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STRUCTURAL CHARACTERIZATION OF SOME 2-(DIMETHYLAMINO)-METHYL-SUBSTITUTED PHENYLCOPPER COMPOUNDS R_4Cu_4 *

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Summary

2-[(Dimethylamino)methyl]phenylcopper and its 5-methyl and 5-methoxy analogues are tetrameric in benzene. 5-Methyl-2-[(dimethylamino)methyl]phenylcopper is tetrameric in the solid state (X-ray structure determination). The bonding in this tetranuclear cluster (Cu—Cu 2.38 Å, multicenter bonded aryl groups) is discussed. NMR spectroscopy provides indications that Cu—N coordination observed in the solid is weak in solution. Mass spectra of 2-[(dimethylamino)methyl]-phenylcopper (R_4Cu_4) and its 5-methyl analogue ($(5\text{-MeR})_4Cu_4$) reveal that the Cu_4 cluster in both compounds has considerable stability. Although the $R_4Cu_4^+$ ions in both spectra are very abundant, the $R_3Cu_4^+$ (even electron species) forms the base peak in the R_nCu_n part of the mass spectra. The occurrence in solution of an intercluster exchange between R_4Cu_4 and $(5\text{-MeR})_4Cu_4$ with formation of the three possible mixed species $R(5\text{-MeR})_3Cu_4$, $R_2(5\text{-MeR})_2Cu_4$ and $R_3(5\text{-MeR})Cu_4$ was confirmed by the mass spectra, which show five patterns in the parent peak region separated by 14 mass units.

Introduction

Until recently, the structure of only a few organocopper compounds had been unambiguously established. X-ray structural determinations are limited to a few acetylenic copper compounds and complexes [2] and two complexes of *pentahapto*-cyclopentadienylcopper(I) with triphenylphosphine [3] and triethylphosphine [4]. Very recently, the solid state structure of Me_3SiCH_2Cu has been reported [5]. The structures of simple alkyl- and aryl-copper compounds are unknown. The general insolubility of these compounds, which suggests a polymeric structure, has hampered the application of physico-chemical techniques. Green [6] envisaged three possible structures for organocopper com-

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* Part XI of the series of papers dealing with Group IB organometallic chemistry. For Part X see ref. 1.

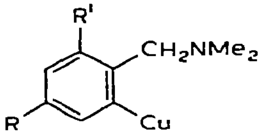
pounds. For alkylcopper compounds, he proposed a metal cluster structure with bridging alkyl groups or, less probably, ionic structures of the type $Cu^+(CuR_2)^-$, while for phenylcopper the possibility of π-bonding by the phenyl nucleus was suggested. Indications of a metal cluster structure were found by Cairncross et al. [7] for octameric *m*-(trifluoromethyl)phenylcopper(I), but this was not confirmed by an X-ray structural determination.

The favourable physical properties (good solubility, and relatively high thermal stability) of the pure 2-(dimethylamino)methyl-substituted arylcopper compounds [1] have made possible the characterization of their structure by physico-chemical techniques*.

Results and discussion

Molecular weights

Cryometric and ebulliometric molecular weight determinations indicate that the 2-[(dimethylamino)methyl]phenylcopper compounds I-V exist in benzene solution as tetrameric species R_4Cu_4.



		Mol. wt. found (calcd.)
I,	R = R' = H	792 (197.5) n = 4.0
II,	R = Me, R' = H	863 (211.5) n = 4.1
III,	R = OMe, R' = H	921 (227.8) n = 4.0
IV,	R = Cl, R' = H	See text
V,	R = H, R' = Cl	See text

The molecular weight of the 5-chloro-derivative, IV, could not be determined because of insufficient solubility at ± 5° and slow decomposition in boiling benzene. For the 3-chloro-derivative, V, values for n of about 3.6 were found; the molecular weight is concentration independent; no impurities were detected. Since the molecular weights of I-III appeared to be concentration independent, these tetramers R_4Cu_4 must be of considerable stability.

Structure and bonding

On the basis of their solubilities, I and II were singled out for further study. Crystallization (see Experimental) of 5-methyl-2-[(dimethylamino)methyl]-phenylcopper (II) from benzene afforded single crystals suitable for X-ray analysis. The structure determination has been carried out by Prof. R. Mason and his co-workers at the University of Sussex, England. The overall structure of II is shown in Fig. 1.

Figure 1 shows that the organocopper compound II is also tetranuclear in the solid. The main features of this structure are:

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* A preliminary account of the X-ray structure determination of 5-methyl-2-[(dimethylamino)methyl]-phenylcopper tetramer has appeared [8].

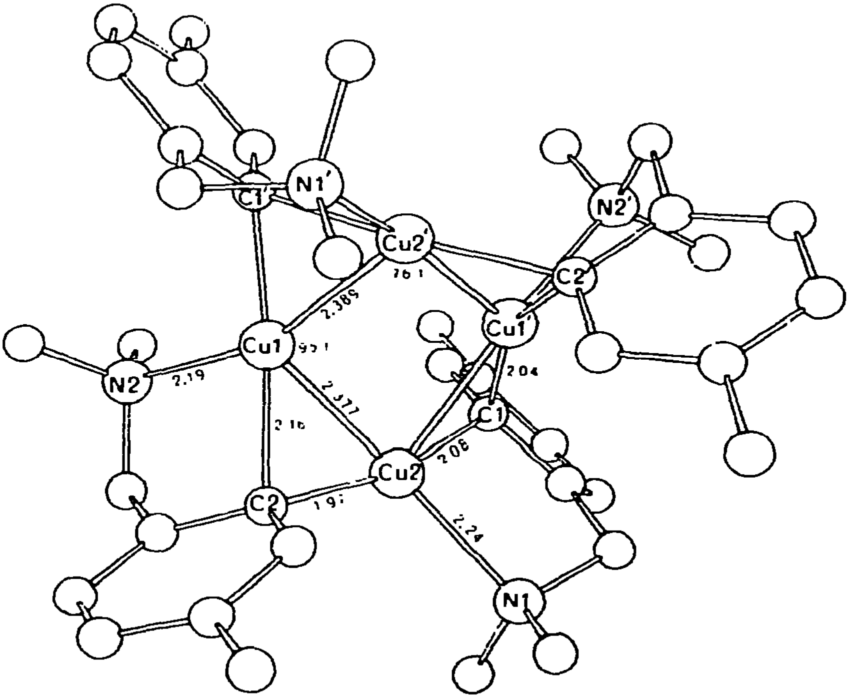

Fig. 1. Structure of 5-methyl-2-[(dimethylamino)methyl] phenylcopper (II). (Crystals are monoclinic with *a* 18.02; *b* 11.35; *c* 19.58 Å; *β* 97.6°; space group *C*2/*c*, *Z* 4.)

1. The Cu—N distances of 2.21 Å (mean) as well as the observed stereochemistry around copper indicate that Cu—N coordination occurs.
2. The four copper atoms are positioned in a butterfly arrangement intermediate between a square planar and a tetrahedral situation. The Cu—Cu distances, which average 2.38 Å, are very short. In copper metal for example the Cu—Cu distance is 2.56 Å.
3. The most remarkable feature is the presence of bridging phenyl groups. The bonds from the aryl ligands to the respective copper atoms are either almost symmetric, 2.04 and 2.08 Å, or asymmetric, 2.16 and 1.97 Å (e.s.d.'s in the Cu—C bond average 0.015 Å).

Bridging phenyl groups have precedents in arylaluminium dimers [9] and in a few osmium trinuclear clusters [10]. The phenyl ligands bridging the metals in the Os, Al and Cu compounds have their plane orientated almost perpendicular to the metal—metal axis.

As for the Cu—Cu bonding, application of the valence bond description shows that a closed shell configuration for the copper atoms is achieved if each copper atom is bonded to its nearest neighbours by a bond order of two. Such metal—metal bonding would imply extensive promotions of *d* electrons to *s* and *p* levels, which is unlikely on promotion energy considerations*.

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[*] Promotion energy of Cu^+: $d^{10} \rightarrow d^9s^1$ 2.72 eV and $d^{10} \rightarrow d^9p^1$ 8.25 eV, see ref. 11.

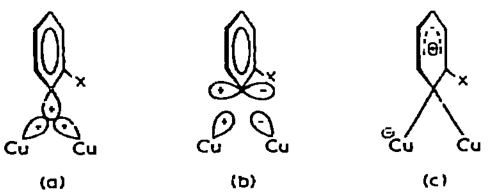

Fig. 2. 3-Center bonding in a C_{bridge} Cu_2 unit; *a*, C_{bridge}-orbital symmetric, bridge orbitals are bonding with respect to the copper atoms; *b*, C_{bridge}-orbital antisymmetric, bridge orbitals are antibonding with respect to the copper atoms; *c*, possible resonance structure if *b* also contributes to the bonding.

In the absence of metal—metal bonding*, the copper atoms in the R_4Cu_4 compound have a distorted trigonal stereochemistry. As discussed by Mason and Mingos [13], the arylcopper bonding can then be described in terms of a localized three center — two electron bond resulting from overlap of sp^2 hybrid orbitals (one on each of the two Cu atoms and one on the C_{bridge} atom of the phenyl group). In this electron-deficient bond the bridge orbitals are bonding with respect to the copper atoms. When other bonding interactions are absent, only this bridge-molecular orbital will be filled and can thus account for the short Cu—Cu distance (Fig. 2a).

However, two other interactions between the ligand and the copper atoms may operate; (*i*) donation of electron density of the π system of the aryl ligand to the bridge bond and (*ii*), back donation from filled metal orbitals of copper to empty $\pi^{\star}$ orbitals of the aryl ligand.

The former interaction (*i*) will result in an increase of the copper—copper separation, because an overlap** of a *p* type orbital of C_{bridge} will involve copper orbitals which are anti-bonding with respect to each other*** (see Fig. 2b). This release of π-electron density from the ligand to the bridged bond will result in a contribution of the resonance structure depicted in Fig. 2c. In consequence, this contribution will influence the intramolecular bond lengths as well as bond angles of the aromatic ring. In view of the very short Cu—Cu distance found in the R_4Cu_4 compound as well as the absence of distortions in the aryl rings, interactions of this type are probably not important.

The second interaction (*ii*) seems to provide a rationalization of the observed higher thermal stability of the 2-(dimethylamino)methyl-substituted phenylcopper compounds compared with phenylcopper☆. Back donation from copper to the aryl ligand enhances the strength of the copper—aryl bond, thus increasing the kinetic stability of the compound by increasing the energy necessary for dissociation of this bond. The degree of back donation will be determined by the electron acceptor properties of the surrounding ligands and by the effective nuclear charge on the copper atom.

The foregoing discussion, which has been restricted to a description of

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* The Raman spectrum of I lacks strong absorptions in the region where metal—metal vibrations are expected [12].

** Such an overlap will be maximal when the phenyl ring is placed perpendicular to the metal—metal vector.

*** Examples in Cu^I-organic chemistry where such MO's are occupied by 2 electrons are: $Cu_2[SC(NCH_3H)_2]_6^{2+}$, Cu—Cu 2.828 Å, Cu—S—Cu′ 72.3° [14] and Diphos · $CuPPh_2$, Cu—Cu 3.34 Å, Cu—P—Cu′ 89.70° [15].

☆ Moreover, back donation of this type will reduce the possibility of non-bonding interactions between the neighbouring copper atoms. The observed short Cu—Cu distance is in line with this view.

the bonding in an isolated $C_{bridge}Cu_2$-unit, is an oversimplification with regard to the total bonding in the R_4Cu_4 compound; each copper atom takes part in two electron-deficient bonds and also in one σ-type bond with the NMe_2 ligand. Such a Cu—N coordination decreases the effective nuclear charge on copper thereby causing an increase of the donor capacity of the Cu^I atom which results in an enhanced back bonding. This interaction, which strengthens the copper—aryl bond, distinguishes the 2-CH_2NMe_2 substituted phenylcopper compounds from the parent phenylcoppers.

In this connection it is of interest that fluoro-substituted arylcopper compounds display high thermal stability. Here enhanced back donation brought about by the better electron acceptor properties [16] of the fluoro-substituted aryl groups as compared with the phenyl group, may be operative.

Mass spectrometry

The mass spectra of I and II have been recorded. In Table 1 the copper-containing ions $R_nCu_n^+$ (calculated on ^{63}Cu) in both spectra are compiled.

These data lead to the following conclusions:

i. Substitution at the 5-site of 2-[(dimethylamino)methyl]phenylcopper does not influence the fragmentation pattern.

ii. No other fragments at higher mass units than that of the tetrameric species are found.

iii. The Cu_4-cluster in both compounds has a considerable stability. This is apparent from the great relative abundance of the Cu_4-containing species. In this respect it is of interest that the ligand R can fragment while the Cu_4-skeleton

TABLE 1

MASS SPECTRAL DATA FOR SOME ARYLCOPPER COMPOUNDS $R_4{}^{63}Cu_4$ [a]

Ion	Relative abundance (%) [b]	
	I, R = 2-$Me_2NCH_2C_6H_4$	II, R = 5-Me-2-$Me_2NCH_2C_6H_3$
R_4Cu_4	59 (788)	54 (844)
R_3Cu_4	100 (654)	100 (696)
$R_3Cu_4 - CH_4$	15 (638)	15 (680)
$R_3Cu_4 - C_2H_6N$	3 (610)	2 (652)
$R_3Cu_4 - C_3H_9N$	5 (595)	4 (637)
R_2Cu_4H	6 (521)	4 (549)
R_3Cu_3	6 (591)	7 (633)
R_2Cu_3	26 (457)	22 (485)
$R_2Cu_3 - CH_4$	4 (441)	3 (469)
$R_2Cu_3 - C_2H_6N$	4 (413)	2 (441)
R_2Cu_2	16 (394)	12 (422)
$R_2Cu_2 - C_2H_6N$		5 (378)
RCu_2	16 (260)	
R_2Cu	6 (331)	7.4 (359)
$RCu - H$	20 (196)	19 (210)

[a] Several patterns in the region below *m/e* 413 (I) and 441 (II) were difficult to interpret. However, their relative intensity [calculated on $I(R_3Cu_4^+)$] does not exceed 10%. [b] *m/e* value between brackets.

remains intact. A similar fragmentation of R occurs in Cu_3- and Cu_2-containing species.

iv. Although the $R_4Cu_4^+$ ions in both spectra are very abundant (about 50%) the $R_3Cu_4^+$ species forms the base peak in the R_nCu_n part of the mass spectrum. Moreover, no ions were detected in the range between *m/e* ($R_4Cu_4^+$) and *m/e* ($R_3Cu_4^+$), which suggests that the following fragmentation occurs exclusively:

$$R_4Cu_4 \xrightarrow{+e;\,-2e} R_4Cu_4^{\cdot +} \xrightarrow{-R^{\cdot}} R_3Cu_4^+$$

These observations point to a higher stability of the $R_3Cu_4^+$ species (even-electron system) as compared with that of the parent ion $R_4Cu_4^{\cdot +}$ (odd-electron system). In other words: removal of one electron from the R_4Cu_4 cluster reduces the bonding between R and Cu. This suggests that in spite of copper having *d* electrons, a valence-electron (from the bridge-bond MO) is removed.

The high abundance of ions of the type $R_{n-1}Cu_n^+$ (even-electron) may be a general feature in the mass spectra of polynuclear compounds containing bridging aryl or alkyl groups. Examples are: $R_2Cu_3^+$ in the spectrum of I and II and of $(C_6F_5Cu)_4$ [17]; $R_3Cu_4^+$ ($R = C_6F_5$), but also $RCu_4F_2^+$ ($R = o$-$CF_3C_6H_4$) [17] and $R_2Cu_4H^+$ in I and II; in the spectra of ethyllithium even-electron $Et_5Li_6^+$ and $Et_3Li_4^+$ species [18] are observed.

v. Worthy of note are the species found at *m/e* 331 (I) and *m/e* 359 (II), which have been assigned to the R_2Cu^+ ion. Obviously in this ion the copper atom has a formal oxidation state of three (even-electron system).

A striking difference with the spectra of $(C_6F_5Cu)_4$ [*] and (o-$CF_3C_6H_4Cu)_4$ is the absence of fragment ions R—R in the spectra of I and II. Most abundant species of the C, H, and N-containing fragments in the spectra I and II are RH^+, R^+ and $R - 2H^+$ [**].

In addition to information about the degree of association in the solid and the stability of the Cu_n skeleton, mass spectrometry can also provide information about the occurrence of interaggregate exchange reactions of organocopper compounds. For example, when the 2-[(dimethylamino)methyl]phenylcopper tetramer I and its 5-methyl derivative II were dissolved in benzene in a 1/1 molar ratio, a mass spectrum of the solution recorded after 24 h showed five patterns separated by 14 mass units ranging from 844 [$(5\text{-MeR})_4{}^{63}Cu_4$] to 788 ($R_4{}^{63}Cu_4$). This observation indicates that intercluster exchange between $(5\text{-MeR})_4Cu_4$ and R_4Cu_4 has taken place[***] with the formation of the three possible mixed species $(5\text{-MeR})R_3Cu_4$, $(5\text{-MeR})_2R_2Cu_4$, and $(5\text{-MeR})_3RCu_4$ with *m/e* ($^{63}Cu_4$) of 804, 818 and 832, respectively. Recently, a number of polynuclear mixed-organocopper compounds of the type $R_4R'_2Cu_6$ have been isolated and characterized [15].

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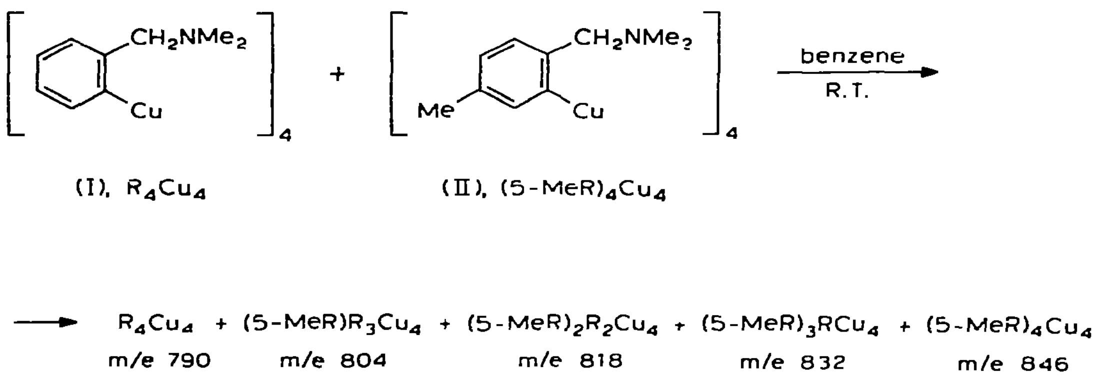
[*] Decafluorobiphenyl is an abundant species in the spectrum of $(C_6F_5Cu)_4$. It is not clear whether this species results from fragmentation or arises from thermal decomposition [17].

[**] Since the mass spectra are recorded at 150° it is believed that these ions result from fragmentation. It is interesting, however, that the observation of these ions parallels the thermal decomposition pattern of solid I at 210°. RH is the major product whereas R—R is a minor product [19].

[***] It seems unlikely that this exchange occurs in the gas phase in view of the low pressures (about 10^{-7} mm) used.



(m/e values of the $(5\text{-MeR})_{4-n}R_n{}^{63}Cu_3{}^{65}Cu$ ions)

^{1}H NMR spectroscopy

The ^{1}H NMR spectra of the tetrameric 2-[(dimethylamino)methyl]phenyl-copper compounds I-V show the expected resonance patterns as well as correct peak area ratios. As an example the spectrum of I in benzene-d_6 is shown in Fig. 3, while the chemical shift data for the other compounds are compiled in Table 2. The assignment of the respective multiplets in the aromatic region is based upon their multiplicity as well as on their relative peak areas.

The NMR spectra are remarkably simple. They give no positive information on the arrangement of the aryl ligands around the Cu_4 cluster or the interaction of the (dimethylamino)methyl ligand with copper*. However, it is assumed that the main structural features for the compounds I-V (multicenter bonded aryl groups; tetranuclear Cu_4 cluster) are retained in solution. This view seems justified, (*i*) by the observation that both in the solid and in solution the compounds are tetranuclear and (*ii*) by the proof [20, 21] for multicenter bonded aryl groups in the related $R_4Cu_2Li_2$ and $R_4Ag_2Li_2$ compounds in solution. As follows from Table 2 and Fig. 3, the benzylic and the *N*-methyl protons appear as singlets. These singlets are shifted upfield (by 0.09-0.27 ppm; see Table 3) with respect to those of the parent arenes. An interpretation of this upfield shift in terms of absence of Cu—N coordination is doubtful because in the NMR spectra of the 2-[(dimethylamino)methyl]phenyl-palladium [22], -platinum [22], -cobalt [23], -copperlithium and -lithium compounds both upfield (Co, CuLi and Li) as well as downfield shifts (Pd and Pt) for the NCH_3 and NCH_2 proton resonances have been observed. For all these compounds M—N coordination is assumed to take place. In contrast with the Co, CuLi and Li compounds the NMR spectra of the organocopper derivatives I and V (3-Cl) are temperature independent. Also at low temperatures (—80°) the CH_2 and CH_3 protons appear as singlets. It would not seem unreasonable to assume that in solution the "hard"

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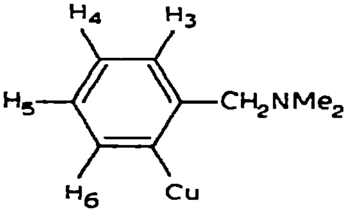
* In contrast, the ^{1}H and ^{13}C NMR spectra of the organo-lithium, -copperlithium [20] and -silver-lithium [21] compounds provide direct information about their structure (bridging aryl groups and Li—N coordination).

TABLE 2

^1H NMR DATA [a] FOR THE 2-[(DIMETHYLAMINO)METHYL]PHENYLCOPPER COMPOUNDS I-V

Compound		δ (ppm)					
		NCH_3	NCH_2	R	H_6	H_3	$H_{4,5}$
							
I		1.90 (s)	3.02 (s)		8.45 (d of d) $J_{5,6} \approx 6$ Hz $J_{4,6} \approx 2$ Hz	6.80 (d of d) $J_{3,4}$ 7 Hz $J_{3,5} \approx 1.5$ Hz	7.0 - 7.35 (m)
II	R = 5-Me	1.98 (s)	3.06 (s)	2.44 (s)	8.37 (d) $J_{4,6} \approx 1$ Hz [b]	6.78 (d) $J_{3,4} \approx 8$ Hz [b]	≈ 6.95 (H_4, d of d)
III	R = 5-OMe	1.99 (s)	3.04 (s)	3.64 (s)	8.20 (d) $J_{4,6} \approx 2.5$ Hz	6.76 (d) $J_{3,4} \approx 8$ Hz	6.58 (H_4, d of d)
IV	R = 5-Cl	1.86 (s)	2.80 (s)		8.43 (d) $J_{4,6} \approx 2.5$ Hz	6.50 (d) $J_{3,4}$ 8 Hz	7.02 (H_4, d of d)
V	R = 3-Cl	1.81 (s)	3.37 (s)		8.10 (d of d) $J_{5,6} \approx 6.5$ Hz $J_{4,6} \approx 1.5$ Hz		6.85 - 7.1 (m)

[a] In benzene-d_6 at ambient temperature; TMS internal standard. [b] Values taken from the spectra recorded at 90°.

CH_2NMe_2-ligand will only weakly coordinate with the "soft" copper(I) atom, as predicted by the HSAB principle.

In Table 3 $\Delta\delta$ ($= \delta_{RH} - \delta_{RCu}$) for the respective protons are given. This table shows that large downfield shifts (about 1.2 to 1.4 ppm) are found for the protons H_6 *ortho* to the C(1)—Cu bond, whereas the protons H_3 *ortho* to the CH_2NMe_2-ligand are shifted slightly upfield (0.3-0.6 ppm). The influence of the solvent on δ is small (about 0.2 ppm) as is apparent from the spectra of I recorded in C_6D_6, C_5D_5N and c-C_6H_{12}. The origin of the large $\Delta\delta$ values for the protons H_3 and H_6 has been discussed for aryl-copper [24], -lithium [25] and -magnesium halide [25] compounds in terms of the magnetic anisotropy of C(1)*.

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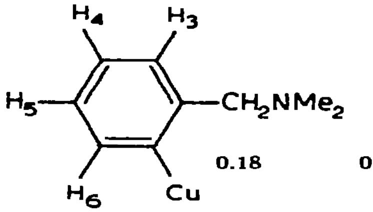
* The large downfield shifts for C(1) and to a lesser extent of C(2) and C(6) in the ^{13}C NMR spectra [20] of R_4Cu_4 (I; R = 2-$Me_2NCH_2C_6H_4$) and the corresponding copperlithium $R_4Cu_2Li_2$ and lithium (5-MeR)$_4$Li$_4$ derivatives are in accord with this view; about 25 {15} for C(1) {C(2, 6)} in R_4Cu_4, 40 {16-20} in $R_4Cu_2Li_2$ and 47 {10-12} ppm in (5-MeR)$_4$Li$_4$ relative to benzene.

TABLE 3

INFLUENCE ON δ OF THE INTRODUCTION OF A COPPER ATOM *ortho* TO THE (DIMETHYLAMINO)-METHYL GROUP IN DIMETHYLBENZYLAMINES

RCu compound	$\Delta(\delta_{arene}-\delta_{RCu})^a$ (ppm)					
	NCH_3	NCH_2	H_6	H_3	$H_{4,5}$	5-Substituent
	0.18	0.14	−1.30	0.35	≈ 0	
5-Me	0.10	0.18	−1.38	0.46	0.04	Me, −0.33
5-OMe	0.09	0.18	−1.43	0.46	0.19	MeO, −0.31
5-Cl	0.12	0.25	−1.44	0.60	≈ 0	
3-Cl	0.27	0.05	≈ −1.16 ± 0.10[b]	[c]		

[a] Arene = *N,N*-dimethylbenzylamine or its *para*- or *ortho*-substituted derivatives; RCu = corresponding organocopper compound. [b] Estimated value. [c] Not determined since the H_4 and H_5 multiplets are partly matching each other.

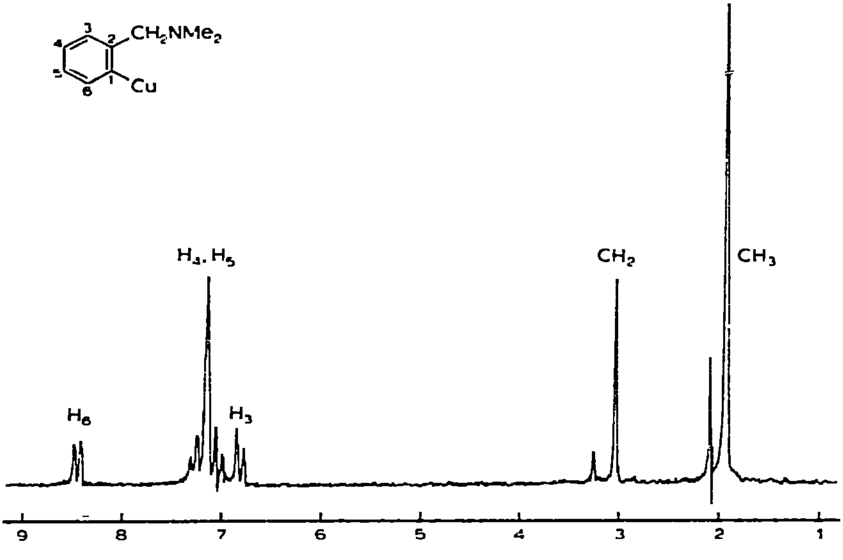


Fig. 3. ^1H NMR spectrum (δ ppm) of 2-[(dimethylamino)methyl]phenylcopper tetramer in benzene-d_6.

Experimental

General

The syntheses of the respective 2-[(dimethylamino)methyl]-substituted phenylcopper compounds (I)-(V) have been reported [1]. ^1H NMR spectra which were run by Miss L. Veldstra, were recorded on a Varian Associates

HA-100 NMR spectrometer. The mass spectra were recorded on an AEI Ms 9 mass spectrometer (70 eV, ionization chamber temp. 150-170°).

Preparation of single crystals of 5-methyl-2-[(dimethylamino)methyl]phenylcopper (II)

An ampoule was charged with about 0.2 g of (II). At 60° benzene was added until a saturated solution was obtained. The ampoule was sealed off, placed in a thermostatted waterbath, and then gradually cooled from 60 to 20° at a rate of 2°/24 h.

Interaggregate exchange reaction between (I) and (II)

A mixture of equimolar amounts (0.18 mmol) of (I) and (II) was dissolved in benzene (1 ml). The resulting solution was stirred at room temperature for 24 h. A sample of this solution was transferred to the direct-insertion probe of the mass spectrometer.

Acknowledgements

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