Tetranuclear Amido Complexes of Copper(I): A Synthetic and Structural Study[‡]

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Reaction of copper(I) halides with lithium amides leads to the formation of thermally stable tetrameric amido derivatives of copper(I), $[\{Cu(NRR')\}_4]$ [NRR′ = NMe_2, (**1**); $\overline{N(CH_2)_3CH_2}$, (**2**); $MeNCH_2CH_2NMe_2$, (**3**); $N(CH_2CH_2NEt_2)_2$, (**4**)]. Compounds (**1**)—(**4**) are tetrameric both in the solid state (*X*-ray analysis) and in solution (cryoscopy in benzene). Copper(I) remains consistently two-co-ordinate without bonding the free amino groups in complexes (**3**) and (**4**). Copper(I) amido complexes did not react with unidentate ligands like PPh_3 and NEt_3, but complex (**2**) undergoes a facile transformation with bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe). The amido group abstracts a proton from dppm forming the known trimeric compound $[Cu_3(PPh_2CHPPh_2)_3]$ (**5**), while it promotes the cleavage of a P–C bond in dppe, forming $[Cu_2(\mu\text{-}PPh_2)_2(dppe)_2]$ (**6**). The structures of complexes (**1**)—(**3**) have been determined by *X*-ray analysis. They each have an eight-membered ring, Cu_4N_4, which is nearly planar for complexes (**1**) and (**2**), but significantly distorted from planarity for (**3**). The average Cu–N bond distances are very similar: 1.890(5) in (**1**), 1.885(4) in (**2**), 1.913(4) Å in (**3**); the Cu • • • Cu separations are 2.702(2) in (**1**), 2.717(2) in (**2**), and 2.618(2) Å in (**3**). Copper(I) has a nearly linear two-co-ordinate geometry in all the complexes, the N–Cu–N angle being 178.5(2) in (**1**), 177.1(2) in (**2**), and 169.4(2)° in (**3**).

Unlike the situation for many other transition metals, there is a close similarity in terms of stability, structural features, and, to some extent, chemical behaviour among the copper(I) organometallic functionalities Cu–R,[1] Cu–OR,[2,3] and $Cu\text{–}NR_2$ (R = alkyl or aryl).[4,5] This may be the consequence of the similar thermodynamic stability of the Cu–C, Cu–O, and Cu–N bonds, which is a unique property of copper.[6] All these functionalities, which are involved in transformations of organic substrates, are synthesized and used *in situ*. The *in situ* conditions are, normally, those promoting the formation of a cuprate-type derivative, $[CuR_2]^-$, $[Cu(OR)_2]^-$, or $[Cu(NR_2)_2]^-$, which is believed to be the active form in the reaction with organic electrophiles.[1,2] The goal of this work was to provide fundamental information concerning the synthesis, stability, environment, and simple ligand-induced transformations of the $Cu\text{–}NR_2$ unit. The first aspect that has to be considered concerns the forms that copper(I) functionalities display; these are summarized as follows.

Homoleptic Compounds: $(Cu\text{–}R)_n$, $(Cu\text{–}OR)_n$, *and* $(Cu\text{–}NR_2)_n$.—In this form copper(I) is normally two-co-ordinate, with the organic fragment displaying a bridging bonding mode. This structural mode is well known for Cu–R and Cu–OR functionalities and can be exemplified by $[\{Cu(CH_2SiMe_3)\}_4]$,[7] $[\{Cu(C_6H_2Me_3\text{-}2,4,6)\}_5]$,[8] $[\{Cu(OBu^t)\}_4]$,[9] and $[\{Cu(OCHBu^t_2)\}_4]$,[10] all having similar cyclic structures. An *X*-ray structure was recently reported for an amido derivative, $[\{Cu(NEt_2)\}_4]$.[5] In this paper a general synthesis and structural information are reported for this class of compounds.

Compounds of Formula $[CuXL_n]$ (X = R, OR, *or* NR_2).—The organometallic functionality can be stabilized by some ancillary ligands (L). In some complexes the donor atom belongs to the organic residue. Numerous examples of this kind are known for the Cu–R functionalities,[1,2] a few for the Cu–OR group,[3,11] while compounds of formula $[Cu(NR_2)L_n]$ are not very common.[4c,12] As demonstrated by the results reported in this paper, this is due to the reluctance of $Cu\text{–}NR_2$ to add ancillary ligands.

Alkyl-, Alkoxo-, and Amido-cuprate Compounds.—These have the simplified formula $[X\text{–}Cu\text{–}X]^-$ (X = R, OR, or NR_2) and can exist either in the ion-pair or in the ion-separated form. A significant number of cuprate ion pairs are known in copper(I)–alkyl[1,2] and only a few in copper(I)–alkoxo chemistry.[3] Amidocuprates of copper(I) have been reported, though not isolated, and used *in situ*.[13] Among their interesting properties there are the reactions with electrophiles and carbon monoxide, which have been used in the functionalization of organic substrates.[13] This paper describes the synthesis and structural properties of homoleptic amido derivatives $[\{Cu(NR_2)\}_4]$ and their reactions with amine and phosphine ligands.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by

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standard methods. CuCl and CuI were prepared by a published procedure.[14] Lithium amides were prepared by reaction of freshly distilled and dried amines with LiMe, and were isolated as crystalline solids. Infrared spectra were recorded with a Perkin-Elmer 983 spectrophotometer. ^{1}H N.m.r. spectra were recorded using a Bruker 300-MHz instrument.

Preparation of $Li(MeNCH_2CH_2NMe_2)\cdot nEt_2O$.—A diethyl ether solution (200 cm^3) of *NN'N'*-trimethylethylenediamine (20.0 cm^3, 157.4 mmol) was treated with $LiNMe_2$ (157.8 mmol). A little solid was filtered off, and the light yellow solution was evaporated almost to dryness. The residue was dissolved in n-hexane (50 cm^3), from which on cooling at −30 °C $Li(MeNCH_2CH_2NMe_2)\cdot nEt_2O$ crystallized (yield *ca.* 50%). Acid–base titration was used to determine the amido content.

Synthesis of $[\{Cu(NMe_2)\}_4]$ (**1**).—Lithium dimethylamide (13.6 mmol) was added to a suspension obtained by mixing solid CuCl (1.28 g, 13.0 mmol) with a tetrahydrofuran (thf) solution (50 cm^3) of tetrahydrothiophene (tht) (4 cm^3). A light brown solution formed, containing some solid, which was filtered while keeping the solution warm. On cooling at room temperature white crystals of (**1**) formed (yield *ca.* 22%) (Found: C, 22.4; H, 5.90; N, 12.6. $C_8H_{24}Cu_4N_4$ requires C, 22.3; H, 5.60; N, 13.0%). ^{1}H N.m.r. (C_6D_6, 300 MHz): δ 2.83 (s).

Synthesis of $[\{Cu(NC_4H_8)\}_4]$ (**2**).—A thf solution (15 cm^3) of $Li(NC_4H_8)$ (13.5 mmol) was added to a thf suspension (50 cm^3) of CuCl (1.39 g, 14.0 mmol). A little solid was filtered off from the resulting solution, which was partially evaporated, then kept at room temperature for a few hours; after which complex (**2**) crystallized (yield *ca.* 38%) [Found: C, 36.1; H, 5.80; N, 10.1%; *M* (cryoscopy in benzene), 504. $C_{16}H_{32}Cu_4N_4$ requires C, 35.95; H, 6.00; N, 10.5%; *M*, 534]. ^{1}H N.m.r. (C_6D_6, 300 MHz): two multiplets of same intensity at δ 3.25 and 1.52.

Synthesis of $[\{Cu(MeNCH_2CH_2NMe_2)\}_4]$ (**3**).—A thf solution (20 cm^3) of $Li(MeNCH_2CH_2NMe_2)$ (7.40 mmol) was added to a thf suspension (50 cm^3) of CuI (1.39 g, 7.30 mmol). The addition was carried out very slowly, and the suspension became colourless at the end of the addition. The solid was filtered off and the resulting solution, cooled to −30 °C, gave a crystalline light yellow solid (yield *ca.* 63%) [Found: C, 36.6; H, 7.70; N, 16.7%; *M* (cryoscopy in benzene), 628. $C_{20}H_{52}Cu_4N_8$ requires C, 36.45; H, 7.95; N, 17.0%; *M*, 658.9]. ^{1}H N.m.r. (C_6D_6, 300 MHz): δ 1.95 (s, 3 H), 2.32 (s, 6 H), 2.73 (t, 2 H), 2.93 (t, 2 H).

Synthesis of $[\{Cu[N(CH_2CH_2NEt_2)_2]\}_4]$ (**4**).—A thf solution (33 cm^3) of $Li[N(CH_2CH_2NEt_2)_2]$ (6.6 mmol) was slowly added to a thf suspension (50 cm^3) of CuI (1.24 g, 6.51 mmol). The solid progressively dissolved during the addition to form a light yellow solution which turned brown when half of the lithium amide had been added. All the CuI was in solution at this stage. When the addition was complete the solution became colourless. A little solid was filtered off and the resulting solution, when concentrated by addition of Et_2O (50 cm^3) and cooled at −30 °C, gave a white crystalline solid (yield *ca.* 30%) [Found: C, 52.0; H, 9.90; N, 14.8%; *M* (cryoscopy in benzene), 1 012. $C_{48}H_{112}Cu_4N_{12}$ requires C, 51.85; H, 10.15; N, 15.2%; *M*, 1 110].

Reaction of (**2**) *with Bis(diphenylphosphino)methane (dppm): Synthesis of* (**5**).—A thf solution (50 cm^3) of dppm (1.91 g, 5.0 mmol) was added to a thf solution (50 cm^3) of (**2**) (0.67 g, 1.20 mmol). The resulting light yellow solution was concentrated and cooled to 0 °C. Complex $[Cu_3(PPh_2CHPPh_2)_3]$ (**5**) (*ca.* 50%) crystallized and was identified by comparison with an authentic sample.[15]

Table 1. Fractional atomic co-ordinates (× 10^4) for complex (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	2 968(1)	403(1)	1 160(1)	C(1)	8 951(9)	1 363(9)	3 187(14)
Cu(2)	5 731(1)	2 031(1)	2 387(1)	C(2)	8 301(10)	2 834(8)	173(14)
N(1)	7 736(6)	1 596(5)	1 255(9)	C(3)	2 893(9)	3 910(7)	3 162(13)
N(2)	3 723(6)	2 406(5)	3 536(9)	C(4)	3 705(10)	2 465(9)	6 129(13)

Table 2. Fractional atomic co-ordinates (× 10^4) for complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	757(1)	1 618(1)	771(1)	C(3)	−792(6)	3 563(5)	2 286(4)
Cu(2)	−2 155(1)	415(1)	−94(1)	C(4)	−1 380(6)	2 156(5)	1 924(4)
N(1)	−1 318(4)	1 982(3)	721(3)	C(5)	3 489(5)	2 190(4)	223(4)
N(2)	2 833(4)	1 226(3)	842(3)	C(6)	4 013(5)	3 359(4)	1 080(4)
C(1)	−1 937(5)	3 277(4)	161(4)	C(7)	4 378(5)	2 750(5)	2 309(4)
C(2)	−1 158(6)	4 296(4)	1 122(4)	C(8)	4 040(5)	1 279(4)	2 069(4)

Table 3. Fractional atomic co-ordinates (× 10^4) for complex (**3**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	2 550(1)	1 513(1)	965(2)	C(3)	3 763(4)	−573(6)	1 299(3)
Cu(2)	3 560(1)	1 862(1)	321(1)	C(4)	3 898(4)	5 496(7)	1 139(4)
N(1)	3 615(2)	991(4)	1 235(2)	C(5)	4 943(4)	3 913(8)	1 246(4)
N(2)	4 154(2)	3 991(4)	1 209(2)	C(6)	1 018(3)	1 708(7)	957(3)
N(3)	1 550(2)	2 409(4)	659(2)	C(7)	1 019(3)	83(7)	888(4)
N(4)	1 797(3)	−549(5)	1 259(3)	C(8)	1 553(3)	3 976(6)	778(3)
C(1)	4 162(3)	1 702(6)	1 888(3)	C(9)	2 040(5)	−511(9)	2 052(4)
C(2)	4 057(3)	3 331(6)	1 858(3)	C(10)	1 807(4)	−2 043(7)	1 003(5)

Reaction of (**2**) *with* 1,2-*Bis(diphenylphosphino)ethane* (*dppe*): *Synthesis of* (**6**).—A thf solution (50 cm^3) of dppe (3.69 g, 9.26 mmol) was slowly added to a thf solution (50 cm^3) of (**2**) (1.33 g, 2.5 mmol). The solution became suddenly orange and was kept overnight at 0 °C. A yellow crystalline solid formed (*ca.* 27%), $[Cu_2(\mu\text{-}PPh_2)_2(dppe)_2]$[16] (**6**) (Found: C, 70.45; H, 5.35; P, 14.0. $C_{76}H_{68}Cu_2P_6$ requires C, 70.5; H, 5.30; P, 14.4%).

Crystal Structure Determinations.—The compounds $[\{Cu(NMe_2)\}_4]$ (**1**), $[\{Cu(NC_4H_8)\}_4]$ (**2**), and $[\{Cu(MeNCH_2CH_2NMe_2)\}_4]$ (**3**) were mounted on a Philips PW 1100 diffractometer (graphite-monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å) in a random orientation. The reduced cells were obtained using the program TRACER.[17] The unit-cell parameters were deduced from least-squares refinement of the 2θ values of 25 reflections having $2\theta > 28°$ for all complexes.

Crystal data for (**1**). $C_8H_{24}Cu_4N_4$, $M = 430.5$, triclinic, $a = 8.553(2)$, $b = 8.383(2)$, $c = 5.638(1)$ Å, $\alpha = 107.04(2)$, $\beta = 96.80(3)$, $\gamma = 87.69(3)°$, $U = 383.8(2)$ Å^3, $Z = 1$, $D_c = 1.863$ g cm^{-3}, $F(000) = 216$, $\mu(\text{Mo-}K_\alpha) = 54.7$ cm^{-1}, space group $P\bar{1}$, crystal dimensions 0.05 × 0.37 × 0.56 mm.

Crystal data for (**2**). $C_{16}H_{32}Cu_4N_4$, $M = 534.6$, monoclinic, $a = 9.058(4)$, $b = 10.105(4)$, $c = 12.065(5)$ Å, $\beta = 111.38(4)°$, $U = 1\,028.3(8)$ Å^3, $Z = 2$, $D_c = 1.727$ g cm^{-3}, $F(000) = 544$, $\mu(\text{Mo-}K_\alpha) = 41.0$ cm^{-1}, space group $P2_1/c$, crystal dimensions 0.21 × 0.40 × 0.42 mm.

Crystal data for (**3**). $C_{20}H_{52}Cu_4N_8$, $M = 658.9$, monoclinic, $a = 18.541(4)$, $b = 9.242(2)$, $c = 19.441(4)$ Å, $\beta = 111.51(2)°$, $U = 3\,099(1)$ Å^3, $Z = 4$, $D_c = 1.412$ g cm^{-3}, $F(000) = 1\,376$, $\mu(\text{Mo-}K_\alpha) = 27.4$ cm^{-1}, space group $I2/a$, crystal dimensions 0.26 × 0.29 × 0.70 mm.

Intensities were collected at room temperature by ω–2θ scans in the ranges 5—58° for complex (**1**) and 6—56° for complex (**2**), and by ω scans in the range 6—58° for (**3**). No crystal decay or experimental instability was indicated by monitoring of standard reflections during the data collection. Ψ-Scans showed that crystal absorption effects could not be neglected, so the data for the three complexes were corrected for absorption by a semiempirical method[18] with maximum corrections of 1.739 for (**1**), 1.251 for (**2**), and 1.189 for (**3**). 2 051 [for (**1**)], 2 486 [for (**2**)], and 4 126 [for (**3**)] unique reflections were measured; of these 1 168, 1 731, and 2 513, respectively, having $I > 3.0\sigma(I)$ were considered observed and used in the structure solution and refinement.

Solution and refinement. The structures were solved by the heavy-atom method (Patterson and Fourier) and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms for complexes (**1**)—(**3**) were located from difference-Fourier maps and isotropically refined, except for those of complex (**1**) which were introduced in the final refinement as fixed contributors ($U_{iso.} = 0.10$ Å^2). The function minimized during the least-squares refinement was $\Sigma w(\Delta F)^2$. Unit weights were used for complexes (**2**) and (**3**) since these gave acceptable agreement analyses. For complex (**1**) data were weighted according to the scheme $w = 1.1484/[\sigma^2(F_o) + 0.000\,470\ F_o^2]$. Final residual indices for (**1**) were $R = 0.039$, $R' = 0.040$, and $S = 1.57$; $R' = \Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$, $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ (N_o = number of observed reflections, N_v = number of parameters to be determined). The final R index was 0.029 and 0.039 for (**2**) and (**3**) respectively. Fractional atomic co-ordinates for non-hydrogen atoms are listed in Tables 1—3 for (**1**)—(**3**) respectively. Complex neutral-atom scattering factors for Cu, N, and C were taken from ref. 19, those for H from ref. 20. All calculations were carried out on the CDC 7600 computer of the Centro di Calcolo dell'Italia Nord-orientale, using the SHELX 76 system of programs.[21]

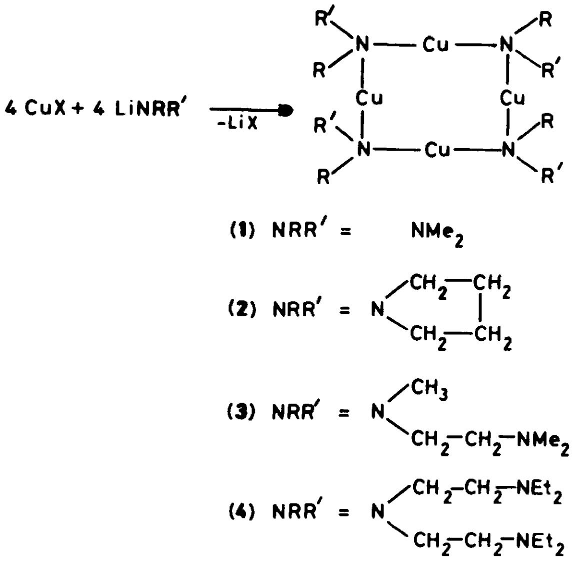
Results and Discussion

Synthesis of the copper(I) amido complexes was performed by a metathesis reaction on copper(I) halides, CuX (X = Cl or I), with lithium amides, reaction (1). Sometimes the use of a CuCl adduct with tetrahydrothiophene, which is a rather labile and weak ligand for the copper(I) ion, can be very helpful, since such an adduct has a good solubility in organic solvents. Reaction (1) is a good and general synthetic method for amido derivatives of copper(I), which do not have any intrinsic instability, though they are very sensitive and reactive to oxygen and water. Compounds (**1**)—(**4**) are very thermally stable since they decompose to metallic copper in boiling tetralin (1,2,3,4-tetrahydronaphthalene) only. Their stability is significantly greater than that of copper alkyls and copper alkoxides.[4a] The synthesis requires very careful control of the CuX:LiNRR′ molar ratio since an excess of LiNRR′ leads to deep coloured (normally deep brown) solutions, which are supposed to contain the cuprate form $Li[Cu(NRR')_2]$. An alternative, though more complex, synthesis uses the reaction of $[\{Cu(C_6H_2Me_3\text{-}2,4,6)\}_5]$ with amines.[4a] This can be an interesting route in the case of a difficult preparation involving functionalized lithium amides. The molecular complexity of

Table 4. Interatomic distances (Å) and angles (°) for complex (**1**)*

Cu(1)–N(1′)	1.891(4)	N(1)–Cu(1)	1.465(9)
Cu(1)–N(2)	1.896(4)	N(1)–C(2)	1.471(10)
Cu(2)–N(1)	1.885(5)	N(2)–C(3)	1.479(8)
Cu(2)–N(2)	1.889(5)	N(2)–C(4)	1.450(9)
Cu(1)–Cu(2)	2.692(2)		
Cu(1)–Cu(2′)	2.712(1)		
N(1′)–Cu(1)–N(2)	178.5(2)	Cu(1′)–N(1)–C(2)	113.5(4)
N(1)–Cu(2)–N(2)	178.4(2)	C(1)–N(1)–C(2)	108.4(6)
Cu(2)–N(1)–Cu(1′)	91.8(2)	Cu(2)–N(2)–C(3)	114.9(4)
Cu(1)–N(2)–Cu(2)	90.7(2)	Cu(2)–N(2)–C(4)	114.6(4)
Cu(2)–N(1)–Cu(1)	112.7(4)	Cu(1)–N(2)–C(3)	113.1(4)
Cu(2)–N(1)–Cu(2)	115.5(4)	Cu(1)–N(2)–C(4)	115.5(4)
Cu(1′)–N(1)–C(1)	114.4(4)	C(3)–N(2)–C(4)	107.7(5)

* Primed atoms are related to the others by the co-ordinates 1 − *x*, −*y*, −*z*.



(1)

Table 5. Interatomic distances (Å) and angles (°) for complex **(2)***

Cu(1)–N(1)	1.894(4)	N(2)–C(5)	1.478(6)
Cu(1)–N(2)	1.893(4)	N(2)–C(8)	1.487(5)
Cu(2)–N(1)	1.872(3)	C(1)–C(2)	1.519(6)
Cu(2)–N(2′)	1.881(3)	C(2)–C(3)	1.514(7)
Cu(1)–Cu(2)	2.742(2)	C(3)–C(4)	1.525(7)
Cu(1)–Cu(2′)	2.692(2)	C(5)–C(6)	1.527(6)
N(1)–C(1)	1.486(5)	C(6)–C(7)	1.526(7)
N(1)–C(4)	1.483(7)	C(7)–C(8)	1.524(6)
N(1)–Cu(1)–N(2)	178.9(2)	Cu(2′)–N(2)–C(5)	117.4(3)
N(1)–Cu(2)–N(2′)	175.2(2)	Cu(2′)–N(2)–C(8)	120.2(3)
Cu(1)–N(1)–Cu(2)	93.4(2)	C(5)–N(2)–C(8)	101.2(3)
Cu(1)–N(2)–Cu(2′)	91.0(2)	N(1)–C(1)–C(2)	104.9(3)
Cu(1)–N(1)–C(1)	113.0(3)	C(1)–C(2)–C(3)	105.1(4)
Cu(1)–N(1)–C(4)	112.5(3)	C(2)–C(3)–C(4)	104.8(4)
Cu(2)–N(1)–C(1)	119.5(3)	N(1)–C(4)–C(3)	104.9(4)
Cu(2)–N(1)–C(4)	117.5(3)	N(2)–C(5)–C(6)	104.5(4)
C(1)–N(1)–C(4)	101.4(3)	C(5)–C(6)–C(7)	104.5(4)
Cu(1)–N(2)–C(5)	114.5(3)	C(6)–C(7)–C(8)	104.6(4)
Cu(1)–N(2)–C(8)	113.3(3)	N(2)–C(8)–C(7)	104.4(4)

* Primed atoms are related to the others by the co-ordinates $-x, -y, -z$.

Table 6. Interatomic distances (Å) and angles (°) for complex **(3)***

Cu(1)–N(1)	1.910(4)	N(3)–C(8)	1.466(7)
Cu(1)–N(3)	1.915(4)	N(2)–C(2)	1.471(8)
Cu(2)–N(1)	1.919(4)	N(2)–C(4)	1.460(8)
Cu(2)–N(3′)	1.908(4)	N(2)–C(5)	1.440(9)
Cu(1)–Cu(2)	2.626(3)	N(4)–C(7)	1.476(7)
Cu(1)–Cu(2′)	2.611(2)	N(4)–C(9)	1.439(9)
N(1)–C(1)	1.459(6)	N(4)–C(10)	1.470(9)
N(1)–C(3)	1.468(7)	C(1)–C(2)	1.516(8)
N(3)–C(6)	1.465(8)	C(6)–C(7)	1.508(9)
Cu(1)–N(4)	2.548(6)	Cu(2)–N(2)	2.583(4)
N(1)–Cu(1)–N(3)	168.6(2)	N(1)–Cu(2)–N(3′)	170.2(2)
N(1)–Cu(1)–N(4)	110.2(2)	N(2)–Cu(2)–N(3′)	109.2(2)
N(3)–Cu(1)–N(4)	81.1(2)	N(1)–Cu(2)–N(2)	80.6(2)
Cu(1)–N(1)–Cu(2)	86.6(2)	Cu(1)–N(3)–Cu(2′)	86.1(2)
Cu(2)–N(1)–C(3)	115.9(3)	Cu(2′)–N(3)–C(6)	115.9(3)
Cu(2)–N(1)–C(1)	113.6(3)	Cu(1)–N(3)–C(6)	113.7(3)
Cu(1)–N(1)–C(3)	114.5(3)	Cu(1)–N(3)–C(8)	115.5(3)
Cu(1)–N(1)–C(1)	116.4(3)	Cu(2′)–N(3)–C(8)	114.3(3)
C(1)–N(1)–C(3)	108.7(4)	C(6)–N(3)–C(8)	109.8(4)
Cu(2)–N(2)–C(5)	99.9(4)	Cu(1)–N(4)–C(9)	103.9(4)
Cu(2)–N(2)–C(4)	128.3(4)	Cu(1)–N(4)–C(10)	123.4(5)
Cu(2)–N(2)–C(2)	95.8(3)	Cu(1)–N(4)–C(7)	96.4(4)

* Primed atoms are related to the others by the co-ordinates $\frac{1}{2} - x, y, -z$.

complexes **(1)**—**(3)** was elucidated in the solid state by *X*-ray crystallography and in solution by cryoscopy in benzene. A detailed discussion of the structures of **(1)**—**(3)** is given later.

The attempts to generate copper(I) amido derivatives of different molecular complexity led us to use polydentate lithium amides. Complexes **(3)** and **(4)** have been found, however, to be tetrameric both in the solid state and in solution (cryoscopy in benzene). The copper(I) ion in complexes **(3)** and **(4)** does not bind the tertiary amino groups, which are free from complexing another metal ion. An indication of such a reaction can be found in the synthesis of **(4)**. The complete solubilization of CuI occurred when half the stoicheiometric amount of the lithium amide only was added to the suspension of the copper salt.

Complexes **(1)**—**(4)** do not react with external nucleophiles, like PPh_3 and NEt_3, but they undergo a very facile transformation with diphosphine ligands. The reaction of **(2)** with dppm is shown in reaction (2). Complex **(5)** is a known compound which forms from the reaction of copper(I) alkyl derivatives with dppm. The amido group in complex **(2)** behaves as an alkyl group, abstracting a proton from the bridging methylene of dppm.[15] This result seems to arise because of a very high nucleophilicity of the NRR′ residue in **(2)**. A related, though more unusual, result was obtained reacting **(2)** with dppe. The amido group at copper(I) is able to displace the bridging ethylene in the dppe ligand. While the structure of **(6)** was established by an *X*-ray analysis,[16] we did not identify any organic product from reaction (3). The intermediate **(A)** we propose in reaction (3) is closely related to the structurally characterized $[Cu_2(OPh)_2(\mu\text{-dppe})(dppe)_2]$ **(7)**. The formation

Table 7. Equations of least-squares planes with deviations (Å) of the atoms given in square brackets

Complex **(1)**
Plane through the Cu_4N_4 core

$$-0.1710x' + 0.7228y' - 0.6696z' = -0.7311$$

[Cu(1) 0.000(1), Cu(2) 0.001(1), N(1) −0.026(5), N(2) −0.014(5), N(1′) 0.026(5), N(2′) 0.014(5)]

Complex **(2)**
Plane through the Cu_4N_4 core

$$0.1414x' + 0.4417y' - 0.8860z' = -0.000$$

[Cu(1) 0.004(1), Cu(2) 0.009(1), Cu(1′) −0.004(1), Cu(2′) −0.009(1), N(1) −0.047(3), N(2) 0.019(3), N(1′) 0.047(3), N(2′) −0.019(3)]

Complex **(3)**
Plane through the copper atoms

$$y' = 1.5560$$

[Cu(1) −0.161(1), Cu(2) 0.161(2), Cu(1′) −0.161(1), Cu(2′) 0.161(1), N(1) −0.644(4), N(3) 0.667(4)]

$$\tfrac{3}{4}[\{Cu(NC_4H_8)\}_4] + 3Ph_2PCH_2PPh_2 \xrightarrow{-HNC_4H_8} [Cu_3(Ph_2PCHPPh_2)_3] \quad (2)$$

(2) **(5)**

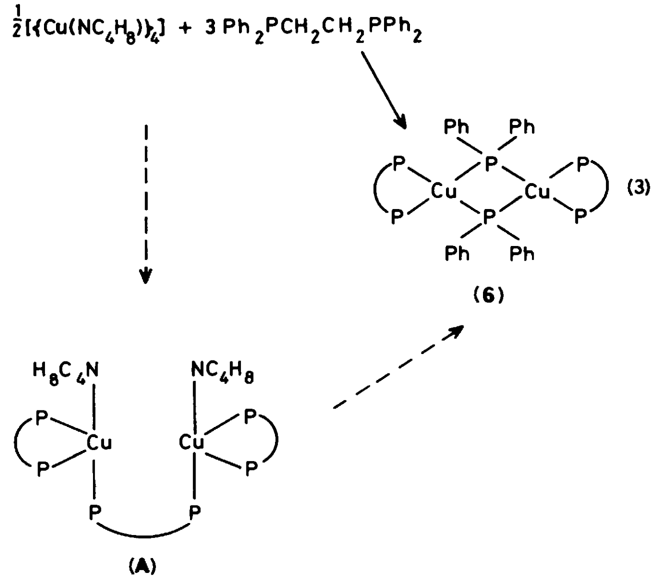


Table 8. Comparison of structural parameters in some copper(I) amido complexes

	(1)	(2)	[{Cu(NEt$_2$)}$_4$] (ref. 5)
Cu $\cdots$ Cu/Å	2.702(2)	2.717(2)	2.664(2)
Cu–N/Å	1.890(5)	1.885(4)	1.904(3)
N–Cu–N/°	178.5(2)	177.1(2)	175.4(1)
Cu–N–Cu/°	91.2(2)	92.2(2)	88.8(1)

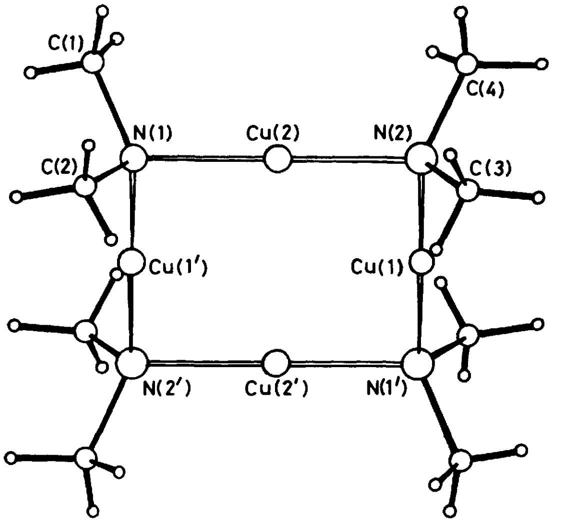


Figure 1. Structure of [{Cu(NMe$_2$)}$_4$]

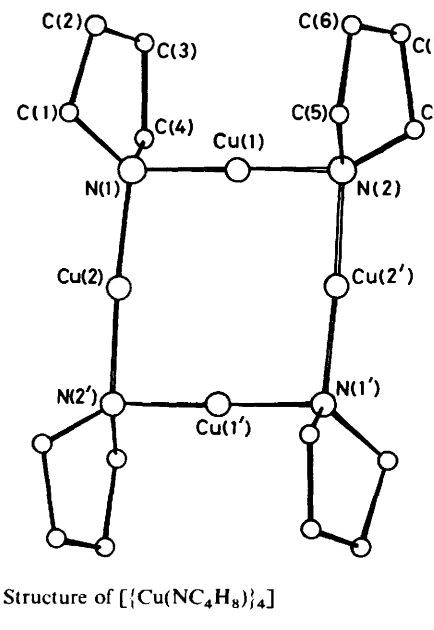


Figure 2. Structure of [{Cu(NC$_4$H$_8$)}$_4$]

of (**A**) is expected on the basis of similar chemistry of the Cu–OR and Cu–NR$_2$ functionalities,[3] though the difference in nucleophilicity of OPh$^-$ *vs.* NC$_4$H$_8$$^-$ leads to the evolution of (**A**) to (**6**), while complex (**7**) is stable.

Description of the Structures of (**1**)—(**3**).—Bond distances and angles are listed in Tables 4—6 for complexes (**1**)—(**3**), respectively; equations of least-squares planes are given in Table 7.

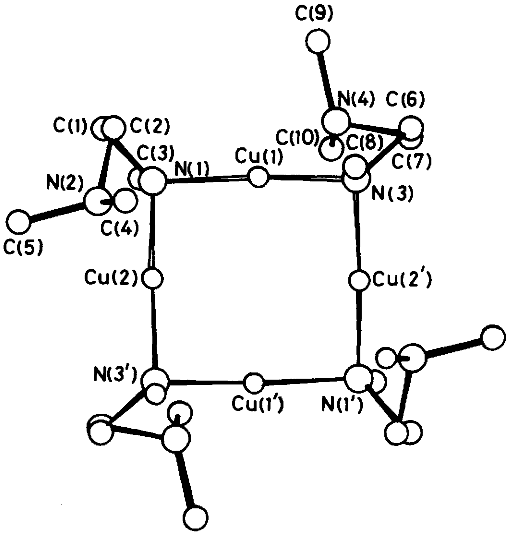


Figure 3. Structure of [{Cu(MeNCH$_2$CH$_2$NMe$_2$)}$_4$]

Complex (**1**) consists of discrete centrosymmetric units with a square plane of copper atoms (Figure 1). The nitrogen atoms symmetrically bridge adjacent pairs of copper atoms giving a nearly planar eight-membered ring [deviations from the Cu$_4$N$_4$ plane of 0.026(5) and 0.014(5) Å for N(1) and N(2) respectively (Table 7)]. The average distance between adjacent copper atoms [2.702(2) Å] is very close to those found in alkoxo and amido derivatives [{Cu(OBu^t)}$_4$] [2.709(3) Å (av.)],[9] [{Cu(mhp)}$_4$] (Hmhp = 2-hydroxy-6-methylpyridine) [2.678(1) Å (av.)],[22] and [{Cu(NEt$_2$)}$_4$] [2.664(3) Å],[5] but significantly longer than those in organometallic derivatives, [{Cu(C$_6$H$_2$Me$_3$-2,4,6)}$_5$] [2.453(9) Å (av.)][8] and [{Cu(CH$_2$SiMe$_3$)}$_4$] [2.418(2) Å].[7] The presence of heteroatoms rather than carbon bonded to copper(I) has a significant influence on the Cu $\cdots$ Cu distance. In view of the rather long Cu $\cdots$ Cu separation, it is possible that the tetrameric unit is held together by donor bonds with little or no d^{10}–d^{10} Cu–Cu interaction. Such a Cu $\cdots$ Cu separation, in any case, seems to involve a very weak metal–metal interaction.[23] The nitrogen co-ordination is tetrahedral with Cu–N–Cu angles close to 90°, so that the Cu$_4$N$_4$ core is near to being a perfect square plane.[5] The Cu–N–C angles are larger than the tetrahedral value, while the C–N–C angles are narrower. The N–C bond distances average 1.466(9) Å, consistent with a N(sp^3)–C(sp^3) bond length. The Cu–N distances [average 1.890(5) Å] are in agreement with those observed in [{Cu(NEt$_2$)}$_4$][5] and [{Cu(mhp)}$_4$].[22]

Both complexes (**1**) and (**2**) have a very similar structure of the Cu$_4$N$_4$ core, which is centrosymmetric, shown by the comparison of the most significant parameters (Table 8).

Complex (**3**) consists of tetrameric units whose geometry significantly differs from those of complexes (**1**) and (**2**). In particular: (*i*) the molecules have a C_2 symmetry; (*ii*) the mean plane through the copper atoms has a tetrahedral distortion (deviations of 0.161 Å) and the bridging ligands are arranged, alternately, above and below it [deviations of 0.644(4) and 0.667(4) Å (Table 7)]; (*iii*) the Cu $\cdots$ Cu separation is significantly shorter [2.618(2) Å (av.)] than in (**1**) and (**2**) and the N–Cu–N angles [169.4(2)° (av.)] deviate significantly from linearity; (*iv*) the Cu–N distances [1.913(4) Å (av.)] are longer than in (**1**) and (**2**). Such differences could be due to steric repulsions between ligands and/or weak interactions between the copper atoms and the unco-ordinated nitrogen atoms. The ligands are twisted [torsion angles: N(1)–C(1)–C(2)–N(2) −58.8(6), N(3)–C(6)–C(7)–N(4) 57.6(7)°] and the terminal nitrogen atoms are at distances of 2.548(6) [Cu(1)–N(4)] and 2.583(4) Å [Cu(2)–N(2)] from the copper atoms. These distances cannot be considered as bonding interactions, however, if compared with usual distances of a tertiary amino group bonded to copper(I) [2.09(1)—2.25(1) Å].[24]

Acknowledgements

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