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# New $d^{10}$ heterometallic coordination polymers based on compartmental Schiff-base ligands. Synthesis, structure and luminescence

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ABSTRACT

The self-assembly processes between binuclear $[Zn_2L^n]^{2+}$ complex cations and complex anions, $[M(CN)_2]^-$ [M(I) = Ag(I), Au(I)], generate new one-dimensional (1-D) coordination polymers: $^1{}_\infty[\{L^1Zn_2(\mu_3\text{-OH})\}_2(H_2O)\{\mu\text{-}[Ag(CN)_2]\}](ClO_4)_3$ THF 0.5MeOH **1**, $^1{}_\infty[\{L^1Zn_2(\mu_3\text{-OH})\}_2(H_2O)\{\mu\text{-}[Au(CN)_2]\}](ClO_4)_3$ THF $H_2O$ **2**, $^1{}_\infty[\{L^2Zn_2(\mu\text{-OH})\}\{\mu\text{-}[Ag(CN)_2]\}][Ag(CN)_2]$ $H_2O$ **3** ($H_2L^n$ are bicompartmental Schiff-base ligands resulting from condensation reactions between 2,6-diformyl-*p*-cresol with 2-aminomethyl-pyridine, and 2-aminoethyl-pyridine, respectively). The luminescence properties of the new heterometallic complexes have been investigated.

## 1. Introduction

The considerable interest in designing new coordination polymers emerges not only from their potential applications in electronics, luminescence, catalysis, magnetism and molecular recognition [1], but also from their intriguing structural topologies [2–7]. The self-assembly process of metal ions with *exo*-dentate (divergent) ligands is an efficient and widely used strategy for the construction of such polymers (node-and-spacer approach) [8]. A major challenge in this approach is to predict the topology of the polymeric structure, since many factors are involved in the framework formation (the stereochemical preferences of the metal ions, the nature of the ligands, the metal-to-ligand ratio, the reaction temperature, the solvent, and the pH of the solution) [9].

The luminescent metal complexes of $d^{10}$ metal ions [*e.g.* zinc(II), cadmium(II), copper(I), silver(I) and gold(I)] have grown into a very active research area. Due to the flexibility of their stereochemistry, they can coordinate various ligands, leading to systems exhibiting interesting structural features and potential applications in light emitting diodes (LEDs), biomedical analyses, fluorescence imaging and cancer phototherapy [10,11].

The Schiff-bases are widely employed as ligands in coordination chemistry [12,13]. These ligands are readily available, versatile and allow a good control over the stereochemistry of the metallic centers, as well as over the nuclearity of the complexes, by the appropriate selection of the starting materials (carbonyl precursors and primary amines) [14]. All these advantages make Schiff bases very good candidates in the effort to synthesize metal complexes of interest in bioinorganic chemistry, catalysis, encapsulation, transport and separation processes, magnetochemistry [14]. An important class of Schiff base ligands is represented by organic molecules able to accommodate two metal ions (compartmental ligands) [14].

In a series of papers, we have shown that tetranuclear complexes and coordination polymers with interesting topologies can be obtained employing binuclear complexes as nodes and various bridging ligands [*e.g.* 4,4′-bipyridine, bis(4-pyridyl)ethane, bis(4-pyridyl)ethylene] [15]. The formation of the dinuclear nodes in a preliminary step succeeds using compartmental ligands, which hold together two metal ions. Such ligands can be either end-off, side-off, or macrocyclic species, some of them being obtained by reacting 2,6-diformyl-*p*-cresol with different diamines (*e.g.* *N*,*N*-dimethyl-ethylenediamine, 2-aminomethyl-pyridine or 2-aminoethyl-pyridine – Scheme 1).

McGillivray and coworkers have reported an 1-D coordination polymers, which undergoes photodimerization in the solid state, by connecting the dinuclear zinc complexes through bis(4-pyridyl)ethylene [16].

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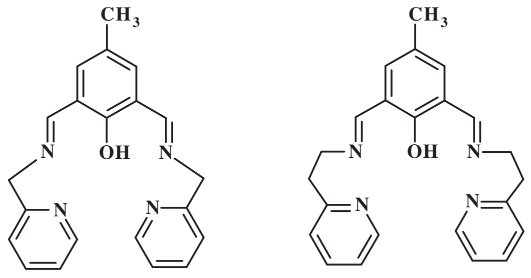

HL$^1$ HL$^2$

**Scheme 1.** Schematic molecular structures of ligands, HL$^1$ and HL$^2$.

In a recent paper, we showed that the self-assembly processes between binuclear [Zn$_2$] complex cation and *exo*-bidentate ligands [*e.g.* 4,4′-bipyridine, bis(4-pyridyl)ethane] generate one-dimensional coordination polymers with interesting luminescence properties [15j].

In this work, we have extended our investigations to other category of spacers namely anionic metal-complexes containing potentially bridging ligands, [M(CN)$_2$]$^-$, M(I) = Ag(I), Au(I). These species carry an additional element which can determine the final crystalline architecture, through the metallophilic interactions, representing also a new luminophoric source.

## 2. Experimental section

Syntheses of ${}^1_\infty$[{L$^1$Zn$_2$(μ$_3$-OH)}$_2$(H$_2$O){μ-[Ag(CN)$_2$]}](ClO$_4$)$_3$·THF·0.5MeOH **1**, ${}^1_\infty$[{L$^1$Zn$_2$(μ$_3$-OH)}$_2$(H$_2$O){μ-[Au(CN)$_2$]}](ClO$_4$)$_3$·THF·H$_2$O **2**, ${}^1_\infty$[{L$^2$Zn$_2$(μ-OH)}{μ-[Ag(CN)$_2$]}][Ag(CN)$_2$]·H$_2$O **3**. All starting materials were of reagent grade and were used without further purification. The binuclear precursors were synthesized *in situ*, by reacting the Schiff bases with zinc perchlorate.

### 2.1. Syntheses of ${}^1_\infty$[{L$^1$Zn$_2$($_3$-OH)}$_2$(H$_2$O){-[Ag(CN)$_2$]}](ClO$_4$)$_3$·THF·0.5MeOH (**1**)

The tetrahydrofuran (THF) solutions containing stoichiometric amounts of 2,6-diformyl-*p*-cresol (0.1 mmol, 10 mL) and 2-aminomethyl-pyridine (0.2 mmol, 5 mL) were mixed and kept under continuous stirring for 30 min at 50 °C. This solution was then reacted with the stoichiometric amounts of LiOH (0.1 mmol, 5 mL H$_2$O) and Zn(ClO$_4$)$_2$·6H$_2$O (0.2 mmol, 10 mL THF) and kept under stirring for 30 min. The yellow single-crystals of the compound **1** were obtained by slow diffusion (in a 20 mm diameter test tube at room temperature), of the THF solution of binuclear compound obtained as above through a methanol layer (2 mL) into an aqueous solution (2 mL) of K[Ag(CN)$_2$] (0.1 mmol), after several days. Yield ca. 75%. Elemental chemical analysis: 37.61% C, 3.42% H, 9.14% N (calc.); 37.70% C, 3.09% H, 9.15% N (found). IR data (KBr, cm$^{-1}$): 3566m, 3394m, 3040w, 2907w, 2174i, 2140w, 1652s, 1553s, 1488m, 1419s, 1327m, 1290m, 1239m, 1092vs, 1024 shoulder, 882w, 826s, 765s, 624s, 557w, 474w.

### 2.2. Syntheses of ${}^1_\infty$[{L$^1$Zn$_2$(μ$_3$-OH)}$_2$(H$_2$O){μ-[Au(CN)$_2$]}](ClO$_4$)$_3$·THF·H$_2$O (**2**)

Compound **2** has been obtained following the same general procedure described for ${}^1_\infty$[{L$^1$Zn$_2$(μ$_3$-OH)}$_2$(H$_2$O){μ-[Ag(CN)$_2$]}](ClO$_4$)$_3$·THF·0.5MeOH (**1**), using K[Au(CN)$_2$] instead of K[Ag(CN)$_2$]. Yield ca. 70%. Elemental chemical analysis: 35.20% C, 3.20% H, 8.55% N (calc.); 35.28% C, 2.90% H, 8.60% N (found). IR data (KBr, cm$^{-1}$): 3510m, 3449m, 2966w, 2901w, 2863w, 2188s, 2145w, 1651vs, 1609s, 1552s, 1489m, 1447w, 1420s, 1332m, 1291m, 1239m, 1108vs, 1069vs, 975w, 873w, 828m, 766s, 624vs, 555w, 471m, 413w.

### 2.3. Syntheses of ${}^1_\infty$[{L$^2$Zn$_2$(μ-OH)}{μ-[Ag(CN)$_2$]}][Ag(CN)$_2$]·H$_2$O (**3**)

Two solutions containing stoichiometric amounts of 2,6-diformyl-*p*-cresol (0.1 mmol, 10 mL of 1:1 methanol:acetonitrile mixture) and 2-aminoethyl-pyridine (0.2 mmol, 5 mL of 1:1 MeOH:ACN mixture) were mixed and kept under continuous stirring for 30 min at 50 °C. The resulting solution was then reacted with the stoichiometric amounts of LiOH (0.1 mmol, 5 mL H$_2$O) and Zn(ClO$_4$)$_2$·6H$_2$O (0.2 mmol, 10 mL MeOH:ACN) and kept under stirring for 30 min. An aqueous solution (10 mL) containing the K[Ag(CN)$_2$] (0.1 mmol) was added to the solution containing the dinuclear precursor [L$^2$Zn$_2$(μ-OH)](ClO$_4$)$_2$. The slow evaporation of the mixture at room temperature, in a dark recipient, led after several days to yellow crystals. Yield ca. 60%. Elemental chemical analysis: 37.84% C, 3.06% H, 13.07% N (calc.); 38.05% C, 2.90% H, 13.12% N (found). IR data (KBr, cm$^{-1}$): 3498s, 3369m, 2921w,

**Table 1**
Crystallographic data, details of data collection and structure refinement parameters for compounds **1**–**3**.

| Compound | 1 | 2 | 3 |
|---|---|---|---|
| Chemical formula | $C_{48.50}H_{52}AgCl_3N_{10}O_{18.50}Zn_4$ | $C_{48}H_{52}AuCl_3N_{10}O_{19}Zn_4$ | $C_{27}H_{26}Ag_2N_8O_3Zn_2$ |
| $M$ (g mol$^{-1}$) | 1546.67 | 1637.76 | 857.02 |
| Temperature, (K) | 293 | 293 | 293 |
| Wavelength, (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | *monoclinic* | *monoclinic* | *triclinic* |
| Space group | *P21/a* | *P21/a* | *P-1* |
| $a$ (Å) | 14.4552(6) | 14.3505(4) | 11.1217(10) |
| $b$ (Å) | 16.8840(8) | 16.8848(4) | 11.9903(9) |
| $c$ (Å) | 25.0547(10) | 25.1038(11) | 13.7892(12) |
| $\alpha$ (°) | 90 | 90 | 74.510(6) |
| $\beta$ (°) | 103.119(3) | 103.418(3) | 76.774(7) |
| $\gamma$ (°) | 90 | 90 | 62.707(6) |
| $V$ (Å$^3$) | 5955.3(4) | 5916.7(3) | 1562.6(20) |
| $Z$ | 4 | 4 | 2 |
| $D_c$ (g cm$^{-3}$) | 1.721 | 1.834 | 1.817 |
| $\mu$ (mm$^{-1}$) | 2.124 | 4.284 | 2.793 |
| F(0 0 0) | 3100 | 3232 | 840 |
| Goodness-of-fit on $F^2$ | 1.065 | 1.065 | 1.095 |
| Final $R_1$, w$R_2$ [I > 2$\sigma$($I$)] | 0.0798, 0.1855 | 0.0650, 0.1576 | 0.0798, 0.2114 |
| $R_1$, w$R_2$ (all data) | 0.1217, 0.2036 | 0.0891, 0.1708 | 0.0926, 0.2183 |
| Largest diff peak and hole (e Å$^{-3}$) | 0.816, −0.783 | 2.198, −2.800 | 1.185, −1.132 |