Inorganica Chimica Acta 435 (2015) 283-291

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and structural characterization of new N₂O₂-donor Schiff base macrocycles and their silver(I) coordination polymers



Inorganica Chimica Acta

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ARTICLE INFO

Article history: Received 26 February 2015 Received in revised form 5 June 2015 Accepted 10 July 2015 Available online 21 July 2015

Keywords: N₂O₂-donor Schiff base macrocycles Silver(1) coordination polymers Polymeric chain Metallacyclic ring

ABSTRACT

Two N₂O₂-donor macrocyclic Schiff bases **mD1** and **mD2** (**mD1** = 1,5-diaza-2,4:7,8:16,17-tribenzo-9,15dioxa-cyclooctadeca-1,5-dien; **mD2** = 1,5-diaza-2,4:7,8:15,16-tribenzo-9,14-dioxa-cycloheptadeca-1,5dien) were prepared by the [1+1] cyclocondensation reaction of the corresponding dialdehyde and diamine. The reactions of the prepared macrocycles with silver nitrate led to formation of unique (regarding the N₂O₂-donors) silver coordination polymers, AgmD1 and AgmD2. All synthesized compounds were characterized by vibrational spectroscopy (IR), thermal methods (TG/DSC) and the ligands additionally by NMR. The crystal and molecular structures of the macrocycles and the silver coordination polymers were determined by the single crystal X-ray diffraction method. The molecular structure of the macrocycles is found to be rather similar, but with significant differences in the crystal packing arrangement due to slight deviations from planarity. In the complex AgmD1 each silver atom is coordinated by two imino nitrogen atoms of the neighboring ligand molecules and, with an oxygen atom of the nitrate group, thus producing an infinite zig-zag polymeric chain. The silver atoms in AgmD2 are tetrahedrally coordinated with two N-bound ligand molecules and two nitrate anions. This form of coordination produces an additional metallacyclic ring. The polymeric structure is formed through connection of the metallacyclic rings by bridging nitrate anions. Slight deviations in the conformation of the macrocyclic ligands have significant impact upon the coordination mode and topology of the silver coordination polymer structures. © 2015 Elsevier B.V. All rights reserved.

1. Introduction

The chemistry of macrocycles has been an attractive scientific field for almost five decades [1]. The quest for elucidation of naturally occurring processes that involve metal centers is the main driving force that motivates scientists for research in this particular area. The macrocycles are usually prepared for their use as specific binding agents and for complexation of charged and neutral species [1,2]. In addition, the unusual stability of macrocyclic complexes, known as the macrocyclic effect, is one of the major features of these compounds. This feature validates application of macrocycles as sensing agents [3] and selective separating agents [4]. However, for this type of applications, due to the nature of the macrocyclic ligands, endo-coordinated macrocyclic complexes (metal ion is bonded inside macrocyclic cavity) are almost exclusively investigated. Considering this type of coordination and donor set atoms (N, O), a large number of investigations were done

on unsymmetrical macrocyclic systems [5–7], particularly on compartmental macrocycles [8,9]. Another, much less investigated binding mode is the exo-coordination, where the metal ion is linked outside the macrocyclic ring. This type of coordination mode is certainly interesting as a potential synthesis route for construction of macrocyclic coordination polymers and metalloorganic frameworks (MOFs). Consequently, these materials are potentially very interesting as building blocks of porous and biporous MOFs.

In the literature we can identify two major strategic approaches for synthesis of exo-coordinated macrocyclic compounds: (i) replacement of weakly coordinated apical ligands in existing endo-macrocyclic complexes with stronger ligands that are ditopic [10,11] and (ii) design of macrocyclic ligands with exo-oriented electron donor atoms. Until now, the ii strategy was less common and there have been only a few known examples of such compounds. Most of the investigations are dedicated to thioether macrocycles that are suitable for coordination of soft metals [4,12,13].



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Herein, we report the synthesis of two N_2O_2 -donor Schiff base macrocyclic ligands (Scheme 1) and their silver coordination polymers. To our knowledge, the prepared silver coordination polymers are unique examples of macrocyclic coordination polymers with this type of donor set atoms (N, O).

The compounds were identified by means of chemical analysis and characterized by IR and NMR spectroscopy. The thermal properties of the compounds were investigated by TG/DSC method. The molecular and crystal structures were determined by the singlecrystal X-ray diffraction.

2. Experimental

2.1. General methods

All commercially available chemicals were of reagent grade and used as purchased. IR spectra were recorded on Shimadzu FTIR 8400S spectrophotometer using the DRS 8000 attachment, in the 4000-400 cm⁻¹ region. Approximately 3 mg of samples were mixed with 100 mg of KBr (IR grade), placed in the sample cup and FTIR data were collected using diffuse reflectance technique. Thermogravimetric analyses were performed using a simultaneous TGA-DSC analyzer (Mettler-Toledo TGA/DSC 1). The samples (approx. 20–30 mg) were placed in aluminum pans (100 μ L) and heated in a nitrogen atmosphere (200 mL min⁻¹) up to 500 °C at a rate of 10 °C min⁻¹. Complex compounds (AgmD1 and AgmD2) were heated in an oxygen atmosphere (200 mLmin^{-1}) up to 550 °C at a rate of 10 °C min⁻¹. The compound **AgmD1** was additionally treated in oxygen atmosphere up to 150 °C and held at that temperature for 10 min. The data collection and analysis was performed using the program package STAR^e Software 10.0 [14]. Elemental analyses were performed on PerkinElmer 2400 Series II CHNS/O system. All NMR measurements were performed on Varian VNMRS 500 MHz and Varian VNMRS 600 MHz spectrometers (Institute of Organic Chemistry PAS, Warsaw), using a broad band 5 mm probe, equipped with a z-gradient coil. The measurements were carried out in CDCl₃, at room temperature. Signal assignments were achieved on the basis of one-dimensional ¹H NMR and ¹³C NMR spectra, and 2D ¹³C,¹H HSQC and ¹³C,¹H HMBC spectra. ¹⁵N NMR spectra have been acquired using 2D inverse technique (¹⁵N,¹H HMBC). ¹H and ¹³C chemical shifts were given with respect to ¹H and ¹³C signals of TMS (0 ppm). The ¹⁵N chemical shifts were given with respect to the ¹⁵N NMR signal of nitromethane (δ (¹⁵N) = 0 ppm). Prediction of the ¹H and ¹³C chemical shifts were performed using ChemDraw Ultra vs. 12.0. Predicted chemical shifts agree satisfactorily with the experimental values. Experimental and predicted chemical shifts are collected in Fig. S7. The powder X-ray diffraction data were collected by the Philips 1840 X-ray diffractometer with CuKα radiation (1.54056 Å) at 295(2) K. Patterns were collected in the scan range $2\theta = 5-50^{\circ}$ with the step size of 0.03° and at 1.5 s per step.

2.2. X-ray crystallography

The single-crystal X-ray diffraction data were collected at room temperature (294 K) for the macrocyclic ligands (**mD1** and **mD2**) and at 190 K for the silver(I) coordination polymers (AgmD1 and AgmD1) on an Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) using ω -scans. Single-crystals of the coordination polymers decomposed in contact with air and were therefore transferred into mineral oil (Paratone N) and scooped with a plastic loop whereas crystals of the macrocyclic ligands were glued to a thin glass needle. The data reduction was performed using the CrysAlis software package [15]. The structures were solved with the SIR2004 program [16]. Refinement and analysis of the structures were done using the programs integrated within the WinGX system [17]. The refinement procedure was performed by the full-matrix least-squares method based on F^2 against all reflections using SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically except the C atom of dichloromethane and chloroform molecules in AgmD1 which were disordered and were refined isotropically. Restraints were used on these two disordered solvent molecules. The occupation factor of disordered dichloromethane and chloroform molecules refined to 0.75(1) and 0.25(1), respectively. The studied crystal of AgmD1 is a racemic twin with the twin ratio 0.55:0.45. Hydrogen atoms in the structures were placed in calculated positions and refined using the riding model. Geometrical calculations were done using PLATON [19,20] and the structure drawings with ORTEP and MERCURY [21] programs. The crystallographic data are summarized in Table 1.

2.3. Synthesis

Synthesis of dialdehydes **D1**, **D2** and the corresponding macrocyclic ligands (*m***D1** and *m***D2**) was previously reported by Larikova et al. [22]. Herein we report synthesis of the above mentioned compounds under the procedure as follows.

2.3.1. Preparation of the dialdehydes

2.3.1.1. 2-[5-(2-Formylphenoxy)pentoxy]benzaldehyde (**D1**). 10.5 ml (0.1 mol) of salicylaldehyde and 13.9 g (0.1 mol) of K₂CO₃, were mixed in 50 ml of dimethylformamide and the mixture was heated to boiling temperature (153 °C). 6.85 ml (0.05 mol) of 1,5-dibromopentane were dissolved in 10 ml of dimethylformamide and slowly added to the mixture of salicylaldehyde and K₂CO₃. The mixture was refluxed at boiling temperature for 4 h and stirred at room temperature for additional 3 h. After the reaction was completed, approximately 500 ml of water were added and the resulting precipitate was filtered and washed with water. The product was recrystallized from absolute ethanol. Yield: 51%. IR ν_{max} (cm⁻¹): 2947(m), 2873(m), 1678(s), 1600(s), 1242(s), 1012(m), 765(s). Melting point: 66 °C (DSC, from EtOH).



Scheme 1. Representation of ligands mD1 and mD2.

Crystallographic data and structure refinement details for all compounds.

| Compound | mD1 | mD2 | AgmD1 | AgmD2 |
|---|----------------------|----------------------|--|--|
| CCD number | 1039600 | 1039601 | 1039602 | 1039603 |
| Formula | $C_{25}H_{24}N_2O_2$ | $C_{24}H_{22}N_2O_2$ | C ₂₆ H _{25.75} Ag Cl _{2.25} N ₃ O ₅ | C ₄₈ H ₄₄ Ag ₂ N ₇ O ₁₃ |
| Formula weight | 384.46 | 370.44 | 647.88 | 1142.64 |
| Crystal system | monoclinic | monoclinic | orthorhombic | monoclinic |
| Space group | P 2 ₁ /n | P 21/c | $P 2_1 2_1 2_1$ | C 2/c |
| T (K) | 294(2) | 294(2) | 190(2) | 190(2) |
| a (Å) | 15.493(1) | 15.671(1) | 8.2540(4) | 12.0290(3) |
| b (Å) | 7.889(7) | 7.4720(7) | 15.7340(6) | 19.8230(5) |
| <i>c</i> (Å) | 16.783(1) | 33.315(2) | 20.5940(8) | 18.9490(5) |
| β(°) | 91.136(9) | 92.029(6) | | 91.619(2) |
| $V(Å^3)$ | 2050.9(3) | 3898.5(3) | 2674.51(19) | 4516.6(2) |
| Ζ | 4 | 8 | 4 | 4 |
| $D_{\rm calc} ({\rm g}{\rm cm}^{-3})$ | 1.245 | 1.262 | 1.609 | 1.680 |
| μ (mm ⁻¹) | 0.079 | 0.081 | 1.020 | 0.944 |
| F(000) | 816 | 1568 | 1312 | 2316 |
| Total data | 13174 | 26701 | 9834 | 16793 |
| Number of unique data | 4009 | 7634 | 5657 | 4877 |
| Number of parameters | 262 | 536 | 348 | 317 |
| Flack parameter | | | 0.55(7) | |
| R_1^{a} , $[F_o \ge 4\sigma (F_o)]$ | 0.0654 | 0.0757 | 0.0601 | 0.0378 |
| wR_2^{b} | 0.1192 | 0.1170 | 0.1555 | 0.0942 |
| Goodness of fit on $F^2(S)$ | 1.063 | 1.072 | 1.065 | 1.091 |
| Minimum and maximum electron density (e ${\rm \AA}^{-3})$ | 0.114; -0.134 | 0.161; -0.138 | 1.070; -0.820 | 0.614; -0.811 |

^a $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$.

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

Table 2

Dihedral angles between benzene rings in mD1 and mD2.

| Compound | A/B | A/C | B/C |
|---|----------------------------------|----------------------------------|----------------------------------|
| mD1 mD2 (conformer 1) mD2 conformer 2 (major part of disordered C | 53.1(1)° 16.6(1)° 17.3(1)° | 59.4(1)° 26.2(1)° 24.3(4)° | 56.1(1)° 21.3(1)° 14.3(4)° |
| conformer 2 (minor part of disordered C ring) | | 30.4(4)° | 26.7(6)° |

2.3.1.2. 2-[4-(2-Formylphenoxy)butoxy]benzaldehyde (**D2**). K₂CO₃ 13.9 g (0.1 mol) and salicylaldehyde 10.5 ml (0.1 mol) were mixed in 50 ml of dimethylformamide. The mixture was brought to the reflux temperature and 5.97 ml (0.05 mol) of 1,4-dibromobutane dissolved in 10 ml of dimethylformamide were then added. The reaction mixture was refluxed for 5 h and then stirred at room temperature for additional 3 h. Approximately 500 ml of water was added to the reaction mixture. The resulting precipitate was filtered and washed with water. The product was recrystallized from absolute ethanol. Yield: 55%. IR v_{max} (cm⁻¹): 2954(m), 2876(m), 1675(s), 1600(s), 1244(s), 1011(m), 754(s). Melting point: 108 °C (DSC, from EtOH).

2.3.2. Preparation of the ligands

2.3.2.1. Preparation of mD1. 0.625 (2 mmol) g of dialdehyde D1 were dissolved in 40 ml of absolute ethanol and 0.274 ml (2 mmol) of triethylamine were added to this solution. The solution was heated to reflux temperature (78 °C) and 0.243 g (2.5 mmol) of *m*-phenylendiamine dissolved in 25 ml of absolute ethanol were gradually added. Resulting solution was heated at reflux temperature for 3 h. After the reaction was completed the suspension was left at room temperature for 24 h. Needle-like crystalline product was filtered. Single crystals suitable for X-ray diffraction experiments were obtained directly from the reaction mixture. The product was recrystallized from chloroform. Yield: 80%. Anal. Calcd for C25H24N2O2: C, 78.1; H, 6.29; N, 7.29; Found: C, 77.7, H, 6.27; N, 6.84%. IR v_{max} (cm⁻¹): 2933(m), 2883(m), 1614(m), 1600(s), 1575(s), 1458(s), 1269(s) 1244(s), 1055(m), 804(m), 754(s). Melting point: 272 °C (DSC, from CHCl₃). NMR data are given in Figs. S7a, S13-S18.

2.3.2.2. Preparation of **mD2**. The macrocyclic ligand **mD2** was prepared by dropwise addition of *m*-phenylenediamine 0.243 g (2.5 mmol) dissolved in 25 ml of absolute ethanol to the ethanol solution of dialdehyde **D2** 0.625 g (2 mmol) and triethylamine 0.274 ml (2 mmol). The resulting solution was heated at the reflux temperature for 3 h. After cooling, a pale yellow suspension was formed. This suspension was left at room temperature for 2 weeks, during which time larger crystals gradually formed. Single crystals suitable for X-ray diffraction experiments were obtained directly from the suspension mixture. Yellow product was recrystallized from dichloromethane/methanol mixture to obtain pale yellow powder. Yield: 45%. Anal. Calcd for C₂₄H₂₂N₂O₂: C, 77.81; H, 5.99; N, 7.56; Found: C, 77.93, H, 5.96; N, 7.51%. IR v_{max} (cm⁻¹): 2955(m), 2875(m), 1615(m), 1600(s), 1574(s), 1240(s), 1456(s), 1041(m), 802(m), 755(s). Thermal decomposition: 405 °C (DSC, from DCM/MeOH). NMR data are given in Figs. S7b, S13-S22.

2.3.3. Preparation of the silver(I) coordination polymers

2.3.3.1. Preparation of $\{Ag[mD1(NO_3)]\)$ -dichloromethane-chloroform $(1/0.75/0.25)\}_n$ (AgmD1). The silver coordination polymer of mD1 was obtained by mixing a dichloromethane solution of ligand mD1 19.2 mg (0.05 mmol) with a methanol solution of silver nitrate 8.45 mg (0.05 mmol). The reaction was performed at room temperature in a U-shaped tube, using chloroform as the diffusion reagent. After 24 h single crystals suitable for diffraction experiments were obtained. The crystals decompose in contact with air. The analysis was done for crystals without solvent molecules. Anal. Calc. for C₂₅H₂₄AgN₃O₅: C, 54.17; H, 4.36; N, 7.58; Found: C, 54.24, H, 4.36; N, 7.42. IR v_{max} (cm⁻¹): 1601(m), 1383(s), 433(w).

2.3.3.2. Preparation of $\{Ag_2[(mD2)_2(NO_3)_3]\}_n$ (AgmD2). 0.1 mmol (37 mg) of mD2 was dissolved in a small amount of dichloromethane and heated. The resulting solution was added to a heated methanol solution of silver nitrate 16.9 mg (0.1 mmol). The yellow solution was cooled to room temperature and filtered. The filtrate was placed in a 10 ml vial and diethylether was diffused into the filtrate. After two weeks color of the solution changed into dark red, and brown hexagonal crystals suitable for diffraction experiments appeared on the edges of the vial. The crystals are unstable

in contact with air, however more stable than **AgmD2**. Anal. Calc. for: $C_{48}H_{44}Ag_2N_7O_{13}$ C, 50.42; H, 3.88; N, 8.58. Found: C, 50.26, H, 3.95; N, 8.22; IR v_{max} (cm⁻¹): 1601(m), 1383(s), 416(w).

3. Results and discussion

3.1. Synthesis

The macrocycles were prepared by the [1+1] cyclocondensation reactions of a dialdehyde and diamine, with a relatively high yield. It should be noted that these reactions do not require employment of the high dilution technique or presence of a template. Furthermore, the preliminary investigations indicate that the synthesis of these macrocycles can be achieved by simple mechanochemical synthesis or by simple mixing of the ethanolic reactant solutions at room temperature.

Silver coordination polymers with the prepared macrocycles were obtained by slow diffusion of the reactant solution through a liquid membrane.

3.2. IR spectroscopy

The IR spectra of the prepared ligands are rather similar. The stretching vibrations of the imine group in the ligands **mD1** and **mD2** appears at 1614 and 1615 cm⁻¹, respectively. The stretching vibrations of the aliphatic C–H are in the region 2945–2874 cm⁻¹. Also, both spectra exhibit strong vibration bands at 1269 cm⁻¹ (**mD1**) and 1240 cm⁻¹ (**mD2**) that are assigned to stretching vibration of the C_{aromatic} –O– $C_{\text{aliphatic}}$ group. C–H bending vibration bands of the *meta* and *ortho* substituted benzene rings

appear in the region 804–752 cm⁻¹. Both spectra are free of vibration bands related to the primary amino and aldehyde groups.

In comparison to the IR spectra of the ligands, spectra of the silver complexes show very strong absorption maxima close to 1385 cm⁻¹, corresponding to the stretching vibrations of the nitrate anion. The stretching vibrations of the imino group in the complexes are shifted to slightly lower values in comparison to the ligand (red shift). This observation indicates that the imino group is involved in the formation of metal-ligand bond. The Ag-N stretching vibrations in **AgmD1** and **AgmD2** appear at 433 cm⁻¹ and 416 cm⁻¹, respectively [23]. Other vibrations previously described in the uncoordinated ligands do not show any significant changes. IR spectra of ligands and complexes can be found in ESI (Figs. S1–S4).

In order to investigate influence of the nitrate anion on the interactions within the polymeric structure, compound **AgmD1** was thermally treated in an oxygen atmosphere up to 150 °C for 10 min. The IR spectrum of the thermally treated coordination polymer **AgmD1**, represented in Fig. S5, indicates absence of the vibrations typical for the nitrate anion (vibrations close to 1380, 830 and 690 cm⁻¹). Other vibrations observed in the thermally untreated **AgmD1** are found to be present in the spectrum of the thermally treated compound.

3.3. NMR spectroscopy of the ligands

The assignment of NMR signals was performed on the basis of 1D and 2D NMR spectra. Some dubious assignments concerning the signal order in the phenol ring were explained by chemical shifts prediction using the ChemDraw module. Observed NMR data fully confirmed the structures of the ligands. Unfortunately, we were not able to acquire NMR spectra of the Ag complexes, due



Fig. 1. TG (full lines) and DSC (dashed lines) curves of AgmD1 (red) and AgmD2 (blue) recorded in oxygen atmosphere. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to their decomposition in solution and precipitation of an insoluble material. Additional information regarding the NMR results of the ligands can be found in the Supplementary material (Figs. S13–S22).

3.4. Thermal analysis (TG/DSC)

The samples of ligands **mD1** and **mD2** were heated from 25 to 500 °C in a nitrogen atmosphere. The silver coordination polymers were heated in reactive atmosphere of oxygen from 25 to 550 °C. Thermoanalytical data for the ligands are represented in Table S1. The TG curve of **mD1** indicates that the compound is stable up to 336 °C. Thermal decomposition occurs in one step which is accompanied by a 68% mass loss. The DSC curve of **mD1** shows two distinctive peaks. The endothermic peak at 272 °C can be attributed to the melting point of the compound. The second, exothermic peak at 407 °C is related to thermal decomposition of the compound. The TG curve of **mD2** reveals a continuous mass loss between 345 and 500 °C. Furthermore, the DSC curve of the same compound shows a broadened exothermic peak at 405 °C that is related to thermal decomposition.

Thermoanalytical data for the complexes (AgmD1 and AgmD2) are given in Table S1 and the corresponding curves are presented in Fig. 1. Measurements of AgmD1 were done on decomposed crystals of since the solvent molecules leave the crystals upon standing at room temperature. The TG curve of AgmD1 shows thermal degradation in three steps. The first step is accompanied by a mass loss of 2.6% and a sharp exothermic peak on the DSC curve. The second step occurs in the temperature interval from 150 to 270 °C with a mass loss of 8.5%. The mass loss of the first two thermal events can be attributed to the loss of the nitrate group (calc. 11.6; found 11.1%). Afterwards, the TG curve shows continuous weight loss between 273 and 550 °C accompanied by a strong broad exothermic peak on the DSC curve corresponding to thermal decomposition of the ligand. The residual mass (22.4%) is elemental silver as found by powder diffraction (calc. 19.5%, assuming that the remaining solid is elemental Ag) [24]. The TG curve of AgmD2 exhibits thermal degradation in two steps. First step shows mass loss of 12.6% and is accompanied by a sharp exothermic peak on the DSC curve. This step can be attributed to the thermal decomposition of two loosely bound nitrate anions (calc. 10.8%). The second step occurs in the temperature range of 247-550 °C, with several broad exothermic peaks detected on the DSC curve. This step corresponds to the thermal decomposition of the ligand and the third (bridging) nitrate group. The residual mass (18.2%) is elemental silver (calc. 18.6%). The melting points of the coordination polymers were not observed and individual TG/DSC curves are given in ESI (Figs. S8–S11).

The results of thermal analysis indicate importance of the nitrate anion in the structure of the coordination polymers. As it can be seen (Fig. 1), the nitrate group in AgmD1 decomposes at a significantly lower temperature then the nitrate group in AgmD2. The results of thermal analysis of thermally treated AgmD1, represented in Fig. S12, indicate absence of the nitrate anion in the thermally treated compound. Thermal decomposition of the ligand is shifted to a lower temperature (242-458 °C) in comparison to the untreated compound, which may be caused by weaker connectivity of the polymeric chains due to absence of the nitrate group. From the results of IR spectroscopy of treated **AgmD1** it can be supposed that the polymeric structure of the compound is present (at least partially) even without presence of the nitrate anion. However, the powder diffraction data of thermally treated AgmD1 display only diffraction maxima that are assigned to elemental silver (Fig. S25) indicating that crystallinity of the complex is lost and that partial decomposition occurs. In the case of AgmD2, the polymeric structure is most probably destroyed upon thermal decomposition of the nitrate groups and therefore the structural integrity of this compound is strongly dependent upon presence of anionic species. In addition, the thermal analysis of these compounds is in very good agreement with the crystal structure studies, i.e., silver–ligand bond lengths.

3.5. Crystal structure of ligands mD1 and mD2

The single crystals of both ligands were obtained directly from the reaction mixture. Conformation of the free oxa-aza macrocycles can be described by considering the orientation of the potential donor atoms, torsion angles associated with these atoms, distance between donor atoms etc. [25]. The above mentioned factors can have a strong effect upon the complexation abilities of the macrocyclic system and thus can influence stability of the derived complexes [4,26]. Theoretical studies [27] have shown that the most stable conformation of donor atoms in the oxa-aza macrocycles is when the oxygen atoms are oriented in an endodentante manner and the nitrogen in an exodentante. This, energetically favorable state can occasionally be altered by coordination of the cation, through conformational switching [28,29]. metal Furthermore, macrocycles can be described in terms of the shape of the molecule and ring puckering. Also it is convenient to describe a macrocyclic ligand by considering the number of atoms in the inner macrocyclic ring and the approximate inner hole size. Selected bond lengths, valence angles and torsion angles for the synthesized ligands are listed in Table S2, and the molecular



Fig. 2. ORTEP plot of **mD1** and **mD2** with displacement ellipsoids of non-hydrogen atoms drawn at the 50% probability level. A, B and C represent aromatic rings.



Fig. 3. Representation of crystal packing in *m***D2**. Blue colored molecules are conformer **1** and red conformer **2**. $\pi \cdots \pi$ interactions of benzene rings in conformer **2** is denoted with violet ellipses. Hydrogen atoms are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. (a) ORTEP plot of AgmD1 with displacement ellipsoids of non-hydrogen atoms drawn at 50% probability level. Only the major dichloromethane solvent molecule is shown. (b) Local coordination geometry of AgmD1 (T-shaped).

structures are represented in Fig. 2 (molecular structure of the conformer 2 molecule is represented on Fig. S6).

Both molecules crystallize in the monoclinic crystal system with Z = 4 and Z = 8 for **mD1** and **mD2**, respectively. Both molecules are tetradentante N₂O₂ macrocyclic Schiff bases with 18 (mD1) and 17 (mD2) atoms in the inner macrocyclic ring. The average hole size in **mD1** is in the interval of 2.44–2.61 Å and 2.35– 2.44 Å for **mD2**. The asymmetric unit of **mD2** is composed of two symmetrically independent conformers, denoted as conformer 1 and conformer **2**. The two conformers are different regarding the orientation of the aliphatic chain and dihedral angles between the benzene rings. Also, in conformer 2, the C18-C23 benzene ring is disordered over two positions with an occupancy factor of 0.52(2). In regard to the orientation of donor atoms the nitrogen atoms are exo-oriented and oxygen atoms endo-oriented, in both molecules. The distances between nitrogen atoms are almost identical in both macrocyles due to the rigidity of the *m*-phenylenediamine precursor. As it can be seen from dihedral angles between the benzene rings (Table 2), there is a more pronounced deviation from planarity in **mD1** then in **mD2**. The **mD1** molecule is in the partial-cone (saddle) conformation that is typical for some other 18-membered macrocyclic compounds [30]. The deviations from planarity can also be seen from analysis of the puckering amplitude of **mD1** and **mD2** (1.843(3)Å and 1.299(4), respectively) [31]. In both ligands the aliphatic chain is arranged in the trans conformation.

In the crystal, the macrocyclic molecules are primarily linked through $\pi \cdots \pi$, C–H··· π and C–H···N interactions. The described deviations of the overall planarity in **mD1** and **mD2** have a significant impact upon the crystal structure arrangement. In **mD1**, the molecules are linked along the crystallographic axis *b* by weak C14–H14A··· π (centroid of C) and C18–H18B··· π (centroid of B) interactions. Due to flattening of the macrocyclic ring in **mD2** (see dihedral angles in Table 2), the benzene rings are connected

via strong $\pi \cdots \pi$ interactions along the crystallographic axis *a*. These interactions are primarily observed between conformer **2** molecules (benzene ring **C**). Furthermore, conformer **1** molecules are linked by weak C-H···N interactions (C17-H17A···N1) along axis *b*. The same type of C-H···N interaction is observed in conformer **2** (C14A-H14D···N2A). Conformer **1** and conformer **2** molecules are linked through a series of weak van der Waals contacts along the *c*-axis (Fig. 3). Hydrogen bond interactions of macrocyclic ligand molecules are summarized in Table S3.

The *Cambridge Structural Database* [32] was searched for related derivatives containing uncoordinated Schiff base macrocyclic ligands containing benzene rings in order to compare crystal packing peculiarities of the ligands. The search resulted with only 2 relevant hits [27,33] in which the molecules exhibit similar weak C-H··· π and C-H···N interactions as in **mD1** and **mD2**.

3.6. Crystal structure of the silver coordination polymers

3.6.1. Crystal structure of AgmD1

X-ray analysis of **AgmD1** has shown that the compound crystallizes in monoclinic crystal system, non-centrosymmetric space group $P \ 2_1 2_1 2_1$. The crystal structure of **AgmD1** is shown in Fig. 4a and the selected bond lengths and angles are presented in Table S4. The asymmetric unit is comprised of one silver atom, one ligand, a coordinated nitrate anion molecule and disordered dichloromethane and chloroform molecules in the ratio of 0.75:0.25 (Fig. 4a).

Each silver atom is coordinated by imino nitrogen atoms of two neighboring ligand molecules and, in addition, with the oxygen atom of the nitrate group (Fig. 4b). This mode of coordination produces an infinite, polymeric structure along the crystallographic axis *b*. The coordination geometry around the silver atom can be described as T-shaped (Fig. 4b), with the N1-Ag-N2 angle slightly deviating from linearity (170.6(2)°) and with the N1-Ag1-O3 and N2-Ag1-O3 angles almost orthogonal (96.4(2)° and 92.4(2)°). The

Ag-N bond distances are identical (2.185(5) and 2.186(5) Å), thus indicating strong coordination of the ligand to the metal center. The nitrate group is loosely bound to the silver center with the Ag-O distance of 2.537(6) Å. Oxygen atoms of ligand remain endo-oriented and do not participate in coordination. There are no significant changes in the conformational or geometrical parameters of the macrocyclic ligand in comparison to free **mD1**.

Due to a slight deviation of the N1-Ag1-N2 angle from linearity and a bowl shape of the macrocyclic ligand the polymeric chain is not linear and can be described as a 1D zig-zag chain typical for some other silver coordination polymers (Fig. 5a) [34].

Two neighboring polymeric chains are connected through nitrate group via a series of weak C–H···O interactions along the *a*-axis (light blue lines in Fig 5b). These interactions form a 2D ribbon-like network with empty spaces in which dichloromethane or chloroform molecules are incorporated. The solvent molecules are linked by C–H···O and Cl···O interactions to the nitrate ion and Cl··· π interactions (C1–C6 benzene ring) to the ligand molecule. The hydrogen bond interactions in **AgmD1** are given in Table S6.

3.6.2. Crystal structure of AgmD2

The crystal structure of **AgmD2** is shown in Fig. 6 and the selected bond lengths and angles are presented in Table S5. The asymmetric unit is composed of the Ag atom, one ligand molecule, the monodentate nitrate anion and half of the bridging bidentate nitrate anion. Each silver atom is coordinated by two ligand molecules and two nitrate anions. The second ligand molecule is generated by symmetry of the inversion center ((i) -x, -y, -z). This symmetry related molecules form a metallacyclic ring along with the two silver atoms. The metallacyclic ring is comprised of two symmetrically related silver atoms, four imino nitrogen atoms (donor atoms) and two *m*-phenylenediamine moieties. The separation of two silver atoms (Ag1 \cdots Ag1^{*i*}, 7.5316(4) Å) is far beyond any argentophilic interactions [35]. The polymeric structure is generated by connection of two metallacyclic rings through the bridging



Fig. 5. (a) Representation of 1D zig-zag chain in **AgmD1** (dichloromethane, chloroform and hydrogen atoms are omitted for clarity). (b) Representation of C-H···O and Cl···O intermolecular interactions (light blue lines) of two neighboring polymeric chains and dichloromethane solvent molecules in **AgmD1** (chloroform molecules are not represented). View down the *c*-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. ORTEP plot of **AgmD2** with displacement ellipsoids of non-hydrogen atoms drawn at 50% probability level. (i) -x, -y, -z; (ii) -x, y, $\frac{1}{2} - z$.

nitrate ion, approximately along the [1-1-3] crystallographic direction. The local coordination environment around each silver center is distorted tetrahedral, with the angles around the silver atom ranging from 76.6(1)° to 123.0(1)°. The Ag-N (Ag1-N1 2.316(2), Ag1-N2 2.349(3)Å) bond distances are considerably elongated and the Ag-O_(nitrate) (Ag-O3 2.4122(9), Ag-O5 2.473(3)Å) are somewhat shorter in comparison to **AgmD1** thus indicating stronger binding of the nitrate anion to the metal center. Nevertheless, both bond distances and angles are within the normal range and comparable to other tetrahedral silver complexes [36]. It should be noted that only conformer **2** of **mD2** is present in the structure of the silver complex. There are no significant changes in geometrical parameters of the ligand in comparison to the free conformer.

The Ag-O_(bridging)-Ag angle is $147.9(1)^{\circ}$ and, therefore, the polymeric chain can be described as non-linear. As it is represented in Fig. 7a the polymeric chain propagates in a 1D sinusoidal manner [37].

Within the crystal structure, the two neighboring sinusoidal chains are interconnected by a series of weak C-H···O interactions along the crystallographic *c* axis that involve monodentate nitrate groups. Furthermore, the bridging nitrate groups and ether oxygen atoms also participate in the intermolecular arrangement by a series of C-H···O interactions along the crystallographic *b*-axis (Fig. 7b, Table S7). These interactions are stacking molecules in the crystal rather densely, so there are no solvent accessible voids, unlike in the case of **AgmD1**.

In addition, it is appropriate to describe the role of the nitrate anion in long-range structural order of the coordination polymers. Nitrate anion has the ability to act as a monodentate and a polydentate ligand, as in **AgmD1** and **AgmD2**, respectively. It can also function as an intermolecular linkage between discrete polymeric chains that can influence long-range order and properties (i.e., porosity) of coordination polymers and MOFs [38]. Recently, it was reported that the nitrate anion can build polymeric structures via hydrogen bond interactions which additionally expand its role in design of coordination polymers [39].



Fig. 7. (a) Representation of 1D sinusoidal chain in **AgmD2** (hydrogen atoms are omitted for clarity) (b) Representation of C–H···O intramolecular interactions (black lines) of neighboring polymeric chains in **AgmD2**. Silver atoms are represented by spheres in **7a** and **7b**.

Considering the intermolecular interactions, the oxygen atoms of the nitrate anion act as hydrogen acceptors, and usually form weak intra/intermolecular C–H \cdots O interactions with aromatics that stabilize the 3D structure of the coordination polymers [40–44], as the nitrate anion in **AgmD1** and **AgmD2**.

3.7. PXRD studies of the silver coordination polymers

The powder diffraction pattern of **AgmD2** is consistent with the simulated one based on the solved crystal structure thus confirming the purity of sample (Fig. S23). The crystals of **AgmD1** decompose at room temperature since the solvent molecules leave the crystal. This is further enhanced by grinding the single crystals for powder diffraction, therefore the diffraction pattern is poorly resolved with low intensity peaks and it was not possible to confirm purity of the bulk material by this method (Fig. S24).

4. Conclusions

Two N₂O₂-donor macrocyclic Schiff bases **mD1** and **mD2** were prepared and their reactions with silver nitrate led to the formation of silver coordination polymers, **AgmD1** and **AgmD2**. The prepared polymers are unique examples of coordination polymers with macrocycles containing this type of donor set atoms. The single crystal structure studies revealed different mode of coordination around silver atoms, linear and tetrahedral for **AgmD1** and **AgmD2**, respectively. The differences in coordination behavior and conformation of the ligands subsequently influence the topology of the polymeric chains.

Appendix A. Supplementary material

CCDC 1039600–1039603 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.07.016.

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