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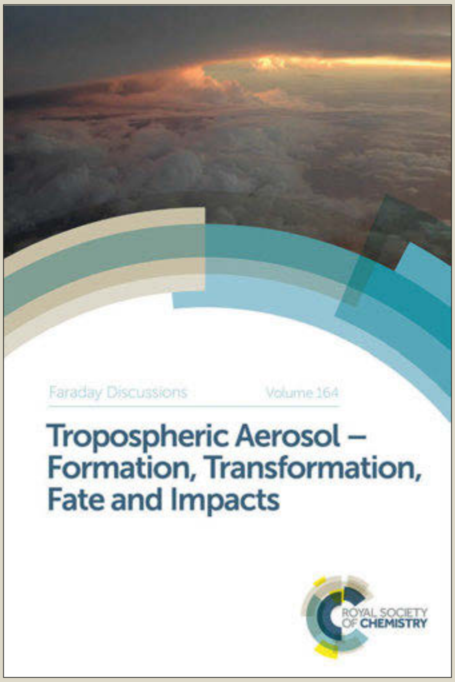

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Mechanochemical preparation of Copper Iodide clusters of interest for luminescent devices.

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The copper iodide complexes are known for their large variety of coordination geometries. Such diversity while making difficult to predict the final structure, permits the preparation of a great number of copper iodide complexes based on the same ligand. The target of the research was that of thoroughly exploring the chemistry of CuI and the ligand diphenyl-2-pyridyl phosphine PN by varying the stoichiometry ratio and/or the aggregation state. Six different compounds have been identified: $[Cu_4I_4(PN)_2]$, $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$, $[CuI(PN)_{0.5}]_\infty$, $[CuI(PN)_3]$ whose structures have been determined during this study, $CuI(PN)_2$ which was characterized by powder diffraction and $[Cu_2I_2(PN)_3]$ which had been already reported. The preparation routes are also different: synthesis in solution yielded $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$ and $[CuI(PN)_3]$ while $[CuI(PN)_{0.5}]_\infty$ and $CuI(PN)_2$ were obtained only via solid state reactions. These two latter examples confirmed that mechanochemistry is a valid route to explore the landscape of the possible structures of CuI derivatives. Crystallization by traditional solution procedures failed to give the desired crystal so structure determination of the new compounds was tackled in two ways: by attempting crystal growth *via* solvothermal synthesis and by resolving the structure from X-ray powder diffraction data with “direct space” methods. What is more the photophysical properties of the complexes that could be obtained as sufficiently pure powders, have also been investigated and are herein reported.

1 Introduction

The complexes based on Copper Iodide are currently at the forefront of coordination chemistry and crystal engineering research because of the quest of active materials for optoelectronic.[1-8] The interest stems from the increasing demand of more affordable complexes in preference to luminescent metal complexes based on precious (i.e. Platinum group) and rare earth metals, which are often quite expensive and environmentally problematic.[9] The copper iodide complexes present several advantages: they are characterized by a large variety of coordination geometries which arise from the many possible combinations of coordination numbers (two, three and four) available for copper(I) and geometries that can be adopted by the halide ions (from terminal to μ^2- and up to μ^8-bridging);[10] they present different luminescent levels which can be of ligand centred, charge transfer or, in the case of polynuclear compounds, even metal-centred nature;[11,12] most of the complexes studied are characterized by a remarkable high quantum yield in solid state;[4, 13, 14] and finally the reagents are cheap and it is relatively easy to obtain the final products.[4, 15]

The luminescent properties of copper(I) halide clusters are strictly related to the geometries adopted by the clusters.[12] In the case of the cubanes $Cu_4I_4L_4$ for example, two distinct emission bands were observed, the high-energy band attributed to halide-to-ligand charge transfer (^{3}XLCT), and the low-energy emission band was attributed to a triplet Cu-I Cluster-Centered (^{3}CC) excited state with the excitation localized to the Cu_4I_4 core, only possible in the presence of an interaction between the metal centres. Recent studies have widened the possibility of the emission properties of Copper(I) compounds. Several Cu(I) compounds with P^N ligands present a low singlet–triplet splitting which allows the emission from both the singlet and the triplet excited state depending on the temperature. The singlet excited state, which is slightly higher in energy than the triplet state, can be thermally activated at the expense of the triplet state, leading to the so-called thermally activated delayed fluorescence (TADF). The TADF emission mechanism allows harvesting of both singlet and triplet excited states generated by charge recombination in electroluminescent devices, therefore light generation efficiency is enhanced. [13, 16]

Due to the increasing interested on CuI(P^N ligands) complexes for OLED application and for photochemistry studies,[3, 13, 15, 17] we exploited the reactivity of the CuI towards diphenyl-2-pyridyl phosphine, hereafter PN. Two crucial aspects of the research will be presented: we will first discuss how the synthetic procedure influences the formation of the final product with particular attention to the mechanochemical synthesis; secondly we will address the different strategies to determine the crystal structure when the final product is a crystalline powder.

The crystal engineering of copper halides is particularly difficult since in solution, halocuprate complexes are involved in kinetically fast dissociative and associative equilibria[18, 19] and the labile coordination numbers and geometries of both copper(I) and halide ions allows an inner-core variability difficult to predict. These complexes are characterized by a flat energy landscape confirmed by the presence of several different copper halides complexes in the CSD[20] which present dramatically different nuclearity of the Cu_xI_y cores such as discrete dimers, cubane tetramers, stepped cubane tetramers to infinity polymeric chains (including split stairs, zigzag, helical, staircase, rack and columnar ones). Although the final structures of the copper(I) halide complexes in crystals could be hardly designed, the reaction stoichiometry allows some degree of control of the copper(I) halide core: reactions with a stoichiometry ratio of CuI/L >>1 higher nuclearity are favoured while CuI/L <<1 promote the formation of monomers.[21] However, to explore all the possible crystal forms it is necessary to vary not only the stoichiometry but also other parameters such as solvent, temperature etc. To overcome the problem of the low solubility of the CuI which restricts the possibility of changing the solvent, the reactions can be performed in solid state which can yield to crystal forms hardly or even not obtainable in solution.[22] The reactivity of CuI towards nitrogen, sulphur or phosphorous based ligands is very high and preliminary work of mechanochemical synthesis with CuI with N-base sature ligands are reported[23, 24] and more extensive studies have been done for Copper thyocyanate complexes,[25-27] in both cases mechanochemical synthesis led to the formation of compounds not obtained by solution synthesis.

The main drawbacks in the mechanochemical reaction methods consist in the formation of microcrystalline products, obviously unsuitable for X-ray single crystal diffraction. The structural characterization is a key point to understand the properties and to design new compounds, that is why a great effort will be devoted to tackle this problem. Most of the times traditional crystallizations from solution, but also triple layer crystallizations, or seeding of solutions with microcrystalline powder of the desired compound fail to yield single crystals of amenable size for single crystal diffraction experiments. However, the structure can be determined from X-ray powder diffraction data, thanks to the development of "direct space" methods.[28] This approach is particularly suited for materials constructed from well-defined modular building units and it is more challenging for Copper Iodide complexes whose coordination is difficult to control. Spectroscopy techniques such as IR or Solid State NMR can give some insights on the coordination or on the asymmetric units but not guarantee the exact structure determination.[26, 29]

The quest of suitable methods to obtain crystals for structure determination of Copper complexes led us to explore different crystallization processes including those based on solvothermal synthesis. Recently, several zeolites, commonly obtained by solvothermal synthesis, have been produced also by grinding or ball milling,[30-33] which suggests that the solid state reactions can have several aspects in common with the solvothermal conditions.[25] Although, for large scale preparations, nowadays researches try to move from solvothermal to solvent–free reactions in order to reduce environmental impact and energy consumption, solvothermal synthesis can still be exploited to obtain single crystals of the desired compound since the high-temperature and high-pressure environments conditions created, would facilitate the crystallization process of complexes with poor solubility.

Herein we report the synthesis of five new crystal forms of copper iodide with the diphenyl-2-pyridyl phosphine (PN): $[Cu_4I_4(PN)_2]$, $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$, $[CuI(PN)_{0.5}]_\infty$, $[CuI(PN)_3]$ and $CuI(PN)_2$; as well as that of the known complex $[Cu_2I_2(PN)_3]$.[14] Mechanochemical synthesis was decisive to obtain the new compounds $[CuI(PN)_{0.5}]_\infty$ and $CuI(PN)_2$ while the monomer $[CuI(PN)_3]$ is formed only by precipitation from solution. Not only the stoichiometry variation but also performing the reaction in solid state or solution allowed us to widen the landscape of crystal forms of copper iodide complexes with PN. The structures of $[Cu_4I_4(PN)_2]$ and $[CuI(PN)_{0.5}]_\infty$ have been determined by single crystals obtained from solvothermal synthesis, while the bulk product has been obtained by reaction in solid state or solution. The structure of $[CuI(PN)_3]$ was determined by direct methods from X-ray powder diffraction data.

All the compounds obtained are luminescent and the photophysical properties of the complexes that could be obtained as sufficiently pure powders, have been studied and reported.

Experimentals

General

All reagents were purchased from Sigma Aldrich and used without further purification.

Synthesis of $[Cu_2I_2(PN)_3]$.

Copper(I) iodide (0.380 g; 2 mmol) and the PN ligand (0.789 g; 3 mmol) were suspended under nitrogen atmosphere in dry dichloromethane (10 mL) and stirred for 12 h at room temperature. The yellowish powder obtained was filtered and washed with a saturated solution of KI_{aq} to remove the unreacted CuI and distilled water to remove KI.

The same titled compound was obtained by grinding CuI (0.190 g; 1 mmol) and PN (0.394 g; 1.5 mmol) with two drops of acetonitrile in a ball mill for 30 minutes at 20 Hz.

Synthesis of $[CuI(PN)_3]$

Copper iodide (0.095 g, 0.5 mmol) was dissolved in saturated aqueous solution of KI (5 mL) then an acetone solution of PN (0,526 g, 2 mmol) was added under stirring. A whitish powder precipitates instantly which was filtered and washed with cold acetone.

Synthesis of $CuI(PN)_2$

Copper iodide (0.190 g ; 1mmol) and PN ligand (1.052 g; 4 mmol) were ground two drops of AcCN in a ball mill for 60 minutes at 20Hz.

Synthesis of $[Cu_4I_4(PN)_2 \cdot (CH_3CN)]$.

CuI (0.760 g; 4 mmol) dissolved in 20 mL of CH_3CN at 40°C was added to a solution of PN (0.263 g; 1mmol) in 20 mL of CH_2Cl_2. The clear solution obtained was left standing at room temperature overnight. The brownish powder obtained was filtered and then washed with aqueous saturated solution of KI_{aq} to remove the unreacted CuI and with distilled water to remove the KI.

Ball milling of CuI (0.760 g; 4 mmol) and PN (0.263 g; 1 mmol) with two drops of acetonitrile for 60 minutes at 20 Hz leaded to mixture of $[Cu_4I_4(PN)_2 \cdot (CH_3CN)]$ and $[CuI(PN)_{0.5}]_{\infty}$.

Synthesis of $[Cu_4I_4(PN)_2]$

$[Cu_4I_4(PN)_2]$ can be easily obtained by heating $[Cu_4I_4(PN)_2 \cdot (CH_3CN)]$ at 170°C.

Crystallization of $[Cu_4I_4(PN)_2]$ and $[CuI(PN)_{0.5}]_{\infty}$.

Crystals of $[Cu_4I_4(PN)_2]$ suitable for SC-XRD analysis were obtained via solvothermal reaction by mixing 0.2 g of CuI with 0.8 g of PN in 1 mL of ethanol at 170°C and slowly cooling down to ambient temperature in 7 days.

Crystals of $[CuI(PN)_{0.5}]_{\infty}$ suitable for SC-XRD were obtained via solvothermal conditions by mixing 0.2 g of CuI with 0.6 g of PN in 1 mL of toluene at 140°C and slowly cooling down to ambient temperature in 7 days.

TGA measurements

TGA measurements were performed using a Perkin Elmer TGA7 in the temperature range 35-700°C under N_2 gas flow and heating was carried out at 5°C min^{-1}.

Photophysics

All determinations made use of powder samples placed between two quartz slides and were done at room temperature. Excitation and emission spectra were obtained with a SPEX Fluorolog fluorometer; excitation spectra were monitored at the maximum emission wavelength and emission spectra were recorded exciting all samples at 350nm.

X-Ray powder diffraction

X-Ray powder diffractograms were collected on a Panalytical X'Pert PRO automated diffractometer with CuKα radiation and an X'Celerator equipped with an Anton Paar TTK 450 low-temperature camera. The program Mercury[34] was used for calculation of X-ray powder patterns. XRPD data of [CuI(PN)$_3$] were collected over the range 3–70° 2θ with a Bruker D8 Advance diffractometer equipped with a LynxEye detector and focusing mirror.

Crystal structure determination

Crystal data for [Cu$_4$I$_4$(PN)$_2$] and [CuI(PN)$_{0.5}$]$_\infty$ were collected on an Oxford Xcalibur S with MoKα radiation, λ= 0.71073, monochromator graphite. Crystal data and details of measurements are summarized in Table 1. SHELX97[35] was used for the structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. The uniqueness of the crystal of [CuI(PN)$_{0.5}$]$_\infty$, synthesized by solvothermal reaction, not allowed to obtain better data. Bad quality data due to the poor cristallinity and high mosaicity of the sample.
The Mercury[34] software package was used for the graphical representation of the resultant structures. CCDC 979008-979010 contains 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.

Table 1 Crystal data

	[Cu$_4$I$_4$(PN)$_2$]	[CuI(PN)$_{0.5}$]$_\infty$.	[CuI(PN)$_3$]^a
Chemical formula	$C_{34}H_{28}Cu_4I_4N_2P_2$	$C_{17}H_{14}Cu_2I_2N_1P_1$	$C_{51}H_{42}Cu_1I_1N_3P_3$
Formula Mass	1288.28	644.15	980.28
Crystal System	Monoclinic	Triclinc	Trigonal
a/Å	16.7222(3)	7.9805(7)	13.6471(2)
b/Å	13.9164(3)	8.5298(8)	13.6471(2)
c/Å	16.4466(3)	14.3667(14)	14.7400(4)
α/°	90	78.092(8)	90
β/°	99.688(2)	85.576(8)	90
γ/°	90	86.494(7)	120
Volume/ Å^3	3772.75(13)	953.05(15)	2377.4
Temperature	RT	RT	RT
Space group	P2$_1$/c	P-1	P-3
No. of independent reflections	11078	2594	-
R_{int}	0.0534	0.046	-
Final R_1 values	0.0489	0.1225	
Final $wR(F^2)$ values	0.0933	0.3395	
Final R_1 values (all data)	0.0621	0.1386	

^{a} Solved from X-ray powder diffraction.

Results and discussion

Synthesis and Crystal Structures

The copper iodide was reacted with PN with different synthetic procedures which differ mainly for the stoichiometric ratio or for the aggregation state (solid state or solution). The reactions in solution are carried out mainly in acetonitrile or saturated aqueous solution of KI in air, while the reactions in solid state were carried out via ball milling with a drop of acetonitrile.

Six different compounds have been isolated so far, $[Cu_2I_2(PN)_3]$ recently described by Zink et al.[13] $[Cu_4I_4(PN)_2]$ and its solvate form $[Cu_4I_4(PN)_2{\cdot}(CH_3CN)]$, $[CuI(PN)_{0.5}]_\infty$ and $[CuI(PN)_3]$ whose structure has been determined during these studies and $CuI(PN)_2$.

The dimer $[Cu_2I_2(PN)_3]$ was easily reproduced by the synthesis described in the literature[13] and it was also obtained by ball milling of CuI and PN with stoichiometry ratio 1:1.5 with a drop of acetonitrile. This complex seems to be very stable and it was obtained as an undesired product in several other reactions (up to stoichiometry ratio CuI:PN 3:1 or 1:3) both in solution and solid state. In many cases to avoid the presence of $[Cu_2I_2(PN)_3]$ the reactions were run with a great excess of one of the reagents.

The dimeric core of $[Cu_2I_2(PN)_3]$ is characterized by a butterfly shape due to the presence of a bridging ligand coordinating with both N and P atoms, and a short copper-copper distance (2.7694(6) Å) consistent with metallophilic interactions (see table 2). The two other ligands coordinated only with the P atoms and they are described as ancillary ligands. The complexes interact via C-H---π and in the case of the ancillary ligands also via π-π interactions (see figure 1). These weak interactions do not affect the photophysical properties since the compound does not suffer of emission quenching.

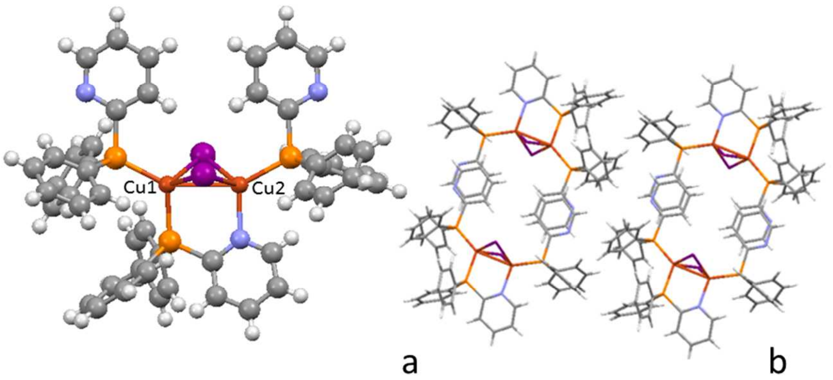


Fig.1 a) $[Cu_2I_2(PN)_3]$ b) π-π interactions present in the crystal packing

Table 2 Copper-copper distances

Compound		Distance/ Å
$[Cu_2I_2(PN)_3]$	Cu1-Cu2	2.7694(6)
$[CuI(PN)_{0.5}]_\infty$	Cu6-Cu7	2.7499(9)
	Cu5-Cu7	2.5883(9)
	Cu6-Cu8	2.574(1)
	Cu5-Cu8	2.699(1)
$[Cu_4I_4(PN)_2]$	Cu3-Cu4	2.771(7)
	Cu3-Cu3	2.900(7)
	Cu4-Cu4	3.485(6)

The reactions carried in excess of CuI (stoichiometry ratio CuI:PN 4:1) leads to the formation of $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$, and $[CuI(PN)_{0.5}]_\infty$; the pure phase of $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$, is obtained by reaction in solution, while by ball milling a mixture of $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$ and $[CuI(PN)_{0.5}]_\infty$ is obtained; it was not possible to isolate the pure phase of $[CuI(PN)_{0.5}]_\infty$. Single crystals of $[Cu_4I_4(PN)_2]$ and $[CuI(PN)_{0.5}]_\infty$ have been obtained by solvothermal reactions while all other attempts to obtain crystals by triple layer crystallization failed. $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$ presents a powder diffraction pattern very similar to $[Cu_4I_4(PN)_2]$; while the structure of the unsolvate form was determined by single crystal X-ray diffraction, it was possible only to index the powder pattern of the $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$. The Pawley refinement converged to R_{wp}=6.65% with a monoclinic cell, space group $P2_1/c$ with parameters a=17.4853(5)Å, b=14.180(2) Å, c=16.303(2) Å, β=97.07(1)° and volume 4011.5(8)$Å^3$ which is about 239$Å^3$ greater than the volume of $Cu_4I_4(PN)_2$. The difference in volume can be ascribed to the presence of one acetonitrile molecule in the asymmetric unit. The presence of the solvent was confirmed by the TGA which shows a 3.06% weight loss at 150°C corresponding to the release of one molecule of acetonitrile (calculated 2.96%) (see figure 2a). The transformation of $[Cu_4I_4(PN)_2\cdot(CH_3CN)]$ into $[Cu_4I_4(PN)_2]$ was observed also with variable temperature X-ray diffraction (see figure 2b).

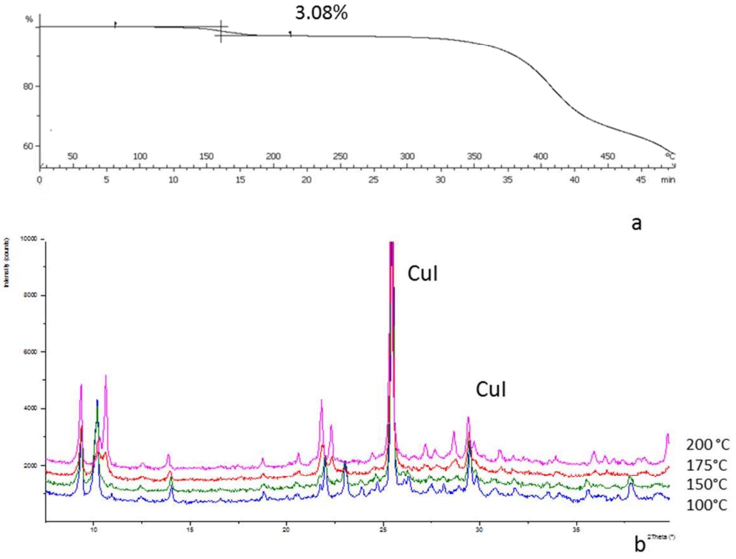


Fig. 2 a) TGA curve of [$Cu_4I_4(PN)_2$·(CH_3CN)], the first step is consistent with the release of one acetonitrile molecule (experimental 3.08%, calculated 2.96%), b) Variable temperature X-ray powder diffraction: pattern reported are at 100°C bottom line, 150°C medium bottom line, 175°C medium top line and 200°top line. Bragg reflections of unreacted CuI are highlighted with the labels.

Instead of the common motif of cubane-like clusters, the [$Cu_4I_4(PN)_2$] cluster adopts an "octahedral" geometry which it has been observed recently by Liu et al.[4] The copper atoms are arranged in a parallelogram with μ^4- iodides above and below the parallelogram and μ^2- iodides bridging the copper atoms on the short edge. All Cu-Cu distances are lower than the sum of the van der Waals radii (see table 2). The aromatic ring interacts mainly via C-H---π interactions and π-π interactions involving the pyridine coordinating ring and a phenyl ring (see figure 3). The crystal packing suggests that the solvent molecules can be placed in the (1 0 0) plane which is the less dense. Further studies will be done to ascertain the crystal packing of [$Cu_4I_4(PN)_2$·(CH_3CN)].

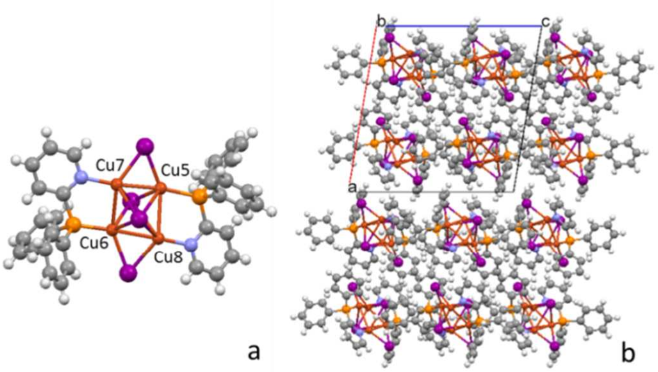


Fig.3 a) Compound $Cu_4I_4(PN)_2$; b) crystal packing view along *b axis*.

It is worth noting that $[CuI(PN)_{0.5}]_\infty$ is easily obtained by mechanosynthesis, although not as a pure phase. Its formation was observed also in solid state reactions with stoichiometry ratio CuI:PN 1:1.5. The low solubility of the compound, which characterizes all the coordination polymers, seems to preclude its formation from the synthesis in solution, while it seems a driving force in the solid state reactions. The solvothermal conditions (high temperature and high pressure) allow to crystallize phase which are known to be poorly soluble, as well, solid state reactions are known to reach phases which can be hard to obtain in solution as observed for the co-crystals.[36] In our case the solvothermal synthesis were explored in order to obtain a single crystal of the desired phase, since the structure determination by X-ray powder diffraction (XRPD) would be really challenging due to the lack of information on the molecular geometry of the complexes.

Despite of all the structures of CuI(P^N ligands) described in the literature[1-4, 13, 15, 37] which show discrete complexes, the structure of $[CuI(PN)_{0.5}]_\infty$ is characterized by a one–dimensional copper iodide polymeric structure. The infinite double chain of CuI presents an alternation of short and long copper–copper distances (see table 2). Usually the tetrahedral coordination of the copper(I) ions is fulfilled by multidentate bridging ligands to construct a 2D sheet network;[24, 38] in our case the PN ligand bridges two copper atoms but on the same chain and brings the two cooper atoms 3.0716(3) Å apart.

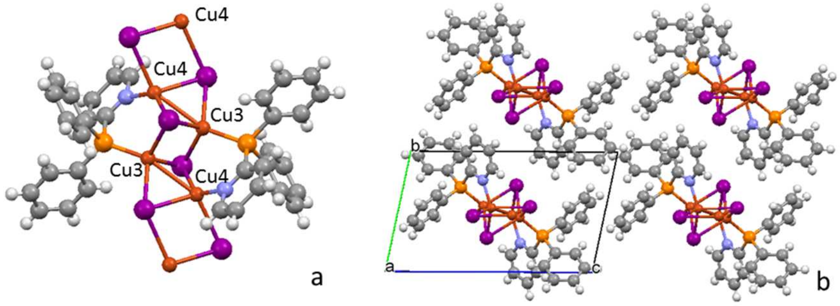


Fig. 4 a) Polymeric structure of $[CuI(PN)_{0.5}]_\infty$; b) crystal packing view along *a axis.* Polymeric chains run parallel to each other.

The reactions carried in excess of the ligand leads to the formation of two new phases: [CuI(PN)$_3$] and CuI(PN)$_2$. The pure compound [CuI(PN)$_3$] is obtained only from reaction in solution carried with a stoichiometry ratio CuI:PN 1:4 while when the same reaction is carried out in solid state only CuI(PN)$_2$ is obtained. The structure of [CuI(PN)$_3$] was solved from powder pattern X-ray diffraction data even if the diffractogram acquired shows peaks of unwashed KI salt. The powder pattern is indexed by a trigonal cell with cell axes a=13.6471(2)Å, c=14.7400(4) Å volume = 2377 Å^3 and space group P-3. The volume of the asymmetric unit, 396 Å^3, is consistent with the volume of the one third of [CuI(PN)$_3$]. The solution is possible only if the monomer is located on the 3-fold axis. The structure was solved with a simulated annealing algorithm using as starting model one molecule of the ligand not bounded to the metal atom and the copper atom and the iodide with site occupancy 1/3. The Rietveld refinement converged to a R_{wp}= 7.681% and R_{exp}= 4.351% (see figure 5). The position of the nitrogen atoms was assumed from the structure solution since the packing features or the Rietveld refinement gave no hints on the possible position (see figure 6). The crystal packing of [CuI(PN)$_3$] does not present important intermolecular interactions. It is worth noting that along the *c axis* the molecular disposition create cavities which can host solvent molecules as suggested also by the TGA curve (see figure 8a).

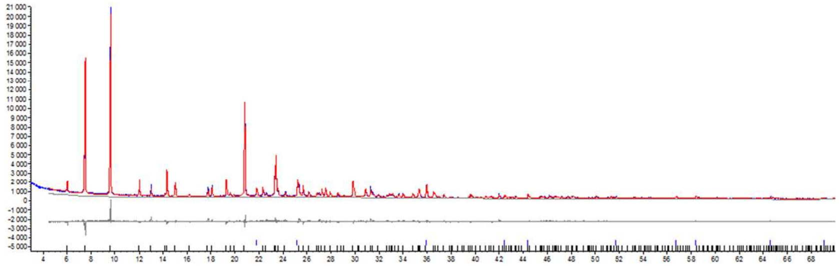


Fig. 5 Rietveld refinement of [CuI(PN)$_3$], red line is the calculated diffractogram, blue line observed diffractogram and bottom line difference plot. Upper ticks correspond to the Bragg peaks of KI, lower ticks correspond to the Bragg peaks of [CuI(PN)$_3$].

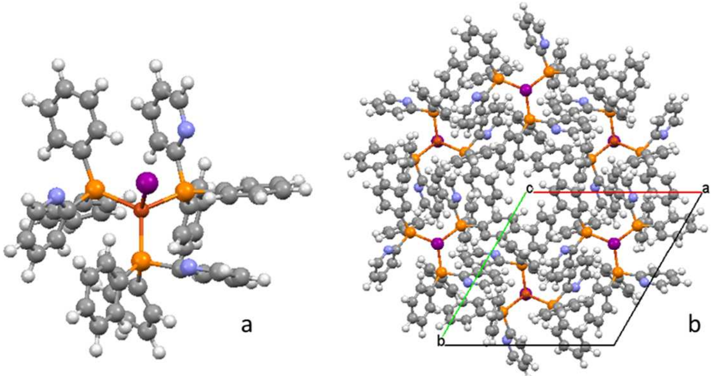


Fig.6 a) Single molecule of [CuIPN$_3$]; b) Packing of [CuIPN$_3$] view along the *c axis.*

Several attempts have been made to determine the crystal structure of CuI(PN)$_2$, although the diffractogram does not present peaks of the reagents or of other known phases we were not able to index it (see figure 7). It is not possible to exclude the presence of more than one phase.

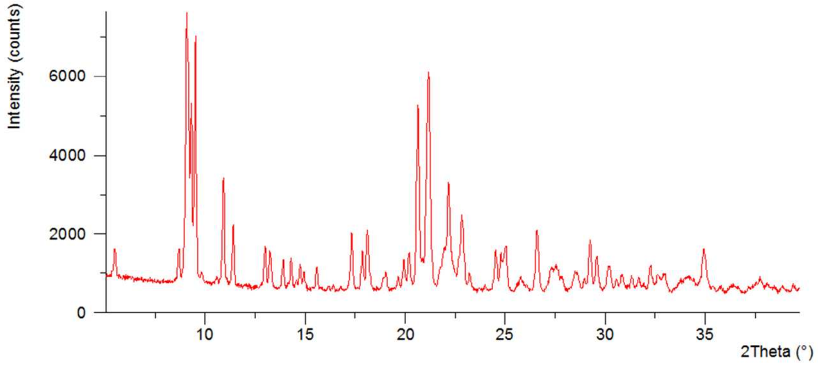


Fig. 7 Powder pattern of CuI(PN)$_2$ obatined by ball milling.

The empirical formula is suggested by TGA and VTXRPD (see figure 8). X-ray diffraction at variable temperature shows that [CuI(PN)$_3$] starts to transform into CuI(PN)$_2$ at 180°C and the complete transformation accompanied by amorphization is observed at 250°C. In the TGA curve the first step which corresponds to weight lost 0.81% is probably due to some solvent trapped in the crystals, the second step due to the release of one ligand (calculated 26.84% weight lost) which is suddenly followed by decomposition and the release of the second and third ligand.

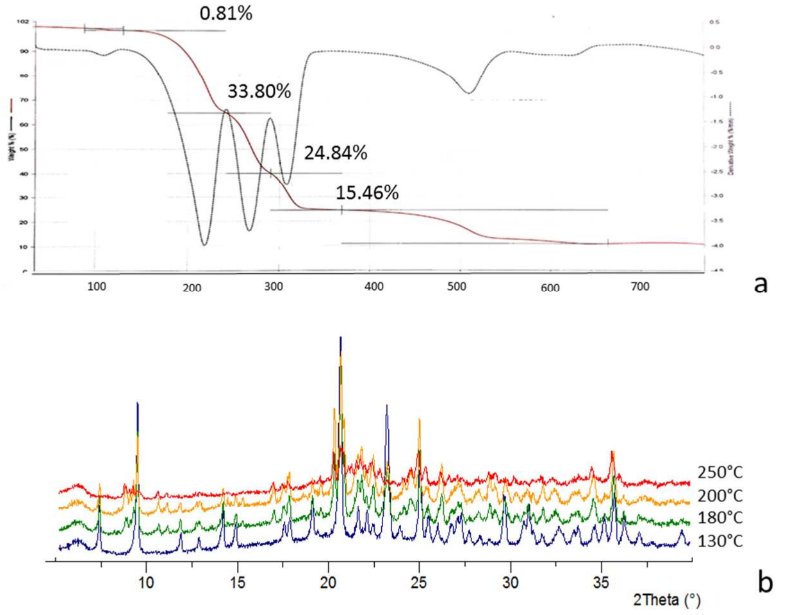


Fig. 8 a) TGA curve of [CuI(PN)$_3$], the first step (0.81%) is due to some solvent release, the second step can be ascribed to the release to one ligand molecule which is suddenly followed by the release of the other ligand molecules; b) VTXRPD of [CuI(PN)$_3$], at 180°C the peaks of CuI(PN)$_2$ appear, the complete transformation is characterized is observed at 250°C. The powder pattern presents a low crystallinity profile.

Photophysical properties

All complexes are luminescent in their solid state at room temperature with emissions spanning from green to yellow. The tetrahedral coordination around the copper(I) ion and the stiff molecular structure assured by rigid ligands hamper the Jahn-Teller distortion of the excited state and allow high emission quantum yields.[39, 40] Examination of the relevant bond angles reveals an only slightly distorted tetrahedral geometry around the Cu ions, demonstrating the fitting bite angle of the bidentate P^N ligand in the polynuclear complexes.[13] The lack of concentration quenching make these complexes attractive for applications in solid state devices as OLEDs or LECs. Moreover their emissions stem from excited states populated by fast intersystem crossing, which allow the so-called “triplet harvesting” or “singlet harvesting” that leads to high electroluminescence efficiencies.[13, 16, 41-43]

The emission lifetimes are relatively short, in the order of microseconds, thus preventing the excited state quenching due to triplet-triplet and triplet-charge interaction processes origin of the typical roll-off in the electroluminescence efficiency decay at high currents.[44]

The frontier orbitals involved in electronic transitions have a (X+M)LCT character, only slightly affected by the halogen/metal orbital ratio contributing to the HOMO, and dependent on the Cu_xI_x nuclearity, and by the number of bridging ligands that contribute to the LUMO.

The emission spectra of the complexes that could be obtained as sufficiently pure powders are represented in figure 9. The dimeric [$Cu_2I_2(PN)_3$] complex shows an emission band with maximum at 525 nm which has been assigned to a temperature assisted delayed fluorescence (TADF) from a (X+M)LCT singlet excited state in thermal equilibrium with the triplet state lying at a very close energy level.[13] The monomer [$CuI(PN)_3$] has a very similar emission band most probably ascribable to a transition akin to the [$Cu_2I_2PN_3$] one. None of the two compounds show radiative decay from excited states generated by cuprophilic interactions. Instead, the red-shifted and broader emission band of the [$Cu_4I_4(PN)_2\cdot(CH_3CN)$] octahedral complex is indicative of a cluster centred (CC) transition at lower energy contributing to the emission.[4]

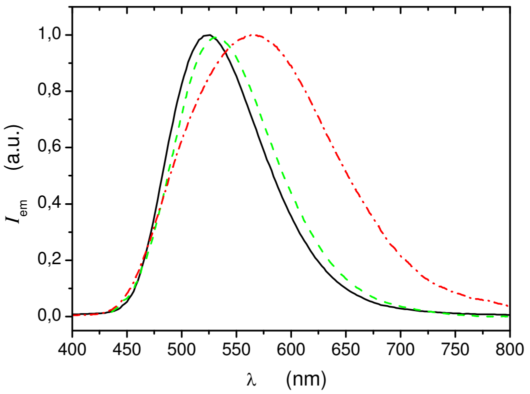
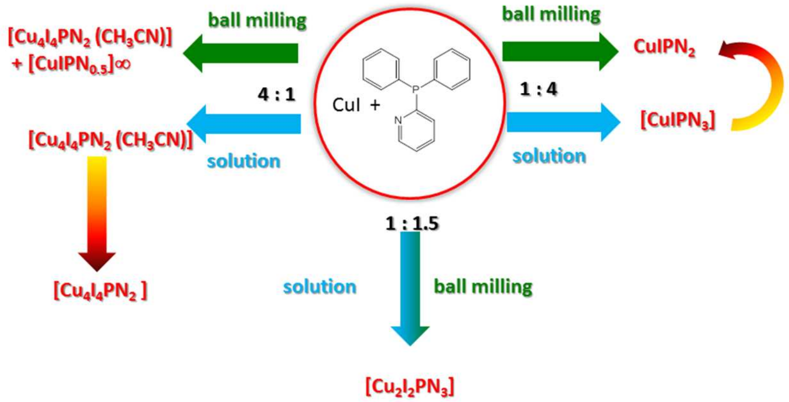


Fig. 9 Emission spectra of $[Cu_2I_2(PN)_3]$ (solid, black), $[CuI(PN)_3]$ (dash, green) and $[Cu_4I_4(PN)_2{\cdot}(CH_3CN)]$ (dash-dot, red) as crystalline powders at room temperature.

Conclusions

The copper iodide complexes are known for their large variety of coordination geometries which allows a great deal of different stoichiometries to be attained with compounds based on the same ligand. One of the targets of the research described in this paper was that of exploring as thoroughly as possible the chemistry of CuI and the ligand diphenyl-2-pyridyl phosphine PN. Five new different compounds have been discussed: $[Cu_4I_4(PN)_2]$, $[Cu_4I_4(PN)_2{\cdot}(CH_3CN)]$, $[CuI\ (PN)_{0.5}]_\infty$, $[CuI(PN)_3]$ whose structure has been determined during this study, and $CuI(PN)_2$ (see scheme 1). Two main synthetic parameters were changed, the stoichiometry and the media in which reactions were carried out, whether in solution or the solid state. Regarding the stoichiometry, we have discovered that only by using great excess of one of the reagents it is possible to move from the dimeric structure $[Cu_2I_2(PN)_3]$ and to obtain new compounds with higher ligand/CuI ratios. In terms of synthetic routes we have shown that solution synthesis yielded $[Cu_4I_4(PN)_2{\cdot}(CH_3CN)]$ and $[CuI(PN)_3]$ while $[CuI(PN)_{0.5}]_\infty$ and $CuI(PN)_2$ were obtained only via solid state reactions, which posed the additional problem of structure determination when only polycrystalline samples are available. One way to circumvent this problem is that of finding an alternative way to grow single crystals of the desired species. This is why in our study we have explored in parallel the solvothermal synthesis with CuI and PN in an attempt to obtain the same species as produced by solid state reactions. In such a way we have obtained single crystals of $[Cu_4I_4(PN)_2]$ and $[CuI(PN)_{0.5}]_\infty$ which allowed full identification of this latter mechanochemical products by comparison of observed and simulated patterns. The observation that $[CuI(PN)_{0.5}]_\infty$ could be obtained by solid state reaction and by solvothermal method suggests that the two processes can reach similar conditions which are not allowed in the traditional synthesis in solution. $[Cu_4I_4(PN)_2]$ and $[Cu_4I_4(PN)_2{\cdot}(CH_3CN)]$ present a very similar powder patterns which suggests that the solvated compound should maintain the same geometry, upon thermal treatment $[Cu_4I_4(PN)_2{\cdot}(CH_3CN)]$ convert into $[Cu_4I_4(PN)_2]$. The crystal structure of $[CuI(PN)_3]$ was solved from powder pattern X-ray diffraction data. Only the empirical formula of $CuI(PN)_2$ was postulate. This compound was obtained by ball milling or upon heating of $[CuI(PN)_3]$ at 180°C, which corresponds in the TGA curve, at the release of one ligand.

All the compounds obtained are luminescent and the photophysical properties of the complexes that could be obtained as sufficiently pure powders, have been reported.



Scheme 1 Scheme of the compounds obtained and their relationship. Plain coloured arrows indicate synthesis in solution and solid state, gradient coloured arrows indicate the thermal treatment.

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