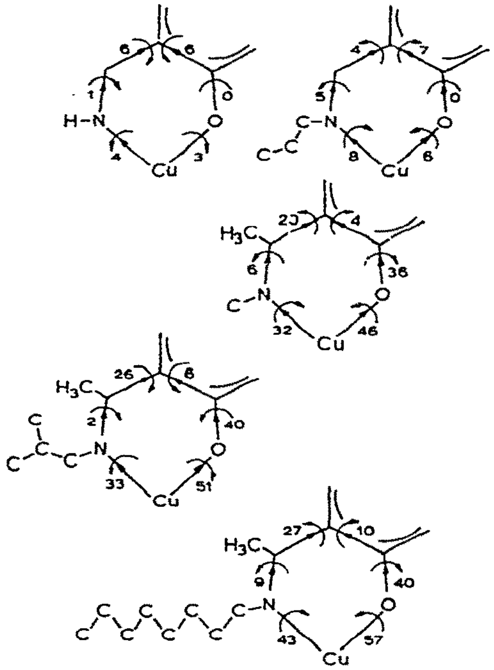


Fig. 6. Bond axis rotations (deg.).

TABLE 5

Selected bond lengths and angles for centrosymmetric molecules

R	σ (Å)	C(1)—C(7) (Å)	O(1)—C(2) (Å)	Cu—O(1)—C(2) (deg.)
Cu(N-R,salim)$_2$	0.15	1.44	1.31	126
—Me(α)	0	1.44(1)	1.32(1)	131(1)
—Me(adduct)	0.38	1.418(8)	1.322(7)	128.9(4)
—*n*-propyl	0.13	1.39(3)	1.32(3)	131(1)
—*n*-butyl	0.37	*1.46(1)*	*1.30(1)*	*130(1)*
—phenyl	0.45	1.436(6)	1.313(4)	128.0(4)
Cu(N-R,hapim)$_2$				
—H	0.24	1.456(5)	1.310(4)	128.5(2)
—Me	0.96	1.473(4)	1.314(4)	121.1(2)
—*i*-butyl	1.12	1.465(4)	1.313(3)	118.4(2)
—*n*-octyl	1.33	1.470(3)	1.321(3)	114.8(2)
Cu(N-R,napim)$_2$				
—Me(β)	0.63	1.416(5)	1.302(4)	126.5(2)
—Me(γ)	0.19	1.42(2)	1.29(1)	131.0(6)

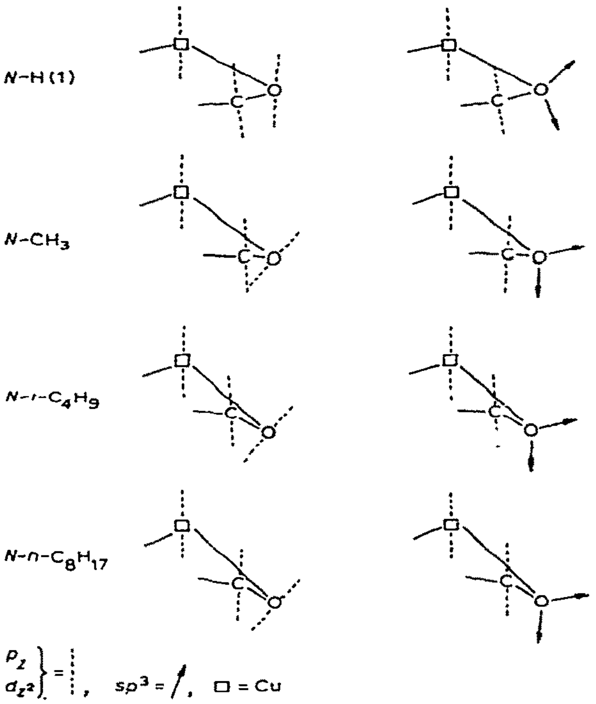
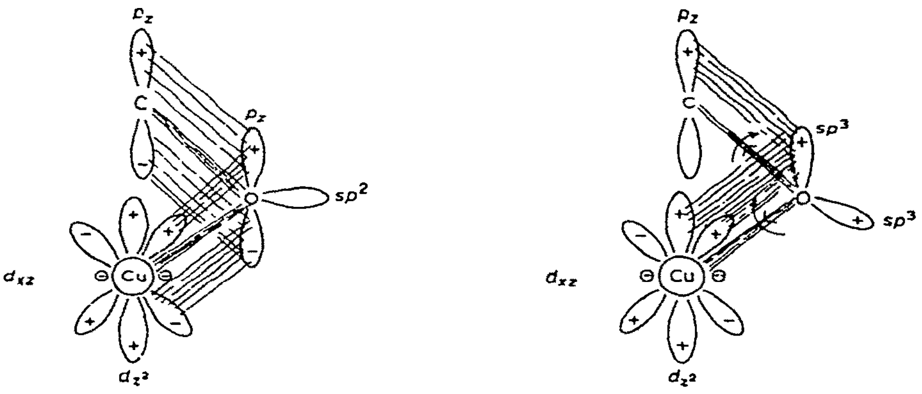


Fig. 7. Orbital overlaps between Cu,O(1) and C(2) in Cu(*N*-R,hapim)$_2$.

its length, but the constancy of the O(1)—C(2) bond gives, in its apparent contradiction, one of the clues to the electronic rearrangement which is occurring. Equally significant is the fact that the O(1)—C(2) bond rotation equals the O(1)—Cu rotation, although of opposite sense, until ca. 40° is reached. At this point (ideally 35° if the complex were initially strictly planar) the O(1)—C(2) rotation reaches a maximum for reasons which Figs. 7 and 8 explain by drawing attention to the consequences of the development of an sp^3 orbital system on O(1). Such a hybrid pattern produces an orbital in the correct orientation to retain conjugative continuity with the benzene ring, by π-overlap with C(2), if a bond rotation of ca. 40° takes place. Hence the length C(2)(p_z)—O(1)(sp^3) remains relatively constant whereas the length of C(1)(p_z)—C(7)(p_z), where π-overlap is being lost, increases with the bond rotation. The sp^3 lobe developing on O(1) would, of course, also maintain overlap with the $4p_z$ and/or the d_{xz}, d_{z^2} orbitals of the copper atom.

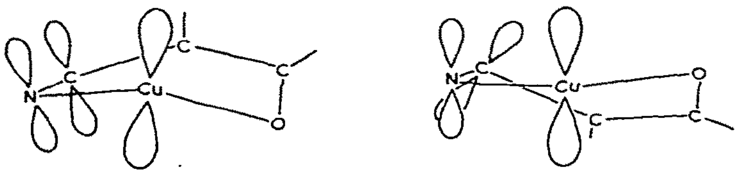
It is therefore suggested that a rehybridisation takes place at O(1) under the influence of an increased electron density within the chelate ring and that this is then accompanied by bond rotations driven by the change in the O(1)—C(2) π-overlap from the p_z—p_z type seen in α-Cu(*N*-Me,salim)$_2$ [47] to the sp^3—p_z situation of Cu(*N*-*n*-octyl,hapim)$_2$ [69]. As noted in Table 5 the bond angle at O(1) also closes as the tetrahedral hybridisation proceeds,



Cu(N-Me,salim)$_2$ Cu(N-n-octyl,hapim)$_2$

Fig. 8. Orbital overlaps in, (a) Cu(N-Me,salim)$_2$ and, (b) Cu(N-n-octyl,hapim)$_2$.

falling from 132° to 115° in the two compounds just mentioned. The primary movement in many complexes is therefore rotation about O(1)—C(2), other compensatory twists then being necessary to maintain ring closure. A rotation of ca. 35° brings full π-overlap with an oxygen sp^3 system and a concomitant half-step, σ, of ca. 1 Å calculated on the assumption that the compensatory twists are such as to bring N(1) into the position which maintains a high degree of C(7)(p_z)—N(1)(p_z) overlap. Figure 9 illustrates this point and the alternative in which this overlap is destroyed, that between C(1) and C(7) much reduced and in which the N(1)—Cu bond direction tends to reduce the step height. Most values are less than ca. 1.0 Å for σ but in two complexes, Cu(N-i-butyl,hapim)$_2$ [90] and Cu(N-n-octyl,hapim)$_2$ [69] they are 1.12 and 1.33 Å even though the rotation about the O(1)—C(2) axis does not increase accordingly. Steric interference between nitrogen-substituted R-groups and neighbouring oxygen donors is not discounted, and probably accounts for much of the step heights in Cu(N-H,salim)$_2$ [91] and in Cu(N-n-propyl,salim)$_2$ [50] where σ = 0.15 and 0.13 Å respectively with an O(1)—C(2) rotation of 0°. It seems unlikely, however, that the i-butyl and n-octyl groups require



a b

Fig. 9. Position of N(1) and N(1)—C(7) π-overlap; (a) overlap maintained, (b) overlap reduced.

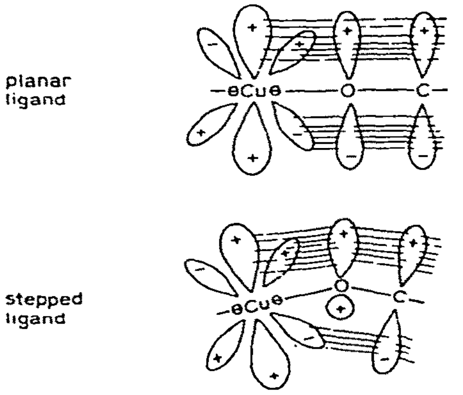


Fig. 10. Overlap between orbitals on Cu and C(2).

different σ-values, or that σ for Cu(N-n-butyl,salim)$_2$ should be only 0.37 Å [51], if steric forces are the primary consideration. The electronic explanation can be extended to account for half-steps larger than 1 Å by noting the spatial orientations of the C(2)(p_z) and the Cu($4p_z$) and (d_{xz}) orbitals. Figure 10 shows that whereas their positive lobes lean away from each other and interact through an intervening sp^3 orbital the axes of their negative lobes interact almost exactly, in "bent bond" fashion, when σ is ca. 1.2 Å. Half-steps greater than the 1.0 Å due to O(1)—C(2) bond axis rotation are thus ascribed to an attractive orbital overlap between C(2) and Cu which will, in terms of Fig. 10, pull the copper atom further beneath the molecule and increase the step height.

The conformations of bis-chelate complexes of copper thus reflect the following factors. When the electron input to the chelate ring is small the oxygen donors maintain sp^2 hybridisation, the O(1)—C(2) bond rotation is very small and the half-step is less than 0.2 Å. This latter value probably reflects the geometrical needs of the chelate rings rather than steric effects since it is noted that both crystalline isomers of bis(salicylaldehydato)copper(II) [92,93], in which steric difficulties are at a minimum, have a half-step height of 0.19 Å. At a certain level of electron input as the number of carbon atoms in the substituents is increased the molecule begins to "unlock" with the oxygen hybridisation changing towards sp^3, a situation reached when the O(1)—C(2) bond rotation is 35° and σ is 1.0 Å. Further electron loading brings a new interaction into significance in the Cu ··· C(2) bent bonds discussed above and σ increases again. Table 6 lists bond rotations and half-step heights for a series of square planar salicylaldiminato and acetophenoneiminato complexes which illustrate these effects. The exceptions seen in the compounds with R = methyl or ethyl will be discussed later in more detail but the special effects already mentioned as occurring in isomers of Cu(N-Et,salim)$_2$ can be recalled here to suggest that there is a very close relationship between overall geom-

TABLE 6

Bond rotation angles and the half-step heights in centrosymmetric molecules

R	σ (Å)	Cu—O(1) (Å)	Cu—N(1) (deg.)	O(1)—C(1) (deg.)
Cu(N-R,salim)$_2$				
—Me(α)	0	0	0	0
—H	0.15	3.6	3.3	0.0
—*n*-propyl	0.13	5.8	8.2	0.4
—*n*-butyl	0.37	22.8	11.9	19.4
—Me(adduct)	0.38	23.0	15.9	18.8
—phenyl	0.45	24.4	17.9	18.4
Cu(N-R,hapim)$_2$				
—H	0.24	9.5	3.1	10.6
—Me	0.96	45.9	31.9	36.4
—*i*-butyl	1.12	51.1	33.3	40.5
—*n*-octyl	1.33	57.0	43.2	40.0

etry and the electronic state of the molecule as indicated by its bond lengths and angles and that the sequence of events just summarised should not be taken as temporal cause and effect but as an explanation of what is observed.

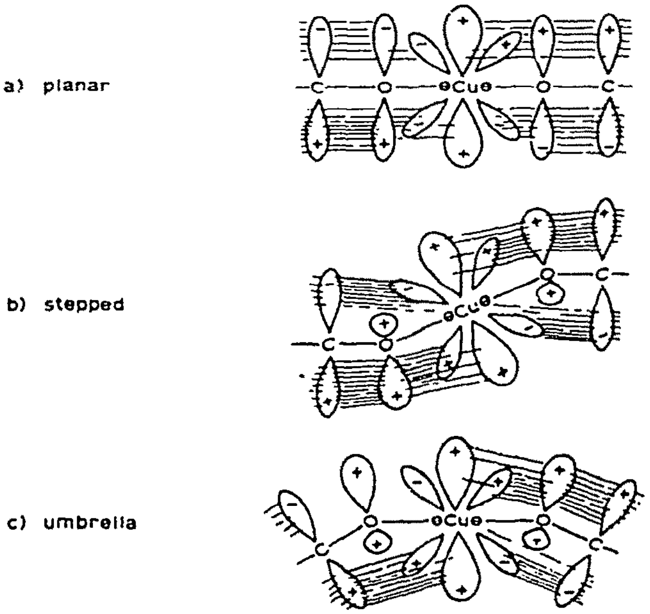


Fig. 11. Orbital overlap for: (a) planar, (b) stepped and (c) umbrella-shaped molecules.

It will be noted that a "stepped" or "umbrella" conformation seems equally probable if the two ligands of a bis-chelate complex are treated separately but as Fig. 11 illustrates the proposed necessity to maintain maximum π-overlap is favoured by stepping when the whole molecule is considered and this is what is observed.

(ii) Quadridentate complexes

A stepped conformation with large values of σ is unlikely with quadridentate ligands since the geometry of the link is an important constraint, especially when the link is short. This follows as a consequence of the rotations about the copper—nitrogen bonds which affect the spatial location of nitrogen substituents. The distance between substituent positions increases much more rapidly with rotations of opposite sense, a "stepping" feature, than with the similar rotations of an "umbrella-shaped" molecule. In the dimethylene complexes, therefore, the single carbon—carbon link is a tie which mitigates against the simultaneous attainment of a stepped molecule and the required bond rotations at the oxygen donors. Thus in a quadridentate complex where rotations indicate full sp^3 hybridisation at oxygen atoms, as in Cu[*N*,*N*'—$CH_2 \cdot CH_2$—(4-OH,salim)$_2$], the "umbrella" conformation is found [80].

As in the bis-chelate compounds the rotations vary between values appropriate for sp^2 and sp^3 hybridisations at the oxygen but unfortunately electron loading cannot now be so obviously correlated with substituents because of the constraining effect of the link or the complications introduced by the dimerisation or adduct formation seen in a number of the complexes for which structural data are available. These and other geometrical data are presented in Table 7 which also draws attention to the length of the carbon—carbon single bond in dimethylene links. With the exception of Cu[*N*,*N*'—$CH_2 \cdot CH_2$—(salim)$_2$]$_2$ which we omit from consideration because of the low accuracy of the two-dimensional analysis [85], it will be noted that these carbon—carbon distances are less than expected. This shortening is also seen in Cu[*N*,*N*'—$CH_2 \cdot CH_2$—(acacim)$_2$] complexes, relevant data also being listed in the Table. An associated effect is to be found in the closing of the dihedral angle, γ, which describes the staggered or *gauche* conformation of a dimethylene link. Ideally 60°, as in coordinated 1,2-diaminoethane [94—98], the Table shows that a fully eclipsed state, $\gamma = 0°$, is attainable and that such a reduction in angle is favoured by an appropriate substitution or by hydrogen bonding between a donor oxygen atom and an adduct. It has already been seen that a strengthening of the canonical forms represented by (11) and (12) leads to a shortening of the dimethylene link and by interference, increased conjugation through the molecule. Increased density at nitrogen will also follow the enhanced importance of these canonical structures and, with the overall increase in conjugation, ensure better metal—ligand π-bonding and a larger ligand field at the donor atoms. This last effect makes a brief consideration of five-coordinate complexes appropriate at this point.

TABLE 7

Selected geometric data for quadridentate complexes

Compound	Coord. No.	Conformation	σ (Å)	C—C length of dimethylene (Å)	γ (deg.)	Ref.
a	5(dimer)	Umbrella?**	0.40 −0.47	1.56	49.6	85
a(1)	5(dimer)	Stepped	0.27 −0.38	1.50(2)	41.3	83
a(2)	4	Stepped	0.01 −0.12	1.49(2)	30.2	82
b	4	Umbrella	0.38 0.49	1.37(2)	22.7	80
c	4	Stepped	0.22 −0.25	1.47(3)	22.5	86
d*	4	Umbrella	0 0.18	1.55(3)	65.2	101
d(1)*	4	Planar	0 0	1.48(2)	0	84
d(2)*	4	Planar	0 0.05	1.43(2)	11.7	81
d(3)*	5	Umbrella	0.20 0.15	1.508(8)	4.1	126
e	5	Umbrella	0.55 0.02	1.61(4)	74.1	102

a = Cu[*N*,*N'*—$CH_2 \cdot CH_2$—(salim)$_2$];
(1) = $CHCl_3$ adduct of a;
(2) = *p*-nitrophenol adduct of a;
b = Cu[*N*,*N'*—$CH_2 \cdot CH_2$—(4-OH,salim)$_2$];
c = Cu[*N*,*N'*—$CH_2 \cdot CH_2$—(hapim)$_2$];
d = Cu[*N*,*N'*—$CH_2 \cdot CH_2$—(acacim)$_2$];
(1) = $MeNH_3^+$ adduct of d;
(2) = hemihydrate of d;
(3) = aquo complex of d;
e = aquo complex of Cu[*N*,*N'*—$CH(CH_3) \cdot CH_2$—(salim)$_2$];
* Half-step, σ, defined as distance of Cu from acetylacetoneimine skeleton $O—C(CH_3)=CH—C(CH_3)=N—$
** Note that σ can be misleading when Cu is not in the basal plane.

(iii) Five-coordination in copper(II) complexes:

Five-coordination has been linked with a diminished ligand field at the donors [83,99], i.e., with a situation in which back-bonding leading to molecular planarity and four-coordination, or electron donation to the metal

TABLE 8

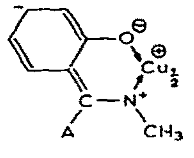
Five coordinate complexes

Compound	"Fifth" bond	Bond length (Å)	Ref.
a[a]	Cu—O′(dimer)	2.41	85
a(1)[a]	Cu—O′(dimer)	2.79(1)	83
d(3)[a]	Cu—H_2O	2.428(4)	126
e[a]	Cu—H_2O	2.53(3)	102
γ-Cu(*N*-Me,salim)$_2$	Cu—O′(dimer)	2.43(2), 2.46(2)	49
Cu(*N*-Me,hapim)$_2$(triclinic)	Cu—O′(dimer)	2.378(2)	69
β-Cu(*N*-Me,napim)$_2$	Cu—O′(dimer)	2.94	76
Cu[(*N*-phenyl,salim)$_2$pyridine]	Cu—pyridine	2.308(6)	127

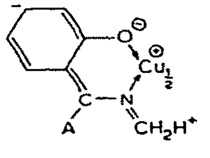
[a] For identification see Table 7.

leading to a tetrahedral stereochemistry, no longer exists. It is seen in dimer formation in the solid state only in the dimethylene linked quadridentate complexes and in the bis-chelate complexes when R = methyl. Compounds are listed in Table 8 and it is interesting to observe that salicylaldiminato, *o*-hydroxyacetophenoneiminato and 2-hydroxy-1-naphthaldiminato ligands are all involved. Solvent bonding can also increase the coordination number and occurs with dimethylene-linked ligands and with Cu(*N*-phenyl,salim)$_2$.

That there is diminished Cu—N bonding in all of these compounds and their various adducts and isomers seems apparent from the increased metal—donor separations relative to those found when R = H, but since these longer values also occur with other substituents, and even in pseudo-tetrahedral molecules, they are not a special feature of five coordination. Their occurrence, ascribed by Lingafelter to steric pressure [47], may nevertheless be an important precondition since it has been demonstrated by Hathaway [100] that extra bonding will occur with copper(II) when the π-bonding to the in-plane donors is reduced. It is our view that the metal—donor interaction is not sufficiently strengthened by a compensatory increase in electron density at the oxygens and nitrogens when R = methyl or when a dimethylene link is involved. Some evidence is presented later to suggest that with the methyl substituents canonical forms such as (14) and (15) are of significance. The

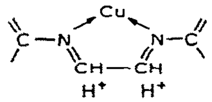


(14)



(15)

same kind of situation can be envisaged in the quadridentate complexes. Unfortunately the three dimeric compounds for which there are structural data have only been subjected to two-dimensional analyses but the best of these, Cu[N,N'—$CH_2 \cdot CH_2$—(acacim)$_2$]$_2$, (giving R-factors of 0.11 and 0.12 [101] against 0.18, 0.20 for Cu[N,N'—$CH_2 \cdot CH_2$—(salim)$_2$]$_2$ [85] and 0.16, 0.18 for the aquo complex of Cu[N,N'—$CH_2 \cdot CH(CH_3)$—(salim)$_2$]) [102] gives some support to a canonical form, 16.


(16)

It will be seen that the density implied by these structures diminishes, rather than strengthens, electron build-up at the donors, particularly the nitrogens. A consequence is that the π-bonding to the in-plane coordinating atoms is reduced to the point of inducing quinque-covalency. Thus, whereas on the basis of the slight tetrahedral twist seen in one of the crystallographically distinct molecules of Cu(N-H,hapim)$_2$ [103] it might have been predicted that electron build-up on the nitrogens would have proceeded in Cu(N-Me,hapim)$_2$ [69] to the point of ensuring an equivocally pseudo-tetrahedral geometry this is not so. In one polymorphic form the molecule is square-planar and stepped, in the other it is dimeric and five-coordinate with only a small tetrahedral twist. It is worth noting here that all the N-methyl complexes for which structural data are available show polymorphism, three crystalline forms being known for Cu(N-Me,salim)$_2$ [44—46] two for Cu(N-Me,hapim)$_2$ [69] and three for Cu(N-Me,napim)$_2$ [74—76]. This diversity would appear to indicate, again, the very close relationship between structure and electronic state, and, particularly, the importance of the electron density on the nitrogen donors in stabilising the planar, for example, α-Cu(N-Me,salim)$_2$ or the dimeric, for example, γ-Cu(N-Me,salim)$_2$, state.

The situation with respect to the quadridentate complexes needs little further comment. Any strengthening of the canonical structures (11) and (12) should lead to a decrease in the tendency toward five-coordination and a shortening of the carbon—carbon bond in the dimethylene link, a feature noted in Table 7.

It must be admitted that our interpretation of the shortening of the link is not without its difficulty since this bond is also less than expected in many simple complexes of ethylenediamine, or its derivatives, which do not have a conjugated system attached to a nitrogen atom. Values range from 1.43 to 1.63 Å over fifty measurements which we have noted from well refined (R-factor $< 10\%$) X-ray investigations. We do not wish to examine these data in detail but attempt to briefly justify our view that these observations are not artifacts of X-ray procedures. Most of the bonds are < 1.54 Å, the mean of the surveyed sample being 1.510 (±0.005) Å, with an e.s.d. of 0.038 Å, so that it is their decrease from simple expectation which most needs comment. In uncomplexed planar molecules of ethylenediamine and those of *gauche* conformation "complexed" to lithium [104] the carbon—carbon bond is 1.53(2) Å in length.

A recent discussion of the dimethylene link of 1.42(3) Å found in the sodium perchlorate "adduct" of the quadridentate complex Cu[*N*,*N'*-—$CH_2 \cdot CH_2$—salim)$_2$] [105] suggests one explanation for such shortening in that the decrease is tentatively ascribed to a slight disorder between two possible (δ and λ) *gauche* conformations for the bridge which thereby brings the apparent positions of the carbon atoms closer to the chelate plane defined by the metal and the two nitrogen donors. However, complete disorder of a "classical" [94] *gauche* link with carbons then averaged into the plane only reduces the C—C bond to 1.38 Å so it is unlikely that the disorder needed to reduce it to 1.42 Å could be overlooked in the X-ray analysis. Judicious use of the 0.03 Å standard deviation could, of course, modify the rebuttal in this particular instance but other examples can be cited. Thus the complex di-μ-hydroxo-bis(*N*,*N*,*N'N'*-tetramethylethylenediamine)copper(II) bromide [106] which has a C—C bond of 1.43(2) Å reveals no evidence for disorder nor for the positioning of the carbons closer to the chelate plane since each is 0.35 Å removed therefrom, a value to be compared with the expected distance of 0.34 Å [94].

The alternative explanation for the observed lengths is that they arise from enhanced thermal motion. We do not believe that the evidence supports this view either, although some of the structures showing short C—C bonds are reported as having their largest thermal parameters associated with these carbon atoms. Where thermal motion has been measured over a temperature range [64—67] or through a full vibrational analysis [63,68] it is not, however, found to affect bond lengths of the type under discussion by more than ca. 0.01 Å. Nor is it easy to see how this explanation accounts for the distances of 1.507(5) and 1.544(9) Å in the isomorphous crystals containing the trigonal molecules of tris(ethylenediamine)copper(II) sulphate [107] and tris(ethylenediamine)nickel(II) sulphate [108]. The *R*-factors are low (4.0 and 4.2% respectively), the thermal parameters are similar [63] (although the orientation of the vibrational ellipsoids differ somewhat) and the N—C distances are identical and normal at 1.472(5) and 1.476(9) Å. Again, the carefully analysed complexes of the tris(ethylenediamine)chromium(III) cation [109,110] have shortened C—C bonds, for example, 1.502(5) Å in one molecule [107], with no evidence for large temperature parameters. In fact, a qualitative perusal of the data shows no correlation between the C—C bond length and the thermal parameters, nor any indication that when the C—C bond is short, the N—C bond lengths correspondingly decrease as a model of the link seems to suggest they should if the carbons undergo any degree of thermal motion perpendicular to the bonds.

In rejecting these explanations we conclude that the C—C length in complexed ethylenediamine is somewhat flexible and responsive to the demands of the chemical system in which it finds itself. It is not obvious what all these demands are, but the asymmetric nature of the *gauche* conformation seen in most of the dimethylene links of cupric complexes is worth noting. This asymmetry can be described as a "step", or a bending about the N ··· N line

[111], which has the result of bringing one N—H bond on each nitrogen more nearly perpendicular to the coordination plane and the other more nearly coplanar with it. The significance in terms of their interaction with copper orbitals, and the effect of normal intermolecular hydrogen bonding in increasing the electron drain away from the dimethylene link, have not yet been seriously studied. We do not, however, believe that these bonds, nor those in the quadridentate conjugated molecules discussed earlier, can be "explained away" as artifacts of their X-ray analyses.

(iv) Tetrahedral complexes

Complexes with a pseudo-tetrahedral donor arrangement, i.e. the angle, θ, is greater than 0°, are expected to be those in which the electron feed into the chelate ring is relatively large and manifest at both donor atoms. This effect is seen with copper complexes in Cu(*N*-Et,salim)$_2$ due, it is proposed, to the hyperconjugative stabilisation of the substituents as incipient carbonium ions. It could therefore be predicted that *i*-propyl and *t*-butyl groups should produce an increasing tetrahedrality and structural data listed in Table 9 show that this is so. The dihedral angle, θ, it is recalled, is defined as the angle between the planes Cu,N(1), O(1) and Cu,N(2), O(2). It is also noted that these pseudo-tetrahedral complexes are expected to show the same deviations from chelate ring planarity as the stepped compounds since the former have, by inference, a larger electron drift into the chelate rings. Table 9 also summarises the displacements of ring atoms from the planes defined by Cu,N(1),C(7) and Cu,N(2),C(27) and Fig. 12 shows some corresponding rotations about bond axes. It is apparent that there is a similar pattern to that seen in square-planar complexes.

A further similarity with the square-planar complexes can also be deduced, namely that interactions between donor oxygen atoms and hydrogens, this time of the nitrogen substituents, can be important and indeed explain the particular values of θ. The pseudo-tetrahedral structures of Cu(*N*-Et,salim)$_2$ are again a useful starting point. It should first be noted that molecules (1) and (2) (see page 141) can be described as substituent-*trans* in that the two ethyl groups of each are oriented towards the opposite sides of the mean molecular plane, whereas molecules (3) and (4) are substituent-*cis*. In the latter two molecules a turning moment at the copper atom is able to impose pseudo-tetrahedrality (an increase in θ) without hindrance (Fig. 13) until substituent—substituent crowding becomes significant. In both, however, the C(9) ··· C(9')* distance is ca. 5 Å, well outside a van der Waal's approach. On the other hand a turning moment in the substituent-*trans* molecules must result in one of the donor oxygens being forced into an ethyl group, Fig. 14. It is found, in fact, that in the molecules (1) and (2) each oxygen atom makes

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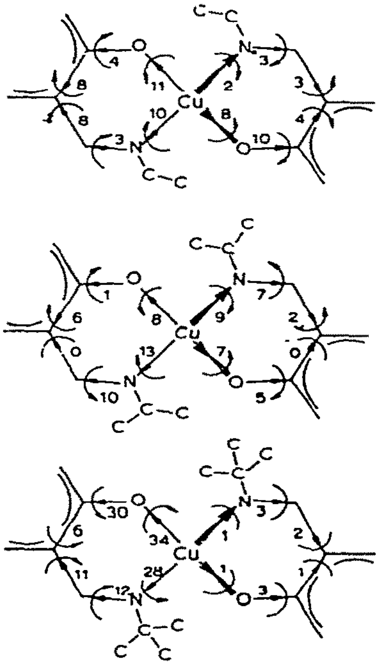
* Numbering scheme of ref. 112.

TABLE 9

Values of the twist, θ, and displacements from the planes Cu, N(1), C(7) and Cu, N(2), C(17) in pseudo-tetrahedral molecules

R		θ (deg.)	σ_1 (Å)	O(1) (Å)	C(1) (Å)	C(2) (Å)	σ_2 (Å)	O(2) (Å)	C(11) (Å)	C(12) (Å)	Ref.
Cu(N-R,salim)$_2$											
—ethyl	1	9.4	0.12	0.33	0.23	0.08	0.08	0.12	0.12	0.04	45
	2	12.8	0.25	0.40	0.32	0.07	0.07	0.22	0.21	0.07	46
	3	35.5	0.11	0.07	−0.05	−0.05	0.23	0.38	0.29	0.09	44
	4	35.9	0.10	0.06	−0.06	−0.06	0.28	0.34	0.31	0.06	45
—*i*-propyl		59.3	0.17	0.41	0.46	0.21	0.08	0.29	0.28	0.14	112
—*t*-butyl		53.6	0.03	0.04	0.09	0.06	0,67	0.91	0.73	0.25	113
Cu(N-R,hapim)$_2$											
—H		7.8	0.37	0.31	0.16	0.02	0.03	0.17	0.16	0.05	103
—benzyl		26.4	0.78	0.24	−0.05	0.15	0.90	0.72	0.25	0.01	69
2-phenylethyl		29.6	0.61	0.64	0.41	0.06	(0.61)	(0.64)	(0.41)	(0.06)	69



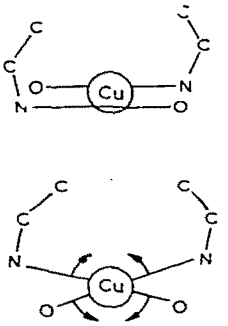
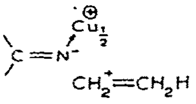


Fig. 12. Rotations about bond axes in three pseudo-tetrahedral molecules.

Fig. 13. The substituent-*cis* structure of Cu(N-Et,salim)$_2$.

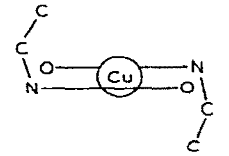
a close approach (2.0—2.7 Å) to two of the hydrogen atoms of its neighbouring ethyl group. That each oxygen is so involved, and not just one as an increase in θ would suggest, indicates that their interactions are other than simple steric clashing and that the geometry finally adopted is one in which the turning moment at the copper is resisted by opposing C—H ··· O attractive forces. The possibility of such an interaction must be regarded as being greatly enhanced by the positive nature of the ethyl substituents deduced by the bond and angle changes already cited. These suggest that electron donation to the chelate ring by canonical forms of the type, (17), is stabilised by hyper-



$$\gt C{=}\overset{\overset{\cdot\oplus}{Cu_{\frac{1}{2}}}}{N^{-}}\underset{CH_2^{+}{=}CH_2H}{} \qquad (17)$$

conjugation and partial carbonium ion formation.

The complex Cu(N-i-propyl,salim)$_2$ [112] has the two dimethylmethine groups oriented as shown in Fig. 15, i.e., the structure is both substituent-*cis* and substituent-*trans*. The pseudo-tetrahedral nature of the compound is much more pronounced in response to the enhanced stabilisation now possible, but



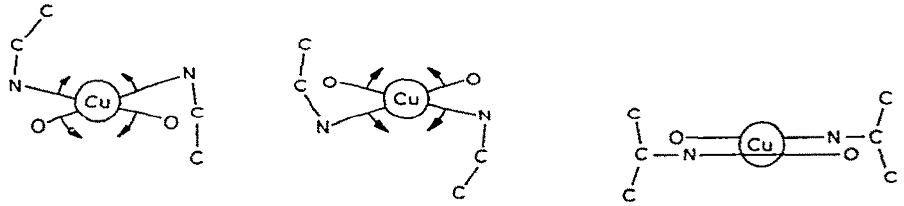


Fig. 14. The substituent-*trans* structure of Cu(N-Et,salim)$_2$.

Fig. 15. Substituent orientation in Cu(N-i-propyl,salim)$_2$.

again evidence of C—H ··· O interactions is apparent. Thus H^{111}-10* is 2.5 Å from O(2) and is located as to interact with an sp^3-hybridised lone pair. A hydrogen atom (not located crystallographically but in a predictable position) on the other methyl group of the same substituent is placed so as to interact with the other lone pair of O(2). A similar situation exists at the other oxygen donor, O(1), as shown in Fig. 16. Hydrogen atoms were not located in Cu(N-t-butyl,salim)$_2$ [113] but the same situation seems evident. For example there are C(of CH_3) ··· O approaches of 3.18 and 3.26 Å and if these are attractive forces they are again in a direction opposing the rotatory movement generating the pseudo-tetrahedral geometry. A feature of this molecule is that one of the chelate rings shows a much closer approach to planarity than does the other and it is noted that a movement of its oxygen atom towards the

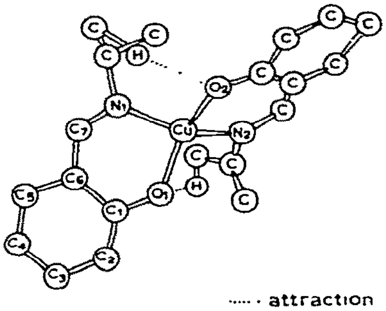


Fig. 16. Hydrogen—oxygen intermolecular interactions in Cu(N-i-propyl,salim)$_2$.

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* Numbering scheme of ref. 112.

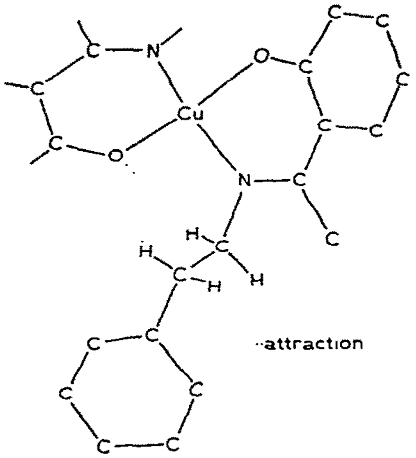

Fig. 17. Hydrogen—oxygen intermolecular interactions in Cu(*N*-2-phenylethyl,hapim)$_2$.

methyl carbon atom 3.26 Å distant, i.e. interaction C(20) ··· O(1)*, would, through its associated bond rotations, flatten the ring in the manner observed.

It has already been suggested that the hydrogen atoms on the substituents are likely to be electropositive through hyperconjugation and partial carbonium ion formation so that attractive C—H ··· O interactions of the type already evidenced by the $CHCl_3$ adducts of quadridentate complexes are to be expected. There are thus two important forces acting in these pseudotetrahedral complexes. One is the drive towards a tetrahedral configuration acting on the metal through the primary coordination sphere, the other is a hydrogen-bonding interaction acting on the reverse direction between the donors and the outer regions of the molecule.

Introduction of a phenyl ring into the substituents has interesting consequences. The complex Cu(*N*-2-phenylethyl,hapim)$_2$ [69] is substituent-*cis* and therefore similar to molecules (3) and (4) of Cu(*N*-Et,salim)$_2$ with a phenyl ring replacing a hydrogen on the β-carbon of each ethyl group. Hyperconjugative stabilisation of a partial carbonium ion $^+CH_2—CH_2Ph$ is apparent in the long N—C$_\alpha$ (1.516(4) Å) and short C$_\alpha$—C$_\beta$ (1.494(4) Å) bonds. (The two substituents are related by a crystallographic two-fold axis.) Electron input at nitrogen, added to that resulting from the methyl substituent at C(7) in this *o*-hydroxyacetophenoneiminato derivative, would suggest a tetrahedral rotation even greater than that seen in Cu(*N*-Et,salim)$_2$. The dihedral angle, θ, is, however, only 29.6°. But C—H ··· O approaches of 2.40 and 2.65 Å are established, Fig. 17, since the sense of rotation about the copper ion is the reverse of that in the *N*-ethyl complex, a movement which brings the oxygens close to hydrogens on C$_\alpha$ and C$_\beta$ of the side chains. It is not inconceivable, therefore, that these C—H ··· O forces, strengthened by the hyperconjugation

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* Numbering scheme of ref. 113.

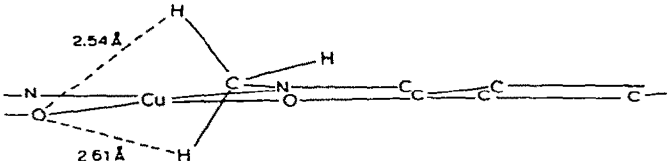


Fig. 18. Hydrogen—oxygen intermolecular interactions in δ-Cu(*N*-Me,napim)$_2$.

effects seen in both substituents —in contrast with the one substituent of Cu(*N*-Et,salim)$_2$ molecules — have succeeded in reversing the sense of the tetrahedral twist. A further balance point (θ = —30°) thus exists substituent-*cis* molecules and indicates the reality of C—H - - - O interactions.

It is worth noting, in passing, that the changes in the N—C_α and C_α—C_β bonds of Cu(*N*-2-phenylethyl,hapim)$_2$ are unlikely to be due to thermal effects since the carbon distances in the phenyl group are all within 0.03 Å of 1.39 Å even though the thermal vibrational parameters are much larger for the benzene atoms.

These opposing effects can be generalised and set in a wider context by noting that in the square-planar complexes there is, in some compounds, a tension between C—H ··· O interactions and the conformational changes leading to stepping. Thus in δ-Cu(*N*-Me,napim)$_2$ [74] it is postulated that the attractive interactions, Fig. 18, "encapsulate" the oxygens thereby overcoming the deforming consequences of electron feed into the chelate ring and perhaps strengthening double-bonding between metal and donors in the manner already suggested as increasing molecular planarity. The same situation exists in the salicylaldiminato series in the polymorph α-Cu(*N*-Me,salim)$_2$ [47]. If these interactions are broken the molecule goes on to take up the stepped β-structure seen in the isomorphous β-Ni(*N*-Me,salim)$_2$ [48] or in the stepped and dimeric structure of γ-[Cu(*N*-Me,salim)$_2$]$_2$ [49]. The same stepped conformation is seen in β-Cu(*N*-Me,napim)$_2$ [76] and the same stepped and dimeric conformation in γ-[Cu(*N*-Me,napim)$_2$]$_2$ [75]. The stepped conformation reappears in one form of Cu(*N*-Me,hapim)$_2$ [69] but in the dimeric, and stepped, isomer there is also a small tetrahedral twist superimposed, presumably as a result of a marginal increase in electron density at the donors through methyl substitution at C(7).

Further electron input, as occurs in Cu(*N*-Et,salim)$_2$, brings the pseudotetrahedral geometry. This is resisted in molecules (1) and (2) of the complex, where substituent orientation is unfavourable, to impose a balance point at about θ = 10°. Removal of this resistance by reorientation of the substituents in the *cis* positions allows θ to increase to 25—35°. A further opportunity for C—H ··· O interactions occurs in Cu(*N*-*i*-propyl,salim)$_2$ and Cu(*N*-*t*-butyl, salim)$_2$ where the extra methyl groups allow a new balance between 50 and 60°.

We have attempted to express some of these results in statistical terms after undertaking an initial survey of the recent literature to establish a C(sp^3)—C(sp^3)

mean bond length for comparison purposes. Light atom structures in which a model containing hydrogen atoms was refined to an $R < 10\%$ were chosen — the mean of the estimated standard deviations of the 251 bonds in the sample was 0.009 Å. A mean value of 1.533 Å was obtained with a standard deviation of 0.002 Å.

The null hypothesis that there is no difference between this "general" length and the C_α—C_β bonds of non-branched nitrogen substituents of pseudo-tetrahedral complexes was then tested by the method outlined by Hamilton [114] in his discussion of the Fisher—Behrens problem. The ten available bonds for these pseudo-tetrahedral complexes have a mean of 1.495 Å ($S = 0.019$ Å) and a preliminary Snedecor's F test [115] for the variance ratio indicates that the difference between the sample standard deviations is not significant. Hamilton's procedure was then applied and gave the statistic 'u' as 6.16 with 10.2 degrees of freedom, leading to the rejection of the hypothesis at the 99.9% confidence level. The test is "two-tailed" and so the probability of such a shortened sample of bonds arising by chance is 1 in 2,000. The null hypothesis that there is no significant difference between the N—C_α bonds available for square planar complexes and twenty N—C_α bonds of pseudo-tetrahedral complexes was also tested. The 'u' statistic here indicates the rejection of the hypothesis at the 97% level.

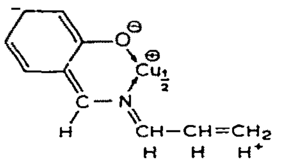
Finally we tested the hypothesis that a pseudo-tetrahedral geometry is associated with a high inductive effect using Wilcoxon's "stratified sum of ranks" test [116]. Six *N*-alkyl substituents were tested, namely methyl, *n*-propyl and *n*-butyl for the square-planar complexes and ethyl, *i*-propyl and *t*-butyl for the pseudo-tetrahedral. Their inductive effects were ranked on the pK_a of their acids R—COOH [117], the carbon—chlorine bond moments of R—Cl [118], the pK_a of monoalkyl substituted anilines [119], the pK_a of aliphatic amines [120], the $-\Sigma\sigma^*$ values in primary amines [120], the E_s values derived by Taft [122] and the σ^* values of Taft [121]. The null hypothesis is that distinction between square-planar and pseudo-tetrahedral complexes has no relationship with the inductive effect of their nitrogen substituents. The statistic, 'z', may be computed from the number of strata (7), the number of pairs in each stratum (3) and the smaller sum of ranks (55). It has a value of 3.05 and the probability of this figure arising by chance may be evaluated from the standard normal distribution as 0.001. Thus the probability that the distinction between square-planar and pseudo-tetrahedral complexes is unrelated to the inductive order of their nitrogen substituents is 0.1%; in other words there is a highly significant correlation.

The chemical and statistical approaches to the situation are thus in agreement, as indeed they should be. The decisive nature of the statistics is, nevertheless, comforting.

D. OTHER MOLECULAR CHANGES

Associated with the main stereochemical changes at the metal atom we have drawn attention to a change at the oxygen donors and to the importance of enhanced electron density at the nitrogens. If such electronic enhancements occur at these atoms, electron shifts elsewhere must be implied and it is our view that these are apparent in small geometrical changes throughout the molecule. Some of these have already been cited as, for example, deviations from "expected" bond lengths, especially in the linking groups of quadridentate complexes, and we have expressed this in terms of the increased significance of particular canonical forms. Similarly we have noted that we believe that structure (8) accounts for the decreased N—C(methyl) distances of 1.44(1) [74], 1.44(2) [75], 1.42(2) [75] and 1.45(1) [76] Å in the polymorphs of Cu(*N*-Me,hapim)$_2$. Further supporting evidence is now presented.

We begin by observing that a structure similar to (8) is also present in Cu-(*N*-*n*-propyl,salim)$_2$ [50] where added hyperconjugation in the propyl group appears to stabilise a planar complex by preventing electronic build-up on the donors (it will be recalled that the half-step, σ, is only 0.13 Å) through reinforcement of canonical forms (18) and (19).



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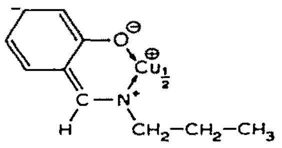
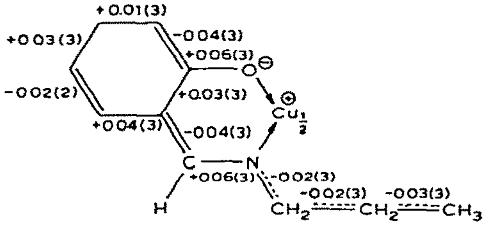


(19)

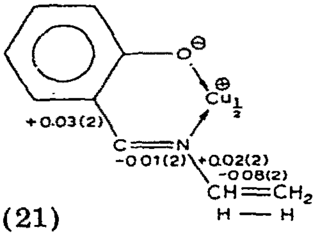
Bond length differences from "expected" values are shown as (20). Although not individually convincing in statistical terms we see the overall pattern of bond changes as being more persuasive. (Expected values are 1.39 Å for the



(20)

benzene ring, 1.48 Å for N(sp^2)—C(sp^3), 1.54 Å for C(sp^3)—C(sp^3) and the mean values over many different complexes for the chelate ring [69]. This latter standard is, of course, open to some objection if each compound has a different electronic distribution. The effect of such structures is to increase the electron density at C(4) on the benzene ring and it is therefore significant that even though the Cu—O bond rotation is 0° and distortions due to a changing oxygen hybridisation are negligible, the aromatic ring has a slight chair conformation. Atoms C(1) and C(4) are respectively −0.086 and +0.084 Å from a plane through C(2), C(3), C(5) and C(6). (The largest deviation of the defining atoms is 0.002 Å.) The picture, then, is one in which the charge density on the donor atoms is dispersed through the system or, in other terms, one in which the nitrogen atom is π-bonded to its substituent as well as within the ring.

A contrasting ground state appears in Cu(N-Et,salim)$_2$ where four measurements support canonical forms (21) and (22). An extreme example [46] is



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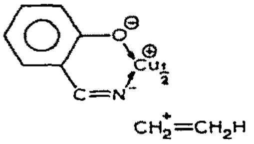
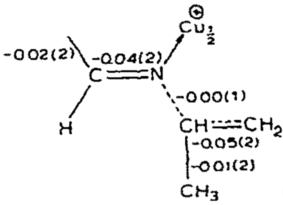


(22)

quoted on the figure, other values are given in Table 1. It has already been noted that the substituent which most shows this effect also undergoes C—C bond rotation towards the elipsed conformation, a result which adds some realism to the "non-bond" structure (22).

It could be concluded that the i-propyl and t-butyl groups should show a similar effect and one such substituent in Cu(N-i-propyl,salim)$_2$ [112] (23),



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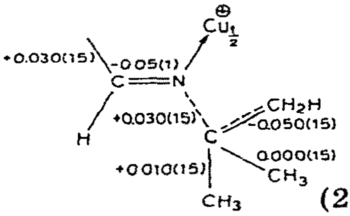
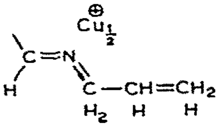


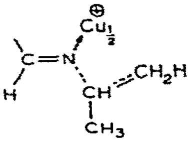
(24)

and Cu(N-t-butyl,salim)$_2$ [113] (24), is found. We again picture the substituent as being a partial carbonium ion stabilised by hyperconjugation. Electron transfer to the nitrogen and a consequent pseudo-tetrahedral stereochemistry is the result. A pictorial explanation can be given in terms of double-bonding at the nitrogen and its ability to interact with the metal atom. Bearing in mind that the terminal methyl group is likely to be involved in the hyperconjugation, the fact that Cu(N-n-propyl,salim)$_2$ has weaker bonding with copper can be rationalised by formal structures similar to (25), and contrasted with Cu(N-i-propyl,



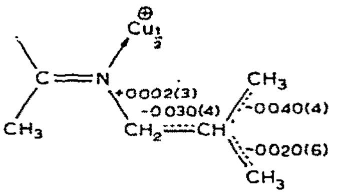
(25)

salim)$_2$ which has the structure (26).



(26)

A similar situation holds with *o*-hydroxyacetophenoneiminato complexes where appreciable bond shortening in *N*-substituents is again apparent. These are shown for Cu(*N*-*i*-butyl,hapim)$_2$ [90] (27), and Cu(*N*-2-phenylethyl, hapim)$_2$ [69] (28). The aromatic to carbon length in the latter is "expected" at 1.51 Å [52]. The former compound is planar, although highly stepped, the latter with a partially stabilised phenylethyl carbonium ion, is pseudo-tetrahedral.



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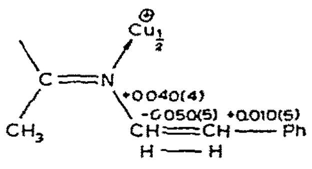
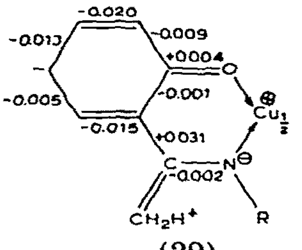
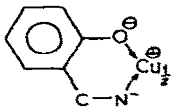


(28)

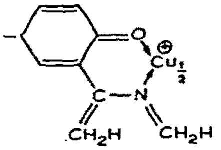
It is appropriate at this point to also consider the methyl substituent on C(7). As mentioned earlier it has an electronic effect of its own, especially on the donors, although that at nitrogen may be in conflict with substituents thereon. It is not clear from the C(7)—C(methyl) bond length, which has a mean value of 1.511 Å (spread = 0.024 Å) over eleven measurements [69], whether this action is inductive or hyperconjugative but it is perhaps significant that the mean value of the C(1)—C(7) bond at 1.461 Å in the *o*-hydroxyacetophenoneiminato complexes is 0.031 Å longer than the corresponding distance in the salicylaldimines [69] and that all the benzene ring bonds are shorter. These differences are shown diagrammatically in (29) and suggest the relative importance in the former system of the canonical structures (29) and (30). It is interesting that when R = methyl the three measurements of N—C(methyl) are 1.471(5), 1.472(6) and 1.464(6) perhaps suggesting some small contribution from structures (31) and (32) as well as from those based on (6)



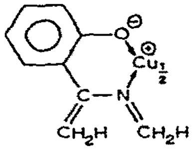
(29)



(30)

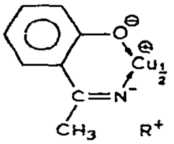


(31)



(32)

and (7). When R = *i*-butyl this length is 1.482(3) Å [69] but with partial carbonium ion formation (R = 2-phenylethyl) it is, as already noted on (28), 0.040(4) Å greater than the "expected" value. An important contributor in this instance is therefore also (33). One consequence of this view of methyl

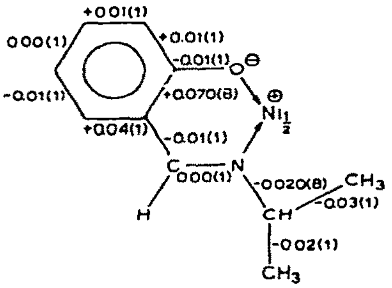


(33)

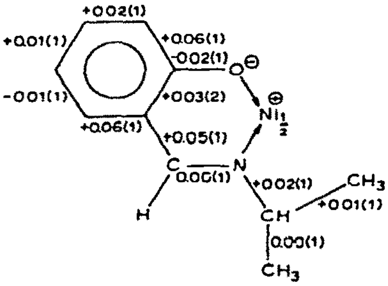
substitution at C(7), which will also be aided by increased density at nitrogen from appropriate R-groups, is that electron loading occurs in the benzene ring. It is therefore encouraging to note that this ring has a small boat conformation in nearly every *o*-hydroxyacetophenoneiminato complex [71]. We thus conclude that the methyl group at C(7) has an electronic effect on the donors and on the aromatic group and that the most obvious explanation involves the processes of hyperconjugation.

We turn to complexes of nickel(II) for final comments. The compound Ni(*N*-*i*-propyl,salim)$_2$ [41] and those of its 3-ethyl [42] and 3-methyl [43] substituents were used to introduce the problems inherent in the steric approach to stereochemistry when it was observed that the latter was planar in the solid state. It is difficult to conceive of this change in other than electronic terms, particularly when it is noted that not only the type of substituent but also its position on the benzene ring appears to be critical [28,29,31,122]. It is therefore again appropriate to expect evidence for electronic shifts in the reported bond geometries.

At first sight the parent complex, Ni(*N*-*i*-propyl,salim)$_2$ is disappointing in this respect since it shows little evidence for the partial carbonium ion formation characteristic of α-branched copper(II) analogues. In fact, differences from expected bond lengths suggest that one *i*-propyl group is essentially unchanged whereas the other is possibly hyperconjugated in a manner thought previously to mitigate against high charge density on the nitrogen. The complex is tetrahedral, θ = 81.3°, the two ligands deviating from "normal" as shown in (34) and (35). These observations suggest strongly that steric inter-



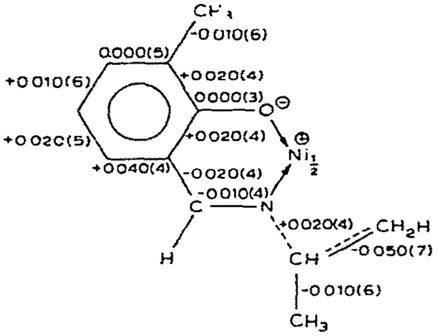
(34)



(35)

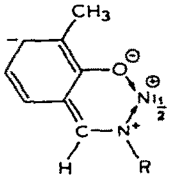
actions are of importance in dictating the tetrahedral stereochemistry of this complex.

On the other hand the substitution of a methyl group at C(3) brings clear changes. The molecule is now centrosymmetric and stepped ($\sigma = 0.298$ Å) with some evidence of partial carbonium ion formation at the *i*-propyl groups as indicated by (36).



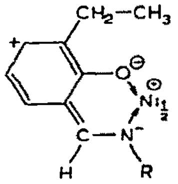
(36)

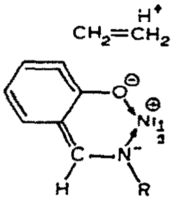
In electron density terms this implies a reduction at the nitrogen donors which then enhances carbonium ion formation. We visualise this as resulting from the slight stabilisation of bonding orbitals at C(2), C(4) and C(6) with respect to orbitals at C(1), C(3) and C(5). This is a consequential effect of the methyl group at C(3) and one which aids the importance of charge-spreading structures similar to (37).

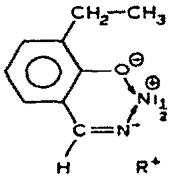


(37)

The complex with the 3-ethyl substituent will have the opposite polarities [77—79] if the ethyl groups are hyperconjugated (the evidence is discussed below) and partially positive. A higher charge accumulation on nitrogen is therefore likely because of the significance of (38)—(40).

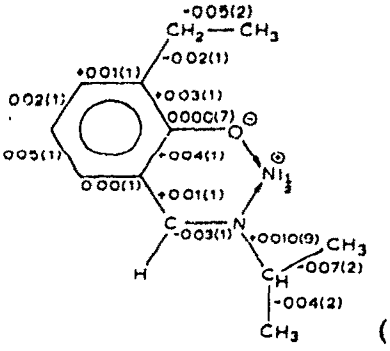




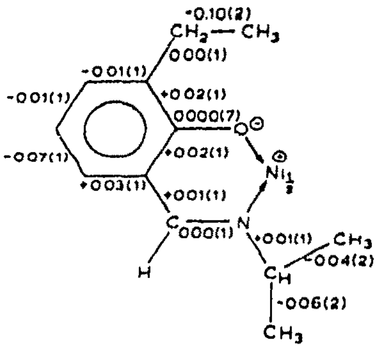


(38) (39) (40)

The evidence for hyperconjugation in at least one ethyl group seems substantial at first sight as deviations from expected bond lengths, (41) and (42), show.



(41)



(42)

The exceptionally short bond in one substituent (atoms C(1) and C(2) of ref. 42) is noteworthy, although explained by the authors as being due to thermal motion. It is always difficult to assess this effect quantitatively however, since possible adjustments will often be large enough to account for observed shortening, particularly when terminal atoms are involved. Thus in the present instance the assumption of riding motion brings the length to 1.467 Å whereas independent motion brings it to 1.61 Å. It is our thesis that the decreases are real, at least partly, since not only is one ethyl group quite close to planarity with benzene, as expected if conjugation were appreciable, with its bond angle C(3)—C(11)—C(12)* at 116.9(9)°, but one of its hydrogen atoms, H(112), which has been located experimentally and subject to positional refinement, is so placed as to make the C(11)—H(112) bond almost perpendicular to the aromatic ring. This is at the expense of some distortion at C(11) since C(3)—C(11)—H(112) is 94°, C(12)—C(11)—H(112) is 118°, C(3)—C(11)—H(111) is 125°, C(12)—C(11)—H(111) is 89° and H(111)—C(11)—H(112) is 116°, and gives the strong impression that in this substituent hyperconjugation of the "classical" σ—π type is present. The other ethyl group is turned perpendicularly to the ring, also a conformation favourable to hyperconjugation [53,54].

One last feature of these three nickel complexes needs comment. It is probably an important one in dictating the stereochemistry and concerns the position of the hydrogen atom on the α-carbon of the *i*-propyl group. Although the C—H bond is approximately coplanar with the N—C(7) bond of its associated ligand in all the compounds H and C(7) are *cis*-disposed in the tetrahedral complexes but *trans* in the planar complex. This means that in the latter instance the hydrogen points towards the oxygen atom of the neighbouring ligand (O ··· H = 2.20 Å) and, because of the postulated positivity of the *i*-propyl group, is assumed to form a hydrogen bond which helps to stabilise the planar conformation. It can be demonstrated that the reverse

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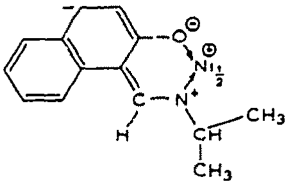
* Numbering scheme of reference 42.

orientation is not likely in a planar molecule because of steric clashing between the *i*-propyl methyl groups and the benzene substituent on C(3) but whether or not the orientation stabilises a planar complex or whether the planar complex forces the orientation is not a question which structural data can readily answer. In either event the electronic effect of the 3-methyl substituent differs from that of its 3-ethyl or the 3-hydrogen analogues in promoting the centrosymmetric structure.

It is possible to extend this simple view of the effect of aromatic substituents to further complexes of the Ni(*N*-*i*-propyl,X-salim)$_2$ type. Table VI of ref. 4 lists thirteen examples, together with their solid state stereochemistries as determined by magnetic moment measurements. All those which favour the same type of charge distributions as outlined above for the 3-methyl complex, namely 5-methyl, 5-*n*-propyl, 5-phenyl and 5-chloro are diamagnetic and planar, whereas the 3-*i*-propyl, 3-*t*-butyl, 4-methyl and 5-ethyl substituents which favour the alternative polarities give complexes which are paramagnetic and presumably tetrahedral. The 3,4- and 5,6-benzo derivatives can be similarly treated by recalling that the α-position of naphthalene has the larger "free valence" and that the 5,6-benzo substituted complex is therefore the one [43], which will disperse the negative charge on the nitrogen. This complex is planar as predicted, the other naphthalene derivative (the 3,4-benzo compound) is tetrahedral. This faithful reflection of the substitution pattern in the crystalline structure lends some support to our thesis and does suggest that the electronic state of a molecule is important in determining which of the planar or tetrahedral configurational isomers known to exist in solution is to be "frozen" in the solid. Again the close relationship between structure and electronics is hinted at. There is one anomaly in the above list in that the 4,6-dimethyl derivative should favour the tetrahedral geometry but is diamagnetic although we note in passing that Berliner [123] has drawn attention to a kinetic situation in which a substituent which enhances reactivity reduces the reaction rate considerably below the expected value when it is duplicated in a position which might be supposed to increase its efficacy.



(43)

We conclude by stressing that our emphasis on an electronic explanation of stereochemistry does not imply that we believe steric effects to be unimportant. Clearly the two will act in concert in many instances — the adoption of a pseudo-tetrahedral geometry when R is an α-branched alkyl group is an example. It may not be too fanciful to suppose that there is a tendency for the overall electronic distribution to match the structure as well as for the structure to match the electronics. Thus, whereas all polymorphic forms of Cu(*N*-Et, salim)$_2$ contain pseudo-tetrahedral molecules, with at least one ethyl group showing marked bond shortening, the corresponding nickel(II) complex is planar and the substituents have "normal" N—C (1.49(2) Å, and C—C (1.55(2) Å) bond lengths. On the other hand the complex Ni(*N*-*i*-propyl, 3-methylsalim)$_2$, although planar, does show evidence of electronic shifts in the *i*-propyl group and it is more likely that it is the change in metal and consequent changes in the electronic interactions with the donor atoms which tips the balance in favour of the hyperconjugative effects in Cu(*N*-Et,salim)$_2$. For the moment the distinction between these two complexes serves to make the point that although it is not erudite to declare that structural data reveal the molecule as it has accommodated to all internal and external forces acting upon it, it is nevertheless very easy to focus too exclusively on just one factor.

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