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## Introduction

Functionalization of polyaza macrocyclic and macrobicyclic compounds by several chemical groups, such as acrylonitrile,<sup>1–6</sup> alkynyl,<sup>7</sup> phosphanylmethyl,<sup>8</sup> carboxyl,<sup>9</sup> and heterocycles,<sup>10</sup> on their secondary N-sites, has attracted a considerable interest, and a number of their complexes has been prepared with different metal ions with interesting properties in the fields of coordination chemistry, electrochemistry, photoluminescence and catalysis.<sup>11–17</sup> We have also engaged in this investigation<sup>9,15</sup> to identify new synthetic procedures that may allow designing a diversity of transition metal

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# Silver coordination polymers with tri- and hexacyanoethyl-functionalized macrocyclic ligands<sup>†</sup>

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Tri- and hexa-cyanoethyl functionalized 17- ( $L^1$ ) and 42-membered ( $L^2$ ) macrocyclic compounds were obtained by [1 + 1] (for  $L^1$ ) or [2 + 2] (for  $L^2$ ) cyclocondensation of the corresponding dialdehyde and diethylenetriamine, followed by hydrogenation by KBH<sub>4</sub> and subsequent cyano-functionalization with acrylonitrile. They react with silver nitrate, leading to the formation of [AgL<sup>1</sup>](NO<sub>3</sub>) (**1**) and of the metal-organic coordination polymers [Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>L<sup>1</sup>]<sub>n</sub> (**2**) and {[Ag<sub>2</sub>L<sup>2</sup>](NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (**3**). The complexes were characterized by elemental analysis, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectroscopies, and ESI-MS; moreover, L<sup>2</sup>, **1**, **2** and **3** were also characterized by single crystal X-ray diffraction. The metal cation in **1** is pentacoordinated with a N<sub>3</sub>O<sub>2</sub> coordination environment; in **2**, the metal cations display N<sub>4</sub>O<sub>2</sub> octahedral and N<sub>2</sub>O<sub>3</sub> square-pyramid coordination and in **3** they are in square-planar N<sub>4</sub> sites. In **1**, the ligand acts as a pentadentate chelator, and in the other two cases, the ligands behave as octadentate chelators in a  $1\kappa^3N:\kappa^2O, 2\kappa N, 3\kappa N, 4\kappa N$  (in **2**) or  $1\kappa^3N, 2\kappa^3N, 3\kappa N, 4\kappa N$  fashion (in **3**). The cyanoethyl strands of the ligands are directly involved in the formation of the 2D frameworks of **2** and **3**, which in the former polymer can be viewed as a net composed of hexametallic 36-membered macrocyclic rings and in the latter generates extra hexametallic 58-membered cyclic sets that form zig-zag layers. The thermal analytical and electro-chemical properties of these silver complexes were also studied.

complexes with such type of ligands and to prepare novel structures with relevance in material and medicinal chemistries.

It is well known that silver complexes are good candidates for antibacterial or antitumor activities and can show interesting electrochemical and catalytic properties.<sup>18</sup> Unfortunately, one shortcoming of the compounds with this metal is their usual instability in air, which limits their applications. In this work, we aim to synthesize stable silver(1) complexes with ligands that combine advantages of macrocyclic and nitrile compounds, which are expected to show effective coordination abilities to this metal ion, and to study their thermal and electrochemical properties.

We report herein two new tri- and hexa-cyanoethyl functionalized macrocycles,  $L^1$  and  $L^2$ , which were synthesized by the reaction of the two polyaza macrocyclic precursors  $L^{1b}$  and  $L^{2b}$ (Scheme 1) with acrylonitrile, according to a previously reported general procedure.<sup>1,19a</sup> Depending on the ligand and on the AgNO<sub>3</sub>: ligand molar ratios, the reaction of  $L^1$  or  $L^2$ with AgNO<sub>3</sub> afforded the mononuclear complex [AgL<sup>1</sup>](NO<sub>3</sub>) (1) or the polymeric compounds [Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>L<sup>1</sup>]<sub>n</sub> (2) or {[Ag<sub>2</sub>L<sup>2</sup>]-(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (3), which represent rare examples of stable silver cyanoethyl functionalized coronand polymeric complexes. In 2, L<sup>1</sup> is coordinated to four silver ions, resulting in hexanuclear



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Scheme 1 Ligands  $L^1$  and  $L^2$  and their precursors.

metallic macrocyclic motifs and a 2-D structure. In 3,  $L^2$  binds two silver ions in its cavity and is coordinated to two other neighbouring ones, forming interesting cylindrical motifs and a 2-D layer.

## **Experimental**

#### Instrumentation and reagents

All reagents were of analytical grade or purified by standard methods. C, H and N elemental analyses were carried out on Vario EL III Elemental Analyzer. Infrared spectra  $(4000-400 \text{ cm}^{-1})$  were recorded using a BIO-RAD FTS 3000MX or a Bruker IFS 1113v using KBr pellets (abbreviations: vs - very strong, s - strong, m - medium, w - weak, br - broad, sh - shoulder). <sup>1</sup>H and <sup>13</sup>C NMR spectra were run on a Varian Unity 400 spectrometer at an ambient temperature. TG-DTA data were collected with a Perkin Elmer STA6000 Thermal Analyzer at a heating rate of 10 K min<sup>-1</sup> under an air atmosphere. Electrospray mass spectra (ESI-MS) were run (in NCMe for L<sup>1</sup> and  $L^2$ , or in a mixture of MeOH/DMSO for complexes 1-3) with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 psi nebulizer pressure. Scanning was performed from m/z 100 to 1200 for L<sup>1</sup>,  $L^{2}$ , 1 and 2 and m/z 100 to 1500 for 3.

The electrochemical experiments were performed using an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammetry (CV) studies were performed in 0.2 M [ $^{n}$ Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe, at a platinum disc working electrode (d = 0.5 mm) and at room temperature. Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the abovementioned composition in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential. A Pt wire was employed as the counter electrode for the CV cell. The CPE experiments were monitored regularly by CV, thus assuring no significant potential drift occurred along the electrolysis. The solutions were saturated by bubbling N<sub>2</sub> before each run. The redox potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and their values are quoted relative to the SCE by using the  $[Fe(\eta^5-C_5H_5)_2]^{0/+}$  redox couple  $(E_{1/2}^{ox} = 0.42 \text{ V} \text{ vs. SCE}).^{20}$ 

#### General synthetic procedure

Scheme 1 represents the two ligands  $L^1$  and  $L^2$ , whose isolation and full characterization were achieved in this work for the first time. Their synthetic precursors ( $L^{1a}$ ,  $L^{1b}$ ,  $L^{2a}$  and  $L^{2b}$ ) were synthesized by following the methods earlier reported,<sup>19</sup> *via* [1 + 1] or [2 + 2] condensation of diethylenetriamine with 2,2'-(ethane-1,2-diylbis(oxy))dibenzaldehyde or 4,4'-(ethane-1,2diylbis(oxy))-dibenzaldehyde, respectively, followed by hydrogenation with KBH<sub>4</sub>.

Synthesis of L<sup>1</sup>. 3.4 g (0.010 mol) of L<sup>1b</sup> were heated to 55 °C in 200 mL of methanol until total dissolution. Upon addition of 0.48 g (9.0 mmol) of acrylonitrile, the mixture was refluxed for 24 h. After most of the solvent (ca. 150 mL) was distilled off and the system stored overnight at room temperature, colourless crystals of  $L^1$  were obtained (4.5 g, yield 90%). m.p. 98-99 °C. Anal. calcd for C29H36N6O2 (500.64): C, 69.57; H, 7.25; N, 16.79. Found C, 69.74; H, 7.51; N, 16.57. ESI-MS:  $[L + H^{\dagger}]^{\dagger}$ : (501.3, 25%),  $[L - C_{3}H_{4}N + H^{\dagger}]^{\dagger}$ : (448.4, 100%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  2.17 (t, J = 6.8 Hz, 2H, -CH<sub>2</sub>CN), 2.43-2.51 (m, 10H,  $-CH_2CH_2CN$ ), 2.59 (t, J = 6.4 Hz, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N), 2.82 (t, J = 7.0 Hz, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N), 3.69 (s, 4H,  $-CH_2$ Ar), 4.37 (s, 4H,  $-OCH_2$ ), 6.91–6.98 (m, 4H, aryl), 7.27–7.32 (m, 4H, aryl). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ ),  $\delta$  16.77 (CH<sub>2</sub>CH<sub>2</sub>-CN), 50.22 (CH<sub>2</sub>CH<sub>2</sub>N), 50.59 (CH<sub>2</sub>CH<sub>2</sub>N), 52.29  $(CH_2CH_2-CN)$ , 53.11 (- $CH_2$ -aryl), 67.00 (O- $CH_2$ ); 111.41 (aryl),

119.40 (-*C*N), 120.90 (aryl), 127.27 (-CH<sub>2</sub>-aryl), 128.74 (aryl), 131.10 (aryl), 157.10 (-O-aryl). IR (KBr disc) (cm<sup>-1</sup>): 3065 (w), 2947 (s), 2908 (s), 2809 (s), 2846 (m), 2810 (vs), 2239 (s), 1599 (s,  $\nu_{aryl-H}$ ), 1587 (m), 1493 (s,  $\nu_{aryl-H}$ ), 1452 (s), 1377 (m), 1340 (m), 1291 (m), 1244 (vs), 1196 (m), 1113 (s), 1100 (s), 1069 (m), 1048 (m), 1009 (m), 954 (s), 925 (m), 951 (s), 758 (s), 721 (w), 620 (w).

Synthesis of L<sup>2</sup>. 0.20 g (0.29 mmol) of L<sup>2b</sup> and 40 mL of ethanol were mixed in a 100 mL flask and a white emulsion was obtained. Upon addition of 0.48 g (9.0 mmol) of acrylonitrile, the mixture was refluxed for 24 h, and the initially colourless solution turned to pale yellow. The hot solution was filtered, and upon cooling, colourless crystals of L<sup>2</sup> were formed, which were separated by filtration and dried (0.20 g, 69%). m.p. 123-125 °C. Anal. calcd for C<sub>58</sub>H<sub>72</sub>N<sub>12</sub>O<sub>4</sub>·C<sub>2</sub>H<sub>5</sub>OH (1047.34): C, 68.81 H, 7.50; N, 16.05. Found C, 68.55; H, 7.65; N, 16.12. ESI-MS:  $[L + H^{\dagger}]^{+}$ : (1001.4, 10%),  $[L - C_{3}H_{4}N + H^{\dagger}]^{+}$ : (948.8, 100%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ),  $\delta$  2.35–2.42 (m, J = 7.0 Hz, 12H,  $-NCH_2$ ), 2.49–2.51 (m, J = 3.2 Hz, 16H,  $-NCH_2CH_2N$ , 2.72–2.77 (q, J = 6.5 Hz, 12H,  $-CH_2CN$ ), 3.47 (s, 8H, -CH<sub>2</sub>Ar), 4.15 (s, 8H, -OCH<sub>2</sub>), 6.85 (d, J = 8.4 Hz, 8H, aryl), 7.20 (d, J = 8.8 Hz, 8H, aryl). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ 16.95 (CH<sub>2</sub>CH<sub>2</sub>-CN), 17.18 (CH<sub>2</sub>CH<sub>2</sub>-CN), 50.15 (CH<sub>2</sub>CH<sub>2</sub>-CN), 50.80 (CH<sub>2</sub>CH<sub>2</sub>-CN), 52.05 (-NCH<sub>2</sub>CH<sub>2</sub>N), 52.74 (-NCH<sub>2</sub>CH<sub>2</sub>N), 58.45 (-CH<sub>2</sub>-aryl), 66.73 (O-CH<sub>2</sub>), 114.75 (aryl), 119.34 (-CN), 130.25 (aryl), 131.16 (CH<sub>2</sub>-aryl), 158.19 (-O-aryl). IR (KBr disc) (cm<sup>-1</sup>): 3043 (w), 2942 (s), 2925 (s), 2923 (s), 2249 (s), 1609 (s,  $\nu_{arvl-H}$ ), 1510 (vs,  $\nu_{arvl-H}$ ), 1456 (s), 1421 (w,  $\nu_{aryl-H}$ ), 1372 (m), 1302 (w), 1244 (s), 1229 (s), 1173 (m), 1119 (s), 1075 (s), 1018 (m), 947 (s), 822 (s), 770 (m), 628 (w), 518 (m).

Suitable crystals for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile solution of  $L^2$ .

Synthesis of [AgL<sup>1</sup>](NO<sub>3</sub>) (1). A solution of AgNO<sub>3</sub> (0.085, 0.50 mmol) in 10 mL acetonitrile in a 50 mL flask was heated to 55 °C to dissolve the silver salt. A 10 mL dichloromethane solution of  $L^1$  (0.25 g, 0.50 mmol) was added dropwise. The system was stirred for 24 h at this temperature. After cooling to room temperature and filtration, diffusion of diethyl ether into the filtrate led to colourless crystals of 1 suitable for X-ray determination (0.17 g, 51% yield based on the silver salt). Anal. calcd for C<sub>29</sub>H<sub>36</sub>Ag<sub>1</sub>N<sub>7</sub>O<sub>5</sub> (670.51): C, 51.95; H, 5.41; N, 14.62. Found: C, 51.94; H, 5.50; N, 14.66. TG-DTA, Ag<sub>2</sub>O% 18.4; Calc. for Ag<sub>2</sub>O% is 17.3. ESI-MS (DMSO):  $[AgL^1]^+$ : (609.2, 100%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  2.29 (s, 2H, -NCH<sub>2</sub>), 2.55-2.93 (m, 18H, CH2N- and -CH2CN), 3.78 (s, 4H, CH2Ar), 4.52 (s, 4H, O-CH<sub>2</sub>), 7.04 (t, J = 7.2 Hz, 2H, aryl), 7.19 (d, J = 8.0 Hz, 2H, aryl), 7.35 (d, J = 7.2 Hz, 2H, aryl), 7.41 (t, J = 6.4 Hz, 2H, aryl). IR (KBr disc) (cm<sup>-1</sup>): 2930 (s), 2851 (s), 2247 (m), 1601 (m, varyl-H), 1494 (s, varyl-H), 1451 (s), 1383 (vs), 1344 (vs), 1238 (s), 1196 (m), 1122 (m), 1053 (m), 943 (s), 766 (s), 624 (w).

Synthesis of  $[Ag_2(NO_3)_2L^1]_n$  (2). A solution of  $AgNO_3$  (0.17 g, 1.00 mmol) in 10 mL acetonitrile in a 50 mL flask was heated to 55 °C to dissolve the silver salt. A 10 mL dichloromethane solution of  $L^1$  (0.25 g, 0.50 mmol) was added dropwise.

The system was stirred for 24 h at this temperature. After cooling to room temperature and filtration, diffusion of diethyl ether into the filtrate led to colourless crystals of 2 suitable for X-ray determination (0.24 g, 57% yield based on the silver salt). Anal. calcd for C<sub>29</sub>H<sub>36</sub>Ag<sub>2</sub>N<sub>8</sub>O<sub>8</sub> (840.38): C, 41.45; H, 4.32; N, 13.33. Found: C, 41.77; H, 4.36; N, 13.26. TG-DTA, Ag<sub>2</sub>O% 27.3; Calc. for Ag<sub>2</sub>O% is 27.6. ESI-MS (DMSO):  $[AgL^{1}]^{+}$ : (607.6, 100%),  $[Ag(DMSO)_{2}C_{2}H_{5}CN]^{+}$ : (319, 13%),  $[Ag(DMSO)C_2H_5CN]^+$ : (243, 13%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  2.08 (s, 6H, -NCH<sub>2</sub>), 2.28 (s, 2H, -CH<sub>2</sub>N), 2.39-2.72 (m, 12H, CH<sub>2</sub>N- and -CH<sub>2</sub>CN), 3.79 (s, 4H, CH<sub>2</sub>Ar), 4.53 (s, 4H, O-CH<sub>2</sub>), 7.04 (t, J = 7.2 Hz, 2H, aryl), 7.20 (d, J = 8.4 Hz, 2H, aryl), 7.35 (d, J = 6.0 Hz, 2H, aryl), 7.42 (t, J = 7.6 Hz, 2H, aryl). IR (KBr disc) (cm<sup>-1</sup>): 3179 (w), 3114 (w), 3077 (m), 2957 (s), 2927 (s), 2863 (s), 2247 (s), 1601 (vs,  $\nu_{arvl-H}$ ), 1587 (s), 1496 (s,  $\nu_{arvl-H}$ ), 1449 (m), 1384 (m), 1292 (m), 1237 (m), 1124 (s), 1084 (m), 1069 (m), 1054 (m), 1030 (m), 935 (s), 819 (m), 778 (s), 760 (s), 723 (m), 632 (m), 552 (m), 479 (w).

Synthesis of  $\{[Ag_2L^2](NO_3)_2\}_n$  (3). A solution of AgNO<sub>3</sub> (0.085 g, 0.50 mmol) in 20 mL acetonitrile was added to 20 mL of a dichloromethane solution of L<sup>2</sup> (0.25 g, 0.25 mmol). The system was stirred for 24 h, and a colourless solution formed. After filtration, diffusion of diethyl ether into the filtrate led to colourless crystals of 3 suitable for X-ray structural determination (0.12 g, 36% yield based on silver nitrate).

Anal. calcd for  $C_{58}H_{72}Ag_2N_{14}O_{10}$  (1341.02): C, 51.95; H, 5.41; N, 14.62. Found: C, 51.45; H, 5.33; N, 14.50. TG-DTA,  $Ag_2O$  17.3%, calc.  $Ag_2O\%$  17.3%. ESI-MS (DMSO):  $[Ag_2L^2(NO_3)]^+$ : (1278.2, 6%),  $[Ag_2L^2-2CH_2CH_2CN + H^+]^+$ (1109.8, 100%),  $[Ag(DMSO)_2]^+$ : (264.6, 11%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  2.54 (s, 20H, -NCH<sub>2</sub>), 2.74 (t, J = 4.8, 20H, - $CH_2N-$  and - $CH_2CN$ ), 3.46 (s, 8H,  $CH_2Ar$ ), 4.16 (s, 8H, O- $CH_2$ ), 6.89 (d, J = 8.4 Hz, 8H, aryl), 7.26 (d, J = 8.0 Hz, 8H, aryl). IR (KBr disc) (cm<sup>-1</sup>): 2931 (m), 2852 (m), 2830 (m), 2427 (w), 2246 (m), 1611 (vs,  $\nu_{aryl-H}$ ), 1511 (vs,  $\nu_{aryl-H}$ ), 1455 (m), 1384 (vs), 1295 (m), 1235 (vs), 1172 (m), 1108 (m), 1072 (m), 941 (s), 830 (s), 776 (m), 522 (w).

#### X-ray crystal structure determinations

Single crystals of  $L^2$ , 1, 2 and 3 were mounted on glass fibers. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation. Data were collected using omega scans of 0.5° per frame, and full spheres of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT<sup>21</sup> on all the observed reflections. Absorption corrections were applied using SADABS.<sup>21</sup> Structures were solved by direct methods using the SHELXS-97 package<sup>22</sup> and refined with SHELXL-97.<sup>23</sup> Calculations were performed using the WinGX System-Version 1.80.03.24 The atomic positions of some methylene groups of 1 as well as of the O4 and O5 atoms of the nitrate counter-ion were disordered over two orientations and were refined with the use of PART instruction. The occupancies of the two components of each atom were refined to a ratio of 69% and 31%. In spite of this, the C57 and C58 carbon atom had to be refined isotropi-

Table 1 Crystallographic data for compounds  $L^2$ , 1, 2 and 3

FormulaC58HFormula Weight999.2Crystal systemMonoCrystal size (mm)0.40 %	<sub>72</sub> N <sub>12</sub> O <sub>4</sub> 26 oclinic	C <sub>29</sub> H <sub>36</sub> AgN <sub>7</sub> O <sub>5</sub> 670.52	$C_{29}H_{36}Ag_2N_8O_8$	C20H26AgN7O5
Formula Weight999.2Crystal systemMonoCrystal size (mm)0.40 %	26 oclinic	670.52	25 00 20 0	
Crystal systemMoneCrystal size (mm)0.40 ×	oclinic		840.40	670.52
Crystal size (mm) 0.40		Monoclinic	Orthorhombic	Monoclinic
•	$\times 0.30 \times 0.10$	$0.37 \times 0.32 \times 0.26$	0.31  imes 0.20  imes 0.14	$0.41 \times 0.19 \times 0.15$
Space group $P2_1/c$		$P2_1/c$	$Pca2_1$	$P2_1/c$
a (Å) 16.37	77(4)	10.8117(6)	17.614(3)	10.3340(6)
$b(\dot{A})$ 17.14	12(5)	21.4389(13)	11.581(2)	34.337(2)
c (Å) 9.573	B(3)	14.0630(6)	31.048(6)	9.4266(3)
$\beta(\circ)$ 93.61	4(8)	118.699(3)	90	106.526(3)
$V(Å^3)$ 2682.	.3(13)	2859.2(3)	6333(2)	3206.7(3)
<i>Z</i> 2		4	8	4
$D_{\rm calc} ({\rm mg}{\rm m}^{-3})$ 1.237	7	1.557	1.762	1.389
$\mu ({\rm mm^{-1}})$ 0.080	)	0.758	1.300	0.676
F(000) 1068		1384	3391	1384
No. Rfl. unique 5128		8758	15 211	5871
No. Rfl. observed 3850		7525	11 699	5141
R 0.053	33	0.0390	0.0506	0.0408
wR 0.173	37	0.0926	0.1260	0.0915
<i>R</i> for all 0.076	59	0.0473	0.0708	0.0473
wR for all 0.201	.0	0.0997	0.1390	0.0941
GOF 1.026	5	1.032	1.042	1.062
CCDC number 78049	99	936855	842196	780498

cally. In compound 2, the positions of the methylene carbons C27 and C28 were also disordered over two orientations and refined with the use of PART instructions as well, their occupancies being refined to ratios of 73%/27% and 60%/40%, respectively. The positions of the hydrogen atoms bonded to the disordered carbon atoms were included in calculated positions by using the PART instructions in SHELXL and treated as riding atoms. The remaining hydrogen atoms were inserted in calculated positions. Least square refinements, with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms, were employed. CCDC 780498, 780499, 842196 and 936855 contain the supplementary crystallographic data of this study. Crystal data and details of data collections are reported in Table 1.

## **Results and discussion**

The macrocyclic compounds  $L^{1b}$  and  $L^{2b}$  (Scheme 1) were prepared in high yields by [1 + 1] or [2 + 2] condensation of diethylenetriamine with 2,2'-(ethane-1,2-diylbis(oxy))dibenzaldehyde or 4,4'-(ethane-1,2-diylbis(oxy))-dibenzaldehyde, respectively, followed by hydrogenation with KBH<sub>4</sub>, in accordance with a known method.<sup>1,2,19</sup>

The cyanoethyl-functionalized ligands  $L^1$  and  $L^2$  were then obtained by reaction of  $L^{1b}$  or  $L^{2b}$  with acrylonitrile under reflux for 24 h in methanol or ethanol, respectively. They were isolated as air-stable white solids in 90% and 69% yields, respectively, and were characterized by elemental analysis, ESI-MS, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies and single crystal structure X-ray diffraction (for  $L^2$ ). The infrared spectra (KBr disc) show strong bands at 2239 ( $L^1$ ) cm<sup>-1</sup> or 2249 ( $L^2$ ) cm<sup>-1</sup>, which are assigned to  $\nu$ (C $\equiv$ N). Note that these features are in accordance with the formation of the cyanoethylated macrocycles. Other absorption bands corresponding to  $\nu$ (C=C) vibrations from the aryl groups occur, as expected, at *ca.* 1609, 1510 and 1456 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectra of L<sup>1</sup> and L<sup>2</sup> confirm the integrity of the ligands and their stability in solution, also showing the chemical equivalence of the different segments of their structures, as one would expect for this type of system. In fact, the singlets at  $\delta$  4.37 (L<sup>1</sup>) or 4.15 (L<sup>2</sup>) are assigned to the O-CH<sub>2</sub> methylene protons, whereas those at  $\delta$  3.69 (L<sup>1</sup>) or 3.47 (L<sup>2</sup>) are due to Ar-CH<sub>2</sub>-N. The set of signals in the  $\delta$  2.17–2.84 (for L<sup>1</sup>) or 2.35–2.77 (for L<sup>2</sup>) range is attributable to the ethylenic fragments of the pendants. The aryl protons exhibit the expected patterns, and the chemical shifts are also consistent with the proposed structures. In the <sup>13</sup>C spectra, the cyano carbon appears at  $\delta$  119.40 for L<sup>1</sup> and 119.34 for L<sup>2</sup>.

The coordination abilities of  $L^1$  and  $L^2$  towards Ag(1) were studied. The reactions of  $L^1$  with silver nitrate in the 1:1 and 2:1 metal-to-ligand ratios led to the formation of the mononuclear and the polymeric macrocyclic metal complexes [AgL<sup>1</sup>]-(NO<sub>3</sub>) (1) and [Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>L<sup>1</sup>]<sub>n</sub> (2), respectively (Scheme 2). The reaction of  $L^2$  with silver nitrate in a 2:1 metal-to-ligand ratio (corresponding to a 1:1 molar ration for the N<sub>3</sub> motif in this ligand and AgNO<sub>3</sub>) led to the formation of the macrocyclic polymeric compound {[Ag<sub>2</sub>L<sup>2</sup>](NO<sub>3</sub>)<sub>2</sub>}<sub>n</sub> (3) (Scheme 2).

Compounds 1–3 were characterized by elemental analysis, IR, NMR spectroscopies, ESI-MS and single crystal X-ray diffraction. The cyano groups are clearly detected by their IR  $\delta$ (C=N) bands at *ca.* 2247 cm<sup>-1</sup>. In their <sup>1</sup>H NMR spectra, the singlets at  $\delta$  4.52 (1), 4.53 (2) or 4.16 (3) are assigned to the O–CH<sub>2</sub> methylene protons, whereas those at  $\delta$  3.78 (1), 3.79 (2) or 3.46 (3) are due to Ar–CH<sub>2</sub>–N. The set of signals in the  $\delta$  2.55–2.93 (for 1), 2.39–2.72 (for 2) or 2.73–2.76 (for 3) range is attributable to the ethylenic fragments of the pendants, and the aryl groups are located in the range of 7.04–7.41 for 1,



7.04–7.42 for 2 or 6.89–7.26 for 3. Their ESI-MS spectra exhibit the silver-containing fragments  $[AgL^1]^+$  (1 and 2) or  $[Ag_2L^2(NO_3)]^+$  (3). Moreover, for 2 and 3, metallic fragments resulting from the coordination of the solvent (DMSO) are also detected.

Compound  $L^2$  (Fig. 1) crystallized in the monoclinic space group  $P2_1/c$ . Its asymmetric unit contains only half of the molecule, and an inversion centre is located in the middle of the macrocycle. Bond lengths and angles are within the normal ranges. The distances between symmetrically equivalent amine N atoms are 14.511(4), 17.722(5) and 18.302(5) Å, whereas those between the oxygen atoms are 4.182(2) and 7.553(3) Å. The distance of 17.723(5) Å between the two bridgehead amine atoms (N1 and N1A) is shorter than that of the Schiff base compound  $L^{1a}$  (18.890(3) Å).<sup>19b</sup>

The asymmetric unit of compound  $[AgL^1](NO_3)$  (1) comprises one unit of the cationic silver complex and one nitrate as a counterion (Fig. 2). The Ag cation is in a square-pyramidal coordination environment ( $\tau_5 = 0.03$ )<sup>25</sup> with the L<sup>1</sup> ligand connecting the metal by means of the three *N*-amine atoms and



**Fig. 1** ORTEP view of L<sup>2</sup>. Ellipsoids were drawn at 30% probability. Symmetry operation to generate equivalent atoms: (A) -x, 1 - y, 2 - z.



**Fig. 2** ORTEP diagram of  $[Ag(L^1)]^+$  (1) with partial atom numbering scheme. Ellipsoids are drawn at 30% probability. H atoms were omitted for clarity, and only one of the disordered components is shown.



**Fig. 3** ORTEP diagram of  $[Ag_2(NO_3)_2(L^1)]_n$  (2) with partial atom numbering scheme. Ellipsoids are drawn at 30% probability. Symmetry operation to generate equivalent atoms: (A) 1/2 + x, 1 - y, z; (B) x, 1 + y, z; (C) x - 1/2, 1 - y, z. H atoms were omitted for clarity, and only one of the disordered components is shown.

the two oxygen atoms; the silver ion stands in the least-square basal plane formed by the O1, O2, N1 and N3 atoms. The average Ag–O bond length is 2.572 Å and that of Ag–N is 2.474 Å. Intermolecular C–H… $\pi$  interactions (average H…*centroid* of 2.85 Å) could be found in the structure of **1** involving both aromatic rings.

Complex  $[Ag_2(NO_3)_2 L^1]_n$  (2) is a 2D coordination polymer (Fig. 3) extended from a metal-organic coordination macrocycle made up of two silver cations, one  $L^1$  ligand and two nitrate anions. The organic ligand acts as an octadentate  $1\kappa^3 N$ : $\kappa^2 O$ ,  $2\kappa N$ ,  $3\kappa N$ ,  $4\kappa N$  chelator to four silver cations, two of them (Ag1 and Ag3) are included in the cavity of the ligands in a N<sub>4</sub>O<sub>2</sub> octahedral location, whereas the coordination geometries of the other two (Ag2 and Ag4) are better considered as N<sub>2</sub>O<sub>3</sub> square-pyramids ( $\tau_5$  parameters of 0.22 and 0.09, respectively) with the oxygen atoms belonging to coordinated nitrate anions. Thus, one of the nitrate ligands binds the metal in a chelating fashion, whereas the other one is monodentate.

The coordination polymer 2 (Fig. 4) runs along the crystallographic *a* and *b* axis, generating infinite 2D layers made of Ag1 and Ag2 metal cations or of Ag3 and Ag4. Moreover, the 2D framework structure of **2** can be viewed as a net composed of hexametallic 36-membered  $-Ag_6(N_2C_3)_6$ - macrocyclic rings (A in Fig. 4), in which the metal cations are linked by the *meta*positioned cyanoethyl strands of four L<sup>1</sup> ligands; two of them furnish one strand each and the remaining ones furnish two strands. The distances involving the six silver ions in these rings range from 6.620(1) to 15.619(2) Å with the former being the minimum metal…metal intralayer length found in this structure; the minimum interlayer one engages Ag1 and Ag4 and reaches 9.309(2) Å.

The asymmetric unit of  $\{ [Ag_2L^2](NO_3)_2 \}_n$  (3) consists of one silver cation, half of a molecule of the  $L^2$  ligand and a nitrate counter anion, and an inversion centre is then located in the middle of the macrocycle (Fig. 5). The organic group acts as an octadentate  $1\kappa^3 N, 2\kappa^3 N, 3\kappa N, 4\kappa N$  chelator to the silver cations that rest in the distorted square planar  $(\tau_4 = 0.24)^{26}$  N<sub>4</sub> environments, each macrocycle bearing four uncoordinated nitrile strands. The  $L^2$  ligand can be viewed in the role of a bridge connecting to four metal cations, which then extends along the crystallographic b and c axis leading to a zig-zag 2D network (Fig. 6). The structure of 3 presents a more complex architecture as compared with that of 2, derived from hexametallic 58-membered  $-Ag_6(N_2C_3)_4(N_2C_{12}O_2)_2$ - cyclic sets (B in Fig. 6; the cyclic set is also represented in Fig. S1<sup>†</sup>), where the metal---metal distances range from 7.9400(4) (the shortest Ag...Ag distance found in 3) to 25.722(1) Å.



Fig. 4 Packing diagram of 2 viewed down the crystallographic a axis (H atoms were omitted for clarity).



**Fig. 5** ORTEP view of complex  $\{[Ag_2(L^2)]^{2+}\}_n$  (3). Ellipsoids are drawn at 30% probability. Symmetry operation to generate equivalent atoms: (A) 2 - x, -y, 1 - z; (B) x, 1/2 - y, z - 1/2; (C) 2 - x, y - 1/2, 3/2 - z. H atoms were omitted for clarity, and only one of the disordered components is shown.

The Ag–N bond distances in 3 range from 2.247(3) to 2.537(3) Å, the shorter one belonging to the metal–N<sub>nitrile</sub> group. The C=N bond distances of the coordinated and uncoordinated nitrile groups are quite similar [1.136(4) and 1.140(5) or 1.152(7) Å, respectively]. The distances between an amine N atom and its symmetrically equivalent analogue range from 15.676(4) to 16.748(3) Å and those between the oxygen atoms are of 4.487(3) and 5.800(3) Å, therefore indicating a clear shrinking of the cavity of L<sup>2</sup> upon coordination. The two silver ions in the cavity are 14.9270(6) Å apart, which is longer than the distance found in the silver N<sub>8</sub>O<sub>6</sub> cryptand compound (14.666(1) Å).<sup>27</sup>

The TG and DTA curves for complexes 1–3 are shown in Fig. S2 (ESI<sup>†</sup>). The decomposition processes include three major weight losses with the final product being Ag<sub>2</sub>O. In the curve of 1, the first decomposition step (in the range 161–348 °C, 38.9% loss) includes the decomposition of one  $NO_3^-$ , three nitrile strands and one  $-C_2H_4N$  group of L<sup>1</sup>. The second step (temperature range of 348–410 °C) is assigned to the loss (5.8%) of another  $-C_2H_4N$  group. The last step within the range of 432–595 °C (36.8% loss) corresponds to the decomposition of the left-over L<sup>1</sup>. In the case of 2, the first

sharp loss in the range of 169–188 °C is assigned to the decomposition of the two nitrate ligands according to the percentage loss (calc. 14.8% for the two NO<sub>3</sub><sup>-</sup>). The second step of loss (temperature range of 225–337 °C) is assigned to the decomposition of the nitrile strands of L<sup>1</sup> (calc. 19.3% for the three  $-C_3H_4N$  groups). The last step is the decomposition of the left-over part of L<sup>1</sup> (30.0% for  $C_{16}H_{16}N_2O$ ). Compound 3 exhibits a mechanism of thermal decomposition similar to the one presented by 1: the first two steps (40.9% loss) include the decomposition of the two NO<sub>3</sub><sup>-</sup>, six nitrile stands and two  $-C_2H_4N$  groups of L<sup>2</sup>; the last step (41.8% loss) is assigned to the decomposition of the left-over L<sup>2</sup> ( $C_{36}H_{40}N_4O_3$ , calc. 43.0%).

## Electrochemical behaviour

The electrochemical behaviours of complexes 1–3, as well as of ligands L<sup>1</sup> and L<sup>2</sup>, were investigated by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), at a platinum working electrode at 25 °C in a 0.2 M [<sup>*n*</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe solution. Complexes 1–3 exhibit one single-electron (as measured by CPE) irreversible reduction wave at potential values (Table 2) in the 0.06–0.15 V *vs.* SCE range, assigned to the Ag(I)  $\rightarrow$  Ag(0) reduction (wave I<sup>red</sup>). Upon scan reversal, after the cathodic process, an irreversible (with desorption) anodic wave (II<sup>ox</sup>) at 0.32–0.39 V *vs.* SCE (Table 2) is observed, corresponding to the oxidation of cathodically generated metallic silver. In 2, no Ag–Ag interaction through the nitrile bridges<sup>28</sup> was detected by CV, on account of the distance between the silver ions.

1–3 also show one irreversible anodic wave in the range 0.93–1.32 V vs. SCE (Table 2), which can involve the ligands  $L^1$  and  $L^2$ . A typical cyclic voltammogram is exemplified in Fig. 7.



Fig. 6 Crystal packing diagram of 3 viewed down the crystallographic *a* axis (H atoms are omitted for clarity) showing the 2D metal–organic skeletons with trapped nitrate ions.

Compound	$E_{\rm p}\left({\rm I}^{\rm red}\right)$	$E_{\rm p} \left( {\rm I}^{\rm ox} \right)$	$E_{1/2}$ (II <sup>ox</sup> )
L <sup>1</sup>	_	0.74	1.03
$L^2$	_	0.98	1.22
$1^{b}$	0.06	1.32	_
$2^b$	0.15	1.13	_
$3^b$	0.13	0.93	—

<sup>*a*</sup> Potential values in Volt  $\pm$  0.02 *vs.* SCE, in a 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe solution, at a Pt disc working electrode determined by using the [Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup> redox couple ( $E_{1/2}^{\circ x} = 0.42$  V *vs.* SCE<sup>20</sup>) as internal standard at a scan rate of 200 mV s<sup>-1</sup>. <sup>*b*</sup> An anodic wave generated upon scan reversal following the reduction wave is observed at 0.32 (1), 0.34 (2) or 0.39 (3).



**Fig. 7** Cyclic voltammogram of **1** in a 0.2 M [<sup>*n*</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe solution, at a Pt disc working electrode (*d* = 0.5 mm), run at a scan rate of 200 mV s<sup>-1</sup>.\* [Fe( $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup>.



E/V vs. SCE

**Fig. 8** Cyclic voltammogram of  $L^2$  in a 0.2 M [<sup>*n*</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe solution, at a Pt disc working electrode (d = 0.5 mm) and run at a scan rate of 200 mV s<sup>-1</sup>.

In fact,  $L^1$  and  $L^2$  are also redox active, exhibiting a first irreversible oxidation wave at 0.74 and 0.98 V vs. SCE, respectively, followed by a reversible one at 1.03 and 1.22 V vs. SCE, correspondingly (Table 2, Fig. 8).

## Conclusion

Cyanoethyl-functionalized 17- and 42-membered macrocyclic compounds were easily synthesized by [1 + 1] or [2 + 2] condensations of the respective dialdehydes with diethylenetriamine followed by hydrogenation with KBH<sub>4</sub> and functionalization by acrylonitrile. They emerge as convenient *N*,*N*,*N*,*O*,*O*-pentapodal and double *N*,*N*,*N*-tripodal ligands towards silver ions.

Stable Ag(1) complexes were obtained (usually in good yields), two of which (2 and 3) are of a polymeric nature, by simple reactions of silver nitrate with such ligands. They show interesting structures, which are markedly dependent on the molar ratios between the silver salts and the ligands and on the structures of the ligands themselves: 1 is a mononuclear complex; 2 has one silver ion in the cavity of the ligand that is coordinated to another three silver ions by the three functionalized cyanoethyl strands, thus generating an infinite 2D layer structure; 3 displays two silver ions in the cavity of the ligand, which binds other two silver atoms by two cyanoethyl strands and, simultaneously, each silver cation in the cavity accepts a cyanoethyl strand, thereby generating an intricate architecture and extending the structure in infinite 2D zig-zag layers. Their thermal and electrochemical properties were also studied, allowing for comparison of their thermal stability, as well as their redox behaviour. It was also found that L<sup>1</sup> and L<sup>2</sup> are redox active.

Complexes 2 and 3 represent rare examples of stable silver cyanoethyl functionalized coronand polymeric compounds, and the work provides good candidates for further assembly of metal ions with the functionalized macrocyclic compounds and deserves to be extended to other substituted macrocyclic metal complexes in attempts to study metal and ligand substituent effects and to establish structure-composition relationships.

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