Polyhedron Vol. 2, No. 12, pp. 1379–1388, 1983
Printed in Great Britain.

0277–5387/83 $3.00 + .00

Studies of Amidino-Complexes of Copper(I) and (II). Carboxylate Analogues

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(Received 25 July 1983; accepted 10 August 1983)

Lithioamidines {R'N(Li)C(R)NR'; R = H, CH_3, C_6H_5; R' = C_6H_5, p-$CH_3C_6H_4$} react with anhydrous copper(II) chloride to form $[Cu\{R'NC(R)NR'\}_2]_n$ complexes, and with anhydrous copper(I) chloride to form $[Cu\{R'NC(R)NR'\}]_m$. The copper(II) complexes are diamagnetic, purple solids, which are air stable in the solid state but very air reactive in solution. Experimental data are consistent with a dimeric or more highly associated structure, and an X-ray structural determination shows $[Cu\{C_6H_5NC(C_6H_5)NC_6H_5\}_2]_2$ to be dimeric with four bridging amidino-groups and a short Cu-Cu distance (2.46Å). The copper(I) complexes are pale yellow solids, which in solution are subject to rapid aerial oxidation, especially in the presence of free amidines, and disproportionation to $[Cu\{R'NC(R)NR'\}_2]_n$ and copper metal. Differences in properties are noted between acetamidino-, benzamidino- and formamidino-complexes, the last complexes of copper(I) being most stable towards disproportionation. $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2$ reacts with pyridine (Py) to form the copper(I) derivative $Cu\{C_6H_5NC(CH_3)NC_6H_5\}.2Py$ and with carbon disulphide to form $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2.CS_2$ which is reduced to form $Cu\{C_6H_5NC(CH_3)NC_6H_5\}.CS_2$.

THE isoelectronic relationship between allyl, amidino, triazeno and carboxylato-groups has been noted previously,[1,2] together with the differences in the mode of bonding to transition metals. The metal assumes a position out of the plane of η^3-allyl groups,[3] whereas for bidentate carboxylato-groups the metal adopts a position in, or close to, the ligand skeletal plane.[4] Amidino-groups have been shown to exhibit structural features similar to those of carboxylato-groups,[5] and also in common with the latter, have a high propensity to bridge between two identical[5-8] or different transition metals.[9,10] For example, amidines and carboxylic acids both react with chromium and molybdenum hexacarbonyls to produce M_2L_4 complexes, and for M = molybdenum the structures of the complexes in the solid state are closely related, both consisting of a quadruple bonded Mo_2 unit bridged symmetrically by four ligand groups.[5] The ability of the amidino-group to encourage metal-metal interactions in binuclear complexes has been studied for other metals, and here we report studies involving copper. Attempts have been made to promote direct copper-copper bonding in complexes analogous to the copper(II) carboxylates.[4,11]

Previous studies of both copper(I) and (II) carboxylates have been extensive,[12] but only limited attention has been paid to amidino-copper complexes. In 1956 copper(II) acetate was treated with N,N'-diarylformamidines in refluxing ethanol to yield the copper(I) complexes $[Cu(RNCHNR)]_n$,[13] reactions which occur only for formamidines. Relevant also to the present work are complexes of the iso-electronic triazeno-group. The crystal structure of 1,3-dimethyltriazenocopper(I)[7] consists of a tetramer based on a diamond Cu_4 unit with single amidino-groups bridging alternate sides of the Cu_4 plane. The 1,3-diphenyltriazeno-complex, in contrast, has a dimeric structure with two triazeno-groups bridging the metals.[6]

Interestingly dimer-tetramer equilibria have been established for related formamidino-complexes.[14] Also bis-1,3-diphenyltriazenocopper(II),[15] unlike the corresponding copper(II) acetate, is diamagnetic and thought to have a similar dinuclear structure with four bridging triazeno-groups. We report here our studies of related acetamidino-, benzamidino-, and formamidino-complexes of both copper(I) and copper(II), together with some attempted ligand addition reactions.

RESULTS AND DISCUSSION

A. Bis-amidinocopper(II) Complexes

These complexes have been synthesised from anhydrous copper(II) chloride and lithioamidines in monoglyme solution as purple solids (see Table 1) which are recrystallised from dichloromethane using Soxhlet extraction. The reaction started below ambient temperature, but was allowed to continue for 18 h. to reach completion. The product slowly precipitated. There was no evidence for an intermediate amidinochloro-complex, Cu(Am)Cl. Yields of the microcrystalline materials, which melted in the range 160-220° with decomposition, were 50-70%. Though the solids are air stable over many months, rapid decomposition occurs in solution in the presence of air. The solutions become cloudy and deposit a brown solid whilst changing to a brown-green colour. At best the materials are only sparingly soluble in organic solvents, a property which restricted structural studies of the complexes. Benzamidino- and formamidino-complexes have a marginally better solubility than acetamidino-complexes, and the best solvents were found to be chlorocarbons (CH_2Cl_2, $CHCl_3$).

Molecular weight measurements by cryoscopy in benzene were undertaken on $Cu\{C_6H_5NC(C_6H_5)NC_6H_5\}_2$, but the level of solubility made the results subject to large errors. Because of the high relative molecular mass (RMM) and low concentration of solutions small variations in temperatures correspond to large differences in RMM values. Never-the-less the values of 985, 892 and 708 which compare with values of 606 for the monomer and 1212 for the dimer raise the question of monomer $\rightleftharpoons$ dimer or monomer oligomer or polymer equilibria occurring in solution, though no data from other sources support such a process. Interestingly Vrieze et al.[14] report dimer $\rightleftharpoons$ tetramer equilibria for a series of formamidino-copper(I) complexes, though the formation of a monomer intermediate is unlikely in this process which requires only the cleavage of one metal-nitrogen bond of the dimer. Magnetic measurements of the solid amidino-copper(II) complexes, $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2$ and $Cu\{C_6H_5NC(C_6H_5)NC_6H_5\}_2$ using a Gouy balance show the complexes to be diamagnetic, and mass spectral studies of the complexes show the presence of Cu_2 species. Every complex exhibits peaks arising from $[Cu_2(Am)_2]^+$ as the highest $^m/e$ fragment in the spectrum implying association of $Cu(Am)_2$ units in the vapour state and possibly in the solid state. A typical breakdown pattern for $Cu\{C_6H_5NC(CH_3)NPh\}_2$ is illustrated in Figure 1. Source temperatures used were slightly lower than the melting points of the complexes at which they tend to decompose (according to thermal gravimetric analysis studies). $[Am]^+$ peaks are the most intense in the spectra, though the peaks due to $[Cu_2Am_2]^+$ are the most intense peaks for a copper containing species). $[CuAm_2]^+$, $[Cu_2Am]^+$ and $[CuAm]^+$ fragments are also commonly observed. Loss of RCN (R = CH_3, C_6H_5) from $[Cu_2\{R'NC(R)NR'\}_2]^+$ is well documented as an important fragmentation step, though it is less important for formamidino-complexes.

Infrared spectroscopic data (Table 2) consist of absorptions at 1568-1463 and 1263-1231 cm.$^{-1}$ characteristic of delocalised amidino-complexes[16] but from such data it is not possible to differentiate between bridging and chelate bonding. Use of ^1H n.m.r. spectroscopy for structural studies was limited by the low solubility of the complexes in suitable solvents, though a spectrum was recorded for $Cu\{\underline{p}\text{-}CH_3C_6H_4NC(CH_3)N\text{-}\underline{p}\text{-}CH_3C_6H_4\}_2$

Table 1. Analytical Data^{+} and Yields for [Cu{R'NC(R)NR'}]$_n$ and [Cu{R'NC(R)NR'}$_2$]$_n$ Complexes.

Complex	% Yield	%C	%H	%N	%Cu
Cu{PhNCHNPh}$_2$	49	68.8 (68.8)	4.73 (4.88)	12.0 (12.3)	14.3 (14.0)
Cu{PhNCHNPh}	62	60.0 (60.3)	4.50 (4.29)	10.6 (10.8)	24.2 (24.5)
Cu{PhNC(CH$_3$)NPh}$_2$	61	69.5 (69.8)	5.46 (5.44)	11.20 (11.62)	13.2 (13.2)
Cu{PhNC(CH$_3$)NPh}	53	67.6 (68.1)	4.81 (4.52)	8.10 (8.37)	18.4 (19.0)
Cu{*p*-CH$_3$C$_6$H$_4$NC(CH$_3$)N-*p*-CH$_3$C$_6$H$_4$}$_2$	67	70.8 (71.4)	6.20 (6.37)	10.5 (10.4)	11.4 (11.8)
Cu{*p*-CH$_3$C$_6$H$_4$NC(CH$_3$)N-*p*-CH$_3$C$_6$H$_4$}	70	64.1 (63.9)	5.95 (5.70)	9.11 (9.31)	20.8 (21.1)
Cu{PhNC(Ph)NPh}$_2$	63	74.5 (75.3)	5.21 (4.99)	9.15 (9.24)	10.4 (10.5)
Cu{PhNC(Ph)NPh}	61	68.0 (68.2)	4.52 (4.48)	8.23 (8.37)	18.8 (19.0)
Cu{*p*-CH$_3$C$_6$H$_4$NC(C$_6$H$_5$)N-*p*-CH$_3$C$_6$H$_4$}$_2$	58	75.5 (76.2)	6.02 (5.78)	8.56 (8.46)	9.53 (9.59)
Cu{*p*-CH$_3$C$_6$H$_4$NC(C$_6$H$_5$)N-*p*-CH$_3$C$_6$H$_4$}	58	68.9 (69.5)	5.37 (5.28)	7.60 (7.72)	17.4 (17.5)

$^{+}$ Calculated % are given in parentheses.

Table 2. Infra-red and Melting Point Data for [Cu{R'NC(R)NR'}$_2$]$_m$ and Cu{R'NC(R)NR'}]$_m$ Complexes.

Compound	Colour	M.p. (decomp) °C	IR data (cm^{-1})			
Cu(DPFA)$_2$	purple	160	1568	1350		1231
CuDPFA	pale yellow	270	1562	1352		1237
Cu(DPAA)$_2$	purple	165	1529	1415	1362	1252
CuDPAA	yellow	210	1513	1415	1368	1259
Cu(DpTAA)$_2$	purple	180	1538	1420	1363	1253
CuDpTAA	pale yellow	220	1518	1420	1360	1260
Cu(DPBA)$_2$	purple	180	1465	1415		1263
CuDPBA	yellow	260	1465 1476	1406		1260
Cu(DpTBA)$_2$	purple	175	1468	1423		1259
CuDpTBA	yellow	210	1463 1470	1439		1260

which was consistent with symmetrical bridging or bidentate amidino-groups. It must however be noted that p-tolyl groups have been shown by one of the authors to be insensitive to different bonding situations occurring at the two nitrogen atoms in such groups.[16] Furthermore the sharp signals provide further evidence for a diamagnetic complex. The diamagnetism of the complex, its low solubility in organic solvents and the m.s. data are consistent with a dimeric (I) or more highly associated complex (II), but not with a monomeric complex.

For one of the complexes, $Cu\{C_6H_5NC(C_6H_5)NC_6H_5\}_2$, suitable crystals for an X-ray crystallographic study were produced which would allow the problem of a dimeric or an oligomeric/polymeric structure in the solid state to be resolved. The crystal structure determined by Halfpenny,[17] shows a dimeric structure (I) with four bridging amidino-groups. The structure is closely related to that of $Mo_2\{C_6H_5NC(C_6H_5)NC_6H_5\}_4$ and is the same as that proposed for the isoelectronic triazenocopper(II) complexes. The copper-copper distance of 2.46Å is consistent with direct bonding between the coppers, and represents a Cu-Cu single bond.

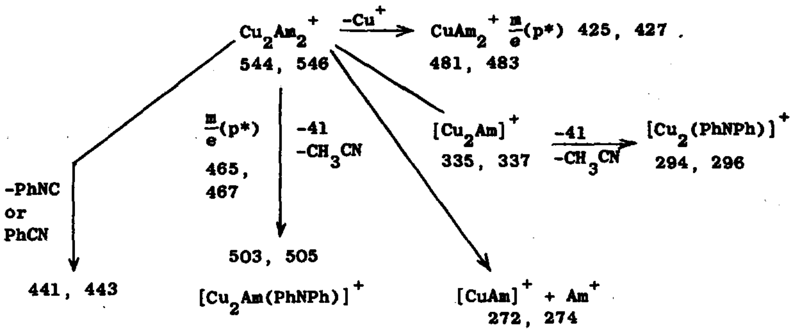
A thermal gravimetric study of the complexes under a nitrogen atmosphere produced the thermograms shown in Figure 2. The benzamidino-complexes and $[Cu_2(DPTAA)_4]$ contained monoglyme of crystallisation, and the initial mass losses for these complexes correspond to the loss of solvent. The curves for the two benzamidino-complexes appear very similar, but assessment of the % mass loss data indicate different modes of decomposition. Three stages occur for each of the benzamidino- and acetamidino-complexes, though the mass loss data show no close relationship between the corresponding stages for each complex. Loss of complete amidino-groups was not a recognisable process, but fragmentation of amidino-groups was common with losses of [PhNCPh], $[CH_3C_6H_4NC(CH_3)N]$ and [PhNCNPh] being typical. The final residue results after a lower mass loss than that expected for formation of copper metal, but in all cases the data is not consistent with a characterisable material.

B. Amidino-Copper(I) Complexes

Copper(I) complexes were synthesised by the reaction of lithioamidines with anhydrous copper(I) chloride in monoglyme as pale yellow, diamagnetic solids in ca. 50-70% yield (see Table 1). Attempts were made to synthesise acetamidine and benzamidino-complexes from copper(II) acetate by the method of Bradley and Wright[13] but without success. The N,N'-diphenylformamidinocopper(I) complexes are apparently stable to disproportionation in solution whereas the acetamidino- and benzamidino-complex are labile. The copper(I) complexes are non-volatile and have higher melting points than their copper(II) counterparts, together with a higher solubility in organic solvents. Amidinocopper(I) complexes readily oxidise in air to the copper(II) complexes, particularly in solution, where the process is noticeably accelerated by the presence of the free amidine. In the solid state, N,N'-diphenylacetamidinocopper(I), on exposure to air develops a bluish-green/red colour on the surface. In solution disproportionation also occurs with deposition of the metal and development of the purple colour characteristic of the copper(II) complexes. This reaction prevented purification of the complexes by recrystallisation methods. Stability of the solutions towards disproportionation in the order acetamidino < benzamidino << formamidino-complexes, and solutions of the last complexes showed virtually no signs of reaction. Interestingly a detailed study of the dimer-dimer and dimer-tetramer equilibria by ^1H and ^{13}C n.m.r. methods has been reported by Vrieze et al.[14] for a series of formamidinocopper(I) complexes, with no reference being made to disproportionation in solution. Indeed solutions of these complexes appear remarkably stable compared with

Figure 1

Mass Spectral breakdown pattern for Cu{PhNC(CH_3)NPh}$_2$



The following abbreviations are used:

AmH = amidine R'NHC(R)NR' (R = H, CH_3, C_6H_5; R = C_6H_5, p-$CH_3C_6H_4$)

Am = amidino-group R'NC(R)NR'

DPAAH = N,N'-diphenylacetamidine, $C_6H_5NHC(CH_3)NC_6H_5$

DPAA = N,N'-diphenylacetamidino, $C_6H_5NC(CH_3)NC_6H_5$

DPTAAH = N,N'-di-p-tolylacetamidine, p-$CH_3C_6H_4NHC(CH_3)N$-p-$CH_3C_6H_4$

DPTAA = N,N'-di-p-tolylacetamidino, p-$CH_3C_6H_4NC(CH_3)N$-p-$CH_3C_6H_4$

DPBAH = N,N'-diphenylbenzamidine, $C_6H_5NHC(C_6H_5)NC_6H_5$

DPBA = N,N'-diphenylbenzamidino, $C_6H_5NC(C_6H_5)NC_6H_5$

DPTBAH = N,N'-di-p-tolylbenzamidine, p-$CH_3C_6H_4NHC(C_6H_5)N$-p-$CH_3C_6H_4$

DPTBA = N,N'-di-p-tolylbenzamidino, p-$CH_3C_6H_4NC(C_6H_5)N$-p-$CH_3C_6H_4$

DPFAH = N,N'-diphenylformamidine, $C_6H_5NHCHNC_6H_5$

DPFA = N,N'-diphenylformamidino, $C_6H_5NCHNC_6H_5$

solutions of benzamidino- and acetamidino-complexes, though it is *conceivable that some* of the minor changes i.e. broadening and weak new signals, could arise from copper(II) derivatives.

The mass spectra of the copper(I) complexes are very similar to those of the copper(II) complexes, with $[Cu_2Am_2]^+$ ions being the highest $^m/e$ value ions detected. $[CuAm_2]^+$ ions are detected for all the complexes. The fragmentation pattern follows closely that shown in Figure 1 for $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2$. The $[Cu_2Am_2]^+$ ion may represent the parent ion for the complex, and indeed for $[Cu(C_6H_5NNNC_6H_5)]_2$[6] a dinuclear complex has been established. However the ion may also represent a thermolysis product of a tetranuclear complex, as established for $[Cu(CH_3NNNCH_3)]_4$.[7] Infrared spectra are strikingly similar to those of copper(II) complexes and n.m.r. spectra provided little structural information which was reliable because of low solubility and disproportionation in suitable solvents.

Thermograms for the copper(I) complexes are given in Figure 3. The benzamidino-complexes decompose in one stage, whereas for the acetamidino-complexes decomposition occurs in a two stage process. A thermogram, intermediate between these two types, with a merging together of the two stages is exhibited by the formamidino-complex. All the complexes decompose to form a residue, which contains, in addition to copper, a small percentage of carbon, hydrogen and/or nitrogen, though in the case of the N,N'-diphenylbenzamidino-complex the % loss in weight corresponds most closely to a residue of copper metal. The intermediate stages in the decomposition of the acetamidino-complexes correspond closely to the loss of three amidino-groups from a Cu_4Am_4 unit (where Am = $R'NC(CH_3)NR'$, R' = C_6H_5, $\underline{p}$-$CH_3C_6H_4$). Though these complexes were too unstable towards disproportionation in solution (to Cu(O) and Cu(II)) to allow relative molecular mass measurements by using colligative properties, this feature in the thermogram possibly provides some evidence for tetramers in the solid state, as found for the isoelectronic N,N'-dimethyltriazino-complex.[7]

C. Reactions of $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2$ with Pyridine and Carbon Disulphide

Pyridine reacts with the bis-amidinocopper(II) complex in monoglyme over 4d to produce a brown powder thought to be $Cu\{C_6H_5NC(CH_3)NC_6H_5\}.2C_5H_5N$ on the basis of elemental analysis. This reduction of a copper(II) complex to a copper(I) complex is a process achieved by many ligands, including phosphines and phosphites, and for example triphenylphosphine reacts with hydrated copper(II) chloride in ethanol to produce $(Ph_3P)_3CuCl$ or $[PPh_3CuCl]_4$ depending on the molar ratios of the reactants.[18]

With carbon disulphide attempts were made to accomplish insertion into a copper-nitrogen bond. The purple solution of the copper(II) complex dissolved in carbon disulphide became brown over ½ h. and deposited a brown solid which though impure showed characteristics of an addition compound. Analytical data suggested the formulation $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2.CS_2$. Recrystallisation of the material from toluene/hexane mixtures led to a decrease in carbon, hydrogen and nitrogen content, but an increase in copper and sulphur contents, the data being consistent with reduction to the copper(I) complex, $Cu\{C_6H_5NC(CH_3)NC_6H_5\}.CS_2$.

Distinct differences occur between the reactions of this bis-amidinocopper(II) complex and the corresponding carboxylato-complex with neutral ligands, and may reflect the weak coordinating properties of ligands <u>trans-</u> to the second metal in the dinuclear unit, or reflect the steric properties of the N-substituents associated with four

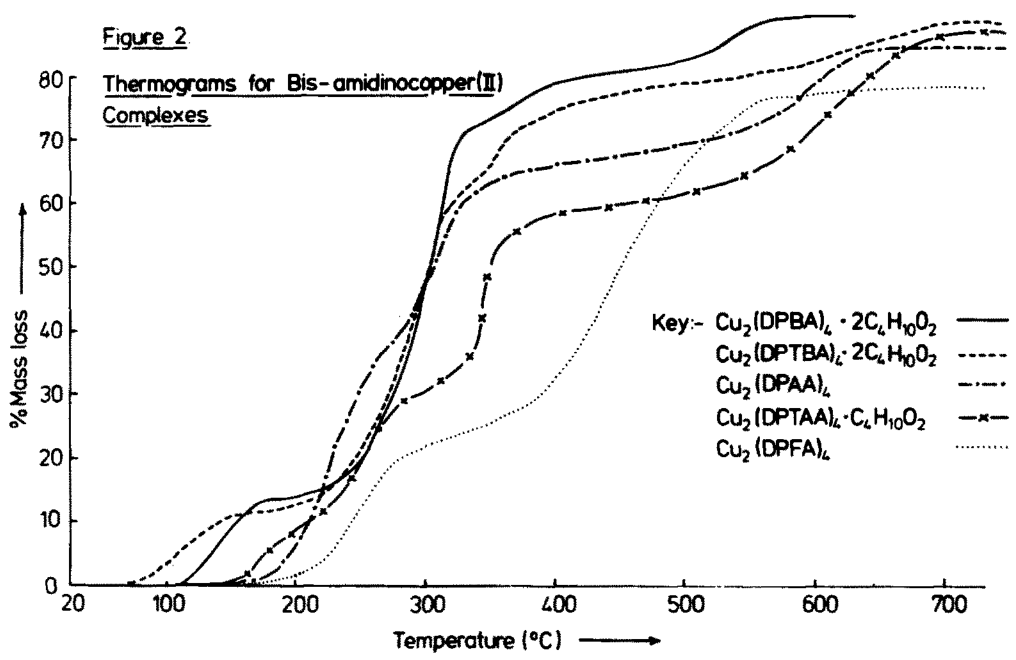


Figure 2. Thermograms for Bis-amidinocopper(II) Complexes.

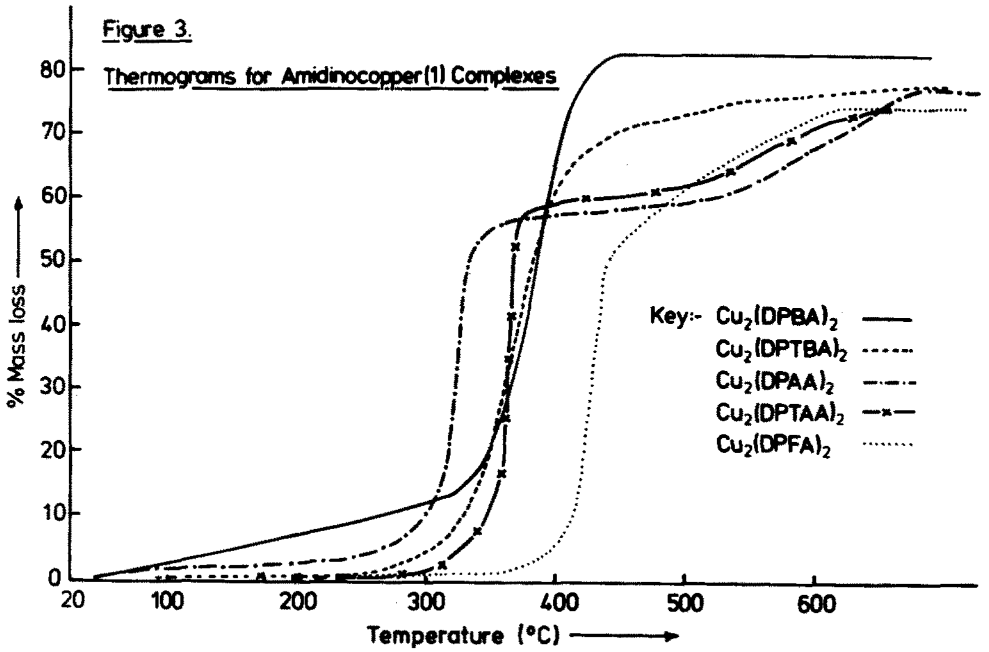


Figure 3. Thermograms for Amidinocopper(I) Complexes.

amidino-groups. It is well established that complexes containing strong metal-metal interactions tend to form weak bonds trans to the metal-metal bond.[19] For metal-metal bonded amidino-complexes pyridine and triphenylphosphine failed to form adducts of the type $Cu_2Am_4L_2$, whereas for the acetato-complex water, dioxane, pyridines and anilines give $Cu_2(OCOCH_3)_4L_2$ derivatives.[20]

EXPERIMENTAL

Anhydrous copper(I) and copper(II) chlorides, triphenylphosphine, pyridine, N,N'-diphenylacetamidine and -formamidine, acetamidinium hydrochloride and benzamidinium hydrochloride were obtained from commercial sources and used without further purification. N,N'-Diphenylbenzamidine, N,N'-di-*p*-tolylbenzamidine, N,N'-dimethylbenzamidine and N,N'-di-*p*-tolylacetamidine were prepared by standard methods.[21] n-Butyllithium, ca. 1.23M in hexane, was used as supplied without purification. Hydrocarbon solvents and diethylether were dried over extruded sodium, and monoglyme was freshly distilled from sodium hydride prior to use. Chlorocarbon solvents and carbon disulphide were dried over molecular sieves. All solvents were de-gassed under reduced pressure, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed with rigorous exclusion of air.

I.r. spectra in the range 4000-400 cm.$^{-1}$ were recorded with a Perkin-Elmer 457 spectrophotometer, and ^1H n.m.r. spectra at 90 MHz with a Bruker HX90E spectrophotometer. Mass spectra were obtained with an A.E.I. MS9 instrument at 70 eV and an accelerating potential of 8 kV. Samples were inserted directly into the ion source at temperatures between 80°-220°C. Thermogravimetric studies were undertaken using a Stanton Redcroft TG750 balance.

Carbon, hydrogen and nitrogen contents of the complexes were determined with a Perkin-Elmer 240 Elemental Analyser, and copper by atomic absorption spectroscopy using a Perkin-Elmer 403 spectrometer. Sulphur content was obtained by combustion of the complex in oxygen to sulphate, followed by the volumetric determination of sulphate using a standard barium perchlorate solution. Phosphorus content was determined by combustion of the sample in air, followed by volumetric determination of phosphate.

Preparation of Bis(N,N'-diphenylacetamidino)copper(II), $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2$.-

n-Butyllithium (5.9 ml; 1.23M in hexane) was added to a frozen solution of N,N'-diphenylacetamidine (1.54 g, 7.31 mmol) in monoglyme (40 ml), and the mixture allowed to warm slowly to ambient temperature and stand for ½ h. The resulting inhomogeneous product mixture was then transferred onto a frozen suspension of anhydrous copper(II) chloride (0.49 g, 3.65 mmol) in monoglyme (40 ml), and the reaction mixture stirred at ambient temperature for 18 h. After filtering the resulting mixture, the purple residue was washed with hexane (2 x 10 ml), dried *in vacuo* and recrystallised from hot dichloromethane using a modified Soxhlet extraction method. A purple microcrystalline solid, $Cu\{C_6H_5NC(CH_3)NC_6H_5\}_2$ (m 165° dec, 61% yield) was obtained, which could be stored in the solid state in air over many months without noticeable change. The complex in solution remains unchanged when stored under nitrogen over many days, but rapid changes occur in the presence of air.

M.s. The highest mass fragment observed gave peaks at $^m/e$ 548, 546, 544 corresponding to $[Cu_2Am_2]^+$ and arising from ^{63}Cu and ^{65}Cu (69 and 31% abundancies respectively).

Preparation of other Bis-amidinocopper(II) Complexes.- The method described above was used generally to prepare the following complexes as purple solids typically in 50-70%

yields.

Bis(N,N'-di-p-tolylacetamidino)copper(II), m. 220° dec.

M.s. The highest mass fragment was observed at $^{m}/e$ 602 and 600 corresponding to $[Cu_2Am_2]^{+}$.

^{1}H n.m.r., $\delta(CDCl_3)$: 2.84(8H), 7.69(6H), 7.91(3H) p.p.m.

Bis(N,N'-di-p-tolylbenzamidino)copper(II), m. 175° dec.

M.s. The highest mass fragment was observed at $^{m}/e$ 726 and 724 corresponding to $[Cu_2Am_2]^{+}$.

Bis(N,N'-diphenylbenzamidino)copper(II), m. 180° dec. M 985, 892, 708 by cryoscopy in benzene (monomer requires 606, dimer 1212).

M.s. The highest mass fragment was observed at $^{m}/e$ 670 and 668 corresponding to $[Cu_2Am_2]^{+}$

Bis(N,N'-diphenylformamidino)copper(II), m. 160° dec.

M.s. The highest mass fragment was observed at $^{m}/e$ 518 and 516 corresponding to $[Cu_2Am_2]^{+}$.

Preparation of N,N'-Di-p-tolylacetamidinocopper(I), Cu{p-$CH_3C_6H_4NC(CH_3)N$-*p*-$CH_3C_6H_4$}.- n-Butyllithium (2.70 ml, 1.84M in hexane) was added to a frozen solution of N,N'-di-*p*-tolylacetamidine (0.89 g, 4.14 mmol) in monoglyme (25 ml), and the mixture allowed to warm slowly to ambient temperature. After ½ h. the resulting reagent was syringed onto a frozen mixture of anhydrous copper(I) chloride (0.41 g, 4.14 mmol) and monoglyme (30 ml), and the mixture allowed to warm to ambient temperature. After stirring for 12 h., the pale yellow precipitate was separated by filtration, washed with hexane (2 x 10 ml), and dried *in vacuo*. Soxhlet extraction using dichloromethane yielded pale yellow microcrystalline N,N'-di-*p*-tolylacetamidinocopper(I), m. 220° dec.

M.s. The highest mass fragment was observed at $^{m}/e$ 602 and 600 corresponding to $[Cu_2Am_2]^{+}$.

Preparation of other Amidinocopper(I) Complexes.- The method described above was used generally to prepare the following complexes as yellow solids typically in 50-70% yields.

N,N'-Diphenylformamidinocopper(I), m. 270° dec.

M.s. The highest mass fragment was observed at $^{m}/e$ 518 and 516 corresponding to $[Cu_2Am_2]^{+}$.

N,N'-Di-*p*-tolylbenzamidinocopper(I), m. 210° dec.

M.s. The highest mass fragment was observed at $^{m}/e$ 726 and 724 corresponding to $[Cu_2Am_2]^{+}$.

N,N'-Diphenylbenzamidinocopper(I), m. 260° dec.

M.s. The highest mass fragment was observed at $^{m}/e$ 670 and 668 corresponding to $[Cu_2Am_2]^{+}$.

N,N'-Diphenylacetamidinocopper(I), m. 210° dec

M.s. The highest mass fragment was observed at $^{m}/e$ 532 and 530, corresponding to $[Cu_2Am_2]^{+}$.

Reaction of Bis(N,N'-diphenylacetamidino)copper(II) with Pyridine.- A suspension of the complex (0.38 g, 0.8 mmol) in monoglyme (15 ml) was stirred with pyridine (0.063 g, 0.8 mmol) for 4d at ambient temperature. The brown precipitate of the product, Cu$\{C_6H_5NC(CH_3)NC_6H_5\}_2.2C_6H_5N$, was separated by filtration, washed with monoglyme and dried *in vacuo*. Found: C, 67.1; H, 5.81; N, 13.0; Cu, 14.8: $C_{24}H_{23}N_4Cu$ requires C, 66.9; H, 5.38; N, 13.0; Cu, 14.7%.

Reaction of Bis(N,N'-diphenylacetamidino)copper(II) with Carbon Disulphide.- The complex was stirred in carbon disulphide for 24 h., the initial purple solution turning brown over ½ h. After filtration the solvent was removed *in vacuo* to produce a brown solid. Found: C, 59.8; H, 4.90; N, 10.4; Cu, 12.4; S, 12.0: Cu(DPAA)$_2$.CS$_2$ requires C, 62.4; H, 4.69; N, 10.0; Cu, 11.4; S, 11.5%. After recrystallisation from toluene/hexane mixtures, found C, 49.7; H, 4.31; N, 8.42; Cu, 17.7; S, 17.6: Cu(DPAA).CS$_2$ requires C, 51.6; H, 3.75; N, 8.03; Cu, 18.2; S, 18.4%.

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