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ARTICLE

A new heterometallic multiligand 3D coordination polymer: synthesis and structure of $[\text{Pb}(\text{OH})]_n[\text{Ag}(\text{SCN})(\text{CN})]_n$.

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Eliano Diana^{*a}, Giuliana Gervasio^a, Emanuele Priola^a and Elisabetta Bonometti^aReceived 00th January 2012,
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The synthesis and structural characterization of a new coordination polymer $[\text{Pb}(\text{OH})]_n[\text{Ag}(\text{SCN})(\text{CN})]_n$, formed by an anionic layer $[\text{Ag}(\text{CN})(\mu_3\text{-SCN})]_n$ linked to the 1D cationic fragment $[\text{Pb}(\text{OH})]_n$ through a bridging cyanide is reported. We have obtained a rational combination of the pattern of laurionite-type structures ($\text{Pb}(\text{OH})\text{X}$, with $\text{X}=\text{halogen, SCN}$) with the 2D hexagonal pattern of the silver thiocyanate. The title compound shows luminescent behaviour, and the analysis of the computed band structure allows us to describe the electronic transitions.

Introduction

The goal to build coordination polymers (CP) can be achieved by a strategic control of both metal and ligand employed. This kind of materials received a great interest in this decade for their peculiar properties, like luminescence, gas storage¹⁻³, sensoristics⁴ magnetic properties and non-linear optical behaviour⁵. Cyanide and thiocyanate ligands are very versatile as building block for the rational construction of these architectures, because of their ambidentate nature. Thiocyanate is completely ambidentate, in terms of both its $\mu\text{-}1,2\kappa\text{S}$ and $\mu\text{-}1\kappa\text{S},2\kappa\text{N}$ bridging bonding capabilities. Pearson and Drago⁶⁻⁸ cite in their work on this ligand 13 different modes.

There are different effects that can influence the coordination behaviour of this anion: 1) the electronic nature of metal sites (hard or soft behaviour) 2) the steric requirements of ligands (sulphur sites prefer to have a larger coordination sphere because of its bigger dimension)⁹.

The coordination modes of the cyanide group in metal complexes show also a considerable diversity¹⁰. By far the two most commonly observed modes are κC bound mode and the linear bridged arrangement. The architectures that this anion can develop in systems with d^{10} metals are of great variety, especially in the form of $\text{M}(\text{CN})_2$ linear complexes that act as building block for heterometallic compounds.

The use of d^{10} metals, with their spherical shell, permits to develop widely all coordination modes of this kind of anions¹⁰. Silver-thiocyanate is able to form 1D, 2D and 3D coordination polymers. 1D polymers are obtained by development of two principal motifs (figure 1 a and b), a $\mu^2\text{-S}$ silver coordination¹¹ and a bridging coordination¹²:

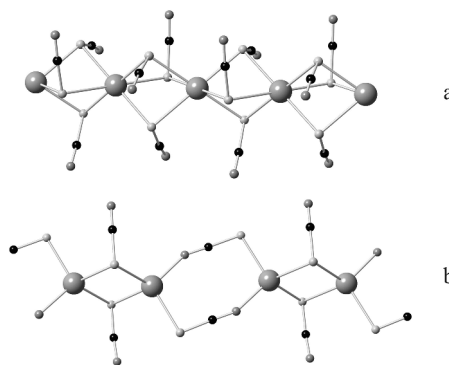


Figure 1: 1D CP obtained from $\text{Ag}(\text{SCN})$, (a) all $\mu^2\text{-S}$ coordinated, (b) $\mu^2\text{-S}$ and bridging SCN

2D polymers are usually built by thiocyanates $\mu_3\text{-}1,2,3\kappa\text{S}$ or $\mu_4\text{-}1,2,3\kappa\text{S},4\kappa\text{N}$ coordinates, that develop a bidimensional pattern formed by rings with different stoichiometry and dispositions (figure 2):

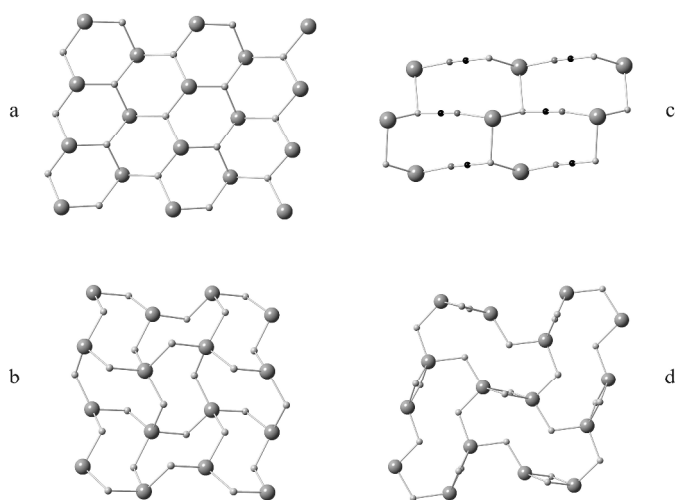


Figure 2: the main 2D pattern built by Ag(SCN) (see text for details). Only sulphur atoms of SCN group is shown.

Ag_3S_3 rings (fig. 2a) have an hexagonal boat disposition^{13,14}; $\text{Ag}_2(\text{SCN})_2\text{S}$ motifs (fig. 2c) that form planar rectangular or hexagonal rings¹⁵; Ag_4S_4 rings with a distorted octagonal geometry¹⁶ (fig. 2b), and bigger Ag_6S_8 rings (fig. 2d) with the typical Ag_2S_2 motif perpendicular to the plane¹⁷.

An analysis of the structures deposited in the CSD and ICSD databases, allows to focus on the main effects that determine the thiocyanate behaviour in these systems.

1) the neutral or anionic nature of the polymer: typically the anionic structures present a pattern created by $\mu^2\text{-S}$ coordination, allowing the interactions with the cationic part of the structure, while neutral polymers are typically generated with bridging coordination.

2) The presence of other metal centres in the compound: if there are other metal atoms, the thiocyanate ligand bridges the polymer and the metal with the N-site. Different patterns of rings in 2D sheets are due to the coordination sphere of the metal and to his dimensions.

3) The presence of hydrogen bonds: the hydrogen bond usually induces distortions of the chains, and typically the thiocyanate use his N-site as acceptor, showing the $\mu^2\text{-S}$ coordination.

4) The steric hindrance of organic ligands coordinated to silver or to other metals: in presence of big ligands, the thiocyanate tends to show a bridging coordination, that maximises the distance between the metal centres. This is also true in presence of other hetero-metals with bulky ligands, and for structures with organic ligands having a supramolecular pattern due to intermolecular forces that needs spatial requirements, like $\pi\text{-}\pi$ stacking.

This great variety of patterns built up with the silver and thiocyanate ligand has been used in the past decades to synthesize several heterobimetallic coordination polymers, formed by an anionic polymer and a cationic metal centre with ancillary ligands. Synthetic work has been developed with Fe^{18-21} , Cu^{22-25} , Zn^{26-30} and Cd^{31-34} , with the formation of new and interesting topological features. Within this background, there are no attempts to investigate the possibility of using anionic

silver thiocyanate fragments as counter ion of another cationic supramolecular fragment, with the aim to build a multipolymeric structure. We decided, in our research about the inorganic mixed salts of d^{10} metals, to explore this supramolecular approach with the use of lead(II) cation. The intrinsic features of Pb(II) inspired chemist's extensive interest in coordination chemistry, photophysics and photochemistry^{35,36}. The presence of the inert pair of 6s electrons leads to interesting topological arrangements, and plays an important role in the luminescent behaviour of the complexes. An important characteristic of Pb(II) exploited in the present research, is the ability to form complex architectures from the species obtained from hydrolysis products. These are often metal clusters but, as in the title compound, they can form 2D or 3D polymers³⁷⁻⁴⁰.

In the present work we have explored the possibility to form a supramolecular architecture with two d^{10} metals, Ag(I) and Pb(II), formed by two different polymeric fragments built up by two pseudohalogenide ligands, CN^- and SCN^- , and the hydroxyl group. One interesting aspect in the study of this kind of CP is the evaluation of luminescence properties typical of d^{10} metal systems in presence of two highly polarizable metals as Ag and Pb, that have been scarcely explored in heterometallic complexes.^{41a-c}

Experimental

All the reagents are used as obtained from the suppliers. Lead (II) thiocyanate (99,5 % purity) was obtained by Aldrich. Potassium dicyanoargentate (99,9 % purity) was obtained from Strem chemicals. We employed deionized water.

Spectroscopic analysis

Raman spectra were obtained with a Horiba JobinYvon HR800 instrument on crystalline sample, equipped with an Olympus BX41 microscope. Samples have been excited with a 633 nm laser radiation with a magnification ratio of 50x.

Infrared spectra have been recorded on the solid sample by means of an anvil cell on a Bruker Vertex 70 FTIR, equipped with the Hyperion 2000 microscope. The UV measurements were recorded on a Perkin Elmer Lambda 900 spectrophotometer in reflectance mode, on a KBr pellet. The photoluminescence measurements were recorded using a Fluorolog F2 Horiba/Jobin-Yvon spectrofluorimeter.

Synthesis of 1: 50 mg of $\text{Pb}(\text{SCN})_2$ and 31 mg of $\text{K}[\text{Ag}(\text{CN})_2]$ have been dissolved in 10 ml of boiling water separately, then the two solutions have been mixed in a Schlenk tube immersed in hot water in a Dewar flask. The pH was at neutral value. The apparatus was closed and leaved to cool down 12 hours. After this time, colourless crystals were formed of two differing habit, one of prismatic shape and one of lamellar shape, suitable for X-ray diffraction experiments. XRPD pattern (see figure S2) showed the presence of compound **1** (lamellar crystals) and of lead hydroxide isothiocyanate (prismatic crystals). Crystals have been mechanically separated and investigated.

X-ray Crystallography

The X-ray data of $[\text{Pb}(\text{OH})]_n[\text{Ag}(\text{SCN})(\text{CN})]_n$ crystal have been collected on a Gemini R Ultra diffractometer. The crystal data and refinement results are collected in Table S1. Data collection and integration has been performed with CrysAlisPro⁴², and SHELXTL⁴³ for the structure solutions and conventional refinement. X-ray powder diffraction (XRPD) intensities of the synthesized compound has been measured at 293 K on the same instrument (Cu-15 K α , $\lambda = 1.54056 \text{ \AA}$). The crystalline powder sample has been prepared by grinding the crystals and scanned from $5\text{-}60^\circ$ with a step of $0.1^\circ/\text{s}$, and calculated patterns were generated with CrysAlisPro. Distances and angles are listed in Table S2. Figure S1 shows the asymmetric unit labelling. Crystallographic data have been deposited to ICSD with CSD number 427447.

Computational analysis: DFT computations on crystalline structure have been performed with Crystal09⁴⁴ code. We used the hybrid B3LYP functional, with empirical Grimme's correction for the dispersive interactions. We employed the 6-311g(d,p) basis set for light elements, the Doll's⁴⁵ ECP with a (8s7p6d)/[6s5p3d]-GTO valence basis set for Ag and the fully relativistic Stoll's⁴⁶ ECP with a (12s12p9d3f2g)/[6s6p4d3f2g]-GTO valence basis set for Pb. We performed a full cell parameter's and atomic position's optimisation, and computed harmonic vibrational frequencies.

Results

Description of the structure

The $\text{Ag}(\text{SCN})(\text{CN})\text{Pb}(\text{OH})$ compound (Table S1 and S2) is formed by two types of polymers linked through weak $\text{N}\cdots\text{Pb}$ interactions ($2.639(7)\text{ \AA}$) (figure 3, top).

One moiety is formed by $[\text{Pb}(\text{OH})]_n^{n+}$ ribbons (parallel to b axis), where OH^- acts as a μ_3 -bridge over three Pb ions (see figure 3, bottom). The other moiety is a corrugated layer (nearly parallel to (100) plane) where the sulphur atom of SCN^- ion bridges three Ag(CN) units; the CN^- ligands lay over and below the $[\text{Ag}(\text{CN})(\mu_3\text{-SCN})]_n^{n-}$ layers and link the $[\text{Pb}(\mu_3\text{-OH})]_n^{n+}$ ribbons.

The coordination sphere of lead(II) is formed by three OH oxygen atoms ($\text{Pb}\cdots\text{O} 2.406(4) \text{ \AA}$ av.) and three nitrogen atoms: two N atoms belong to the cyanide ion and the contact is quite short ($2.639(7) \text{ \AA}$) with respect to the third N atom at the tip of the thiocyanate ion ($2.972(7) \text{ \AA}$). Pb ions show an hemispheric coordination due to the stereochemically active 6s lone pair, similar for example to that found in other compounds of Pb(II)⁴⁷.

Silver atoms of $[\text{Ag}(\text{CN})(\mu_3\text{-SCN})]_n^{n-}$ show the typical tetrahedral coordination and, as metal ions softer than Pb^{2+} , bond the soft sulphur atom of thiocyanate ion. In fact, the borderline Pb(II) interacts better with nitrogen and oxygen atoms.

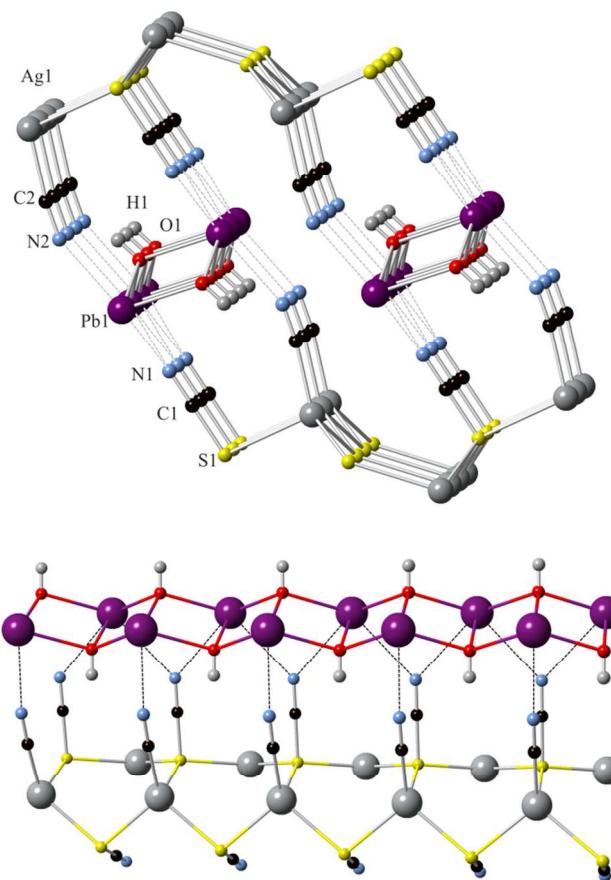


Figure 3: view of 3D network of **1** (top) and the detail of the stacking of the $[\text{Pb}(\text{OH})]_n^{n+}$ and $[\text{Ag}(\text{CN})(\mu_3\text{-SCN})]_n^{n-}$ layers (bottom)

Vibrational analysis

The FT-IR and Raman spectra of solid **1** are shown in figure 4.

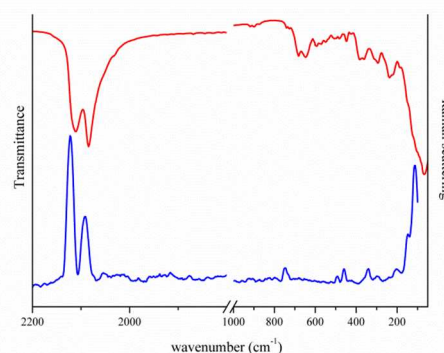


Figure 4: infrared (top) and Raman (bottom) spectra of **1**

The region 4000-300 cm^{-1} is largely dominated by internal modes, while the low frequency region is characterized by lattice modes. Vibrational spectra of crystalline **1** could be interpreted by considering that the Bravais cell contains 36 atoms, and has at the Γ -point of the Brillouin zone $3 \times 36 - 3 = 105$ normal modes. These 105 vibrations are classifiable into symmetry species by considering the D_{2h}^{16} factor group of the $Pnma$ space group:

$$\Gamma = 18 A_g (\text{Raman}) + 9 B_{1g} (\text{Raman}) + 9 B_{2g} (\text{Raman}) + 18 B_{3g} (\text{Raman}) + 9 A_u (\text{n.a.}) + 17 B_{1u} (\text{IR}) + 17 B_{2u} (\text{IR}) + 8 B_{3u} (\text{IR})$$

The spectral selection rules predict 42 infrared and 54 Raman active modes. Observed spectra are rather simple, and this is justified by the negligible intermolecular coupling. The vibrational spectra (figure S2 and table S3) are mainly characterized by the vibrational modes of the cyanide and thiocyanate ligands. In order to do a vibrational assignment we have compared the SCN^- interactions in crystalline AgSCN and in **1** (figure S3), and performed a periodic DFT computation of vibrational spectra of **1** in crystalline state. All results are reported in table S2. The C-N stretching region is usually considered diagnostic of the metal-ligand interaction⁴⁸. The unit cell has one CN and one SCN ligand, with a multiplicity of 4, and so we expect 4 $\nu(\text{CN})$ and 4 $\nu\text{S}(\text{CN})$. Computed spectra indicate a negligible vibrational coupling for these modes, and this justifies the two infrared and two Raman bands detected in the 2200-2000 cm^{-1} region. Frequency values are meaningful of the coordination mode of the ligands. Free SCN^- ion has Raman $\nu(\text{CN})$ frequency at 2066 cm^{-1} ⁴⁹, that becomes 2146 cm^{-1} in the AgSCN compound because of the metal coordination and of the bridging arrangement of the ligand⁴⁷. In **1** SCN^- ligand is linked with the sulfur atom to three silver, as in AgSCN , but the $\text{N} \cdots \text{Pb}$ distance is 2.97 Å, longer than 2.16 Å of $\text{d}(\text{N} \cdots \text{Ag})$ in AgSCN ⁵⁰, that makes the SCN^- ligand in **1** more terminal like. This is reflected on the Raman $\nu(\text{CN})$ frequency, that decreases to 2092 cm^{-1} . The $\nu(\text{CS})$ vibrational mode shows a smaller sensitivity, with a shift from 744 cm^{-1} in AgSCN ⁵¹ to 735 cm^{-1} in **1**. The cyanide ligand behaves similarly: in crystalline AgCN the ligand has a linear bridge coordination and a $\nu(\text{CN})$ frequency at 2164 cm^{-1} ⁵². Compound **1** has a similar arrangement of CN^- , with a $\text{Pb} \cdots \text{N}$ distance of 2.64 Å, greater than $\text{Ag} \cdots \text{N}$ distance in AgCN compound (1.86 Å), and a non-linear Pb-N-C angle of 158°. The elongation of the bridge disposition induces a lowering of the $\nu(\text{CN})$ frequency, that we assign to the 2122 cm^{-1} mode.

The low frequency region contains bands attributable to stretching and deformation modes involving the metal atoms. Vibrational modes involving the μ^3 -OH groups bonded to Pb atoms are expected similar to those present in the analogous $[\text{PbOH}]^+$ polymers⁵³: the two bands at 345 and 294 cm^{-1} are attributed to O-Pb stretching. The modes of cyanide ligand show a very weak feature at 380 cm^{-1} , attributable to $\nu(\text{Ag-C})$, and a weak broad band at 236 cm^{-1} , assignable to the silver cyanide bending $\delta(\text{Ag-CN})$ ⁵². These modes are very similar to those found in crystalline AgCN , and this is reasonable by considering the equal (within the high e.s.d.'s) bond distance ($\text{d}(\text{Ag-C}) = 2.12(1) \text{ \AA}$ in **1**, 2.15(6) Å in AgCN). Two main bands

are assignable to modes involving the SCN ligand, the medium band at 460 cm^{-1} , attributable to SCN bending, and the band at 147 cm^{-1} , assigned to Ag-S stretching. The computed data allow to assign also the O-H modes. A strong and sharp infrared feature at 3557 cm^{-1} is assigned to $\nu(\text{OH})$ modes.

Luminescence

The absorption spectrum of **1** in the solid state shows a broad feature at near 240 nm, and a band at 301 nm. Electronic excitation and emission spectra of **1** are reported in fig. 5, the intense emission at 360 nm comes from the excitation at 240 nm, and the weak emission at 495 nm is obtained by excitation at 301 nm. The absorption spectrum is very similar to that of AgSCN (that has an absorption around 290 nm)⁵⁴ that shows two phosphorescence emissions at near 400 and 550 nm. The phosphorescence has been assigned to a $T^1 \rightarrow S_0$ transition of the SCN^- ion.

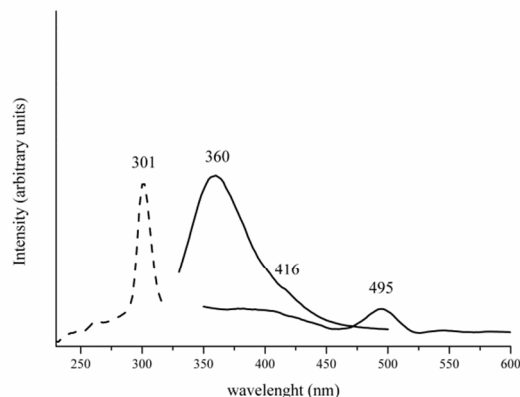


Figure 5: excitation (dot line) and emission spectra of **1**

Also lead coordination polymers show a typical luminescence pattern, that is very sensitive to the Pb-ligand interactions: luminescence transitions have been attributed to transitions localised on Pb, as in the case of 1D lanarkite structures⁵⁵, or in 2D coordination polymers, to a charge transfer that involves the delocalised cluster formed by Pb-O ⁵⁶.

A guess to the composition of computed density of states of crystalline **1** can address toward a qualitative description of the electronic transitions. We explored the path $\Gamma \rightarrow Y \rightarrow R \rightarrow Z \rightarrow \Gamma$ of the Brillouin zone (figures S4 and S5). The top of valence band has main contribution from silver and sulphur atoms, while the bottom of conduction band derives mainly from lead and thiocyanate atoms. The composition of states suggests a charge transfer from the $\text{Ag}(\text{SCN})$ fragment to Pb, but further investigations are needed in order to better evaluate the nature of the emission.

Discussion

The ribbons motif of $[\text{Pb}(\text{OH})]_n^{n+}$ in **1** is characteristic of the compounds isomorphous to the laurionite^{57a-c}, $\text{Pb}(\text{OH})\text{X}$ ($\text{X}=\text{Cl}$, Br , I , SCN). This structure has all atoms in the asymmetric unit on a glide plane on $b/4$ and the same space group of **1**. The structure of **1** can be described as derived from that of $[\text{Pb}(\text{OH})(\text{SCN})]_n^{57b}$ by substitution of thiocyanate ligands with the 2D $[\text{Ag}(\text{CN})(\mu_3\text{-SCN})]_n^{n-}$ polymers. The formation of $\text{Pb}(\text{OH})(\text{NCS})$ is in competition with the compound **1**, and this could explicate the combined crystallisation of **1** and $\text{Pb}(\text{OH})(\text{NCS})$. In **1** the shorter $\text{Pb}\cdots\text{Pb}$ distance 3.906(3) Å, is less than the sum of the Van der Waals radius of the lead (2.02 Å), indicating a metal-metal interaction between these d^{10} centres through the ribbons. The hydrogen bonded $-\text{OH}$ of the laurionite^{57c} is also peculiar in the structure of **1**, with a short interaction with the cyanide's nitrogen (2.521(7) Å) and a typical angular interaction (104.5°). The $[\text{Ag}(\text{CN})(\mu_3\text{-SCN})]_n^{n-}$ are characterised by Ag_3S_3 hexagons with a boat configuration and a $\mu_3\text{-}1,2,3\kappa\text{S}$ coordination for the thiocyanate: the presence of hydrogen bond donors and of other metal centres contribute both to favour this coordination mode.

The formation of $[\text{Pb}(\text{OH})]_n^{n+}$ layers are attributable to the experimental conditions: dissolution of $\text{Pb}(\text{SCN})_2$ in hot water (required by his low solubility) favours the formation of hydrolysis species of lead^{58a-c}. The released thiocyanate enters in competition with the formation of silver complexes ($\log K_1=0.54$ for $\text{Pb}(\text{SCN})^{+59a-c}$, and $\log K_1=4.6$ for $\text{Ag}(\text{SCN})^{60a-c}$. Silver(I) is in equilibrium with mixed complexes of cyanide and thiocyanate, while $\text{Pb}(\text{II})$ already hydrolyses at neutral condition to form hydroxyl complexes^{58c}, especially $[\text{Pb}(\text{OH})]^+$, that probably is the building block for the formation of the chain; the presence of the silver that sequester the thiocyanate ligand favours probably their formation. The $[\text{Pb}(\mu_3\text{-OH})]_n^{n+}$ polymer has been formed probably during the dissolution of lead thiocyanate in boiling water, acting consequently as aggregation centre of the crystalline packing. The effect of the temperature on this equilibriums, is to enhance the acidity of $\text{Pb}(\text{II})$, favouring the formation of hydroxyl complexes⁶¹.

This metathesis reaction suggests a useful method for the synthesis of the anionic silver-thiocyanate fragments. The low solubility of AgSCN in water and common organic solvents is a difficulty in the synthetic procedures, that has been bypassed by several methods: 1) an increase of concentration of the thiocyanate anion to form soluble $[\text{Ag}_n(\text{SCN})_m]^{(m-n)-}$ species^{62a-b}; 2) incorporation of organic ligands to generate neutral AgSCN-L_n species^{63a-b}; 3) dissolution of AgSCN in presence of other silver salts to form mixed inorganic salts⁶⁴. The use of an external source of the anion in equilibrium with a silver complex in our knowledge has not yet reported as method to obtain a supramolecular architecture of this kind.

Conclusions

The synthesis and structural and spectroscopic characterization of a new hetero-metallic Ag-Pb coordination polymer is reported. Compound **1** can be described as derived from the polymeric laurianite structure, $\text{PbX}(\text{OH})$ ($\text{X}=\text{halogen}$, SCN), through substitution of the X ion with an anionic 2D $[\text{Ag}(\text{CN})(\mu_3\text{-SCN})]_n^{n-}$ fragment. The two polymeric layers are connected by bridging cyanides. Compound **1** shows luminescent properties, analysed with the auxilium of computational modelling. The band structure analysis permits to discriminate the differing contribution of metals, with a main involvement of silver into the valence band and of lead into the conduction band.

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^a Dipartimento di Chimica and Centro Interdipartimentale di Cristallografia Diffraattometrica (CrisDi), Università di Torino, Via Pietro Giuria 7, Turin 10125, Italy. Fax: +3901167078550 Tel: +390116707572; E-mail: eliano.diana@unito.it

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A 3D luminescent coordination polymer built by cyanide linkage of 2D polymers of $[\text{Pb}(\text{OH})]_n$ and $[\text{Ag}(\text{SCN})\text{CN}]_n$ has been synthesized and characterized.

