Chemistry of the copper(I)-water bond. Some new observations

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One-dimensional polymeric copper(1) complexes of the type $\{[CuL(H_2O)]BF_4 \cdot H_2O\}_n$, where L = 2,3diphenylquinoxaline, and { $[CuL'(H_2O)]X_{ln}$, where L' = 2,3-dimethylquinoxaline and X⁻ = ClO₄⁻ or BF₄⁻, containing a rare copper(i)-water bond were synthesised. From the X-ray crystal structures of two of them, the copper(i) centres in these complexes are found to have a planar T-shaped N₂O coordination sphere. It is concluded from the observed Cu(I)–O(water) bond lengths [2.167(7)–2.307(14) Å] that the copper(I)–water bonds in these complexes are rather weak. With L, a monomeric complex of the type CuL_2ClO_4 has also been synthesised. But it has not been possible to obtain such a monomeric copper(1) complex with the BF_4^- anion or the ligand L'. In CuL₂ClO₄ the metal is also found to have, from the X-ray crystal structure, a planar T-shaped N₂O coordination sphere with the perchlorate anion very weakly bound to the metal through an oxygen atom [Cu(1)-O(perchlorate) = 2.442(8) Å]. While in the solid state electronic spectra, CuL₂ClO₄ displays a band at 346 nm, the aqua complexes show additional band(s) in the 400–480 nm range. CuL_2ClO_4 reacts with water in dichloromethane to yield an aqua copper(1) complex: $CuL_2ClO_4 + H_2O \rightarrow [CuL_2(H_2O)]ClO_4 \rightarrow 1/n \{[CuL_2(H_2O)]ClO_4 \rightarrow 1/n \}$ (H_2O)]ClO₄ $_n$ + L. In cyclic voltammetry at a glassy carbon electrode in anhydrous dichloromethane under N₂ atmosphere, CuL_2ClO_4 shows a quasi-reversible $Cu^{n/1}$ couple with a very high redox potential of 0.91 V vs. SCE, which is lowered to 0.79 V vs. SCE upon addition of water. This indicates that binding of water destabilises copper(I), a result expected on the basis of Pearson's HSAB Principle.

Water is a very common ligand in the chemistry of copper(II), but this is not so for copper(I). The reason can be understood when Pearson's Hard and Soft Acids and Bases Principle¹ is considered. In terms of Pearson's hard-soft classification of Lewis acids and bases, copper(I) is a "soft" acid while water is a "hard" base and copper(II) a "borderline" acid. Since hardsoft interactions are not particularly favoured, copper(I) and water are not compatible with each other. This is manifested in the experimental observation that in water² simple Cu⁺ ion disproportionates into Cu²⁺ ion and metallic copper with a disproportionation constant of ~10⁶. In an earlier communication,³ we have reported the synthesis and structure of a polymeric copper(I) complex {[CuL(H₂O)]ClO₄ · 0.5C₂H₅OH}_n (**1a**, L = 2,3-diphenylquinoxaline) containing a discrete copper(I)–water bond. Herein we expound the chemistry of the copper(I)–water bond further.



Results and discussion

Earlier, by reacting $Cu(ClO_4)_2 \cdot 6H_2O$ with L in ethanol in equimolar proportions in the presence of a slight excess of the reducing agent hydrazine hydrate, we have obtained **1a**. Now we report that when the anion is changed to tetrafluoroborate or the substituents at the 2 and 3 positions of the quinoxaline fragment are changed from phenyl to methyl, the copper(I)– water bond is retained. Reaction of L with Cu(BF₄)₂ · xH₂O in ethanol in equimolar proportions (assuming x = 4.5) in the presence of hydrazine hydrate yields the reddish orange $\{[CuL(H_2O)]BF_4 \cdot H_2O\}_n$ (1b). Reaction of 2,3-dimethylquinoxaline (L') with $Cu(ClO_4)_2 \cdot 6H_2O$ and $Cu(BF_4)_2 \cdot xH_2O$ carried out in a similar fashion yields ${[CuL'(H_2O)]ClO_4}_n$ (2a) and $\{[CuL'(H_2O)]BF_4\}_n$ (2b), respectively, which are brownish yellow in colour. Of the three new complexes, the structures of 1b and 2b have been determined by X-ray crystallography; the structures of the cations in 1b and 2b are shown in Fig. 1 and 2, respectively. The cations in both the complexes are onedimensional polymers, 1b along the y axis and 2b along the z axis, both aligned around the 2_1 screw axis. In both the cations, the copper atoms have essentially a planar, T-shaped N₂O coordination sphere with the N atoms coming from two adjacent ligands and the oxygen atom from a water molecule. The dimensions of the two coordination spheres are slightly different with the two Cu-N distances in 1b being significantly longer at 1.957(6) and 1.988(6) Å than those [1.917(10) and 1.894(9) Å] in **2b**. This might well be due to the larger steric effects of the substituent phenyl rings in 1b compared to the methyl groups in 2b. However, as if to compensate, the longer Cu-N distances in 1b are accompanied by a shorter Cu-O distance as this is 2.167(7) Å in **1b** compared to 2.307(14) Å in **2b.** For comparison, we mention that the Cu(I)-water bond length in **1a** is 2.154(6) Å.³ From the bond valence sum (BVS) models,^{4,5} which correlate the bond lengths around a metal with its oxidation state, the ideal Cu(I)-O bond length in a symmetric Cu¹O₃ chromophore is calculated to be 1.99 Å. Thus, the copper(I)-water bond in all the complexes 1a, 1b and 2b is longer than expected and hence somewhat weak. Bond length considerations indicate that of all the three complexes the copper(I)-water bond is weakest in 2b. Incidentally, from BVS calculations, the ideal Cu(I)-N bond length in a symmetric $Cu^{I}N_{3}$ moiety is expected to be 1.98 Å.



Fig. 1 The structure of the one-dimensional polymeric cation in 1b with ellipsoids at 20% probability. The hydrogen atoms on the water molecule were not located. Selected bond distances (Å) and angles (°): Cu(1)–N(1) 1.957(6), Cu(1)–N(4)^{*a*} 1.988(6), Cu(1)–O(100) 2.167(7), N(1)–Cu(1)–N(4)^{*a*} 150.6(2), N(1)–Cu(1)–O(100) 109.9(3), N(4)^{*a*} –Cu(1)–O(100) 99.4(3). Symmetry element (*a*): -x, y = 0.5, z = 0.5.

Earlier, when we reported 1a we indicated that it was the first example of a copper(1) complex containing a discrete copper(I)-water bond. However, while pursuing this problem, we have come across two copper(I) complexes containing such a bond.^{6,7} These are monomeric [Cu(phenazine)₂H₂O]ClO₄ reported by Munakata et al.⁶ in 1993 and [Cu(1.4-thioxane)₃H₂O]BF₄ reported by Olmstead *et al.*⁷ in 1982. Of these two complexes, that of Munakata et al. is directly comparable with our complexes. In $[Cu(phenazine)_2H_2O]ClO_4$, the metal has a T-shaped, planar N₂O coordination sphere with an average Cu-N bond length of 1.949(3) Å and a Cu-O distance of 2.241(3) Å. Thus, the Cu(1)-water bond length in [Cu(phenazine)₂H₂O]ClO₄ falls in-between our complexes of types 1 and 2. In [Cu(1,4-thioxane)₃H₂O]BF₄, the metal has a tetrahedral S₃O coordination sphere with the Cu-O bond length being 2.234(7) Å.

Planar T-shaped tricoordinate copper(1) complexes seem to be quite common. For a pioneering example, see ref. 8. Several mercury(11) complexes are known with somewhat distorted T-shaped N₂O coordination spheres in which the oxygen atom belongs to a water molecule.^{9,10}

When the reaction between L and $Cu(ClO_4)_2 \cdot 6H_2O$ is carried out in ethanol in the presence of hydrazine hydrate in n: 1(n=2-4) molar proportions, we obtain the lemon yellow $CuL_2 \cdot ClO_4$ (3a). Its structure as determined by X-ray crystallography is shown in Fig. 3. It is a monomer in which the metal atom is bonded to two nitrogen atoms of two different ligands in trans positions [1.933(7) and 1.942(8) Å] and to the perchlorate anion through one oxygen atom at a distance of 2.442(8) Å. From our preceding discussion on Cu(I)–O bond lengths, it is evident that the perchlorate anion is very weakly bound to the metal in 3a. This is reflected in the solution conductivity of 3a also; it behaves as a 1 : 1 electrolyte in methanol. However, we have not been able to synthesise its tetrafluoroborate analogue. Use of $Cu(BF_4)_2 \cdot xH_2O$ in a procedure similar to that adopted for synthesising 3a has always led to 1b. Further, all our attempts to obtain a monomer like 3a with the ligand L' have so far failed. Irrespective of the proportion of the metal and L' used in the synthetic procedure, 2a has been obtained consistently when starting with $Cu(ClO_4)_2 \cdot 6H_2O$ and **2b** with $Cu(BF_4)_2 \cdot xH_2O$. The reasons for this are not understood.



Fig. 2 The structure of the one-dimensional polymeric cation in **2b** with ellipsoids at 20% probability. The hydrogen atoms on the water molecule were not located. Selected bond distances (Å) and angles (°): Cu(1)-N(1) 1.917(10), $Cu(1)-N(4)^a 1.894(9)$, Cu(1)-O(100) 2.307(14), $N(1)-Cu(1)-N(4)^a 164.4(4)$, N(1)-Cu(1)-O(100) 92.1(5), $N(4)^a -Cu(1)-O(100) 102.3(4)$. Symmetry element (*a*): -x + 1, y + 0.5, z - 0.5.



Fig. 3 The structure of 3a with ellipsoids at 20% probability. Only one set of positions of the disordered perchlorate is shown. Selected bond distances (Å) and angles (°): Cu(1)–N(1B) 1.933(7), Cu(1)–N(1A) 1.942(8), Cu(1)–O(11) 2.442(8), N(1B)–Cu(1)–O(11) 100.0(3), N(1A)–Cu(1)– O(11) 93.6(3), N(1B)-Cu(1)-N(1A) 166.3(3).

(1)

The complexes of type 1 and 2 are indefinitely stable in air in the solid state. But in solution, almost immediately they undergo aerial oxidation giving rise to faint green solutions. Complex 3a is also indefinitely stable in air in the solid state; its stability in solution in the presence of air is somewhat better than that of complexes of type 1 and 2. An interesting feature is revealed when the solid state electronic spectrum of 3a is compared with those of the complexes of types 1 and 2. Complex 3a shows a band at 346 nm; from its intensity in methanol, it is recognised as being a charge transfer band that may arise from a metal to guinoxaline charge transfer. In the solid state electronic spectra of the complexes of types 1 and 2, this band is present with minor variations in the position; additionally they display band(s) at wavelengths longer than 400 nm (Fig. 4) assignable to some kind of charge transfer between copper(I) and water. The complex 2a, which we have not been able to characterise structurally, shows an electronic spectra essentially similar to that of 2b. [Cu(phenazine)2- $H_2O[ClO_4]$, the complex reported by Munakata et al.,⁶ also displays two bands in the solid state at comparable positions, 372 and 420 nm.

We have found that 3a can be converted to an aqua complex by adding water to a solution of **3a** under N₂ atmosphere:

$$n\operatorname{CuL}_2\operatorname{ClO}_4 + n\operatorname{H}_2\operatorname{O} \to \{[\operatorname{CuL}(\operatorname{H}_2\operatorname{O})]\operatorname{ClO}_4\}_n + n\operatorname{L} \quad (1)$$



Fig. 4 The room temperature solid state electronic spectra of (a) 1a, (b) 2a and (c) 3a in the region 800-300 nm.

The reaction is irreversible and occurs smoothly and almost instantaneously in dichloromethane. Based on the change in colour of a dichloromethane solution of 3a, from lemon yellow to orange with the addition of water, it appears that first a monomeric species of the type [CuL₂(H₂O)]ClO₄ is formed, but the compound that precipitates from the reaction mixture by the addition of diethyl ether (see Experimental) is the polymer { $[CuL(H_2O)]ClO_4$ }_n. Thus reaction (1) can be decomposed into:

$$n \operatorname{CuL}_2\operatorname{ClO}_4 + n \operatorname{H}_2\operatorname{O} \to n [\operatorname{CuL}_2(\operatorname{H}_2\operatorname{O})]\operatorname{ClO}_4$$
 (1a)

$$n[\operatorname{CuL}_2(\operatorname{H}_2\operatorname{O})]\operatorname{ClO}_4 \to \{[\operatorname{CuL}(\operatorname{H}_2\operatorname{O})]\operatorname{ClO}_4\}_n \downarrow + n\operatorname{L} \quad (1b)$$

Incidentally, the polymers 1a and 1b are insoluble in dichloromethane. It is noted that reaction (1) does not proceed in methanol, in which 3a is poorly soluble. In any case, reaction (1) shows that the copper(I) centre in **3a** has a considerable affinity for water. The electrochemistry of the various complexes described here has been examined by cyclic voltammetry at a glassy carbon electrode under dry N2 atmosphere. While in methanol complexes of types 1 and 2 show voltammograms characteristic of adsorbed species, complex 3a displays an oxidative, quasi-reversible voltammogram with an $E_{1/2}$ of 0.91 V vs. SCE (saturated calomel electrode) in dry dichloromethane (Fig. 5). Comparison of the voltammetric peak currents with those of the ferrocene-ferrocenium couple under the same experimental conditions establishes that the oxidative response in 3a involves only one electron. Since L is not electroactive in the potential range of interest here, the electrode process observed for 3a is metal based:

$$Cu^{II} + e^{-} \rightleftharpoons Cu^{I}$$
 (2)

The redox potential of the couple in eqn. (2) is quite high. To our knowledge, no electrochemical data on a Cu¹N₂O chromophore (though in a polar solvent like methanol CuL₂ClO₄ behaves as a 1:1 electrolyte, it is very likely that the ClO₄ anion in 3a remains bound to the metal in the non-polar dichloromethane solvent used for cyclic voltammetry) are available with which we can compare the potential. For comparison, we mention that the $Cu^{{\rm i}{\rm n}/{\rm i}}$ potential for the $Cu^{{\rm i}}N_4$ moiety in [Cu(pyridine)₄]⁺ is ca. 0.06 V vs. SCE, for that in [Cu(bipyridine)₂]⁺ it is ca. 0.01 V vs. SCE in 50% dioxanewater¹¹ and the highest potential of the $Cu^{\pi/1}$ couple for a



Fig. 5 Cyclic voltammograms of **3a** in anhydrous dichloromethane (—) and in dichloromethane saturated with water (-----) at a glassy carbon electrode under N₂ atmosphere. Supporting electrolyte: 0.1 mol dm⁻³ tetrabutylammonium perchlorate; concentration of **3a**: 1.4 mmol dm⁻³; scan rate: 50 mV s⁻¹. Under the same experimental conditions, the ferrocene–ferrocenium couple appears at 0.47 V vs. SCE with a peak-to-peak separation of 95 mV.

 $Cu^{II}N_2O_2$ chromophore recorded so far is -0.30 V vs. SCE in acetonitrile.¹² For a tetracoordinate copper complex, the potential of the Cu^{$\pi/1$} couple is believed to increase with the π acidity of the ligand and the extent of tetrahedral distortion in the corresponding copper(II) species.^{12,13} The highest $Cu^{II/I}$ potential hitherto recorded for any copper complex is 1.55 V vs. SCE;¹⁴ the relevant copper complex has a Cu¹N₄ chromophore. Since the π -acidity of quinoxaline is likely to be comparable to that of pyridine,^{15,16} the high magnitude of the Cu^{1/1} couple in **3a** is attributable to the tricoordination of the metal in **3a**, which preferentially stabilises copper(I) over copper(II)to a great extent. It should be noted that the electrode process in eqn. (2) generates a tricoordinate copper(II) species in solution. Until now, apart from biological systems, only two structurally characterised tricoordinate copper(II) complexes are known; in one case the metal ion has a $Cu^{II}N_2Cl$ moiety and in the other Cu^{II}N₂S.¹⁷ The potential of the Cu^{II/I} couple in the Cu^{II}N₂S chromophore was found to be -0.42 V vs. SCE in tetrahydrofuran. A type 1 copper site in human ceruloplasmin, in which the coordination sphere around the metal is presumably trigonal N₂S, has a Cu^{II/1} potential of ca. 0.78 V vs. SCE.¹⁸

When water is added to the dichloromethane solution of **3a** used for cyclic voltammetry, the potential of the couple in eqn. (2) is lowered. Fig. 5 shows that in dichloromethane saturated with water, the Cu^{n/1} potential in **3a** becomes 0.79 V vs. SCE. In reaction (1) we have indicated that water replaces the coordinated perchlorate anion in **3a**. Thus, from Fig. 5 it is apparent that coordination of water destabilises copper(1). This is an expected result.

Concluding remarks

Herein we have reported three new one-dimensional copper(1) polymers containing a copper(1)-water bond synthesized using 2,3-diphenylquinoxaline (L) and 2,3-dimethylquinoxaline (L') as ligands. The structures of two of them have been determined by X-ray crystallography. From the observed Cu(1)–O(water) bond lengths, it is apparent that the bonding between copper(1) and water is rather weak in these copper(1) aqua complexes. With L, we have been able to isolate a monomer of the type CuL₂ClO₄ (**3a**), which does not have a copper(1)–water bond. We have demonstrated that it is possible to convert **3a** to a polymeric aqua complex of copper(1) by reacting it with water in dichloromethane. However, it has not been possible to synthesise the tetrafluoroborate or L' analogue of **3a**. Pearson's HSAB Principle predicts that bonding between copper(1) and water is not particularly favoured. This we have

demonstrated in the lowering of the Cu^{II/1} potential in **3a** upon addition of water. We now mention that earlier work with unsubstituted quinoxaline (Q), a polymeric copper(I) complex of the type {[Cu(Q)₃ClO₄]ClO₄}_n, in which the bridging Q moieties give rise to a three dimensional network, has been reported.¹⁹ Some structurally uncharacterised polymeric copper(II) complexes of the type CuX₂(L or L') with X = Cl⁻, Br⁻ and NO₃⁻ are also known.²⁰

Experimental

General

All reagents were procured commercially. The melting points reported here are uncorrected. Copper was estimated gravimetrically as CuSCN. Microanalyses were performed by a Perkin–Elmer 2400II elemental analyser. FTIR spectra (KBr) were recorded on a Nicolet Magna-IR spectrophotometer (Series II) and UV-VIS spectra on a Shimadzu UV-160A spectrophotometer. Cyclic voltammetry was performed at a planar EG&G PARC G0229 glassy carbon milli electrode using an EG&G PARC electrochemical analysis system (model 250/5/0) in conventional three-electrode configurations.

Syntheses

2,3-Diphenylquinoxaline (L). Recrystallised *o*-phenylenediamine (OPDA; 0.54 g, 5 mmol and benzil (1.05 g, 5 mmol) were taken in 25 ml of ethanol and refluxed for 5 h. Then the yellow reaction mixture was left in air overnight. The white needles that deposited were filtered off, washed with a few drops of ethanol and dried *in vacuo* over fused CaCl₂. Yield 1.15 g (80%), mp 120–122 °C. Anal. found (calcd): C, 85.05 (85.07); H, 5.17 (5.00); N, 9.90 (9.92)%.

2,3-Dimethylquinoxaline (L'). Recrystallised OPDA (0.54 g, 5 mmol) and 0.434 ml (5 mmol) of diacetyl were taken in 25 ml of ethanol and refluxed for 5 h. Then the intense brown reaction mixture was left in air for 4 days. The shiny white crystals that deposited were filtered off, washed with a few drops of ethanol and dried *in vacuo* over fused CaCl₂. Yield 0.25 g (30%), mp 102–104 °C. Anal. found (calcd): C, 74.00 (74.02); H, 8.62 (8.70); N, 17.37 (17.27)%.

 $\{[CuL(H_2O)]BF_4 \cdot H_2O\}_n$ (1b). Hydrated Cu(BF₄)₂ (0.24 g), dissolved in 5 ml of ethanol, was added to 0.28 g (1 mmol) of L dissolved in 20 ml of ethanol. The resulting bluish green solution was heated to boiling. To this hot solution, 0.05 ml of hydrazine hydrate (4 mmol) was added dropwise with constant stirring. The resulting red solution was stirred for 5 min and the reaction mixture was left in air. After 10 min, the brownish yellow crystalline compound that precipitated was filtered, washed with 5 ml of ethanol and dried in vacuo over fused CaCl₂. Yield 0.19 g (40%). Direct diffusion of diethyl ether into the filtrate afforded shiny reddish orange single crystals suitable for X-ray crystallography. Anal. found (calcd): C, 51.09 (51.23); H, 3.77 (3.87); N, 6.09 (5.98); Cu, 13.50 (13.56)%. FTIR (KBr) ν/cm^{-1} : 1642w (C=N); 1131w, 1102w, 1066s, 1025s, 981m (BF₄). UV-VIS (nujol) $\lambda_{\rm max}/\rm{nm}$: 480, 402, 354.

{[CuL'(H₂O)]ClO₄}_n (2a). 2a was prepared in a manner similar to that used for 1b by starting with 0.18 g (0.5 mmol) of Cu(ClO₄)₂.6H₂O and 0.08 g (0.5 mmol) of L'. The resulting compound was brownish yellow. Yield 0.05 g (30%). Anal. found (calcd): C, 35.46 (35.38); H, 3.50 (3.57);

	1b	2b	3a
Chemical formula	$C_{20}H_{18}BCuF_4N_2O_2$	$C_{10}H_{12}BCuF_4N_2O$	C40H28ClCuN4O4
Formula weight	468.48	326.44	727.26
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	P22 ₁ 2 ₁	$Pn2_1a$	$P\overline{1}$
a/Å	9.166(12)	15.08(2)	11.052(14)
b/Å	13.014(17)	9.895(14)	11.696(14)
c/Å	17.57(2)	8.700(14)	14.049(17)
α/°	_	_ ``	78.445(10)
$\dot{\beta}/^{\circ}$	_	_	74.361(10)
v/°	_	_	73.854(10)
$U/Å^3$	2096(5)	1298(3)	1664(4)
z	4	4	2
μ/mm^{-1}	1.095	1.722	0.786
No. data collected	6913	1248	5463
No. unique data	3874	1248	5463
R _{int}	0.0539	0.065	
R indices $[I > 2\sigma(I)]$			
R_1	0.0726	0.0721	0.1162
wR_2	0.1863	0.1833	0.3027
<i>R</i> indices (all data)			
R_1	0.1221	0.0948	0.1829
wR_2	0.2103	0.1949	0.3402

N, 8.16 (8.26); Cu, 18.76 (18.74)%. FTIR (KBr) ν/cm^{-1} : 1632w (C=N); 1105vs, 1055m, 999w, 620vs (ClO₄). UV-VIS $\lambda_{\text{max}}/\text{nm}$ (nujol): 425, 350.

{[CuL'(H₂O)]BF₄}_n (2b). 2b was prepared in a manner similar to that used for 1b by starting with 0.16 g (1 mmol) of L' and 0.24 g of hydrated Cu(BF₄)₂. The resulting compound was brownish yellow. Yield 0.06 g (20%). Direct diffusion of diethyl ether into the filtrate gave shiny orange single crystals suitable for X-ray crystallography. Anal. found (calcd): C, 36.83 (36.76); H, 3.64 (3.71); N, 8.53 (8.58); Cu, 19.50 (19.46)%. FTIR (KBr) ν/cm^{-1} : 1630w (C=N); 1196m, 1178m, 1137m, 1002s, 980w (BF₄). UV-VIS (nujol) λ_{max}/nm : 425, 359.

CuL₂ClO₄ (3a). L (0.11 g, 0.4 mmol), dissolved in 20 ml of ethanol, was added to 0.07 g (0.2 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ dissolved in 5 ml of ethanol. The resulting bluish green solution was heated to boiling. To this hot solution, 0.04 ml (3.2 mmol) of hydrazine hydrate taken in 3 ml of ethanol was added dropwise with constant stirring. Within a minute, a shiny lemon yellow compound started precipitating from the orange solution. After 5 min, the compound was filtered, washed with 5 ml of diethyl ether and dried in vacuo over fused CaCl₂. Yield 0.11 g (75%). Direct diffusion of diethyl ether into the filtrate afforded lemon yellow crystals suitable for X-ray crystallography. Anal. found (calcd): C, 65.97 (66.00); H, 3.95 (3.88); N, 7.68 (7.70); Cu, 8.71 (8.74)%. FTIR (KBr) v/cm⁻¹: 1642w (C=N); 1145m, 1067vs, 1060m, 1040m, 620s, split (ClO₄). $\Lambda_{\rm M}$ (CH₃OH): 97 Ω^{-1} cm² mol⁻¹ UV-VIS (nujol) λ_{max}/nm (ε/dm^3 mol⁻¹ cm⁻¹): 346; (anhydrous, degassed CH₃OH): 345 (1100), 255 (3000).

Conversion of 3a to $\{[CuL(H_2O)]ClO_4\}_n$. Solid lemon yellow 3a (0.22 g, 0.30 mmol) was added to a mixture of 25 ml of dichloromethane and 0.075 ml (4.2 mmol) of water with constant stirring under nitrogen atmosphere. Almost immediately an orange turbid solution was obtained, which was stirred for 5 min. Then 10 ml of deaerated diethyl ether was added and stirring continued for another 5 min. The light orange precipitate that appeared was then filtered off, washed with 5 ml of diethyl ether and dried *in vacuo* over fused CaCl₂. Yield 0.11 g (75%). The solid analysed as CuL(H₂O)ClO₄. Anal. found (calcd): C, 51.79 (51.82); H, 3.41 (3.48); N, 6.15 (6.05); Cu, 13.69 (13.72). FTIR (KBr) ν/cm^{-1} : 1639w (C=N); 1138m, 1115s, 1089vs, 1079vs, 625s (ClO₄). UV-VIS (nujol) $\lambda_{\text{max}}/\text{nm}$: 470, 402, 360.

Caution! Though we have not met with any incident while working with the perchlorate compounds described here, care should be taken in handling them as perchlorates are potentially explosive. They should not be prepared and stored in large quantities.

X-Ray crystallography

Details for the structure determinations of 1b, 2b and 3a are given in Table 1. Intensity data were collected with Mo-Ka radiation using a MAR research image plate system at 293(2) K. The crystals were positioned at 70 mm from the image plate. One hundred frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.²¹ The structures were solved using direct methods with the SHELXS-86 program.²² 1b contains three water molecules, each given 33.3% occupancy. In 3a the perchlorate is disordered; the oxygen atom bonded to the copper atom is ordered but the other three oxygen atoms are disordered over two sites. In the three structures the nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Hydrogen atoms of water molecules were not located. An empirical absorption correction was carried out using DIFABS.²³ The structures were refined on F^2 using SHELXL.24

CCDC reference number 174164–174166. See http:// www.rsc.org/suppdata/nj/b1/b105443k/ for crystallographic data in CIF or other electronic format.

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