Formamide as a Precursor to Cyanide in Mixed-valence Copper(I,II) Cyanide Complexes

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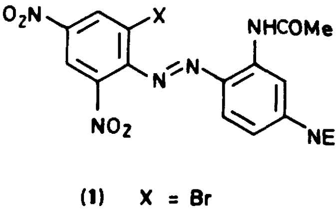
Copper(I) acetate reacts with acetic anhydride–formamide (1 : 1) in acetonitrile solution to give $[Cu_2(O_2CMe)(CN)]$ or $[Cu_2(CN)_2(NCMe)]$. Anhydrous copper(II) acetate reacts with the same reagent to give $[Cu(NCMe)_4][Cu_2(CN)_4]$ and $[Cu(O_2CMe)_2(HCONH_2)]$. The influence of various polar solvents on the products of the reaction is evaluated. The complex $[Cu(NCMe)_4)][Cu_2(CN)_4]$ reacts with unidentate nitrogen-donor ligands, L, to form $[CuL_4][Cu_2(CN)_4]$ (L = pyridine or 4-methylpyridine) or $[CuL_3][Cu_2(CN)_4]$ (L = 2-methylpyridine or 2,6-dimethylpyridine). With bidentate nitrogen-donor ligands, L–L, substitution in $[Cu(NCMe)_4][Cu_2(CN)_4]$ gives $[Cu(L\text{–}L)_2(NCMe)][Cu_2(CN)_4]$ (L–L = 1,2-diaminoethane or 2,2′-bipyridine). The insoluble complex products are obtained in good yield and characterized by microanalysis and spectroscopy (i.r. and visible reflectance). The role of copper ions in promoting the dehydration of formamide by acetic anhydride is assessed.

The use of copper(I) cyanide to substitute halogen in aryl halides by cyanide is well known and widely used.[1] Polar donor solvents are known to assist the reaction,[2] but very little is known about either the copper species which effects the substitution or the mechanism of the reaction. Efforts have been made in recent years to avoid the direct use of copper(I) cyanide and to improve the efficiency of this useful reaction because of increasingly significant environmental and economic considerations. The patent literature describes[3] a mild and efficient cyanation process in which copper(I) iodide, sodium acetate, formamide, and acetic anhydride are used in the synthesis of aryl cyanides.

From the outset it was assumed that the role of the copper salts is to promote the dehydration of formamide by acetic anhydride [equation (1)], but the fate of the hydrogen cyanide

$$HCONH_2 + (MeCO)_2O \longrightarrow HCN + 2\,MeCOOH \quad (1)$$

produced was not known. A survey of various simple copper compounds as promoters of the cyanation of the 2-halogenodiarylazo compound (1) to give (2) by formamide in the presence of acetic anhydride under standard conditions showed that



(1) X = Br
(2) X = CN

the rate of reaction decreased in the order $[Cu_2(O_2CMe)_4] >$ CuI $\sim Cu(O_2CMe) > [Cu(NCMe)_4][PF_6]$, although the differences are not great (*ca.* three-fold). Some copper compounds (*e.g.* $CuBr_2$) are inactive. Investigation of the reaction between CuI or $[Cu(NCMe)_4][PF_6]$ and acetic anhydride–formamide (1 : 1) in acetonitrile gave in each case a golden-yellow solution of a thermally labile, air- and moisture-sensitive species which effects the cyanation of (1), but from which no cyanide- or formamide-containing copper complex could be isolated. Therefore we have concentrated attention on acetate-containing systems. We shall show that a variety of cyanide-containing complexes of copper are formed when either copper(I) acetate or copper(II) acetate reacts with formamide in the presence of acetic anhydride.

Results and Discussion

(*a*) *Reactions of Copper*(I) *Acetate*.—Heating equimolar proportions of copper(I) acetate, acetic anhydride, and formamide in acetonitrile solution at reflux produces a very pale blue solution from which a very air- and moisture-sensitive bluish white solid complex $[Cu_2(O_2CMe)(CN)]$ was isolated in good yield. The complex dissolves in acetonitrile in the presence of a trace of acetic acid or acetic anhydride and can be recovered intact. In other polar solvents (acetone, ethanol) the complex dissociates to its components, copper(I) acetate and copper(I) cyanide. In addition to two strong, broad carboxylate absorptions (1 525 and 1 430 cm^{-1}), the i.r. spectrum of the complex contains two absorptions assigned to CH_3 deformation (1 352m and 1 341m cm^{-1}) and two ν(CN) absorptions (2 153s and 2 142s cm^{-1}) which are close to, but different from, the corresponding values for $Cu(O_2CMe)$ (1 345 cm^{-1}) and CuCN (2 172 cm^{-1}) under the same conditions. A consistent interpretation would indicate a structure in which the $\{Cu_2(O_2CMe)_2\}$ dimeric unit found[4] in the structure of copper(I) acetate is linked to a polymeric[5] CuCN chain.

If the ratio of acetic anhydride–formamide (1 : 1) to copper(I) acetate is increased from 1 : 1 to 2 : 1 a different product is obtained by refluxing the mixture in acetonitrile. Air- and moisture-sensitive colourless crystals of $[Cu_2(CN)_2(NCMe)]$ are obtained in good yield by cooling the pale blue-green reaction solution. This complex can also be prepared by cooling a hot solution of copper(I) cyanide in acetonitrile. The i.r. spectrum of this complex contains three absorptions (2 165m, 2 098s, and 2 067w cm^{-1}) which are assigned to anionic cyanide, and one absorption (2 265m cm^{-1}) assigned to co-ordinated acetonitrile. The former group of wavenumbers is similar to that reported[6] for $[Cu_2(CN)_2(NH_3)]$ (2 135, 2 090, and 2 065 cm^{-1}).

(*b*) *Reactions of Copper*(II) *Acetate.*—Anhydrous copper(II) acetate (1 mol) reacts with acetic anhydride–formamide (1 : 1) (4 mol) in acetonitrile at reflux to form a green precipitate in a dark green solution. The green solid, isolated in good (80%) yield, is the mixed-valence copper(I,II) complex $[Cu_3(CN)_4(NCMe)_4]$. When the ratio of acetic acid–formamide (1 : 1) to copper(II) acetate is reduced from 4 : 1 to 3 : 1 the yield of $[Cu_3(CN)_4(NCMe)_4]$ is also reduced and the formamide adduct of copper(II) acetate $[Cu(O_2CMe)_2(HCONH_2)]$ can be isolated from the mother-liquor. When the formamide adduct is heated at reflux in acetonitrile solution with acetic anhydride the adduct is converted into $[Cu_3(CN)_4(NCMe)_4]$ only. When the reaction between copper(II) acetate and acetic anhydride–formamide is done in air rather than dinitrogen, neither of the previously mentioned products is isolated. Instead, an off-white precipitate of $[Cu(CN)(NCMe)]$ is produced which gradually decomposes in air, losing acetonitrile to form $[Cu_2(CN)_2(NCMe)]$. Similar behaviour has been observed[6] for $[Cu(CN)(NH_3)]$ which decomposes in air to $[Cu_2(CN)_2(NH_3)]$.

The i.r. spectrum of $[Cu_3(CN)_4(NCMe)_4]$ contains two ν(CN) absorptions (2 151vs and 2 112vs cm^{-1}) which are at very similar frequencies to those reported[6] for $[Cu_3(CN)_4(NH_3)_4]$ (2 130 and 2 100 cm^{-1}) and for $[Cu_3(CN)_4(NH_3)_3]$ (2 136 and 2 111 cm^{-1}). The crystal structure of $[Cu_3(CN)_4(NH_3)_3]$ shows[7] that it is $[Cu(NH_3)_3][Cu_2(CN)_4]$. By analogy, we suggest that the complex $[Cu_3(CN)_4(NCMe)_4]$ is to be represented as $[Cu(NCMe)_4][Cu_2(CN)_4]$. The weak ν(CN) absorptions (2 265 and 2 252 cm^{-1}) are assigned to the acetonitrile ligands in this complex. The splitting may be explained by the inequivalence of the ligands bound to tetragonally distorted copper(II). This could be produced if the $[Cu(NCMe)_4]^{2+}$ ion is not square planar as in $[Cu(NCMe)_4][SnCl_6]$ [which shows only one ν(CN) absorption in the i.r.],[8] but is distorted octahedral as a result of co-ordination through nitrogen to two cyanides of the polymeric $[Cu_2(CN)_4]^{2-}$ ion. The nitrile ν(CN) absorption wavenumbers of $[Cu(NCMe)_4][Cu_2(CN)_4]$ are the lowest recorded for any acetonitrile complex of copper(II) to date and are not much different from that of free acetonitrile (2 250 cm^{-1}). This indicates that the acetonitrile is only weakly bound to copper(II) in the cation. Consistent with this, the complex decomposes very readily in air, releasing acetonitrile. The visible reflectance spectrum of $[Cu(NCMe)_4][Cu_2(CN)_4]$ contains a broad absorption centred at 16 700 cm^{-1}, the asymmetry of which is typical of tetragonally distorted copper(II) complexes. The rather high energy of this absorption is consistent with the *cis*-octahedral geometry proposed.

It is known that the particular solvent used does influence the rate of halide substitution by cyanide in aryl halides.[2] We have examined the influence of various polar solvents on the copper(II) acetate–acetic anhydride–formamide (1 : 4 : 4) reaction at 355 K (a common temperature, close to the boiling point of acetonitrile, was chosen for the purpose of comparison). In most cases (propionitrile, benzonitrile, benzyl cyanide, ethyl acetate, and nitromethane) a precipitate of copper(I) cyanide was isolated from the reaction mixture. Apart from acetonitrile, which gives $[Cu(NCMe)_4][Cu_2(CN)_4]$, only isobutyronitrile and pyridine (py) produce complexes of copper(I) cyanide. The former is a pale pink solid, $[Cu_4(CN)_4(Pr^iCN)]$ and the latter is the yellow complex $[Cu(CN)(py)_2]$ which decomposes in air to give the well known white adduct[9] $[Cu(CN)(py)]$. The i.r. spectrum of $[Cu_4(CN)_4(Pr^iCN)]$ contains ν(CN) absorptions at 2 243m cm^{-1}, assigned to the co-ordinated Pr^iCN, and at 2 142s and 2 105s cm^{-1} assigned to co-ordinated cyanide. Free Pr^iCN absorbs at 2 237 cm^{-1}; the small frequency difference suggests that the ligand is not strongly bound to copper in the complex.

(*c*) *Reactions of* $[Cu(NCMe)_4][Cu_2(CN)_4]$ *with Unidentate Donor Ligands.*—The lability of co-ordinated acetonitrile in $[Cu(NCMe)_4][ClO_4]$ which is displaced by pyridine to give[10] $[Cu(py)_4][ClO_4]$, suggested that it might be possible to carry out similar substitution reactions at copper(II) in $[Cu(NCMe)_4][Cu_2(CN)_4]$. Addition of an excess of any one of the unidentate ligands pyridine, 2-, 4-methylpyridine, and 2,6-dimethylpyridine to a suspension of $[Cu(NCMe)_4][Cu_2(CN)_4]$ in acetonitrile causes precipitation of the substitution product. When only 4 equivalents of the unidentate ligand are used no reaction is observed. With excess of pyridine and 4-methylpyridine (4Me-py) the product is $[Cu_3(CN)_4L_4]$ (L = py or 4Me-py), which are purple solids insoluble in acetonitrile. When $[Cu_3(CN)_4(py)_4]$ is suspended in acetonitrile the colour gradually changes from purple to the green of $[Cu_3(CN)_4(NCMe)_4]$; the colour reverts to purple when pyridine is added to the suspension. The complex $[Cu_3(CN)_4(py)_4]$ is air stable and insoluble in most common solvents. The purple colour of the complexes $[Cu_3(CN)_4L_4]$ corresponds to that of $[CuL_4]X_2$ ($X = ClO_4$ or BF_4)[11] and is evidence that the complexes have the form $[CuL_4][Cu_2(CN)_4]$ (L = py or 4Me-py). In the case of $[Cu(4Me\text{-}py)_4][Cu_2(CN)_4]$, the violet solid decomposes quite rapidly in the solid state to give the known[9] beige-brown $[Cu(CN)(4Me\text{-}py)]$. The i.r. spectrum of $[Cu(py)_4][Cu_2(CN)_4]$ shows two strong ν(CN) absorption bands at 2 101 and 2 088 cm^{-1} which are at significantly lower wavenumbers than for $[Cu(NCMe)_4][Cu_2(CN)_4]$ described above, and closer to those (2 095 and 2 088 cm^{-1}) reported[12] for $[Cu(en)_2][Cu_2(CN)_4]$ (en = 1,2-diaminoethane). This suggests that there are discrete $[Cu(py)_4]^{2+}$ ions within the polymeric $[Cu_2(CN)_4]^{2-}$ framework. The pyridine absorptions in the i.r. spectrum of this mixed-valence complex are generally shifted to higher wavenumbers relative both to free pyridine and to the co-ordinated pyridine in the copper(I) complex $[Cu(CN)(py)_2]$, which provides further evidence for the co-ordination of py to copper(II) in $[Cu(py)_4][Cu_2(CN)_4]$. The pyridine i.r. absorptions, particularly the ring-deformation modes, are split. This is consistent with the expected tetragonal distortion of the cation located in the voids of the polymeric $[Cu_2(CN)_4]^{2-}$ structure such as is found[13] in the structure of $[Cu(en)_2(OH_2)][Cu_2(CN)_4]$. Splitting of the absorptions due to pyridine ring-deformation vibrations is not observed[14] in the i.r. spectra of $[Cu(py)_4]X_2$ (X = Cl, Br, SCN, or BF_4), presumably because of geometrical constraints imposed by the small monoanion on the copper(II) cation. The visible reflectance spectrum of $[Cu(py)_4][Cu_2(CN)_4]$ contains pyridine-to-copper(II) charge-transfer (c.t.) transitions above 22 000 cm^{-1} and two bands at 14 500 and 13 300 cm^{-1}. The energies of these bands are significantly lower than in other $[Cu(py)_4]X_2$ ($X = ClO_4$, BF_4, or PF_6) complexes,[11,15] in agreement with a change in geometry. There is no evidence of intervalence c.t. absorption at low energy in the visible/near-i.r. absorption spectrum of this complex.

The addition of either 2-methylpyridine or 2,6-dimethylpyridine in excess to $[Cu(NCMe)_4][Cu_2(CN)_4]$ produces a green precipitate of $[Cu_3(CN)_4L_3]$ (L = 2Me-py or $2,6Me_2$-py). The fact that four acetonitrile ligands are replaced by only three 2-methyl-substituted pyridine ligands is an indication of the steric crowding at copper(II). Similar observations have been reported[16] for the substitution of aquo-ligands in copper(II) perchlorate which produces $[Cu(py)_4][ClO_4]$ and $[Cu(2Me\text{-}py)_3][ClO_4]$. The i.r. spectrum of $[Cu_3(CN)_4(2Me\text{-}py)_3]$ contains three strong ν(CN) absorptions (2 148, 2 133, and 2 122 cm^{-1}) and that of $[Cu_3(CN)_4(2,6Me_2\text{-}py)_3]$ contains two strong absorptions (2 145 and 2 130 cm^{-1}) of which the one at lower wavenumbers is remarkably broad, which may suggest that the envelope contains two bands which are close together. The relatively high frequencies of these vibrations indicate that both bridging and terminal cyanide ligands are linked to the three-co-ordinate copper(I) sites in the polymeric

$[Cu_2(CN)_4]^{2-}$ ion. The i.r. absorptions of the neutral heterocyclic ligand in both these complexes are shifted to higher wavenumbers from the free-ligand values, and the ring-deformation modes show small splittings indicating once again that these neutral ligands attached to copper(II) are not equivalent. In the structure[7] of $[Cu_3(CN)_4(NH_3)_3]$ the copper(II) atom is octahedral because the three NH_3 ligands are distributed over four positions with the other two *cis* positions occupied by nitrogen atoms of CN groups. The visible reflectance spectrum of $[Cu_3(CN)_4(2,6Me_2\text{-}py)_3]$ contains lutidine-to-copper(II) c.t. transitions above 22 000 cm^{-1} and an asymmetric absorption centred at 14 800 cm^{-1}. Evidence from the spectra[17] of $[Cu(NCS)_2L_3]$ (L is a methyl-substituted pyridine) suggests that the cation in $[Cu_3(CN)_4(2,6Me_2\text{-}py)_3]$ has a distorted trigonal-bipyramidal structure which is consistent with the evidence from i.r. spectroscopy.

(*d*) *Reaction of* $[Cu(NCMe)_4][Cu_2(CN)_4]$ *with Bidentate Donor Ligands*.—The green, air-sensitive $[Cu_3(CN)_4(NCMe)_4]$ suspended in acetonitrile reacts with 1,2-diaminoethane at room temperature to give a violet solution from which a violet solid complex $[Cu_3(CN)_4(en)_2(NCMe)]$ is isolated. This complex is only sightly soluble in 1,2-diaminoethane, otherwise it is insoluble in most common solvents. The solid must be stored in an inert atmosphere. A change of colour from violet to lilac indicates that the solid complex reacts with moist air to give $[Cu_3(CN)_4(en)_2(OH_2)]$ which has been prepared[18] by addition of 1,2-diaminoethane to an aqueous solution of $[Cu_3(CN)_4(NH_3)_n]$ (n = 2—3). The i.r. spectrum of $[Cu_3(CN)_4(en)_2(NCMe)]$ shows three absorbances which are assigned to ν(CN) (2 090m, 2 072s, and 2 053m cm^{-1}). Two of these are at wavenumbers close to those in the i.r. spectrum of $[Cu_3(CN)_4(en)_2(OH_2)]$ (2 090 and 2 075 cm^{-1}). A five-co-ordinate $[Cu(en)_2(NCMe)]^{2+}$ ion, analogous to the distorted square-pyramidal $[Cu(en)_2(OH_2)]^{2+}$ structure established[13] by *X*-ray diffraction analysis of $[Cu_3(CN)_4(en)_2(OH_2)]$, appears to be most likely.

2,2′-Bipyridine reacts with $[Cu_3(CN)_4(NCMe)_4]$ suspended in acetonitrile at room temperature. The green suspension gradually turns dark brown. The brown solid product $[Cu_3(CN)_4(bipy)_2(NCMe)]$ is insoluble in all common solvents and slowly absorbs moisture from the air. The i.r. spectrum of this complex shows two cyanide ν(CN) absorptions (2 125s and 2 102vs cm^{-1}) which are at higher wavenumbers than those of $[Cu_3(CN)_4(py)_4]$ and $[Cu_3(CN)_4(en)_2(NCMe)]$ and are close to the values reported[12] for $[Cu_3(CN)_4(NH_3)_4]$ (2 130 and 2 100 cm^{-1}). The ν(CN) of the co-ordinated acetonitrile ligand (2 305m cm^{-1}) implies that this is bound quite strongly. The bipy ligand vibrations in the complexes are generally shifted to higher wavenumbers and many of the bands show splittings which are consistent with the two bipy ligands being in slightly different environments.

Conclusions

The dehydration of formamide by acetic anhydride forms hydrogen cyanide which reacts rapidly with copper(I) acetate to form simple cyano-complexes of copper(I), and with copper(II) acetate to produce either a copper(I) or a mixed-valence copper(I,II) cyano-complex, depending on the solvent used. The release of free HCN was not detected. The structure of the mixed-valence complex $[Cu_3(CN)_4(NCMe)_4]$ is formulated as $[Cu(NCMe)_4][Cu_2(CN)_4]$ on the basis of spectroscopic comparisons, in which there is a *cis*-octahedral structure at the copper(II) cation as a result of its being linked through two terminal cyano-groups in the polymeric $[Cu_2(CN)_4]^{2-}$ ion.

The co-ordinated acetonitrile ligands in $[Cu(NCMe)_4][Cu_2(CN)_4]$ are substituted by various unidentate ligands, L, to give $[CuL_4][Cu_2(CN)_4]$ (L = py or 4Me-py) or, when the ligand is sterically demanding, $[CuL_3][Cu_2(CN)_4]$ (L = 2Me-py or 2,6Me-py). Substitution of acetonitrile by bidentate ligands, L–L, produces $[Cu_3(CN)_4(L\text{–}L)_2(NCMe)]$ (L–L = en or bipy): the structures of these could not be reliably deduced from their spectra, but it is likely that they should be formulated as $[Cu(L\text{–}L)_2(NCMe)][Cu_2(CN)_4]$ with a five-co-ordinate cation.

We have examined the reactions of some of these cyano-complexes with aryl halides. We find that they can cause the substitution of halide by cyanide at room temperature. This work will be reported elsewhere.

Experimental

All reactions were carried out using reagents of the highest available purity and solvents were purified by distillation, dried, and then purged with dry, deoxygenated dinitrogen prior to use. Reactions were always carried out under dinitrogen unless specifically stated otherwise, using Schlenk techniques and a gas/vacuum manifold. I.r. spectra were recorded on KBr plates as Nujol and as hexachlorobutadiene mulls. Anhydrous copper(II) acetate was prepared by heating the reagent-grade hydrated compound *in vacuo* (0.1 mmHg) at 363—373 K for 8—10 h. Dehydration was confirmed by i.r. spectra of the solid. Anhydrous copper(I) acetate was prepared by reduction of anhydrous copper(II) acetate with copper bronze in excess, in acetonitrile to which acetic anhydride and glacial acetic acid were added.

Acetato(cyano)dicopper(I).—Copper(I) acetate (1.22 g, 10 mmol) was stirred in acetonitrile (100 cm^3) forming a yellow suspension. Acetic anhydride (0.94 cm^3, 10 mmol) and formamide (0.40 cm^3, 10 mmol) were stirred into the mixture and this was heated to reflux (355 K) for 2 h. The pale blue solution was cooled to room temperature and the acetonitrile solvent removed by distillation under reduced pressure. The residue was washed with light petroleum (b.p. 40—60 °C) dichloromethane (2:1 v/v) (100 cm^3) and then with diethyl ether before being dried *in vacuo* (0.80 g, 75% yield) (Found: C, 18.0; H, 1.6; Cu, 59.4; N, 6.1. Calc. for $C_3H_3Cu_2NO_2$: C, 17.0; H, 1.4; Cu, 59.9; N, 6.6%). I.r.: 2 950m, 2 910m, 2 855m, 1 040m, 686s, and 604s cm^{-1}.

Acetonitrile(dicyano)dicopper(I).—Copper(I) acetate (1.22 g, 10 mmol) was stirred at room temperature in acetonitrile (100 cm^3). Acetic anhydride (1.88 cm^3, 20 mmol) and formamide (0.80 cm^3, 20 mmol) were added and the mixture heated at reflux for 4 h, forming a very pale blue-green solution. Small needle-like colourless crystals separated on cooling to room temperature (0.75 g, 68% yield) (Found: C, 21.8; H, 1.5; Cu, 58.4; N, 18.3. Calc. for $C_4H_3Cu_2N_3$: C, 21.8; H, 1.4; Cu, 57.7; N, 19.1%). I.r.: 2 994m, 2 929m, 1 372m, 1 025m,br, and 723w cm^{-1}.

Tetrakis(acetonitrile)copper(II) *Tetracyanodicuprate*(I).—Anhydrous copper(II) acetate (1.81 g, 10 mmol) in acetonitrile (100 cm^3) was stirred at room temperature. Formamide (1.59 cm^3, 40 mmol) and acetic anhydride (3.78 cm^3, 40 mmol) were added to the blue-green solution, and the mixture was then heated at reflux (355 K) for 17 h (overnight) to give a green precipitate in a dark green solution. The green solid was isolated by filtration, washed with diethyl ether, and then dried (1.22 g, 80% yield) (Found: C, 31.7; H, 2.5; Cu, 40.8; N, 25.0. Calc. for $C_{12}H_{12}Cu_3N_8$: C, 31.4; H, 2.6; Cu, 41.5; N, 24.4%). I.r.: 2 917m, 1 376m, 1 026m, 939m, 920m, 487s, 422m, and 418m cm^{-1}. The mother-liquor contained $[Cu(O_2CMe)_2(HCONH_2)]$ (Found: C, 26.5; H, 4.0; Cu, 28.2; N, 6.2. Calc. for $C_5H_9CuNO_5$: C, 26.5; H, 4.0; Cu, 28.0; N, 6.2%).

$[Cu_4(CN)_4(Pr^iCN)]$.—Anhydrous copper(II) acetate (1.81 g, 10 mmol) was suspended in dry isobutyronitrile (100 cm^3) and then formamide (1.59 cm^3, 40 mmol) and acetic anhydride (3.78 cm^3, 40 mmol) were added. The mixture was heated at 355 K overnight. The solid product precipitated and was isolated by filtration, washed with ether, and dried (Found: C, 21.5; H, 1.4; Cu, 61.1; N, 16.0. Calc. for $C_8H_7Cu_4N_5$: C, 22.5; H, 1.6; Cu, 59.5; N, 16.4%). I.r.: 2 980m, 2 925m, 1 442m, 1 360m, and 1 305m cm^{-1}. The yellow solid complex $[Cu(CN)(py)_2]$ was prepared in a similar manner (Found: C, 53.7; H, 4.2; Cu, 25.1; N, 17.0. Calc. for $C_{11}H_{10}CuN_3$: C, 53.3; H, 4.1; Cu, 25.6; N, 17.0%). I.r.: 3 080m, 3 050m, 2 100vs, 2 080m (sh), 1 607w, 1 596vs, 1 567m, 1 478s, 1 439vs, 1 381w, 1 350w, 1 239vw, 1 208m, 1 143s, 1 064s, 1 028s, 996s, 752s, 699vs, 668w, 615w, 610m, and 415m cm^{-1}.

Tetrakis(pyridine)copper(II) *Tetracyanodicuprate*(I).—A suspension of $[Cu_3(CN)_4(NCMe)_4]$ (0.46 g, 1 mmol) in acetonitrile (50 cm^3) was stirred at room temperature. Pyridine (5 cm^3) was added to the mixture which was stirred for 1 h, after which the precipitated purple solid was isolated by filtration, washed with ether, and then dried *in vacuo* (Found: C, 46.6; H, 3.3; Cu, 31.5; N, 18.6. Calc. for $C_{24}H_{20}Cu_3N_8$: C, 47.2; H, 3.3; Cu, 31.2; N, 18.3%). I.r.: 1 605s, 1 597s, 1 580m, 1 548w, 1 537w, 1 475m, 1 461w, 1 447vs, 1 441s, 1 221w, 1 214m, 1 156m, 1 071s, 1 042m, 1 033w, 1 017m, 1 008w, 1 004 (sh), 762s, 756m, 749m, 699vs, 638m, 628w, and 440m cm^{-1}.

Tris(2-methylpyridine)copper(II) *Tetracyanodicuprate*(I).—2-Methylpyridine (5 cm^3) was added to a suspension of $[Cu_3(CN)_4(NCMe)_4]$ (0.46 g, 1 mmol) in acetonitrile and the mixture was stirred at room temperature for 1 h, after which the emerald-green precipitate was isolated by filtration, washed with ether, and dried *in vacuo* (Found: C, 45.4; H, 3.7; Cu, 34.1; N, 16.8. Calc. for $C_{22}H_{21}Cu_3N_7$: C, 46.0; H, 3.7; Cu, 33.2; N, 17.1%). I.r.: 1 606vs, 1 567m, 1 489s, 1 482s, 1 461s, 1 424w, 1 383w, 1 377w, 1 303m, 1 295w, 1 158s, 1 110m, 1 060m, 1 023m, 1 017w, 803w, 765vs, 760vs, 724s, 647w, 479m, and 437m cm^{-1}. Using the same procedure with 2,6-dimethylpyridine gave *tris(2,6-dimethylpyridine)copper*(II) *tetracyanodicuprate*(I) (Found: C, 48.4; H, 4.4; Cu, 31.7; N, 15.5. Calc. for $C_{25}H_{30}Cu_3N_7$: C, 48.7; H, 4.4; Cu, 30.9; N, 15.9%). I.r.: 1 609s, 1 579s, 1 557w, 1 484m, 1 466vs, 1 450m, 1 433m, 1 383m, 1 372w, 1 196w, 1 162m, 1 159m, 1 120vw, 1 104m, 1 053w, 1 033m, 785vs, 722w, 706m, 481m, and 436m cm^{-1}.

Acetonitrilebis(1,2-diaminoethane)copper(II) *Tetracyanodicuprate*(I).—Anhydrous 1,2-diaminoethane (0.13 cm^3, 2 mmol) was added to a stirred suspension of $[Cu_3(CN)_4(NCMe)_4]$ (0.46 g, 1 mmol) in acetonitrile (50 cm^3). The mixture became violet in colour over 7 h of stirring at room temperature. The violet solid precipitate was isolated by filtration, was washed with ether, and dried *in vacuo* (Found: C, 26.3; H, 4.3; Cu, 41.6; N, 27.8. Calc. for $C_{10}H_{19}Cu_3N_9$: C, 26.3; H, 4.2; Cu, 41.8; N, 27.7%). I.r.: 3 321s, 3 303s, 3 269m, 3 225m, 1 582s, 1 321w, 1 038s, and 1 016s cm^{-1}.

Acetonitrilebis(2,2′-bipyridine)copper(II) *Tetracyanodicuprate*(I).—2,2′-Bipyridine (0.31 g, 2 mmol) was added gradually to a stirred suspension of $[Cu_3(CN)_4(NCMe)_4]$ (0.46, g 1 mmol) in acetonitrile. The colour of the suspension changed gradually from green to dark brown during 1 h. The suspension was isolated by filtration, washed with acetone and then ether, and then dried *in vacuo* (Found: C, 49.6; H, 2.8; Cu, 29.0; N, 18.6. Calc. for $C_{26}H_{19}Cu_3N_9$: C, 48.2; H, 3.0; Cu, 29.4; N, 19.4%). I.r.: 3 060w, 2 925m, 1 610m, 1 597s, 1 470w, 1 448m, 1 440m, 1 317w, 1 309w, 1 260w, 1 250w, 1 220w, 1 160w, 1 155w, 1 027w, 761s, 731m, and 651m cm^{-1}.

Acknowledgements

We thank the S.E.R.C. and I.C.I. plc, Organics Division for the award of a C.A.S.E. studentship (to D. G.).

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Received 13*th May* 1985; *Paper* 5/790