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1. University of Torino, Department of Chemistry and NIS Centre of Excellence Via Pietro Giuria 7, 10125, Turin, Italy.

\* Corresponding Author E-mail: michele.chierotti@unito.it. Tel: +39011-6707523

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Vibrational-Structural combined Study into Luminescent mixed Cu(I)/Cu(II) CuCN Coordination Polymers

F. Grifasi,a E. Priola,a M. R. Chierotti,a,\* E. Diana,a C. Garinoa and R. Gobettoa

**ABSTRACT** This paper reports the characterization of a series of CuCN-based coordination polymers that display different crystal packing and electronic properties, namely [Na2Cu(CN)3·3H2O]n (**1**), [Cu4(CN)5(NH3)2(H2O)]n (**2**), [Cu3(CN)4(NH3)3]n (**3**), [Cu3(CN)3(O0.1)(NH3)]n (**4**), [Cu5(CN)6(NH3)4]n (**5**) and [Cu5(CN)6(NH3)2]n (**6**). Spectroscopic evidence of the presence of ammonia molecules coordinated to the metal is provided, in particular for compound **4** which is a new structure. The characterization has been carried out using X-Ray Single Crystal Diffraction (XRSCD), micro-Infrared (IR) and micro-Raman spectroscopies (RAMAN), Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA). Photophysical properties have been studied using solid-state luminescence by acquiring emission and excitation spectra and evaluating emission quantum yields, which is an approach that has recently grown in importance in the solid-state field. The goals of this work are: (a) an elucidation of the correlation between luminescent properties and the presence of either Cu(I) or mixed Cu(I)/Cu(II) oxidation states; (b) the evaluation, *via* a crystallographic-spectroscopic combined study, of the presence of NH3 and/or H2O in the polymers; (c) the rationalization of the supramolecular architecture and its influence on the resulting luminescence. text goes here.

**Introduction**

Coordination polymers have recently drawn great interest because of their peculiar topologies and, more importantly, because of their possible applications in numerous fields, ranging from catalysis to molecular sensing and from optics to magnetism.1–8

As far as molecular sensing applications are concerned, both the design of photoactive materials and the investigation of their luminescent properties are fundamental in the field of Organic Light Emitting Devices (OLEDs). Copper is therefore a highly promising metal because of its limited toxicity, higher availability and low costs, when compared to the traditional heavy metals involved in coordination complexes (such as ruthenium, rhenium, platinum and iridium).9–19

The literature provides a wide range of compounds prepared starting from Cu(I) and various organic ligands.20 Different luminescence pathways have been detected and thoroughly studied in order to correlate metal to ligand charge transfer, which can give rise to variations in emission range and quantum yields. On the other hand, the rational design and preparation of mixed-valence Cu(I)/Cu(II) coordination complexes, which are of great biological importance and display interesting electronic properties, is still a challenge.21–24 Cu(I)/Cu(II) cyanide complexes have received wide recognition for their unique physical and chemical properties, which include long-range magnetic order, luminescence, electron-transfer as well as bioinorganic chemistry relative to blue copper proteins and type I copper-containing enzymes.25–28

The cyanide group is a versatile ligand that can act as a mono-dentate, as well as μ2-,μ3- and μ4-bridging multi-dentate, ligand. The copper atom, meanwhile, possesses several coordination modes (two-, three-, four-, five-, or six-) and can form diverse geometries. The self-assembly of copper cyanide can therefore generate long-lived and highly efficient luminescent materials with variable structures, which sometimes exhibit intriguing topological architectures.29,30

CuCN is not a common inorganic salt from the structural point of view. Its 1D chain structure, which is based on two-coordinated metal centers and bridging cyano ligands, means that CuCN differs from many other inorganic salts that are characterized by 2D or 3D arrays.31 The compound gives a weak luminescence,32 which generally shifts from the near UV (392 nm) into the visible region upon the coordination of nucleophiles, such as thioamide ligands, which also increases emission intensity.33 In general, small differences in ligands can cause significant differences in polymer emission colors, providing us with suitable luminescence tuning ability.34 On the other hand, very little attention has been paid to the luminescence of CuCN itself and the variations that occur at different coordination degrees. Two CuCN polymorphs have been reported in literature, both displaying crystallographically disordered carbon and nitrogen sites. The metal-metal interaction, common in Cu(I)-based compounds, is very indicative of luminescence properties, and is 3.09 Å and 3.78 Å for the low- and high- temperature polymorph, respectively in the case of CuCN.35,36

In this contribution, we report a series of CuCN-based coordination polymers: [Na2Cu(CN)3·3H2O]n (**1**), [Cu4(CN)5(NH3)2(H2O)]n (**2**), [Cu3(CN)4(NH3)3]n (**3**), [Cu3(CN)3(O0.25)(NH3)]n (**4**), [Cu5(CN)6(NH3)4]n (**5**) and [Cu5(CN)6(NH3)2]n (**6**). Although all these compounds, with the exception of **4**, have already been reported in literature (ICSD database codes 2168, 16460, 9139, 83704, 16459)37–42 their characterization is still lacking the precise spectroscopic determination of the presence and quantity of H2O/NH3 and a solid-state luminescence study. This article grants us the opportunity to report the new sample **4** and its X-ray crystal structure and to revisit all the other compounds' X-ray structures, which are quite dated and characterized by poor R factors. Moreover, this article allows us to investigate the supramolecular architecture of these compounds using modern coordination polymer research and clarify some obscure points, like the disorder in **3** and the nature of the solvent molecule in **5**. The compounds were therefore characterized using a combined SCXRD and spectroscopic approach (micro-IR and micro-RAMAN spectroscopies) in addition to calorimetric data from Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA). The combined vibrational and diffractometric approach allowed us to explore the conversions between different coordination polymers occurring when they are left in the mother liquor. These structural rearrangements, due to the exchange of molecular fragments or ligands, have already been reported in several systems in the literature.43,44 Finally, luminescence properties have been evaluated using emission, excitation and quantum yield measurements.

We address the following issues in this article:

a) we correlate luminescent properties with the presence of either Cu(I) or mixed Cu(I)/Cu(II) metal oxidation states;

b) we evaluate both the presence of NH3 and/or H2O in the metal coordination sphere and their influence on the resulting luminescence;

c) we carry out a to carry out a complete assignment of the cyano bands in the IR and RAMAN spectra, which are very complex and often misunderstood.

The comparative structural and luminescence study of this series allows a relationship between the crystal structure and emission pathways to be established for this class of compounds thus opening the way for several possible applications in luminescent devices.45,46

**Experimental Part**

All reagents and solvents were purchased from Sigma Aldrich and used without further purification. All samples were obtained using thehydrothermal technique and traditional crystallization to obtain crystals suitable for XRSCD. Sodium cyanide must be handled with care since highly toxic (can affect the body through ingestion, inhalation, skin contact, or eye contact).

[Na2Cu(CN)3·3H2O]n (**1**) was obtained by heating (100°C, 8 hours) 30 ml of a saturated water solution of CuCN (400 mg, 4.5 mol) and NaCN (221.4 mg, 4.5 mol) (stoichiometric ratio 1:1). White prism crystals were collected after 15 hours of slow room temperature evaporation. Yield 95%.

[Cu4(CN)5(NH3)2(H2O)]n (**2**) was obtained by stirring (room temperature, 6 hours) 30 ml of water solution of CuCN (400 mg, 4.5 mol), NaCN (221.4 mg, 4.5 mol) and CuSO4 (1.120 g, 4.5 mol) (stoichiometric ratio 1:1:1). Green needle crystals were collected after 7 days of slow room temperature evaporation. Yield 89%. Compound **2** can also be obtained from conversions of **3**, **5** and **6** in their mother solution after 7-10 days.

[Cu3(CN)4(NH3)3]n (**3**) was obtained by stirring (room temperature, 3 hours) 30 ml of an ammonium hydroxide solution (3% v/v NH4OH) of CuCN (400 mg, 4.5 mol), NaCN (221.4 mg, 4.5 mol) and CuCl2 (1.528 g, 9.0 mol) (stoichiometric ratio 1:1:2). Blue needle crystals were obtained after 6 days of slow room temperature evaporation. Yield 23%.

[Cu3(CN)3(O)0.25(NH3)]n (**4**) was obtained using hydrothermal synthesis (100°C, 8 hours) from the dissolution of CuCN (400 mg, 4.5 mol), NaCN (221.4 mg, 4.5 mol) and CuCl2 (1.528 g, 9.0 mol) (stoichiometric ratio 1:1:2) in 30 ml of an ammonium hydroxide solution (1.5 % v/v NH4OH). Orange needle crystals were collected after 4 hours of slow room temperature cooling. Yield 49%.

[Cu5(CN)6(NH3)4]n (**5**) was obtained by hydrothermal synthesis (100°C, 8h) *via* the dissolution of CuCN (400 mg, 4.5 mol) and NaCN (221.4 mg, 4.5 mol) (stoichiometric ratio 1:1) in 30 ml of an ammonium hydroxide solution (1.5 % v/v NH4OH). Violet prism crystals were collected after 3 days of slow room temperature cooling. Yield 58%.

[Cu5(CN)6(NH3)2]n (**6**) was achieved *via* hydrothermal synthesis (100°C, 8h) and the dissolution of CuCN (400 mg, 4.5 mol), NaCN (221.4 mg, 4.5 mol) and CuCl2 (1.528 g, 9.0 mol) (stoichiometric ratio 1:1:2) in 30 ml of an ammonium hydroxide solution (5 % v/v NH4OH). Red prism crystals were obtained after 4 days of slow room temperature cooling. Yield 37%.

Compounds **2**, **3**, **5** and **6** can also be obtained in the absence of NH3, as already reported in the literature.47–49

**Single crystal X-ray diffraction measurements.** Crystallographic information are deposited in the CCDC database with numbers 1424443, 1424444, 1424445, 1424446, 1424447 and 1424448.

Single crystal data were collected on a Gemini R Ultra diffractometer,50 using graphite-monochromated Mo Kα radiation (λ=0.71073) and the ω-scan method. Cell parameters were retrieved using CrysAlisPro51 software and the same program was used to perform data reduction, with corrections for Lorenz and polarizing effects. Scaling and absorption corrections were applied using the CrysAlisPro multi-scan technique. All structures were solved with direct methods using SHELXS-9752 and refined with full-matrix least-squares on F2 using the SHELXL-97. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located in the final Fourier-difference maps and refined with coordinates and Uiso free or calculated and riding on the corresponding N atom. Bond distances are reported in **Table S1a**-**S1b**, while crystal data and refinement results can be found in **Table S2a-S2b** of the Supporting Information. Cyanides have been refined for end-for-end disorder. The disorder has been detected only in **4** and **6** due to the symmetry of the space group. Refining structures **1**, **2**, **3** and **5** with end-for-end disorder for cyanides led to negative occupations for the other configuration. The structure of **1** presents disorder in the position of Cu(2)-C(2)-N(2) (see **Figures S1** in Supporting Information), with the alternating presence of a water molecule (O(2)) that has been interpreted with a supercell by Kappenstein and Hugel.37 Compound **3** is characterized by positional disorder in the ammonia molecules bonded to Cu(1). This fact may be correlated to the difficulties in assigning the exact space group. Williams et al.,38 assigned this structure to space group Cmca, orthorhombic, although a more recent determination assigned it to P21/n which was found to be correct.41 We tried to refine the model for the same crystal in the orthorhombic space group, resulting in a poorer R1 factor of 0.12. Further evidence of the correct space group can be found in the analysis of the systematic absences and of the obtained structural model. Indeed, the violation of systematic absences of the family h,0,l with h=2n, connected to the m plane, confirms that the orthorhombic space group is only partially filled by the structure. The presence of the same disordered ammonia and additional end-for-end disorder on cyanides was observed when analyzing the orthorhombic model. Thermal ellipsoids of the two ammonia in the cyanide plane, that correspond to N13 and N14 (see **Figure S3** in the Supporting Information) in the monoclinic model, are oblate in the direction of the bisecting mirror plane. We studied the pseudosymmetry of the structure with the PSEUDO program on the Bilbao crystallographic service,53 which allows the analysis of pseudosymmetry through group-subgroup decomposition and comparison. We found good structural similarity (strain= 0.001) between our monoclinic cell and a Cmce orthorombic cell with dimensions -1/2a + 1/2b, c, a (origin translated of a vector -1/4, 1/4, 0) (12.2026, 14.5050, 12.6319, 90.0, 90.0, 90.0, very similar to that obtained by Williams et al.). This orthorombic space group is a 2-order t-supergroup of P21/n. By modeling the structure in the supergroup as ordered (only one ammonia molecule in one of the two possible sites),the best higher symmetry fit is reached when using a triangular bipyramid geometry for Cu(1) with the equatorial ammonia lying on the m plane (Wyckoff position: 8f). Due to Cu(II)'s preference for a square pyramid geometry, the disorder in ammonia sites probably tends towards simulating the reflection symmetry of the m plane, averaging two mirror image-like square pyramidal geometries. The more similar the occupancies of the N13 and N14 sites (belonging to the two symmetrical geometries) are, the more filled the orthorhombic symmetry becomes and the more systematic absences of the m plane are fitted. However, seeing as the N14 site is less occupied than the N13, the overall structure only simulates orthorombic symmetry. There is substitutional disorder in the position of atom O1, in structure **4**, with an occupation of 25%. The structure of **5** had been reported with the formula [Cu5(CN)6(H2O)4]n,54 but we have corrected the assignment of the solvent molecules to ammonia, using IR and Raman evidence, and we highlight the existence of strict N-H vibrational mode similarities with the other ammonia-containing compounds in the series. The structure of **5** was obtained by a two domain non-merohedric twinned crystal, so the overall refinement parameters are worse than that of the other structures. However they are still good enough to study the pattern behaviors.

**IR and Raman spectroscopies.** Raman spectra for crystalline samples were obtained using a Horiba Jobin Yvon HR800 instrument, equipped with an Olimpus BX41 microscope. The samples were excited using 633 nm laser radiation with a magnification ratio of 50x. The infrared spectra and FT-Raman spectra were recorded on the solid samples by means of an anvil cell on a Bruker Vertex 70 FTIR, equipped with a Hyperion 2000 microscope and a RamII module (λ= 1064 nm; Nd:YAG source).

**Calorimetric analysis.** Differential Scanning Calorimetry (DSC) analyses were performed on a TA instrument Q200. The samples (5–10 mg) were placed in sealed alumina pans and heated at a rate of 10 °C·min–1 (temperature range: 50–400 °C). Thermogravimetric (TGA) measurements were performed under N2 flow at a heating rate of 10 °C·min–1 (temperature range: 50–400 °C) on a TA instrument Q600 SDT Simultaneous DSC-TGA heat flow analyzer. The samples (5–10 mg) were placed in alumina pans.

**Luminescence measurements.** Solid-state emission and excitation spectra, together with luminescence lifetimes and quantum yields, were acquired at room temperature using a HORIBA Jobin Yvon IBH Fluorolog-TCSPC spectrofluorimeter equipped with a Quanta-ϕ integrating sphere. Luminescence lifetimes were determined by time-correlated single-photon counting; an excitation *via* nanosecond pulses of 270 nm light generated by a NanoLED pulsed diode was used. All emission data were collected using a spectral bandwidth ranging from 4–4 to 10–10 nm. Emission decay data were collected into 2048 channels to 10000 counts in the peak channel and analyzed using the software DAS6 (TCSPC Decay Analysis Software)

**Results and Discussion**

Compounds **1–6** were synthesized using solvothermal techniques and traditional crystallization. The architecture of these compounds is usually strictly related to the CN/Cu ratio. An empirical rule shows that polymeric structures are characterized by CN/Cu ratios that are equal to or less than 2. For instance, the 1D wavelike chain structure of the alfa55 and beta56 polymorphs of CuCN is preserved in M[Cu(CN)2] (M=Na,57 K58), with CN/Cu=2. On the other hand, CN/Cu ratios higher than 2 are typical of discrete monomeric complexes as observed in K3[Cu(CN)4].59

In our case, compounds **2**–**6** are characterized by a CN/Cu ratio of lower than 2 and are coordination polymers, while compound **1** (CN/Cu=3) is monomeric.

In general, the crystallochemistry of Cu(I)CN systems is strongly complex.60,61 Some recurrent structural motives are presented in **Figure** **1**: a) linear chains similar to pure CuCN, with possible disorder in the cyanide groups; b) dimeric 6-metal center connectors with stoichiometry Cu2(1,1,2-µ3-CN)2(CN)4, showing Cu–Cu distances typical of cuprophilic interactions; c) rings of (CuCN)x, with squared, pentagonal or hexagonal geometry. These rings can be planar or deformed with peculiar geometries similar to the conformations of the corresponding cycloalkanes.62

The structures of **1**–**6** can be rationalized with the new structural information and knowledge recently developed in the field of Cu(I)CN coordination polymers. The structural patterns of compounds **1**–**6** are reported in **Figure 2**, while all the asymmetric units are depicted in **Figures S1**-**S6** of the Supporting Information with corresponding atom labels and numbers.

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**Fig. 1** Main structural motifs typical of cyanocuprate crystallochemistry: a) linear chains b) Cu2(1,1,2-µ3-CN)2(CN)4 fragments and c) cycles of (CuCN)x. (Cu: orange; C: yellow; N: blue).

The presence of mixed Cu(I)/Cu(II) centers, in **2**–**6**, provides multiple coordination geometries allowing even more complex crystallochemistry. Indeed, Cu(II) can act as part of the polymeric structure or as a template of channels intercalated as a separate complex in the Cu(I)CN framework.63,64 The former case is observed in **2**, **3**, **4**, **6** while the latter is present in **5**. Moreover, when the Cu(II) ion coordinates water or ammonia it typically displays square planar (compounds **5**, **6**), square pyramid (compounds **2**, **3**) or octahedral coordination geometry (not observed in our compounds).

Compound **1** is formed by the monomeric anionic complex Cu(CN)32–, a rare case of a D3h trigonal planar Cu(I) complex. The structure is deeply disordered with partially occupied tricyanocuprate sites and has been interpreted as an ordered superstructure with alternating Cu(CN)32– units and water molecules.37 The anion Cu(CN)32– forms a coordination polymer through bridging water molecules coordinated to Na cations.

While compound **2** was reported as accidentally found in Cu(II) + CN- solutions, in this work we rationalized its synthesis. The structure of **2** is characterized by squared (CuCN)4 rings. Each Cu site is also part of a Cu2(1,1,2-µ3-CN)2(CN)4 group which is linked to a third Cu(I) through a further cuprophilic interaction. In each ring, one Cu2(1,1,2-µ3-CN)2(CN)4 unit bonds, through a μ2-bridging cyanide, a Cu(II)(NH3)2(H2O) fragment that is characterized by the square pyramid coordination geometry already found in (CH3)4N[Cu(H2O)(NH3)4][Cu4(CN)7].63 This last moiety propagates the structure through two trans cyanide groups. The overall architecture is a 3D polymer.

Compound **3** was previously reported as orthorhombic or monoclinic. The interpretation of this space group ambiguity is described in the Experimental Section, where our structural analysis confirms the second hypothesis. The resulting structure is based on chains of pentagonal (CuCN)5 rings that share specular sides and have an envelope conformation similar to cyclopentane. The endo position is occupied by a Cu(II)(NH3)3 unit. The 3D structure is generated by the connection of nearby chains linked by two Cu2(1,1,2-µ3-CN)2(CN)4 units for each ring. This kind of topology has also been found in CsCu3(CN)465 and (CH3)4N[Cu(H2O)(NH3)4][Cu4(CN)7].63 The coordination geometry of the Cu(II)(NH3)3 fragment is square pyramidal, but the disorder in the N13 and N14 positions (see **Figure S3** in the Supporting Information) simulates an octahedron.

Compound **4** presents finite linear CuCN chains composed by 4 CuCN units.66 The cyanides are partially end-for-end disordered lying on symmetry elements. The chains are connected by Cu2(1,1,2-µ3-CN)2(CN)4 fragments which propagate the structure in two dimensions: along the chains, although staggered, and perpendicularly to them. μ2-bridging cyanides of the Cu2(1,1,2-µ3-CN)2(CN)4 moieties are coordinated to Cu(NH3) fragments that propagate the architecture in the third dimension through an uncommon linear bridging oxygen.67–69 The oxygen site is only partially occupied (25%), and this points to partial Cu(I) oxidation (50% of the sites are occupied by Cu(II)). Owing to the low oxygen occupation, hydrogen atoms could not be detected. However, the geometry of the Cu-O bond rules out the presence of coordinated water molecules in agreement with the lack of νOH bands in the IR and Raman spectra (see below). Cu(I) atoms interact by means of cuprophilic interaction where the



**Fig. 2** Structural patterns for compounds **1**–**6**.(Cu: orange; C: yellow; N: blue; H: white; O: red).

oxygen atoms are not present.

Compound **5** has the most regular structure. Uncertainty around this compound can be found in the literature since the Cu(II)(NH3)4 complex has also been reported as Cu(II)(H2O)4.54 However, an in-depth vibrational analysis (see below) clearly indicates the presence of ammonia molecules rather than water allowing for very precise structure solution. The structure presents a 2D architecture based on graphite-like planar hexagonal (CuCN)6 rings with an intercalated Cu(II)(NH3)4 complex in the channels. The layers are the inverse of each other, two by two, forming smaller pentagonal channels that connect the entire structure. The hexagonal layers are common to other salts like MCu2(CN)3.H2O (M=K+ both the polymorphs, Cs+ and NH4+)62,70,71 or Cu3(CN)4(NH3)2Hg(CN)2.72

Compound **6** is characterized by chains of alternating Cu(II)(NH3)2 and Cu2(1,1,2-µ3-CN)2(CN)4 fragments. The chains are linked through linear CN groups and other Cu2(1,1,2-µ3-CN)2(CN)4 units to form a 3D structure.

Compound **2** appears to be the most stable sample: indeed **3**, **4** and **6** all convert to **2** after 7-10 days if kept in the mother liquor, as confirmed by vibrational spectroscopy, powder diffraction and single crystal X-ray diffraction.On the other hand, compounds **1** and **5** are stable and do not convert to any other forms. Furthermore, compound **4** slowly (more than 1 month) converts to **2** if left in air.

**Infrared and RAMAN characterization**

All the studied complexes (except for **1**) are coordination polymers where the dominant features in the vibrational spectra are the cyanide and ammonia vibrational modes. The polymeric chains in complex **1** propagate trough Cu(CN)32– units bridged to sodium cations, while the polymeric chains propagate through bridged Cu(I)–CN–Cu(I) and Cu(I)–CN–Cu(II) units in all the other complexes.

The band frequencies of **1**–**6** are reported in **Table S3** of the Supporting Information. IR and RAMAN spectra of **1**–**6** are depicted from **Figure S7** to **Figure S12** of the Supporting Information. Vibrational spectra (4000–300 cm–1) are characterized by the internal modes of the ligands and can be divided into three main regions: 3600–3200 cm–1 (ν(OH) and ν(NH) stretching), 2200–2000 cm–1 (ν(CN) stretching) and 500–300 cm–1 (ν(Cu–C/N) stretching). The vibrational modes of coordinated water and ammonia are assigned according to Nakamoto.73

The two sharp features near 3370 and 3270 cm–1 in complexes **2**–**6** are attributed to asymmetric and symmetric ν(NH) stretching respectively. Compound **5**, already reported to have a [Cu(OH2)4]2+ fragment,54 only shows two strong features in this region at 3334 and 3257 cm–1, which are attributable to N–H stretching, thus definitely confirming the accuracy of structure solution found by us (see above). The lower frequency value with respect to the other complexes is probably ascribable to a Cu(II) charge effect in the [Cu(NH3)4]2+ unit, that has a higher charge if compared to the other complexes where Cu(II) is also bound to cyanide ligands. The presence of water is evident in complex **1**, where a broad strong band is seen at 3443 cm–1, and in complex **2**, with a similar band at 3450 cm–1. The sharpness and the similar frequencies of ν(NH) stretching in complexes **2–6** do not indicate the presence of significant hydrogen bonds. Complex **1** has broad ν(OH) and ν(NH) bands, with the lowest N–H stretching values, indicative of a strong hydrogen-bond interaction.

A structure-spectrum correlation is often regarded as invaluable in cyanide complexes, both because of the different cyanide group environments possible64,74 and the difficulty in correlating the spectral features to the number of non-equivalent CN groups in the solid structure.75 The vibrational spectra of complexes **1**–**6**, that have common structural features, allow us to correlate the IR and Raman bands to the crystalline structural properties. We focused our attention principally on the ν(CN) stretching region because of the superposition, in the low frequency region, of Cu–N stretching of ammonia and cyanide ligands and, where present, of Cu–O stretching.

The vibrational spectra of complex **1** have already been assigned: the compound has two non-equivalent cyanides in the unit cell, but shows four bands, that have been assigned by considering the local D3h symmetry of two differing Cu(CN)32– units, one ordered and one disordered, that give two sets of A1’(Raman)+E’(IR, Raman) modes.60

Compound **2** is more complex: the asymmetric unit has five CN– and three structural motifs: (a) Cu2(I)–CN–Cu(II)–NC–Cu2(I), with two coupled cyanides linked to a Cu(II); (b) Cu(I)–CN–Cu(I); (c) Cu(I)–CN–Cu2(I). Vibrational spectra show four bands, two at lower frequency (2099 and 2113 cm–1), and two at higher frequency (2128 and 2139 cm–1). The vibrational behavior of bridging cyanides has recently been rationalized,76 and an increase in the charge on the metal connected to the cyanide usually raises the ν(CN). For this reason, we can attribute the 2139 and 2128 cm–1 bands to fragment (a), where the almost linear CN–Cu(II)–NC cyanides give origin to the strongest Raman band at 2139 cm–1 and the strongest IR mode at 2129 cm–1. μ2 coordination in fragment (c) weakens the bond order of cyanide, and we attribute the 2113 cm–1 to fragment (b) and the 2099 cm–1 bands to fragment (c) for this reason.

Compound **3** has four CN– in the asymmetric unit, which are nevertheless organized in a triangular Cu(CN)32– motif, with two cyanides bridging Cu(I) atoms, and one cyanide bridging Cu(I)–CN–Cu(II). Vibrational spectra are quite simple and show a band at 2136 cm–1 and a band at 2117 cm–1, which is slightly split in the infrared. By considering the triangular motif as having C2v symmetry, we assigned 2136 cm–1 to the Cu(I)–CN–Cu(II) cyanides, similarly to compound **2**, and the weakly coupled 2117–2114 cm–1 modes to the Cu(I)–CN–Cu(I) cyanides.

Compound **4** has four CN– in the asymmetric unit, organized in three structural fragments: (a) Cu(I)a–NC–Cu(I)b–CN–Cu(I)b–CN–Cu(I)a, (where subscripts indicate differently coordinated coppers); (b) Cu(I)c–CN–Cu(I)c; (c) Cu2(I)a–CN–Cu(II). The vibrational spectra show four bands, with a reversed intensity pattern with respect to complex **2**. The two bands at 2109 and 2099 cm–1 may be attributed to the coupled cyanides of fragment (a); the higher frequency mode at 2155 cm–1 could be assigned to fragment (c), containing Cu(II), and the remaining mode at 2139 cm–1 to the cyanide of fragment (b).

Compound **5** has three CN– in the asymmetric unit and is built upon a 2D polymeric structure formed of linked Cu(I)(CN)32– units. Vibrational spectra show two bands in the Raman (the strongest at higher frequency) and a split band in the infrared. The intensity pattern of the bands is coherent with the a+e symmetry components of a weakly coupled cyanide in the triangular units.

Compound **6** has four CN– in the asymmetric unit, organized in three fragments: (a) Cu(I)–CN–Cu(I) chains; (b) Cu2(I)–CN–Cu2(I); (c) Cu2(I)–CN–Cu(II). These fragments are similar to those in complex **4**, and the vibrational spectra are also mostly analogous: the high frequency mode at 2155 cm–1 is attributed to the Cu(II) containing fragment (c), the 2141 cm–1 mode to fragment (b) and the 2110 and 2098 cm–1 modes to the coupled cyanide of fragment (a).

The comparison of infrared and Raman data allowed us to correlate the vibrational data to the main structural feature of the crystalline structure, which is almost impossible when only considering the infrared data. Similar motifs show analogous modes, with a blue shift due to coordination to Cu(II).

**Differential Scanning Calorimetry (DSC) and Thermogravimetric (TGA) Analyses**

All analyses were carried out from 25 to 400°C, when all the structures start to collapse, giving CuO and HCN as principal products. The calorimetric data are summarized in **Table 1** while the curves are reported in the Supporting Information (**Figures S13–S18**). All the compounds show very similar calorimetric behavior with a decomposition point between 166 and 197°C. The only exception is **1** which is characterized by very high thermal stability (up to 400°C). This particular calorimetric behavior is due to the tricyanocuprate nature of **1.** Indeed, it loses its 3 water molecules in the first 140°C and then it remains stable up to 400°C.

The TGA curve of **2** presents two main losses around 136 and 180°C which are related to the release of one H2O and two NH3 molecules, respectively. It starts to decompose around 205.0°C.

Compounds **3** and **6** lose one ammonia molecule around 124 and 180°C, respectively. Then, they start to decompose at 199 and 197°C, respectively, although both possess several ammonia molecules. On the other hand, **4** and **5** lose all their NH3 molecules (1 and 4, respectively) and then start to decompose at 202 and 166°C, respectively.

**Table 1**. TGA and DSC data for CuCN, **1–6**.

|  |  |  |
| --- | --- | --- |
| **Sample** | ***T*s [°C]** | ***Tdec* [°C]** |
| **1** | 88/108/127 | >400 |
| **2** | 136/180 | 205 |
| **3** | 89/124 | 199 |
| **4** | 180 | 202 |
| **5** | 142 | 166 |
| **6** | 180 | 197 |

*T*s: desolvation temperature; *T*dec: decomposition temperature

**Luminescence Measurements**

In opposition to the quenching behavior of Cu(II),77,78 Cu(I)-based compounds display significant photophysical properties that are ascribed to several electronic excited states: MLCT (Metal to Ligand Charge Transfer), XLCT (halide to Ligand Charge Transfer), CC (metal Cluster-Centered Transition), MC (single Metal Centered transition) and LC (Ligand Centered transition). CuCN itself is characterized by an emission band at 392 nm in the solid state.32,34 This luminescence results from electronic excitation between π character orbitals, in particular from the dCu/πCN HOMO to the pCu/π\*CN LUMO.31 After the coordination of ligands with N or S, as the binding site, the luminescence moves towards the visible region, due to the presence of two different transitions which lead to two possible emissive paths: metal to CN and metal to S/N-ligand, ruling out the CC transitions if the Cu···Cu distance is above 2.8 Å.33,79

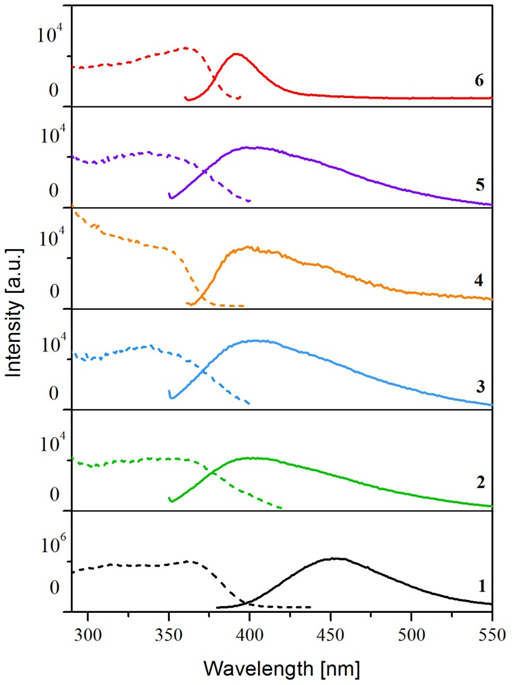
The emission and excitation spectra of the studied compounds are reported in **Figure 3**, while the corresponding data are listed in **Table 2** together with the emission quantum yields. All the coordination polymers exhibit a broad excitation feature in the 300–375 nm range which is similar to that displayed by the parent CuCN. After excitation with UV-light, compound **1** shows outstanding emission at 452 nm, characterized by an excellent quantum yield of 90% (2 orders of magnitude higher than the other coordination polymers), which makes it very promising for possible applications in luminescent devices. All the other coordination polymers show a broad unstructured emission band in the 390–400 nm range, and are characterized by quantum yields of lower than 1%. The Stokes’ shifts are of the order of 106 cm–1. The lifetime of the emissive excited state falls in the nanosecond range for all compounds which is of the same order of magnitude as CuCN.

**Table 2**. Luminescence data for **1–6**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **Excitation**  **λmax [nm]** | **Emission**  **λmax [nm]** | **Stokes shift**  **[cm–1]** | **ϕ** |
| **1** | 366 | 452 | 116279 | 90% |
| **2** | 363 | 400 | 270270 | <1% |
| **3** | 355 | 401 | 217391 | <1% |
| **4** | 351 | 392-550 | 243902-502510 | <1% |
| **5** | 357 | 402 | 222222 | <1% |
| **6** | 365 | 392 | 370370 | <1% |

ϕ: quantum yields

The presence of Cu(I) in compound **1** and of different ratios of Cu(I)/Cu(II) mixed sites in all the other samples provides a likely explanation for the emission band intensity trend. The relative percentages of Cu(I) and Cu(II) have been obtained from the stoichiometry of SCXRD structures and are used for giving a quantification of the quenching effect of Cu(II) sites on the luminescence of the presented coordination polymers. In compound **1**,the presence of 100% Cu(I) sites corresponds with outstanding luminescence. A Cu···Cu distance of larger than 3.6 Å supports the absence of CC transitions, while the MLCT transition is the most plausible pathway for the emission process. Conversely, compounds **2, 3** and **4** display cuprophilic interactions (see **Table 3**) that affect luminescence behavior through CC deactivation pathways. Although an accurate evaluation of emission quantum yields for **2**–**6** is not possible due their low value (< 1%), a qualitative estimation of emission



**Fig. 3** Luminescence emission (solid line) and excitation (dotted line) spectra of **1**–**6**.

intensity reveals a correlation between luminescence and Cu(II) percentage. In particular, compound **4** displays the most intense emission thanks to the presence of 84% of Cu(I) and 16% of Cu(II), while the Cu(II) percentages are 25% and 33%, in compounds **2** and **3** respectively. Finally, **5** and **6** display emission intensities that lie between compounds **2** and **4,** explained by the presence of 80% of Cu(I) and 20% of Cu(II). These data definitively correlate the luminescence properties to the oxidation state of Cu.

Although the presence and number of H2O and NH3 molecules seem completely uncorrelated to coordination polymer luminescent behavior, the presence of NH3 is however related to the number of Cu(II) sites due to its higher affinity for Cu(II) with respect to Cu(I). In this sense, the quenching effect increases with increasing NH3 molecule number. Thus, NH3 molecules are functional to Cu(I) site oxidation, the formation of new structures and packing, that are responsible for the remarkable luminescent behavior of the compounds.

**Table 3.** Cu–Cu distances from SC XRD of **2**–**4** and **6**. Compounds **1** and **5** do not present Cu–Cu interactions.

|  |  |  |  |
| --- | --- | --- | --- |
| **2** | **3** | **4** | **6** |
| Cu1–Cu2  2.6901(5) | Cu2–Cu2  2.6559(10) | Cu2–Cu2  2.6336(10) | Cu1–Cu1  2.7069(14) |
| Cu2–Cu3  2.6483(5) | - | Cu2–Cu3  3.0423(9) | Cu1–Cu2  2.7202(10) |

Conclusions

A series of CuCN-based coordination polymers, with different crystal packing and electronic properties, has been revised from the structural and spectroscopic points of view. The synthesis and the structure of compound **4** have been reported for the first time. The combined presence of Cu(I) and Cu(II) in different percentages in the coordination polymers provides us with a reliable occasion to correlate the oxidation states of copper to the resulting luminescence and, more importantly, to evaluate the effect of Cu(II) in this type of system. Cu(II) is characterized by a quenching behavior, while Cu(I) is the driving force for numerous emission pathways. Indeed, a decrease in luminescence intensity is proportional to an increase in Cu(II) percentages.

Compound **1** was found to be the most attractive compound thanks to its outstanding luminescence and its particular crystal structure. The “tricyanocuprate nature” of this compound reveals the importance of charge transfer between copper and cyanide in strengthening luminescent properties: highest shift with respect to CuCN emission, highest intensity and extraordinary quantum yield. The costs of reagents and preparation are relatively low, making **1** promising for engineering applications. All the other samples show emissions around 400 nm, with low intensities and non-evaluable quantum yields. Compounds **3**, **4** and **6** convert to the most stable form **2**. No direct effects can be traced to the presence of H2O or NH3 molecules rather than them inducing the oxidation of Cu(I) leading to different structures and packing. Due to its low cost, copper is a promising starting material for a number of industrial applications. In particular, copper has shown to be an interesting source of luminescent materials, when combined with CN ligands and various solvent molecules, and one that can be modulated by the oxidation state of the metal site.

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