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Cyanosilylation of Aldehydes Catalyzed by Ag(I)- and Cu(II)-Arylhydrazone Coordination Polymers in Conventional and in Ionic Liquid Media

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Abstract: The novel Ag(I) and Cu(II) coordination polymers $[Ag(\mu_3\text{-}1\kappa O;2\text{:}3\kappa O';4\kappa N\text{-HL})]_n \cdot n/2H_2O$ (**1**) and $[Cu(en)_2(\mu\text{-}1\kappa O;2\kappa N\text{-L})]_n \cdot nH_2O$ (**2**) $[HL^- = 2\text{-}(2\text{-}(1\text{-cyano-2-oxopropylidene})hydrazinyl)benzene sulfonate]$ were synthesized and characterized by IR and ESI-MS spectroscopies, elemental and single crystal X-ray diffraction analyses. Compounds **1** and **2** as well as the already known complex salt $[Cu(H_2O)_2(en)_2](HL)_2$ (**3**) have been tested as homogenous catalysts for the cyanosilylation reaction of different aldehydes with trimethylsilyl cyanide, to provide cyanohydrin trimethylsilyl ethers. Coordination polymer **2** was found to be the most efficient one, with yields ranging from 76 to 88% in methanol, which increases up to 99% by addition of the ionic liquid [DHTMG][*L*-Lactate].

Keywords: Ag(I) and Cu(II) coordination polymers; arylhydrazone; catalysis; ionic liquids; cyanosilylation reaction

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1. Introduction

Cyanohydrins are industrially valuable substrates and important intermediates for the preparation of α-aminonitriles, α-hydroxyketones, α-hydroxyacids, β-hydroxyamines, and β-aminoalcohols, among others [1]. The main synthetic route for the synthesis of cyanohydrins is the catalytic addition of the cyano group to a carbonyl compounds. Trimethylsilyl cyanide (TMSCN) is a frequently explored substrate for catalytic cyanation reaction since it is easy to handle, it has a high atom economy without providing side reactions, and its Si–C bond has low dissociation energy (Scheme 1) [2–7], therefore, contrasting with the toxic nature of other cyanide sources such as HCN, NaCN, KCN, etc. Numerous catalysts, including Lewis acids [8–10], Lewis bases [11–13], oxazaborolidinium ion [14,15], amino-thiourea [16,17], organic-inorganic salts [18–22], N-heterocyclic carbenes [23,24], nonionic bases [25,26], Ti,Al-phosphine oxide bifunctional species with carbohydrate or binaphthol scaffolds [27–29], Ti,Al-N-oxide bifunctional catalysts with proline, pyrrolidine and 1,2-diamino ligands [30–32], V-, Mn-, Al-, and Ti-salen complexes [33–36], chiral Ti-α,α,α,α-1,3-dioxolane-tetraaryl-4,5-dimethanols [37,38], Cu(II) and Co(II/III) hydrazone complexes [39,40] and also metal organic frameworks (MOFs) [41–44], have been developed for this transformation. According to the proposed reaction mechanism [1], the coordination or

noncovalent bond acceptor behavior of the oxygen atom of an aldehyde enhances the electrophilic character of the carbon atom at C=O, which makes it more susceptible to a nucleophilic attack by the cyano group. Thus, the reaction rate and yield of cyanohydrin trimethylsilyl ethers are strongly dependent on the nature of metal center and the coordinated ligand in the metal complex catalyzed cyanation reaction [1].
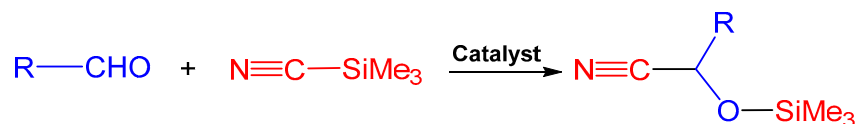

Scheme 1. Cyanosilylation of aldehydes.

MOFs or coordination polymers are attractive not only as storage, transporter, magnetic and luminescence materials [45–48], but also as catalysts for various catalytic transformations, such as alkane/alcohol oxidation [49,50], C–C bond formation [40,44], etc., from the viewpoint of green chemistry. The design and synthesis of coordination polymer catalysts, in particular being inexpensive, highly efficient and selective with a wide range of substrates, remains a challenging goal in cyanosilylation reaction. Having this objective in mind, we intend to report the synthesis of new copper(II) and Ag(I) coordination polymers bearing an arylhydrazone ligand and their application in cyanosilylation reaction of different aldehydes with trimethylsilyl cyanide.

Moreover, ionic liquids (ILs) have wide applications in catalysis, namely as green solvents or reaction promoters [51], being able, in some cases, to enhance the reaction rate, improve the yield and selectivity in organic transformations under mild conditions. To date, a few ILs have been reported in the cyanosilylation of aldehydes [52,53]. Thus, another aim of this work is to use a cooperative action of ILs and coordination polymers in cyanosilylation reaction, a type of approach that we have successfully applied in the oxidation of alkanes [54,55] and oxidation of alcohols [56].

2. Results and Discussion

2.1. Synthesis and Characterization of **1**–**3**

Sodium 2-(2-(1-cyano-2-oxopropylidene)hydrazinyl)benzenesulfonate (NaHL) and $[Cu(H_2O)_2(en)_2]$ $(HL)_2$ (**3**) were synthesized as previously reported [57]. Reaction of $AgNO_3$ or $Cu(NO_3)_2 \cdot 2.5H_2O$ with NaHL in methanol in the presence of nitric acid or ethylenediamine (en) led to the novel coordination polymer $[Ag(\mu_3\text{-}1\kappa O;2:3\kappa O';4\kappa N\text{-}HL)]_n \cdot n/2H_2O$ (**1**) or $[Cu(en)_2(\mu\text{-}1\kappa O;2\kappa N\text{-}L)]_n \cdot nH_2O$ (**2**), respectively (Scheme 2). Both polymers were characterized by IR spectroscopy, ESI-MS, elemental analysis, and single crystal X-ray diffraction.
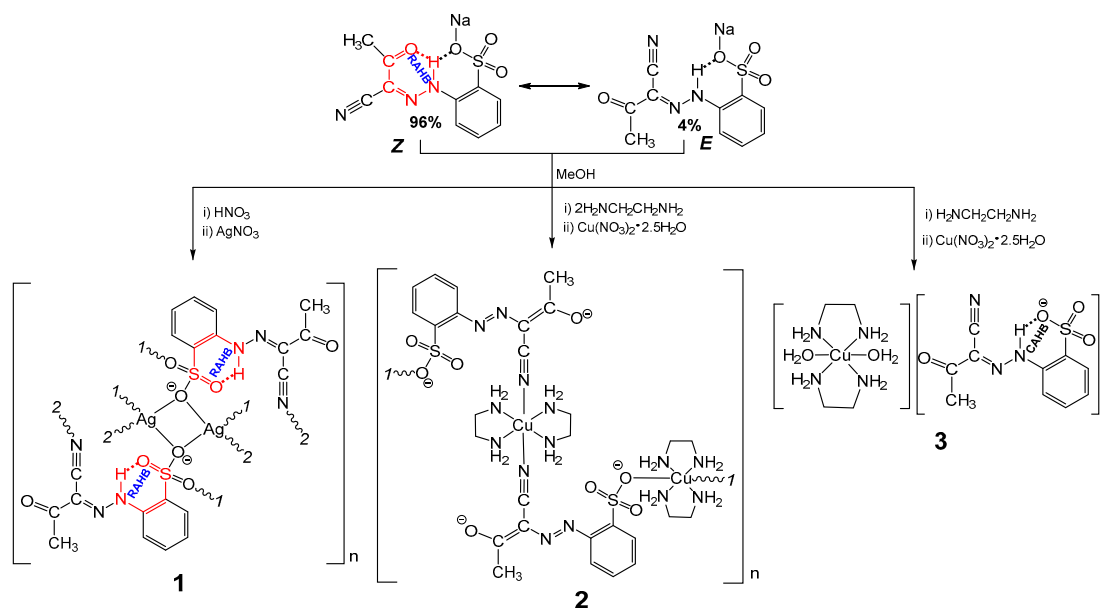
Scheme 2. Synthesis of **1**–**3**. Hydrate water molecules were omitted in **1** and **2**.

The IR spectra of **1** and **2** (see experimental section) show the expected N≡C, C=O and C=N vibrations which generally occur at wavenumbers different from those of the proligand (i.e., 2206, 1645, and average 1570 cm^{-1}, respectively [57]), therefore attesting the involvement of the compound in coordination to the metals. The nitrile group stretching frequency ν(C≡N) in **1** is 8 cm^{-1} above that measured for NaHL which is consistent with its coordination. In **2**, that frequency is 2 cm^{-1} below. Concerning the ketone vibrations, ν(C=O), they occur 16 (for **1**) and 30 (for **2**) cm^{-1} above those of the NaHL reference value, whereas ν(C=N) assume values 13 (for **1**) and 26 (for **2**) cm^{-1} above the average one for NaHL. Fragmentation peaks in MS-ESI of the compounds are related as follows: 749.20 [*Mr*–H$_2$O+H]$^+$ (for **1**) and 450.05 [*Mr*–H$_2$O+H]$^+$ (for **2**), accounting for the existence of the dinuclear and mononuclear species in solution, respectively. Elemental analyses and X-ray crystallography experiments are also in accordance with the proposed formulations.

The asymmetric unit of **1** contains one Ag^{I} cation, a HL$^-$ anion and a crystallization water molecule. Upon symmetry expansion, a 2D polymer is revealed with every silver cation adopting a distorted trigonal pyramidal geometry (τ_4 = 0.48) [58] filled by one N$_{cyano}$- and three O$_{sulfonate}$-atoms (Figure 1). Each organic ligand behaves as a bridging three donor chelators. Polymer **1** contains four membered {AgO}$_2$ fragments which side-share with two eight-membered {AgO$_2$S}$_2$ metallacycles thus giving rise to infinite chains connected by the organic ligands (Figures S1 and S2). The water molecules are trapped in these metal-organic sheets, each one donating to the O$_{keto}$ atoms of two hydrazones (Figure S3 and Table S1).
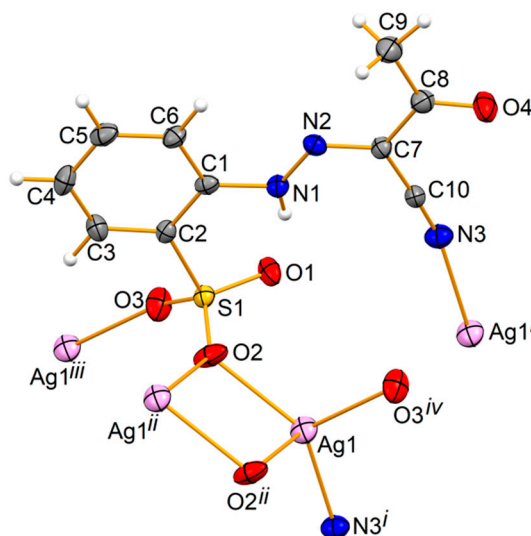
Figure 1. Ellipsoid plot of a fragment of polymer **1**, drawn at 30% probability level and with atom numbering scheme. Crystallization water molecule is omitted for clarity. Symmetry operations to generate equivalent atoms: (*i*) $1 - x, 2 - y, 1 - z$; (*ii*) $1.5 - x, 1.5 - y, 1 - z$; (*iii*) $x, -1 + y, z$; (*iv*) $x, 1 + y, z$.

The asymmetric unit of **2** comprises a hydrazine ligand bridging two copper cations that stand in special positions, half a chelating ethylenediamine molecule and a crystallization water molecule. Symmetry expansion reveals a 1D polymer (Figure 2) featuring wave-like chains (base vectors [101]) with the copper cations alternating N_6 and N_4O_2 coordination environments every 7.6836(4) Å (see Figure S4 and Table 1). The octahedral geometries of the two metals are roughly similar in terms of volume and of quadratic elongation (13.319 and 13.935 Å^3; 1.021 and 1.046, in this order), but differ in the angle variances (10.77 for **1** against 36.53 $^{\circ 2}$ for **2**) [59]. The water molecules in **2** are trapped between the metal-organic chains (Figure S4 and Table S1), each one donating to an O_{keto} and accepting from a N_{amine} in a chain, and interacting with an $O_{sulfonate}$ atom in a vicinal one.

The NN and $C_{keto} - C_{hydraz}$ distances (Table 1) in the compounds considered in this work vary in the order **3 > 1 > 2** and approach single bond characters, while the $C - N_{hydraz}$ and $C - O_{keto}$ lengths follow the reverse sequence **2 > 1 > 3** therefore pending to double bond types. Such observations suggest electronic delocalization along the $OC_{keto}C_{hidraz}NN$ skeleton of the hydrazo ligand of polymer **2**. This is further supported by the presence of the NH groups in polymer **1** and in complex salt **3,** which are involved in RAHB interactions with $O_{sulfonate}$ atoms (see also Table S1). The dianionic nature of this ligand in **2** is thus allocated to their O atoms. Since the $C \equiv N$ groups in **1** and **2** are engaged in coordination, their lengths slightly increased as compared to that found in **3**. The $M - N_{amine}$ distances in **2** and **3** are comparable (Table 1) indicating that in the former this parameter was not affected by the coordination of the L^{2-} ligand. In **2** the axial $M - N_{cyano}$ (eventually, also the $M - O_{sulfonate}$) length considerably exceeds the equatorial $M - N_{amine}$, conceivably due to Jahn-Teller effect. Despite the planarity of the hydrazone ligand in **1** and **2**, the $C \equiv N - M$ angle in the latter is considerably lower than that in the former (126.5(6) against 165.2(7)°, see Table 1). As it was found in the complex salt **3**, polymer **1** is stabilized by the intramolecular $N - H \cdots O_{sulfonate}$ resonance assisted hydrogen bond (RAHB) system. The $N - H \cdots O$ angle of 150(11)° is significantly higher than the average $O - H \cdots O$ value of 149° found in β-diketones involved in similar intra-molecular interactions [60].
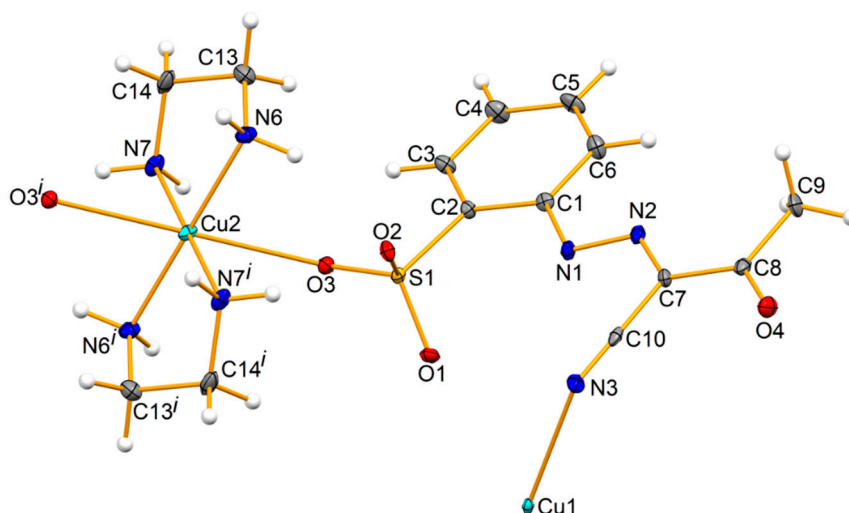
Figure 2. Ellipsoid plot of a fragment of polymer **2**, drawn at 30% probability level and with atom numbering scheme. Crystallization water molecule is omitted for clarity. Symmetry operation to generate equivalent atoms: (*i*) −1 + x,y,−1 + z.

Table 1. Selected bond distances (Å) and angles (°) for polymers **1** and **2**, and for complex salt **3** [57].

	1	2	3
Involving the hydrazone skeleton			
NN	1.294(9)	1.277(10)	1.312(3)
C−N$_{hydraz}$	1.310(10)	1.359(11)	1.303(3)
C$_{keto}$−C$_{hydraz}$	1.449(11)	1.432(12)	1.479(3)
C$_{keto}$−O	1.237(10)	1.246(11)	1.218(4)
C≡N	1.142(10)	1.148(12)	1.139(4)
Involving the metal centre			
M−N$_{cyano}$	2.249(7)	2.458(7)	-
M−N$_{amine}$	-	1.994(7) to 2.027(7)	2.002(2) 2.020(2)
M−O$_{sulfonate}$	2.364(6) 2.402(6) 2.580(6)	2.635(3)	-
C≡N−M	165.2(7)	126.5(6)	-
*Intra*molecular M⋯M	3.871(1) {Ag$_2$O$_2$} 5.861(1) {Ag$_2$O$_4$S$_2$}	7.6836(4)	-
*Inter*molecular M⋯M	>10	6.0884(4)	6.9798(4)

2.2. Catalytic Activity of **1**–**3** in Cyanosilylation Reaction

Polymers **1** and **2**, mononuclear complex **3** and NaHL have been tested as homogeneous catalysts in cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide (model reaction) in different organic solvents (tetrahydrofurane, dichloromethane, or methanol), and at room temperature

(Scheme 1, Table 2). In all the experiments, higher yields are observed in MeOH (entries 1–12, Table 2). Polymer **1** can be considered as inactive towards the reaction under study in view of the obtained yields (entries 1–3, Table 2) being identical to those attained in the absence of any metal catalyst (entries 16–18, Table 2). The catalytic activities of polymer **2** and the complex salt **3** are also comparable (compare entries 4–6 with 7–9 in Table 2) suggesting disaggregation of **2** in solution giving rise to **3**. Polymer **2** was chosen as the catalyst (it provides 79.9% product yield, slightly above that of **3**, 75.3%) and methanol as the solvent for the following studies (Table 3). Reaction of benzaldehyde with TMSCN provides low product yield in the presence of a metal salt, $AgNO_3$ or $Cu(NO_3)_2 \cdot 2.5H_2O$ (maximum yield of 33%), and without metal catalyst (maximum yield of 25%) (entries 13–18, Table 2). With catalyst **2**, a high yield of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile is already obtained (79.0%) after 8 h, which did not increase considerably for longer times (entries 1–6, Table 3). The amount of this catalyst was varied from 1 to 9 mol %, and no considerable yield increase was observed for a catalyst load above 5% (entries 7–11, Table 3). The temperature (in the 15–55 °C range) had not a marked effect on the product yield (entries 12–15, Table 3).

Table 2. Catalyst and solvent screening for the cyanosilylation of benzaldehyde [a].

Entry	Catalyst	Solvent	Yield (%) [b]
1		THF	15.1
2	**1**	CH_2Cl_2	15.9
3		MeOH	26.8
4		THF	26.1
5	**2**	CH_2Cl_2	28.7
6		MeOH	79.9
7		THF	25.9
8	**3**	CH_2Cl_2	28.3
9		MeOH	75.3
10		THF	22.0
11	NaHL	CH_2Cl_2	25.2
12		MeOH	28.3
13	$AgNO_3$	MeOH	30.0
14	$Cu(NO_3)_2 \cdot 2.5H_2O$	MeOH	32.9
15 [c]	-	-	20.0
16 [c]	-	THF	14.0
17 [c]	-	CH_2Cl_2	14.4
18 [c]	-	MeOH	24.7

[a] Reaction conditions: 5 mol % catalyst, 2 mL solvent, 0.12 mmol TMSCN and 0.10 mmol aldehyde, in air at room temperature, 24 h reaction time. [b] Determined by ^{1}H NMR analysis of crude products. [c] From Reference [39].
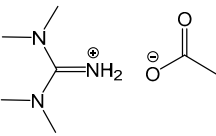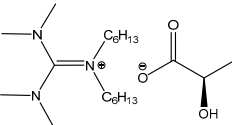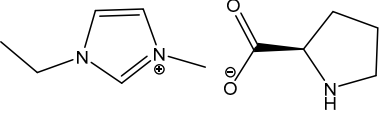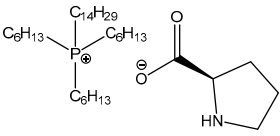
Table 3. Optimization of the parameters of the cyanosilylation reaction of benzaldehyde and TMSCN with catalyst **2** [a].

Entry	Time (h)	Amount (mol %) of Catalyst	T (°C)	Yield [b] (%)
1	1	5	25	42.6
2	4	5	25	65.4
3	6	5	25	73.5
4	8	5	25	79.0
5	12	5	25	78.9
6	24	5	25	79.9
7	8	1	25	44.9
8	8	3	25	72.9
9	8	5	25	79.0
10	8	7	25	78.9
11	8	9	25	79.0
12	8	5	15	70.3
13	8	5	35	79.2
14	8	5	45	80.8
15	8	5	55	82.5

[a] Reaction conditions: MeOH (2 mL), TMSCN (0.6 mmol) and benzaldehyde (0.4 mmol), in air. [b] Determined by ^{1}H NMR analysis of crude products (see the Experimental part).

Among the common organic solvents that we tested, methanol is the best one for this system. However, this solvent is considerably toxic. In order to use a greener solvent, we applied several room temperature ionic liquids (Table 4). In all experiments, the reaction proceeded smoothly to produce 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile in a moderate yield (68.7–75.2%) under catalyst-free conditions (entries 1, 6, 11, and 16), which increases (75.1–82.2%) in the presence of **2** (entries 2, 7, 12, and 17). The use, as reaction medium, of a mixture of IL with MeOH afforded the product in a higher yield in comparison to the IL alone (Table 4). In general, ILs with guanidinium cations shows a higher catalytic performance than imidazolinium or phosphonium cations (Table 4). The ionic liquid [DHTMG][*L*-Lactate] afforded the product in the highest yield (92.6% yield; Table 4, entry 9).

Table 4. Cyanosilylation of benzaldehyde with TMSCN in the absence or presence of catalyst **2** in IL or IL + MeOH media [a].

Entry	Ionic Liquid	IL or IL:MeOH (*v/v*)	Yield,% [b]
1 [c]		[TMGH][OAc]	70.8
2		[TMGH][OAc]	76.7
3		1:1	79.0
4		1:10	78.3
5	1,1,3,3-Tetramethylguanidine acetate **[TMGH][OAc]**	1:20	77.7
6 [c]		[DHTMG][*L*-Lactate]	75.2
7		[DHTMG][*L*-Lactate]	82.2
8		1:1	86.5
9		1:10	92.5
10	1′,1′-Dihexyl-3,3,3′,3′-tetramethylguanidine *L*-Lactate **[DHTMG][L-Lactate]**	1:20	91.3
11 [c]		[EMIM][*L*-Prolinate]	70.4
12		[EMIM][*L*-Prolinate]	76.6
13		1:1	78.6
14		1:10	78.1
15	1-Ethyl-3-methylimidazolium *L*-Prolinate **[EMIM][L-Prolinate]**	1:20	77.6
16 [c]		[P$_{6,6,6,14}$][*L*-Prolinate]	68.7
17		[P$_{6,6,6,14}$][*L*-Prolinate]	75.1
18		1:1	78.2
19		1:10	77.3
20	Trihexyl(tetradecyl)phosphonium *L*-Prolinate **[P$_{6,6,6,14}$][L-Prolinate]**	1:20	75.9

[a] Reaction conditions: 5 mol % of catalyst **2**, IL or a mixture of IL + MeOH (2 mL), TMSCN (0.6 mmol) and aldehyde (0.4 mmol). Reaction time: 8 h. [b] Determined by ^{1}H NMR analysis of crude products (see Experimental part). [c] Without catalyst **2**.

Subsequently, the cyanosilylation reaction of *para*-electron-withdrawing or -donating aromatic aldehyde substrates in the presence of catalyst **2** was tested under optimized reaction conditions (entries 1–3 and 5–6 in Table 5, respectively), in MeOH or in IL+MeOH mixture. With 4-nitro-, 4-chloro- or 4-bromobenzaldehyde, higher yields were obtained (Table 5, entries 1–3), as compared to the benzaldehyde derivatives having an electron-donating substituent (methoxy or methyl) (Table 5, entries 5 and 6), due to an increase of the electrophilicity of the carbon atom at C=O in the former case. The use of linear aliphatic aldehydes (acetaldehyde, propionaldehyde and hexanal) as substrates (entries 7–9, Table 5) allowed to reach higher yields than in the case of the aromatic aldehydes, in MeOH or in a mixture of [DHTMG][*L*-Lactate]:MeOH (1:10, *v/v*), which decrease with the growth of the aliphatic fragment. In all cases, **2** shows higher catalytic performance in a mixture of [DHTMG][*L*-Lactate]:MeOH (1:10, *v/v*) than in the conventional organic solvent MeOH (Table 5).

Table 5. Cyanosilylation of different aldehydes with TMSCN using catalyst **2**, in MeOH or in IL+MeOH mixture [a].

Entry	Substrate	Yield,% [b]	
		MeOH Solvent	**[DHTMG][L-Lactate]:MeOH (1:10, *v/v*) Medium**
1	4-Nitrobenzaldehyde	83.4	97.8
2	4-Chlorobenzaldehyde	79.7	94.0
3	4-Bromobenzaldehyde	79.6	93.3
4	Benzaldehyde	79.0	92.6
5	4-Methylbenzaldehyde	78.0	92.1
6	4-Methoxybenzaldehyde	76.4	90.7
7	Acetaldehyde	87.7	99.0
8	Propionaldehyde	87.4	98.5
9	Hexanal	85.2	97.9

[a] Reaction conditions: 5 mol % of catalyst **2**, MeOH or a mixture of [DHTMG][L-Lactate]:MeOH (1:10, *v/v*) (2 mL), TMSCN (0.6 mmol) and aldehyde (0.4 mmol). Reaction time: 8 h. [b] Determined by ^{1}H NMR analysis of crude products (see Experimental part).

Up to now, a solvent capable of extracting effectively the products from the IL+catalyst system was not found. Therefore, no recycling experiments were made and the reaction analysis with IL was made by using a sample of the reactional mixture containing the product and the IL (see Experimental). This method was accurate because the ^{1}H NMR peaks of ILs do not overlap with those of the product.

Comparing with reported homogeneous catalytic systems for the cyanosilylation reaction, there are several advantages in using **2** as a catalyst in this transformation: (i) It is available from relatively cheap starting materials (arylhydrazone and copper nitrate); (ii) it shows a higher activity (79.0%) in methanol medium in comparison to Zn(II) (30%) [61], Cu(II) (27%) [62], potassium salt of *L*-proline (83%) [63], etc.; and (iii) a shorter reaction time (8 h) and the convenient room temperature can be used favorably, in comparison to other cases operating for a longer reaction time (96 h) [64], at higher (40 °C) [62] or lower (even negative) (−50 °C) [65] temperatures.

The reaction mechanism can be similar to that proposed for some reported examples with related catalytic systems [1,66,67]. Moreover, the reaction possibly can be promoted by cooperative action of coordination and noncovalent interactions, which increase the electrophilic character of carbon atom at the carbonyl group of the aldehyde towards the nucleophilic addition of the cyano moiety with the assistance of a tetrel bonding (Scheme 3), and migration of the silyl group to the oxygen followed by product liberation.
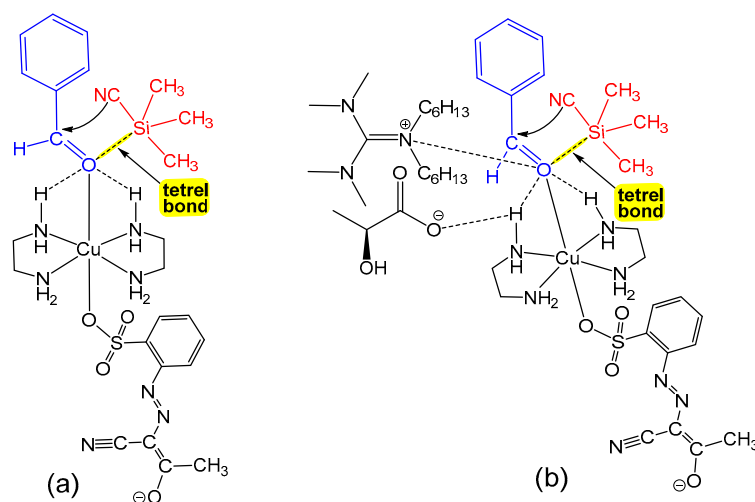
Scheme 3. Proposed intermediates in the absence (**a**) or presence (**b**) of [DHTMG][*L*-Lactate].

3. Experimental

3.1. Materials and Instrumentation

All the chemicals were obtained from commercial sources (Aldrich, St. Louis, MO, USA) and used as received. Sodium 2-(2-(1-cyano-2-oxopropylidene)hydrazinyl)benzenesulfonate (NaHL) and $[Cu(H_2O)_2(en)_2](HL)_2$ (**3**) were synthesized according to the reported procedures [57]. Infrared spectra (4000–400 cm^{-1}) were recorded on a Vertex 70 (Bruker, Billerica, MA, USA) instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were carried out by the Microanalytical service of Instituto Superior Técnico. The ^{1}H and ^{13}C NMR analyses were performed on a Bruker Avance II + 300 (Bruker, Billerica, MA, USA) spectrometer, which operates at 300.130 and 75.468 MHz for ^{1}H and ^{13}C, respectively. The chemical shifts are recorded in ppm in reference to tetramethylsilane. Electrospray mass spectra (ESI-MS) experiments were run by using an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer, Palo Alto, CA, USA) containing an electrospray ion source. In order to perform the electrospray ionization, the optimization of the drying gas and flow rate was undertaken in accord to the particular sample with 35 p.s.i. of nebulizer pressure. Scanning was recorded from *m/z* 0 to 1100 in a methanol solution. The compounds were seen in the positive mode (capillary voltage = 80–105 V).

3.2. Synthesis

3.2.1. Synthesis of **1**

1 mmol (289 mg) of NaHL was dissolved in 25 mL of methanol, and 2 drops of HNO$_3$ (70%) and 1 mmol (170 mg) of AgNO$_3$ were added, and the system was then stirred for 10 min. After ca. 3 d at room temperature, orange crystals precipitated and were filtered off and dried in air.

1: Yield, 49% (based on Ag). Calcd. for $C_{20}H_{18}Ag_2N_6O_9S_2$ (*Mr* = 766.26): C 31.35, H 2.37, N 10.97; found C 31.22, H 2.40, N 10.89. MS (ESI, positive ion mode), *m/z*: 749.20 [*Mr*–H$_2$O+H]$^+$. IR (KBr): 3470 ν(OH), 3406 ν(NH), 2214 ν(C≡N), 1661 ν(C=O), and 1583 ν(C=N) cm^{-1}.

3.2.2. Synthesis of **2**

1 mmol (289 mg) of NaHL was dissolved in 25 mL of methanol, 0.12 mL (2 mmol) en and 1 mmol (232 mg) of Cu(NO$_3$)$_2$·2.5H$_2$O were added, and the system was then stirred for 10 min. After ca. 2 d at room temperature, greenish yellow crystals precipitated and were filtered off and dried in air.

2: Yield, 53% (based on Cu). Calcd. for $C_{14}H_{25}CuN_7O_5S$ (*Mr* = 467.00): C 36.01, H 5.40, N 21.00; found C 35.96, H 5.43, N 20.93. MS (ESI, positive ion mode), *m/z*: 450.05 [*Mr*–H$_2$O+H]$^+$. IR (KBr): 3450 ν(OH), 3340, 3286, 3266 and 3134 ν(NH), 2204 ν(C≡N), 1675 ν(C=O), and 1596 ν(C=N) cm^{-1}.

3.3. Crystal Structure Determination

Intensity data for compounds **1** and **2** were collected at 150 K using a Bruker SMART APEX-II diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT [68] on all the observed reflections. Absorption corrections were applied using the SADABS program [69]. The structures were solved by direct methods using SIR97 package [70] and refined with SHELXL-2018/3 [71]. Calculations were performed using the WinGX System-Version 2014-1 [72]. The hydrogen atoms of water molecules and hydrazine (in **1**) or ethylenediamine (in **2**) were found in the difference Fourier map and the isotropic thermal parameters were set at 1.5 times the average thermal parameters of the belonging oxygen or nitrogen atoms, with their distances restrained by using the DFIX and DANG commands. Hydrogen atoms bonded to carbon atoms were included in the refinement using the riding-model approximation with the Uiso(H) defined as 1.2 Ueq of the parent aromatic atoms, and 1.5U$_{eq}$ of the parent carbon atoms for methyl. Compound **2** was refined as a 2-component twin; the unaccounted

twinning was resolved by using the TwinRotMat program in Platon [73]. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms were employed. The details of the crystallographic data for **1** and **2** are summarized in Table 6. Selected bond distances and angles for polymers **1** and **2** as well as, for comparative purposes, complex salt **3** are shown in Table 1. Ellipsoid plots are presented in Figures 1 and 2, while Figures S1–S5 in the Supplementary Material File illustrate packing properties for both polymers.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center: CCDC 1891994 for **1** and 1891993 for **2**. Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).

Table 6. Crystallographic data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{18}Ag_2N_6O_9S_2$	$C_{14}H_{25}CuN_7O_5S$
fw	766.26	467.01
Temperature (K)	150(2)	150(2)
Cryst. Syst.	monoclinic	triclinic
Space group	C 2/c	P-1
a (Å)	12.982(2)	7.2744(8)
b (Å)	5.7571(10)	11.7588(14)
c (Å)	33.603(6)	11.8024(13)
α, °	90	83.559(4)
β, °	98.673(6)	75.174(3)
γ, °	90	84.810(4)
V (Å^3)	2482.7(7)	967.78(19)
Z	4	2
ρ_{calc} (g cm^{-3})	2.050	1.603
μ(Mo Kα) (mm^{-1})	1.810	1.279
F (000)	1512	486
R_{int}	0.0554	0.0594
R1 [a] (I $\geq$ 2σ)	0.0572	0.0718
wR2 [b] (I $\geq$ 2σ)	0.1304	0.2039
GOOF	1.190	1.114

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] wR2 = $[\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$.

3.4. Synthesis of ILs

1-Ethyl-3-methylimidazolium *L*-prolinate [EMIM][*L*-Prolinate] and 1′,1′-dihexyl-3,3,3′,3′-tetramethylguanidine *L*-lactate [DHTMG][*L*-Lactate] were prepared by known procedure [74,75]. 1,1,3,3-Tetramethylguanidine acetate [TMGH][OAc] and trihexyl(tetradecyl)phosphonium *L*-prolinate [P$_{6,6,6,14}$][*L*-Prolinate] were synthesized by the same methodology (see below).

3.4.1. Synthesis of 1,1,3,3-tetramethylguanidine acetate [TMGH][OAc]

To a solution of 35 mmol of 1,1,3,3-tetramethylguanidine in 20 mL of methanol, 35 mmol of acetic acid were added dropwise. The mixture was then stirred at room temperature for 24 h. Then, the methanol was evaporated, and the product was dried under vacuum during 24 h. A colorless oil was obtained (98% yield). ^{1}H NMR (CDCl$_3$): δ 1.91 (s, 3H, CH$_3$), and 3.01 (s, 12H, 4CH$_3$) ppm.

3.4.2. Synthesis of trihexyl(tetradecyl)phosphonium *L*-prolinate [P$_{6,6,6,14}$][L-Prolinate]

This IL was synthesized in two steps: (i) 3.6 mmol of *L*-proline were dissolved in 50 mL of methanol and 3.6 mmol of crystalline NaOH were added. The reaction was left stirred for 24 h; (ii) After sodium prolinate was formed, 3 mmol of [P$_{6,6,6,14}$]Cl were added, and the mixture was stirred for 24 h at room temperature. After that time, methanol was removed under low pressure

and the mixture was re-dissolved in dichloromethane. The precipitated NaCl was filtered off and the dichloromethane was evaporated. Then, the product was dried under vacuum during 24 h. A yellow oil was obtained (67% yield). ^{1}H NMR (CDCl$_3$): δ 0.89 (t, 12H, 4CH$_3$), 1.25 and 1.30 (m, 40H, 20CH$_3$, peaks very messy and overlapped), 1.50 (m, 16H, 8CH$_3$), and 2.42 (m, 8H, 3CH$_2$, NH, and CH, these peaks correspond to the anion and are all overlapped) ppm.

3.5. General Procedure for Catalytic Studies

In a typical cyanosilylation experiment, to a solution of benzaldehyde (0.4 mmol), catalyst (**1**–**3**) (1–8 mol %) in any of the solvents [CH$_2$Cl$_2$, THF, MeOH or IL; 2 mL], trimethylsilyl cyanide (TMSCN) (0.6 mmol) was added dropwise. The mixture was stirred continuously for a certain amount of time. The solvent was then evaporated (in the case of CH$_2$Cl$_2$, THF and MeOH) and the residue was analyzed by ^{1}H-NMR spectroscopy in CDCl$_3$, in order to evaluate the yield of the products [39,40]. In the case of the reactions with IL, the analysis was made by taking directly a sample of the reactional mixture, which was analyzed by ^{1}H-NMR in CDCl$_3$. For the reactions in a IL+MeOH mixture, MeOH was evaporated and a sample of products+IL was taken for analysis. The adequacy of this procedure was confirmed by using blank ^{1}H NMR analyses with 1,2-dimethoxyethane (0.10 mmol) as an internal reference [benzaldehyde (0.10 mmol) and TMSCN) (0.15 mmol)] (Figure S6). The internal standard method showed the absence of side products

4. Conclusions

We have prepared two new silver(I) and copper(II) coordination polymers **1** and **2**, and applied them, with the known mononuclear copper(II) complex **3**, as catalysts in cyanosilylation reaction of several aldehydes with TMSCN. The Cu^{II} coordination polymer **2** showed the highest activity for the cyanosilylation reaction in methanol and in a mixture of [DHTMG][*L*-Lactate]:MeOH (1:10, *v/v*) achieving yields up to 99% at room temperature. Electron-withdrawing substituents, such as –NO$_2$, –Cl, –Br, in the para position of the aromatic aldehyde provide higher product yields, whereas electron-donating groups (–CH$_3$, –OCH$_3$) inhibit the reaction. Cooperative actions of coordination and noncovalent interactions are proposed for the C=O activation in the aldehyde substrate. The use of a IL+MeOH mixture also increases the catalytic activity in comparison with the case of MeOH alone or another organic solvent.

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