129. *Metal Derivatives of* NN′*-Diarylamidines.*

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The ability of *NN*′-diarylamidines to form compounds with metals has been investigated. Four kinds of metal derivatives have been recognized. Their structures are discussed.

In a previous communication[1] the preparation of *NN*′-di-2-anthraquinonylformamidine and two of its metal derivatives was described, and reference was made to the stability of the cuprous compound towards chemical reagents. The present investigation is a more detailed study of the metal derivatives of *NN*′-diarylamidines and some related compounds, in particular the cuprous and silver derivatives.

Of the methods of preparing *NN*′-diarylformamidines[2] two—the reaction of ethyl orthoformate or ethyl*iso*formanilide with primary amines—have been used most frequently in the present work. The ethyl orthoformate method gave satisfactory results with all symmetrical *NN*′-diarylformamidines except those derived from the weakest bases such as 2 : 4-dinitroaniline and 2-amino-1- and 2-amino-3-nitroanthraquinone.[3] Ten new symmetrical *NN*′-diaryl derivatives of formamidine were thus prepared. Two others, the 2 : 4-dimethylphenyl and 2-anthryl derivatives, were prepared for the first time by the ethyl orthoformate method; the second had been prepared and analysed by Bollert[4] who, however, did not record the melting point. Ethyl*iso*formanilide and benzidine gave the 4 : 4′-di-(*N*-phenylformamidine) derivative of diphenyl. Several unsymmetrical *NN*′-diarylformamidines were prepared from primary amines and ethyl*iso*formanilide.

A number of related benzamidines have been prepared, the majority by the reaction of benzotrichloride with amines, and also a series of acetamidines from imidoyl chlorides by reaction with amines.[2] In addition some metal derivatives of compounds related to the amidines have been investigated; these included the dianil and the di-(*p*-chloroanil) of glutacondialdehyde, 2-*p*-nitroanilinoquinoline, 2 : 4 : 6-triarylaminotriazines, the dianils of dimedone and indane-1 : 3-dione, benziminazole, and di-(2-methyl-3-indenyl)methine.

NN′-*Diarylformamidines.*—Most of the formamidines were colourless or pale yellow crystalline solids. A few were more deeply coloured, such as the symmetrical compounds derived from *p*-aminoazobenzene (orange), 2-aminofluorenone (red), and 3-aminofluorenone (reddish-orange). *N*-2-Anthraquinonyl-*N*′-phenylformamidine was orange-yellow.

Cuprous derivatives. Most of these were obtained from the parent formamidines by one or both of two methods.

(1) Reaction with cupric acetate in ethanol. This succeeded with compounds which were readily oxidised, *e.g.*, the di-*p*-alkylphenyl and di-*p*-alkoxyphenyl members, but the more stable ones, *e.g.*, *NN*′-di-*p*-nitrophenylformamidine, which did not reduce cupric acetate, did not yield cuprous derivatives by this method. The maximum molar yield obtainable did not exceed one-half of the amount of formamidine employed. In several

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[1] Bradley and Leete, *J.*, 1951, 2147.
[2] Shriner and Neumann, *Chem. Rev.*, 1944, **35**, 351.
[3] Cf. Mizumo and Nishimura, *J. Pharm. Soc. Japan*, 1948, **68**, 58.
[4] Bollert, *Ber.*, 1883, **16**, 1639.

instances, as with the *NN'*-di-*p*-acetylphenyl and *NN'*-di-*p*-methylsulphonyl members, there was evidence that the formamidines were decomposed by the solvent.[5] *NN'*-Di-*p*-chlorophenylformamidine formed a stable addition compound with cupric acetate.

With the less soluble symmetrical formamidines, *e.g.*, those derived from 2-aminoanthraquinone and 2-aminoanthracene, nitrobenzene was preferred to alcohol, but even in this medium scission of the formamidine to the component amines was observed with the *NN'*-di-*p*-nitrophenyl and *NN'*-di-2-fluorenonyl compounds. Yields obtained by reaction in boiling nitrobenzene sometimes exceeded those obtained in alcohol; it may be mentioned in this connection that cupric acetate yields cuprous acetate at high temperatures.[6]

(2) A more general method was to mix pyridine solutions of the formamidines and cuprous chloride, the latter in twice the theoretical amount, to add then sufficient of a standard solution of potassium hydroxide or methoxide in methanol, and finally to add the whole to water. After purification 80—90% yields of the cuprous derivatives were obtained.

The cuprous derivatives were solids, mostly crystalline, which gave analyses correct for the expected compound. Solubility varied with structure, the di-*p*-*n*-butoxyphenyl member being soluble in cold benzene, whilst cuprous *NN'*-di-2-anthraquinonylformamidine was insoluble in hot nitrobenzene; the majority were soluble to some degree in benzene or chlorobenzene. In a series of *pp'*-disubstituted derivatives of *NN'*-diphenylformamidine the solubility in organic solvents diminished in the order $Bu^nO > Bu^tO > EtO > MeO > Me > H > Cl > Ac > NO_2$. All the cuprous derivatives melted and then decomposed, the majority in the range 220—360°. That of *NN'*-di-*p*-*n*-butoxyphenylformamidine melted without decomposition at 163°. Colour was generally similar to that of the parent formamidine except with *NN'*-di-2-anthraquinonyl (red-violet), *NN'*-di-2-fluorenonyl (blue-violet), and *NN'*-di-3-fluorenonyl (red-violet); *N*-2-anthraquinonyl-*N'*-phenylformamidine afforded a violet cuprous derivative. Stability towards chemical reagents varied with structure; none was so inert as cuprous *NN'*-di-2-anthraquinonylformamidine.[1] All were stable towards cold, N-potassium hydroxide, but all reacted slowly with cold aqueous sodium sulphide, potassium cyanide, and N-hydrochloric acid except the *NN'*-di-2-anthraquinonyl compound. The cuprous derivatives showed no tendency to oxidation by air, even when moist. Their behaviour in hot pyridine varied considerably. Cuprous *NN'*-diphenylformamidine could be crystallised from this medium, though decomposition occurred when the heating was more than brief, but the cuprous compounds of *NN'*-di-*p*-nitrophenyl- and *NN'*-di-*p*-acetylphenyl-formamidine were transformed into cupric derivatives which then crystallised with 4 mols. of the solvent.

Silver derivatives. These were usually prepared by the addition of a solution of silver acetate in pyridine to one of the formamidine in pyridine or methanol. All were obtained crystalline. Their solubilities in organic solvents were generally higher than those of the cuprous derivatives; the silver compounds of the 4 : 4'-dimethoxy-, 4 : 4'-diethoxy-, and 4 : 4'-di-*n*-butoxy-derivatives of *NN'*-diphenylformamidine were soluble in benzene and the di-*n*-butoxy-compound was soluble also in light petroleum (b. p. 60—80°). All decomposed on being heated. Their colours varied with structure in the same way as the cuprous compounds, and in the several examples investigated the absorption spectra of the silver and the cuprous compounds were closely similar. None was markedly sensitive to light.

NN'-*Diarylacetamidines and* NN'-*Diarylbenzamidines.*—Most of the methods of preparing the cuprous derivatives of *NN'*-diarylformamidines failed with the corresponding acetamidines and benzamidines. The cuprous derivatives of *NN'*-di-2-anthraquinonyl- and *NN'*-di-*p*-nitrophenyl-benzamidine resulted when the parent compounds were heated with copper bronze in nitrobenzene but the method was not generally useful. The cuprous derivatives which were isolated resembled the corresponding formamidine compounds closely, except that cuprous *NN'*-di-2-anthraquinonylformamidine was much more stable than the related benzamidine.[1] Silver derivatives could not be prepared.

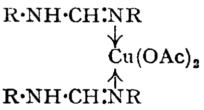
Related Compounds.—2-*p*-Nitroanilinoquinoline afforded a yellow cuprous derivative with copper in nitrobenzene. Benziminazole gave a grey product by method (2), but this

[5] Cf. Dains, *Ber.*, 1902, **35**, 2498.
[6] Sidgwick, " Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, p. 126.

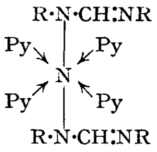
changed to the known red cupric compound[7] on contact with ammonia and ammonium chloride. Glutacondialdehyde dianil afforded a violet cuprous derivative by method (2), and an analogous compound was prepared from the di-*p*-chloro-anil; unlike the parent dianils both cuprous derivatives were stable and also unaffected by ammonia–ammonium chloride. Acetylacetone dianil gave a cupric derivative when it was brought into contact with an ammoniacal cupric solution. Indane-1 : 3-dione dianil and cupric acetate in ethanol or cuprous chloride in pyridine gave a deep red cuprous derivative which was unstable towards aqueous ammonia.

Cupric Derivatives of NN′-*Diarylformamidines.*—*NN*′-Diphenyl- and *NN*′-di-*p*-tolyl-formamidine combined with cupric acetate to form green, unstable complexes having the composition (I). Attempts to replace two atoms of hydrogen by one atom of copper in two mols. of *NN*′-di-2-anthraquinonylformamidine were unsuccessful, but tetrapyridine adducts of analogous copper and nickel compounds of *NN*′-di-*p*-nitrophenylformamidine were prepared; the copper compound readily lost two mols. of pyridine on being heated.

Structure of the Metal Derivatives of NN′-*Diarylamidines.*—*NN*′-Diarylamidines form potassium derivatives which have the properties of salts of weak acids; as such they are easily hydrolysed by water with liberation of the parent amidine. In addition *NN*′-diphenyl- and *NN*′-di-*p*-tolyl-formamidine are able to function as simple donors. They yield adducts with cupric acetate which contain two mols. of the amidine to one of the cupric salt and are soluble in benzene and decomposed by water; the adducts behave as fully covalent compounds. Thus the *NN*′-diphenylformamidine–cupric acetate compound has a molecular weight of 506 in benzene (cryoscopic) [$C_{26}H_{24}N_4,Cu(C_4H_6O_4)$ requires 574]. The cupric and nickel derivatives, in which one atom of metal replaces two atoms of hydrogen in two mols. of an amidine and the product combines with pyridine, are presumably co-ordination compounds also, the nickel derivative being represented by (II).



(I)



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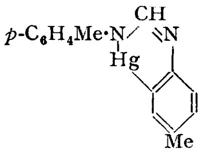

(III)

Mercuric acetate reacts with *NN*′-di-*p*-tolylformamidine to form a derivative, $C_{15}H_{14}N_2Hg$, which with iodine affords *N*-(2-iodo-4-methylphenyl)-*N*′-phenylformamidine. The most probable structure of the mercury compound appears to be (III).

Especially interesting are the cuprous and silver derivatives which are formed by all the formamidines investigated. They have the character of inner complexes.[1] Unlike the cupric compounds referred to they are stable to water, aqueous ammonia, and generally also aqueous ammonia containing ammonium chloride. In cuprous *NN*′-di-2-anthraquinonylformamidine the metal has replaced hydrogen which was attached to nitrogen in the parent compound, because the same cuprous derivative results whether *NN*′-di-2-anthraquinonylformamidine or its *N*-methyl derivative is used in the preparation; when the *N*-methyl derivative is used the methyl group is eliminated.[1] The close correspondence in properties suggests that the same kind of Cu–N bond is present in all the cuprous derivatives and an analogous Ag–N bond in the related silver compounds. The decomposition of cuprous *NN*′-diphenylformamidine with hydrochloric acid under nitrogen liberates copper in the form of cuprous ions only. As to the size of the molecules, determinations of the molecular weights of cuprous and silver compounds in benzene by the ebullioscopic method gave the results shown in the following Table. The three compounds investigated are thus tetrameric in boiling benzene but this is not necessarily so for all cuprous and silver compounds under all circumstances. The parent *NN*′-diarylformamidines are associated[8] and cyclic dimeric and linear polymer forms have been proposed.[8, 9] Similar considerations

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[7] Cf. Skraup, *Annalen*, 1919, **419**, 70.

[8] Roberts, *J. Amer. Chem. Soc.*, 1950, **72**, 3608

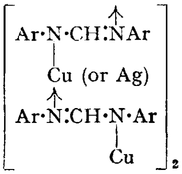
[9] Hunter and Marriott, *J.*, 1941, 777.

apply to the *NN′*-diarylacetamidines and *NN′*-diarylbenzamidines.[9] In associating, the *NN′*-diarylformamidines resemble the analogously constituted 1 : 3-diaryltriazens.[10] The metal derivatives of the latter have been examined by Dwyer [11] who concludes that the cuprous and silver derivatives of 1 : 3-diphenyltriazen are monomeric in benzene and contain a 4-membered ring. Under the conditions we have employed we found cuprous 1 : 3-diphenyltriazen to be considerably associated (Found : *M*, 1136, 998, 804. Calc. for $C_{12}H_{10}N_3Cu$: *M*, 260·6). A decision as to the structure of the tetrameric cuprous and silver derivatives of the *NN′*-diarylformamidines is not possible in the absence of *X*-ray crystallographic measurements but a cyclic form involving four molecules of the metal derivative in which each atom of copper or silver is linked to nitrogen, the nitrogen–metal bonds being linear, appears most probable (cf. IV). Other metal derivatives may be linear polymers which contain the same repeating unit as (IV); indeed a linear polymer form appears to be the more probable for such compounds as the dicuprous derivatives (V) and the cuprous derivatives of glutacondialdehyde dianil and the di-*p*-chloro-anil (VI; Ar = Ph or *p*-C_6H_4Cl).

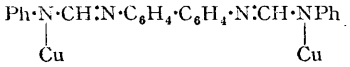
Derivative	Mol. wt. found	4 × Formula weight
Cuprous *NN′*-di-*p*-*n*-butoxyphenylformamidine	1650	1610
Silver *NN′*-di-*p*-methoxyphenylformamidine	1450	1451
Silver *NN′*-di-*p*-*n*-butoxyphenylformamidine	1875	1788

Inner complexes have been prepared previously from a number of cyclic vinylogues of the formamidines. *o*-Aminobenzaldimine forms a green, and pyrrole-2-aldimine a red, cupric derivative.[12] Similar properties are shown by 2-2′-pyridylpyrrole,[13] 2-alkylimino-methylpyrroles,[14] the 2 : 2′-dipyrrylazomethines,[15] the 2 : 2′-dipyrrylmethines,[16] and the phthalocyanines.[17] Indeed, cuprous complexes appear to be restricted to those derived from 1 : 3-diphenyltriazen,[11] di-(2-methyl-3-indenyl)methine,[18] di-(3 : 5-dimethyl-2-pyrryl)*meso*phenylmethine,[15] and those now reported. With the formamidines the ready polarizability of the anion doubtless contributes to the stability of the cuprous form.[19]

(IV)

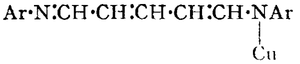


$$\left[\begin{array}{l} \text{Ar·N·CH:}\overset{\uparrow}{\text{N}}\text{Ar} \\ \quad | \\ \quad \text{Cu (or Ag)} \\ \quad \uparrow \\ \text{Ar·N:CH·N·Ar} \\ \qquad\quad | \\ \qquad\quad \text{Cu} \end{array}\right]_2$$



$$\underset{\substack{|\\ \text{Cu}}}{\text{Ph·N}}\text{·CH:N·C}_6\text{H}_4\text{·C}_6\text{H}_4\text{·N:CH·}\underset{\substack{|\\ \text{Cu}}}{\text{N}}\text{Ph}$$

(V)



$$\text{Ar·N:CH·CH:CH·CH:CH·}\underset{\substack{|\\ \text{Cu}}}{\text{N}}\text{Ar}$$

(VI)

EXPERIMENTAL

NN′-*Diarylformamidines.*—Several *NN′*-diarylformamidines were prepared by methods described in the literature. New symmetrical compounds were prepared by heating ethyl orthoformate with primary amines; all unsymmetrical compounds were obtained by the action of ethyl*iso*formanilide on primary amines (Table 1). Additional details are given in Table 2. 2-Aminoanthraquinone (2·2 g.) and ethyl*iso*formanilide (2·0 g.) gave *N*-2-anthraquinonyl-*N′*-phenylformamidine (1·0 g.; orange-yellow needles from chlorobenzene, readily soluble in pyridine) and *NN′*-di-2-anthraquinonylformamidine (0·9 g.).

NN′-*Di*-(N-*phenylformimidoyl*)*benzidine.*—Benzidine (4·5 g.) and ethyl*iso*formanilide (8 g.) were heated to 180° during 0·5 hr. and kept thereat for 0·5 hr. The solid product was cooled and extracted with benzene; the *diformamidine* separated and was crystallised from benzene

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[10] Hunter, *J.*, 1937, 320.
[11] Dwyer, *J. Amer. Chem. Soc.*, 1941, **63**, 78, *J. Soc. Chem. Ind.*, 1939, **58**, 110.
[12] Pfeiffer, *J. prakt. Chem.*, 1937, **149**, 217.
[13] Emmert and Brandl, *Ber.*, 1927, **60**, 2211.
[14] Emmert, Diehl, and Gollwitzer, *Ber.*, 1929, **62**, 1733.
[15] Rogers, *J.*, 1943, 596.
[16] Fischer and Schubert, *Ber.*, 1923, **56**, 1202; 1924, **57**, 611; Fischer and Ammann, *Ber.*, 1923, **56**, 2319; Porter, *J.*, 1938, 368; Rogers, *J.*, 1943, 596.
[17] Barrett, Dent, and Linstead, *J.*, 1936, 1719.
[18] Kunz and Stühlinger, *Ber.*, 1925, **58**, 1860; Schmitz-Dumont and Motzkus, *Ber.*, 1928, **61**, 580.
[19] Randles, *J.*, 1941, 802.

TABLE 1. NN′-*Diarylformamidines.*

NN′-Subst.	H·C(OEt)$_3$ (g.)	Amine (g.)	Yield (g.)	Colour [a]	Solvent
p-$C_6H_4Bu^t$	5	7·5	3·0	Colourless	Pet [b]
p-C_6H_4·OBu^n	5	8·25	7·0	,,	,,
o-C_6H_4·NO_2	7	10·3	1·0	Yellow	EtOH
p-C_6H_4Ac	7·5	6·8	5·9	Yellow	C_6H_6
p-C_6H_4·SO_2·Me	5	8	7·5	White (amorphous)	
p-C_6H_4·CO_2Et	5	8	7·5	Colourless	C_6H_6
2-Fluorenyl	2	3·6	1·9	Yellow	PhCl
2-Fluorenonyl	3	4	2	Red	$PhNO_2$
5-Quinolyl	0·8	1·4	0·7	Colourless	C_6H_6

[a] Needles, except as stated. [b] Light petroleum of b. p. 60—80°.

TABLE 2. NN′-*Diarylformamidines.*

		Found (%)				Required (%)		
NN′-Subst. [a]	M. p.	C	H	N	Formula	C	H	N
p-$C_6H_4Bu^t$	163°	81·5	9·3	9·2	$C_{21}H_{28}N_2$	81·8	9·1	9·1
p-C_6H_4·OBu^n	98—99	74·2	7·9	8·4	$C_{21}H_{28}O_2N_2$	74·1	8·2	8·2
o-C_6H_4·NO_2	161	54·1	3·3	19·7	$C_{13}H_{10}O_4N_4$	54·5	3·5	19·6
p-C_6H_4Ac	172	72·7	5·7	10·1	$C_{17}H_{16}O_2N_2$	72·9	5·7	10·1
p-C_6H_4·SO_2·Me	218—221	51·3	4·9	8·2	$C_{15}H_{16}O_4N_2S_2$	51·1	4·6	8·0
p-C_6H_4·CO_2Et	191	67·5	6·0	8·2	$C_{19}H_{20}O_4N_2$	67·1	5·9	8·2
2-Fluorenyl	253—254	87·4	4·9	7·6	$C_{27}H_{20}N_2$	87·1	5·4	7·5
2-Fluorenonyl	264—265	81·3	3·8	6·8	$C_{27}H_{16}O_2N_2$	81·0	4·0	7·0
5-Quinolyl	203	—	—	18·5, 18·9	$C_{19}H_{14}N_4$	—	—	18·8

[a] N-2-*Anthraquinonyl*-N′-*phenylformamidine* has m. p. 235—236° (Found: C, 77·3; H, 4·1; N, 8·9. $C_{21}H_{14}O_3N_2$ requires C, 77·3; H, 4·3; N, 8·6%).

(m. p. 225—226°) and then from chlorobenzene (5 g.; m. p. 225°) (Found: C, 79·8; H, 5·9; N, 14·1. $C_{26}H_{22}N_4$ requires C, 80·0; H, 5·6; N, 14·4%).

N-(2-*Iodo*-4-*methylphenyl*)-N′-p-*tolylformamidine*.—2-Iodo-4-methylaniline (4·6 g.) and ethyl-4-*iso*formamidotoluene (3·5 g.) were heated for 2 hr. at 180°. The cooled product was a thick oil which crystallised on being stirred with light petroleum (15 c.c.; b. p. 60—80°). The solid product was collected, washed with light petroleum (yield, 3·4 g.), and crystallised from benzene; it had m. p. 154—155° (Found: C, 52·1; H, 4·1; N, 7·7; I, 35·8. $C_{15}H_{15}N_2I$ requires C, 51·4; H, 4·3; N, 8·0; I, 36·3%).

Cuprous NN′-*Diphenylformamidine*.—(*a*) Cupric acetate (1 g.) and *NN*′-diphenylformamidine (1 g.; m. p. 139°, cf. Claisen [20]) were refluxed for 1 hr. in ethanol (40 c.c.). Needles (0·3 g.) separated and were collected and washed with hot ethanol. *Cuprous* NN′-*diphenylformamidine* crystallised from benzene and chlorobenzene in pale yellow needles, m. p. 310° (decomp.) (Found: C, 60·2; H, 4·3; N, 10·8; Cu, 24·5. $C_{13}H_{11}N_2Cu$ requires C, 60·3; H, 4·3; N, 10·8; Cu, 24·6%). It was insoluble in alcohol and water. (*b*) The same product (0·5 g.) resulted in the following experiment. Cupric acetate (0·5 g.) was dissolved in dilute aqueous ammonia. Air was displaced from the solution by means of nitrogen and an excess of hydrazine sulphate was added. The resulting colourless solution was mixed under nitrogen with one of *NN*′-diphenylformamidine (0·5 g.) in ethanol. The voluminous precipitate was collected and then kept in contact with aqueous ammonia–ammonium chloride for 48 hr. The residue was collected, washed with water, then with ethanol, and crystallised from chlorobenzene.

Silver NN′-*diphenylformamidine* resulted when a filtered solution of silver acetate (0·9 g.) in pyridine (10 c.c.) was added slowly to one of *NN*′-diphenylformamidine (1 g.) in methanol (15 c.c.). The precipitate was collected, washed with a small volume of pyridine and methanol, and then kept in contact with cold dilute ammonia for 24 hr. Silver *NN*′-diphenylformamidine crystallised from a small volume of pyridine as needles, m. p. 260° (decomp.) (Found: C, 51·8; H, 3·8; N, 9·2; Ag, 35·8. $C_{13}H_{11}N_2Ag$ requires C, 51·5; H, 3·6; N, 9·2; Ag, 35·7%). The same derivative was formed on addition of an alcoholic solution of *NN*′-diphenylformamidine to one of silver acetate in dilute ammonia.

Cuprous NN′-*di*-p-*methoxyphenylformamidine*.—Equimolar amounts of cuprous chloride and *NN*′-di-*p*-methoxyphenylformamidine were refluxed for 1 hr. in dry ethanol. The suspension, filtered while hot, gave a grey residue and this was stirred with dilute aqueous ammonia. The

[20] Claisen, *Annalen*, 1895, **287**, 366.

insoluble derivative crystallised from benzene as greenish-yellow needles, m. p. 269—270°, without prior decomposition, and as pale yellow needles, m. p. 269—270°, from dioxan or dioxan–ethanol (Found : C, 56·5; H, 5·0; N, 9·2; Cu, 19·8. $C_{15}H_{15}O_2N_2Cu$ requires C, 56·5; H, 4·7; N, 8·8; Cu, 20·0%).

Cuprous NN'-*Di*-o-*chlorophenylformamidine*.—Cuprous chloride (1 g.) was dissolved in hot pyridine under nitrogen, and the resulting solution was passed into a warm solution of *NN'*-di-*o*-chlorophenylformamidine (1·3 g.) in pyridine. Methanolic potassium hydroxide (2·5 c.c. of 2N) was added, and the mixture was shaken and poured into water. Concentrated aqueous ammonia was added to the resulting suspension and after some hours the solid was collected, washed with aqueous ammonia, then with ethanol, and finally boiled with ethanol (150 c.c.). The white insoluble residue of *cuprous* NN'-*di*-o-*chlorophenylformamidine* crystallised from chlorobenzene as colourless needles (0·7 g.), m. p. 287° (decomp.) (Found : C, 47·7; H, 3·0; N, 8·4; Cl, 22·0; Cu, 19·1. $C_{13}H_9N_2Cl_2Cu$ requires C, 47·6; H, 2·8; N, 8·6; Cl, 21·7; Cu, 19·4%). This product was identical with the cuprous derivative prepared from *NN'*-di-*o*-chlorophenylformamidine (1 g.) and cupric acetate (1 g.) in ethanol (40 c.c.) (Found : C, 47·7; H, 2·9%).

Details of other cuprous and silver compounds are given in Tables 3 and 4. *NN'*-Di-(*N*-phenylformimidoyl)benzidine (0·9 g., 0·0025 mol.) and cuprous chloride (2·0 g.) in pyridine under nitrogen gave a greenish-yellow *dicuprous derivative* (Found : Cu, 22·5. $C_{26}H_{20}N_4Cu_2$ requires Cu, 24·7%) on addition to a fine suspension of potassium methoxide (0·005 mol.) in pyridine. *Cuprous* N-p-*nitrophenyl*-N'-*phenylformamidine*, yellow needles (from *o*-dichlorobenzene), m. p. >300° (Found : C, 51·5; H, 3·4; N, 13·9, Cu, 20·7. $C_{13}H_{10}O_2N_3Cu$ requires C, 51·4; H, 3·3; N, 13·8; Cu, 21·0%) and N-2-*anthraquinonyl*-N'-*phenylformamidine*, a violet powder (Found : N, 7·4; Cu, 17·1. $C_{21}H_{13}O_2N_2Cu$ requires N, 7·2; Cu, 16·4%), were prepared by method (*c*) (see Table 3). *Silver* N-p-*nitrophenyl*-N'-*phenylformamidine*, yellow needles (from pyridine), has m. p. 264—265° (Found : C, 45·1; H, 3·0; N, 12·4; Ag, 31·0. $C_{13}H_{10}O_2N_3Ag$ requires C, 44·8; H, 2·9; N, 12·1; Ag, 31·0%).

TABLE 3. *Cuprous derivatives of* NN'-*diarylformamidines.*

	Method	M. p.	Found (%)					Required (%)			
NN'-Subst.	of prep.	(decomp.)	C	H	N	Cu	Formula	C	H	N	Cu
p-C_6H_4Me	(*a*)	330—332°	63·0	5·4	9·9	21·8	$C_{15}H_{15}N_2Cu$	62·8	5·2	9·8	22·2
p-$C_6H_4Bu^t$	(*a*)	397 *	67·7	7·3	7·2	17·2	$C_{21}H_{27}N_2Cu$	68·0	7·3	7·6	17·2
p-$C_6H_4{\cdot}OEt$ ...	(*a*)	220	—	—	7·8	18·0	$C_{17}H_{19}O_2N_2Cu$	—	—	8·1	18·4
p-$C_6H_4{\cdot}OBu^n$ ...	(*a*)	163	63·0	6·9	7·4	15·4	$C_{21}H_{27}O_2N_2Cu$	62·6	6·7	7·0	15·8
p-C_6H_4Cl	(*c*)	318—320	47·4	3·1	8·3	—	$C_{13}H_9N_2Cl_2Cu$	47·6	2·8	8·6	—
p-$C_6H_4{\cdot}NO_2$ ...	(*c*)	>400	44·8	2·8	15·8	17·8	$C_{13}H_9O_4N_4Cu$	44·7	2·6	16·1	18·2
p-C_6H_4Ac	(*c*)	†	59·1	4·7	18·3	18·1	$C_{17}H_{15}O_2N_2Cu$	59·5	4·4	8·2	18·6
p-$C_6H_4{\cdot}CO_2Et$	(*c*)	320	56·5	4·7	6·8	15·7	$C_{19}H_{19}O_4N_2Cu$	56·6	4·7	7·0	15·8
p-$C_6H_4{\cdot}N_2Ph$ ...	(*c*)	336—338	64·2	4·2	17·9	—	$C_{25}H_{19}N_6Cu$	64·3	4·1	18·0	—
2-Anthryl	(*d*)	—	75·4	3·9	6·0	13·9	$C_{29}H_{19}N_2Cu$	75·9	4·1	6·1	13·9
2-Fluorenonyl	(*c*)	—	—	—	6·0	13·8	$C_{27}H_{15}O_2N_2Cu$	—	—	6·1	13·7
5-Quinolyl	(*c*)	235 ‡	—	—	—	17·9	$C_{19}H_{13}N_4Cu$	—	—	—	17·6

* Decomp. from 350°. † Decomp. without melting above 220°. ‡ Darkens at 230°.

Methods of prep.: (*a*) cupric acetate in alcohol; (*b*) cuprous chloride in alcohol; (*c*) cuprous chloride in pyridine; (*d*) cupric acetate in nitrobenzene.

TABLE 4. *Silver derivatives of* NN'-*diarylformamidines.*

	M. p.	Found (%)					Required (%)			
NN'-Subst.	(decomp.)	C	H	N	Ag	Formula	C	H	N	Ag
p-$C_6H_4{\cdot}OMe$	205°	49·7	4·3	7·9	29·8	$C_{15}H_{15}O_2N_2Ag$	49·5	4·1	7·7	29·7
p-$C_6H_4{\cdot}OEt$	215	52·4	4·9	7·1	27·6	$C_{17}H_{19}O_2N_2Ag$	52·2	4·9	7·2	27·6
p-$C_6H_4{\cdot}OBu^n$	185	56·6	6·6	6·1	24·4	$C_{21}H_{27}O_2N_2Ag$	56·4	6·0	6·3	24·2
p-$C_6H_4{\cdot}NO_2$	318	39·5	2·2	14·2	27·1	$C_{13}H_9O_4N_4Ag$	39·7	2·3	14·3	27·5
p-C_6H_4Ac	—	52·9	3·8	7·3	27·3	$C_{17}H_{15}O_2N_2Ag$	52·7	3·9	7·2	27·9

Oxidation State of Copper in Cuprous NN'-*Diphenylformamidine*.—The copper derivative of *NN'*-diphenylformamidine (0·07 g.) was dissolved in concentrated hydrochloric acid (5 c.c.) under nitrogen. The solution so obtained was passed into 20 c.c. of an aqueous solution of sodium acetate (10 g.); a fine white suspension of the metal-free formamidine resulted. On the addition of potassium iodide (1 g.) in water (5 c.c.) there was no liberation of iodine, and on the further addition of aqueous ammonia only a very faint blue colour developed; contact with air caused rapid oxidation of the cuprous ion to the cupric state.

Silver NN′-*Di*-2-*anthraquinonylformamidine*.—An equivalent of potassium dissolved in methanol was added to a suspension of *NN′*-di-2-anthraquinonylformamidine (0·4 g.) in dry pyridine (100 c.c.). A deep blue colour developed; conversion into the potassium salt was completed by heating the suspension for 15 min. under reflux. A solution of silver acetate (0·2 g.) in pyridine (25 c.c.) was then added and refluxing was continued for 5 min.; the colour changed to violet-brown. The cooled suspension was then filtered, and the residue washed with water, then with cold aqueous ammonia. On being dried the *product* became paler and browner (Found: Ag, 18·5. $C_{29}H_{16}O_4N_2Ag$ requires Ag, 19·2%). Exposure of the dry solid to ammonia fumes restored the dark violet-brown colour.

NN′-*Di*-p-*nitrophenylacetamidine*.—*p*-Nitroacetanilide (1·8 g.) was added to a solution of phosphorus pentachloride (2·3 g.) in nitrobenzene (30 c.c.) which had been prepared at 100° and then cooled. The mixture was heated at 120° until a clear solution resulted (2 hr.). *p*-Nitroaniline (1·4 g.) was added and the heating was continued at 140° for 3 hr. On being cooled and kept the solution afforded crystals; these were collected and decomposed by the addition of ammonia. NN′-*Di*-p-*nitrophenylacetamidine* crystallised from ethanol as yellow needles, m. p. 261—262° (softening at 252°) (Found: C, 56·2; H, 4·3; N, 18·9. $C_{14}H_{12}O_4N_4$ requires C, 56·0; H, 4·0; N, 18·7%).

NN′-*Di*-2-*anthraquinonylacetamidine*.—Prepared analogously from 2-acetamidoanthraquinone (13·25 g.) and phosphorus pentachloride (12 g.) in nitrobenzene (100 c.c.) with subsequent addition of 2-aminoanthraquinone (12 g.), this *product* (10 g.) crystallised from pyridine as yellow needles, m. p. 350—352° (Found: C, 76·5; H, 3·7; N, 5·9. $C_{30}H_{18}O_4N_2$ requires C, 76·6; H, 3·8; N, 6·0%).

p-*Nitro*-NN′-*diphenylbenzamidine*.—Prepared from *p*-nitrobenzanilide (6 g.) by heating with a solution of phosphorus pentachloride (6 g.) in nitrobenzene and further treatment of the product with aniline (2·4 g.), this *amidine* crystallised from ethanol as yellow plates, m. p. 157° (Found: C, 71·4; H, 4·8; N, 13·1. $C_{19}H_{15}O_2N_3$ requires C, 71·9; H, 4·7; N, 13·2%). The cuprous derivative resulted when the benzamidine (3·6 g.) and copper bronze (1 g.) were refluxed for 3·5 hr. in nitrobenzene (25—30 c.c.). On being filtered the suspension yielded a residue; this was washed with acetone and then treated for 72 hr. with a concentrated solution of ammonium chloride in ammonia (*d* 0·88). The resulting solid was collected, washed free from copper salts, and extracted with acetone. *Cuprous* p-*nitro*-NN′-*diphenylbenzamidine* forms brown needles (yellow on being crushed) (Found: C, 53·3; H, 3·4; N, 13·0; Cu, 15·0. $C_{19}H_{13}O_4N_4Cu$ requires C, 53·7; H, 3·1; N, 13·2; Cu, 15·0%).

Reaction of Cuprous Chloride with Glutacondialdehyde Dianil.—A solution of cuprous chloride (1 g.) in pyridine was added to one of glutacondialdehyde dianil[21] (1 g.) in pyridine. Methanolic potassium methoxide (1·4 c.c. of 2N) was added, all the manipulations being done under nitrogen. The mixture was shaken, then added to water; a brown precipitate was formed. Concentrated aqueous ammonia was added, and the precipitate was collected, then stirred with ammonia, again collected, then dried *in vacuo*. The resulting solid was extracted with acetone; a purple residue remained which decomposed at 175° (Found: C, 61·1, 64·5; H, 4·5, 4·0; N, 9·0; Cu, 19·9, 19·6. $C_{17}H_{15}N_2Cu$ requires C, 65·7; H, 4·8; N, 9·0; Cu, 20·5%). The combined copper was not removed on extraction with aqueous ammonia–ammonium chloride. The copper derivative was slightly soluble in benzene with a deep red-violet colour which rapidly faded to yellow.

Similar treatment of glutacondialdehyde di-(*p*-chloroanil) hydrochloride[21] (1 g.) with cuprous chloride (1 g.) and methanolic potassium methoxide (3 c.c. of 2N) gave a purplish-brown, copper-containing product which decomposed at 200—201° (Found: Cu, 15·9. Calc. for $C_{17}H_{13}N_2Cl_2Cu$: Cu, 17·1%).

Copper Derivative of Acetylacetone Dianil.—(*a*) Application of the procedure used with glutacondialdehyde dianil to acetylacetone dianil hydrochloride (1·43 g.), cuprous chloride (1 g.), and methanolic potassium methoxide (5 c.c. of 2N) gave dark green material most of which was soluble in acetone. Evaporation of the extract under reduced pressure gave black plates which afforded the *cupric derivative* as a green powder, m. p. 157—158° (on being crushed); the m. p. was unaltered after further crystallisation from acetone (Found: C, 72·5; H, 6·0; N, 9·9; Cu, 11·3. $C_{34}H_{34}N_4Cu$ requires C, 72·6; H, 6·1; N, 10·0; Cu, 11·3%). (*b*) The same cupric compound, m. p. and mixed m. p. 157—158°, resulted from the action of ammoniacal cupric acetate on acetylacetone dianil hydrochloride.

[21] Zincke, *Annalen*, 1904, **333**, 296.

2-p-*Nitroanilinoquinoline*.—2-Chloroquinoline (5 g.) and *p*-nitroaniline (5 g.) were heated at 180° for 1·5 hr. The cooled melt was crushed and then extracted with alcohol (600 c.c.). The filtered solution afforded crystals (5·5 g.) and these on further purification from alcohol gave 2-p-*nitroanilinoquinoline* as yellow-orange needles, m. p. 229° (Found : C, 68·2; H, 4·4; N, 16·0. $C_{15}H_{11}O_2N_3$ requires C, 67·9; H, 4·2; N, 15·9%). On being refluxed for 5 hr. with copper bronze (0·25 g.) and nitrobenzene (20 c.c.) 2-*p*-nitroanilinoquinoline (0·6 g.) afforded a *cuprous derivative*. This was obtained, mixed with copper bronze, when the suspension was cooled. The unchanged metal was dissolved by treatment with a solution of ammonium chloride in concentrated aqueous ammonia, and the residual yellow needles were collected, washed, and then extracted with alcohol (Found : C, 54·6; H, 3·3; N, 12·9; Cu, 19·7. $C_{15}H_{10}O_2N_3Cu$ requires C, 55·0; H, 3·1; N, 12·8; Cu, 19·4%). In hot pyridine it gave a solution which was red initially but changed to yellow on boiling.

Mercury Derivative of NN′-*Di*-p-*tolylformamidine*.—Mercuric acetate (1·6 g.) and *NN*′-di-*p*-tolylformamidine (1·1 g.) were refluxed in ethanol (40 c.c.). After 30 mins. a clear yellow solution resulted, from which on further heating a yellow solid separated. The solid was collected from the hot suspension and crystallised from pyridine. The *mercury derivative* formed pale yellow needles, m. p. 320° (Found : C, 42·9; H, 3·5; N, 6·8. $C_{15}H_{14}N_2Hg$ requires C, 42·6; H, 3·3; N, 6·6%), insoluble in water and unaffected on brief heating with aqueous ammonia or sodium sulphide.

Reaction with iodine. A suspension of the mercury derivative (2·5 g.) in ethanol (50 c.c.) was refluxed with an ethanol solution (18 c.c.) of iodine (2·28 g.); reaction was complete in 15 min. The resulting solution was cooled, a small amount of solid was filtered off, and water was added to the filtrate. A sticky reddish precipitate formed; this was stirred with potassium iodide and the resulting granular solid was collected, treated with charcoal in alcohol, and reprecipitated by addition to aqueous potassium iodide. The yellow solid was collected, dried (yield, 0·9 g.), and crystallised from benzene–light petroleum (b. p. 60—80°). It formed white crystals, m. p. 151—152° (Found : N, 8·2; I, 36·2. Calc. for $C_{15}H_{15}N_2I$: N, 8·0; I, 36·3%), which did not depress the m. p. of *N*-(2-iodo-4-methylphenyl)-*N*′-*p*-tolylformamidine. Iodine (0·127 g.) in ethanol (1 c.c.) did not react with *NN*′-di-*p*-tolylformamidine (0·45 g.) in boiling ethanol (20 c.c.) during 2 hr.

Cupric Complexes.—(*a*) A solution of cupric acetate (0·5 g.) and *NN*′-diphenylformamidine (1 g.) in methanol was evaporated under reduced pressure until crystallisation occurred. The resulting suspension was cooled in ice-salt and the deep green crystals which separated were collected, dried *in vacuo*, and recrystallised (yield, 0·7 g.) by dissolution in benzene and addition of light petroleum (b. p. 60—80°). *Bis*-(NN′-*diphenylformamidine*)*cupric acetate* shrinks at 164° (Found : C, 63·0; H, 5·3; N, 9·6; Cu, 10·8. $C_{30}H_{30}O_4N_4Cu$ requires C, 62·8; H, 5·2; N, 9·8; Cu, 11·1%); it is dissociated into *NN*′-diphenylformamidine and cupric salt by contact with water.

(*b*) Similar treatment of *NN*′-di-*p*-tolylformamidine (1 g.) gave *bis*-(NN′-*di*-p-*tolylformamidine*)-*cupric acetate* (1 g.) as green crystals which shrink at 173° (Found : C, 65·3; H, 6·0; N, 8·9; Cu, 10·0. $C_{34}H_{38}O_4N_4Cu$ requires C, 64·8; H, 6·0; N, 8·9; Cu, 10·1%).

(*c*) (i) A hot solution of cupric acetate (1 g.) in pyridine was added to one of *NN*′-di-*p*-nitrophenylformamidine (2·86 g.) in hot pyridine; a deep red colour developed. On the addition of methanolic potassium methoxide (5 c.c. of 2N) the colour changed to deep red-violet and crystals separated when the solution was kept for 12 hr. These were heated with pyridine (150 c.c.), and the solution was then filtered; blue-violet rhomboidal plates of *bis*-(NN′-*di*-p-*nitrophenylformamidine*)*tetrapyridinecopper* separated, which were red by transmitted light and lost 2 mols. of pyridine at 120° in 144 hr. [Found : Cu, 6·9; di-*p*-nitrophenylformamidine, 60·6; C_5H_5N, 31·5. $(C_{13}H_9O_4N_4)_2Cu(C_5H_5N)_4$ requires Cu, 6·7; di-*p*-nitrophenylformamidine, 60·0; C_5H_5N, 33·3. Loss on being heated, C_5H_5N, 16·4. Required : $2C_5H_5N$, 16·63%]. (ii) the same compound resulted when cuprous *NN*′-di-*p*-nitrophenylformamidine (1·5 g.) was refluxed for 15 min. with pyridine (150 c.c.). A suspension was formed and the whole was filtered. A yellow residue (0·6 g.) was obtained and a blue-green filtrate from which bis-(*NN*′-di-*p*-nitrophenylformamidine)tetrapyridinecopper separated (Found : Cu, 7·1; di-*p*-nitrophenylformamidine, 58·4; C_5H_5N, 32·1%).

Bis-(NN′-*di*-p-*nitrophenylformamidine*)*tetrapyridinenickel*.—In a similar preparation to (*c*) (i) but with anhydrous nickel acetate (0·86 g.), the corresponding *nickel compound* resulted. Repeated crystallisation from pyridine gave hexagonal prisms which were deep blue-violet by reflected and ruby-red by transmitted light (Found : C, 56·4; H, 4·3; N, 17·9. $C_{46}H_{38}O_8N_{12}Ni$ requires C, 58·3; H, 4·0; N, 17·8%). This compound was readily decomposed by water, dilute acid, or ammonia; pyridine was liberated on contact with dilute aqueous sodium hydroxide [Found: Ni, 6·4; C_5H_5N, 33·0; di-*p*-nitrophenylformamidine, 58·9. Calc. for $(C_{13}H_9O_4N_4)_2$, $Ni(C_5H_5N)_4$: Ni, 6·2; C_5H_5N, 33·5; di-*p*-nitrophenylformamidine, 60·5%].

Absorption Spectra.—See Table 5.

TABLE 5. *Absorption spectra* $\lambda_{max.}$ (mμ) ($10^{-4}\varepsilon$ in parentheses).

Compound	In dioxan	In benzene	In *cyclo*hexane
NN'-Diphenylformamidine	—	284 (1·95)	—
Cu(I) derivative	—	324 (1·67)	—
NN'-Di-*p*-*n*-butoxyphenylformamidine	294 (2·74)	296 (2·45)	291 (2·48)
Cu(I) derivative	256 (2·3), 317 (1·9)	318 (1·82)	256 (2·33), 315 (1·74)
Ag derivative	245 (1·25), 310 (1·88)	—	256 (1·65), 307 (1·75)

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