New heterometallic coordination polymers based on zinc(II) complexes with Schiff-base ligands and dicyanometallates: synthesis, crystal structures, and luminescent properties

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New heterometallic coordination polymers based on zinc(II) complexes with Schiff-base ligands and dicyanometallates: synthesis, crystal structures, and luminescent properties

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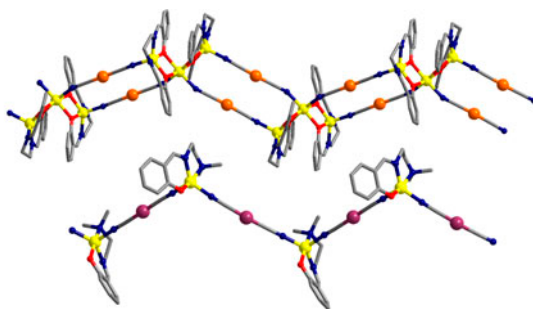
The self-assembly processes between homotrimetallic, $\{Zn_3(salen)_2\}^{2+}$, and mononuclear, $\{Zn(Saldmen)\}^+$, $\{Zn(Salampy)\}^+$, units and dicyanometallates, generate new polymeric 1-D chains. In compound **1** the homotrimetallic units, $\{Zn_3(salen)_2\}^{2+}$, are connected by two $[Au(CN)_2]^-$ bridges, forming 1-D double chain. In compounds **2–4** the crystal structures show polymeric 1-D chains generated by the mononuclear zinc(II) nodes and $[M(CN)_2]^-$ spacers.

Four new d^{10} heterometallic coordination polymers have been obtained using three Schiff-base ligands, zinc(II) nitrate, and dicyanometallates: $_1^\infty[\{Zn_3(Salen)_2\}\{\mu\text{-}Au(CN)_2\}_2]$ (**1**); $_1^\infty[Zn(Saldmen)\{\mu\text{-}Ag(CN)_2\}]\cdot2H_2O$ (**2**); $_1^\infty[Zn(Salampy)\{\mu\text{-}Ag(CN)_2\}]$ (**3**); $_1^\infty[Zn(Salampy)\{\mu\text{-}Au(CN)_2\}]$ (**4**). The Schiff bases are obtained from condensation of salicylaldehyde with ethylenediamine (H_2Salen); N,N-dimethyl-ethylenediamine (HSaldmen) and, respectively, 2-aminomethyl-pyridine (HSalampy). The dicyanometallates are $K[Ag(CN)_2]$ and $K[Au(CN)_2]$. The compounds were characterized by X-ray single-crystal diffraction, infrared spectroscopy, UV–vis spectroscopy, and elemental analysis. In compound **1**, the homotrimetallic units, $\{Zn_3(salen)_2\}^{2+}$, are connected by two $[Au(CN)_2]^-$ bridges, forming a 1-D double chain. In compounds **2–4**, the crystal structures show polymeric zigzag chains generated by the mononuclear zinc(II) nodes and $[M(CN)_2]^-$ spacers. The luminescence properties of the new heterometallic polymers have also been investigated.

Keywords: Zinc–silver heterometallic complexes; Zinc–gold heterometallic complexes; Schiff-base ligands; Luminescence

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1. Introduction

In the synthesis of coordination polymers, Schiff bases are frequently used as auxiliary or blocking ligands to control the topology of the network. The wide diversity of this category of polydentate ligands allows blocking specific positions in the coordination sphere of the metal ions, depending on the number, relative position, and HSAB properties of the donor atoms within the Schiff-base ligands. The coordination polymers based on transition metal ions and multifunctional Schiff-base ligands have been extensively investigated due to their intriguing network topologies and their potential applications (for example, bioinorganic, catalysis, magnetic, luminescent materials) [1].

In this context, our interests were oriented toward the synthesis of discrete or polymeric metal complexes involving symmetrical or asymmetrical Schiff-base ligands derived from salicylaldehyde, 3-methoxysalicylaldehyde, or 2,6-diformyl-p-cresol with interesting magnetic and/or luminescent properties [2]. The salicylaldehyde and its derivatives are very useful precursors for the synthesis of a large variety of Schiff bases, which result by condensation with various amines.

Along with Schiff-base blocking ligands, the spacers used in the synthesis of coordination polymers determine the topology of the resulting networks. Dicyanoargentate(I) and dicyanoaurate(I) anions, $[M(CN)_2]^-$ $[M(I) = Ag(I), Au(I)]$, with linear geometry and two potential cyano-coordination sites, are used as bridging units to generate a large variety of coordination polymers with interesting structures and magnetic properties [3]. Moreover, the d^{10} silver(I) and gold(I) metal centers in the dicyanoargentate and dicyanoaurate ions are frequently involved in metallophilic interactions (known as argentophilic or aurophilic interactions) sustaining the supramolecular solid-state architectures. These short interactions can lead also to interesting optical properties [4].

Herein we report the synthesis and characterization of four new heterometallic coordination polymers, $_1^\infty[\{Zn_3(Salen)_2\}\{\mu\text{-}Au(CN)_2\}_2]$ (1), $_1^\infty[Zn(Saldmen)\{\mu\text{-}Ag(CN)_2\}]\cdot 2H_2O$ (2), $_1^\infty[Zn(Salampy)\{\mu\text{-}Ag(CN)_2\}]$ (3), and $_1^\infty[Zn(Salampy)\{\mu\text{-}Au(CN)_2\}]$ (4), in which the dicyanometallates $[M(CN)_2]^-$ ions act as bridging ligands.

2. Experimental

Synthesis of $_1^\infty[\{Zn_3(Salen)_2\}\{\mu\text{-}Au(CN)_2\}_2]$ (1), $_1^\infty[Zn(Saldmen)\{\mu\text{-}Ag(CN)_2\}]\cdot 2H_2O$ (2), $_1^\infty[Zn(Salampy)\{\mu\text{-}Ag(CN)_2\}]$ (3), and $_1^\infty[Zn(Salampy)\{\mu\text{-}Au(CN)_2\}]$ (4). All starting materials were reagent grade and used without purification. The mono- and trinuclear precursors were synthesized *in situ* by reacting the Schiff bases with zinc(II) nitrate.

2.1. Synthesis of $_1^\infty[\{Zn_3(Salen)_2\}\{\mu\text{-}Au(CN)_2\}_2]$ (1)

A methanolic solution (5 mL) of $Zn(NO_3)_2\cdot 4H_2O$ (0.2 mmol) was added to a solution (15 mL) of H_2Salen (0.1 mmol, 10 mL methanol) and triethylamine (0.1 mmol, 5 mL MeOH), and the resulting mixture was stirred for 30 min at room temperature. This solution was gently layered on top of the aqueous solution (2 mL) of $K[Au(CN)_2]$ (0.2 mmol). Upon slow evaporation at room temperature, yellow single crystals of **1** were obtained after several days, in quantitative yield. Anal. Calcd for $C_{36}H_{28}Au_2N_8O_4Zn_3$: 35.21% C, 2.28% H,

9.13% N. Found: 35.50% C, 2.32% H, 9.15% N. IR data (KBr, cm^{-1}): 2868w, 2844w, 2178s, 2155w, 1660m, 1639vs, 1597s, 1546m, 1470m, 1446s, 1388m, 1337m, 1287vs, 1195m, 1152m, 1036w, 901m, 852w, 755m, 742s, 647m, 608w.

2.2. *Synthesis of $_1^{\infty}$[Zn(Saldmen){μ-Ag(CN)$_2$}]·2H$_2$O (2)*

The methanolic solutions containing stoichiometric amounts of salicylaldehyde (0.1 mmol, 10 mL) and N,N-dimethyl-ethylenediamine (0.1 mmol, 5 mL) were mixed and kept under continuous stirring for 30 min at 50 °C. This solution was then reacted with stoichiometric amounts of triethylamine (0.1 mmol, 5 mL MeOH) and Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol, 10 mL MeOH) and kept under stirring for 30 min. The resulting solution was gently layered on top of the aqueous solution (2 mL) of K[Ag(CN)$_2$] (0.1 mmol). Yellow single crystals of **2** were obtained after several days. Yield ca. 75%. Anal. Calcd for C$_{13}$H$_{19}$AgN$_4$O$_3$Zn: 34.47% C, 4.19% H, 12.37% N. Found: 35.00% C, 4.15% H, 11.97% N. IR data (KBr, cm^{-1}): 3192m, 2998w, 2967w, 2888m, 2840w, 2175s, 2143m, 1637vs, 1598s, 1539m, 1470vs, 1450s, 1398w, 1343m, 1315w, 1255w, 1192m, 1154m, 1074m, 1032w, 904s, 795w, 764m, 641w.

2.3. *Synthesis of $_1^{\infty}$[Zn(Salampy){μ-Ag(CN)$_2$}] (3)*

Methanolic solutions containing stoichiometric amounts of salicylaldehyde (0.1 mmol, 10 mL) and 2-aminomethyl-pyridine (0.1 mmol, 5 mL) were mixed and kept under continuous stirring for 30 min at 50 °C. Then the solution was reacted with stoichiometric amounts of triethylamine (0.1 mmol, 5 mL MeOH) and Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol, 10 mL MeOH) and kept under stirring for 30 min. This solution was gently layered on top of the aqueous solution (2 mL) of K[Ag(CN)$_2$] (0.1 mmol). Yellow single crystals of **3** were obtained after several days. Yield ca. 80%. Anal. Calcd for C$_{15}$H$_{11}$AgN$_4$OZn: 41.23% C, 2.52% H, 12.82% N. Found: 41.00% C, 2.30% H, 12.97% N. IR data (KBr, cm^{-1}): 3065w, 2910w, 2881w, 2177s, 2150w, 1640vs, 1606m, 1571w, 1483w, 1453s, 1420m, 1406m, 1350s, 1286m, 1190w, 1144m, 1129s, 1064m, 1047w, 1018w, 1005w, 911w, 850w, 761s, 742m, 658w.

2.4. *Synthesis of $_1^{\infty}$[Zn(Salampy){μ-Au(CN)$_2$}] (4)*

Compound **4** has been obtained following the same general procedure described for **3**, using K[Au(CN)$_2$] instead of K[Ag(CN)$_2$]. Yield ca. 85%. Anal. Calcd for C$_{15}$H$_{11}$AuN$_4$OZn: 34.24% C, 2.09% H, 10.65% N. Found: 34.89% C, 2.29% H, 11.03% N. IR data (KBr, cm^{-1}): 3077w, 2910w, 2185s, 2152w, 1640vs, 1606m, 1572w, 1535s, 1482w, 1463s, 1453m, 1405m, 1350m, 1286m, 1190w, 1145m, 1129w, 1066w, 1048w, 1020w, 911w, 852w, 761s, 743m, 659w.

2.5. *Physical measurements*

IR spectra were recorded as KBr pellets on a JASCO FTIR 4100 spectrophotometer from 4000 to 400 cm^{-1}. Absorption spectra were made with a JASCO V-670 spectrophotometer. The photoluminescence measurements were carried out at room temperature using a JASCO FP 6500 spectrofluorometer.

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Table 1. Crystallographic data, details of data collection, and structure refinement parameters for **1–4**.

Compound	1	2	3	4
Chemical formula	$C_{36}H_{28}Au_2N_8O_4Zn_3$	$C_{13}H_{19}AgN_4O_3Zn$	$C_{15}H_{11}AgN_4OZn$	$C_{15}H_{11}AuN_4OZn$
M (g M^{-1})	1226.71	452.56	436.52	525.61
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Monoclinic*
Space group	*C2/c*	*C2/c*	*P21/a*	*P21/a*
a (Å)	20.5923(15)	21.903(4)	8.8799(15)	8.8855(13)
b (Å)	10.2400(8)	10.271(2)	13.1209(15)	13.2788(15)
c (Å)	18.0535(12)	17.428(4)	13.631(2)	13.4533(19)
α (°)	90	90	90	90
β (°)	109.631(5)	101.34(3)	92.469(13)	93.374(12)
γ (°)	90	90	90	90
V (Å^3)	3585.6(5)	3844.2(13)	1586.7(4)	1584.6(4)
Z	4	8	4	4
D_{Calcd} (g cm^{-3})	2.272	1.564	1.827	2.203
μ (mm^{-1})	10.185	2.280	2.750	10.766
$F(000)$	2320	1808	856	984
Goodness of fit on F^2	1.087	0.901	0.957	1.022
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0510, 0.1028	0.0532, 0.1157	0.0671, 0.1273	0.0790, 0.1885
R_1, wR_2 (all data)	0.0725, 0.1098	0.1329, 0.1414	0.1416, 0.1501	0.1160, 0.2082
Largest diff. peak/hole (e Å^{-3})	0.922/−3.658	0.641/−0.561	1.472/−0.535	3.190/−1.691

2.6. *X-ray structure determination*

X-ray diffraction measurements were performed on a STOE IPDS II diffractometer, operating with a Mo-Kα ($\lambda = 0.71073$ Å) X-ray tube with a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least squares based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. A summary of the crystallographic data and the structure refinement for crystals **1**–**4** is given in table 1. CCDC reference numbers: 1023950-1023953.

3. Results and discussion

The work presented in this study is based upon the employment of three Schiff-base ligands, which are obtained by reacting salicylaldehyde with ethylenediamine, N,N-dimethyl-ethylenediamine, and 2-aminomethyl-pyridine (scheme 1).

3.1. *Description of the structures*

The crystallographic investigation of **1** reveals a 1-D coordination polymer with the formula $_1^\infty[\{Zn_3(Salen)_2\}\{\mu\text{-}Au(CN)_2\}_2]$. Its structure consists of a 1-D double chain formed by trinuclear $[Zn_3]^{2+}$ nodes connected by two spacer molecules of $[Au(CN)_2]^-$. Within the chain, the trinuclear $[Zn_3]^{2+}$ nodes are built by two mononuclear moieties, [Zn(Salen)], which are connected to the third Zn(II) ion by the oxygen atoms of the Schiff-base ligands (figures 1 and 2).

There are two different crystallographic types of zinc ions. The Zn1 and Zn1′ ions ($' = 1 - x$, y, $1.5 - z$) are five coordinated with a square-pyramidal stereochemistry while Zn2 is six coordinated in a distorted octahedral geometry. The basal plane of each Zn1 ion is formed by the phenoxo oxygen atoms and by the imino nitrogen atoms of the Schiff-base ligands, Zn1–O1 = 2.016(4), Zn1–O2 = 1.992(4), Zn1–N1 = 2.073(6), and Zn1–N2 = 2.071 (6) Å. The apical position is occupied by a nitrogen from the $[Au(CN)_2]^-$ bridge, Zn1–N3 = 2.047(6) Å.
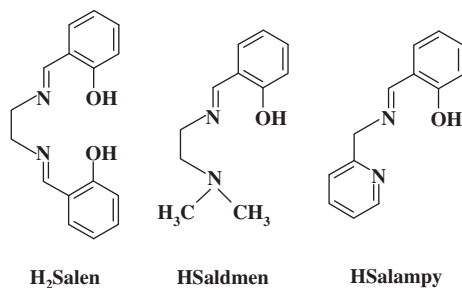
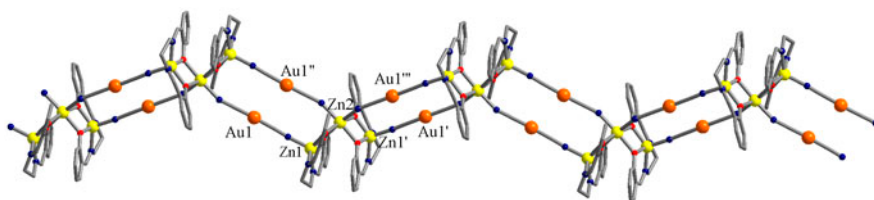Scheme 1. Structures of ligands: H$_2$Salen, HSaldmen, and HSalampy.

Figure 1. View of the coordination polymer in **1** (symmetry codes: $' = 1 - x, y, 1.5 - z$; $'' = 0.5 - x, 0.5 - y, 1 - z$; $''' = 0.5 + x, 0.5 - y, 0.5 + z$).

The Zn2 is coordinated by four phenoxo oxygen atoms from the two Schiff-base ligands and by two nitrogen atoms from the two $[Au(CN)_2]^-$ bridges, Zn2–O1 = 2.096(4), Zn2–O2 = 2.167(4), and Zn2–N4″ = 2.142(6) Å ($'' = 0.5 - x, 0.5 - y, 1 - z$). The angles for the phenoxo bridges are Zn1–O1–Zn2 = 100.71(18) and Zn1–O2–Zn2 = 99.11(19)°. Within the nodes, the two Salen^{2-} ligands establish weak π–π stacking interactions (3.52–3.66 Å). In the crystal, the zigzag chains with a parallel arrangement form layers [figure 3(a)], and the Schiff-base ligands are involved in π–π stacking interactions (3.30–3.56 Å) with similar ligands from neighboring layers [figure 3(b)].

Both dicyanoaurate units have nearly linear geometries. The intra- and internode Zn···Zn distances are 3.167 and 10.35 Å, respectively. The Au···Au distance is 3.659 Å, and there are no significant gold–gold interactions. It is known that the sum of the van der Waals radii of two gold(I) ions is 3.60 Å and is thus considered to be the upper limit of the distance for significant aurophilic interactions [5]. In the literature, gold–gold distances from 3.14 to 3.59 Å were attributed to aurophilic interactions between the gold centers, while compounds with Au···Au distances larger than 3.60 Å were not considered to involve significant aurophilic interactions [4(a), 6, 7].

$_1^\infty$[Zn(Saldmen){μ-Ag(CN)$_2$}]·2H$_2$O (**2**) crystallizes in the *C2/c* monoclinic space group. The structure of **2** consists of neutral [Zn(Saldmen){μ-Ag(CN)$_2$}] zigzag chains and crystallization water molecules (figure 4).

The cationic Zn(II) centers are five coordinated with a distorted trigonal bipyramidal geometry. The equatorial plane is formed by three nitrogen atoms, one imino from the Schiff-base ligand and two from the two $[Ag(CN)_2]^-$ bridges, Zn1–N1 = 2.040(4),
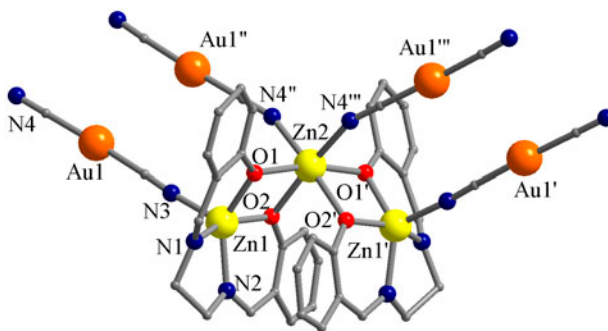

Figure 2. Detailed view of the trinuclear [Zn$_3$]$^{2+}$ node in **1** along with the atom labeling scheme (symmetry codes: $' = 1 - x, y, 1.5 - z$; $'' = 0.5 - x, 0.5 - y, 1 - z$; $''' = 0.5 + x, 0.5 - y, 0.5 + z$).
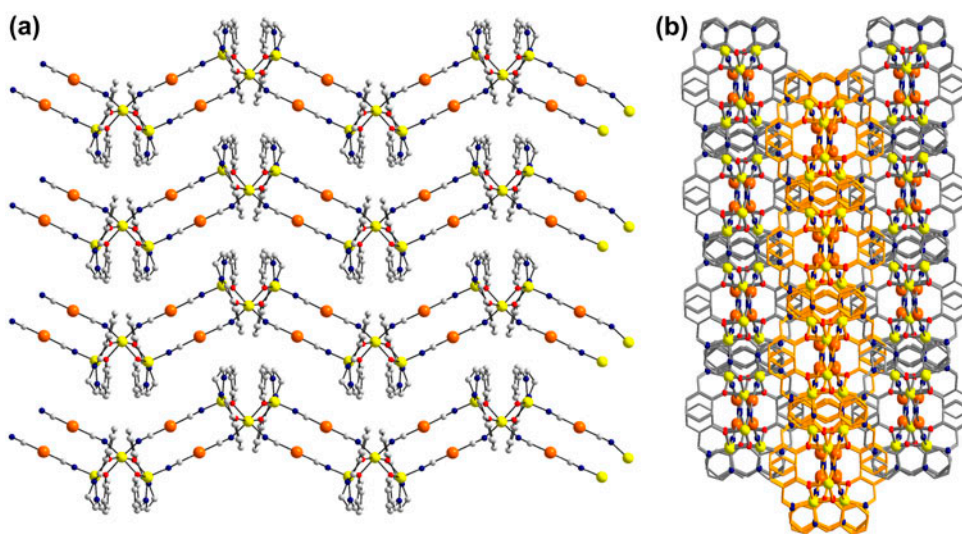
Figure 3. Views of the packing diagrams in **1** showing the layers (a) and the π–π interactions between the layers (b).

Zn1–N3 = 2.031(4), and Zn1–N4 = 2.012(4) Å. The axial positions are occupied by the amino nitrogen of Saldmen$^-$ and the phenoxo oxygen atom, Zn1–N2 = 2.324(4) and Zn1–O1 = 2.026(3) Å. The internode Zn$\cdots$Zn distance is 10.41 Å.

In this case, the silver(I) ions from neighboring chains are involved in argentophilic interactions with Ag$\cdots$Ag separation of 3.274 Å (the sum of the van der Waals radii for silver(I) is 3.44 Å [8]), generating supramolecular double chains (figure 5). Strong interactions are typically <3.0 Å, whereas distances >3.3 Å are considered to be weak interactions [9]. The chains run along the crystallographic *c* axis. The packing diagram shows formation of channels on the same direction in which the solvent water molecules are hosted (figure 6).

Complexes **3** and **4** are isomorphous, and only the structure of **3** is discussed here. It is also a 1-D polymeric chain (figure 7). The Zn(II) centers are five coordinated with a distorted trigonal bipyramidal geometry. The equatorial plane is formed by three nitrogen atoms, one imino from the Schiff-base ligand and two from the two [Ag(CN)$_2$]$^-$ bridges, Zn1–N1 = 2.058(6), Zn1–N3 = 2.047(7), and Zn1–N4′ = 2.068(7) Å; symmetry code: ′ = 0.5 − *x*,
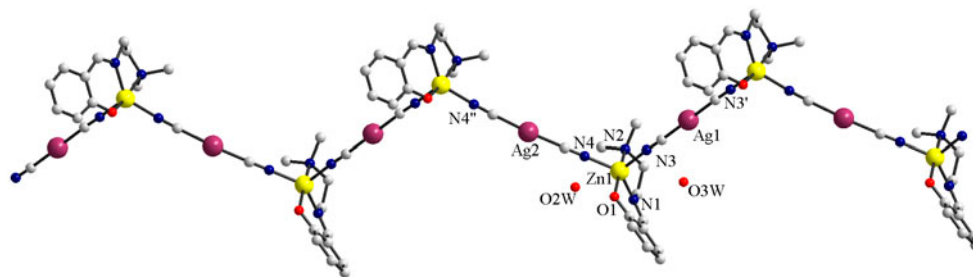

Figure 4. Perspective view of {Zn–Ag}$_n$ zigzag chain in **2** (symmetry codes: ′ = −*x*, *y*, 0.5 − *z*; ″ = −*x*, *y*, −0.5 − *z*).
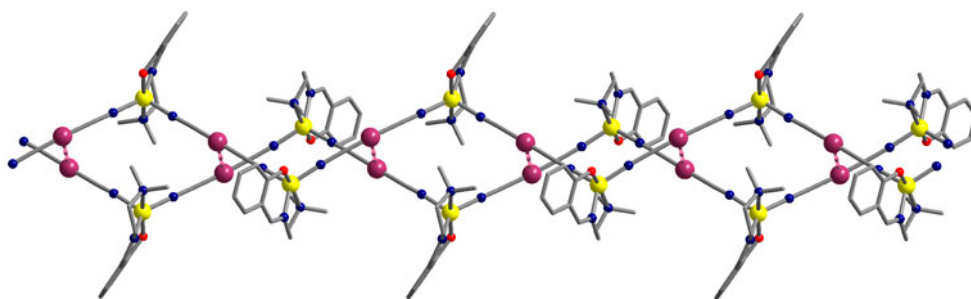
Figure 5.   Supramolecular double chain in **2** through argentophilic interactions (Ag···Ag = 3.274 Å). Dotted lines represent the Ag···Ag interactions.

$-0.5 + y$, $1 - z$. The axial positions are occupied by the pyridine nitrogen of Salampy$^-$ and by the phenoxo oxygen, Zn1–N2 = 2.194(7) and Zn1–O1 = 1.982(5) Å.

The [Zn(Salampy)]$^+$ units are equatorially connected by NC–Ag–CN bridges with a Zn···Zn distance of 10.37 Å. The Ag···Ag (in **3**) and, respectively, Au···Au (in **4**) separations of 4.551 and 4.556 Å are significantly longer than 3.44 and 3.60 Å, respectively, the sum of van der Waals radii, indicating the absence of Ag···Ag and Au···Au interactions in these compounds. The Salampy$^-$ ligands are involved in π–π stacking interactions (3.51–3.60 Å) with similar ligands from neighboring chains (figure 8).

3.2. Spectral properties

The IR spectra of all complexes contain the bands corresponding to cyanide bridges. The absence of any bands corresponding to nitrate anion in the IR spectra of all the complexes confirmed the replacement of the NO$_3^-$ by [M(CN)$_2$]$^-$ units.
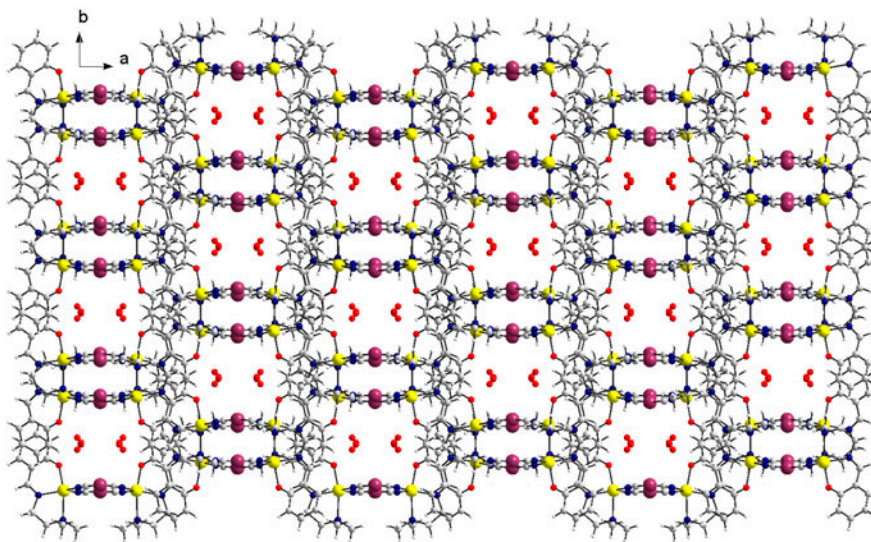

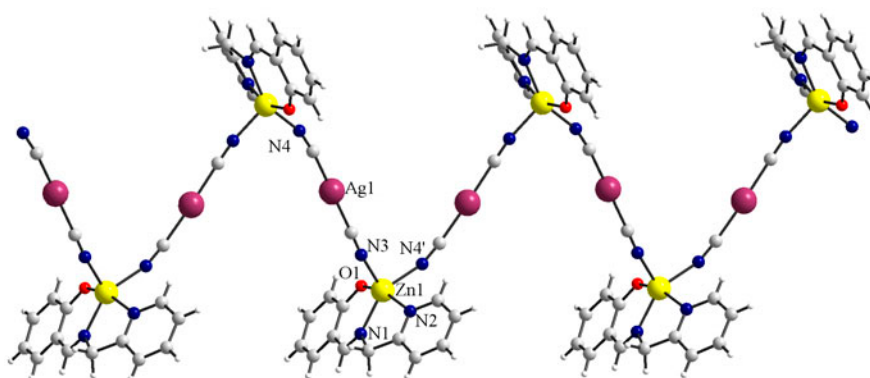Figure 6.   View of the packing diagram in **2** showing the channels along the crystallographic c axis.

Figure 7. Perspective view of 1-D chain in $_1^{\infty}$[Zn(Salampy){μ-Ag(CN)$_2$}] (**3**).

The electronic spectra of **1**–**4** display bands located in the 200–500 nm region. Usually, π–π^* transitions of the organic ligand appear at higher energies, but in dicyanoaurate and dicyanoargentate polymers, strong MLCT (d–π^*) transitions are expected in the same spectral region [10].

3.3. *Luminescence properties*

Silver(I) and gold(I) complexes have attracted much attention in the field of photophysics of metal complexes. The structures (discrete or infinite) constructed through metallophilic interactions are known to be potentially luminescent materials [4(e), 11]. Aurophilic interactions have been involved in several luminescent characteristics of gold(I) complexes,
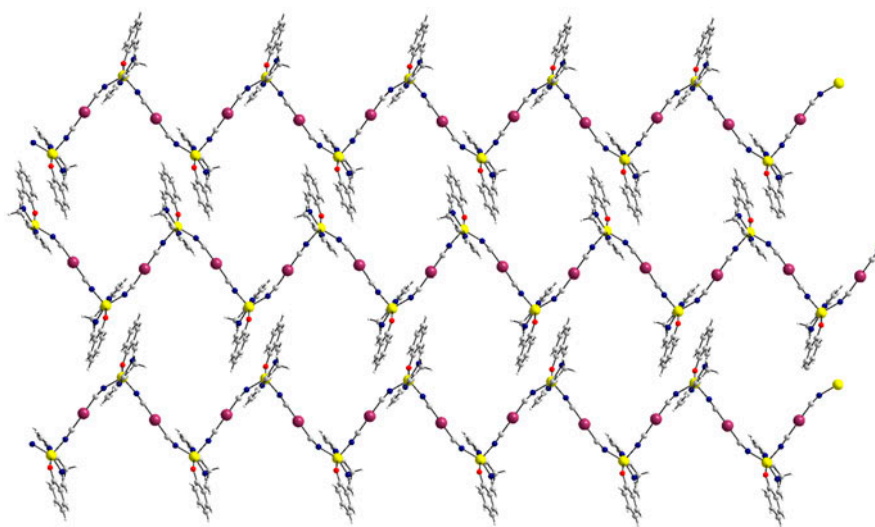

Figure 8. View of the packing diagram in **3** showing a supramolecular layer generated by the π–π interactions.

including emission from dimers [12] and luminescence from $[Au(CN)_2]^-$ in a variety of environments [4(e, f)]. The emission energies of these luminescent compounds are extremely sensitive to the distance between neighboring gold ions [4(e), 13, 14]. Zinc(II) complexes with Schiff-base ligands exhibit interesting luminescence, with emission bands between 390 and 590 nm [2(a–g), 15]. The role of the zinc ion is to make the ligand more rigid upon complexation, reducing the loss of energy by thermal vibrational decay.

Considering all these aspects, the luminescent properties of Schiff-base ligands (in MeOH) and 1–4 (in solid state), at room temperature, have been investigated. The emission spectra of 1–4 resemble the Schiff-base ligands except for the intensity and peak positions, indicating that the fluorescence of 1–4 is given by the ligand emission. For the free Schiff-base, a green emission was observed for 370 nm excitation, with the maximum emission wavelength at 504 nm (for H_2Salen), 475 nm (shoulder at 512 nm) (for HSaldmen), and 472 nm (shoulder at 515 nm) (for HSalampy), respectively.

The emission and the absorption spectra of 1–4 are depicted in figure 9. Upon excitation at 370 nm, all compounds exhibit luminescence with peak maxima at $\lambda_{em} = 464$ nm for 1, $\lambda_{em} = 445$ nm and 555 nm for 2, $\lambda_{em} = 488$ nm for 3, and $\lambda_{em} = 482$ nm for 4. Compared with the emission spectra of the corresponding ligands, the emission spectra of the complexes are slightly shifted as a result of the coordination of zinc(II) centers to the ligand. The incorporation of Zn(II) effectively increases the conformational rigidity of the ligand and reduces the loss of energy via vibration.
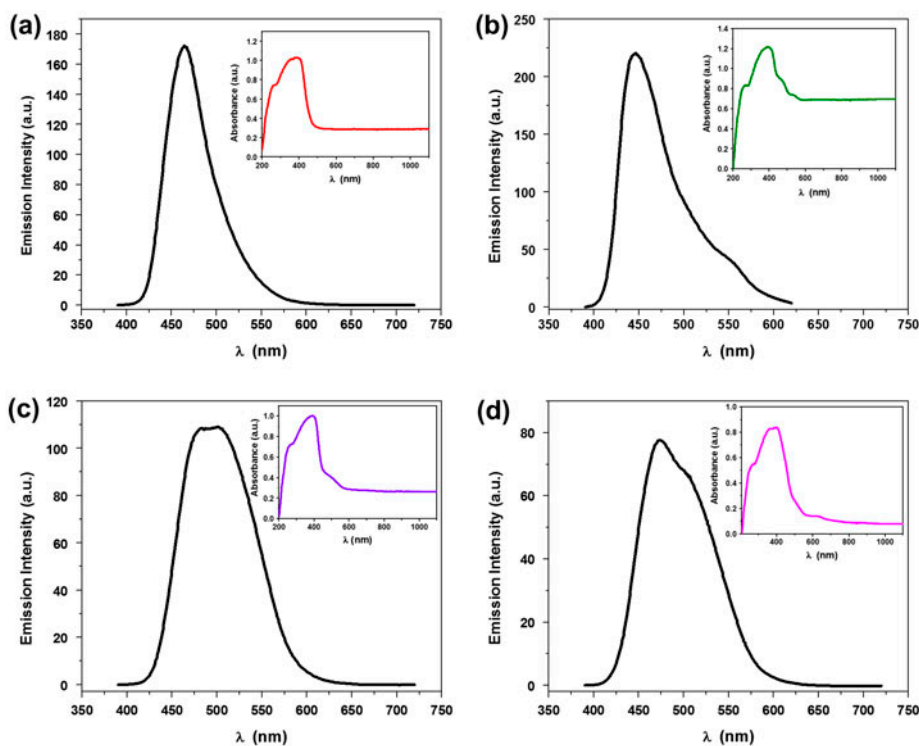

Figure 9.   Solid-state emission spectra of 1 (a), 2 (b), 3 (c), and 4 (d) at room temperature ($\lambda_{exc} = 370$ nm). The inset shows the UV–vis spectra.

The band located in the region 200–500 nm in the absorption spectra of complexes is most probably due to a π–π^* transition of the organic ligand. Due to long distance M$\cdots$M (Ag$\cdots$Ag or Au$\cdots$Au), this type of interaction is not responsible for the emission. In this case, the luminescence is most probably due to intraligand $^1(\pi^*$–$\pi)$ fluorescence.

4. Conclusion

We described the synthesis and characterization of new d^{10} coordination polymers containing Schiff bases and $[M(CN)_2]^-$ [M(I) = Ag(I), Au(I)] ligands. We have illustrated that mononuclear, $[Zn(Saldmen)]^+$, $[Zn(Salampy)]^+$, and homotrinuclear, $[Zn_3(Salen)_2]^{2+}$, complexes can be used as nodes in designing bimetallic coordination polymers. The linear spacers $[M(CN)_2]^-$ ($D_{\infty h}$ linear) favor the formation of 1-D coordination polymers. The structural studies for **1**–**4** show that ligand-unsupported metallophilic interactions exist only in **2** and play an important role in forming supramolecular double chains.

Supplementary material

CCDC reference numbers: 1023950-1023953. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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