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Coordination Polymers of Polycarboxylates: Design, Synthesis and Structures

PhD thesis abstract

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Key Words:

- Polycarboxylate ligands
- Complexes as building blocks
- Coordination polymers
- Transition metals
- Hydrothermal
- TG/DTA

1 *Introduction*

The chemistry of coordination polymers has received much attention during the last decade not only due to their fascinating architectures but also due to their applications in many fields like: catalysis, gas storage, magnetism, ion exchange and non−linear optics.

For the synthesis of coordination polymers, multidentate ligands are suitable, that contain several donor sites which allow the extension of the structure of the polymer in one, two or three directions. Among them, polycarboxylate ligands have received special attention. Two kinds of polycarboxylate ligands have been generally used in the field of coordination polymers: either flexible ligands like succinic or glutaric acid and analogous compounds, or rigid ligands such as benzenedicarboxylate, benzenetricarboxylate and so on. A lesser amount of work has been reported using polycarboxylate ligands which combine the characteristics of both flexibility and rigidity. Therefore, the objectives of this work focused on studying the coordination chemistry towards transition metals of polycarboxylate multidentate ligands which present a semiflexible behavior such as 1,4−phenylenebis(oxy)diacetic acid, 1,2−phenylenebis(oxy)diacetic acid and the hybrid multidentate ligands 1,2− phenylenebis(thio)diacetic acid and *N,N,N'N'* − 1,2− phenylene − diaminetetraacetic acid which contain different donor sites (S, O and N, O, respectively) being in this way suitable for selective coordination to specific transition metals.

The first part of the thesis (**Chapter 2**) presents literature data concerning these ligands, their steric properties as well as their coordination chemistry with accent on transition metals complexes, as well as generalities about the synthesis of coordination polymers, their chemical and structural diversity and applications. While the coordination chemistry of 1,4−phenylenebis(oxy)diacetic acid has received a lot of attention in recent years, much less is known about the coordination chemistry of the 1,2−substituted polycarboxylate ligands.

Although molecular self−assembly is a promising route to synthesize coordination polymers, the controlling factors and experimental conditions for the preparation of the polymers are not yet completely understood. In recent years, a rational synthetic approach for the assembly of the target structures from molecular building blocks has been taken into consideration. The key step in the rational approach is the design of molecular building blocks which can direct the formation of the desired architecture and functionality of the target compound. The synthesis of mononuclear building blocks for the rational preparation of coordination polymers was also taken into consideration in this work.

Chapter 3 presents the synthesis of the ligands according to literature methods as well as the molecular structure of 1,2−phenylenebis(thio)diacetic acid.

Beginning with the fourth chapter the original contributions regarding the synthesis and characterization of molecular building blocks, the synthesis and characterization of new coordination polymers of transition metals as well as the synthesis and characterization of heterobimetallic (Ca/Zn, Ca/Ni and Cd/Ag) and mixed ligand (polycarboxylate/4,4'−bipyridine) coordination polymers are presented.

In **Chapter 4** the synthesis and characterization of a silver complex of 1,2−phenylenebis(oxy)diacetic acid, a nickel complex of 1,2−phenylenebis(thio)diacetic acid and a palladium complex of *N,N,N'N'*−1,2−phenylene−diaminetetraacetic acid as well as a tetranuclear palladium complex are discussed as potential building blocks for the rational synthesis of coordination polymers.

In **Chapters 5−8** the synthesis and characterization of coordination polymers starting from the polycarboxylate ligands are presented. The general preparation procedures are described. A number of seven cadmium, one copper, one zinc, three nickel and two manganese as well as two heterobimetallic calcium/zinc and calcium/nickel coordination polymers were synthesized but also a manganese binuclear complex starting from 1,2−phenylenebis(thio)diacetic acid. All compounds were obtained in hydrothermal conditions except one cadmium coordination polymer starting from 1,2−phenylenebis(oxy)diacetic acid which was obtained at room temperature. All synthesized compounds were characterized by X−ray crystallography. Except the cadmium coordination polymer obtained at room temperature and the heterobimetallic Ca/Ni polymer which could not be reproduced, all compounds were structurally characterized by IR spectroscopy and elemental analysis. The thermal behavior of eleven polymers has also been studied by thermogravimetric/differential thermal analysis (TG/DTA), the results being presented in **Chapter10**.

Chapter 9 is dedicated to the use of building blocks as starting materials for the rational synthesis of coordination polymers. The synthesis and structural characterization of a heterobimetallic Cd/Ag coordination polymer is presented.

The last chapter (**Chapter 11**) includes the experimental part and it is followed by General Conclusions, Appendix and List of Publications. The Appendix contains the list of abbreviations and tables with crystallographic data.

2 *Generalities*

What are Coordination Polymers?

Coordination polymers which are also known as metal−organic coordination networks (MOCNs), hybrid organic−inorganic frameworks or metal−organic frameworks (MOFs) are metal−ligand compounds that extent infinitely in at least one, two or three dimensions (1D, 2D or 3D, respectively) via metal−ligand bonding (Figure 1).[1]

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[1] A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; S. Kitagawa and K. Uemura, *Chem. Soc. Rev.* 2005, **34**, 109; S. Bureekaev, S. Shimomura and S. Kitagawa, *Sci.*

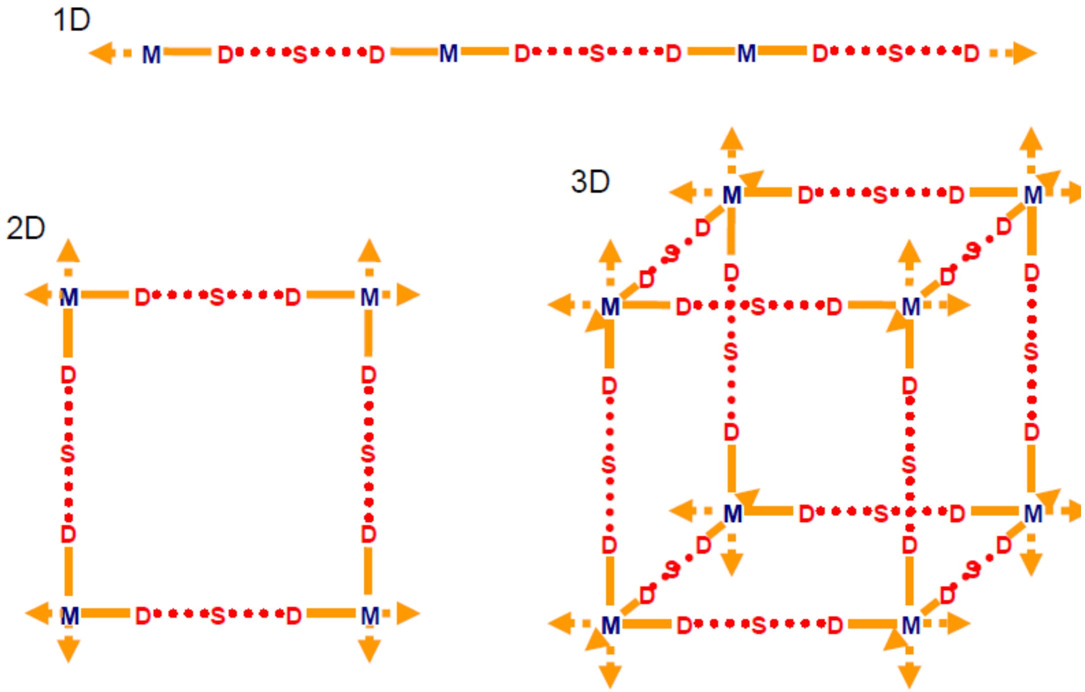

Figure 1 Dimensionality of the coordination polymers (M = metal ions, D = donor groups of the ligand, S = spacer within the ligand)

Technol. Adv. Mater. 2008, **9**, 014108; B. Moulton and M. J. Zawarotko, *Chem. Rev.* 2001, **101**, 1629; S. Noro, S. Kitagawa, T. Akutagawa and T. Nakamura, *Progress in Polymer Science*, 2009, **34**, 240

Weaker non−covalent interactions such as hydrogen bonding or π−π stacking have an important role in the packing pattern of the one−dimensional chains, two−dimensional nets and three−dimensional frameworks.[2]

4. Synthesis and molecular structure of monomeric complexes as building blocks

Starting from the polycarboxylate ligands several transition metal complexes were synthesized and characterized as potential buiding-blocks for the rational synthesis of coordination polymers.

4.1 Synthesis of $[Ag_2\{1,2-(HOOCCH_2O)_2C_6H_4)-\kappa^2O,O'\}_2\{THF\}_2](BF_4)_2$ (5)

Compound **2** was reacted with silver tetrafluoro borate in a 1:1 molar ratio using as solvent THF and refluxed for 30 minutes in the absence of light to give the dimeric silver complex **5**. The reaction pathway is outlined in Scheme 5.

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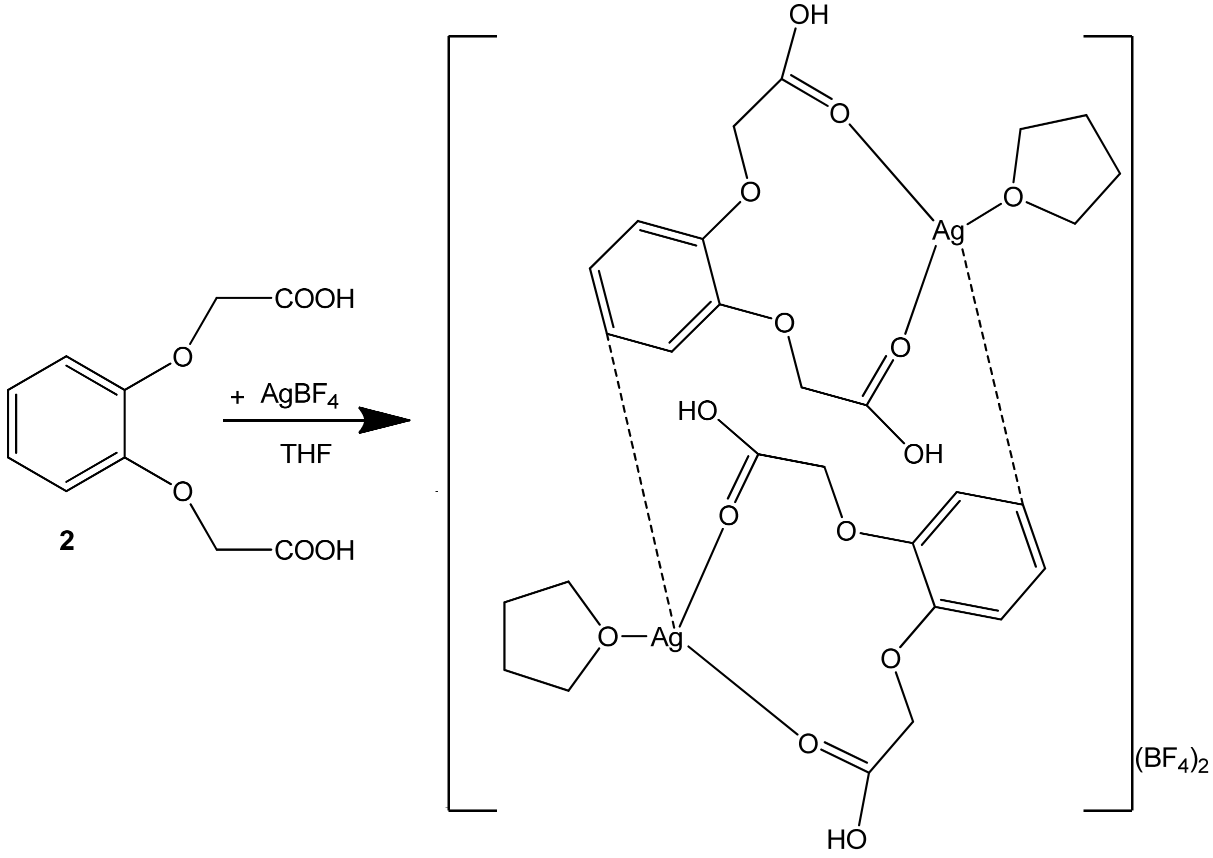
[2] C. Janiak, *Angew. Chem. Int. Ed.*, 1997, **36**, 1431; M. J. Rosseinsky, *Microporous and Mesoporous Materials*, 2004, **73**, 15; J. L. C. Rowsell and O. M. Yaghi, *Microporous and Mesoporous Materials*, 2004, **73**, 3



5

Scheme 5 Reaction pathway for the synthesis of **5**

The molecular structure of **5** (Figure 19) reveals the formation of a dimeric complex where the tetracoordinate silver ions are bridged by two molecules of **2**. Each ligand coordinates to a silver ion in a monodentate manner with two carboxylate oxygen atoms. Additionally, each silver ion is coordinated by a THF molecule. Moreover, the distance of 2.533(2) Å between the silver ions and one aryl carbon atom (C(4) and C(4'), respectively) of the second ligand molecule implies the formation of a Ag···C interaction.[3,4]

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[3] H.−F. Zhu, J. Fan, T. Okamura, Z.−H. Zhang, G.−X. Liu, K.−B. Yu, W.−Y. Sun and N. Ueyama, *Inorg. Chem.*, 2006, **45**, 3941

[4] M. Munakata, L. P. Wu, T. Kuroda−Sawa, M. Maekawa, J. Suenaga and K. Sugimoto, *Inorg. Chem.*, 1997, **36**, 4903

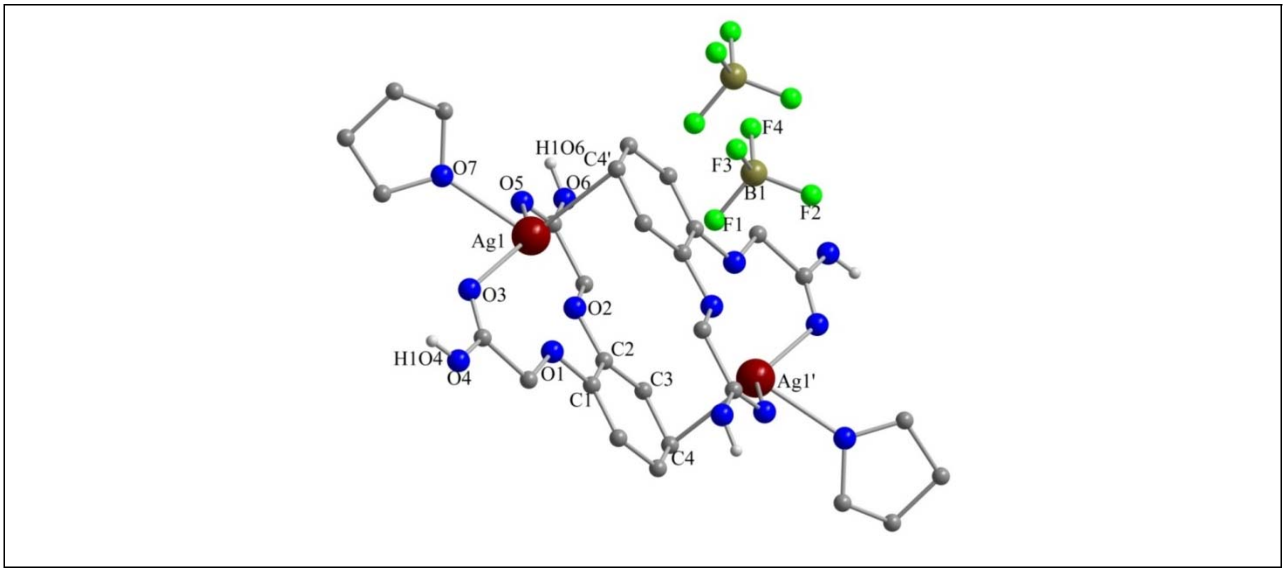
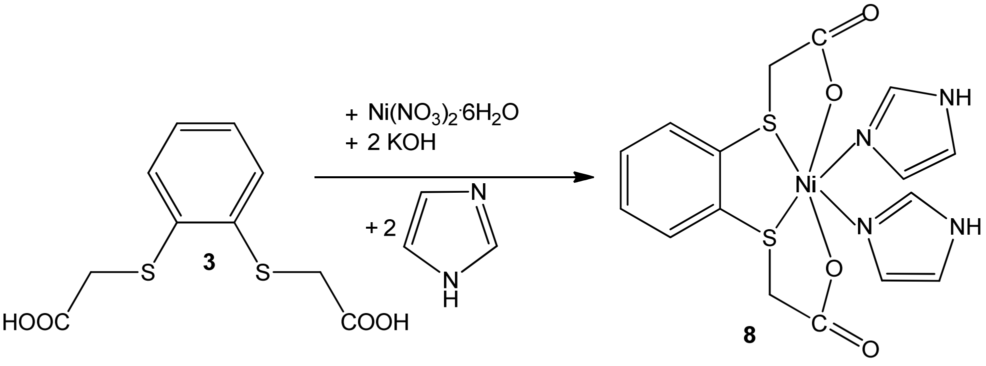


Figure 19 Molecular structure and atom labeling of **5**. H atoms other than O-H were omitted for clarity

4.2 Complexes of 1,2–phenylenebis(thio)diacetic acid **3**

Aiming to obtain a mixed–ligand nickel(II) complex, and providing in this way diverse donor sites for further coordination,[5] **3** was reacted with $Ni(NO_3)_2{\cdot}6H_2O$ in a 1:1 molar ratio in water, using 2 equivalents of KOH as base in order to deprotonate the carboxylic groups. Two equivalents of imidazole were also employed in the reaction as coligands.



Scheme 6 Reaction pathway for the synthesis of **8**

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[5] K. C. Majumdar, B. Chattopadhyay, B. Sinha, *Tetrahedron Letters*, 2008, **49**, 1319; X. Zhang, Z. Xi, A. Liu, W. Chen, *Organometallics*, 2008, **27**, 4401

In **8**, the 1,2−phenylenebis(thio)diacetate ligand acts as a dianionic tetradentate ligand for nickel(II) with the two sulfur atoms in a *cis* (Ni–S 2.4311(4) Å and 2.4527(4) Å) and two oxygen atoms in a *trans* arrangement (Ni–O 2.0443(9) Å and 2.0431(9) Å). In addition, two nitrogen atoms of two imidazole ligands are also coordinated to nickel in a *cis* arrangement (Ni–N 2.035(1) Å and 2.037(1) Å) (Figure 20). Thus, the resulting slightly distorted (O(1)–Ni(1)–O(3) 175.74(4)°, N(1)–Ni(1)–N(3) 95.55(4)°, N(1)–Ni(1)–S(1) 92.23(3)°, N(3)–Ni(1)–S(2) 88.28(3)° and S(1)–Ni(1)–S(2) 85.03(1)°) octahedral complex is chiral, forming Δ and Λ isomers.

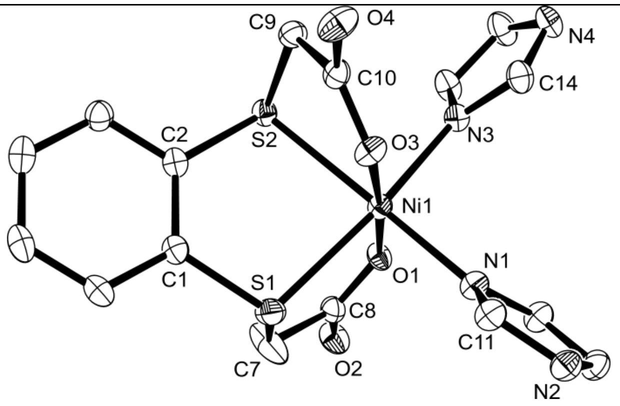
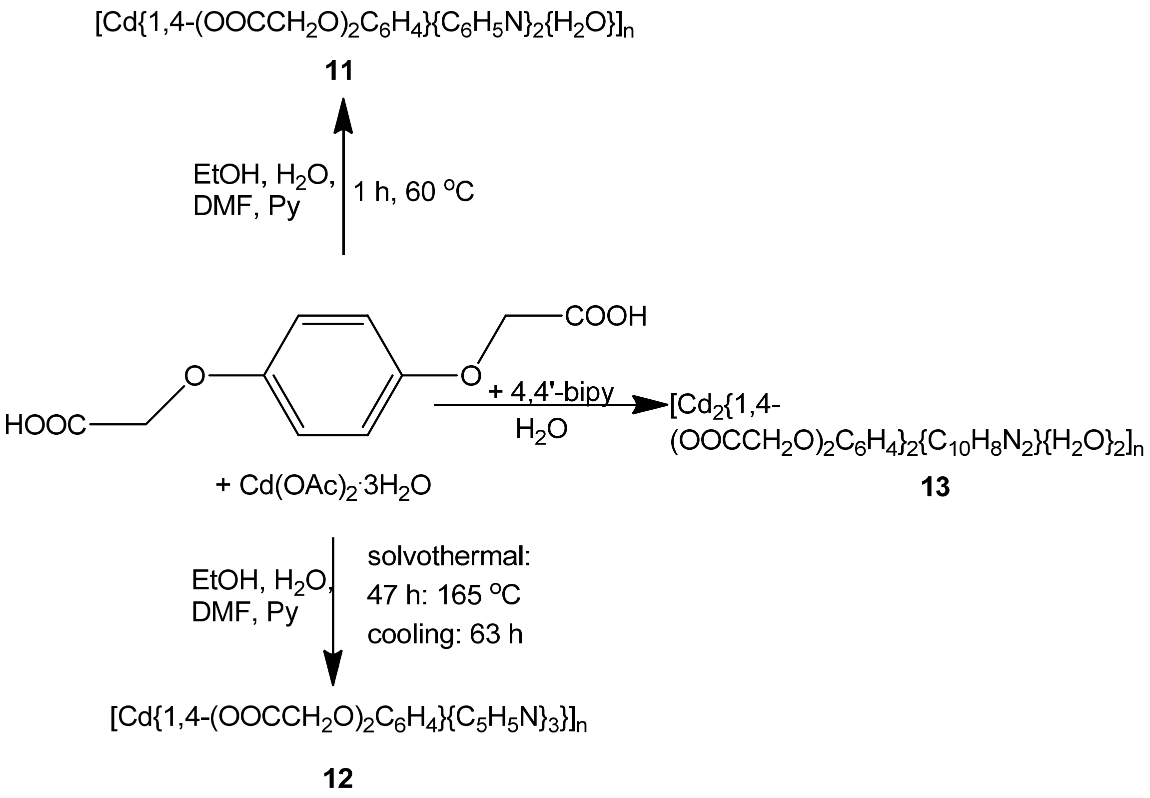


Figure 20 Molecular structure and atom labeling scheme for **8** with thermal ellipsoids at 50% probability. Only the Δ isomer is shown.

5 Coordination polymers of 1,4−phenylenebis(oxy)diacetic acid **1**

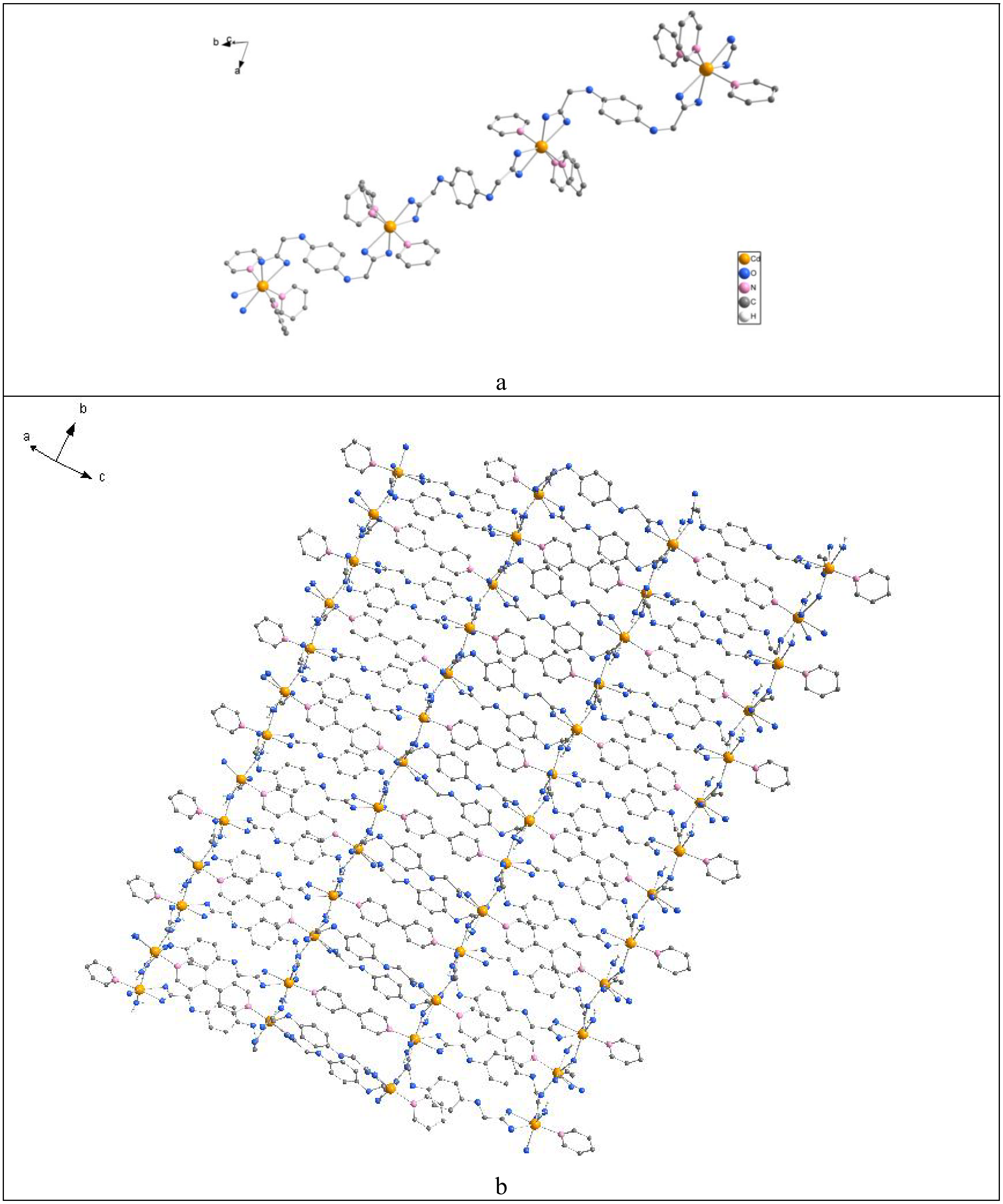
Starting from 1,4−phenylenebis(oxy)diacetic acid and reacting it with cadmium diacetate trihydrate, three new coordination polymers **11−13** were obtained depending on the reaction conditions and the use of coligand. The reaction pathway for the synthesis of polymers **11−13** is presented in Scheme 8.

When reacting ligand **1** with cadmium diacetate trihydrate in a 1:1 molar ratio using as solvent a 1:1:1:2.5 mixture of ethanol, water, pyridine and dimethylformamide, two different one−dimensional polymers were obtained depending on the reaction conditions. When heating the reaction mixture at 60 °C for one hour, light brown crystals of **11** were obtained in three months by allowing the solvent to slowly evaporate in air. When solvothermal conditions were used, the polymer **12** was obtained as brown crystals.



Scheme 8 Reaction pathway for the synthesis of polymers **11-13**

The molecular structures of polymers **12** and **13** reveal the fact that when using pyridine as coligand a 1D polymer with a chain-like motif is formed but when employing in the reaction a bidentate coligand (4,4’-bipyridine) the dimensionality of the polymer increases giving rise to a 2D polymer.(Figure 24)



a

b

Figure 24 a) 1D chain of **12** b) 2D sheet of **13** (H atoms other than O-H were omitted for clarity)

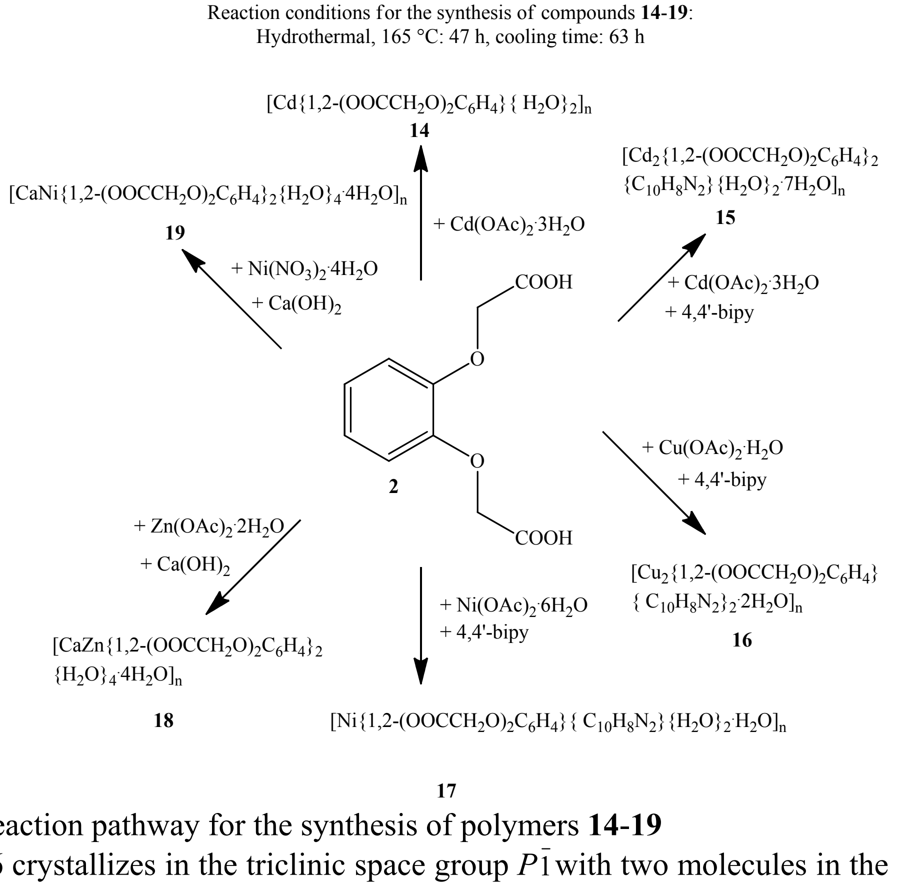
In both **12** and **13**, the cadmium ions are heptacoordinated presenting a distorted pentagonal bipyramidal geometry.

6 Coordination polymers of 1,2−phenylenebis(oxy) diacetic acid **2**

By reacting 1,2−phenylenebis(oxy)diacetic acid with cadmium diacetate trihydrate in hydrothermal conditions in a 1:1 molar ratio, polymer **14** was obtained. Using the same conditions in the reaction of **2** with cadmium diacetate trihydrate, copper diacetate monohydrate and nickel diacetate hexahydrate, respectively, but using 4,4’−bipyridine as coligand in a 1:1:1 molar ratio, three new coordination polymers **15**, **16** and **17** were obtained.

Two heterobimetallic coordination polymers **18** and **19** were also obtained under the same reaction conditions by reacting ligand **2** with calcium hydroxide and zinc diacetate dihydrate or nickel hexanitrate tetrahydrate, respectively, in a 1:1:1 molar ratio.

The reaction pathway for the synthesis of compounds **14−19** is outlined in Scheme 10.



Scheme 10 Reaction pathway for the synthesis of polymers **14-19**

Compound **16** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The coordination environment of the copper(I) ions is presented in Figure 31a.

Due to the fact that the reaction was carried out under hydrothermal conditions and in the presence of 4,4’−bipyridine, the copper(II) ions were reduced to copper(I). The reduction of copper under hydrothermal conditions and in the presence of pyridine derivatives was observed before in the literature.[6] The structure of **16** (Figure 31a) consists of two copper(I) atoms, one dicarboxylate ligand and two 4,4’−bipyridine units. Both copper(I) ions display a T−shaped trigonal geometry being coordinated by two pyridine nitrogen atoms and one oxygen atom belonging to a carboxylate group of the dianion of **2**.

In the coordination polymer there are two types of 4,4’− bipyridine ligands which are distinguished by the torsion angles between the $C_{aryl}-C_{aryl}$ bonds between the pyridyl rings. (11.73(2)° and 20.61(2)°, respectively). Two different 4,4’−bipyridine ligands and two distinct copper(I) atoms are linked generating 1D chains which are crosslinked by ligand **2** molecules to form a 1D ladder structure with large rings (Figure 31b).

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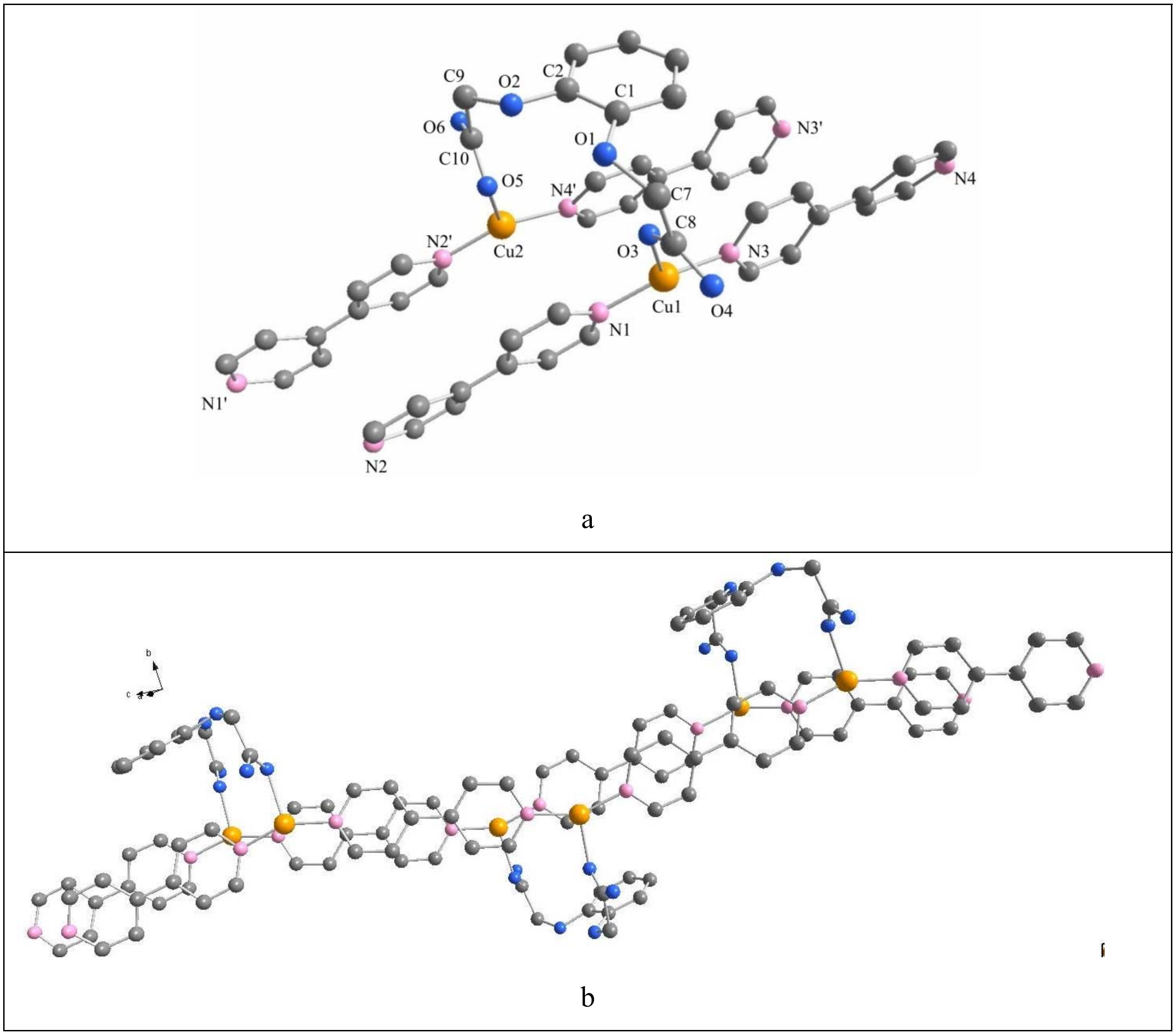
[6] J. Tao, Y. Zhang, M.−L. Tong, X.−M. Chen, T. Yuen, C. L. Lin, X.−Y. Huang and J. Li, *Chem. Commun.*, 2002, 1342; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; J. Y. Lu, B. R. Cabrera, R.−J. Wang and J. Li, *Inorg. Chem.*, 1998, **37**, 4480; S. M.−F. Lo, S.S.−Y. Chui, L.−Y. Shek, Z. Lin, X. Zhang, G. Wen and I. D. Williams, *J. Am. Chem. Soc.*, 2000, **122** , 6293



a

b

Figure 31 a) Coordination environment of the copper ions in 16 and atom labeling. b) Ladder structure of 16, a view along the *a*–axis. H atoms were omitted for clarity.

The two coordination polymers **18** and **19** are isotypical and they will be discussed together. Both compounds crystallize in the monoclinic space group *P*2/n with two molecules in the unit cell.

The coordination environments around the metal ions in **18** and **19** are presented in Figure 36a.

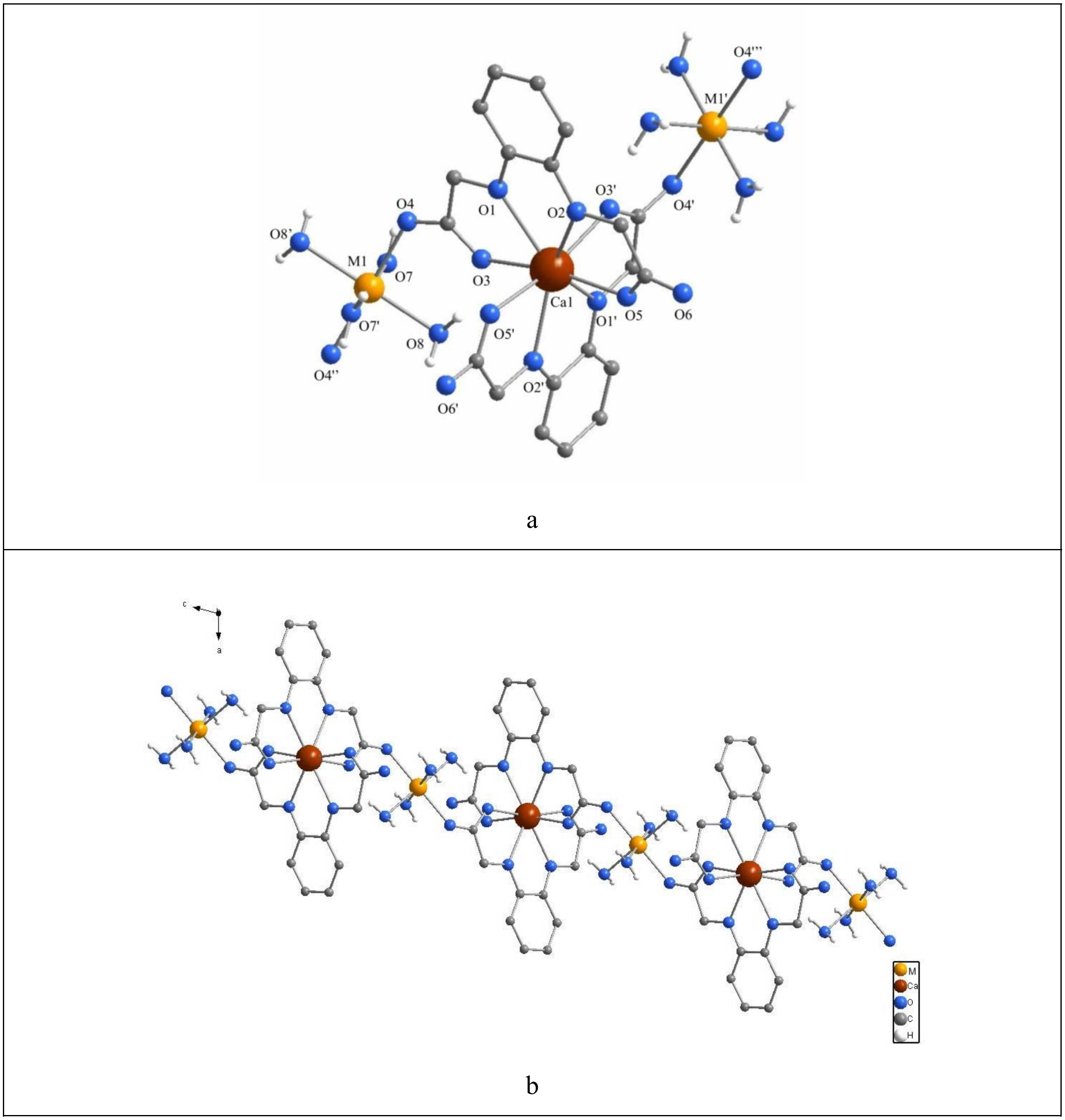


Figure 36 a) Coordination environment of the metal ions in **18** and **19** and atom labeling. b) 1D double chain of **18** and **19**, a view along the *a*–axis. H atoms, other than O–H were omitted for clarity.

The Ca^{2+} ions are octacoordinated by two dianions of **2**. These units are linked via one carboxylate oxygen atom from each dianion through $M(H_2O)_4$ complexes to give 1D chains (Figure 36b). The coordination sphere around the Ca^{2+} ions is fulfilled by four ether oxygen atoms from the two dianions and by four carboxylate oxygen atoms, one from each carboxylate unit of the two dianions. The coordination environment around the calcium ions can be described as distorted octahedral.

The coordination geometry around the Zn^{2+} ions in **18** and Ni^{2+} ions in polymer **19** is distorted octahedral. Both ions are hexacoordinated by two carboxylic oxygen atoms belonging to two different dianions of **2** and four oxygen atoms from four water molecules.

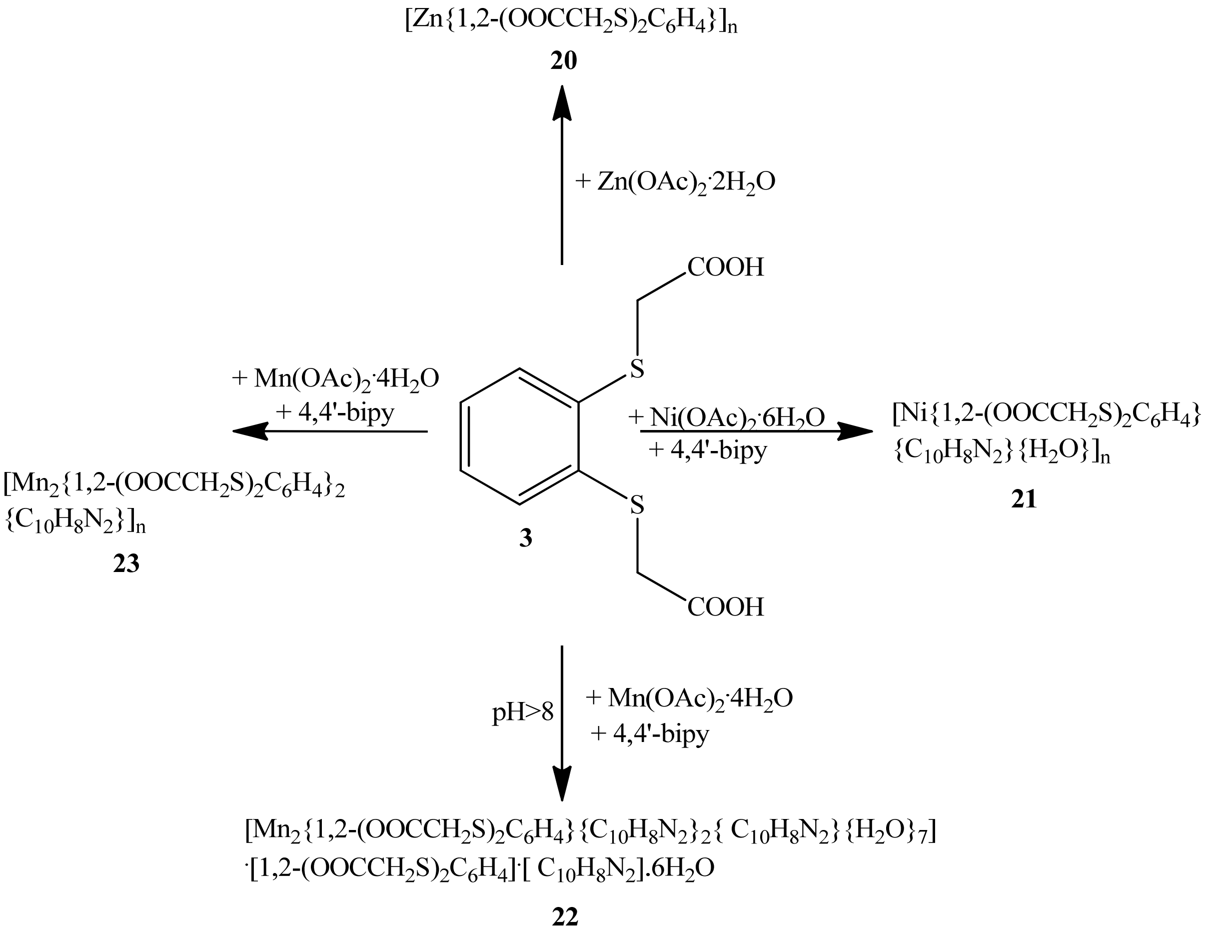
In both polymers the Ca^{2+} ions lie on an inversion center while the second metal ions lie on a two–fold axis.

7 Coordination polymers of 1,2–phenylenebis(thio)diacetic acid **3**

Starting from ligand **3**, four new compounds were obtained under hydrothermal conditions when reacting it with the corresponding starting metal complexes: one zinc 1D coordination polymer **20** was obtained when reacting **3** with $Zn(OAc)_2 \cdot 2H_2O$ in a 1:1 molar ratio, one 2D nickel coordination polymer **21** was obtained when ligand **3** was reacted with $Ni(OAc)_2 \cdot 6H_2O$ and 4,4'–bipyridine as coligand in a 1:1:1 molar ratio and two different manganese compounds by reacting **3** with $Mn(OAc)_2 \cdot 4H_2O$ and 4,4'–bipyridine in a 1:1:1 molar ratio depending on the pH value of the reaction mixture. The binuclear manganese complex **22** was obtained when the pH value of the reaction mixture was adjusted with triethylamine to values higher than 8, and the coordination polymer **23** was the reaction product when no base was used.

The reaction pathway for the synthesis of compounds **20–23** is presented in Scheme 12.

Reaction conditions for the synthesis compounds **20-23**: Hydrothermal, 165 °C: 47 h, cooling time: 63 h



Scheme 12 Reaction pathway for the synthesis of compounds **20-23**

Complex **22** crystallizes in the triclinic space group *P*1 with one molecule in the unit cell. In the asymmetric unit of **22**, six water molecules as well as one uncoordinated 4,4'−bipyridine are also present.

Compound **22** is a complex salt which contains a chain of $\{[Mn_2\{(OOCCH_2S)_2C_6H_4\}\{(NC_5H_5)_2\}_3(H_2O)_7]^{2+}\}_n$ cations and an isolated $[(OOCCH_2S)_2C_6H_4]^{2-}$ anion (Figure 42).

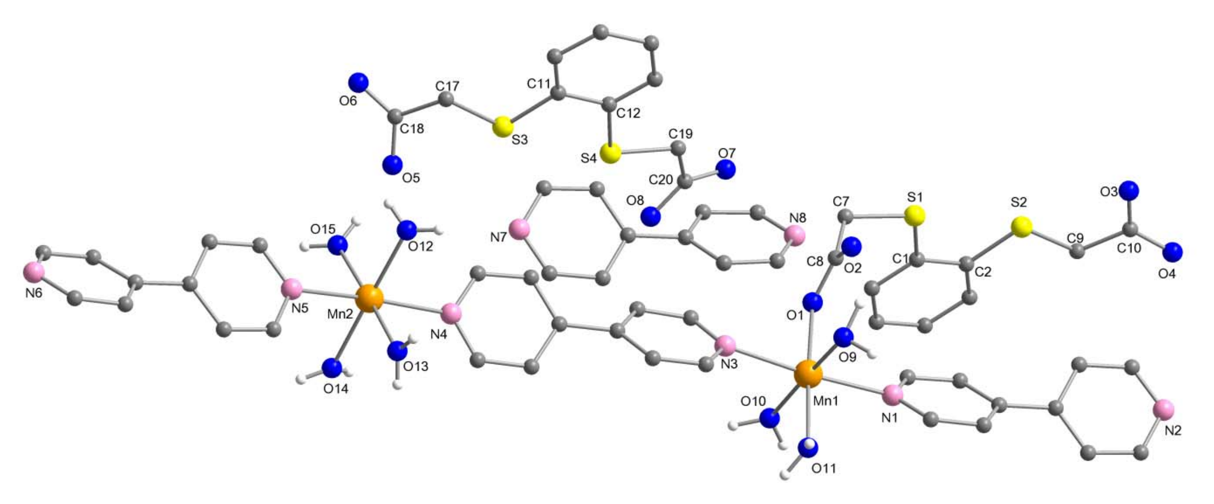


Figure 42 Molecular structure and atom labeling of **22**. H atoms other than O-H were omitted for clarity

There are two types of Mn^{2+} ions bridged by one 4,4'−bipyridine.The Mn^{2+} ions differ from each other by their coordination environment. Both manganese ions are hexacoordinated in a slightly distorted octahedral fashion. The Mn(1) ion is coordinated by two nitrogen atoms from two different 4,4'−bipyridine molecules and by four oxygen atoms, three of them belonging to three coordinated water molecules, while the fourth oxygen atom belongs to a carboxylate group of ligand **3**. The Mn(2) ion is coordinated by two nitrogen atoms from two coordinated 4,4'−bipyridine ligands and by four oxygen atoms belonging to four water molecules which coordinate to the metal center.

Although the $[(OOCCH_2S)_2C_6H_4]^{2-}$ anion does not coordinate to the metal ions, it plays an important role as template in the crystallization process of **22** being involved in intramolcular and intermolecular (when packing) hydrogen bonding.

Compound **23** crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell. The Mn^{5+} ions are hexacoordinated and present a distorted octahedral geometry which is found in many Mn^{5+} complexes.[7] Each manganese ion is coordinated by five carboxylate oxygen

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[7] C. Qi, D. Zhang, S. Gao, H. Ma, Y. He, S. Ma, Y. Chen and C. Yang, *J. Mol. Struct.*, 2008, **891**, 357; S. Zartilas, E. E. Moushi, V. Nastopoulos and A. Boudalis, *Inorg. Chim. Acta*, 2008, **361**, 4100

atoms each belonging to a different dianion and by one nitrogen atom from a 4,4’−bipyridine ligand (Figure 44).

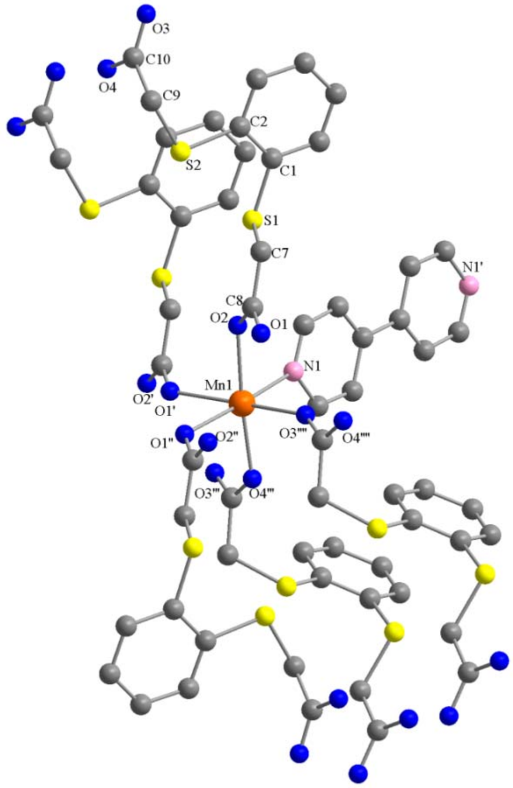
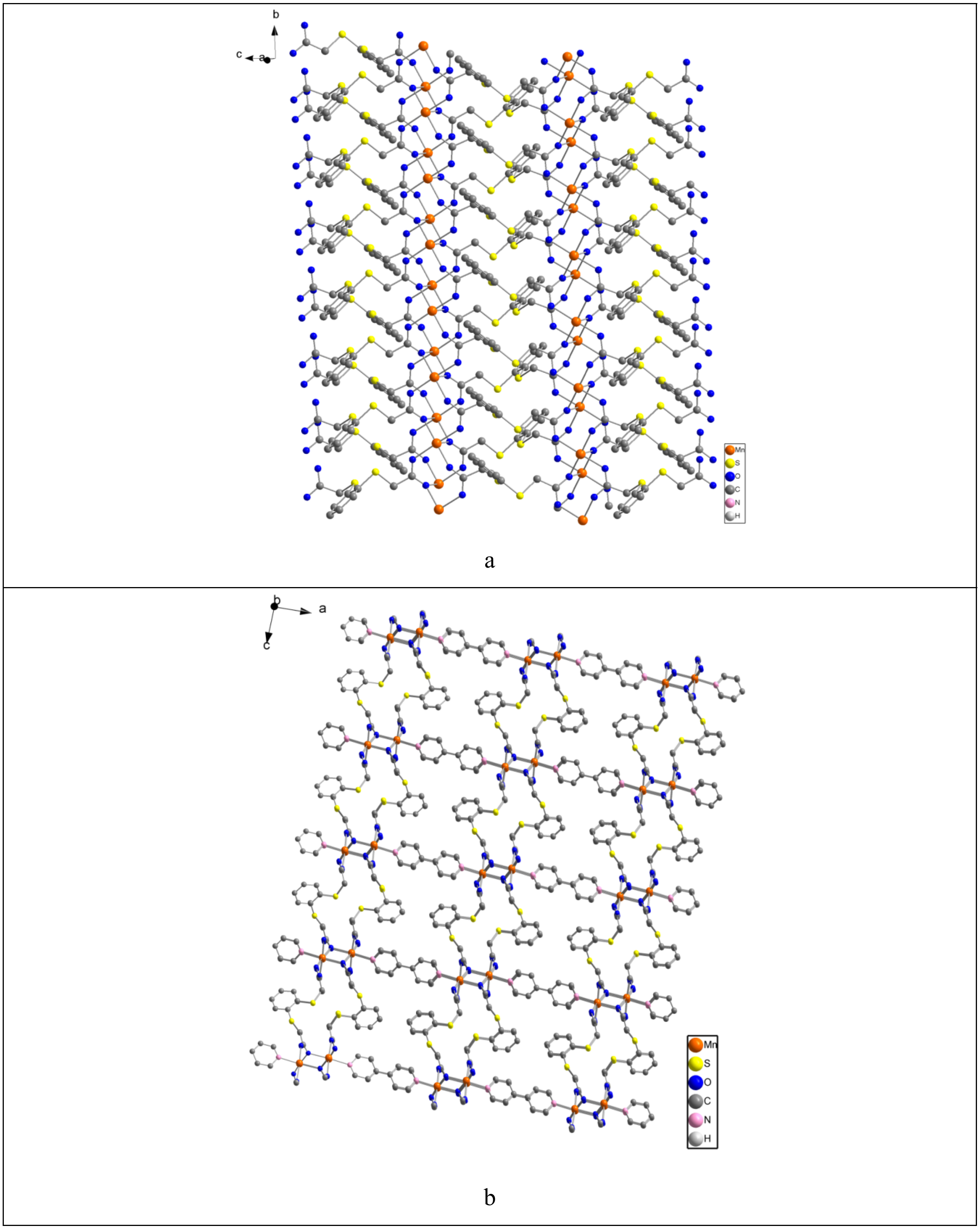


Figure 44 Coordination environment of the manganese ions in **23** and atom labeling. H atoms other than O-H were omitted for clarity

The Mn^{5+} ions and the carboxylate oxygen atoms form infinite 1D chains along the b−axis (Figure 45a). Two manganese ions and two carboxylate oxygen atoms from two different dianions of **3** form four−membered rings. In the rings, the distance between the two Mn^{2+} ions is 3.50(1) Å. These rings are connected through the other carboxylate oxygen atoms which coordinate to the metal centers. The distance between two manganese ions belonging to neighboring rings is 4.44(1) Å. These Mn−O chains are linked by ligand molecules giving rise to 2D sheets (Figure 45a). Moreover, the 2D sheets are linked by the 4,4’−bipyridine ligands, each nitrogen atom coordinating to a manganese ion from different 2D sheets (Figure 45b) giving rise to a porous 3D network.



a

b

Figure 45 a) 2D sheet of **23** formed by Mn_2O_2 chains linked by ligand 3 molecules. b) 3D porous network of **23**

Along the *c*−axis, the distances between two manganese ions are 12.624(2) Å and 14.360(2) Å while along the *a*−axis, the distance between two manganese ions bridged by 4,4'−bipyridine ligands is 13.282(2) Å.

8 *Coordination polymers of* N,N,N'N'*−1,2−phenylene−diaminetetraacetic acid* **4**

Ligand **4** was reacted with cadmium diacetate trihydrate in a 1:2 molar ratio under hydrothermal conditions to obtain the 3D coordination polymer **24**. When one equivalent of 4,4'−bipyridine was employed in the reaction, the mixed ligand 3D polymer **25** was obtained. Under the same reaction conditions, a nickel− based mixed ligand (**4** and 4,4'− bipyridine) 3D coordination polymer was obtained.

Ligand **4** was reacted with manganese diacetate tetrahydrate under hydrothermal conditions in a 1:2 molar ratio and the binuclear complex $[Mn_2(C_{14}H_{12}N_2O_8)(H_2O)_6]$ synthesized previously by Tanaka et al.[8] was obtained. The employment of one equivalent of 4,4'−bipyridine in the reaction led to the formation of polymer **27** although no 4,4'−bipyridine can be found in the structure of the polymer. Apparently, 4,4'−bipyridine acts as a base favoring the formation of a polymeric structure, but the use of other bases like triethylamine, potassium hydroxide or sodium hydroxide did not yield the desired compound. However, the compound could be reproduced in small yield when using 4,4'−bipyridine.

The reaction pathway for the synthesis of polymers **24**−**27** is outlined in Scheme 14.

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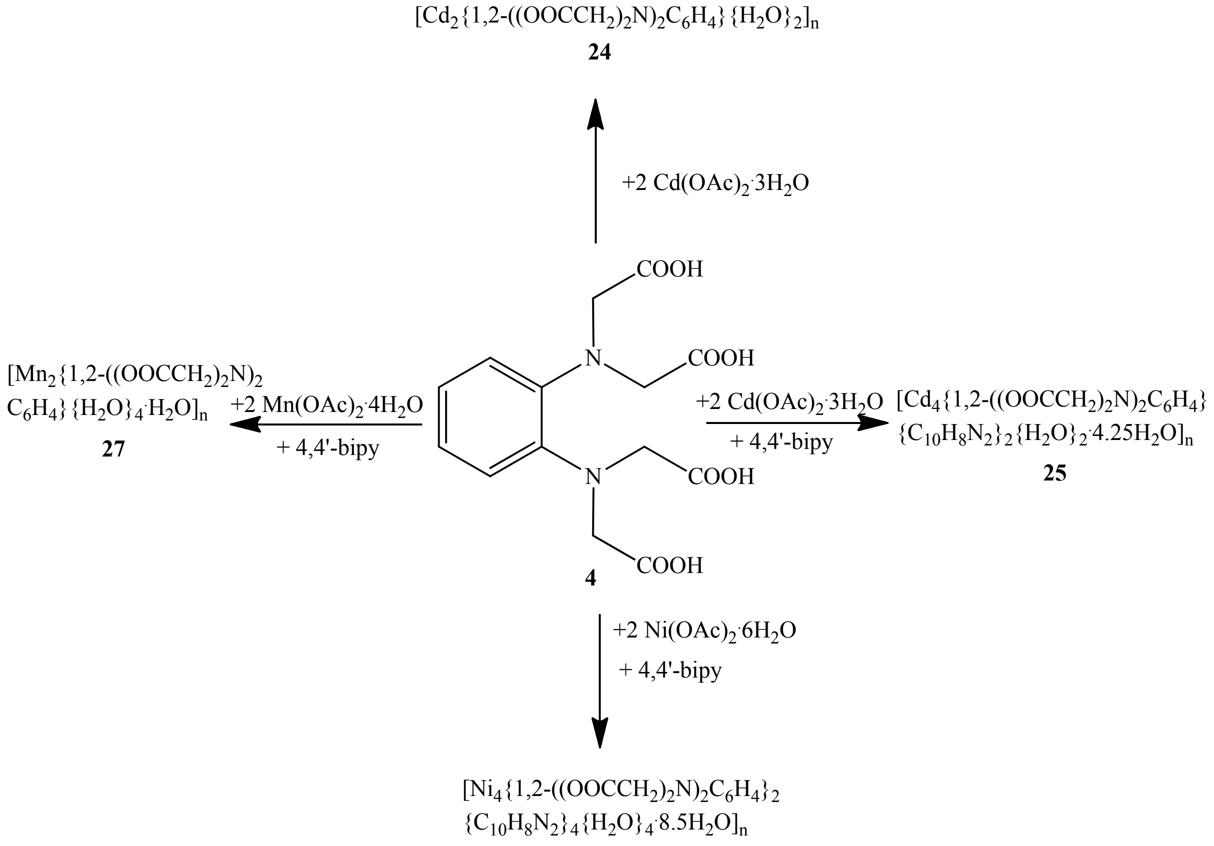
[8] N. Nakasuka, S. Azuma, C. Katayama, M. Honda, J. Tanaka and M. Tanaka, *Acta Cryst.*, 1985, **C41**, 1176

Reaction conditions for the synthesis compounds **24-27**: Hydrothermal, 165 °C: 47 h, cooling time: 63 h



Scheme 14 Reaction pathway for the synthesis of polymers **24-27**

The molecular structure of **24** reveals the existence of two different types of Cd^{2+} ions could be distinguished and their coordination environments are presented in Figure 47a.

Both Cd(1) and Cd(2) are heptacoordinated and present a distorted pentagonal−bipyramidal geometry. The Cd(1) ions are coordinated by two nitrogen atoms and four carboxylate oxygen atoms each of them belonging to a carboxylate group of the same $C_6H_4(N(COO)_2)_2^{4-}$ unit and one oxygen atom from one water molecule. Cd(2) is coordinated by six carboxylate oxygen atoms from four different tetraanions and one oxygen atom from a water molecule. The Cd(1) and Cd(2) ions are bridged by one carboxylate oxygen atom (O(5’’)), the distance between the two being 4.568(1) Å. The structure is extended in all three directions to give a layered supramolecular network (Figure 47b).

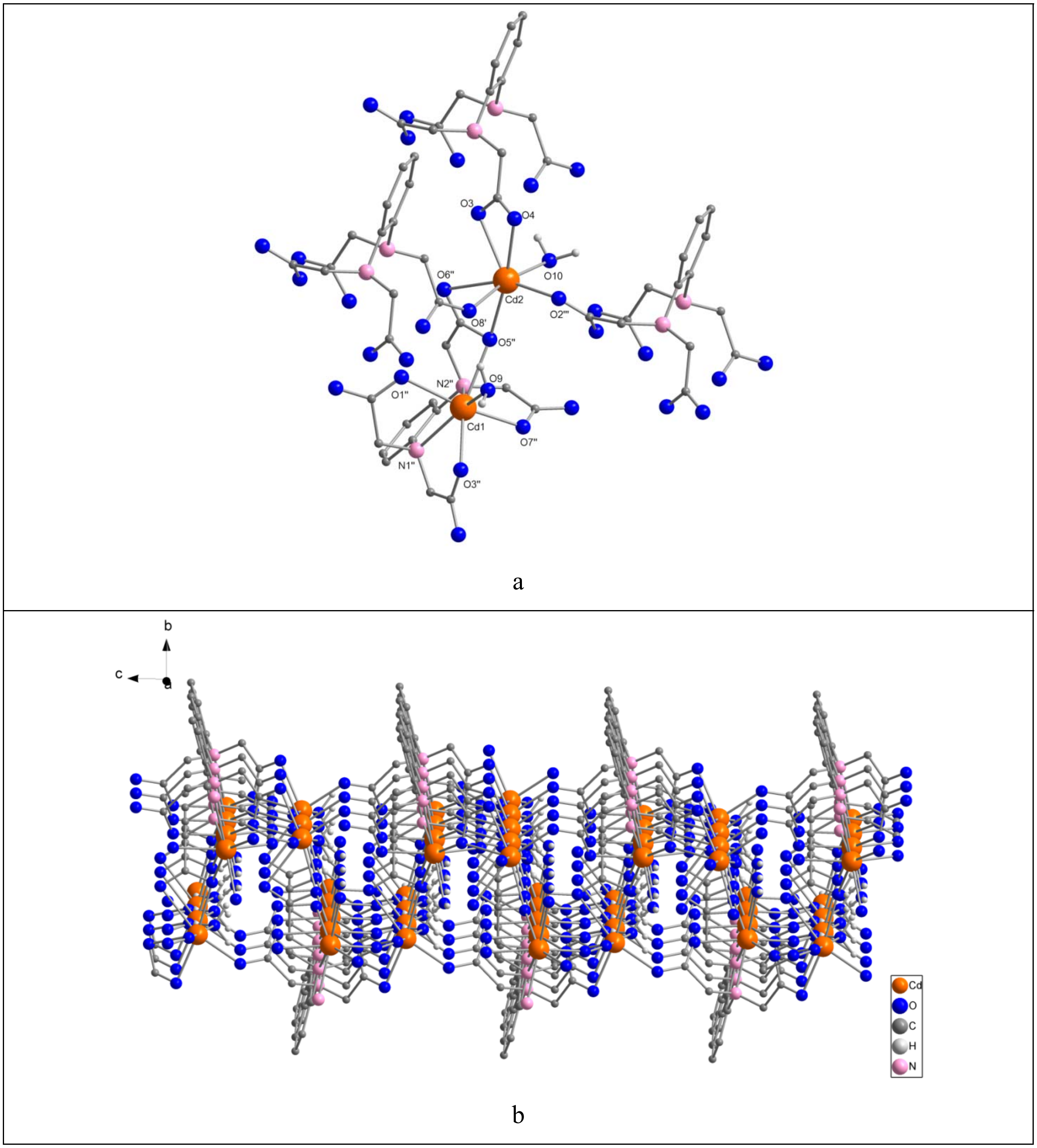


Figure 47a) Coordination environment of the cadmium ions in 24 and atom labeling. b) 3D layered structure of 24. H atoms other than O–H were excluded for clarity

Along the *a*–axis, small channels are formed, the dimensions of these channels are 8.578(2) Å along the *b*–axis and 8.085(1) Å along the *c*–axis.

Compound **26** crystallizes in the monoclinic space group *C*2/c with four molecules in the unit cell. The molecular structure of polymer **26** reveals the existence of two types of nickel ions which differ from each other in their coordination environment (Figure 52).

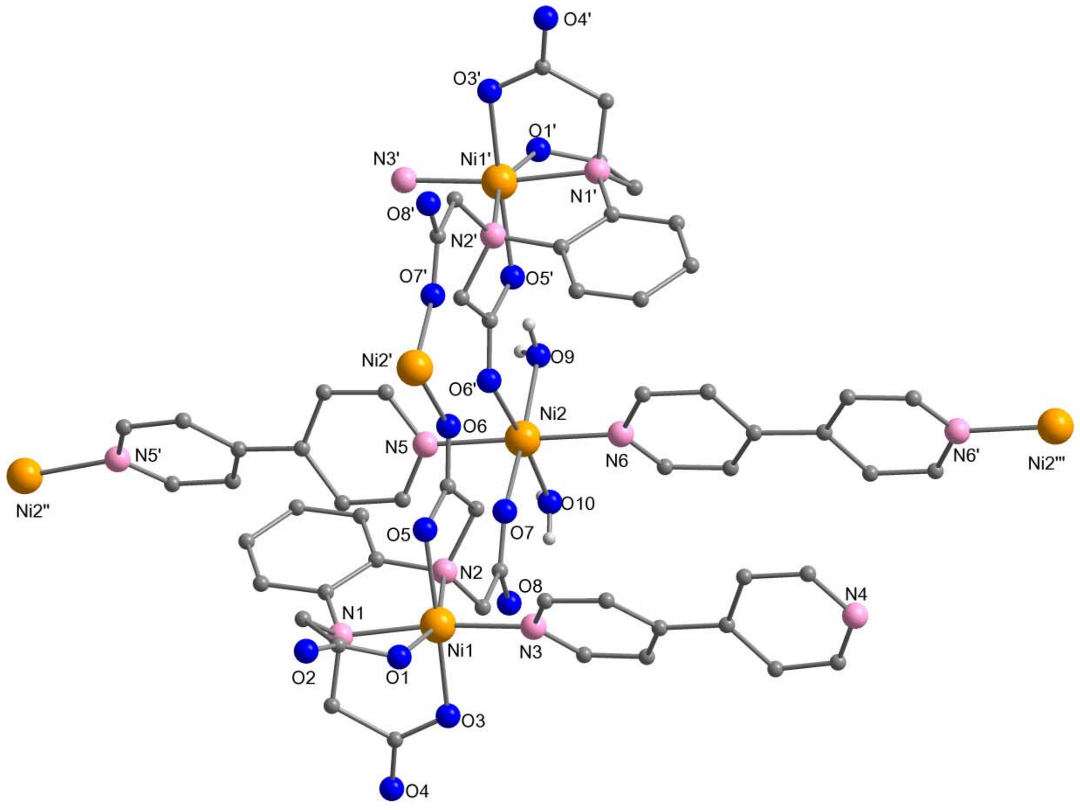


Figure 52 Atom labeling and coordination environment of the Ni^{2+} ions in polymer 25. The (C−H) atoms were omitted for clarity.

Both Ni(1) and Ni(2) are hexacoordinated in a distorted octahedral fashion. The ions Ni(1)$^{2+}$ are coordinated in a chelating manner by two nitrogen atoms of one $C_6H_4(N(COO)_2)_2^{4-}$ unit , three carboxylate oxygen atoms which belong to three carboxylate groups from the same tetraanion and one nitrogen atom from a 4,4'−bipyridine coligand. The ions Ni(2)$^{2+}$ are coordinated by two nitrogen atoms from to two different 4,4'−bipyridine molecules, and two carboxylate oxygen atoms from two different ligand **4** molecules. The coordination sphere is completed by two oxygen atoms belonging to two water molecules which are coordinated to the Ni(2) ions.

Moreover, in the structure of polymer **26** three types of 4,4’−bipyridine molecules are observed: the 4,4’−bipyridine molecules which coordinate to the Ni(1) ions act as monodentate ligands, the second nitrogen atom remains uncoordinated and the torsion angle around the $C_{aryl}-C_{aryl}$ bond has the value of −23.79(5)°, while the other two types of 4,4’− bipyridine molecules, although they act as bidentate ligands bridging two Ni(2) ions, differ from each other in the torsion angles between the pyridyl rings, which are 3.90(6)° and −42.93(5)°, respectively.

Each $C_6H_4(N(COO)_2)_2^{4-}$ is bridging three different nickel ions, while the Ni(2) ions are also bridged by one 4,4’−bipyridine molecule leading to the extension of the structure of **26** to a 3D network (Figure 53). Along the *c*−axis, cavities which are filled with non−coordinating water molecules are formed. The distances between two Ni(1) ions along the *a*−axis is 13.068(5) Å and between two Ni(2) ions 16.803(9) Å. Along the *b*−axis the distances are 15.097(5) Å and 11.512(4) Å, respectively. The distances between the Ni(1) and Ni(2) ions along the *b*−axis is 6.917(2) Å.

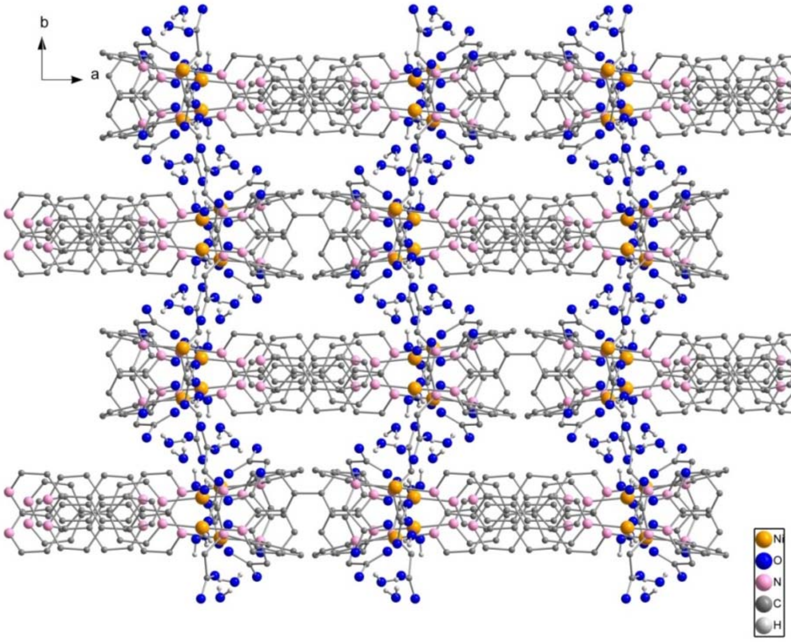


Figure 53 3D structure of 26, a view along the *c*−axis

10 DTA Measurements

Differential thermal analysis (DTA) measurements were performed for the following compounds: **13, 14**, **16**, **17** and **20−27** in a helium atmosphere in order to check their thermal stability. The thermogravimetric analysis of compounds **17**, **20**, **21**, **23**, **24**, **26** and **27** were performed parallel with mass spectrometric analysis. The MS data were recorded with a QMS 403C Aeolos Netzsch spectrometer. The heating rate in the thermogravimetric experiments was 10 °C/minute in all experiments and the sample weight was 18–26 mg.

The TG curve of **21** (Figure 67) consists of two steps; in the first step, water is lost at about 150 °C, the mass loss of 3.63% suggesting the elimination of one included water molecule per formula unit, while the second step which represents the decomposition of the polymer starts at 320 °C with a mass loss of 73.81%. The decomposition occurs with elimination of water, carbon monoxide and carbon dioxide.

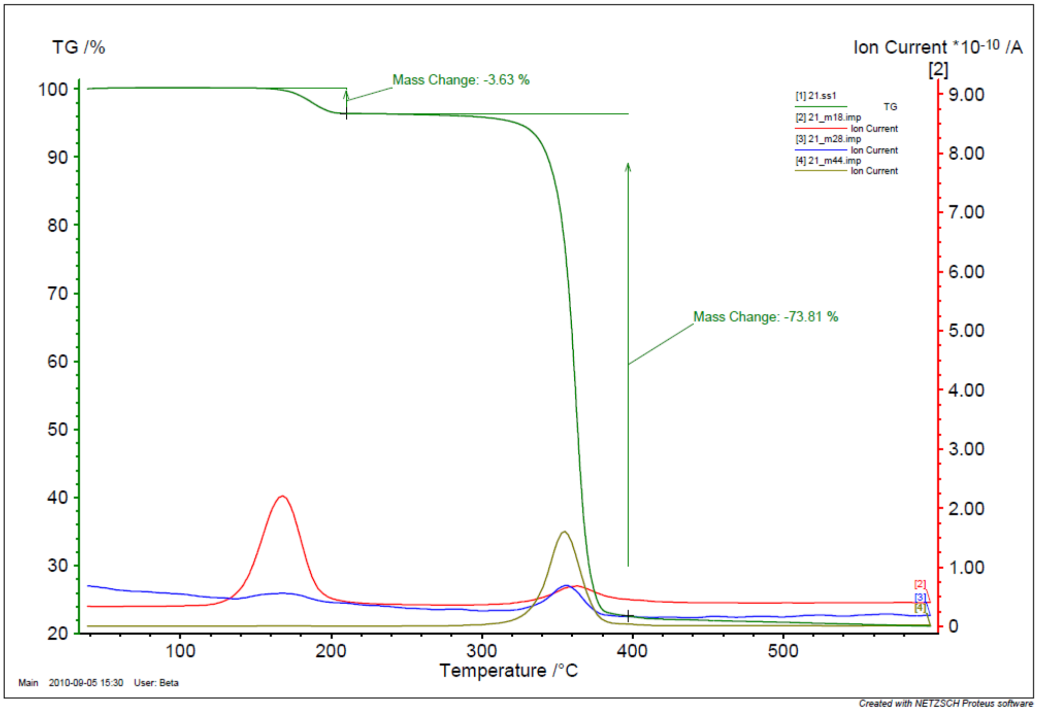


Figure 67. TG curve (green) and mass ion current curves of water (red), carbon monoxide (blue) and carbon dioxide (olive) of **21**

12 General Conclusions

In this thesis, the coordination properties of polycarboxylate ligands towards transition metals are studied with the aim to obtain coordination polymers. Coordination polymers have promising applications in many fields like gas storage, catalysis, magnetism and luminescence.

The personal contributions are related to the synthesis of structural characterization of the polycarboxylate ligands, and of silver, palladium and nickel complexes as potential building blocks for the rational synthesis of coordination polymers. The synthesis and structural characterization of monometallic and heterobimetallic coordination polymers is also presented. Generally, the coordination polymers were obtained by treating the polycarboxylate ligands with the corresponding metal salt in a 1:1 molar ratio in the case of the dicarboxylate ligands, and in a 1:2 molar ratio when starting from the tetracarboxylate ligand under solvothermal conditions. When 4,4'–bipyridine was used as coligand, coordination polymers with mixed ligands were also obtained. All compounds were characterized by single X– ray diffraction and/or by IR spectroscopy, elemental analysis, and the building blocks have also been characterized by ^{1}H, $^{13}C\{^{1}H\}$–NMR spectroscopy and by mass spectrometry. The thermal properties of some of the coordination polymers have also been studied. The results are summarized here:

- **three** new complexes $[Ag_2\{1,2-(HOOCCH_2O)_2C_6H_4)-\kappa^2 OO'\}_2\{THF\}_2](BF_4)_2$ (**5**), $[Ni\{1,2-(OOCCH_2S)_2C_6H_4-\kappa^4 O,O'S,S'\}\{cis-(C_3H_4N_2)\}_2]$ (**8**) and $cis-[PdCl_2\{1,2-((MeOOC)_2N)_2C_6H_4-\kappa^2 N,N'\}]$ (**10**) were synthesized and characterized as potential building blocks
- **seven** cadmium–based coordination polymers were synthesized: **three** one–dimensional coordination polymers ($[Cd\{1,4-(OOCCH_2O)_2C_6H_4\}\{C_6H_5N\}_2\{H_2O\}]_n$ (**11**), $[Cd\{1,4-(OOCCH_2O)_2C_6H_4\}\{C_5H_5N\}_3\}]_n$ (**12**) and $[Cd\{1,2-(OOCCOOCCH_2O)_2C_6H_4\}\{H_2O\}_2]_n\cdot(H_2O)_n)$, **two** two – dimensional mixed – ligand polymers ($[Cd_2\{1,4-(OOCCH_2O)_2C_6H_4\}_2\{C_{10}H_8N_2\}\{H_2O\}_2]_n$ (**13**) and $[Cd_2\{1,2-(OOCCH_2O)_2C_6H_4\}_2\{C_{10}H_8N_2\}\{H_2O\}_2\cdot 7H_2O]_n$ (**15**)) and **two** three – dimensional coordination polymers ($[Cd_2\{1,2-((OOCCH_2)_2N)_2C_6H_4\}\{H_2O\}_2]_n$ (**24**) and the mixed ligand polymer $[Cd_4\{1,2-((OOCCH_2)_2N)_2C_6H_4\}\{C_{10}H_8N_2\}_2\{H_2O\}_2\cdot 4.25H_2O]_n$ (**25**))

- **one** one– dimensional copper– based mixed– ligand coordination polymer $[Cu_2\{1,2-(OOCCH_2O)_2C_6H_4\}\{C_{10}H_8N_2\}_2\cdot 2H_2O]_n$ (**16**) was synthesized; here,hydrothermal conditions and the presence of 4,4'–bipyridine led to reduction of copper(II) to copper(I).
- **three** nickel– based mixed– ligand coordination polymers were obtained: **two** two–dimensional ($[Ni\{1,2-(OOCCH_2O)_2C_6H_4\}\{C_{10}H_8N_2\}\{H_2O\}_2\cdot H_2O]_n$ (**17**) and $[Ni\{1,2-(OOCCH_2S)_2C_6H_4\}\{C_{10}H_8N_2\}\{H_2O\}]_n$ (**21**)) and **one** three– dimensional polymer ($[Ni_4\{1,2-((OOCCH_2)_2N)_2C_6H_4\}_2\{C_{10}H_8N_2\}_4\{H_2O\}_4\cdot 8.5H_2O]_n$ (**26**))
- **Three** manganese–based compounds have been synthesized: **one** mixed–ligand three–dimensional polymer ($[Mn_2\{1,2-(OOCCH_2S)_2C_6H_4\}_2\{C_{10}H_8N_2\}]_n$ (**23**)), **one** two–dimensional coordination polymer ($[Mn_2\{1,2-((OOCCH_2)_2N)_2C_6H_4\}\{H_2O\}_4\cdot H_2O]_n$ (**27**)) and **one** dinuclear complex ($[Mn_2\{1,2-(OOCCH_2S)_2C_6H_4-\kappa^1S\}\{C_{10}H_8N_2-\kappa^1N\}_2\{C_{10}H_8N_2-\kappa^2N',N''\}\{H_2O\}_7]\cdot[1,2-(OOCCH_2S)_2C_6H_4]\cdot[C_{10}H_8N_2]\cdot 6H_2O$ (**22**))
- **three** heterobimetallic coordination polymers have also been obtained: **one** Ca/Zn–based one–dimensional polymer $[CaZn\{1,2-(OOCCH_2O)_2C_6H_4\}_2\{H_2O\}_4\cdot 4H_2O]_n$ (**18**) and **one** Ca/Ni–based one–dimensional polymer $[CaNi\{1,2-(OOCCH_2O)_2C_6H_4\}_2\{H_2O\}_4\cdot 4H_2O]_n$ (**19**), both were obtained under hydrothermal conditions. Additionally, **one** two–dimensional Ag/Cd– based coordination polymer $[Ag_2Cd_2\{1,2-(OOCCH_2S)_2C_6H_4\}_3\{H_2O\}_3\cdot 5H_2O]_n$ (**28**) was obtained at room temperature starting from the silver complex **7** as building block.

An overview of these new complexes is given below:

- Ligands **1**–**4** adopt different coordination modes depending on the metal to which they coordinate and the use of coligand. The dicarboxylate ligands **1**–**3** adopt semiflexible conformations while the tetracarboxylate ligand **4** adopts a flexible conformation.
- The use of 4,4'–bipyridine as coligand increases the dimensionality of the cadmium–based coordination polymers starting from the dicarboxylate ligands **1** and **2** (see **12** vs **13** and **14** vs **15**).
- The synthesis of the manganese–based compounds, the dinuclear complex **22**, the three–dimensional coordination polymer **23** and the two–dimensional polymer **27**, depends on the pH value of the reaction mixture (see **22** vs **23**) or the presence of 4,4'–bipyridine in the reaction media (see **27**).

- Intermolecular hydrogen bonding interactions between solvate water molecules and/or carboxylate oxygen atoms and coordinated water molecules as well as between carboxylate oxygen atoms and coordinated water molecules lead to the formation of hydrogen–bonded supramolecular networks of superior dimensionalities.