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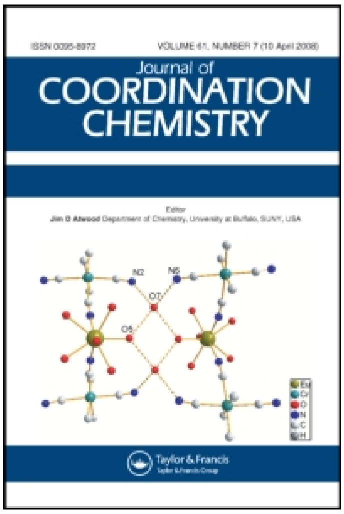

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Synthesis and co-crystallisation behaviour of copper(II) complexes of two isomeric *p*-tolyl-terpyridines§

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Copper(II) complexes incorporating the isomeric tolyl-derivatised terpyridine ligands, 4′-*p*-tolyl-2,2′:6′,2″-terpyridine (L^1) and 6′-*p*-tolyl-2,2′:2″,4′-terpyridine (L^2) have been prepared and characterised by X-ray diffraction. The first of these is a co-crystal of type $[Cu(L^1)(NO_3)_2]\cdot[Cu(L^1)(NO_3)(EtOH)]NO_3\cdot MeOH$ while the second is a single complex of type $[Cu(L^2)_2(NO_3)]NO_3\cdot 0.5MeOH\cdot 1.5H_2O$. Crystallisation of a mixture of both products from ethanol/methanol (1 : 1) yields an unusual co-crystalline product of stoichiometry $[Cu(L^2)_2NO_3]_2[Cu(L^1)(NO_3)_2](NO_3)_2$ whose structure was also confirmed by an X-ray stucture determination.

Keywords: Co-crystal; Terpyridine; Copper(II); Supramolecular; X-ray

1. Introduction

The metal ion chemistry of polypyridine ligands has been extensively studied since the beginnings of coordination chemistry, in part, due to the ability of such ligands to coordinate to a wide variety of metal ions, often leading to complexes with unusual electronic and/or structural properties [1–3]. In particular, the metal ion chemistry of 2,2′:6′,2″-terpyridine (terpy) and its substituted derivatives has received a great deal of attention over many decades [4, 5]. Much of this work and many of the applications have been summarised in a recent book [6]. In the present study we have investigated the interaction of copper(II) nitrate with a *p*-tolyl

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§Dedicated to Professor Peter Williams in honour of his contribution to chemistry over many years.

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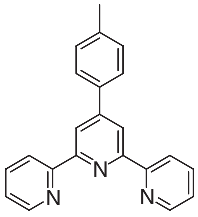
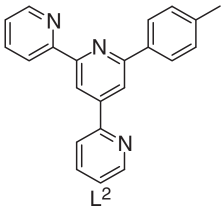
derivative of terpy, 4′-p-tolyl-2,2′:6′,2″-terpyridine L^1, as well as its lower symmetry isomer 6′-*p*-tolyl-2,2′:2″,4′-terpyridine L^2.



L^1



L^2

Copper(II) complexes of L^1 have been synthesised previously in isolated studies. A complex of stoichiometry $Cu(L^1)Cl_2$ was obtained as part of an enzymatic study and shown to be an inhibitor for furin [7]; more recently, an investigation of its interaction with DNA has also been reported [8]. In another study, a mixed ligand species $\{[CuL^1](HO_3P(CH_2)_4PO_3)]\cdot H_2O$ was shown by X-ray diffraction to have the copper(II) in a square pyramidal, O_2N_3 coordination environment [9]. A complex of type $[Cu(L^1)_2](ClO_4)_2$ has also been reported and was shown to contain the copper in an axially compressed, distorted six-coordinate environment [10] consisting of six N-donors from the two terpyridyine ligands. Copper(II) complexes of many other 4′-substituted terpyridines have been also reported. For example, in one structural study [11], the copper(II) nitrate complex of 4′-(2-pyridyl)-2,2′:6′,2″-terpyridine was shown to contain a six-coordinate copper(II), with three nitrogens from the terpyridine and three oxygens from two nitrates (one bidentate, one monodentate) filling the coordination sites. Complexes of L^1 incorporating different metal ions (including mixed metal and mixed ligand species) have also been reported by a number of groups as exemplified, for example, by recent reports by Zubieta *et al.* [9], McDonagh *et al.* [12] and Yin *et al.* [13].

Ligand L^2 was characterised in1991 as a by-product of the synthesis of L^1 [14] and other reports of its isolation have also appeared subsequently [15–17]. While the hydrochloric acid salt of L^2 has been reported to show potential as a therapeutic agent for neurodegenerative disorders [17], there appear to be no reports of the interaction of this potential ligand with metal ions.

We now report the synthesis of new copper(II) nitrate complexes of both L^1 and L^2 together with the isolation and characterisation of co-crystals incorporating each of these metal derivatives.

2. Experimental

2.1. *Materials and Measurements*

Melting points were measured using a Gallenkamp Electrothermal apparatus and are uncorrected. ^1H NMR spectra were recorded on Bruker Avance DPX300 or DPX200 spectrometers operating at 300 and 200 MHz, respectively. ^{13}C NMR spectra were recorded on a Bruker Avance DPX300 spectrometer operating at 75.5 MHz. Chemical shifts are reported in parts per million downfield from tetramethylsilane.

Low resolution electrospray mass spectra (ESI-MS) were obtained on a Finnigan LCQ-8 spectrometer. FTIR spectra were determined on a Bio-Rad FTS-40 spectrometer. TGA analyses were performed under nitrogen using a TA Instruments HI-Res TGA 2850 thermogravimetric analyser. All commercially available reagents were used as received.

2.2. *Synthesis*

2.2.1. Preparation of L^1 and L^2. The syntheses of both L^1 and L^2 were based on a published procedure [14, 15]. A mixture of acetamide (183g, 3.1 mol), ammonium acetate (118 g, 1.5 mol), *p*-tolualdehyde (12.4 g, 103 mmol) and 2-acetylpyridine (25 g, 206 mmol) was refluxed for 4 h. The mixture was then cooled to 100°C, and a solution of sodium hydroxide (90 g) in water (200 ml) was slowly added. The solution was allow to cool and left to stand overnight. A dark brown solid formed and the mother liquor was decanted. The solid was washed with water and then dissolved in glacial acetic acid (75 ml). The hydrogen bromide salt was precipitated by adding 48% HBr (60 ml) and the resulting green solid was filtered off and dissolved in water (200 ml). This solution was basified to pH 10 with potassium hydroxide solution and the resulting suspension extracted with dichloromethane (3×200 ml). The combined extracts were dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The residue was recrystallised from ethanol to give white needles (12.2 g). This product was dissolved in ethanol/dichloromethane (1 : 1; 400 ml) and iron(II) ammonium sulfate hexahydrate (6.45 g) in water (80 ml) was added to give a deep purple solution. The dichloromethane was removed under reduced pressure and potassium hexafluorophosphate (6.15 g) in water (50 ml) was added. The purple precipitate that formed was collected by filtration and the solid was washed with warm ethanol (3×100 ml). The combined ethanol fractions were taken to dryness and the residue was recrystallised from ethanol to yield L^2 (2.2 g, 6.6%) as a by-product. The remaining purple precipitate was suspended in methanol/water (5 : 1, 300 ml), and the pH of the suspension was increased to pH 12 with potassium hydroxide pellets. Excess sodium sulfide nonahydrate was added to the suspension and the mixture was heated to reflux for 48 h. The resulting solid was removed by filtration through celite. The celite was washed with methanol (150 ml), the filtrates were combined and then the methanol was removed. The aqueous solution that remained was extracted with dichloromethane (3×100 ml) and the combined extracts dried over anhydrous sodium sulfate then evaporated to dryness under reduced pressure. L^1 was obtained as white needles (7.1 g, 21%) after recrystallisation from ethanol. The MS and ^{1}H NMR spectra were consistent with the literature for both compounds [14, 15].

L^1: ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 8.73 (2H, s), 8.71 (2H, m), 8.67 (2H, d), 7.87 (2H, td), 7.82 (2H, d), 7.35 (2H, dd), 7.32 (2H, d), 2.43 (3H, s). MS (ESI): $m/z = 324.4$ $(M + H)^+$; m.p. 170°C (lit. m.p. 174–176°C) [14].

L^2: ^{1}H NMR (200 MHz, $CDCl_3$, 300 K): δ 8.89 (1 H, s), 8.79 (1H, d), 8.73 – 8.65 (3 H, m), 8.51 (1H, s), 8.18 (2H, d) 8.04 (1H, d), 7.85 (2H, q), 7.34 (4H, m), 2.44 (3H, s). MS (ESI): $m/z = 324.4$ $(M + H)^+$; m.p. 140–141°C (lit. m.p. 142°C) [14].

2.2.2. Preparation of co-crystal $[Cu(L^1)(NO_3)_2] \cdot [Cu(L^1)(NO_3)(EtOH)]NO_3 \cdot MeOH$ (1). Copper(II) nitrate dihydrate (36 mg, 0.16 mmol) in hot methanol (5 ml) was added dropwise to a solution of L^1 (50 mg, 0.16 mmol) in hot ethanol (5 ml). The volume of the resulting deep green solution was reduced to 5 ml on a hotplate. The solution was left to stand overnight and the dark blue crystalline product was filtered off and washed with cold ethanol and ether (64 mg, 81%). M.p. 154 °C (decomp.). MS (ESI): $m/z = 448.2$ $(M - NO_3)^+$. Anal. Calcd. for $C_{44}H_{34}Cu_2N_{10}O_{12} \cdot CH_3OH \cdot C_2H_5OH$ (%): C, 51.35; H, 4.03; N, 12.75. Found: C, 51.46; H, 3.96; N, 12.71. Crystals for the X-ray crystal structure analysis were obtained by slow evaporation of an ethanol/methanol (1 : 1) solution of the above product over 24 h.

2.2.3. Preparation of $[Cu(L^2)_2NO_3]NO_3 \cdot 0.5MeOH \cdot 1.5H_2O$ (2). Copper(II) nitrate dihydrate (72 mg, 0.32 mmol) in hot methanol (5 ml) was added dropwise to L^2 (100 mg, 0.31 mmol) in hot ethanol (6 ml). This solution was left to cool and slowly evaporate, resulting in bright green crystals of the desired complex (34 mg, 13%). M.p. 180°C (decomp.). MS (ESI): $m/z = 709.47$ $[Cu\,(L^2)_2]^+$, 419.73 $[Cu(L^2)\,NO_3]^+$. Anal. Calcd. for $C_{44}H_{34}CuN_8O_6 \cdot 0.5MeOH \cdot 1.5H_2O$ (%): C, 60.94; H, 4.49; N, 12.79. Found: C, 61.29; H, 4.50; N, 12.96.

2.2.4. Preparation of co-crystal $[Cu(L^2)_2NO_3]_2[Cu(L^1)(NO_3)_2](NO_3)_2 \cdot 2.5H_2O$ (3). Method 1: Complexes **1** and **2** were dissolved in hot ethanol/methanol (2 ml, 1:1). The resulting solution was left to evaporate slowly, resulting in the formation of emerald green crystals. An X-ray structure determination confirmed that this was the same co-crystalline product as obtained by method 2 below.

Method 2: Ligands L^1 (20 mg, 0.006 mmol) and L^2 (80 mg, 0.25 mmol) were dissolved in hot ethanol (6 ml) and $Cu(NO_3)_2 \cdot 2.5H_2O$ (72 mg, 0.31 mmol, 1 equiv. with respect to the sum of L^1 and L^2) dissolved in hot methanol (5 ml) was then added drop-wise. The solution was left to cool and evaporate slowly to yield emerald green crystals of the co-crystalline product (110 mg, 64%). An X-ray structure determination was obtained using a crystal from this batch. The remaining product was dried in vacuum over P_2O_5 and stored in air. Microanalysis indicated that this bulk sample corresponded to the 2.5 hydrate. Anal. Calcd for $C_{110}H_{85}Cu_3N_{21}O_{18} \cdot 2.5H_2O$ (%): C, 59.39; H, 4.08; N, 13.22. Found: C, 59.45; H, 3.97; N, 13.27.

2.2.5. Crystal structure determinations. X-ray structural data for **1** and **2** were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans. Data for **3** were collected with ω scans using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a sealed tube (0.71073 Å). Data were collected at 150 K to approximately 56° 2θ. Data integration and reduction were undertaken with SAINT and XPREP [18] and subsequent computations were carried out using the WinGX-32 graphical user interface [19]. The structures were solved by direct methods using SIR97 [20]. Multi-scan empirical absorption corrections were applied to the data set using the program SADABS or TWINABS [21]. Data were refined and extended with SHELXL-97 [21]. Non-hydrogen atoms with occupancy greater than 0.5 were refined anisotropically. Carbon-bound and non-water oxygen-bound hydrogen atoms were included in idealised positions and refined using a riding model. Water-bound hydrogen atoms were first located in the difference Fourier map and then modelled with bond length restraints. Where they could not be located they were not modelled.

2.2.6. X-ray details for $[Cu(L^1)(NO_3)_2] \cdot [Cu(L^1)(NO_3)(EtOH)]NO_3 \cdot MeOH$ (1).

The coordinated ethanol molecule is disordered over three positions with occupancies of 0.6, 0.25 and 0.15 respectively.

Formula $C_{47}H_{44}Cu_2N_{10}O_{14}$, *M* 1100.00, Monoclinic, space group $P2_1/n$(#14), *a* 17.9568(11), *b* 8.7661(4), *c* 30.5083(19) Å, β 99.212(3), *V* 4740.4(5) Å^3, D_c 1.541 g cm^{-3} *Z*4, crystal size 0.223 by 0.062 by 0.037 mm, colour blue, habit blade, temperature 150(2) Kelvin, λ(Mo-Kα) 0.71073 Å, μ(Mo-Kα) 0.977 mm^{-1}, $T(\mathrm{SADABS})_{\mathrm{min,max}}$ 0.8432736, 0.960000, $2\theta_{\mathrm{max}}$ 56.84, *hkl* range −24 23, −11 11, −40 40, *N* 82435, N_{ind} 11916(R_{merge} 0.0824), N_{obs} 7562($I > 2\sigma(I)$), N_{var} 678, residuals $R1(F)$ 0.0592, $wR2(F^2)$ 0.1669, GoF(all) 1.023, $\Delta\rho_{\mathrm{min,max}}$ −0.653, 1.868 e− Å^{-3}. The refinement residuals are defined as $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w(Fc^2)^2)^{1/2}$ all reflections where $w = 1/[\sigma^2(F_o^2) + (0.0866P)^2 + 2.0499P]$ where $P = (F_o^2 + 2F_C^2)/3$.

2.2.7. X-ray details for $[Cu(L^2)_2NO_3]NO_3 \cdot 0.5MeOH \cdot 1.5H_2O$ (2).

The N(3) containing pyridine ring is disordered over two positions, modelled with equal occupancy. Bond length and FLAT restraints were required to facilitate realistic modeling of this disorder. The hydrogen atoms on C(44) were modelled over two positions. There is some disordered solvent in the lattice which was modelled as a combination of methanol (two positions, occupancies 0.4 and 0.2) and water (five positions, occupancies 0.55, 0.3, 0.15, 0.25, 0.15). There is hydrogen bonding between the 0.55 occupancy water molecule and the pyridine (N(3)) nitrogen.

Formula $C_{44.60}H_{39.20}CuN_8O_8$, *M* 878.78, triclinic, space group *P*1(#2), *a* 11.1102(8), *b* 14.1407(11), *c* 14.5496(12) Å, α88.870(7), β73.995(5), γ75.426(5)°, *V* 2123.5(3) Å^3, D_c 1.374 g cm^{-3}, *Z*2, crystal size 0.45 by 0.178 by 0.163 mm, colour green, habit prism, temperature 150(2) Kelvin, λ(Mo-Kα) 0.71073 Å, μ(Mo-Kα) 0.578 mm^{-1}, $T(\mathrm{SADABS})_{\mathrm{min,max}}$ 0.783, 0.910, $2\theta_{\mathrm{max}}$ 60.96, *hkl* range −15 14, −20 20, −20 20, *N* 51380, N_{ind} 12546(R_{merge} 0.0575), N_{obs} 8176($I > 2\sigma(I)$), N_{var} 562, residuals $R1(F)$ 0.0626, $wR2(F^2)$ 0.1814, GoF(all) 1.060, $\Delta\rho_{\mathrm{min,max}}$ −1.248, 1.341 e$^-$ Å^{-3}. The refinement residuals are defined as $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w(Fc^2)^2)^{1/2}$ all reflections where $w = 1/[\sigma^2(F_O^2) + (0.0866P)^2 + 2.0499P]$ where $P = (F_o^2 + 2F_C^2)/3$.

2.2.8. X-ray details for X-ray structure of $[Cu(L^2)_2NO_3]_2[Cu(L^1)(NO_3)_2](NO_3)_2$ (3).

Despite appearing (at least visually) to be single crystals, the crystal employed for this determination proved to be twinned by a two-fold rotation about the *a*-axis. The twinning was resolved using GEMINI [23] and resulted in a final BASF value of 0.24027. The two uncoordinated anions are disordered. The N(20)-containing anion is rotationally disordered, with the oxygens modelled on two positions with occupancies of 0.75 and 0.25. The N(21)-containing anion is disordered over two non-overlapping positions each with 50 percent occupancy. Bond length and flat restraints were applied to facilitate realistic modeling. The remaining electron density in the structure was modelled as a combination of disordered methanol (two positions, occupancies 0.5 and 0.3) and water (six positions, occupancies 0.5, 0.3, 0.3, 0.2, 0.2, 0.2). Some of the positions of the water molecules overlap with those of the disordered methanol and nitrate groups. The non-solvent/anion sections of the structure have larger than ideal $U_{\mathrm{eq}\ max/min}$ ratios for both carbons and hydrogens, which is not unexpected in structures of this type, given the large ligand size.

Formula $C_{110.80}H_{91.60}Cu_3N_{21}O_{20.50}$, M 2235.87, Triclinic, space group $P1$(#2), a 14.782(2), b 14.927(2), c 23.678(4) Å, α 83.842(3), β 80.473(3), γ 88.565(3)°, V 5122.7(14) $\mathrm{Å}^3$, D_c 1.451 g cm^{-3}, Z 2, crystal size 0.450 by 0.300 by 0.150 mm, colour green, habit multi-face, temperature 150(2) Kelvin, λ(MoKα) 0.71073 Å, μ(Mo-Kα) 0.701 mm^{-1}, T(TWINABS (BRUKER, 2003))$_{\mathrm{min,max}}$ 0.673, 0.903, $2\theta_{\mathrm{max}}$ 56.72, hkl range −18 19, −19 19, 0 31, N 25626, N_{ind} 25197(R_{merge} 0.0577), N_{obs} 14522(I > 2σ(I)), N_{var} 1415, residuals $R1(F)$ 0.0591, $wR2(F^2)$ 0.1539, GoF(all) 0.931, $\Delta\rho_{\mathrm{min,max}}$ −0.657, 1.082 e− $\mathrm{Å}^{-3}$. The refinement residuals are defined as $R1 = \Sigma\|F_\mathrm{o}|-|F_\mathrm{c}\|/\Sigma|F_\mathrm{o}|$ for $F_\mathrm{o} > 2\sigma(F_\mathrm{o})$; $wR2 = (\Sigma w(F_\mathrm{o}^2 - F_\mathrm{c}^2)^2/\Sigma(w(Fc^2)^2)^{1/2}$ all reflections where $w = 1/[\sigma^2(F_\mathrm{O}^2) + (0.0866P)^2 + 2.0499P]$ where $P = (F_o^2 + 2F_\mathrm{C}^2)/3$.

3. Results and discussion

Reaction of copper(II) nitrate with L^1 or L^2 in a methanol/ethanol mixture resulted in blue and bright green crystalline products respectively. The crystal structure of the first of these (figure 1), confirmed the stoichiometry obtained from microanalysis and showed the presence of two independent molecules with different coordination geometries in the unit cell such that the product is a co-crystal of type $[Cu(L^1)(NO_3)_2]\cdot[Cu(L^1)(NO_3)(EtOH)]NO_3\cdot MeOH$. In the first of the two complexes present, the terpyridine coordinates to copper(II) in its normal tridentate manner with the remaining coordination sites occupied by two nitrates, one as a bidentate ligand and the other monodentate. The second complex is positioned adjacent to the first but rotated through 180°. The copper centre in this case is also six-coordinate. The terpyridine again occupies three coordination sites, with two of the remaining sites filled by a bidentate nitrate group, while the sixth site is occupied by the oxygen of an ethanol. The remaining nitrate in this case is located nearby in the lattice, as is an unbound methanol. There is hydrogen bonding in the structure between the coordinated ethanol and the free nitrate and also between the methanol and the free nitrate. There is also offset face-to-face π–π stacking between adjacent molecules and a number of close CH–O distances indicative of weak hydrogen bond interactions.

TGA analysis of the co-crystalline product **1**, conducted at 2 deg/min to 500°C, revealed a slow loss of weight on heating above ambient temperature with the weight loss accelerating from 150 to 165 °C at which temperature a loss of 7.3 percent had occurred (figure 2), corresponding to the combined loss of coordinated ethanol and non-coordinated methanol. No further loss occurs up to ~347°C, at which point ~70 percent of the original mass is lost, indicating complex decomposition.

The crystal structure of **2** (figure 3) shows the presence of a $[Cu(L^2)_2(NO_3)]^+$ cation. The two L^2 ligands coordinate to the copper(II) via bipyridine in an identical (*cis*)

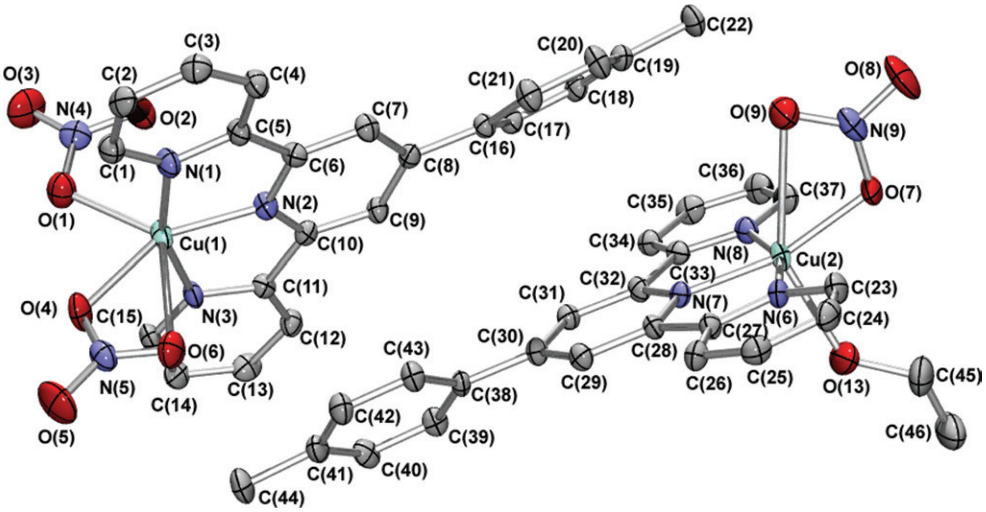


Figure 1. ORTEP plot of $[Cu(L^1)(NO_3)_2]\cdot[Cu(L^1)(NO_3)(EtOH)]NO_3\cdot MeOH$.(**1**) Both molecules in the unit cell are shown. Regions of disorder, uncoordinated nitrate, hydrogens and methanol solvate have been removed for clarity. Thermal ellipsoids shown at the 50 percent probability level. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.027(3); Cu(1)–N(2) 1.942(3); Cu(1)–N(3) 2.013(3); Cu(1)–O(1) 2.179(3); Cu(1)–O(4) 2.051(3); Cu(1)–O(6) 2.747(3); Cu(2)–N(6) 2.044(3); Cu(2)–N(7) 1.922(3); Cu(2)–N(8) 2.032(3); Cu(2)–O(7) 1.978(3); Cu(2)–O(13) 2.239(3); Cu(2)–O(9) 2.578(3); N(2)–Cu(1)–N(3) 79.64(11); N(2)–Cu(1)–N(1) 79.92(11); N(3)–Cu(1)–N(1) 159.54(12); N(2)–Cu(1)–O(4) 148.65(11); N(3)–Cu(1)–O(4) 98.78(11); N(1)–Cu(1)–O(4) 98.16(11); N(2)–Cu(1)–O(1) 134.47(11); N(3)–Cu(1)–O(1) 94.70(11); N(1)–Cu(1)–O(1) 100.26(11); O(4)–Cu(1)–O(1) 76.83(10); N(7)–Cu(2)–O(7) 164.28(11); N(7)–Cu(2)–N(8) 80.32(11); O(7)–Cu(2)–N(8) 100.34(12); N(7)–Cu(2)–N(6) 80.25(11); O(7)–Cu(2)–N(6) 97.76(11); N(8)–Cu(2)–N(6) 160.44(12); N(7)–Cu(2)–O(13) 103.92(11); O(7)–Cu(2)–O(13) 91.79(11); N(8)–Cu(2)–O(13) 90.51(12); N(6)–Cu(2)–O(13) 96.32(12).

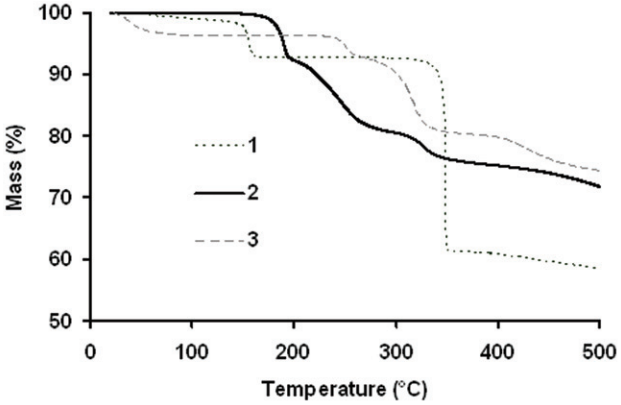


Figure 2. Thermograms for $[Cu(L^1)(NO_3)_2]$ $[Cu(L^1)(NO_3)(EtOH)]NO_3\cdot MeOH$ (**1**), $[Cu(L2)_2NO_3]NO_3\cdot 0.5MeOH\cdot 1.5H_2O$ (2) and $[Cu(L^2)_2NO_3]_2[Cu(L^1)(NO_3)_2](NO_3)_2\cdot 2.5H_2O$ (**3**).

manner, with the remaining two coordination sites occupied by a bidentate nitrate. It is anticipated that *trans* coordination of L^2 in an octahedral coordination environment would be inhibited by severe steric hindrance arising from the presence of tolyl groups. With respect to this, a search of the literature revealed no examples in which the related substituted ligand, 6′-phenyl-2,2′-bipyridine [24–27], was demonstrated to coordinated

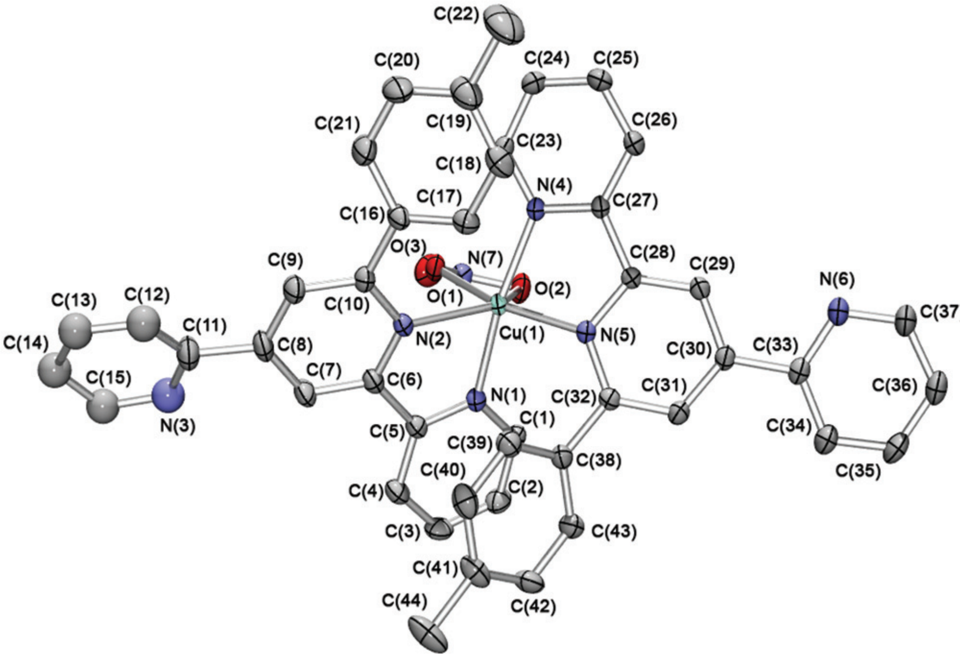


Figure 3. ORTEP plot of $[Cu(L^2)_2NO_3]NO_3 \cdot 0.5MeOH \cdot 1.5H_2O$ (**2**). Regions of disorder, uncoordinated nitrate, hydrogens and solvent molecules have been removed for clarity. Thermal ellipsoids shown at the 50% probability level. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.986(2); Cu(1)–N(2) 2.254(2); Cu(1)–N(4) 1.975(2); Cu(1)–N(5) 2.064(2); Cu(1)–O(1) 2.0416(19); Cu(1)–O(2) 2.665(2); N(4)–Cu(1)–N(1) 165.77(9); N(4)–Cu(1)–O(1) 90.42(8); N(1)–Cu(1)–O(1) 87.37(8); N(4)–Cu(1)–N(5) 81.19(9); N(1)–Cu(1)–N(5) 96.88(9); O(1)–Cu(1)–N(5) 162.17(8); N(4)–Cu(1)–N(2) 114.46(9); N(1)–Cu(1)–N(2) 79.17(9); O(1)–Cu(1)–N(2) 82.16(8); N(5)–Cu(1)–N(2) 115.63(8).

in a *trans* fashion around an octahedral metal ion – consistent with the expected steric hindrance arising from the presence of the bulky phenyl substituent in the 6′-position of the bipyridine.

In the present complex, each of the tolyl groups are π-stacked in an offset-face-to-face orientation with the coordinated non-central pyridine ring of the other L^2 ligand which presumably contributes to the stability of the coordination environment (centroid-centroid distances are 3.5 Å and 3.8 Å for the N(1) – C(38)-containing rings and N(4) – C(16) containing rings, respectively). The third pyridine ring, located at the 'back' of the ligand, is also sterically hindered with respect to approach of a further metal ion and remains uncoordinated. There is extensive offset face-to-face and edge-to-face π–π stacking between adjacent molecules throughout the lattice forming an infinite three-dimensional array (for example, the respective intermolecular C to C distances for C(2) to C(3) are 3.4 Å and intermolecular H – centroid distances for H(18) to the centroid of the C(38)-containing ring are 3.1 Å). Once again, there are also some close CH–O distances indicating weak hydrogen bond interactions.

The TGA for **2** (figure 2) shows that the complex is thermally stabile to180°C at which point the material losses ~7 percent of its mass (corresponding to loss of the 0.5 methanol and 1.5 water solvating molecules); immediately after this decomposition appears to occur.

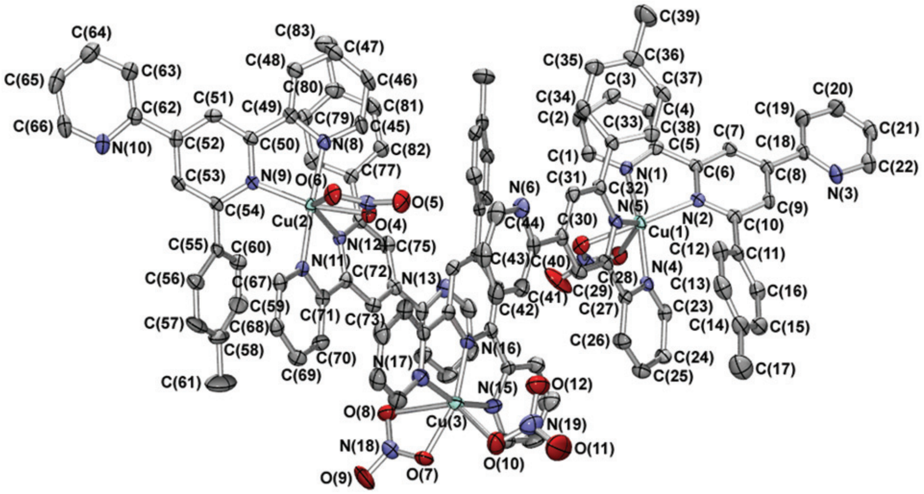


Figure 4. ORTEP representation of the X–ray structure of [Cu(L^2)$_2$NO$_3$]$_2$ · [Cu(L^1)(NO$_3$)$_2$](NO$_3$)$_2$ (**3**). The three molecules present in the unit cell are shown. Uncoordinated anions have been removed for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.962(4); Cu(1)–N(2) 2.093(4); Cu(1)–N(4) 1.983(4); Cu(1)–N(5) 2.195(3); Cu(1)–O(1) 2.146(3); Cu(1)–O(2) 2.584(4); Cu(2)–N(8) 1.974(4); Cu(2)–N(9) 2.060(3); Cu(2)–N(4) 1.999(4); Cu(2)–N(12) 2.221(4); Cu(2)–O(4) 2.058(3); Cu(2)–O(6) 2.710(3); Cu(3)–N(15) 2.028(4); Cu(3)–N(16) 1.922(4); Cu(3)–N(17) 2.035(4); Cu(3)–O(7) 1.976(3); Cu(3)–O(10) 2.182(4); Cu(3)–O(8) 2.605(4); N(1)–Cu(1)–N(4) 168.27(15); N(1)–Cu(1)–N(2) 80.79(14); N(4)–Cu(1)–N(2) 105.52(14); N(1)–Cu(1)–O(1) 88.51(13); N(4)–Cu(1)–O(1) 81.97(13); N(2)–Cu(1)–O(1) 156.66(13); N(1)–Cu(1)–N(5) 106.77(14); N(4)–Cu(1)–N(5) 79.19(14); N(2)–Cu(1)–N(5) 118.60(13); O(1)–Cu(1)–N(5) 84.29(12); N(8)–Cu(2)–N(11) 168.36(15); N(8)–Cu(2)–O(4) 87.17(14); N(11)–Cu(2)–O(4) 85.51(13), N(8)–Cu(2)–N(9) 81.12(14), N(11)–Cu(2)–N(9) 102.84(14); O(4)–Cu(2)–N(9) 158.50(13); N(8)–Cu(2)–N(12) 109.45(14); N(11)–Cu(2)–N(12) 78.80(14); O(4)–Cu(2)–N(12) 84.23(12); N(9)–Cu(2)–N(12) 116.64(13); N(16)–Cu(3)–O(7) 157.77(15); N(16)–Cu(3)–N(15) 79.94(16); O(7)–Cu(3)–N(15) 103.11(15); N(16)–Cu(3)–N(17) 80.22(16); O(7)–Cu(3)–N(17) 94.95(15); N(15)–Cu(3)–N(17) 160.14(16); N(16)–Cu(3)–O(10) 119.18(15); O(7)–Cu(3)–O(10) 82.81(15); N(15)–Cu(3)–O(10) 93.94(15); N(17)–Cu(3)–O(10) 96.48(15).

Co-crystal **3** was produced by two different routes. In the first of these, a 1:1 mixture of **1** and **2** was dissolved in hot ethanol/methanol which upon cooling (and allowing to stand) led to isolation of **3**. The second method involved dissolving a mixture of L^1 and L^2 in a 1:4 ratio in hot ethanol followed by addition of a hot methanol solution of copper(II) nitrate. Slow evaporation of this solution also resulted in crystallisation of emerald green crystals of **3**. The products from each procedure were confirmed to be identical by separate X-ray crystal structure determinations, for the sake of brevity details of only one determination are presented.

The X-ray structure of co-crystal **3** (figure 4) confirmed that it contained one complex of type [Cu(L^1)(NO$_3$)$_2$] (that is, one component of the co-crystal **1**) and two complexes of type **2.** The six coordinate structure of the former complex within **3** is quite similar to that for [Cu(L^1)(NO$_3$)$_2$] discussed previously. Similarly, in **3** the coordination environments of the complexes of type **2** are almost identical to that occurring in **2;** each copper is again six-coordinate being bound to two bidentate L^2 ligands and a bidentate nitrate. As found for **2**, π–π stacking between coordinated ligands also occurs in **3**. Once again, there is extensive offset face-to-face and edge-to-face π–π stacking present between adjacent complexes, together with CH–O hydrogen bonding that results, overall, in a three-dimensional network arrangement.

As expected, the TGA behaviour of each of **1** and **2** differs from that of co-crystal **3** (figure 2). In the latter case there is a gradual loss of weight over the temperature range 45 to ~60°C of about 2.7 percent. This approximates the loss of the 2.5 water molecules formulated for **3** on the basis of elemental analysis. The complex is then stable to 250°C, at which temperature decomposition clearly occurs.

4. Conclusion

Co-crystals are a class of materials which, although appearing in the literature for a considerable time under various guises, have of late been receiving increased attention [28, 29], in part, attributable to developments in the pharmaceutical industry. These studies has tended to focus on the isolation of organic co-crystals – with, overall, less emphasis being given to metal-containing co-crystal systems. In this manuscript we describe the synthesis and X-ray structures of two new examples of the latter type, namely co-crystals incorporating copper(II) complexes of the isomeric polypyridine ligands L^1 and L^2. The first example of metal complexation by the unsymmetric ligand isomer L^2 is also reported.

Supplementary data

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre. CCDC 656669 (for **1**) and CCDC 656670 (for **2**) and CCDC 656671 (for **3**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 1223 336033; or deposit@ccdc.cam.ac.uk).

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