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# Formaldehyde Oxime as a Precursor to Cyanide in Mixed-valence Copper(I,II) Complexes. Hydration of Nitrile Solvents

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Copper(II) acetate reacts with formaldehyde oxime (1 : 1) in a nitrile solvent, RCN at *ca.* 350 K to give a pale blue-green complex $[Cu_3(O_2CMe)_5(RCONH_2)(CH_2NOH)_2]$ (R = Me or Ph). The complex having R = Me reacts with acetic anhydride in acetonitrile to give CuCN, $[Cu_2(O_2CMe)_4(OH_2)_2]$, and $[Cu_2(CN)_2(NCMe)]$, and with pyridine (py) to give $[Cu(O_2CMe)(CH_2NOH)_2]$, $[Cu_2(O_2CMe)_4(py)_2]$, and acetamide.

The patent literature describes a mild and efficient cyanation process in which a copper salt, and either formaldoxime (formaldehyde oxime) or formamide are used in the synthesis of aryl cyanides from a corresponding aryl halide.[1] We have described some features of the co-ordination chemistry of copper in the presence of formamide and acetic anhydride which acts as a dehydrating agent.[2] We have investigated the use of formaldoxime which also acts as a precursor of cyanide under similar conditions.

## Experimental

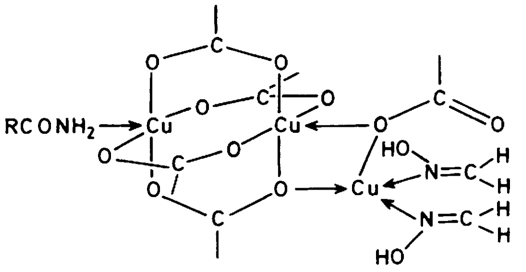
General experimental methods used are described in an earlier paper.[2] Formaldoxime polymer[3] was prepared as follows. Potassium carbonate (69.1 g, 0.5 mol) was added gradually to a mixture of hydroxyammonium chloride (69.6 g, 1 mol) in water (50 $cm^3$). When effervescence had ceased, the mixture was cooled in ice and then aqueous formaldehyde solution (73 $cm^3$ of approximately 37% v/v) was added dropwise. The mixture was stirred overnight at room temperature; the white precipitate was isolated by filtration, washed well with hot water, and then suspended in ethanol (100 $cm^3$). The fine white suspension was isolated, washed with diethyl ether (100 $cm^3$), and dried in air. Yield 24.4 g, 0.54 mol.

*Reaction of Copper*(II) *Acetate with Formaldoxime Polymer* (1:1) *in Nitrile Solvents,* RCN (R = Me *or* Ph).—Copper(II) acetate (1.81 g, 10 mmol) was stirred with the nitrile RCN (100 $cm^3$). Formaldoxime polymer (0.45 g, 10 mmol) was added and the mixture was heated at 350 K for *ca.* 17 h (overnight), then allowed to cool to room temperature. The blue-green reaction mixture contained a precipitate which was isolated as a pale green solid by filtration. The mother-liquor was evaporated under reduced pressure to form an oil which was triturated with diethyl ether, producing a pale blue-green solid. Investigation of the diethyl ether extracts revealed the presence of the amide, $RCONH_2$ (R = Me or Ph). The blue-green solid complex isolated from acetonitrile was shown to be (acetamide)penta-acetatobis(formaldoxime)tricopper(I,II) (Found: C, 26.8; H, 4.1; Cu, 29.9; N, 6.3. Calc. for $C_{14}H_{26}Cu_3N_3O_{13}$: C, 26.5; H, 4.1; Cu, 30.0; N, 6.6%). I.r.: 3 435s, 3 333m, 2 925m, 1 692m, 1 648s, 1 637s, 1 597vs br, 1 430vs bs, 1 395s, 1 356m, 1 348m, 1 043m, 1 034m, 721m, 683s, 640s, 623s, and 580m $cm^{-1}$. $\nu_{max.}$ (*k*/*s*) (*k* = absorption coefficient and *s* = scattering coefficient[4]): 24 400 (0.40), 15 600 (1.06), 14 900 (1.22), 14 600 (1.25), and 13 900 (1.14) $cm^{-1}$. Fast-atom bombardment mass spectrum (f.a.b.m.s.) ($MeCN-Me_2SO$ matrix): *m*/*z* 634 $(M + H)^+$, 588 $(M - CH_2NOH)^+$, and 543 $[M - 2(CH_2NOH)]^+$. The blue-green solid complex isolated from benzonitrile was shown to be penta-acetato(benzamide)bis(formaldoxime)tricopper(I,II) (Found: C, 32.0; H, 3.8; Cu, 26.8; N, 5.2. Calc. for $C_{19}H_{28}Cu_3N_3O_{13}$: C, 32.7; H, 4.1; Cu, 27.3; N, 6.0%). I.r.: 3 415s, 3 330m, 3 301m, 3 250m, 3 065w, 2 928m, 1 675m, 1 648s, 1 610vs br, 1 574s, 1 447s, 1 429s br, 1 351w, 1 098w, 768w, 721w, 690m, 680m, and 630m $cm^{-1}$. $\nu_{max.}$ (*k*/*s*): 24 400 (0.44), 18 200 (0.2), 14 900 (1.40), 14 600 (1.58), and 13 500 (1.38) $cm^{-1}$.

*Reaction of* $[Cu_3(O_2CMe)_5(MeCONH_2)(CH_2NOH)_2]$ *with Pyridine.*—Pyridine (1 $cm^3$) was added to the tricopper complex (0.64 g, 1 mmol) in acetonitrile (50 $cm^3$) solution and the mixture was stirred at room temperature for 1 h. The reaction mixture was filtered and then evaporated under reduced pressure to give an oil. The oil was treated with diethyl ether to precipitate a solid which was isolated by filtration. The filtrate was evaporated to leave a white solid which was identified as acetamide. The solid was treated with methanol which resulted in the separation of $[Cu(O_2CMe)(CH_2NOH)_2]$, a pale green solid (Found: C, 22.8; H, 3.8; Cu, 30.3; N, 12.9. Calc. for $C_4H_9CuN_2O_4$: C, 22.6; H, 4.3; Cu, 29.9; N, 13.2%). I.r.: 3 270s br, 2 925m, 1 685 (sh), 1 580s br, 1 410s br, 1 375s, 1 146m, 1 036m, 966s, 838s, and 719m $cm^{-1}$. $\nu_{max.}$ (*k*/*s*): 28 900 (1.10), 25 900 (0.72), and 24 400 (0.45) $cm^{-1}$. F.a.b.m.s. ($MeCN-Me_2SO$ matrix): *m*/*z* 211 $(M - H)^+$, 167 $(M - CH_2NOH)^+$, and 122 $[M - 2(CH_2NOH)]^+$. $[Cu(O_2CMe)_2(py)]$ was also separated, as a green-blue solid from the mother-liquor (Found: C, 40.8; H, 4.3; Cu, 24.0; N, 5.4. Calc. for $C_9H_{11}CuNO_4$: C, 41.5; H, 4.2; Cu, 24.4; N, 5.4%).

## Results and Discussion

The reaction between copper(II) acetate and formaldoxime polymer (1:2) was performed in various polar solvents at 350 K. When dry nitrile solvents RCN (R = Me, Et, Ph, or $PhCH_2$) are used, an insoluble copper(I) cyanide complex is produced together with the corresponding amide, $RCONH_2$. The i.r. spectra of the copper cyanide complexes produced in this way show that they contain co-ordinated amide and possibly formaldoxime also. The elemental microanalyses of these complexes suggest that they are mixtures; however, all attempts to separate the components of these insoluble solids were unsuccessful. Addition of acetic anhydride to the copper(II) acetate–formaldoxime (1:2) mixture in acetonitrile solution produces $[Cu(CN)(NCMe)]$.



**(1)**

Copper(II) acetate was mixed with formaldoxime polymer (1:1) at 350 K in acetonitrile and in benzonitrile solution. Pale green solid precipitates were isolated on cooling the blue-green solutions. These precipitates are probably mixtures. Their i.r. spectra show the presence of cyanide, acetate, formaldoxime, and amide. Concentration of the mother-liquors produced oils from which pale blue-green solids were isolated by trituration with dry, deoxygenated diethyl ether. Elemental microanalyses and i.r. spectra of the pale blue-green solid complexes indicate that they have the composition $[Cu_3(O_2CMe)_5(RCONH_2)(CH_2NOH)_2]$ (R = Me or Ph). Further elaboration of the mother-liquors produced colourless solids which were identified (i.r. and m.p.) as the amide, $RCONH_2$ (R = Me or Ph).

The copper-assisted hydration of nitriles to form amides is well known.[5] The copper complexes are sensitive to moist air and decompose with effervescence in water or ethanol. The separation of the carboxylate stretching frequencies in these complexes (167 $cm^{-1}$ for R = Me; 181 $cm^{-1}$ for R = Ph) indicates that the acetate groups are bridging the copper atoms in a manner similar to that in $[Cu_3(O_2CMe)_5\{P(OEt)_3\}_2]$, in which a conventional copper(II) acetate unit with *syn,syn* bridging acetates is linked to a copper(I) moiety through an acetate bridge forming a one-dimensional polymer.[6] It is likely that the amide ligand is co-ordinated to the more acidic copper(II) site, and that these complexes have the structure (**1**).

The acetamide complex $[Cu_3(O_2CMe)_5(MeCONH_2)(CH_2NOH)_2]$ reacts with acetic anhydride (1:2) in acetonitrile at reflux to produce $[Cu_2(CN)_2(NCMe)]$ as a white precipitate from the solution. Both $[Cu_2(O_2CMe)_4(OH_2)_2]$ and CuCN were isolated from the pale blue-green mother-liquor at the end of the reaction. Neither acetamide nor formaldoxime was recovered from the reaction. It is probable that, in the presence of acetic anhydride, both of these co-ordinated ligands are dehydrated; formaldoxime to give cyanide, acetamide to give acetonitrile, and any excess water becoming co-ordinated to the copper(II) acetate.

Addition of pyridine (py) to $[Cu_3(O_2CMe)_5(MeCONH_2)(CH_2NOH)_2]$ in acetonitrile solution at ambient temperature results in the formation of a pale green precipitate of $[Cu(O_2CMe)(CH_2NOH)_2]$. The complex $[Cu_2(O_2CMe)_4(py)_2]$ was isolated from the reaction solution, together with acetamide, and characterised by elemental analysis and i.r. spectra. The i.r. spectrum of $[Cu(O_2CMe)(CH_2NOH)_2]$ shows that the acetate is bridging ($\Delta\nu$ 170 $cm^{-1}$). A dimeric structure is proposed, with two *syn,syn* acetate groups bridging two copper(I) atoms and two formaldoxime molecules co-ordinated through nitrogen to each of the copper(I) atoms. A similar structure has been proposed[6] for $[Cu(O_2CMe)\{P(OEt)_3\}_2]$.

## Conclusions

When nitrile solvents are used for the reaction between anhydrous copper(II) acetate and formaldoxime, in the *absence* of a dehydrating agent such as acetic anhydride, hydration of the nitrile to the carboxamide occurs. The pale green copper-containing product of the reaction is a mixture which contains both cyanide and the amide; these may be bound to copper because they are not separated by ether washing of the solid. The formation of this product suggests that hydration of the nitrile may accompany dehydration of formaldoxime in the presence of copper(II) acetate. The other stoicheiometric product of the reaction, $[Cu_3(O_2CMe)_5(RCONH_2)(CH_2NOH)_2]$ (R = Me or Ph), requires acetic anhydride as a dehydrating agent to convert co-ordinated formaldoxime to cyanide. The hydration of nitriles in the presence of copper compounds is well known.[5]

These experiments present an instructive contrast to those we have reported[2] on the formamide–acetic anhydride–copper salt system. In that system, the role of acetic anhydride as a dehydrating agent dominates any alternative paths for the dehydration of formamide. In the formaldoxime system, it is possible to isolate complexes which contain co-ordinated formaldoxime such as $[Cu_3(O_2CMe)_5(RCONH_2)(CH_2NOH)_2]$. The formamide system produces complexes containing the tetracyanodicuprate(I) ion as a result of dehydration. The formation of this anion is not observed when the formaldoxime-containing complexes are dehydrated by the action of acetic anhydride; the cyanide-containing products of these reactions include copper(I) cyanide and $[Cu_2(CN)_2(NCMe)]$ (for R = Me). Dehydration of formamide in the presence of copper(II) acetate in nitrile solvents does not result in hydration of the solvent.

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