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Syntheses of Cu^I polymetallic assemblies from reaction of ligands bearing the 2,5-bis(2-pyridyl)phosphole fragment with Cu^{II} precursors[†]

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Upon reaction with ligands A, 1 and 3 bearing the 2,5-bis(2-pyridyl)phosphole fragment, an unexpected conversion of Cu^{II} metal centers to Cu^I centers is observed affording either bimetallic complexes bearing a bridging phosphane coordination mode or hexametallic metallacycles.

Electron transfer processes in Cu^I/Cu^{II} complexes involve significant internal reorganisation energies due to the geometry constraints imposed by the specific coordination spheres of the Cu^I and the Cu^{II} metal centers (respectively, mostly four-coordinate and five- or sixcoordinate).¹ Hence the relative stability of Cu^I and Cu^{II} complexes can be greatly modulated by the specific features of the ligands reacting with the Cu^I/Cu^{II} metal precursors, arousing interest in the investigation of the reaction of these metal centers with new multitopic ligands. The bis(2-pyridyl)phosphole ligand A^2 (Fig. 1) recently emerged as a powerful 6-electron donor N,P,N-chelate for the stabilization of a series of Cu^{I} bimetallic complexes^{3a} due to the formation of a very rare bridging phosphane coordination mode B.³ These results motivated us to perform the reaction of divalent Cu^{II} metal centers with ligand A to investigate: (i) the stability of the Cu^{II} complex compared to the Cu^I derivative based on ligand A; (ii) the impact of the introduction of a divalent metal center on the



Fig. 1 Structure of the derivatives A, 1–3 and bridging phosphane coordination mode B.

coordination mode adopted by ligand **A**. This study was extended also to the reaction of Cu^{II} metal centers with the heterotritopic N,X,N ligands 1–3 (Fig. 1: 1, X = S; 2, X = O, 3, X = Se) easily synthesized from ligand **A**. Compared to ligand **A**, these new multitopic ligands present alternative coordination geometries and modes⁴ with a central donor chalcogenide atom bearing modulated Lewis basicity that should impact the reactivity of the Cu^{II} precursors.

The room temperature (RT) stoichiometric reaction⁵ of ligand A with Cu(OTf)₂ (OTf⁻: CF₃SO₃⁻) in CH₂Cl₂ afforded a dark green solution that changed within a few minutes to a light orange clear solution. After purification upon precipitation, an orange powder of complex 4 was collected. Despite the introduction of paramagnetic Cu^{II} metal centers in the reaction, the RT ³¹P{¹H} NMR spectrum of 4 in CD₂Cl₂ shows two broad doublets at +17.9 and -3.5 ppm $(J_{PP} = 94.2 \text{ Hz})$. The ¹H NMR spectrum of 4 in CD₂Cl₂ presents a single set of broad signals⁶ with chemical shifts comparable to those recorded for the free ligand A, bearing therefore no significant chemical shift differences that could witness the formation of paramagnetic Cu^{II} complexes. These data clearly suggest that ligand A reacts with the Cu^{II} metal centers to afford a new diamagnetic complex 4. However, these multinuclear spectroscopic data do not allow a structure to be proposed and dark-red single crystals for the X-ray diffraction study were grown in a 39% yield by diffusion of pentane in a CH₂Cl₂ solution of 4.

Complex 4 is a monocationic Cu^I-dimer featuring two bis(2pyridyl)phosphole ligands **A**, one acting as a μ -1 κ N:1,2 κ P:2 κ N bridging phosphane donor and one acting as a 1 κ N:2 κ P P,N chelate (Fig. 2). The coordination sphere of the metal ions is completed by two oxygen atoms of a OTf⁻ counter-anion acting as a 1 κ O:2 κ O chelate (Cu–O distances, 2.143(5) Å and 2.331(5) Å), while another non-coordinated OTf⁻ counter-anion is present in the asymmetric unit together with three CH₂Cl₂ solvent molecules. Metric parameters of the (Cu^I)₂(**A**)₂ core in the derivative **4**, including the metalmetal (2.5228(12) Å, revealing a metallophilic interaction between the metal centers that is among the shortest recorded to date for a Cu^I₂(**A**)₂ core)³ and metal– μ P distances (2.3115(19) Å and 2.341(2) Å) are similar to those measured for the corresponding dicationic Cu^I dimers resulting from the reaction of ligand **A** with Cu^I salts.³ Note that this solid state structure is in agreement with the solution RT

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[†] Electronic supplementary information (ESI) available: Preparation of **3**, **4**, **5**, **5**' and **6**, spectroscopic and X-ray diffraction data. CCDC 927129–927123. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc42955e



Fig. 2 Views of the crystal structure of the monocationic derivative 4 (H atoms, counter-anions and included solvant molecules have been omitted).

 ${}^{31}P{}^{1}H$ NMR spectrum as the signal at -3.5 ppm is typical of ligand A acting as an N,µP,N ligand on a Cu^I dimer, while the signal at +17.9 ppm is assigned to ligand A acting as a P,N chelate on the Cu^{I} dimer.^{3a} Therefore, along this reaction, a Cu^I bimetallic complex is formed despite the fact that a Cu^{II} metal precursor was initially used. A redox reaction between the Cu^{II} metal center and ligand **A** is not thermodynamically favored since the redox potential of ligand A $(+0.83 \text{ V} vs. \text{ ferrocene/ferrocenium})^2$ is high compared to the redox potential usually described for the Cu^{II}/Cu^I couple.⁷ In the first stage of the reaction, the dark green color observed is most probably because of a preliminary coordination of ligand **A** to the Cu^{II} metal center affording a transient Cu^{II} complex that may take part in the formal redox process. Hence, this Cu^{II} complex could be the electron source that reduces the free Cu^{II} center to afford Cu^I ions leading to very stable bimetallic complexes3 bearing bridging phosphane coordination mode **B** with ligand **A**.⁸ This assumption has motivated us to slightly modify the core of ligand A by oxidation of its P atom with oxygen, sulfur and selenium, affording the heterotritopic N,X,N ligands (Fig. 1: 1, X = S; 2, X = O, 3, X = Se) whose coordination chemistry has been less comparatively studied⁴ and for which the formation of bimetallic Cu^I complexes bearing bridging phosphane coordination mode B (Fig. 1) is excluded.

Derivatives 1–3 were obtained in high yields by the oxidation of the P-centre of ligand **A** with elemental sulfur,^{2b} NaIO₄^{2b} and elemental selenium respectively. In the first step, ligand 1 reacted in a 1:1 ratio in CH₂Cl₂ at room temperature with Cu(OTf)₂ affording a dark red clear solution of complex 5.⁵ In the case of this reaction also, despite the introduction of paramagnetic Cu^{II} metal centers in the reaction, derivative 5 in CD₂Cl₂ exhibits a broad singlet at +50.1 ppm in its ³¹P{¹H} NMR spectrum (shifted to low frequencies relatively to the signal of free ligand 1, a sharp singlet at δ = +52.5 ppm in CD₂Cl₂). This suggests that coordination of the ligand 1 on metal centers proceeded during the reaction without a significant modification of the P-center hybridization. The ¹H NMR spectrum presents one single set of broad signals comparable to those of the free derivative 1.

Upon diffusion of pentane vapors into a solution of 5 in CH_2Cl_2 , single crystals suitable for the X-ray diffraction study having two different morphologies (5a, dark red prisms; 5b, light red plates) were obtained in a comparable amount and in a 27% overall yield. Both crystal structure resolutions revealed that 5 is a $[Cu_6(1)_6](OTf)_6 Cu^I$ hexametallic derivative. Unit cells contain in addition two $[Cu(H_2O)_4(OTf)_2]$ complexes, four CH_2Cl_2 and six H_2O molecules in 5a, and three CH_2Cl_2 molecules in 5b. In crystals 5a,b, $[Cu_6(1)_6]^{6+}$ units are metallacycles (Fig. 3a) having very similar geometrical parameters and do not present short contacts with the OTf^- counter anions and



Fig. 3 (a) View of the X-ray crystal structure of the metallacycle 5 (H atoms, counter-anions and included molecules have been omitted), (b) view highlighting the μ -1 κ N:1,2 κ S:2 κ N coordination mode of the ligand 1 in 5 (the remaining atoms in the coordination sphere of the Cu¹ atom owing to neighbouring ligands are shown in white), (c) 'front' and 'side' views of the Cu₆S₆ ring observed in 5.

the other molecules included in the unit cells. The building unit of derivative 5 is based on two distorted tetrahedral Cu^I metal centers tethered by one ligand 1 acting as an 8-electron µ-1kN:1,2kS:2kN donor (Fig. 3b). Each of the metal centers is coordinated to two different ligands 1 affording a metallacycle structure bearing a Cu₆S₆ ring (Fig. 3c). The dihedral angles between the coordinated pyridine and the phosphole moieties range from 35.2° to 62.9° and are markedly larger than those observed in the Cu^I bimetallic complexes bearing ligand A in a bridging phosphane coordination mode (ca. 30°). This demonstrates the high ability of the 2,5-bis(2-pyridyl)phosphole fragment to adapt its conformation in order to fit the geometric constraints fixed by the metal ions and by the overall molecular geometry. The P=S, the Cu-N and the Cu-S bond lengths (ca. 1.99, 2.01 and 2.35 Å, respectively), as well as the (S-Cu-S) and (N-Cu-N) angles (ca. 119° and 101° respectively), are standard.^{2b,3a,4} Conversely, the S atoms present an original distorted T-shape geometry, with acute (P-S-Cu) angles (ranging from 93.34(8)° to 100.02(8)°) and obtuse (Cu-S-Cu) angles (from 140.72(7)° to 162.51(10)°). The S atoms are located out of the plane defined by the P and Cu atoms (from 0.21 to 0.63 Å, Fig. 3b). The Cu₆S₆ ring is non-planar (Fig. 3c, maximal deviation from the mean plane: 5a, 0.54 Å; 5b, 0.55 Å) and presents a distorted '6-pointed star' shape (Fig. 3c) with opposite edge to edge Cu-Cu and S-S distances ranging from 8.72 Å to 9.31 Å and from 6.68 Å to 7.68 Å respectively. Using Cu(BF₄)₂·xH₂O instead of $Cu(OTf)_2$, a soluble dark red material 5' having multinuclear NMR data that compare with those of 5 was obtained. Therefore the synthesis of the macrocyclic structure 5 is not dependent on the templating effect of the counter anion associated with the Cu^{II} metal center. A few examples of high nuclearity $(Cu^{I})_{n}$ metallacycles (n = 6, 8)based on bidentate bulky organophosphorus ligands have been previously described, but the metal source is always a Cu^I metal salt.⁹ The unexpected formation of this new Cu^I macrocycle triggered us to study the impact of the variation of Lewis basicity of the heteroatom grafted on the P-atom of the bis(2-pyridyl)phosphole moiety on the reaction's fate, by reacting ligands 2 and 3 with Cu(OTf)2. The reaction of the oxophosphole ligand 2 with a stoichiometric amount of Cu(OTf)2 at room temperature in CH2Cl2 did not induce any color change in the clear solution obtained. The ³¹P{¹H} NMR spectrum shows a sharp singlet at +42.5 ppm at the same chemical shift as recorded for the free ligand 2 in CH2Cl2 demonstrating that this



Fig. 4 (a) View of the X-ray crystal structure of the metallacycle **6** (H atoms, counter-anions and included molecules have been omitted), (b) view highlighting the μ -1 κ N:1,2 κ Se:2 κ N coordination mode of the ligand **3** in **6** (the remaining atoms in the coordination sphere of the Cu¹ atom owing to neighbouring ligands are shown in white), (c) 'front' and 'side' views of the Cu₆Se₆ ring observed in **6**.

ligand did not react with Cu(OTf)₂ (vide infra). Conversely, as observed in the case of the synthesis of the derivative 5, the stoichiometric reaction at room temperature of ligand 3 with Cu(OTf)₂ in CH₂Cl₂ solution resulted instantaneously in a dark red clear solution affording after purification the derivative 6 as a dark red powder.⁵ The derivative 6 is characterized at room temperature in CD₂Cl₂ by a broad singlet at +34.4 ppm, shifted to high frequencies relatively to the signal of the free ligand 3 (δ = +40.4 ppm in CD₂Cl₂) and by a single set of broad signals in the ¹H NMR spectrum that compares well with those of the free derivative 3. Similarly to what was observed in the case of the derivative 5, single crystals having different morphologies (6a, dark red blocks 6b, light red plates) were grown in a moderate yield from the diffusion of pentane vapors into a CH₂Cl₂ solution of 6. In both cases, the crystal structure resolution revealed that derivative 6 is a novel $[Cu_6(3)_6](OTf)_6$ macrocycle having gross geometric parameters closely related to those of the thioxophosphole based macrocycle 5 (unit cell of 6a is completed by two [Cu(H₂O)₅(OTf)](OTf) complexes, six CH2Cl2 and two H2O molecules while the unit cell of **6b** is completed by eight CH_2Cl_2 and two pentane molecules).

In the derivative 6, ligand 3 acts as an 8-electron μ-1κN:1,2κSe:2κN donor on two Cu^I metal centers. Therefore, the basic units in 5 and 6 are structurally similar. Nevertheless, the PX and Cu-X (P = Se, ca. 2.14 Å; Cu-Se, ca. 2.50 Å) bonds are, as expected, longer. The T-shape geometry of the chalcogen atoms in 6 is less distorted than in 5: the Se atoms are kept out of the plane made of the Cu and the P atoms (from 0.01 Å to 0.78 Å), the (P–Se–Cu) angles (from $87.08(7)^{\circ}$ to 95.91(5)°) are markedly smaller while the (Cu-Se-Cu) angles are similar (from $139.52(4)^{\circ}$ to $175.99(3)^{\circ}$) to those observed in the derivative 5. Within these macrocycles, a non-planar Cu₆Se₆ ring (Fig. 4c, maximal deviation from the mean plane: 6a, 0.51 Å; 6b, 0.52 Å) is formed. This ring is markedly distorted compared to the '6-pointed star' shaped Cu₆S₆ ring in 5a,b with opposite edge to edge Cu-Cu and Se-Se distances ranging from 8.82 Å to 10.29 Å and from 6.70 Å to 9.23 Å respectively. Therefore, the reaction of the selenoxophosphole N,Se,N ligand 3 affords a hexametallic Cu^I macrocycle that is similar to the derivative 5 obtained from the thioxophosphole N,S,N ligand 1.

The difference in reactivity of the ligands 1-3 towards a Cu^{II} metal center clearly suggests that these reactions are not driven

by oxidation-reduction processes between the free ligands and the metal centers. This point is supported by the fact that ligands 1-3 have been reported to present very similar oxidation potentials that are markedly higher than those of the related phosphole derivative.^{2b} Furthermore, as hypothesized for the formation of complex 4, the pre-coordination of the Cu^{II} metal center in ligands 1 and 3 is probably necessary to afford transient Cu^{II} complexes that can reduce the free Cu^{II} metal centers supplying Cu^I ions in the reaction media.⁸ The effect of the Lewis basicity of the chalcogen atoms carried by the P-atoms in 1-3 supports the hypothesis that the pre-coordination of the Cu^{II} centers plays a key role in these reactions. In the case of the thioxophosphole ligand 1 and the selenophosphole ligand 3, the central chalcogen atoms being soft Lewis donors can fit the geometrical constraints imposed by the metal ions and the overall molecular geometry, driving the first step of the reaction to the formation of a macrocyclic structure bearing distorted tetrahedral Cu^I metal centers. This is supported by the observation that the chalcogen atoms in 5 or 6 tolerate significant bond lengths and angle differences within the overall similar macrocycle architecture. Conversely, the central oxygen atom of the oxophosphole ligand 2 is a hard Lewis donor that can probably not tolerate such structural constraints and does not afford related stable complexes.

These results highlight how the subtle balance of the stability of the Cu^{II} and Cu^{I} oxidation states in the coordination chemistry of multitopic ligands bearing different heteroatoms can drive the formation of complex and original molecular architectures. We are currently investigating the mechanism of the formal redox processes occurring along the syntheses of the discrete polymetallic assemblies **4–6** together with the coordination chemistry of ligands **A** and **1–3** with other divalent metal centers.

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