Synthesis, structure and luminescence of new dinuclear cyanido-bridged Ag^I–Au^I one-dimensional coordination polymer

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ABSTRACT

A new alternating chain compound consisting of gold(I) and silver(I) bridged by cyanides is reported. The Ag(I) ion is functionalized by 2 triphenyl phosphane ligands, resulting in the formula $[Au(C\equiv N)_2(PPh_3)_2Ag]_n$. The compound has been prepared by room temperature reaction of triphenyl phosphane with the cyanide salts of silver(I) and gold(I). The product has been characterized and its single crystal X-ray structure was determined. In the molecular structure of the complex, the Au(I) centers exhibit the expected linear, two-coordinate geometry with C-bound cyanides, whereas the Ag(I) centers adopt a tetrahedral geometry in a AgN_2P_2 chromophore. The shortest *hetero* intermetallic separation distance is 4.94(7) Å. No aurophilic interactions are observed, but only the non-conventional C–H…Au hydrogen interactions are present. Upon excitation at 325 nm, a quite intense luminescence at 475 nm, assigned on the basis of *DFT* calculations to MMLCT, is observed, which amounts to *ca.* 10% of the luminescence intensity of the best known luminescent compounds.

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The design and construction of coordination polymers have been evolved as an important cornerstone in supramolecular chemistry [1]. Since the venerable Prussian Blue coordination polymers [2,3] and due to their strong bonds with transition-metal ions, the hexa-, tetra- and di-cyanidometallate anions have been effectively employed as molecular *tectons* in homo- and hetero-metallic multi-dimensional coordination polymers [4–7]. Meanwhile, the construction of new compounds employing the linear anions $[Au(CN)_2]^-$, for the synthesis of new functional materials with the advantage of closed-shell metal ions electronic interaction, continues to generate a great interest [8–10]. In addition, Leznoff and others also demonstrate a moderate to strong anti-ferromagnetic coupling, in materials synthesized using $[Au(CN)_2]^-$ with capping diamine ligands, for a variety of Cu^{II} [11–16], Ni^{II} and Mn^{II} [17–19] scaffolds, and also with bi- and tri-pyridine-based donor ligands [20–24]. Moreover, Real and coworkers have described functional materials in a series of Fe^{II} complexes, by employing the $[Au(CN)_2]^-$ building units, revealing solid state three-dimensional coordination polymers showing Hoffman-like spin crossover and reversible ligands exchange [25–28]. According to CSD version 5.33 [29], the combination of Ag^I complexes with the linear $[Au(CN)_2]^-$ has been yet unexplored.

In the current communication, we describe a new compound with the formula $[AgAu(CN)_2(PPh_3)_2]_n$ (**I**) and we report the synthesis, structure and luminescence of the first example of a Ag^I–Au^I cyanido-bridged one-dimensional coordination polymer.

By stirring AuCN, AgCN and PPh$_3$ in toluene at a 1:1:3 molar ratio under ambient aerobic conditions, the dinuclear Ag^I–Au^I complex (**I**) is formed. Details of synthesis and characterization are available in [30]. Details of the X-ray crystallography are summarized in [31–34]. A thermal ellipsoid plot of the structure is depicted in Fig. 1 and a packing diagram is given in Fig. 2. Figs. 1 and 2 were created with DIAMOND package [35]. Luminescence experimental details are described in [36] and the spectrum is depicted in Fig. 3.

The Ag^I ion adopts a distorted tetrahedral geometry (main angles are: 103.55(2), 111.47(2), 98.94(2) and 117.69(2)°). The Au^I ions are two-coordinated in an almost linear geometry (174.95(4)°). See Fig. 1. The hetero intermetallic separation distances are 4.94(7) and 5.366(6) Å. The Ag–Ag intermetallic node length is 9.935(9), while that of Au–Au is 9.546(7) Å.

The molecular array is best described as a *zig-zag* like chain along the crystallographic *[101]* vector, with the chain nodes propagation angle of 146.93 (7)°. See Fig. 2.

Although clearly-defined now as either agostic bonds or non-conventional hydrogen bonds; the electrostatic interactions involving hydrogen bond donor and metal empty *d*-orbitals acceptor have been investigated during the last decade [37–39]. The C–H…Au interactions in (**I**) arise from the phenyl ring hydrogen atoms, are in short contacts (D–A (Å): 3.668, 3.662 and 3.645) to the gold(I) ions, with apparently no aurophilic interactions are visible, which may be ascribed to the bulky phosphane ligand on Ag^I.

Excitation of the solid-state compound of (**I**) with UV radiation results in the appearance of a rather intense blue luminescence band centered around 475 nm and a shoulder near 450 nm. The compound

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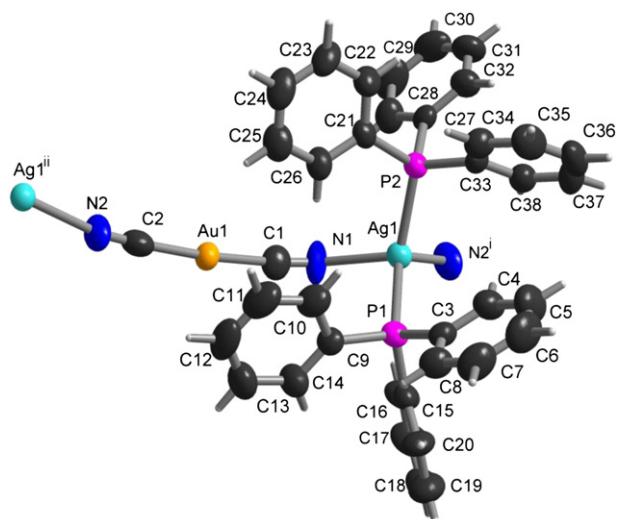 E-mail address: mghazzali@ksu.edu.sa (M. Ghazzali).

Fig. 1. Thermal ellipsoidal of 50% probability level with atomic numbering scheme for a part of the polymeric structure of (I). Hydrogen atoms are presented as spheres of arbitrary radii. Selected bond distances (Å); Au1–C1:1.983(10), Au1–C2: 1.987(9), Ag1–P1: 2.473(2), Ag1–P2: 2.474(2), Ag1–N1: 2.402(7), Ag1–N2^i: 2.280(7), P1–C3: 1.824(8), P1–C9: 1.822(7), P1–C15: 1.829(7), P2–C21: 1.820(7), P2–C27: 1.827(8),P2–C33: 1.832(8), N1–C1: 1.143(12), N2–C2: 1.134(11). Selected bond angles (°); C1–Au1–C2: 175.0(4), P1–Ag1–P2: 123.73(7), P1–Ag1–N1: 98.94(19), P2–Ag1–N: 111.5(2), Ag1–P1–C3: 114.2(3), Ag1–P1–C9: 112.3(3), Ag1–P1–C15: 115.5(3), C3–P1–C9: 103.3(3), C3–P1–C15: 105.1(4), C9–P1–C15: 105.3(3), Ag1–P2–C21: 1116.9(2), Ag1–P2–C27: 116.0(2), Ag1–P2–C33: 111.6(2), C21–P2–C27: 101.2(3), C21–P2–C33: 105.8(3), C27–P2–C33: 103.9(3), Ag1–N1–C1: 128.8(7), C2–N2–Ag1^{ii}:169.2(7), Au1–C1–N1: 174.4(8), Au1–C2–N2: 176.2(9). P1–Ag1–N2^i: 117.7(2), P2–Ag1–N2^i: 103.6(2), N1–Ag1–N2^i: 98.6(3). Symmetry codes: (i) −1/2 + x, 1/2 − y, − 1/2 + z (ii) 1/2 + x, 1/2 − y, 1/2 + z.

features a broad excitation spectrum ranging from 220 to 350 nm with two maxima at 240 and 325 nm. Excitation of the compound at these maxima results in a luminescence intensity that is about 10% of that obtained for one of the best known luminescent coordination compounds, triethylammonium tetrakis(dibenzoylmethanate)europate [40]. In order to assign the electronic transitions associated with these emission bands, we carried out *DFT* calculation on the dinuclear [Ag^I(PPh$_3$)$_2$Au^I(CN)] molecular fragment [41,42]. The relevant HOMOs and LUMOs are depicted in Fig. 4.

Fig. 3. Excitation (left) and emission (right) spectrum of the compound (I).

(a)

(b)

Fig. 4. Isodensity surface diagrams of LUMO with LUMO{+1} (a) and HOMO with HOMO{−1} (b) for the compound cationic fragment. HOMO/LUMO are in solid, HOMO{−1}/LUMO{+1} are in mesh.
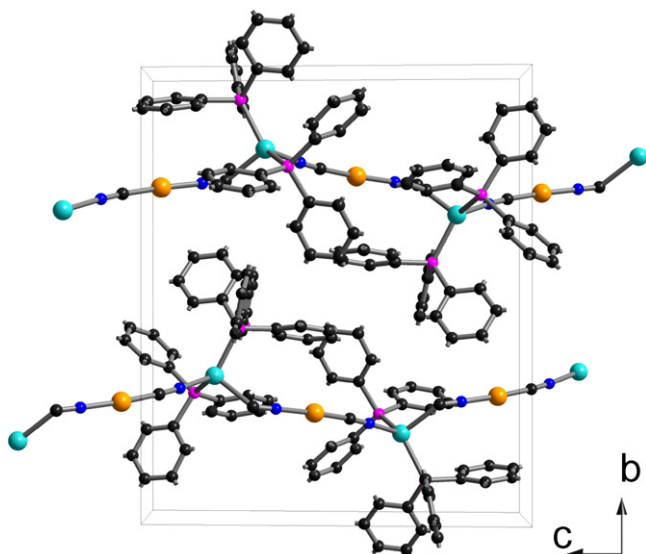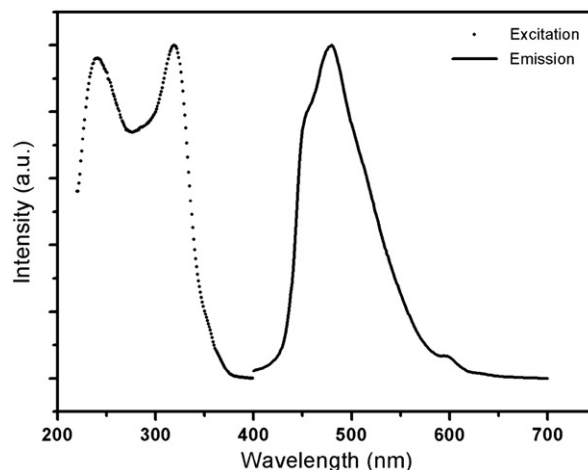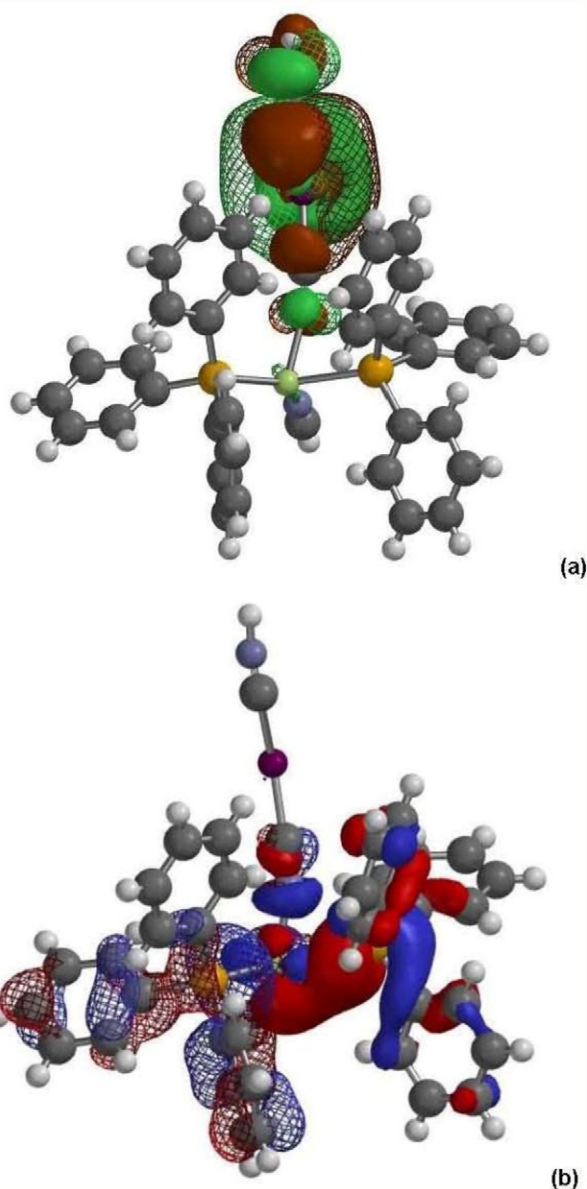

Fig. 2. *a*-axis projection of the molecular chains in (I), with hydrogen atoms are omitted for clarification purpose.

The d^{10} cyanidometallate luminescence is frequently attributed to MLCT or MMLCT transitions [43–45]. In the 1D-chain compound of **I**, The two lowest singlet excitations are dominated by the combination of HOMO–LUMO and HOMO{−1}–LUMO{+1} transitions, in which both HOMO{−1} and HOMO are containing the character of Ag(I) d-orbitals. The HOMOs are localized on the silver metal center (namely the d$_{xy^2}$ orbital), mixing with ð-(Ag–P) and (C≡N) bondings as well as π-orbital contribution from phenyl rings on the PPh$_3$ chromophore. The last one can be also relevant with the existence of C–H…Au interaction. The cyanide π*-orbital mixes with an Au p*-orbital in bonding fashion to form the LUMOs. The small HOMO/LUMO gap of *ca.* 0.031 a.u. can be attributed to the HOMO's and LUMO's large metallic characters. It is expected that during a MLCT transition, the mixing of the π*(C≡N) with the empty p-orbitals of Au and the phenyl π-orbitals is capable of defining the direction of the structural variations along the chain compound. This is also similar to recent results of others [45].

In conclusion, the structure of new bimetallic Au^I–Ag^I one dimensional coordination compound is presented, and its luminescence is ascribed as due to MMLCT.

Acknowledgments

Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2012.03.005.

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[30] The starting chemicals were commercially available (BDH-Analar grade). Hexane was dried and distilled before use; toluene and dichloromethane were kept over molecular sieves and used without distillation. The elemental analysis was performed by Perkin Elmer Series II-2400 analyzer. The FT-IR spectrum was recorded by Shimadzu FT-IR prestige-21 spectrophotometer. Triphenyl phosphane (0.786 g, 3 mmol) was added to yellow suspension of gold cyanide AuCN (0.223 g, 1 mmol) in toluene (30 ml). Stirring continued for 20 min till a clear solution is obtained. Silver cyanide AgCN (0.134 g, 1 mmol) was added then stirring continues for one day. The white precipitate is filtered off, washed with toluene (10 ml) and collected. The recrystallisation with dichloromethane/hexane gives crystals suitable for X-ray single crystal diffraction. Yield of [AgAu(C≡N)$_2$(PPh$_3$)$_2$]$_n$ (0.820 g, *ca.* 93%), m.p. 218 °C, Elemental Analysis for C$_{38}$H$_{30}$AgAuN$_2$P$_2$; Found (calc.): 52.05 (51.78) %C, 3.40 (3.43) %H, 3.18 (3.19) %N v_{max} cm^{-1} (KBr disk) 503 (s), 515 (s) cm^{-1} (Au–C), 2170 (m), 2141 (m) cm^{-1} (C≡N).
[31] X-ray crystallography: Crystal Data: C$_{38}$H$_{30}$AgAuN$_2$P$_2$, Monoclinic, P2$_1$/n, a = 9.7145(6) Å, b = 20.4203(13) Å, c = 17.3735(12) Å, β = 95.666(2)º, V = 3429.6(4) Å^3, D$_{calc}$ = 1.707 g cm^{-3}, A total of 39826 reflections were collected, of which 7809 were independent. Rint = 0.099, Dataset (h;k;l) = −12;12; −26:26; −22:22, Observed data [I > 2σ(I)] = 4715, 398 parameters, R(F) [I > 2σ(I)] = 0.0518, R$_w$ = 0.1444, S = 0.99, min. and max. Residual density (e/Å^3) = −2.48 and 1.26 (0.90 Å from Au1 and 1.18 Å from C1 or 1.4 Å from Au1, respectively). A colorless plate was selected, mounted and glued on a thin capillary tip. Diffraction data were collected using Rigaku R-axis RAPID diffractometer equipped with an imaging plate area detector utilizing Mo-Kα radiation (λ = 0.71075 Å) with graphite monochromator. The data were collected using ω-scans at a temperature of 294 ± 2 K to a maximum 2θ of 55.0°. The intensity data were corrected for Lorentz and polarization effects, for absorption and extinction. The structure was solved by direct method [33] and refined by the SHELX package [34]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically fixed and refined by riding atom approximation.
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