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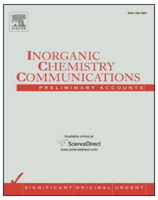

Short communication

A novel 1-D coordination polymer constructed from disilver-1,3,4-oxadiazole nodes and perchlorato bridges

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ABSTRACT

The reaction of silver perchlorate with 2-phenyl-5-(*p*-tolyl)-1,3,4-oxadiazole (**L**) affords a 1-D coordination polymer, $[Ag_3\mathbf{L}_4(ClO_4)_3]$ (**1**). Two silver ions are bridged by two **L** ligands, through the nitrogen atoms of the oxadiazole ring, resulting in binuclear units. The coordination polymer is constructed from binuclear nodes, $\{Ag_2\mathbf{L}_2\}$, connected by perchlorato bridges. The investigation of the optical properties of compound **1** indicates a slight change in the emission profile compared to the organic ligand, showing blue luminescence upon excitation at $\lambda = 300$ nm.

2,5-Diaryl-1,3,4-oxadiazoles represent a class of organic compounds with interesting potential applications as electron-transporting and luminescent materials in the fabrication of the Organic Light Emitting Diodes (OLEDs) [1].The nitrogen atoms of the heterocyclic core and the angular shape of the 2,5-diaryl-1,3,4-oxadiazoles are appealing tectons for designing coordination polymers with original network topologies [2]. Generally, the coordinating abilities of these molecules are reinforced when better donor atoms are incorporated or attached to the aryl moieties (Fig. 1a). In such cases, the nitrogen atoms of the oxadiazole ring are less involved in the interaction with the metal ions. For example, when two 4-pyridyl groups are attached to the oxadiazole ring, most of the extended networks result from the interaction of the metal ions with the pyridyl nitrogen atoms. Several nice examples were thus constructed from 2,5-*bis*(4-pyridyl)-1,3,4-oxadiazole and Cu(I) [3], Mn(II), Fe(II) and Co(II) [4]. Moreover, the employment of 2,5-*bis*(2-pyridyl)-1,3,4-oxadiazole provides complexes of type $[Fe^{II}(L)_2(NCS)_2]$, where one of the nitrogen atoms of the oxadiazole ring is involved in the coordination [5]. 1-D and 2-D coordination polymers of Ag(I) have been reported as well [6], using pyridyl-substituted-1,3,4-oxadiazoles, or ligands such as depicted in Fig. 1a, which involve none, one or both oxadiazole nitrogens as donor atoms. Alternatively, 1,3,4-oxadiazole-based coordination polymers could be prepared by addition of co-ligands such as dicarboxylate ions [7]. In these cases, the heterocyclic nitrogen atoms are not involved in the coordination. To the best of our knowledge, no coordination polymers based on 2,5-diaryl-1,3,4-oxadiazoles containing no other donor atoms/functional groups, or formed without addition of any co-ligands, have been reported so far.

In this context, we report herein the synthesis and characterization of a new Ag(I)-coordination polymer which was obtained from 2-phenyl-5-(*p*-tolyl)-1,3,4-oxadiazole (**L**) (Fig. 1b) and $AgClO_4$. The ligand was synthesized following a previously described procedure and the spectroscopic data correspond to those reported in literature [8]. The 1-D coordination polymer with the empirical formula $[Ag_3\mathbf{L}_4(ClO_4)_3]$ (**1**) has been assembled from the reaction of **L** with $AgClO_4$ in MeOH, followed by slow evaporation of the solvent [9].

The infrared spectrum of compound **1** shows the characteristic bands of the organic ligand, as well as those of the perchlorate anion. It is interesting to note that the intense ν_2 band (antisymmetric stretch of the perchlorate anion) splits into 2 components (1096 and 1031 cm^{-1}), indicating that the symmetry of the anion is lower than T_d (free ion) and, consequently, it acts as a ligand.

The crystal structure of **1** has been solved [10]. There are three crystallographically non-equivalent silver atoms. Two silver atoms, Ag2 and Ag3, are simultaneously bridged by two ligand molecules, resulting in a binuclear unit, with silver-nitrogen bond lengths varying between 2.229(5) and 2.292(5) Å (Fig. 2a).The distance between the two silver ions is $Ag2\cdots Ag3 = 3.231$ Å. This distance is lower than the sum of the van der Waals radii of two silver ions (3.44 Å) suggesting the occurrence of weak argentophilic interactions [11]. Another binuclear unit is formed by two Ag1 atoms related by symmetry (Ag1, Ag1′; ′ = 2-x, 1-y, -z.), which are bridged again by two ligand molecules (Fig. 2b). Each Ag1 ion is also coordinated by a monodenate ligand. The Ag1–N1 distance, 2.422(6) Å, is longer than the distances between the

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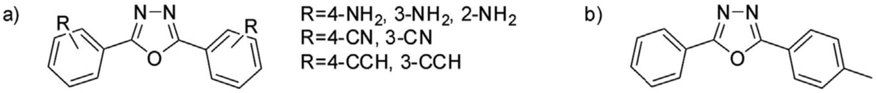

Fig. 1. Examples of functionalised 2,5-diaryl-1,3,4-oxadiazoles used as ligands for Ag(I)-coordination polymers (a), and the ligand used in this work (b).

silver ions and the nitrogen atoms arising from the bridging **L** ligands, 2.306(5) and 2.289(5) Å. The Ag1⋯Ag1′ distance (3.388 Å) is slightly longer than the one between Ag2 and Ag3.

The perchlorate ions act as bridging and terminal ligands. Two {Ag2Ag3} units are connected by two perchlorato bridges, forming a tetranuclear fragment (Fig. 3a). Each silver ion has a coordination number of four (two nitrogen atoms from the ligands and two oxygen atoms from the perchlorate bridging and terminal ligands), with a distorted tetrahedral geometry (Fig. 3a). The silver–oxygen distances are longer than the silver-nitrogen ones, ranging between 2.470(7) and 2.669(9) Å. The {Ag1Ag1'} units are connected to a {Ag2Ag3} unit by one perchlorato bridge (Fig. 3b). The Ag1 ions also display a distorted tetrahedral geometry, being coordinated by three nitrogen atoms arising from the organic ligands and one oxygen atom from the perchlorate bridge. The tetranuclear $\{Ag2Ag3\}_2$ and the binuclear, {Ag1Ag1′}, units, are alternatively connected by single perchlorato bridges, resulting in infinite chains (Fig. 4). The dihedral angles between the mean planes of the five- and six-membered rings of the ligands vary between 2.0 and 7.0°.

The analysis of the packing diagram reveals the occurrence of π–π stacking interactions established between the phenyl rings belonging to the oxadiazole ligands from adjacent chains (3.31–3.54 Å), resulting in supramolecular layers paralleling to the crystallographic *ab* plane (Fig. 5). Selected bond distances and angles for compound **1** are collected in Table 1.

The solid-state excitation and emission properties of ligand and compound **1** were also investigated and the spectra are displayed in Fig. 6. The excitation spectra display wide bands with maxima between 300 and 335 nm, which can be attributed to π–π* transitions of the oxadiazole moiety [12]. The emission spectrum of the ligand indicates two maxima at $\lambda_e = 364$ nm and $\lambda_{em} = 382$ nm. In the case of the complex **1** the emission spectrum slightly changes upon excitation at $\lambda_{ex} = 300$ nm, by exhibiting a maximum at $\lambda_{em} = 372$ nm and a small shoulder around 350 nm. The coordination to the silver ions re-

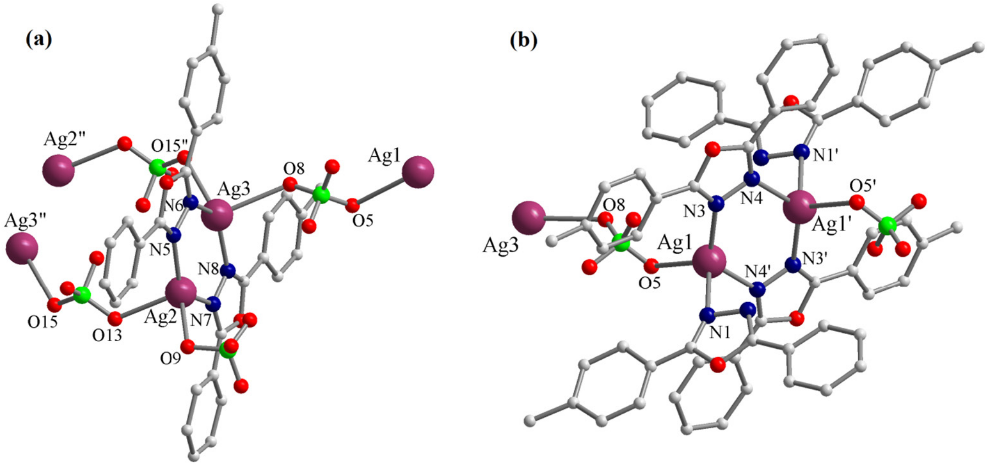

Fig. 2. (a) Binuclear units resulting from Ag2, Ag3 and organic ligands; (b) binuclear units resulting from Ag1 ions and bridging and terminal **L** ligands. Symmetry operations: ′ = 2-x, 1-y, -z; ″ = 1-x, −y, −z.

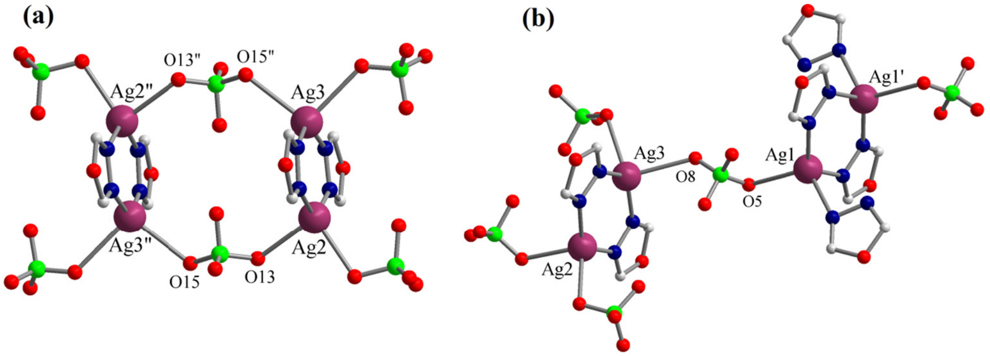

Fig. 3. (a) Tetranuclear fragments resulted from {Ag2Ag3} units and two perchlorato bridges; (b) connection between the tetranuclear, $\{Ag2Ag3\}_2$, and the binuclear {Ag1Ag1′} fragments. For the sake of clarity, the substituents attached to the oxadiazole ring have been removed. Symmetry codes: ′ = 2-x, 1-y, -z; ″ = 1-x, -y, -z.

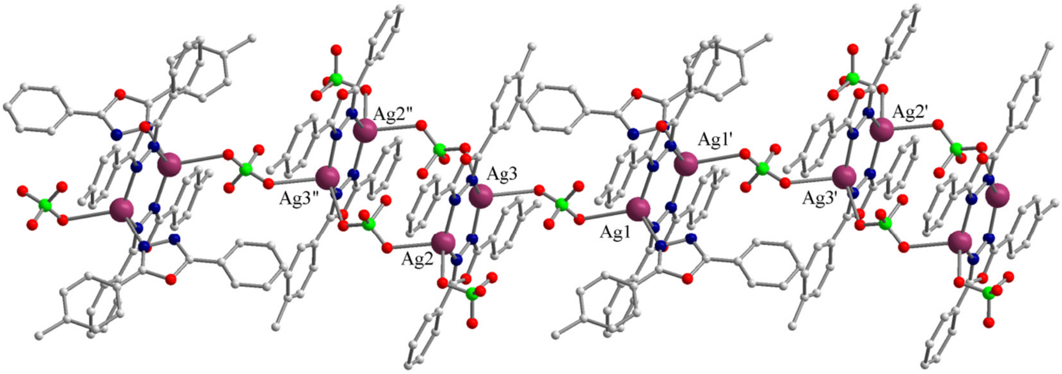

Fig. 4. Perspective view of the coordination polymer **1**.Symmetry codes: = 2-x, 1-y, -z; ″ = 1-x, -y, -z.

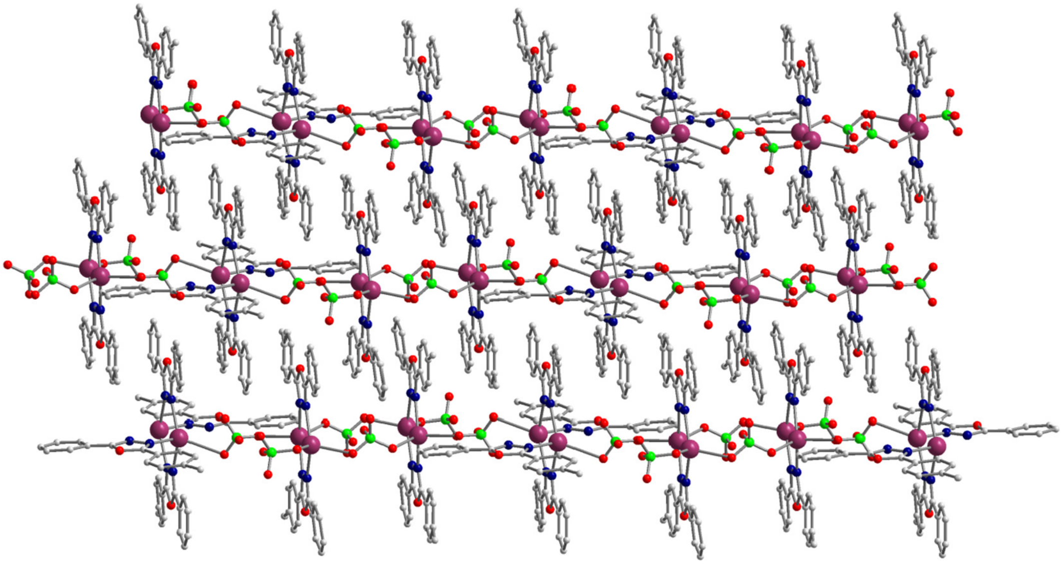

Fig. 5. Detail of the packing diagram showing a supramolecular layer.

duces significantly the intensity of the luminescence of the organic ligand.

In conclusion, we have illustrated the ability of the oxadiazole-based ligands, bearing non-coordinating substituents, to generate binuclear building-blocks for designing new coordination polymers. The binuclear fragments resulted from two silver(I) ions and two oxadiazole ligands can act as nodes for the construction of other coordination polymers with interesting topologies, by selecting various neutral or anionic spacers. Further work is in progress in our laboratories on the synthesis of new suitable oxadiazole-based ligands that are able, in conjunction with metal-ions, to provide coordination polymers with various properties (magnetism, luminescence, catalysis).

Table 1
Selected geometric parameters of coordination surroundings of the metal ions: bond lengths (Å) and angles (°) for compound **1.**

Metal ion	Ag1	Ag2	Ag3
Bond length (Å)	Ag1—N1 = 2.422(6)	Ag2—N5 = 2.292(5)	Ag3—N6 = 2.229(5)
	Ag1—N3 = 2.306(5)	Ag2—N7 = 2.283(5)	Ag3—N8 = 2.237(5)
	Ag1—N4′ = 2.289(5)	Ag2—O9 = 2.470(7)	Ag3—O8 = 2.669(9)
	Ag1—O5 = 2.793(17)	Ag2—O13 = 2.548(8)	Ag3—O15″ = 2.611(8)
Angles (°)	N4′—Ag1—N3 = 128.62(18)	N7—Ag2—N5 = 130.6(2)	N6—Ag3—N8 = 133.4(2)
	N4′—Ag1—N1 = 98.83(18)	N7—Ag2—O9 = 112.7(2)	N6—Ag3—O8 = 105.18(28)
	N3—Ag1—N1 = 100.19(19)	N5—Ag2—O9 = 107.4(2)	N6—Ag3—O16″ = 99.36(23)
	N4′—Ag1—O5 = 87.62(25)	N7—Ag2—O13 = 94.2(2)	N8—Ag3—O8 = 101.26(23)
	N3—Ag1—O5 = 123.31(31)	N5—Ag2—O13 = 112.2(2)	N8—Ag3—O16″ = 114.7(2)
	N1—Ag1—O5 = 117.22(37)	O9—Ag2—O13 = 92.1(3)	O8—Ag3—O16″ = 96.93(28)
Symmetry code	′ = 2-x, 1-y, -z		″ = 1-x, -y, -z

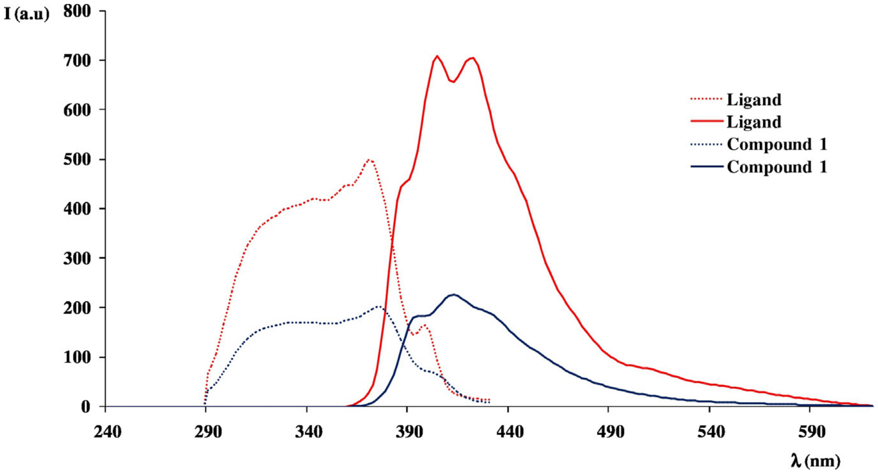

Fig. 6. Excitation (dotted lines) and emission (plain lines) spectra of the ligand and compound **1** performed in solid state.

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Appendix A. Supplementary material

CCDC 1502286 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

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[9] Preparation of **1**: A solution of ligand **L** (0.17 mmol, 40 mg) in MeOH (15 mL) was mixed with a solution of silver perchlorate (0.17 mmol, 36.2 mg) dissolved in MeOH (5 mL). Slow evaporation of the solvent yielded the crystalline compound (40 mg). FTIR data (KBr, cm^{-1}): 3081(w), 1606(m), 1581(s), 1551(s), 1496(m), 1190(w), 1096(vs), 1031(vs), 818(w), 781(w), 724(s), 688(w), 619(m).

[10] X-ray diffraction measurements were performed on a STOE IPDS II diffractometer, operating with Mo-Kα ($\lambda = 0.71073$ Å) X-ray tube with graphite monochromator. The structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package. Crystal data: Compound **1**: $C_{60}H_{48}Ag_3Cl_3N_8O_{16}$, $M = 1567.02$ g·mol^{-1}, crystal system: *monoclinic*, space group: $P2_1/n$, $a = 10.1789(4)$ Å, $b = 20.6964(8)$ Å, $c = 29.0726(16)$ Å, $\alpha = 90.00$, $\beta = 96.129(4)$, $\gamma = 90.00$, $V = 6089.6(5)$ Å^3, $Z = 4$, $D = 1.709$ g.cm^{-3}, $\mu = 1.163$ mm^{-1}, $F(000) = 3136$, $GOF = 0.867$, final $R_1 = 0.0584$, wR_2 [I > 2σ(I)] = 0.1526, R_1 (all data) = 0.1345, wR_2 (all data) = 0.1832.

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