## Accepted Manuscript

Investigation of complexation behavior of the dithiocarbamates of  $N^1, N^n$ -dicinnamylalkane-1,*n*-diamines with metals

Azim Ziyaei Halimehjani, Farzaneh Soleymani Movahed, Mohammad B. Fathi, Rasoul Daliri Asbforoushani, Mohammad R. Saidi

PII: S0022-2860(18)31415-7

DOI: https://doi.org/10.1016/j.molstruc.2018.11.102

Reference: MOLSTR 25931

To appear in: Journal of Molecular Structure

Received Date: 8 May 2018

Revised Date: 17 November 2018

Accepted Date: 28 November 2018

Please cite this article as: A.Z. Halimehjani, F.S. Movahed, M.B. Fathi, R.D. Asbforoushani, M.R. Saidi, Investigation of complexation behavior of the dithiocarbamates of  $N^1$ ,  $N^n$ -dicinnamylalkane-1,*n*-diamines with metals, *Journal of Molecular Structure* (2018), doi: https://doi.org/10.1016/j.molstruc.2018.11.102.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



## ACCEPTED MANUSCRIPT



Chilling with

# Investigation of complexation behavior of the dithiocarbamates of $N^{I}, N^{n}$ -dicinnamylalkane-I, n-diamines with metals

Azim Ziyaei Halimehjani,<sup>a,\*</sup> Farzaneh Soleymani Movahed,<sup>b</sup> Mohammad B. Fathi,<sup>c</sup> Rasoul Daliri Asbforoushani,<sup>d</sup> Mohammad R. Saidi<sup>b,\*</sup>

<sup>a</sup>Faculty of Chemistry, Kharazmi University, 49 Mofateh St., Tehran, Iran. E-mail: ziyaei@khu.ac.ir

<sup>b</sup>Department of Chemistry, Sharif University of Technology, PO Box 11465-9516, Tehran, Iran. Email: saidi@sharif.edu

<sup>c</sup>Solid State Department, Faculty of Physics, Kharazmi University, 49 Mofateh St., Tehran, Iran

<sup>d</sup> Department of Chemistry, Wayne State University, Detroit, Michigan 48202, USA

## Abstract

Synthesis and characterization of metal dithiocarbamate complexes of  $N^{l}$ ,  $N^{3}$ -dicinnamylpropane-1,3-diamine,  $N^{l}$ ,  $N^{4}$ -dicinnamylbutane-1,4-diamine and  $N^{l}$ ,  $N^{6}$ -dicinnamylhexane-1,6-diamine are reported. The ligands are prepared using cinnamaldehyde and primary diamines to provide the corresponding diimines, followed by reduction with NaBH<sub>4</sub> to afford the corresponding secondary diamines. Diamines react with carbon disulfide in basic medium to furnish the corresponding bis(dithiocarbamate) salts, which underwent complexation with metals. The prepared complexes were characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR, TGA and elemental analyses. Although the dinuclear metal dithiocarbamate macrocyclic complexes were obtained from  $N^{l}$ ,  $N^{6}$ dicinnamylhexane-1,6-diamine, the propane and butane diamines afforded the corresponding polymers. The synthesized complexes do not show any crystalline phase even in long lasting terms. Electron microscopy obviously shows that the material is amorphous, and X-ray diffraction technique is employed to investigate atom-atom distances in the molecule via the Fourier transform analysis of XRD data collected from powder sample.

**Keywords:** Dithiocarbamate, Transition metals, cinnamaldehyde, diamine, radial distribution function, X-ray diffraction

#### 1. Introduction

Dithiocarbamates (DTCs) are one of the key components in the field of chemistry science. These compounds have myriad applications that range over a variety of scientific subjects, such as medicine, agriculture, organic synthesis, biochemistry, rubber industry, *etc.* [1-5]. The function of DTCs is not limited to these fields, and in fact, their full potential is yet to be discovered. In recent years, these compounds have also been utilized as beneficial intermediates for the synthesis of electron donor polymers in plastic solar cells [6-8].

The very existence of two sulfur atoms in a DTC group has bestowed an extraordinary feature upon these materials which provides the possibility to stabilize a panoramic variety of metal ions. Due to the fact that these compounds have a considerable sturdy complexion ability, DTCs are known as bidentate ligands, whose high yields and complex diversities with various metals have been well documented [9].

Besides their complexation behavior, they were applied in many fields, such as producing chemical drugs [10], functioning as intermediates in organic synthesis [11], and protecting groups in peptide synthesis [12]. Being particularly beneficial forerunners for the development of metal nanoparticles, dithiocarbamate complexes have shown diverse applications in the realm of nanoscience [13-16]. These complexes are also applied as catalysts in the chemoselective reduction of azides [17]. In fact, with several important applications for DTC complexes, it seems that any progress in this field has been utterly vindicated by the fact that these complexes are effective agents to metal-extraction studies [18-19]. Interestingly, they have a particular capability to react with NO that makes them ideal NO-trapping agents [20-21].

In addition to the mentioned applications, DTC ligand has proved to be an efficient and robust motif for the formation of extremely useful structures, such as macrocycles, cages, catenanes, and nano-dimensional assemblies. Dinuclear macrocyclic complexes of DTCs can be simply formed by coordination of transition metals with appropriate bis(dithiocarbamate) salts. Such cyclic complexes with tunable internal dimensions can be applied as host for cationic, anionic, and neutral guest species [22]. Recently, dinuclear diorganotin (IV) dithiocarbamate macrocycles have been synthesized from  $R_2SnCl_2$  and the bis(dithiocarbamate) derivative of N,N'-dibenzylhexamethylene-1,6-diamine [23]. In addition, pioneering works in this field by Paul D. Beer research group are noteworthy [24].

In continuation of our research on the chemistry of dithiocarbamates [25], in the present work, the complexation behavior of the DTCs of  $N^l, N^n$ -dicinnamylalkane-1,*n*-diamines with transition metals is investigated. We report the complexation reaction of dithiocarbamates of  $N^l, N^3$ -dicinnamylpropane-1,3-diamine,  $N^l, N^4$ -dicinnamylbutane-1,4-diamine and  $N^l, N^6$ -dicinnamylhexane-1,6-diamine with various metal ions at room temperature. To the best of our knowledge, there has been no report for complexation reaction of these ligands with metal ions up to now. At last, the structures of the complexes are verified by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, CHN, and TGA analyses. The electron microscopy is utilized to investigate the probable formation of crystalline phase with a clear look at the topography of powder. The powder sample is analyzed by X-ray diffraction and the Radial Distribution Function (RDF) analysis of the specimen shows quantitative real space typical lengths formed in the molecule.

## 2. Experimental Section

## 2.1. General

The solvents and reagents were of analytical grade. The NMR spectra were recorded on a Bruker 500 MHz spectrometer. FT-IR spectra were recorded on ABB Bomem, MB 100 spectrometer. Elemental analyses were conducted with a Perkin-Elmer 2004 (II) CHN analyzer. Thermogravimetric analysis (TGA) was performed using Agilent Technology (HP) Quadrupole Analyzer (Netzsch - TGA 209 F1) on samples (6.80 mg for **7a**, 6.08 mg for **8a** and 5.74 mg for **8b** by weight) at a heating rate of 20°C min<sup>-1</sup> between room temperature and 600 °C under a flow of nitrogen. FESEM elecron microscopy is utilized to investigate probable formation of any crystalline phase. The results show obviously that no crystalline phases are present in the sample and the material is grown in completely amorphous form. This result is justified by XRD experiments showing the diffuse peaks in the diffracted data, too.

## 2.2. General procedure for synthesis of diimines

Cinnamaldehyde (2 mmol) was dissolved in 0.5 mL of dry ethanol and diamine (1mmol) was added to the reaction flask. The mixture of the reaction was refluxed for 2 hours at 80 °C. The product was simply achieved by evaporation of the solvent as a yellow solid. The yield of the reaction was 79% for 1,3-propane diamine, 82% for 1,4-butane diamine and 75% for 1,6-hexane diamine.

 $[(0E,4E)-N^1,N^3-bis((E)-3-phenylallylidene)propane-1,3-diamine]$  (**3a**): IR (KBr) *v* 689, 749, 1164, 1620, 1639, 3028 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (dd, 2H, *J*= 1 and 7 Hz, 2CH=N), 7.36-7.52 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>), 6.96-6.97 (m, 4H, C<sub>6</sub>H<sub>5</sub>-CH=CH\*2), 3.63 (t, 4H, *J*= 6.7 Hz, 2NCH<sub>2</sub>), 2.08 (m, 2H, NCH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  163.4, 141.9, 136.2, 129.5, 129.2, 128.6, 127.6, 59.5, 32.4 ppm.

[(9*E*,14*E*)-N<sup>1</sup>,N<sup>4</sup>-bis((*E*)-3-phenylallylidene)butane-1,4-diamine] (**3b**): IR (KBr) *v* 689, 749, 1184, 1620, 1639, 3028 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.07 (dd, 2H, *J*= 1 and 7 Hz, 2CH=N), 7.30-7.51 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>), 6.94-6.96 (m, 4H, C<sub>6</sub>H<sub>5</sub>-CH=CH\*2), 3.60-3.63 (t, 4H, *J*= 6.7 Hz, 2NCH<sub>2</sub>), 1.78-1.79 (m, 4H, 2NCH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 163.1, 141.8, 136.2, 129.5, 129.2, 128.6, 127.6, 61.8, 29.1 ppm.

[(9*E*,16*E*)-N<sup>1</sup>,N<sup>6</sup>-bis((*E*)-3-phenylallylidene)hexane-1,6-diamine] (**3c**): IR (KBr) *v* 689, 745, 1176, 1620, 1635, 3052 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (dd, 2H, *J* = 1 and 7 Hz, 2CH=N), 7.30-7.52 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>), 6.94-6.96 (m, 4H, C<sub>6</sub>H<sub>5</sub>-CH=CH\*2), 3.54-3.57 (t, 4H, *J*= 6.7 Hz, 2NCH<sub>2</sub>), 1.71-1.74 (m, 4H, 2NCH<sub>2</sub><u>CH<sub>2</sub></u>), 1.43-1.45 (m, 4H, 2NCH<sub>2</sub><u>CH<sub>2</sub>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  162.8, 141.6, 136.2, 129.4, 129.2, 128.7, 127.6, 61.9, 31.3, 27.6 ppm.

## 2.3. General procedure for synthesis of diamines

Diimine (1 mmol) was dissolved in methanol and sodium borohydride (4 mmol) was added to the reaction in 0°C. The mixture was stirred overnight at room temperature. In completion, water (10 mL) was added and the product was extracted by dichloromethane (10 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and the pure diamine was produced after evaporating the solvent as a yellow viscous liquid in 95% for 1,3-propane diamine (**4a**), 87% for 1,4-butane diamine (**4b**) and 90% for 1,6-hexane diamine (**4c**).

 $N^1$ , $N^3$ -dicinnamylpropane-1,3-diamine (**4a**): IR (KBr) v 693, 741, 967, 1120, 1635, 3422 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.20-7.36 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>), 6.50 (d, 2H, *J*= 16 Hz, C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.28 (dt, 2H, *J*= 6.5 and 16 Hz, C<sub>6</sub>H<sub>5</sub>-CH=<u>CH</u>), 3.39-3.42 (m, 4H, 2NCH<sub>2</sub>), 2.70-2.76 (t, *J*= 6.5 Hz, 4H, 2NCH<sub>2</sub>), 1.72-1.74 (m, 2H, NCH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  137.6, 131.6, 128.9, 127.8, 127.7, 126.7, 52.4, 48.4, 30.8 ppm.

 $N^1, N^4$ -dicinnamylbutane-1,4-diamine (**4b**): IR (KBr) v 693, 741, 971, 1124, 1647, 3471 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.43 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>), 6.55 (d, 2H, *J*=16 Hz, 2C<sub>6</sub>H<sub>5</sub>- <u>CH</u>=CH), 6.31 (dt, 2H, J= 16 and 6.5 Hz, 2C<sub>6</sub>H<sub>5</sub>-CH=<u>CH</u>), 3.45-3.46 (dd, 4H, J= 6.4 and 1.5 Hz, 2NCH<sub>2</sub>), 2.71-2.74 (t, 4H, J= 6.5 Hz, 2NCH<sub>2</sub>), 1.61-1.63 (m, 4H, 2NCH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  137.5, 131.6, 128.9, 128.5, 127.7, 126.6, 52.3, 49.7, 28.4 ppm.

 $N^1$ ,  $N^6$ -dicinnamylhexane-1,6-diamine (**4c**): IR (KBr) *v* 697, 745, 967, 1128, 1651, 3426 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.24-7.42 (m, 10H, 2C<sub>6</sub>H<sub>5</sub>), 6.54-6.58 (d, 2H, *J*=16 Hz, 2C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.31-6.37 (dt, 2H, *J*= 16.0 and 6.5 Hz, 2C<sub>6</sub>H<sub>5</sub>-CH=<u>CH</u>), 3.43-3.45 (d, 4H, *J*=6.5 Hz, 2NCH<sub>2</sub>), 2.67-2.7 (t, 4H, *J*= 6.5 Hz, 2NCH<sub>2</sub>), 1.55-1.58 (m, 4H, 2NCH<sub>2</sub><u>CH<sub>2</sub></u>), 1.4-1.41 (m, 4H, 2NCH<sub>2</sub>CH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  137.6, 131.6, 129.0, 128.9, 127.7, 126.7, 52.4, 49.9, 30.6, 27.8 ppm.

### 2.4. General procedure for synthesis of DTC complexes

Diamine (1 mmol) was dissolved in 2 mL methanol and sodium hydroxide (2 mmol) was added to the reaction container. After 10 minutes,  $CS_2$  (3 mmol) was added to the flask and the reaction was continued for 4-5 hours to complete the sodium bis(dithiocarbamate) salt formation. Finally, the ultimate complexes were produced with the in situ addition of metal salts solutions (1 mmol in appropriate solvent in Tab. 1). The complexes were readily filtered and washed with methanol and water for several times to remove any unreacted starting materials and dried in vacuum at 70 °C for 24h to provide the complexes as stable solids in high yields of 73-92%.

(**6a**): IR (KBr) *v* 693, 749, 967, 1220, 1422, 1490, 1655 cm<sup>-1</sup>; Anal. Calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>S<sub>4</sub>Zn: C, 52.91; H, 4.63; N, 5.37. Found: C, 50.36; H, 4.83; 5.94.

(**6b**): IR (KBr) *v* 696, 745, 962, 1220, 1429, 1496, 1601 cm<sup>-1</sup>; Anal. Calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>S<sub>4</sub>Ni: C, 53.60; H, 4.69; N, 5.44. Found: C, 52.15; H, 5.27; N, 6.50.

(**6c**): IR (KBr) *v* 693, 741, 963, 1220, 1418, 1486, 1623 cm<sup>-1</sup>; Anal. Calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>S<sub>4</sub>Pd: C, 49.06; H, 4.30; N, 4.97. Found: C, 46.65; H, 4.50; N, 5.38.

(**6d**): IR (KBr) *v* 698, 747, 965, 1204, 1417, 1492, 1625 cm<sup>-1</sup>; Anal. Calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>S<sub>4</sub>Hg: C, 42.03; H, 3.68; N, 4.26. Found: C, 41.80; H, 3.70; N, 5.01.

(**6e**): IR (KBr) *v* 605, 737, 967, 1212, 1406, 1474, 1643 cm<sup>-1</sup>; Anal. Calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>S<sub>4</sub>Pb: C, 41.61; H, 3.64; N, 4.22. Found: C, 40.8; H, 3.66; N, 4.98.

(7a): IR (KBr) v 697, 749, 967, 1212, 1422, 1490, 1636 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSOd<sub>6</sub>)  $\delta$  7.24-7.31 (m, 20H, 4C<sub>6</sub>H<sub>5</sub>), 6.58-6.64 (d, 4H, *J*= 16.0 Hz, 4C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.33 (m, 4H, 4C<sub>6</sub>H<sub>5</sub>-CH=<u>CH</u>), 4.62 (m, 8H, 4NCH<sub>2</sub>), 3.84 (t, 8H, *J*= 6.5 Hz, 4NCH<sub>2</sub>), 1.75 (m, 8H, 4NCH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; Anal. Calcd for C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>S<sub>4</sub>Zn: C, 53.77; H, 4.89; N, 5.23. Found: C, 52.47; H, 5.22; N, 6.0.

(**7b**): IR (KBr) v 697, 745, 963, 1216, 1434, 1502, 1644 cm<sup>-1</sup>; Anal. Calcd for  $C_{24}H_{26}N_2S_4Ni$ : C, 54.45; H, 4.95; N, 5.29. Found: C, 51.4; H, 5.2; N, 5.48.

(**7c**): IR (KBr) *v* 693, 745, 967, 1212, 1430, 1498, 1636 cm<sup>-1</sup>; Anal. Calcd for C<sub>48</sub>H<sub>52</sub>N<sub>4</sub>S<sub>8</sub>Pd<sub>2</sub>: C, 49.94; H, 4.54; N, 4.85. Found: C, 50.17; H, 4.89; N, 5.33.

(**8a**): IR (KBr) *v* 697, 745, 967, 1212, 1430, 1494, 1643 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35-7.45 (m, 20H, 4C<sub>6</sub>H<sub>5</sub>), 6.59-6.63 (d, 4H, *J*= 15.6 Hz, 4C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.29-6.35 (m, 4H, 4C<sub>6</sub>H<sub>5</sub>-CH=<u>CH</u>), 4.64-4.65 (brs, 8H, 4NCH<sub>2</sub>), 3.86 (brs, 8H, 4NCH<sub>2</sub>), 1.84 (brs, 8H, 4NCH<sub>2</sub><u>CH<sub>2</sub></u>), 1.43 (brs, 8H, 4NCH<sub>2</sub>CH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 25.8, 26.2, 53.7, 56.6, 121.8, 126.6, 127.8, 128.6, 134.4, 135.9, 203.9 ppm; Anal. Calcd for C<sub>52</sub>H<sub>60</sub>N<sub>4</sub>S<sub>8</sub>Zn<sub>2</sub>: C, 55.35; H, 5.36; N, 4.97. Found: C, 55.70; H, 5.36; N, 5.16.

(**8b**): IR (KBr) *v* 693, 749, 967, 1220, 1434, 1498 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.61 (m, 20H, 4C<sub>6</sub>H<sub>5</sub>), 6.54-6.59 (d, 4H, *J*= 16.0 Hz, 4C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.11-6.12 (m, 4H, 4C<sub>6</sub>H<sub>5</sub>-CH=<u>CH</u>), 4.33 (brs, 8H, 4NCH<sub>2</sub>), 3.49-3.53 (brs, 8H, 4NCH<sub>2</sub>), 1.43-1.64 (brs, 8H, 4NCH<sub>2</sub><u>CH<sub>2</sub></u>), 1.22-1.31 (brs, 8H, NCH<sub>2</sub>CH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  25.9, 26.7, 48.5, 51.0, 121.2, 126.6, 128.2, 128.7, 134.9, 135.8, 207.1 ppm; Anal. Calcd for C<sub>52</sub>H<sub>60</sub>N<sub>4</sub>S<sub>8</sub>Ni<sub>2</sub>: C, 56.02; H, 5.42; N, 5.02. Found: C, 57.45; H, 5.80; N, 5.24.

(8c): IR (KBr) v 692, 745, 962, 1216, 1429, 1474 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.25-7.35 (m, 20H, 4C<sub>6</sub>H<sub>5</sub>), 6.55-6.60 (d, 4H, *J*= 15.8 Hz, 4C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.11-6.15 (m, 4H, 4C<sub>6</sub>H<sub>5</sub>-CH=CH), 4.42 (brs, 8H, 4NCH<sub>2</sub>), 3.48-3.63 (brs, 8H, 4NCH<sub>2</sub>), 1.66 (brs, 8H, 4NCH<sub>2</sub><u>CH<sub>2</sub></u>), 1.25-1.32 (brs, 8H, 4NCH<sub>2</sub>CH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  26.0, 26.7, 48.9, 51.3, 121.2, 126.6, 128.2, 128.9, 134.9, 135.7, 211.2 ppm; Anal. Calcd for C<sub>52</sub>H<sub>60</sub>N<sub>4</sub>S<sub>8</sub>Pd<sub>2</sub>: C, 51.6; H, 5.0; N, 4.63. Found: C, 52.65; H, 5.44; N, 4.88.

(8d): IR (KBr) v 689, 745, 959, 1200, 1414, 1486, 1679 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.35-7.45 (m, 20H, 4C<sub>6</sub>H<sub>5</sub>), 6.59-6.62 (d, 4H, *J*= 15.5 Hz, 4C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.33-6.39 (m, 4H,  $4C_6H_5$ -CH=<u>CH</u>), 4.60-4.61 (d, 8H, J= 6.5 Hz, 4NCH<sub>2</sub>), 3.79-3.82 (t, 8H, J= 6.7 Hz, 4NCH<sub>2</sub>), 1.87-1.89 (m, 8H, 4NCH<sub>2</sub><u>CH<sub>2</sub></u>), 1.44-1.45 (m, 8H, 4NCH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; Anal. Calcd for  $C_{52}H_{60}N_4S_8Hg_2$ : C, 44.65; H, 4.32; N, 4.01. Found: C, 44.40; H, 4.29; N, 4.50.

(8e): IR (KBr) v 701, 741, 963, 1200, 1418, 1474 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.22-7.6 (m, 20H, 4C<sub>6</sub>H<sub>5</sub>), 6.47-6.52 (d, 4H, J = 15.7 Hz, C<sub>6</sub>H<sub>5</sub>-<u>CH</u>=CH), 6.23-6.28 (m, 4H, C<sub>6</sub>H<sub>5</sub>-CH=<u>CH</u>), 4.53 (brs, 8H, 4NCH<sub>2</sub>), 3.84-3.88 (brs, 8H, 4NCH<sub>2</sub>), 1.61-1.75 (brs, 8H, 4NCH<sub>2</sub><u>CH<sub>2</sub></u>), 1.25-1.36 (brs, 8H, NCH<sub>2</sub>CH<sub>2</sub><u>CH<sub>2</sub></u>) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  25.9, 26.5, 48.5, 51.0, 121.2, 126.6, 127.9, 128.6, 133.8, 136.2, 202.9 ppm; Anal. Calcd for C<sub>52</sub>H<sub>60</sub>N<sub>4</sub>S<sub>8</sub>Pb<sub>2</sub>: C, 44.23; H, 4.28; N, 3.97. Found: C, 45.24; H, 4.55; N, 4.52.

## **3. Results and Discussion**

### 3.1. Synthesis of ligands and complexes

First, we focused on the synthesis of secondary diamines. For this purpose, three diverse primary diamines including 1, 3-propane diamine, 1, 4-butane diamine, and 1, 6-hexane diamine are surveyed. The diamines were reacted with cinnamaldehyde to provide the corresponding diimines in high to excellent yields. The diimines then were reduced with NaBH<sub>4</sub> to afford the final secondary N,N'-dicinnamyl alkanediamines in excellent yields (Scheme 1).



Scheme 1. Synthesis of  $N^{l}$ ,  $N^{n}$ -dicinnamylalkane-l, n-diamines.

After characterization of the synthesized diamines and confirmation of their structures, these diamines were applied in other reaction with carbon disulfide in alkaline medium in methanol as

the solvent to provide the corresponding bis(dithiocarbamate) salts. The *in situ* prepared dithiocarbamate salts then reacted with various transition metal salts including  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Pd^{2+}$ ,  $Hg^{2+}$  and  $Pb^{2+}$  salts to provide the corresponding cage-like (macrocyclic) complexes (Scheme 2). Finally, the ultimate products were simply filtered.



Scheme 2. Synthesis of ligands and complexes.

The resulting complexes **6** produced from *N*,*N*'-dicinnamyl propanediamine had no solubility in common organic and NMR solvents. Although, the CHN data of complexes are in accord with theoretical calculations, as a result of outcomes of solubility test, we suggest that these compounds might have become polymerized. Due to the fact that the cage constructed from sulfur atoms and the metal ions is not enough big to produce and the metals may have been placed close to each other, polymerization might be a more plausible way for the molecules to be arranged with one another. In the case of *N*,*N*'-dicinnamyl butanediamine, only the complex with Zn had a little solubility in DMSO that enabled us to study its <sup>1</sup>H NMR spectrum.

Literature survey revealed that all the dinuclear macrocyclic dithiocarbamate complexes reported to date are synthesized using a  $N^1$ , $N^6$ -diamine [26]. As the next step, the chain size of the initial diamine is increased by two more carbon atoms. We utilized  $N^1$ , $N^6$ -dicinnamylhexane-1,6-diamine to assure that the two metals didn't trigger steric hindrance. The corresponding

macrocyclic complexes **8a-e** were obtained in excellent yields. By performing the solubility test, it can be established that the ultimate complexes have sufficient solubility in chloroform.

## 3.2. Characterization of DTC complexes by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and TGA analyses

The structure of the synthesized complexes was verified by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, CHN, and TGA analyses.

## 3.2.1. IR spectral studies

The characteristic band in IR spectra of DTC complexes can be assigned in the range of 940-1050 cm<sup>-1</sup>, without any splitting, which is related to the symmetrical mode of DTC ligand acting in a bidentate mode [27]. In all of the synthesized complexes, a single band at 960 cm<sup>-1</sup> was observed, which completely confirms a bidentate symmetrical behavior of the DTC moiety. Other characteristic bands for synthesized complexes were observed in ranges of 1450-1550 cm<sup>-1</sup> and 1620-1650 cm<sup>-1</sup>, which are attributed to the thioureide and the C=C double bond groups, respectively.

## 3.2.2. NMR spectral studies

<sup>1</sup>H NMR spectra of the complexes show a doublet peak at 4.6 ppm and a broad peak at 3.8 ppm for the methylene groups attached to the nitrogen. These protons in the diamine were assigned at 3.4 and 2.7 ppm, respectively. The other protons of the complexes were observed at the similar chemical shift in comparison to the diamine. The observed deshielding for the NCH<sub>2cinnamyl</sub> and NCH<sub>2chain</sub> of the methylene protons (around 1 ppm) in the complexes indicates the formation of the dithiocarbamate complexes which is related to the release of the electrons from the nitrogen atoms of the DTC group towards the sulfur atoms (or the metal) via the thioureide  $\pi$  system. The proton signals of the macrocyclic products appeared as broad in <sup>1</sup>H NMR spectra which may be attributed to the existence of dynamic processes in the solution. The presence of a peak at 203.9 ppm for **8a**, 207.1 ppm for **8b** and 211.2 ppm for **8c** in <sup>13</sup>C NMR spectra is assigned for the N<sup>13</sup>CS<sub>2</sub> carbon atoms in the complexes [26, 28].

## 3.2.3. TGA analyses

The thermogravimetric analysis (TGA) was applied to evaluate the physical behavior of bis(dithiocarbamate) complex of nickel prepared from 1,6-hexane diamine **8b** (Figure 1). The

TGA curve shows three weight losses: in the temperatures range above 100 °C (mass loss 3.25%) that may be assigned for the loss of moisture and solvent residue from the sample; 200–280 °C (mass loss 30.54%) that may be assigned for the loss of two cinnamyl isothiocyanate groups (calculated mass loss 33.9%) and 270-440 °C (mass loss 46.38%) was attributed to the loss of other organic parts (calculated mass loss 48.9%). The remaining residue (20%) may be assigned for the values calculated (22%) for the mass percentage of two NiS<sub>2</sub>. [25a, 29]. Similar behavior was observed for the Zn complexes **7a** and **8a** with 1,4-butanediamine and 1,6-hexanediamine, but the final remaining residue may be attributed to the formation of two ZnS (see Supplementary material).[30]



Figure 1. TGA of complex 8b.

## 3.3. Electron microscopy and X-ray diffraction studies

In order to have a valid picture of our final products, we attempted to make crystals suitable for X-ray crystallography. To do so, we applied two common methods of crystallization: tank crystallization and diffusion method. Inasmuch as the complexes of 1, 6-hexane diamine had shown an appropriate solubility in chloroform, we chose this solvent as the "good" solvent. In diffusion method, we employed a spectrum of volatile solvents as the anti-solvent: ethanol, methanol, and ethyl acetate. Despite all these efforts, there were not any crystals in the crystallization tanks. In addition, attempt to obtain HRMS analysis of complexes was unsuccessful. Therefore, we tried to analyze the structure by X-ray diffraction intensity showing diffuse peaks typical of amorphous materials (vide infra).

## **3.3.1.** Establishment of the atomic configuration of the molecule 8a (C<sub>52</sub>H<sub>60</sub>N<sub>4</sub>S<sub>8</sub>Zn<sub>2</sub>) by electron microscopy and X-ray diffraction

Characterization of amorphous materials can be performed by a variety of techniques. As the experiments by electron microscopy and X-ray diffraction will show, any attempts to crystallize the molecule led to any crystalline form. FESEM is employed to make maps of real space geometry of the morphology of the material under question and to recognize whether the probable crystalline phases of micro-molecule are formed or not. As the results of electron microscopy will show, no crystallization is observable in the powder of the synthesized complex.

Furthermore, XRD experiments contain diffuse peaks typical of amorphous materials that confirm the result obtained via electron microscopy (see below). Due to its ability for obtaining the characteristic lengths in amorphous materials, X-ray diffraction is applied to confirm atomatom distances in the molecule via the Fourier transforming, and the XRD data collected by two different lab source facilities.

## 3.3.1.1. FESEM Data

Here, data collected from FESEM facility are reported. The sample is coated with a thin layer of gold to produce the conductivity. Figure 2 shows a  $2\mu m$  size image of the sample. As shown in Figure 2, the amorphous nature of the specimen is obvious and no crystalline phases are seen in the sample.



Figure 2. Image of the sample (2µm size)

Figure 3 is 200nm size image of the sample and confirms that no crystalline phase is present in the sample.



Figure 3. Image of the sample with 29.00kV high voltage (200nm size)

Interestingly, the samples of sizes down to 12 nm show no crystallization phases (see Supplementary material). Therefore, we employ the XRD technique in order to progress towards quantitatively investigating the geometry of the molecule in the next subsection.

## 3.3.1.2. Local structure in 8a (C<sub>52</sub>H<sub>60</sub>N<sub>4</sub>S<sub>8</sub>Zn<sub>2</sub>) from X-ray Radial Distribution Analysis

X-ray experimental intensity scattered by the specimen,  $I_{exp}(q)$ , contains the maximum information about the atomic configuration of asymmetric units. The groundwork of Debye for the intensity analysis scattered by a non-crystalline array of atoms makes it possible to establish the correct atomic configuration. This is well performed by comparing the computed theoretical function for the predicted model with the experimental intensity function obtained in X-ray diffraction experiment.

Debye scattering equation (DSE) for the intensity scattered by a collection of atoms with a given arbitrary arrangement in electron unit is given by [31]

$$I = \mathop{\text{a}}_{i} \mathop{\text{a}}_{j} f_{i}f_{j} \frac{\sin 2pqr_{ij}}{2pqr_{ij}}$$

where,  $f_i$  and  $f_j$  are the atomic scattering factor of *i* and *j*, and  $r_{ij}$  is the magnitude of the vector separating *i* and *j*. The integral has been taken over all orientations of atomic arrangement in space, to include the effect of the specimen rotation. The comparing procedure of Debye function analysis and the trial-and-error contained in this method can be bypassed by obtaining radial distribution function (RDF) of the sample directly, which is the real-space interatomic distance correlation function [32]. RDF is the main machinery for the study of non-crystalline materials through Fourier transformation analysis of X-ray diffraction data.

Two experiments are done in two different laboratories which show close results for atom-atom distances. As shown in Figures 5 and 7, the materials' XRD patterns contain diffuse peaks typical of amorphous materials. The data were collected with X-ray lab-sources having Cu lamps, which lack large scattering wavenumbers. According to the results shown below, the quantitative establishment of the typical distances in the molecule can be realized. The polarization and geometry effects are subtracted from the experimental data in both experiments.

Figure 4 shows experimental diffraction data from the powder specimen which is collected by PANAlytic lab source in KEFA COMPANY.



Figure 4. Experimental X-ray diffraction data from the powder specimen

Corresponding RDF of experimental X-ray diffraction data is shown in Figure 5.



Figure 5. Corresponding RDF of experimental X-ray diffraction data

A parallel data collected by a different lab source experiment (XRD-PM) is shown in Figure 6.



Figure 6. Experimental X-ray diffraction data from the powder specimen

Experimental RDF of X-ray diffraction collected in XRD-PM laboratory is shown in Figure 7.



Figure 7. Corresponding RDF of experimental X-ray diffraction data

Lower distances corresponding to the peaks of RDF in two graphs are tabulated in Table 1. These distances are plausibly attributed to atom-atom lengths in the molecule, which are also reported in the Table 1.

Peak Number	1	2	3	4	5	6	7	
Distance (Å) (XRD- KEFA)	1.34	5.25	8.90	12.51	16.03	19.63	23.24	
Distance (Å) (XRD- PM)	1.34	5.48	8.59	12.45	15.80	19.08	22.53	
Number of $d_{C=C}$ length		5	6	9	12	14	17	
Plausible Bond	C=C	Zn-Zn	N-N (longitudina	N-N l) (diagonal)				

Table 1. Plausible attributed atom-atom lengths in the molecule

First we define firstly typical C=C bond length, which mediates between different atoms by sp<sup>2</sup> overlapping, as  $d_{C=C} = \cos 30^{\circ} \cdot 1.34$ ; 1.16Å. The second peak can be attributed plausibly to M-M length for the complex with 5 C=C bonds, since the distance can be calculated through  $d_{M-M} = 5 \cdot \cos 30^{\circ} \cdot 1.34$ ; 5.80Å. The first peak contains different distances contributing to the peak, for example, C=C bond and sulfur-nitrogen bonds and other similar-distant bonds may overlap to yield a diffuse peak with relatively large height. The third peak is ascribed to mean $d_{N-N}$ ; four N atoms construct a simple tetragon rectangle whose width and length are respectively 5 and 6  $d_{C=C}$ . The fourth peak is about 9  $d_{C=C}$  mediating length, so we attribute it to the diagonal of the rectangle constructed by N atoms. Because the diffuse peaks in RDF contain different contributing atom-atom lengths, other parts cannot be inferred clearly. Other parts can't be inferred clearly.

## 4. Conclusion

Being able to stabilize transition metals with a variety of oxidation states, dithiocarbamate (DTC) complexes have attracted scientists' attention. This article described the synthesis and characterization of DTC complexes based on  $N^l$ ,  $N^n$ -dicinnamylalkane-*1*, *n*-diamines. For this purpose, cinnamaldehyde was condensed with diamines (1, 3-diaminopropane, 1, 4-diaminobutane, 1, 6-diaminohexane) in ethanol as the solvent in order to form the related diimines. Sodium borohydride reduction of the diimines in methanol afforded the related diamines as yellow viscous liquids. The final complexes were prepared via the *in situ* reaction of the diamines, CS<sub>2</sub>, and related metal salts. Although macrocyclic compounds were proved for 1,6-hexane diamine, polymerization can be assumed for the shorter chained diamines due to the insolubility of the corresponding complexes in diverse organic solvents.

Electron microscopy clearly shows the formation of clusters of the molecule without having any crystalline phase. XRD intensities collected by various lab source facilities, also, show clearly diffuse peaks typical of amorphous materials. Therefore, we employed the Radial Distribution Function (RDF) analysis of X-ray diffracted data and investigate the atomic local structure of the molecular complex. Atom-atom distances are calculated via Fourier transform analysis of XRD intensity to yield a real-space visualization of the structure of the molecule.

#### Acknowledgement

We are grateful the research council of Kharazmi University for supporting this work. We also thank Sharif University of Technology for financial support.

## References

[1] Cao, S. L.; Feng, Y. P.; Jiang, Y. Y.; Liu, S. Y.; Ding, G. Y.; Li, R.T. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1915-1917.

[2] Len, C.; Postal, D.; Ronco, G.; Villa, P.; Goubert, C.; Jeufrault, E.; Mathon, B.; Simon,
H. J. *J. Agric. Food Chem.* **1997**, *45*, 3-6.

[3] Rafin, C.; Veignie, E.; Sancholle, M.; Postel, D.; Len, C.; Villa, P.; Ronco, G. J. Agric. *Food Chem.* **2000**, *48*, 5283-5287.

[4] Dooghe, M.; De Kime, N. *Tetrahedron* **2006**, *62*, 513-535.

[5] Engels, H. W.; Weidenhaupt, H. J.; Pieroth, M.; Hofmann, W.; Menting, K. H.; Mergenhagen, T.; Schmoll, R.; Uhrlandt, S. Rubber, *Chemicals and Additives. In Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Winheim. **2007**.

[6] Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; De Bore, B. *Polym. Rev.* **2008**, 48, 531-582.

[7] Dilien, H.; Palmaerts, A.; Martijn, L.; Boer, B.; Blom, P.; Cleij, T.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2010**, *43*, 10231-10240.

[8] Banishoeib, F.; Adriaensens, P.; Berson, S.; Guillerez, S.; Douheret, O.; Manca, J.;
Fourier, S.; Cleij, T. J.; Lutsen, L.; Vandersarde, D. Sol. Energy Mater. Sol. Cells 2007, 91, 1026-1034.

[9] (a) Vichers, M. S.; Cookson, J.; Beer, P. D.; Bishop, P.T.; Thiebaut, B. J. Mater. Chem.
2006, 16, 209-215. (b) Hogarth, G.; Rainford-Brent, E.; Richards, I. Inorg. Chem. Acta. 2008, 362, 1361-1364. (c) G. Hogarth, Prog. Inorg. Chem. 2005, 53, 71-561 and references are therein.
(d) Y. S. Tan, A. L. Sudlow, K. C. Molloy, Y. Morishima, K. Fujisawa, W. J. Jackson, W. Henderson, S. N. Bt. A. Halim, S. W. Ng, E. R. T. Tiekink, Crystal Growth & Design 2013, 13, 3046–3056. (e) Jamaludin, N. S.; Goh, Z. J.; Cheah, Y. K.; Ang, K. P.; Sim, J. H.; Khoo, C. H.; Fairuz, Z. A.; Halim, S. N. Bt. A.; Ng, S. W.; Seng, H.-L.; Tiekink, E. R. T. *Eur. J. Med. Chem.* 2013, 67, 127–141. (f) Ishak, D. H. A.; Ooi, K. K.; Ang, K. P.; Akim, A. Md.; Cheah, Y. K.; Nordin, N.; Halim, S. N. B. A.; Seng, H.-L.; Tiekink, E. R. T. J. Inorg. Biochem. 2014, 130, 38–51.

[10] (a) Berry, D. J.; de Rosales, R. T. M.; Charoenphun, P.; Blower, P. J. *Mini Rev. Med. Chem.* 2012, *12*, 1174.

[11] (a) Ziyaei-Halimehjani, A.; Maleki, H.; Saidi, M. R. *Tetrahedron Lett.* 2009, *50*, 2747–2749. [b] Jamir, L.; Sinha, U. B.; Nath, J.; Patel, B. K. *Synth Commun.* 2012, *42*, 951–958. (c) Ziyaei Halimehjani, A.; Marjani, K.; Ashouri, A. A. *Tetrahedron Lett.* 2012, *53*, 3490–3492. (d) Ziyaei Halimehjani, A.; Ashouri, A.; Marjani, K. *J. Heterocycl. Chem.* 2012, *49*, 939–942. (e) Aryanasab, F.; Ziyaei Halimehjani, A.; Saidi, M. R. *Tetrahedron Lett.* 2010, *51*, 790–792. (f) Ziyaei Halimehjani, A.; Hasani, L.; Alaei, M. A.; Saidi, M. R. *Tetrahedron Lett.* 2016, *57*, 883–886. (g) Ziyaei Halimehjani, A.; Hajiloo Shayegan, M.; Hashemi, M. M.; Notash, B. Org Lett.

**2012**, *14*, 3838–3841. (h) Ziyaei Halimehjani, A.; Ranjbari, M. A.; Pasha Zanussi, H. *RSC Adv*. **2013**, *3*, 22904–22908.

[12] Greene, T. W.; Wuts, P. G. M. *Protective groups in organic synthesis*. 3rd ed. New York (NY): Wiley-Interscience 1999.

[13] (a) Tong, M. C.; Chen, W.; Sun, J.; Ghosh. D.; Chen, S. J. Phys. Chem. B 2006, 110, 19238-19242. (b) Guerrini, L.; Garicia-Ramos, J. V.; Domingo, C.; Sanchez-Cortes, S. J. Phys. Chem. 2009, 11, 1787-1793.

[14] Srinivasan, N.; Thirumaran, S. Superlattices Microstruct. 2012, 51, 912-920.

[15] Ajibade, P. A.; Onwudiwe, D. C.; Moloto, M. J. Polyhedron 2011, 30, 246-252.

[16] Thomas, P. J.; Fan, D.; O'Brien, P. J. Colloid Interface Sci. 2011, 354, 210-218.

[17] Maddani, M. R.; Moorthy, S. K.; Prabhu, K. R. *Tetrahedron* **2010**, *66*, 329-333.

[18] Venkatesan, K. A.; Srinivasan, T. G.; Vasudev Rao, P. R. *Physicochem. Eng. Aspects.***2001**, 180, 277-284.

[19] Mahmoud, M. E. Anal. Chim. Acta 1999, 398, 297-304.

[20] Fujii, S.; Yoshimura, T. Coord. Chem. Rev. 2000, 198, 89-99.

[21] Paschenko, S. V.; Khramtsov, V. V.; Skatchkov, M. P.; Plyusnin, V. F.; Bassenge, E. *Biochem. Biophys. Res. Commun.* **1996**, 225, 577-584.

[22] Cookson, J.; Evans, E. A. L.; Maher, J. P.; Serpell, C. J.; Paul, R. L.; Cowley, A. R.;Drew, M. G. B.; Beer, P. D. *Inorg. Chim. Acta* 2010, 363, 1195-1203.

[23] Reyes-Martínez, R.; Mejia-Huicochea, R.; Guerrero-Alvarez, J. A.; Höpfl, H.; Tlahuext, H. *ARKIVOC* 2008, (v), 19-30.

[24] Wong, W. W. H.; Curiel, D.; Cowley, A. R.; Beer, P. D. Dalton Trans. 2005, 2, 359-364.

[25] (a) Ziyaei, A.; Marjani, K. Ashouri, A.; Amani, V. *Inorg. Chem. Acta.* 2011, *373*, 282-285. (b) Ziyaei Halimehjani, A.; Torabi, S.; Amani, V.; Notash, B.; Saidi, M. R. *Polyhedron* 2015, *102*, 643–648.

[26] Sathiyaraj, E.; Thirumaran, S. Spectrochim. Acta Part A: Mol. Biomol. Spectrosc. 2012, 97, 575–581.

- [27] Bonati, F.; Ugo, R.; J. Organomet. Chem. 1967, 10, 257–268.
- [28] (a) Ivanov A. V., Rodina T. A., Antzutkin O. N., Polyhedron 1998, 17, 3101-3109. (b)
  Ivanov A.V., Antzutkin O.N., *Top. Curr. Chem.*, 2005, 246, 271-337.
- [29] Sathiyaraj, E.; Gurumoorthy, G.; Thitumaran, S. New J. Chem., 2015, 39, 5336-5349.
- [30] Onwudiwe, D. C.; Ajibade, P. A. Int. J. Mol. Sci. 2012, 13, 9502-9513.
- [31] Debye, P. J. W. Ann. Phys. **1915**, *351*, 809–823.
- [32] Warren, E. B. J. Appl. Cryst. 1996, 29, 309-310.

Dithiocarbamate complexes base on  $N^l, N^n$ -dicinnamylalkane-1,*n*-diamine were prepared  $\blacktriangleright$  The structure of complexes were assigned as polymer or macrocyclic complexes  $\blacktriangleright$  Complexes were characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR, TGA and elemental analyses  $\triangleright$  Complexes do not show any crystalline phase even in long lasting terms  $\triangleright$  X-ray diffraction technique is employed to investigate atom-atom distances  $\triangleright$ 

CERTIN MARINE