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Synthesis and Coordination Chemistry of 1,1,1-Tris-(pyrid-2-yl)ethane†

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A new synthesis of 1,1,1-tris(pyrid-2-yl)ethane (L), and a survey of its coordination chemistry, are reported. The complexes [ML]n (M = Fe2+, Co3+, Cu2+ and Ag+), [PdCl2L] and [Cu(L)] have all been crystallographically characterised. Noteworthy results include an unusual square planar silver(I) complex [Ag(L)X] (X = NO3− and SbF6−); the oxidative fixation of aerobic CO2 by [Cu(L)] to yield [Cu3(L)2(μ-CO3)]2[CuI]3 and [Cu(CO3)(L)]; and, water/carbonato tape and water/iodo layer hydrogen bonding networks in hydrate crystals of two of the copper(II) complexes. Cyclic voltammetric data on [Fe(L)2]2+ and [Co(L)2]2+/3+ imply that the peripheral methyl substituent has a weak influence on the ligand field exerted by L onto a coordinated metal ion.

Introduction

Tris-(pyrid-2-yl)methane, tris-(pyrid-2-yl)amine, tris-(pyrid-2-yl)phosphine and related compounds were first synthesised in the first half of the 20th century,1 and developed as tripodal ligands for transition ions in the 1960-1980s.2-4 Despite this long-standing chemistry, they continue to find use as facial protecting groups in organometallic chemistry,5-7 transition metal photochemistry,8 catalysis,8 molecular magnetism9-14 and other aspects of coordination chemistry.15 A number of such ligands py3X (py = 2-pyridyl) have been prepared, with different bridgehead groups ‘X’ (Scheme 1).

During our continuing research into the coordination chemistry of polydentate heterocyclic ligands,16 we have fortuitously found a convenient synthesis of 1,1,1-tris-(pyrid-2-yl)ethane (L, Scheme 1). The synthesis of L by a different route has only been recently reported, and its coordination chemistry has been little explored.7 We report here a survey of complexes of this ligand, and a comparison with other complexes from this family.

![Scheme 1](image-url)  
Scheme 1  Examples of tripodal tris-pyridyl ligands that have been used in coordination and organometallic chemistry (py = 2-pyridyl).

Results and Discussion

Ligand L has been previously prepared by alkylation of deprotonated, pre-formed tris-(pyrid-2-yl)methane with MeI.7 We have obtained it through an alternative one-pot procedure, by treatment of monolithiated 2-ethylpyridine with 2 equiv of 2-fluoropyridine.17 This procedure afforded microanalytically pure ligand L in 78% yield following the usual work-up, without further purification. The addition of two pyridyl groups to 2-ethylpyridine, despite the presence of only one equiv of base in the reaction mixture, was unexpected but may reflect deprotonation of the acidic intermediate Py3CHMe by the excess 2-fluoropyridine reagent, or by liberated F−.18 The identity of L was also confirmed crystallographically (ESI†).

The synthesis of [ML]2[ClO4]2 (M = Fe, 1; M = Co, 2) was performed by reaction of 2 equiv of L with the appropriate hydrated M[ClO4]2 salt, in MeCN under an N2 atmosphere. Performing the cobalt synthesis in air afforded instead the cobalt(III) complex product [CoL2][ClO4]3 (3) in good yield. The tetrakis-acetonitrile solvates of all three complex salts, and a second monohydrate form of 3, were all crystallographically characterised (Fig. 1, Table 1 and ESI†). The complex molecules in all four structures have the expected six-coordinate geometry, with crystallographically imposed inversion symmetry. The metric parameters in all the complexes are consistent with low-spin iron(II), cobalt(II) and cobalt(III) centres (Table 1 and ESI†). Unusually, a crystallographically ordered Jahn-Teller elongation is evident in the [CoL2]2+ molecule in 2. Low-spin cobalt(II) complexes of Py3X and other N-heterocyclic chelates often exhibit dynamic...
The Jahn-Teller distortion around the different N–Co–N axes (see below), which is only frozen out at very low temperatures. The Fe–N and Co–N distances in 1-3 are similar to other published compounds of the [M(Py3X)2]2+ type (M = Fe(II), Co(II) or Co(III), Scheme 1), showing that the L methyl substituent has little steric influence on the stereochemistry of the bound ligand.

The midtemperature of this spin-crossover (T_m) is estimated as >400 K. Comparable, gradual spin-crossover equilibria are shown by some salts of other [Co(Py3X)2]2+ complexes (X = N, Scheme 1). Cyclic voltammograms of 1 and 2 in MeCN/0.1 M NBut4ClO4 exhibit chemically reversible M(II/III) oxidations at E_{1/2} = +0.61 V (1, M = Fe) and −0.31 V (2, M = Co) vs. Fe/Ce+ (ESI†). These half-potentials are both ca. 0.1 V more negative than those reported for [M(Py3CH2)2]2+ (M = Fe, Co, Scheme 1), bearing in mind the different reference electrodes used in literature studies. Given the lack of any steric influence of the L methyl group on the coordination spheres of 1-3 in the crystal, this cathodic shift probably reflects the electron donating properties of the L methyl substituent. A chemically reversible Co(II/I) couple is also shown by 2 at E_{1/2} = −1.54 V, which is similar to that in [Co(Py3CH2)2]2+.

Treatment of [PdCl2(NCMe)2] with 1 equiv L in MeCN affords [PdCl2L] (4) as a yellow solid. This is a typical square planar palladium(II) complex by X-ray crystallography, containing a bidentate L ligand with one uncoordinated pyridyl group (ESI†). Complexation of AgNO3 or AgSbF6 by either 1 or 2 equiv L under the same conditions affords the salts [AgL2]Y (Y− = NO3−, 5a; Y− = SbF6−, 5b). While the nitrate salt 5a afforded X-ray quality single crystals, the more soluble 5b was used for solution measurements. The single crystal structure of 5a reveals an unusual square planar silver(I) centre (Fig. 3, Table 2), which is stereochemically comparable to the literature compound [Pd(Py3CH2)2][NO3]2.27 While the bond angles about the silver ion show only small deviations from the idealised 90° symmetry imposed by this ligand geometry, the Ag–N distances show more variation. The bonds to one L ligand are strongly inequivalent, with Ag(1)–N(1) being 0.207(2) Å shorter than Ag(1)–N(2). In contrast the other ligand is bound more symmetrically, with Ag(1)–N(4) being 0.414(2) Å shorter than Ag(1)–N(5) (Table 2). The axial silver coordination sites are sterically shielded by the two pendant pyridyl groups. However the closest Ag...C distances to these
groups are Ag(1)...C(13) = 2.9478(18) and Ag(1)...C(30) = 2.9430(18) Å, which are too long to be considered Ag...π contacts. The nitrate ion does not interact with the silver centres and occupies a hydrophobic pocket in the lattice (the closest Ag...O distance is 5.3942(16) Å). The assignment of 5a as a silver(I) complex, despite its unexpected coordination geometry, was supported by a bond valence sum (BVS) analysis which yielded an oxidation state of +1.00 for the silver ion. Notably, square planar silver(I) complexes have also been obtained with other [Cu(L)₂] complexes, which have proven useful for stabilising unusual oxidation states of transition ions, and Ag...π centres favour tetragonal coordination geometries, the cyclic voltammmogram of 5b in MeCN/0.1 M NBu₄BF₄ was investigated. An oxidation at \( E_{1/2} = +1.71 \) V vs. Fe/Fc⁺ was observed, and assigned to an Ag(I/II) couple. This process was partly reversible at 298 K at a scan rate of 500 mVs⁻¹ and its chemical reversibility diminished at lower scan rates, becoming essentially irreversible at 50 mVs⁻¹. Because of its low stability and positive potential, the chemical characterisation of [AgL₂] was not pursued further.

Complexation of CuI by 1 equiv L in MeCN afforded [CuI(L)](6), which has a distorted tetrahedral geometry by X-ray crystallography (ESI†). Although air-stable in the solid state and in solution under an inert atmosphere, 6 undergoes a series of colour changes in acetonitrile upon exposure to air. Three products were isolated from these solutions under different conditions. Green, dinuclear [Cu₂L₂(μ-CO₂)]₂[CuI₂]·2H₂O (7a) precipitates from aerobic acetonitrile containing L. This was crystallised from dmF/Et₂O as a solvate of [Cu₂L₂I₃(OH)₃]·(μ-CO₂)[CuI] (7b; \( m \approx 0.5 \)), in which the terminal iodo ligand has been partially substituted by exogenous hydroxide. Solutions of 6 or 7a in water/acetonitrile mixtures crystallise more slowly, affording blue [Cu(CO₂)L₂]·4.25H₂O (8) and [CuL₂I₂·8H₂O (9). While 9 was isolated in pure form, 8 was always contaminated by 9 which prevented a successful microanalysis from being obtained. Hence only the crystal structure of 8 is reported here.

Compounds 7a and 8 arise from the fixation of atmospheric CO₂ by an aerobically oxidised [CuL]²⁺ fragment. Consistent with that, no reaction was observed when 6 was incubated with dry or wet CO₂ under an inert atmosphere, showing that aerobic oxidation to copper(II) is an essential first step of the transformation. A comparable reaction of the [Cu(Py₃N)]²⁺ system under an atmosphere of CO₂ has been previously reported. A dinuclear [(Cu(Py₃N)]₂(μ-CO₂)]²⁺ product was proposed in that study, but not crystallographically characterised; other [Cu₂(μ-CO₂)]²⁺ complexes are well known, since Py₃X ligands have proven useful for stabilising unusual oxidation states of transition ions, and Ag...π centres favour tetragonal coordination geometries.
however, with a variety of carbonate coordination modes. No crystallographically authenticated mononuclear Cu/CO$_3$ complex with a tridentate co-ligand has been reported before.

The complex cation in 7b contains two five-coordinate [CuL]$^{2+}$ centres (Fig. 5). Atom Cu(1) is also ligated by monodentate coordination of the bridging carbonate ligand and a mono-atomic donor that was refined as a mixture of iodide and an oxygen donor, which should be a hydroxo group on charge neutrality grounds. The Cu(1)−I(1) [2.5102(17) Å] and Cu(1)−O(1) [2.031(10) Å] distances are consistent with that interpretation. In contrast, the coordination sphere of Cu(2) is completed by bidentate coordination of the carbonato ligand. This $\kappa^1\kappa^2\mu$-CO$_3^{2−}$ coordination mode has been observed in several complexes of copper(II) and other transition ions. Both copper ions have near-ideal square-pyramidal geometries according to their $\tau$ parameters [0.172(4)/0.217(6) for Cu(1), calculated from I(1) and O(1) respectively, and 0.019(4) for Cu(2)]. The [CuI$_3$]$^{2−}$ counterion in 7b has crystallographically imposed $C_2$ symmetry, and shows only small deviations from a triangular geometry.

The asymmetric unit of 8·4.25H$_2$O contains four formula units of the compound ($Z' = 4$); that is, four independent molecules of the complex and seventeen water molecules. The connectivity of the complex is the same as for Cu(2) in 7b (Fig. 5), but the unique molecules differ in their coordination geometry with $\tau$ ranging from 0.001(3) to 0.275(3). The water molecules are crystallographically ordered and occupy channels in the lattice running parallel to the [100] vector. The channels are roughly rectangular in shape, and have the approximate dimensions 2.8 x 5.0 Å. The network has a complicated tape topology, composed of fused four-, five- and six-membered rings of water molecules; and, four-, five-, six-, seven- and eight-membered hydrogen-bonded rings containing one or two carbonato groups (Fig. 6).

The [CuL]$^{2+}$ dication in 9·8H$_2$O has a typical six-coordinate geometry, comparable to [ML$_2$]$^{n+}$ (M = Fe, Co) in 1-3 (Fig. 1). The cation has crystallographic $2/m$ symmetry, with an apparently compressed Jahn-Teller distortion along the unique N−Cu−N axis. However, a mean square displacement amplitude (MSDA) analysis of the metal coordination sphere implies that this is a crystallographic artifact. Rather, the complex probably exhibits symmetry-imposed disorder of a more typical Jahn-Teller elongation along the other two, crystallographically equivalent N−Cu−N directions (ESI†).

Such Jahn-Teller disorder is a well-known phenomenon in copper(II) complexes, including [Cu(Py$_3$CH)$_2$][NO$_3$]$_2$ and a hydrate of [Cu(Py$_3$P)$_2$]Br$_2$. The hydrogen bond network in 9·8H$_2$O is complicated by symmetry-imposed disorder of the water H atoms, but forms 2D sheets in the (001) plane with an L4(6)S(6)8(10) topology comprised of [$\text{H}_2\text{O}$]$_2$, [I($\text{H}_2\text{O}$)$_4$] and [I$_2$(H$_2$O)$_6$] rings (Fig. 7 and ESI†).

**Conclusions**

A new synthesis of $L$ has been achieved, which may be a useful new facial protecting group for coordination and
organometallic chemistry. The methyl substituent protects the bridgehead C atom in L from external attack more effectively than the C–H group in tris-(pyrid-2-yl)methane, which is somewhat acidic, but has only a small influence on the coordinating properties of L. While surveying the coordination chemistry of L we have obtained an unusual square planar silver complex [AgL₂]⁺; observed two complicated and attractive water networks in hydrated crystals; and shed further insight into a previously reported CO₂ fixation reaction.

The dinuclear nature of the initial product of the transformation, 7a, has been confirmed crystallographically. However, we have also now shown that aqueous solutions of 7a react further, forming mononuclear copper/carbonato (8) and ligand disproportionation products (9).

**Experimental**

The precursor [PdCl₂(NCMe)₂] was prepared by the literature procedure. Unless otherwise stated, all other reagents and solvents were used as commercially supplied without further purification. **CAUTION** Although we have experienced no problems with the perchlorate salt products in this work, metal-organic perchlorates are potentially explosive and should be handled with due care in small quantities.

**Synthesis of tris-(2-pyridyl)methylmethane (L).** 2-Ethylpyridine (2.13 cm³, 18.7 mmol) was dissolved in dry THF (60 cm³) and cooled to −78°C in a dry ice-acetone bath. n-Buthylithium (7.5 cm³ of a 2.5M solution in hexanes) was added dropwise, and the mixture was left to stir for 15 min. 2-Fluoropyridine (3.6 g, 37.4 mmol) was added slowly, keeping the reaction temperature below −30°C. After the addition was complete, the mixture was warmed to room temperature, then heated to reflux for 12 h. After cooling to room temperature, the reaction was quenched with excess water. The resultant off-white precipitate was collected, air-dried, then re-suspended in hexane and stirred for 2 h. The solid was re-collected by filtration, affording L as an analytically pure off-white solid. Yield 3.8 g, 78 %. Found C, 77.9; H, 5.80; N, 16.1 %. Calcd for C₁₇H₁₅N₃C, 78.1; H, 5.79; N, 16.1 %. ES MS m/z 262.13 ([LH]⁺), 545.24 ([Na(L)₂]⁺). ¹H NMR ([CD₃]SO δ 2.20 (s, 3H, CC₃H₃), 7.02 (d, 8.1 Hz, 3H, PyH₃), 7.21 (ddd, 1.1, 4.8 and 7.5 Hz, 3H, PyH₅), 7.67 (pseudo-dt, 1.9 and 7.7 Hz, 3H, PyH₆); 7.61 (d, 8.1 Hz, 3H, PyH₃); 7.21 (ddd, 1.1, 4.8 and 7.5 Hz, 3H, PyH₃), 7.61 (pseudo-dt, 1.9 and 7.7 Hz, 3H, PyH₆); 7.67 (pseudo-dt, 1.9 and 7.7 Hz, 3H, PyH₆). ¹³C NMR ([CD₃]SO δ 27.1 (1C, CCH₃), 56.9 (1C, CCH₃), 121.3 (3C, Py C⁵), 123.3 (3C, Py C⁵), 136.0 (3C, Py C⁶), 148.3 (3C, Py C⁶), 165.5 (3C, Py C⁶).

**Synthesis of [Fe₂][ClO₄]₂** (1). A solution of L (500 mg, 1.90 mmol) and Fe[ClO₄]₂·6H₂O (242 mg, 0.95 mmol) in acetonitrile (15 cm³) was stirred at room temperature under N₂ until all the solid had
dissolved. Addition of excess water precipitated the product, which was collected by filtration. The red-brown complex was recrystallised from an acetonitrile-water mixture. Yield 453 mg, 61 %. Found C, 52.5; H, 3.85; N, 10.7; Cl, 9.3 %.

Calcd for C₃₅H₃₀ClFeN₅O₆, C, 52.5; H, 3.89; N, 10.8; Cl, 9.1 %. MS m/z 289.09 ([FeL²⁺]).

1H NMR (CD₃NO₂) δ 3.07 (s, 6H, CH₃), 7.17 (pseudo-t, 6.3 Hz, 6H, Py H¹), 7.47 (dd, 1.3 and 6.9 Hz, 6H, Py H²), 8.07 (pseudo-dt, 1.7 and 8.2 Hz, 6H, Py H³), 8.21 (d, 5.9 Hz, 6H, Py H⁴).

13C NMR (CD₃NO₂) δ 21.4 (2C, C₂H₅), 55.0 (2C, CH₃), 121.9 and 124.8 (both 6C, Py C³ and C⁵), 138.5 (6C, Py C⁴), 158.1 (6C, Py C⁶), 163.6 (6C, Py C⁷).

Synthesis of [CoL₂][ClO₄]₂ (2). CoCl₂·6H₂O (104 mg, 0.29 mmol) and L (150 mg, 0.57 mmol) were dissolved in dry acetonitrile to afford orange crystals of the product. Yield 159 mg, 71 %. Found C, 51.7; H, 3.80; N, 10.5; Cl, 8.8 %. Calcd for C₂₅H₂₀ClN₂O₆, C, 52.3; H, 3.87; N, 10.8; Cl, 9.1 %. MS m/z 290.58 ([CoL²⁺]).

1H NMR (CD₃NO₂) δ 11.4 (s, 6H), 17.5 (s, 6H), 19.9 (s, 6H), 28.8 (s, 6H), 46.8 (s, 6H).

Synthesis of [CoL₂][ClO₄]₃ (3). An acetonitrile solution (15 cm³) of L (300 mg, 1.14 mmol) and CoCl₂·6H₂O (209 mg, 0.57 mmol) was stirred in air until all the solid had dissolved. Slow dissolution of diethyl ether vapour into this solution afforded yellow single crystals of the product. Yield 159 mg, 71 %. Found C, 51.7; H, 3.80; N, 10.5; Cl, 8.8 %. Calcd for C₂₅H₂₀ClN₂O₆, C, 52.3; H, 3.87; N, 10.8; Cl, 9.1 %. MS m/z 290.58 ([CoL²⁺]).

1H NMR (CD₃NO₂) δ 3.24 (s, 6H, CH₃), 7.40 (d, 6.8 Hz, 6H, Py H¹), 7.45 (pseudo-t, 6.2 Hz, 6H, Py H²), 8.38 (pseudo-dt, 7.3 Hz, 6H, Py H³), 8.50 (d, 5.9 Hz, 6H, Py H⁴).

Synthesis of [PdCl₂(L)] (4). Addition of [PdCl₂(NCMe)₂] (148 mg, 0.57 mmol) to a solution of L (150 mg, 0.57 mmol) in acetonitrile (20 cm³) afforded the product as a yellow precipitate, that was collected by filtration and analysed without further purification. Yield 190 mg, 76 %. Found C, 46.45; H, 3.40; N, 9.6; Cl, 16.2 %.

Calcd for C₁₅H₁₂Cl₂Pd C, 46.6; H, 3.45; N, 9.6; Cl, 16.2 %. MS m/z 473.73 ([PdCl₂(L)]⁺).

Synthesis of [AgL₂]NO₃ (5a). A mixture of AgNO₃ (98 mg, 0.57 mmol) and L (150 mg, 0.57 mmol) in MeCN (15 cm³) rapidly formed a white precipitate. This was stirred for 30 mins, then collected by filtration. Yield 74 mg, 61 %. Found C, 58.6; H, 4.30; N, 14.1 %. Calcd for C₁₅H₁₆AgN₂O₃ C, 59.0; H, 4.37; N, 14.2 %.

ES MS m/z 369.03 ([AgL⁺]).

Synthesis of [AgL₂]SbF₆ (5b). Method as for 5a, using AgSbF₆ (98 mg, 0.29 mmol). The product was a white solid. Yield 165 mg, 67 %. Found C, 47.3; H, 3.50; N, 9.6 %.

Calcd for C₁₅H₁₆Ag₈F₆Sb C, 47.1; H, 3.49; N, 9.7 %. MS m/z 262.13 ([LH⁺]), 369.03 ([AgL⁺]).

1H NMR ([CD₃]₂CO) δ 2.28 (s, 6H, CH₃), 7.29 (pseudo-t, 7.1 Hz, 6H, Py H¹), 7.49 (d, 7.8 Hz, 6H, Py H²), 7.86 (pseudo-dt, 1.4 and 7.7 Hz, 6H, Py H³), 8.35 (d, 5.4 Hz, 6H, Py H⁴).

13C NMR ([CD₃]₂CO) δ 28.0 (2C, CH₃), 59.9 (2C, CH₂), 123.2 and 124.1 (both 6C, Py C³ and C⁵), 138.9 (6C, Py C⁴), 150.5 (6C, Py C⁶), 164.8 (6C, Py C⁷).

Synthesis of [CuL(L)] (6). A solution of CuI (145 mg, 0.76 mmol) in MeCN (10 cm³) was added to a solution of L (200 mg, 0.76 mmol) in MeCN (10 cm³), under an N₂ atmosphere. The reaction stirred at room temperature for two hrs, giving a yellow precipitate that was collected by filtration. Yield 170 mg, 50 %.

Found C, 45.2; H, 3.50; N, 8.9 %. Calcd for C₁₅H₁₈CuI₅N₃ C, 45.2; H, 3.35; N, 9.3 %. MS m/z 450.96 ([CuL(L)]⁺).

Synthesis of [CuI(L)]₃[µ-CO₃][CuI]·2H₂O (7a·2H₂O). A filtered solution of 6 in MeCN was exposed to air. A green precipitate began to form after a period of few minutes, which was collected and dried in vacuo. Found C, 38.9; H, 3.30; N, 8.1 %.

Calcd for C₁₅H₁₈CuI₅N₃O₂·2H₂O C, 39.0; H, 3.00; N, 7.8 %. Recrystallisation of this material from dmf/Et₂O afforded green single crystals of 7b·4dmf·0.4H₂O, in which the iodide ligand in the cation has been partially substituted by hydroxide.

Synthesis of [Cu(CO₂)₂L]·4.25H₂O (8·4.25H₂O) and [Cu₂L]₁·8H₂O (9·8H₂O). A solution of 6 in 1:1 MeCN:H₂O was filtered, and left to slowly evaporate under ambient conditions. This afforded two morphologies of crystals. The majority of the crystals were blue prisms of 9·8H₂O, which were sometimes contaminated by a smaller number of darker blue blocks (8·4.25H₂O). Both compounds were crystallographically analysed, but only 9 was isolated in analytical purity. Found C, 41.5; H, 4.70; N, 8.5 %. Calcd for C₁₅H₁₈CuI₅N₃·8H₂O C, 41.5; H, 4.71; N, 8.5 %. ES MS m/z 292.59 ([CuL⁺]), 585.18 ([CuL₂⁺]).

Single crystal X-ray structure determinations

All diffraction data were collected with an Agilent Supernova dual-source diffractometer using monochromated Cu-Kα (λ = 1.54184 Å) or Mo-Kα radiation (λ = 0.71073 Å). The diffractometer is fitted with an Oxford Cyosystems low-temperature device. Experimental details of structure determinations of each compound at 100 K are given in Table 3. The structures were solved by direct methods (SHELXS9715), and developed by full least-squares refinement on F² (SHELX9716). Crystallographic figures were prepared using X-SEED,46 which incorporates POV-Ray.47 The MSDA analysis of 9·8H₂O was performed using PLATON.48

X-ray structure refinements. Unless otherwise stated, all non-H atoms in the structures were refined anisotropically, and C-bound H atoms were placed in calculated positions and refined using a riding model. No disorder is present in the structure of L, and no restraints were applied. H atoms were located in the Fourier map and allowed to refine, with Uiso values of 1.2xUeq of the corresponding C atoms for aromatic H atoms, or 1.5xUeq(C) for the methyl group.

The isostructural crystals 1·4MeCN and 2·4MeCN have half a formula unit in their asymmetric unit, with Fe(1) or Co(1)
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*Collected with Cu-Kα radiation. †Collected with Mo-Kα radiation. \(^{2}R = \Sigma |F_0| - |F_\text{c}| / \Sigma |F_\text{c}|\) \(^{4}wR = \Sigma (w(F_\text{c}^2 - F_\text{c}^2)) / \Sigma wF_\text{c}^2\)
by a disordered mixture of iodide [I(1)] and an oxygen ligand [O(1)], which is hydroxide on charge neutrality grounds. The occupancies of these two fragments refined to 0.44 and 0.56 respectively. In addition to two ordered dmf molecules, a weak Fourier peak that is not associated with any other fragment was included in the model as 0.2 equiv of water. This peak is within hydrogen bonding distance of two different carbonato ligands. No restraints were applied to the model during the final least squares cycles. All wholly occupied non-H atoms were refined anisotropically.

The asymmetric unit of 8·4.25H₂O contains four unique complex molecules and seventeen water molecules. No disorder is present in the model, and no restraints were applied. The water H atoms were all located in the Fourier map and allowed to refine, subject to the fixed restraints O−H = 0.90(2) Å, with UH...H = 1.47(2) Å, and with Uiso equal to 1.5xUeq for the corresponding O atom.

The asymmetric unit of 9·8H₂O contains one-quarter of a formula unit, with Cu(1) lying on the 2/m site ½, ½, 1; atoms C(1)−C(8) lying on the mirror plane x, ½, z; one half-iodide ion and a half-water molecule lying on the same mirror plane; half a water molecule on the C₂ axis ½, y, ½ and a whole water molecule on a general crystallographic site. The water H atoms were located in the Fourier map and allowed to refine, with Uiso constrained to 1.5xUeq for the equivalent O atom. The H atoms for the two half-water sites are disordered about those special positions, leading to significant disorder in the hydrogen bonding network.

Other measurements
Elemental microanalyses were performed by the University of Leeds School of Chemistry microanalytical service. Electrospray mass spectra (ESMS) were obtained on a Bruker MicroTOF spectrometer, from MeCN feed solutions. All mass peaks have the correct isotopic distributions for the proposed assignments. Room temperature ¹H and ¹³C NMR spectra were obtained using a Bruker Avance 500 FT spectrometer, operating at 500.1 MHz (¹H) or 75 MHz (¹³C). The variable temperature ¹H study was performed on a Bruker DRX500 spectrometer.

Electrochemical measurements were carried out using an Autolab PGSTAT20 voltammetric analyser, under an argon atmosphere in predried CH₃CN containing 0.1 M NBu₄ClO₄ as supporting electrolyte. Voltammetry experiments used a Pt disk working electrode, a Pt rod counter-electrode, and an Ag/AgCl reference electrode. All potentials quoted are referenced to an internal ferrocene/ferrocnium standard, and were obtained at a scan rate of 100 mVs⁻¹.

Magnetic susceptibility measurements were performed on a Quantum Design VSM SQUID magnetometer, in an applied field of 5000 G. A diamagnetic correction for the sample was estimated from Pascal’s constants;⁴⁹ a diamagnetic correction for the sample holder was also applied to the data.

Acknowledgements
This work was funded by the EPSRC (EP/K012568/1). The authors thank Simon Barrett (University of Leeds) for help with the variable temperature NMR spectra.

Notes and references


26 Although it suffers from twinning, a preliminary structure solution of 5b also demonstrated the presence of square planar [AgL2]+ centres.

Unit cell data C12H16AgF4N2Sb, M = 866.24, orthorhombic, a = 32.1182(12), b = 22.3288(9), c = 18.1232(7) Å.


