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A Fluxional $Cu^IN_2O_2$ Core: Binding of a Keto Oxygen Atom to Cu^I and Ag^I

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[Cu(2-acetylpyridine)$_2$]ClO$_4$ (**1**), characterised here, has a novel $Cu^IN_2O_2$ core in the solid state. Variable-temperature ^{1}H NMR studies show that the two chelate rings open up in solution at room temperature and the keto oxygen atoms dangle freely. As the temperature is lowered, the O atoms tend to bind to the metal atom. The corresponding silver(I) complex, [Ag(2-acetylpyridine)$_2$]ClO$_4$ (**4**), characterised by single-crystal X-ray crystallography, has an Ag^IN_2 core in the solid state as well as in solution. Thus, while **1** is fluxional, **4** is not. In cyclic voltammetry, complex **1** displays a quasireversible $Cu^{II/I}$ couple with a half-wave potential of 0.40 V vs. SCE. Complex **1** is easily oxidised by air and H_2O_2 in methanol to give rise to a dinuclear copper(II) complex where the ligand framework is not simple acetylpyridine.

Introduction

The bonding between copper(I) and an aldehyde/ketone oxygen atom has received little attention. While simple Cu^+ ion disproportionates into Cu^{2+} and metallic copper in most O-donor solvents like water, methanol etc., it is considerably more stable towards disproportionation in acetone.[1] Consequently, a copper(I)–keto oxygen bond may not be thermodynamically unfeasible. However, to date, there is only one example of a copper(I) complex where the metal atom has a discrete bond with a keto oxygen atom; the oxygen atom belongs to an acetone molecule.[2] This copper(I) complex was not synthesised deliberately. There is a report by Lin et al.,[3] where the authors have claimed to observe bonds between Cu^I and the keto oxygen atoms in bis(triphenylphosphane)bis(phenalenone)copper tetrafluoroborate. In reality, however, they have observed bonds between Cu^I and the O^- ends of the zwitterionic phenalenone fragments. However, in the oxidation of benzyl alcohol catalysed by a copper(II) complex, a copper(I) species having a bond between the metal atom and the O atom of benzaldehyde was proposed by Kitajima et al. as a possible intermediate.[4] On the other hand, several structurally characterised examples of copper(II) complexes containing bonds between Cu^{II} and the carbonyl O atom of some aldehydes/ketones are known.[5–8] For example, in azurin – a blue copper-containing protein – there is a peptide carbonyl O atom in close proximity to the metal ion [mean Cu^I–O distance = 3.22 Å; mean Cu^{II}–O distance = 3.13 Å],[9] although it is doubtful whether this O atom is bonded to the copper atom in azurin.[10] Thus, the possibility of a copper(I)–keto oxygen bond is of biological relevance as well. Recently, we have undertaken a project to study the chemistry of this bond, and here we make the first report of our efforts by describing some properties of a homoleptic copper(I) complex of 2-acetylpyridine (ACPY) containing copper(I)–keto oxygen bonds. For comparison, we have also studied the homoleptic silver(I) complex of ACPY.

Results and Discussion

Reaction of ACPY with [Cu(CH$_3$CN)$_4$]ClO$_4$ in anhydrous methanol under N_2 in a 2:1 molar ratio yields reddish brown [Cu(ACPY)$_2$]ClO$_4$ (**1**). This complex is stable in air for more than a week in the solid state, although in solution it is not at all stable towards aerial oxidation: the reddish colour of the solution first changes to green and then to pink.

Luo et al.[8] have reported the synthesis and X-ray crystal structure of a mixed-ligand copper(II) complex containing ACPY as one of the ligands. Prior to them, El-Hilaly and El-Zaby reported that reaction of 2-pyridinecarboxaldehyde (PYCA) with hydrated Cu(NO$_3$)$_2$ in aqueous medium at pH = 8.0 yielded a pink complex which analysed as Cu(pyridin-2-ylmethanediolate monoanion)$_2$, thus indicating aquation of PYCA.[11] However, when we followed the procedure of El-Hilaly and El-Zaby with ACPY, metallic copper was precipitated. Further, reaction of Cu(ClO$_4$)$_2$·6H$_2$O with ACPY in methanol in a 1:2 molar proportion yields a blue copper(II) complex which seems to contain pyridin-2-ylmethanediolate monoanion as one of the ligands. Thus, we have not yet been able to characterise any pure homoleptic copper(II) complex of ACPY.

That the keto oxygen atoms of the two ACPY moieties in **1** are bonded to copper(I) is unequivocally revealed in

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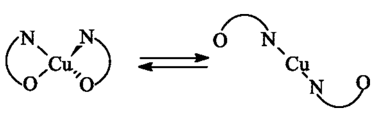
the FTIR spectra. The ν(C=O) absorption of the free ligand appears at 1697 cm^{-1} as a very strong band, whereas in the complex two ν(C=O) bands are observed at 1689 and 1672 cm^{-1} as moderately strong with unequal intensities. The lowering of the ν(C=O) absorption in the complexes compared to that of free ACPY suggests that π back-bonding between copper(I) and the keto fragments is possible. Since two C=O stretching frequencies are observed in the complex, we can say that there are two types of keto groups in the complex which may be due to the difference in the two Cu^I–O bond lengths [a shorter Cu^I–O bond being associated with the ν(C=O) of 1672 cm^{-1}]. The ν(C=N) absorption of pyridine in ACPY (1583 cm^{-1}) moves to higher energy (1591 cm^{-1}) upon binding to copper(I), therefore it is reasonable to assume that there is a distorted tetrahedral $Cu^IN_2O_2$ chromophore in **1**.

A variable-temperature ^1H NMR study of **1** in CD_2Cl_2 (Figure 1) shows that **1** undergoes a dynamic equilibrium according to Equation (1) in solution leading to broadening of the proton signals at room temperature.



(1)

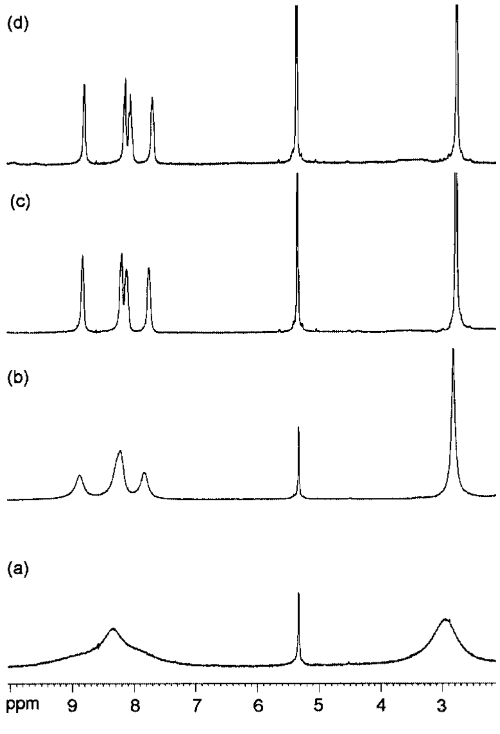


Figure 1. Variable-temperature 300 MHz ^1H NMR spectra of $[Cu(ACPY)_2]ClO_4$ (**1**) in CD_2Cl_2: (a) 298, (b) 253, (c) 213 and (d) 193 K. Assignments: δ [ppm] = 2.2–3.7 (methyl protons), 5.3 (residual protons of the solvent), 7–10 (pyridyl protons).

Since only one type of methyl signal is observed in the temperature range 298–193 K, equilibrium processes involving dissociated and undissociated ligands can be ruled out. We can therefore speculate that **1** is two-coordinate in solution at room temperature, with the ligands bound to the metal atom through the pyridine nitrogen atoms, and at low temperature it is four-coordinate with the keto oxygen atoms also participating in the bonding. This implies that Cu^I–keto oxygen bonds are very weak. Equilibrium (1) indicates that our copper(I) complex **1** is stereochemically nonrigid in solution, i.e. fluxional. Incidentally, the methyl protons in the free ligand ACPY resonate as a singlet at δ = 2.72 ppm and the pyridyl protons at δ = 7.35–7.70 (m), 7.80–8.10 (m) and 8.65–8.72 (d) ppm in $CDCl_3$.[12]

In an attempt to grow single crystals of **1**, we allowed direct diffusion of diethyl ether into its dilute methanolic solution (reddish). After two weeks, there was deposition of shiny, dark-green single crystals of **2**. This green compound is paramagnetic. X-ray crystallography revealed that it is a diperchlorate salt of a dinuclear copper(II) complex where the original ligand, ACPY, has been chemically changed to a monoanionic form of **3**. The formulation of compound **2** is $[Cu_2(\mathbf{3}\text{-}H^+)_2](ClO_4)_2$ (Figure 2). It has a crystallographic centre of symmetry with a Cu···Cu distance of 3.002(3) Å. It is an alkoxo-bridged dinuclear copper(II) complex where each copper atom is five-coordinate; the bridging angle is 101.6(2)°. The coordination sphere of each metal ion is an approximate square pyramid with the alcoholic oxygen atom O(30) in an axial site at a distance of 2.249(6) Å. The atoms in the equatorial plane form shorter bonds [Cu–O(1) = 1.956(5), Cu–O(1) (2 – *x*, –*y*, 2 – *z*) = 1.918(5), Cu(1)–N(11) = 1.982(6) and Cu(1)–N(24) = 1.999(6) Å]. While reports of coordination of an alcoholic oxygen atom to copper(II) are rare,[13,14] many examples of alkoxo-bridged dinuclear copper(II) complexes are known.[15,16]

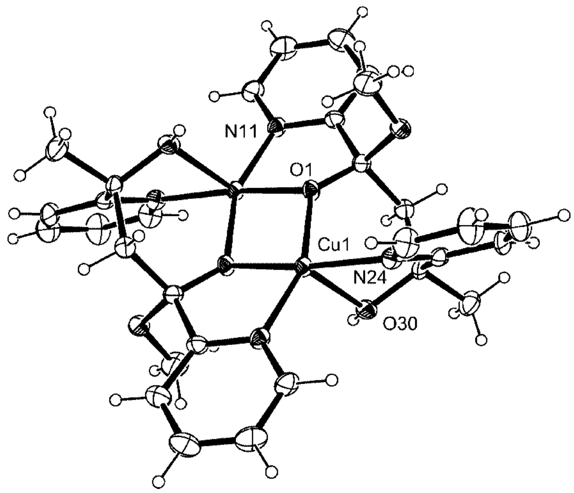
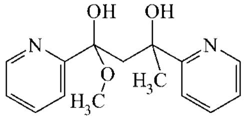


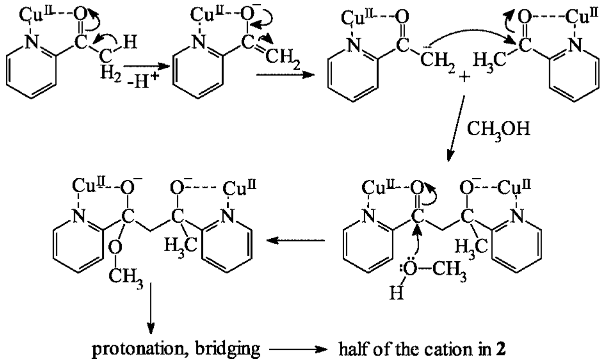
Figure 2. Centrosymmetric structure of the cation in **2** with ellipsoids at 25% probability. Selected bond lengths [Å] and angles [°]: Cu1–O1 1.956(5), Cu1–O30 2.249(6), Cu1–N11 1.983(6), Cu1–N24 2.000(7); O1–Cu1–O30 86.1(2), O1–Cu1–N24 93.6(2), O30–Cu1–N24 76.0(2).

Oxidation of copper(I) to copper(II) is a prerequisite for the conversion of **1** into **2**. In our above experiment, aerial oxygen brings about the required oxidation; the conversion **1** → **2** does not occur under N_2. Later, we found that $[Cu_2(\mathbf{3}\text{-}H^+)_2](ClO_4)_2$ can be easily generated by oxidising **1**



3

with dilute H_2O_2 in methanolic medium. However, our attempts to isolate the free ligand **3** from $[Cu_2(\mathbf{3}\text{-}H^+)_2](ClO_4)_2$ always led to the isolation of ACPY only. A tentative mechanism for the conversion of **1** into **2** is proposed in Scheme 1. The mechanism is shown explicitly for one half of **2**; it is the same for the other half. Oxidation of the metal atom from copper(I) to copper(II) facilitates the enolisation and subsequent formation of the carbanion in Scheme 1.



Scheme 1. Proposed mechanism for the conversion of complex **1** into **2** in methanol followed by oxidation of the metal centre from copper(I) to copper(II).

Having failed to obtain single crystals of **1**, we decided to synthesise its silver(I) analogue, as the structure of the Ag^I complex is found to be similar[17] to that of the Cu^I variety for many ligands. Stirring of $AgClO_4 \cdot xH_2O$ with ACPY in tetrahydrofuran (THF) in the required proportion yielded $[Ag(ACPY)_2]ClO_4$ (**4**). Its X-ray crystal structure is given in Figure 3. There are two pyridyl nitrogen atoms and two keto oxygen atoms in close proximity to the silver atom. The Ag^I–N distances are 2.213(6) and 2.214(5) Å and the Ag^I–O distances 2.544(6) and 2.554(6) Å. The two pyridine rings intersect at 71.2(1)°.

The Ag^I–O bonds in **4** are rather long. In order to find out whether the two keto O atoms are at all bonded to the silver atom, we decided to use the bond valence sum (BVS) model,[18,19] which relates the bond lengths around a metal ion with its oxidation state. Our BVS calculations with a bond valence parameter, r_0, for the Ag^I–N bond of 1.859 Å[20] show that the valency of the silver(I) atom in **4** is well satisfied by the two N atoms; inclusion of the two keto oxygen atoms in the coordination sphere of the silver atom in **4** is unnecessary. This conclusion is also supported by the FTIR spectrum of **4**, where ν(C=O) appears at 1700 cm^{-1}, thus indicating no bonding between the metal atom and the keto oxygen atoms. No silver(I) complex with an Ag^I–keto oxygen bond is known in the literature. In 1997, Lin et al.[21] reported the crystal structure of bis(triphenylphosphane)bis(diphenylcyclopropenone)silver(I) tetrafluoroborate, where there is a bond between Ag^I and the O atom of the diphenylcyclopropenone moiety. However, because of the possible resonance structures of this complex, the O atom behaves more as O^- of the zwitterionic diphenylcyclopropenone fragment. In our case, since the keto oxygen atoms do not bind Ag^I in **4**, no fluxional behaviour is observed in its variable-temperature ^1H NMR spectra in CD_2Cl_2 (Figure 4), in contrast to the copper(I) complex **1**.

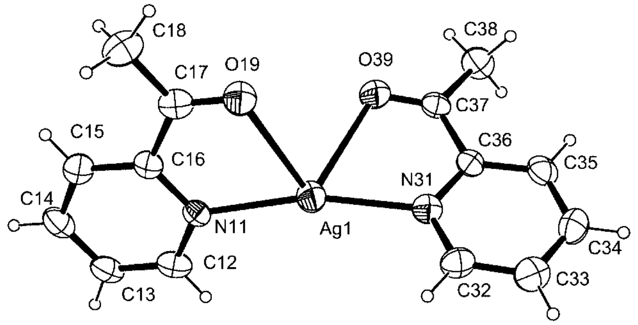


Figure 3. Structure of the cation in **4** with ellipsoids at 25% probability. Selected bond lengths [Å] and angles [°]: Ag1–N11 2.214(5), Ag1–N31 2.213(6), Ag1–O19 2.554(6), Ag1–O39 2.544(6); N31–Ag1–N11 165.8(2), O39–Ag1–O19 84.0(2), N31–Ag1–O39 69.6(2), N11–Ag1–O19 68.83(19).

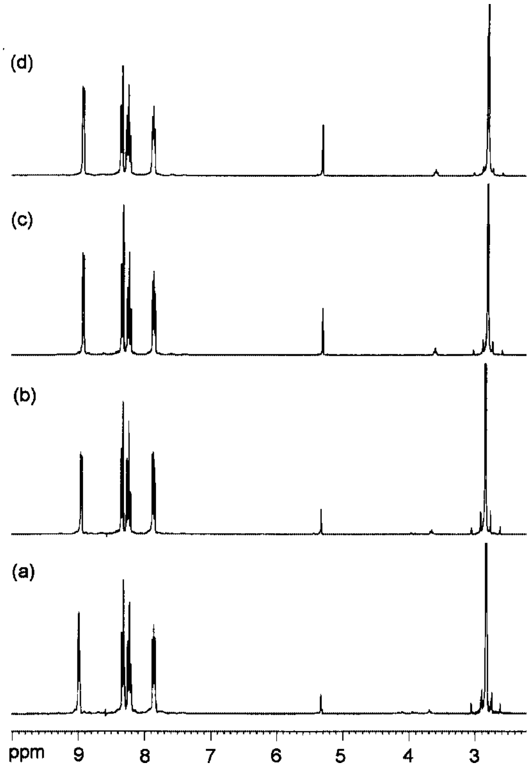
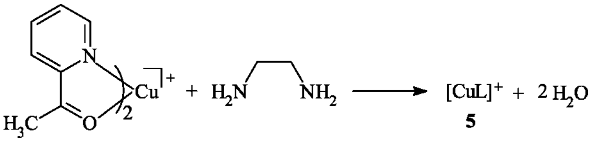


Figure 4. Variable-temperature 300 MHz ^1H NMR spectra of $[Ag(ACPY)_2]ClO_4$ (**4**) in CD_2Cl_2: (a) 298, (b) 253, (c) 213 and (d) 193 K. Assignments: δ [ppm] = 2.83 (methyl protons), 5.3 (residual protons of the solvent), 7.75–9.25 (pyridyl protons).

The keto groups in **1** are capable of forming Schiff bases. This is evidenced by the fact that reaction of ethylenediamine (en) with **1** in an equimolar proportion in anhydrous methanol results in $[CuL]^+$ (**5**), where L is the 2:1 condensate of ACPY and en [Equation (2)]. Previously, we have shown by means of X-ray crystallography that the 2:1 condensate of PYCA and en yields a homotopic dicopper(I) cationic double helicate when treated with $[Cu(CH_3CN)_4]ClO_4$ in a 1:1 molar proportion.[22] We believe that **5** has a similar structure.



(2)

We have examined the electrochemical behaviour of **1** by cyclic voltammetry and coulometry in purified dichloromethane under dry N_2. At a glassy carbon electrode in cyclic voltammetry, it displays a quasi-reversible oxidative electrode process (Figure 5) with an average half-wave potential, $E_{1/2}$, of 0.40 V vs. SCE (saturated calomel electrode). The involvement of one electron in the electrode process was confirmed by coulometry at a platinum wire gauge electrode (4.35 mg of **1** was electrolysed at 0.65 V vs. SCE in CH_2Cl_2; 1.069 coulomb was collected, against the theoretical count of 1.036. The oxidised solution was almost colourless.). Thus, the couple observed in Figure 5 is a $Cu^{II/I}$ one.

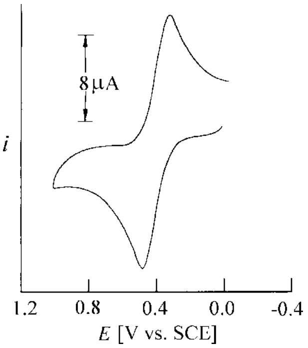


Figure 5. Cyclic voltammogram of $[Cu(ACPY)_2]ClO_4$ (**1**) in dichloromethane (concentration 1.20 mM) containing 0.1 M tetrabutylammonium perchlorate at a glassy carbon electrode at a scan rate of $50\ mV\,s^{-1}$. Under the same experimental conditions, the ferrocene–ferrocenium couple appears at 0.47 V vs. SCE with a peak-to-peak separation of 80 mV.

As revealed by the ^1H NMR spectra, our copper(I) complex is two-coordinate in solution at room temperature. The metallophore in **1** in solution can be represented as $[Cu^IN_2]O_2$, thus indicating that the O atoms of the two ACPY fragments are not bound to the metal atom. The oxidative electrode process observed for **1** can then be described by Equation (3), where the corresponding Cu^{II} species is four-coordinate with the two keto oxygen atoms ligated to the metal atom.

$$Cu^{II}N_2O_2 + e^- \rightleftharpoons [Cu^IN_2]O_2 \qquad (3)$$

Since the coordination number of the metal ion changes so much with the change in the oxidation state, the peak-to-peak separation in Figure 5 is quite large (0.17 V). The reasons for assuming that the Cu^{II} species in Equation (3) is four-coordinate are as follows:

(i) While a number of structurally characterised copper(I) complexes having a Cu^IN_2 core are known,[10] no one has ever observed a quasi-reversible cyclic voltammogram for such a core (an irreversible voltammogram with possible characteristics of adsorption is expected for a Cu^IN_2 core).

(ii) No example of a two-coordinate copper(II) complex is known in the literature; hence, the copper(II) species in Equation (3) cannot have a $Cu^{II}N_2$ core.

(iii) The keto oxygen atom of ACPY is known to bind Cu^{II}.[8]

The $Cu^{II/I}$ potential indicates that complex **1** can be oxidised by aerial oxygen, as the potential of the couple according to Equation (4) at pH = 7 is 0.57 V vs. SCE.[23a]

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \qquad (4)$$

Concluding Remarks

We have characterised a copper(I) complex, $[Cu(ACPY)_2]ClO_4$ (**1**), with a novel $Cu^IN_2O_2$ core and having two Cu^I–keto oxygen bonds. These Cu^I–keto oxygen bonds exist in the solid state, where complex **1** provides the first example of a $Cu^IN_2O_2$ core. However, the Cu^I–keto oxygen bonds in **1** are so weak that, even in a non-coordinating solvent like dichloromethane, the two chelate rings open up and the keto ends dangle freely in solution. However, with the lowering of temperature, the keto oxygen atoms tend to bind the metal atom. Thus, the $Cu^IN_2O_2$ core is stereochemically non-rigid in solution. Accordingly, our copper(I) complex **1** is "fluxional". We wish to point out that, so far, to the best of our knowledge, no other fluxional copper(I) complex is known in inorganic chemistry. We have also demonstrated that the silver(I) counterpart of **1** is not fluxional. This is because the keto oxygen atoms do not bind Ag^I even in the solid state. Incidentally, Ag^I shows a pronounced tendency to exhibit linear twofold coordination.[23b] In **4**, the N–Ag–N angle is 165.8(2)°.

Complex **1** has a low-potential $Cu^{II/I}$ couple and is easily oxidised by air in solution. Oxidation by air or H_2O_2 in methanol results in a dinuclear copper(II) complex, although the organic moiety in this dinuclear compound no longer remains as simple ACPY: it undergoes a chemical transformation, which is facilitated by the oxidation of the metal centre, to yield a novel dinucleating ligand.

Experimental Section

General: $[Cu(CH_3CN)_4]ClO_4$ was prepared by a reported procedure.[24] Copper was estimated gravimetrically as CuSCN. Microanalyses were performed with a Perkin–Elmer 2400II elemental analyser. FTIR spectra (KBr disc) were recorded with a Nicolet Magna-IR spectrophotometer (Series II), UV/Vis spectra with a

Shimadzu UV-160A spectrophotometer and NMR spectra (in CD_2Cl_2) with a Bruker DPX300 spectrometer. Cyclic voltammetry and coulometry were performed using an EG&G PARC electrochemical analysis system (model 250/5/0) in purified dichloromethane, under dry nitrogen, in a conventional three-electrode configuration. A planar EG&G PARC G0229 glassy carbon milli electrode was used as the working electrode in cyclic voltammetry and a platinum wire gauge electrode in coulometry. Magnetic susceptibility was determined at room temperature with a PAR 155 vibrating sample magnetometer. The magnetometer was calibrated with $[Hg\{Co(SCN)_4\}]$ and the susceptibility data were corrected for diamagnetism using Pascal's constants.

Synthesis of $[Cu(ACPY)_2]ClO_4$ (1): ACPY (0.6 mL, 5.36 mmol) was dissolved in anhydrous, degassed methanol (15 mL) to which freshly prepared $[Cu(CH_3CN)_4]ClO_4$ (0.88 g, 2.68 mmol) was added under dry N_2 and stirred for 30 min. The reddish-brown compound precipitated was filtered, washed thoroughly with diethyl ether (50 mL) and stored in vacuo over fused $CaCl_2$. Yield: 0.65 g (60%). $C_{14}H_{14}ClCuN_2O_6$ (405.2): calcd. C 41.46, H 3.48, Cu 15.68, N 6.91; found C 41.43, H 3.60, Cu 15.61, N 7.08. FTIR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1689 (s), 1672 (s) [ν(C=O)], 1591 (m) [ν(C=N)], 1568 (m) [ν(C=C)], 1088 (vs), 625 (s) [ν(ClO_4)]. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε_{max} [M^{-1}cm^{-1}]) = 233 (1.5×10^4), 267 (1.0×10^4), 321 (2.1×10^3); (nujol mull): 260, 350, 465 sh.

Synthesis of $[Cu_2(3\text{-}H^+)_2](ClO_4)_2$ (2): Solid **1** (0.405 g, 1 mmol) was suspended in 10 mL of methanol to obtain a reddish-brown suspension. 30% (w/v) hydrogen peroxide solution (0.11 mL, 1 mmol) was then added with stirring. A green colour appeared immediately and, after 5 min of stirring, a green solution was obtained from which a dark-green compound started to separate. The reaction mixture was left in the air undisturbed for another 30 min. The precipitated green compound was then filtered, washed thoroughly with 15 mL of methanol cautiously and dried in vacuo over fused $CaCl_2$. Yield: 0.156 g (36%). $C_{30}H_{34}Cl_2Cu_2N_4O_{14}$ (872.61): calcd. C 41.27, H 3.93, Cu 14.57, N 6.42; found C 40.79, H 4.20, Cu 14.55, N 5.98. FTIR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3383 (vs) [ν(OH)], 1609 (sh) [ν(C=N)], 1570 (m) [ν(C=C)], 1146–1053 (vs), 625 (s) [ν(ClO_4)]. μ [μ_B] = 1.05 (per Cu; at 298 K). UV/Vis (DMF): λ_{max} [nm] (ε_{max} [M^{-1}cm^{-1}]) = 268 (1.5×10^4), 324 (2.5×10^3), 674 (9.9×10); (nujol mull): 267, 311, 677 sh. Single crystals were grown by direct diffusion of diethyl ether into a methanol solution of the complex.

Attempted Isolation of 3 from $[Cu_2(3\text{-}H^+)_2](ClO_4)_2$: 30 mL of 25% ammonia was added to a suspension of $[Cu_2(\mathbf{3}\text{-}H^+)_2](ClO_4)_2$ (3.2 g, 3.67 mmol) in 75 mL of chloroform with stirring. The stirring was continued for 3 h. The aqueous layer was then discarded and the organic layer was washed thoroughly with 2 × 25 mL of water and then dried with anhydrous Na_2SO_4. The brown ligand solution thus obtained was concentrated in a rotary evaporator to obtain a dense liquid. The FTIR spectrum of the isolated ligand matched that of ACPY.

Synthesis of $[Ag(ACPY)_2]ClO_4$ (4): Solid $AgClO_4{\cdot}xH_2O$ (1.04 g) was added to ACPY (1.12 mL, 10 mmol) in THF (15 mL) and stirred for 30 min. The white compound precipitated was filtered, washed with diethyl ether (10 mL) and dried in vacuo over fused $CaCl_2$. Yield: 1.48 g (66%). $C_{14}H_{14}AgClN_2O_6$ (449.6): calcd. C 37.38, H 3.14, N 6.23; found C 37.49, H 3.05, N 6.20. FTIR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1700 (vs) [ν(C=O)], 1583 (m) [ν(C=N)], 1099 (vs), 630 (s) [ν(ClO_4)]. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε_{max} [M^{-1}cm^{-1}]) = 232 (1.2×10^4), 270 (1.0×10^4). Single crystals suitable for X-ray crystallography were grown by direct diffusion of *n*-hexane into a dilute CH_2Cl_2 solution of **4**.

Reaction 2: Freshly distilled en (0.06 mL, 0.89 mmol) was added to **1** (0.36 g, 0.89 mmol), dissolved in anhydrous methanol (20 mL). The resulting red solution was refluxed for 4 h and then kept in the refrigerator overnight. The red compound, [**5**]$ClO_4{\cdot}0.5H_2O$, precipitated was filtered, washed with diethyl ether (5 mL) and stored in vacuo over fused $CaCl_2$. Yield: 0.30 g (67%). $C_{16}H_{19}ClCuO_{4.5}N_2$ (410.2): calcd. C 43.82, H 4.37, Cu 14.50, N 12.78; found C 43.85, H 4.42, Cu 14.45, N 12.70. FTIR (KBr): $\tilde{\nu}$ [cm^{-1}] = 1589 (s) [ν(C=N)], 1088 (vs), 627 (s) [ν(ClO_4)]. UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε_{max} [M^{-1}cm^{-1}]) = 229 (1.9×10^4), 258 (2.2×10^4), 277 (1.3×10^4), 382 (3.5×10^3), 471 (8.3×10^3). ^{1}H NMR (300 MHz, CD_2Cl_2, TMS): δ [ppm] = 3.41–3.82 (alkyl protons), 7.67–8.58 (pyridyl protons).

Caution! *Although we have not met with any incident during our studies, care should be taken in handling these compounds as perchlorate salts are potentially explosive. They should not be prepared and stored in large amounts.*

X-ray Crystallography: Data were measured with Mo-K_α radiation with an MARresearch Image Plate System at 293(2) K. The crystals were positioned at 70 mm from the image plate; 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program[25] to provide 3352 independent reflections for **2** and 2951 for **4**. The structures were solved by direct methods with the Shelx86 program.[26] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2-times those of the atom to which they are attached. The hydrogen atom on O30 in **2** was located in the difference Fourier map and refined with a distance constraint. The perchlorate anion in **4** was disordered with two sets of oxygen tetrahedra being refined with half occupancy. An empirical absorption correction was applied using DIFABS.[27] The structures were refined on F^2 using Shelxl.[28] Selected crystallographic data for complexes **2** and **4** are given in

Table 1. Crystallographic data for complexes **2** and **4**.

	2	**4**
Empirical formula	$C_{30}H_{34}Cl_2Cu_2N_4O_{14}$	$C_{14}H_{14}AgClN_2O_6$
Formula mass	872.61	449.6
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	10.412(14)	7.342(9)
b [Å]	12.500(14)	9.884(11)
c [Å]	13.877(16)	11.922(13)
α [°]	90	85.60(1)
β [°]	97.096(10)	81.39(1)
γ [°]	90	75.02(1)
Volume [Å^3]	1792(4)	825.7(2)
Z	2	2
Calculated density [g cm^{-3}]	1.617	1.808
Absorption coefficient [mm^{-1}]	1.408	1.415
F(000)	892	448
Θ range [°]	2.2–25.8	2.90–26.01
Index ranges	–12/12	0/8
	–15/15	–11/12
	–16/16	–14/14
Unique reflections	3352	2951
Observed reflections [$I > 2\sigma(I)$]	2649	2951
Parameters	257	269
R indices (observed data)	$R1$ = 0.0837	$R1$ = 0.0601
	$wR2$ = 0.1699	$wR2$ = 0.1619
R indices (all data)	$R1$ = 0.1155	$R1$ = 0.1018
	$wR2$ = 0.2104	$wR2$ = 0.1805
Largest difference peak/hole [e Å^{-3}]	0.48/–0.69	0.74/–0.83

Table 1. CCDC-267815 (**2**) and -249100 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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