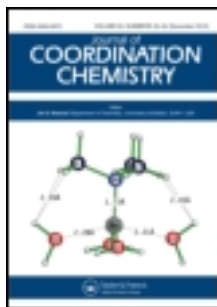


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## Bridging nitrile groups in a metal–organic framework

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This article describes two coordination polymers based on sodium and nickel triflates, respectively, and the linker adiponitrile (1,4-butanedinitrile). Sodium triflate forms a coordination network with adiponitrile, where the nitriles bridge the sodium ions, a rare coordination mode for a nitrile. Crystal structures of alkali metal complexes of linear aliphatic dinitriles have not been reported previously. With nickel triflate, a cationic 1-D coordination polymer results upon coordination of adiponitrile.

*Keywords:* Dinitrile; Coordination polymer; MOF

### 1. Introduction

The expected coordination mode of a nitrile is  $\eta^1$  with a linear, or less frequently, bent metal–nitrogen–carbon arrangement as found in the vast majority of nitrile complexes. However, as seen from figure 1, this is not the only possible way for a nitrile to coordinate to a metal ion. The most obvious alternative is side-on  $\eta^2$  coordination, as represented by structure II in figure 1 [1]. Compared to the large number of structures of arylene  $\pi$ -complexes, this is relatively rare; 30 crystal structures with neutral side-on  $\eta^2$  coordinating nitrile ligands have been reported for nickel, ruthenium, rhodium, tungsten, molybdenum, niobium, and cesium complexes. This mode of coordination is always associated with large deviations from linearity in the nitrile and leaves the lone pair of the nitrile free to coordinate a second metal. Eight structures of type III, which can be thought of as a combination of types I and II, have been reported [2]. The two metals may or may not form a metal–metal bond and these complexes have the nitrile coordinated to nickel, zirconium, technetium, tungsten, or manganese; there is also an example of a complex with a  $\pi$ -coordinating nickel and a  $\sigma$ -coordinating aluminum. Structures of type IV have been called crosswise-bridging and are restricted to coordination of a single nitrile to a pair of molybdenum and tungsten atoms [3]. Eight structures of this type have been reported. The lone pair of nitrogen can coordinate one

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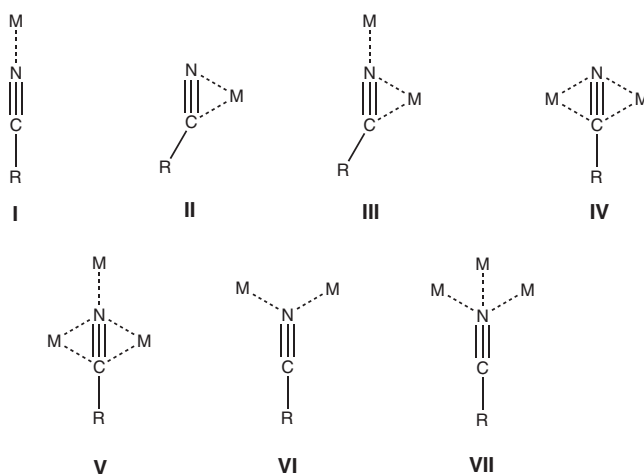


Figure 1. Schematic diagram depicting different possible coordination modes for nitrile ligands.

additional metal giving complexes of type V [4]. There are six crystal structures of this type, one of which is a mixed molybdenum/ruthenium complex, the rest are iron complexes. With a lone pair directed along the  $C\equiv N$  axis, coordination modes VI and VII in figure 1 are less obvious. There are 35 structures of type VI involving sodium, potassium, rubidium, cesium, copper, silver, europium, mercury, and zirconium, and was first observed for an acetonitrile ligand in a europium(II) aryloxide complex in 1998 [5]. Type VII is restricted to four mercury complexes [6]. This article describes the coordination of a dinitrile, adiponitrile (1,4-butandinitrile), to sodium and nickel triflates. Coordination polymers displaying coordination modes VI and I, respectively, are observed.

## 2. Experimental

Nickel(II) triflate hexahydrate was prepared by published procedures [7]. Sodium triflate, pyridine, and adiponitrile were purchased from Sigma-Aldrich and used as received.

### 2.1. $[Na_2(OTf)_2(C_6H_8N_2)]_n$ (**1**)

Sodium triflate (0.172 g, 1 mmol) was dissolved in a mixture of acetone (2 mL), adiponitrile (0.40 mL, 3.5 mmol), and pyridine (0.10 mL, 1.2 mmol). The solution was layered with diethyl ether (10 mL). Colorless crystals of **1** formed within a few days. Yield: 0.20 g (86%). IR: 2962 (m), 2889 (w), 2255 (s), 1466 (m), 1421 (m), 1262 (s), 1228 (s), 1165 (s), 1041 (s), 908 (w), 895 (w), 643 (s), 585 (m), 574 (w), 525 (m), 516 (m)  $cm^{-1}$ . Anal. Calcd for  $NaC_8H_8S_2N_2O_6F_6$ : C, 21.24; H, 1.91; N, 6.20. Found: C, 21.37; H, 1.67; N, 6.27.

## 2.2. $[Ni(H_2O)_2(C_6H_8N_2)]_n(OTf)_{2n}$ (**2**)

Nickel(II) triflate hexahydrate (0.23 g, 0.5 mmol) was dissolved in acetone (2 mL). Adiponitrile (0.54 mL, 5 mmol) was added and the solution was layered with diethyl ether (10 mL). Blue crystals of **2** started to grow, and after five days the mixture was filtered, the crystals were washed with diethyl ether (5 mL) and dried by suction. Yield: 0.26 g (85%). IR: 3381 (bs), 2947 (s), 2304 (s), 1685 (m), 1465 (m), 1413 (w), 1251 (s), 1228 (s), 1167 (s), 1032 (s), 905 (w), 759 (m), 638 (s), 576 (w), 519 (m)  $cm^{-1}$ .

## 2.3. X-ray crystallography

Diffraction data were collected using a Bruker-Nonius X8 APEX-II instrument (Mo-K $\alpha$  radiation). Structures were solved using SIR-92 [8] and refined using SHELXL-97 [9]. All non-H atoms were refined anisotropically. A semi-empirical absorption correction was applied using SADABS. Carbon-bonded hydrogen atoms were placed in calculated positions and refined using a riding model. Diagrams were drawn using ORTEP-3 [10] for Windows and Pluton [11]. SIR-92, SHELXL, and ORTEP-3 operated under the WinGX program suit [12]. Crystal and refinement data are collected in table 1. Selected bond distances and angles for **1** and **2** are collected in tables 2 and 3, respectively.

Table 1. Crystal and refinement data for **1** and **2**.

Parameter	<b>1</b>	<b>2</b>
Empirical formula	C <sub>8</sub> H <sub>8</sub> F <sub>6</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>14</sub> H <sub>20</sub> F <sub>6</sub> N <sub>4</sub> NiO <sub>8</sub> S <sub>2</sub>
<i>M</i>	452.26	609.17
Temperature (K)	298(2)	150(2)
Crystal system	Monoclinic	Triclinic
Space group	<i>C</i> 2/ <i>m</i>	<i>P</i> -1
Unit cell dimensions (Å, °)		
<i>a</i>	20.982(2)	8.1362(3)
<i>b</i>	7.8411(6)	9.2795(4)
<i>c</i>	4.9905(4)	9.5305(4)
$\alpha$	90	66.260(1)
$\beta$	99.331(4)	66.986(2)
$\gamma$	90	84.300(2)
Volume (Å <sup>3</sup> ), <i>Z</i>	810.2 (1), 2	604.80(4), 1
Calculated density (g cm <sup>-3</sup> )	1.854	1.673
Absorption coefficient (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	0.478	1.067
Crystal size (mm <sup>3</sup> )	0.34 × 0.20 × 0.20	0.22 × 0.08 × 0.06
$\theta$ range for data collection (°)	3.93–25.98	3.76–26.06
Reflection collected	11,395	13,533
Unique reflection	856 [ <i>R</i> (int) = 0.0268]	2365 [ <i>R</i> (int) = 0.0217]
Number of parameters	73	168
Final <i>R</i> <sub>1</sub> ( <i>F</i> ) <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]; <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) <sup>b</sup>	0.0375; 0.1108	0.0205; 0.0523
<i>R</i> <sub>1</sub> <sup>a</sup> ; <i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) <sup>b</sup> (all data)	0.0387; 0.1121	0.0218; 0.0530
Largest difference peak and hole (e Å <sup>-3</sup> )	0.575 and -0.502	0.354 and -0.322

<sup>a</sup> $R_1(F) = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ . <sup>b</sup> $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ .

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

N(1)–Na(1)	2.769(2)
O(1)–Na(1)	2.359(1)
O(2)–Na(1)	2.418(1)
O(1) <sup>i</sup> –Na(1)–O(1)	179.998(1)
O(1)–Na(1)–O(2) <sup>ii</sup>	91.83(6)
O(1)–Na(1)–O(2) <sup>iii</sup>	88.17(6)
O(2) <sup>ii</sup> –Na(1)–O(2) <sup>iii</sup>	180.0
O(1)–Na(1)–N(1) <sup>iii</sup>	97.48(7)
O(2) <sup>ii</sup> –Na(1)–N(1) <sup>iii</sup>	77.13(6)
O(2) <sup>iii</sup> –Na(1)–N(1) <sup>iii</sup>	102.87(6)
O(1)–Na(1)–N(1) <sup>ii</sup>	82.52(7)
N(1) <sup>iii</sup> –Na(1)–N(1) <sup>i</sup>	180.0

Symmetry transformations used to generate equivalent atoms: <sup>i</sup>– $x+1/2$ ,  $-y+3/2$ ,  $-z+2$ ; <sup>ii</sup>– $x+1/2$ ,  $-y+3/2$ ,  $-z+1$ ; <sup>iii</sup> $x$ ,  $y$ ,  $z+1$ .

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

N(1)–Ni(1)	2.055(1)
N(2)–Ni(1)	2.076(1)
O(4)–Ni(1)	2.064(1)
N(1) <sup>iv</sup> –Ni(1)–N(1)	180.0
N(1)–Ni(1)–O(4) <sup>iv</sup>	88.57(5)
N(1)–Ni(1)–O(4)	91.43(5)
O(4) <sup>iv</sup> –Ni(1)–O(4)	180.0
N(1) <sup>iv</sup> –Ni(1)–N(2)	89.31(5)
N(1)–Ni(1)–N(2)	90.69(5)
O(4) <sup>iv</sup> –Ni(1)–N(2)	91.39(4)
O(4)–Ni(1)–N(2)	88.61(4)
O(4)–Ni(1)–N(2) <sup>iv</sup>	91.39(4)

Symmetry transformations used to generate equivalent atoms: <sup>iv</sup>– $x+2$ ,  $-y$ ,  $-z$ .

### 3. Results and discussion

There are relatively few crystal structures of compounds containing aliphatic dinitrile ligands, even though these appear to be useful linkers in the construction of coordination polymers and are commercially available at low cost. For straight-chain aliphatic dinitriles with three to twelve carbons, there are 79 crystal structures. The majority of the structures are coordination polymers based on copper(I) and silver(I) and all of the complexes display an end-on (type I, figure 1) coordination of nitrile to the metal. There are no alkali metal complexes with straight-chain aliphatic C<sub>3</sub>–C<sub>12</sub> dinitrile ligands, and indeed, attempts to crystallize sodium triflate (sodium trifluoromethylsulfonate; NaOTf) from neat adiponitrile or from acetone containing an excess of adiponitrile by layering with diethyl ether invariably yielded NaOTf as the sole product. If, on the other hand, pyridine or triethylamine is added to a solution of sodium triflate and adiponitrile in acetone, layering with diethyl ether gave large colorless crystals of a coordination polymer, [Na<sub>2</sub>(OTf)<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)]<sub>n</sub> (**1**) (figure 2). Compound **1** was also identified by powder diffraction, albeit in an impure state, in the products obtained by layering a solution of NaOTf, NaSbF<sub>6</sub>, and adiponitrile in a 1:1:8 ratio or Fe(OTf)<sub>2</sub>, NaClO<sub>4</sub>, and adiponitrile in a 1:2:8 ratio in acetone with diethyl ether. Compound **1** is a rare example of an alkali metal complex with bridging



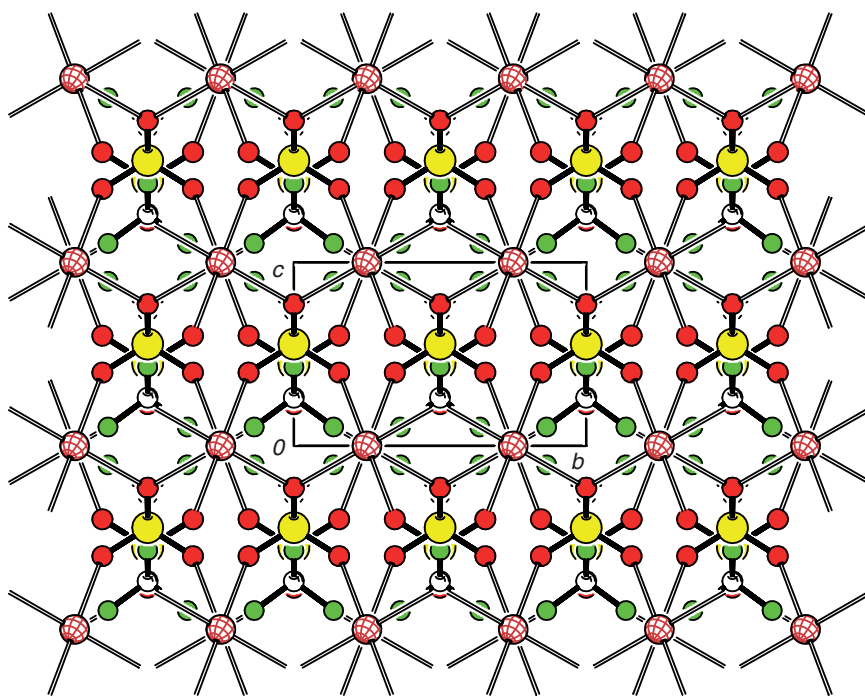


Figure 3. Layers of sodium cations and triflate anions in **1** viewed along the crystallographic *a*-axis. Note: The adiponitrile ligands, extending parallel to the line of sight, have been removed for clarity. Color code: C: white, F: green, Na: brown, O: red, S: yellow. (Color version available online.).

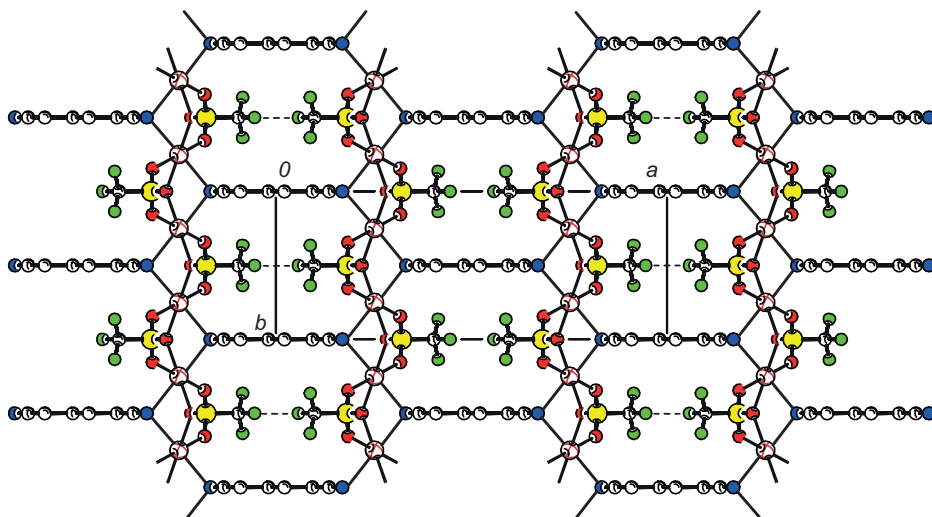


Figure 4. The crystal structure of **1** viewed along the crystallographic *c*-axis. Notes: Four adjacent layers of sodium cations and triflate anions are connected by adiponitrile ligands. Short contacts between fluorines are indicated by dashed lines. All hydrogen atoms have been omitted for clarity. Color code: C: white, F: green, N: blue, Na: brown, O: red, S: yellow. (Color version available online.).



Substituting sodium triflate for nickel(II) triflate hexahydrate gave the coordination polymer  $[\text{Ni}(\text{H}_2\text{O})_2(\text{C}_6\text{H}_8\text{N}_2)]_n(\text{OTf})_{2n}$  (**2**). The synthesis of **2** is more straightforward than the synthesis of **1**, in the sense that no additional additives are required. If a solution of nickel(II) triflate hexahydrate and adiponitrile in acetone is layered with diethyl ether, small blue crystals of **2** form within a few days. The structure of **2** shows few similarities with that of **1**; the central nickel atom in **2** is located at an inversion center and displays octahedral coordination geometry (figure 5). In **2**, nickel atoms are connected by two bridging adiponitrile ligands giving chains extended parallel to the crystallographic *c*-axis. In contrast to **1**, triflate anions in **2** are non-coordinated, and the coordination sphere around nickel is completed by two *trans* water ligands. The hydrogen atoms in water ligands are involved in hydrogen-bonding with triflate oxygen atoms; H1W interacts with O1 and H2W interacts with O2( $2-x, 1-y, -z$ ). The third triflate oxygen has a short contact with H5A( $-1+x, y, z$ ), which may be indicative of an attractive interaction.

Of the previously published crystal structures of aliphatic dinitrile complexes, a vast majority is based on silver(I) and copper(I), the first structure reported in 1959 [13]. These complexes generally give coordination networks with a 1 : 2 metal–dinitrile ratio with four dinitrile ligands forming a tetrahedral coordination sphere around the metal (structure A in figure 6). Although having the same ligand arrangement around the central metal ion, a diversity of network topologies has been reported for compounds of this type [14]. Adiponitrile complexes of  $\text{AgBF}_4$ ,  $\text{AgPF}_6$ ,  $\text{AgAsF}_6$ , and  $\text{AgSbF}_6$  all form this type of framework, while in the case of silver(I) triflate, a mixture of two compounds was obtained, one with an A-type structure and one complex with a 1 : 1 ratio, where coordinating triflates fill the coordination spheres around silver (structure B in figure 6) [14b]. This structure is unusual in that silver is five-coordinate with a coordination geometry close to trigonal bipyramidal with the two adiponitrile ligands in apical positions. Four-coordinate structures with two coordinating triflates (structure C in figure 6) have been reported with  $\text{C}_9$  and  $\text{C}_{10}$  dinitriles [14]. There is only one example of a six-coordinate central atom surrounded by six dinitrile ( $\text{C}_{12}$ ) ligands (structure D in figure 6) [15]. 1-D polymers displaying terminal dinitriles like in **2** are surprisingly rare,

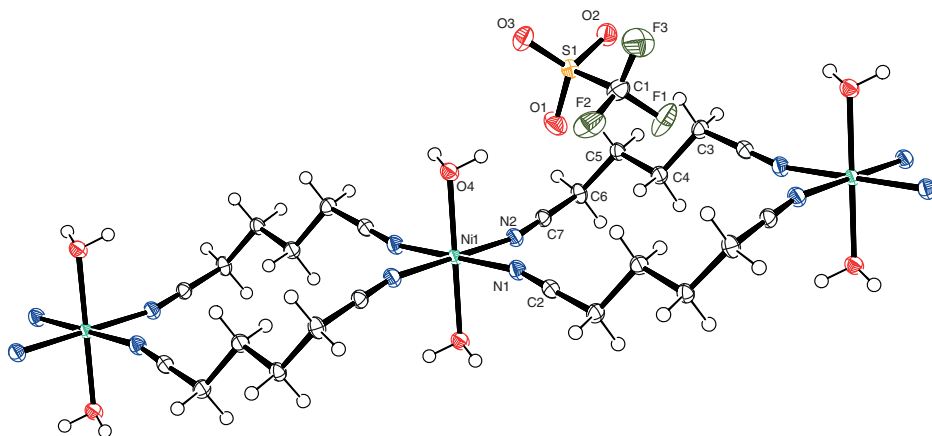


Figure 5. Molecular structure of **2** displaying the crystallographic-numbering scheme.

Notes: The figure depicts the asymmetric unit and a part of the polymeric chain. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii.



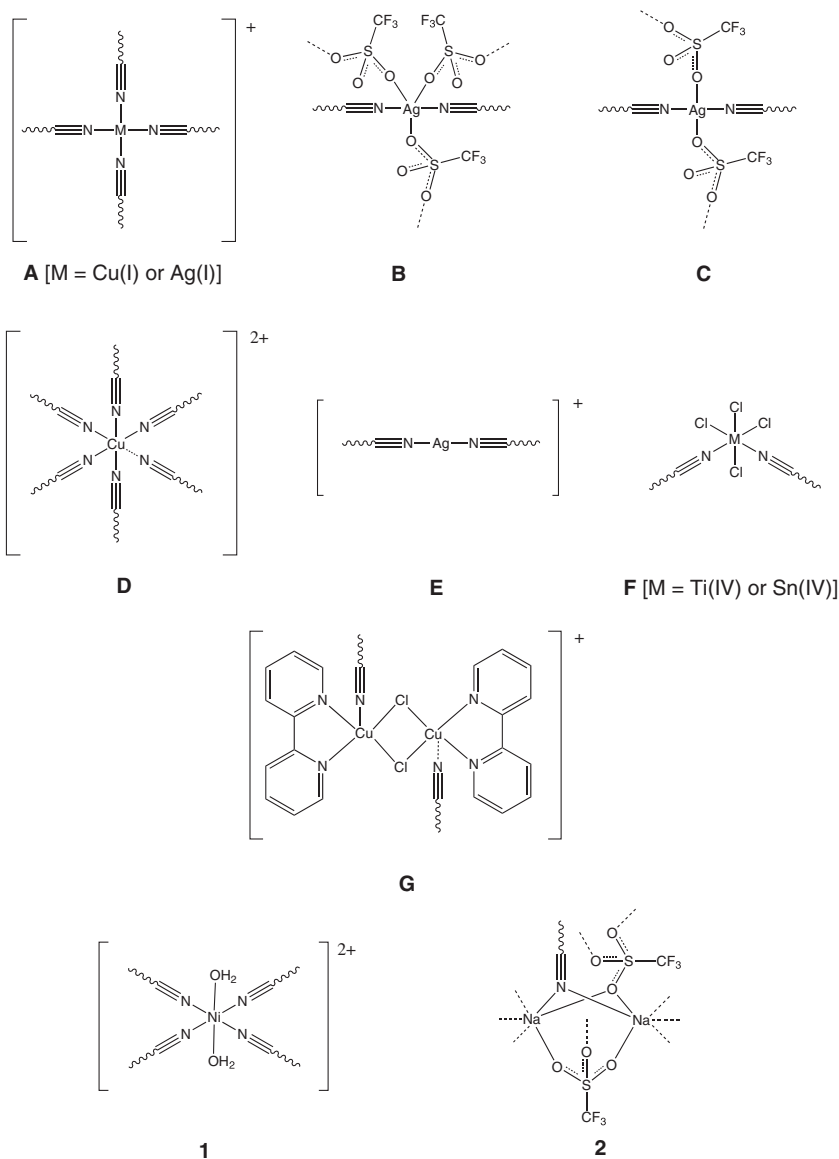


Figure 6. Schematic representation of coordination polymers with aliphatic dinitrile ligands. Note: Structures A–G illustrate the previously reported structure types; **1** and **2** are included for comparison.

with few reported structures in the CSD. There is only one structure of a complex with a two-coordinate metal ion linked by dinitriles (the 1,8-dicyano-octane complex of silver(I) hexafluoroarsenate; structure E in figure 6) [14a]. There are two structures corresponding to structure F in figure 6 [16, 17] and one more example is found in structure G [18]. Cationic 1-D chains as found in **2** are previously unknown.

IR spectra of **1** and **2** have  $\text{C}\equiv\text{N}$  stretching vibrations with  $\nu = 2255$  and  $2304\text{ cm}^{-1}$ , respectively, shifted by 8 and  $57\text{ cm}^{-1}$ , respectively, compared to neat adiponitrile, with  $\nu = 2247\text{ cm}^{-1}$ . Information in the literature about the shift in  $\nu_{\text{C}\equiv\text{N}}$  for different nitrile

coordination modes is relatively scarce, and from the available data there seems to be no clear trend. In  $[\text{KB}(\text{CN})_4\text{MeCN}]_n$ , which displays bridging acetonitrile ligands,  $\nu_{\text{C}\equiv\text{N}}$  is shifted by  $+10\text{ cm}^{-1}$  [19], while an acetonitrile ligand bridging two mercury atoms in an organomercury compound showed no shift in  $\nu_{\text{C}\equiv\text{N}}$  compared to the neat nitrile [20].

### Supplementary material

CCDC 885409 (1) and 885410 (2) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary material associated with this article can be found in the online version.

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