

# Thiocyanate complexes of the group 12 metals with pyridine-2-carboxamide: Synthesis and structural characterization

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## Abstract

Three complexes of picolinamide (pyridine-2-carboxamide, pia) and metal thiocyanates,  $M(\text{SCN})_2$  ( $M = \text{Zn}, \text{Cd}, \text{Hg}$ ), namely two polymorphs of bis(picolinamide-*N,O*)-bis-(thiocyanato-*N*)zinc(II) (**1a** and **1b**), *catena*-[bis( $\mu$ -thiocyanato-*S,N*)-picolinamide-*N,O*-cadmium(II)] (**2**) and bis[ $(\mu_2$ -thiocyanato-*S*-thiocyanato-*S*-picolinamide-*N,O*)mercury(II)] (**3**) have been prepared and characterized by spectroscopic, thermal and X-ray crystallographic methods. The IR and thermal data correlate with the structures of the complexes in the solid state. The vibration bands of diagnostic value are compared to the values of the free ligands.

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**Keywords:** Metal complexes of the group 12; Picolinamide; Thiocyanate; X-ray crystal structure; IR; NMR spectra; TGA/DTA analysis

## 1. Introduction

The carboxamide group,  $[-\text{C}(\text{O})\text{NH}-]$ , ubiquitous throughout Nature in the primary structure of proteins, is an important ligand construction unit for coordination chemists. The behavior of pyridine carboxamides towards biologically relevant d-block metals has been widely investigated while much lesser attention had been paid toward exclusively toxic metals such as cadmium and mercury. In our recent research we examined the behavior of pyridinemono- and dicarboxylic acids and their derivatives and established that they act as efficient competitive ligands toward halides for coordination sites of these metal centres coexisting as anionic *N,O*-bidentate [1–4], *N,O,O*-tridentate [5], *O*-monodentate [3] and *O,O*-bidentate ligands [6], as well as neutral molecules [2]. Our interest is currently

engaged with exploring not only the coordination abilities of picolinamide with thiocyanate complexes of group 12 metals but also in getting some information possibly useful in understanding the role of the thiocyanate ion in biologically important processes recently discovered [7,8]. Here we report the synthesis of thiocyanate complexes of group 12 metals with picolinamide, their structural characterization by spectroscopic and diffraction methods as well as their thermal stability using TGA/DTA methods. The crystal and molecular structures of the two polymorphs  $[\text{Zn}(\text{NCS})_2(\text{pia})_2]$  (**1a** and **1b**), and  $[\text{Cd}(\text{SCN})_2(\text{pia})_n]$  (**2**) and  $[\text{Hg}(\text{SCN})_2(\text{pia})_2]$  (**3**) were determined by single crystal X-ray diffraction.

## 2. Experimental

### 2.1. Materials and physical measurements

All reagents were supplied by Aldrich Chemical Co. and were used as received without further purification. The

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CHNS-microanalyses were performed by the Chemical Analytical Service of the Ruđer Bošković Institut, Zagreb.

Infrared spectra were obtained from KBr pellets within the range 4000–400  $\text{cm}^{-1}$  with a Perkin–Elmer FTIR spectrometer 1600 Series.

The one-dimensional  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker AV 600 spectrometer, operating at 600.133 MHz and 150.971 MHz for the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively. Samples were measured in  $\text{DMSO-}d_6$  solution and chemical shifts (ppm) are referred to TMS.

The thermal measurements were performed using a simultaneous TGA–DTA analyzer (*TA Instruments*, SDT Model 2960). The TGA and DTA curves were obtained by placing samples of about 6 mg in mass, in small open platinum pans, with a heating rate of 10  $^\circ\text{C}/\text{min}$  and nitrogen (purity above 99.996%) pouring at a flow rate of 50 mL/min. All samples were heated from room temperature up to 700  $^\circ\text{C}$ . The SDT was calibrated with indium and silver.

## 2.2. Preparation of the complexes

### 2.2.1. Preparation of $[\text{Zn}(\text{NCS})_2(\text{pia})_2]$ (**1a** and **1b**)

A warm solution (50 mL) of picolinamide (0.24 g; 0.2 mmol) in water was slowly added to an aqueous solution (10 mL) of zinc nitrate hexahydrate (0.30 g; 0.1 mmol). Into the resulting solution was then added an aqueous solution (10 mL) of potassium thiocyanate (0.18 g; 0.2 mmol). After keeping the mother liquid for few days, white crystals suitable for further X-ray diffraction experiments were obtained. Total yield corresponds to 88% (0.37 g; 0.88 mmol) based on Zn. *Anal. Calc.* for  $\text{C}_{14}\text{H}_{12}\text{ZnN}_6\text{O}_2\text{S}_2$  (**1**): C, 39.49; H, 2.84; N, 19.74; S, 15.06. Found: C, 39.61; H, 2.98; N, 19.95; S, 15.16%. Selected IR data ( $\text{cm}^{-1}$ , KBr pellets): 3330s, 3184s, 2096vs, 1688s, 1666vs, 1624m, 1612m, 1593s, 1585s, 1569s, 1423s, 1184w, 1160w, 1124w, 1109m-w, 1074w, 1056w, 1024m, 798w, 780w, 755m, 744m, 724m-w, 528w. From the reaction mixture, in which an excess of a picolinamide was present, **1a** together with a few crystals of another polymorph **1b** were obtained.

### 2.2.2. Preparation of $[\text{Cd}(\text{SCN})_2(\text{pia})]_n$ (**2**)

Compound **2** was prepared in an analogous way to **1**, only using cadmium nitrate tetrahydrate (0.31 g; 0.1 mmol) as the starting metal salt. Total yield corresponds to 77% (0.28 g; 0.77 mmol) based on Cd. *Anal. Calc.* for  $\text{C}_8\text{H}_6\text{CdN}_4\text{O}_2\text{S}_2$  (**2**): C, 27.40; H, 1.72; N, 15.98; S, 18.29. Found: C, 27.48; H, 1.81; N, 16.03; S, 18.32%. Selected IR data ( $\text{cm}^{-1}$ , KBr pellets): 3408s, 3343m, 3284m, 3203s, 2119vs, 2094vs, 1669vs, 1610m-s, 1584s, 1571s, 1419s, 1181w, 1161w, 1117m, 1092w, 1054w, 1016s, 782w, 747s, 659s, 638m-w, 541m.

### 2.2.3. Preparation of $[\text{Hg}(\text{SCN})_2(\text{pia})]_2$ (**3**)

Into an aqueous solution (100 mL) of mercury(II) nitrate monohydrate (0.68 g; 2 mmol) with a few drops of diluted nitric acid (20% by weight), an aqueous solution (10 mL) of potassium thiocyanate (0.36 g; 4 mmol) was slowly

added. After several hours colourless crystals of mercury(II) thiocyanate were obtained. The crystals were filtered off, washed with water and dried. Total yield 85% (0.54 g; 1.7 mmol).  $\text{Hg}(\text{SCN})_2$  was then dissolved in ethanol (0.32 g; 1 mmol in 100 mL) by gentle heating and the ethanol solution (30 mL) of picolinamide (0.24 g; 2 mmol) was added in it. The resulting mixture was refluxed for 1 h. The clear solution thus formed was allowed to stand for a few days to yield colourless crystals of compound **3** suitable for X-ray investigations. Total yield corresponds to 82% (0.36 g; 0.82 mmol) based on Hg. *Anal. Calc.* for  $\text{C}_{16}\text{H}_{12}\text{Hg}_2\text{N}_8\text{O}_2\text{S}_4$  (**3**): C, 21.89; H, 1.38; N, 12.77; S, 14.61. Found: C, 21.95; H, 1.40; N, 12.82; S, 14.73%. Selected IR data ( $\text{cm}^{-1}$ , KBr pellets): 3409s, 3292s, 2130vs, 1691vs, 1616m-s, 1583s, 1568m, 1142w, 1095m, 1044w, 999m, 749s, 676m-w, 636m-w, 617m-s, 559m-s, 496m, 462m.

## 2.3. X-ray structural analysis

The general and crystal data, and summary of intensity data collection and structure refinement for compounds **1–3** are given in Table 1.

Data for structure **1a** were collected at 200 K on a Nonius KappaCCD diffractometer with a crystal-detector distance of 30 mm. The extraction and correction of the intensity data, absorption correction and the refinement of the unit cell parameters were performed with the program package DENZO-SMN [9].

Data for structures **1b**, **2** and **3** were collected at 293 K on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with a Sapphire 3 CCD detector, by applying the CrysAlis software system [10]. The crystal-detector distance was 60 mm. Data reduction, including absorption correction, was done by the CrysAlis RED application of the CrysAlis software system [10].

The structures were solved by direct methods using the SHELXS97 program [11]. The coordinates and the anisotropic thermal parameters for all non-hydrogen atoms were refined by the least-squares methods based on  $F^2$  using the SHELXL97 program [12]. The hydrogen atoms were generated geometrically using the riding model with the isotropic factor set at  $1.2U_{\text{eq}}$  of the parent atom. Hydrogen atoms on the amide nitrogen atom, as well as on the oxygen atom of the  $\text{H}_2\text{O}$  molecule were located in the difference Fourier map at the final stage of the refinement and were refined freely. Graphical work has been performed by the program ORTEP-3 for Windows [13] and Mercury 1.4.1 [14]. The thermal ellipsoids are drawn at the 50% probability level.

## 3. Results and discussion

### 3.1. Preparation of the complexes

The zinc and cadmium thiocyanato complexes **1** (**1a** and **1b**) and **2** were prepared *in situ* from aqueous solutions. The mercury complex **3** could not be obtained in the same way due to very low solubility of mercuric thiocyanate in

Table 1  
Crystal data and structure refinements for complexes **1–3**

| Complex  | <b>1a</b>  | <b>1b</b>  | <b>2</b>   | <b>3</b>   |
|--|--|--|--|--|
| Empirical formula  | C <sub>14</sub> H <sub>12</sub> ZnN <sub>6</sub> O <sub>2</sub> S <sub>2</sub> | C <sub>14</sub> H <sub>12</sub> ZnN <sub>6</sub> O <sub>2</sub> S <sub>2</sub> | C <sub>8</sub> H <sub>6</sub> CdN <sub>4</sub> OS <sub>2</sub> | C <sub>16</sub> H <sub>12</sub> Hg <sub>2</sub> N <sub>8</sub> O <sub>2</sub> S <sub>4</sub> |
| Formula weight   | 425.83   | 425.83   | 350.72   | 877.80   |
| Temperature (K)  | 200  | 296  | 296  | 296  |
| Wavelength (Å)   | 0.71073  | 0.71073  | 0.71073  | 0.71073  |
| Crystal system   | monoclinic   | monoclinic   | triclinic  | triclinic  |
| Space group  | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>C</i> 2/ <i>c</i>   | <i>P</i> $\bar{1}$   | <i>P</i> $\bar{1}$   |
| <i>a</i> (Å)   | 6.754(2)   | 17.1396(5)   | 9.4097(6)  | 7.3949(7)  |
| <i>b</i> (Å)   | 16.643(3)  | 8.2446(2)  | 10.4414(7)   | 7.4560(4)  |
| <i>c</i> (Å)   | 17.384(4)  | 13.5627(4)   | 12.2651(4)   | 10.757(1)  |
| $\alpha$ (°)   | 90   | 90   | 99.259(5)  | 100.124(8)   |
| $\beta$ (°)  | 110.18(3)  | 109.243(3)   | 90.292(4)  | 105.538(9)   |
| $\gamma$ (°)   | 90   | 90   | 93.124(5)  | 91.343(8)  |
| Volume (Å <sup>3</sup> )   | 1838.0(7)  | 1809.46(9)   | 1187.5(1)  | 560.97(9)  |
| <i>Z</i>   | 4  | 4  | 4  | 1  |
| $\rho_{\text{calc}}$ (g/cm <sup>3</sup> )                              | 1.542  | 1.563  | 1.962  | 2.598  |
| <i>F</i> (000)   | 864  | 864  | 680  | 404  |
| Crystal size (mm)  | 0.15 × 0.20 × 0.24   | 0.07 × 0.28 × 0.42   | 0.13 × 0.31 × 0.32   | 0.10 × 0.22 × 0.32   |
| Reflections collected  | 21 352   | 20 139   | 30 651   | 17 933   |
| Unique reflections   | 5585   | 2637   | 6914   | 3264   |
| Parameters   | 253  | 122  | 306  | 154  |
| <i>R</i> <sub>1,all data</sub>   | 0.0434   | 0.0541   | 0.0296   | 0.0338   |
| <i>R</i> <sub>1<sup>a</sup></sub> [ <i>I</i> > 2σ( <i>I</i> )]         | 0.0307   | 0.0312   | 0.0214   | 0.0280   |
| <i>wR</i> <sub>2,all data</sub>  | 0.0788   | 0.0813   | 0.0534   | 0.0712   |
| <i>wR</i> <sub>2<sup>b</sup></sub> [ <i>I</i> > 2σ( <i>I</i> )]        | 0.0735   | 0.0703   | 0.0496   | 0.0677   |
| <i>g</i> <sub>1</sub> , <i>g</i> <sub>2</sub> in <i>w</i> <sup>c</sup> | 0.0355, 0.6356   | 0.0389, 0.3787   | 0.0259, 0.3511   | 0.0345, 1.4834   |
| <i>S</i> <sup>d</sup> on <i>F</i> <sup>2</sup>                         | 1.047  | 1.053  | 1.073  | 1.049  |
| $\Delta\sigma_{\text{min/max}}$ (e Å <sup>-3</sup> ) <sup>e</sup>      | −0.410/0.399   | −0.402/0.368   | −0.549/0.692   | −1.819/2.359   |
| Extinction coefficient   | 0.0053(6)  | none   | 0.0042(3)  | 0.027(1)   |

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

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

<sup>c</sup>  $w = 1/[\sigma^2(F_o^2) + [(g_1P)^2 + g_2P]]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>d</sup>  $S = \sum [w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$ .

<sup>e</sup> The maximum electron density in the last difference Fourier map is near Hg.

water, while *in situ* reaction from an ethanol solution gave a mixture of products. Complex **3** was the only product from the reaction performed by refluxing the mixture of ethanolic solutions of mercuric thiocyanate and picolinamide. It was also established that in **1–3** the reaction products were not influenced by the molar ratio of the reactants (1:1 or 1:2 metal thiocyanate versus picolinamide). All complexes are soluble in solvents with pronounced coordination properties such as dimethyl sulfoxide (DMSO) and *N,N*-dimethyl formamide (DMF).

### 3.2. Structure descriptions

All crystals were grown by slow evaporation of the reaction mixture under ambient conditions in periods from two days to one week. Selected bond distances and bond angles relevant to the coordination of the central metal ions are given in Table 2, while the hydrogen bonds are presented in Table 1. The structures are shown in Figs. 1–4.

#### 3.2.1. Crystal structure of [Zn(NCS)<sub>2</sub>(pia)<sub>2</sub>] (**1a**) and (**1b**)

The compound **1** crystallizes in two polymorphic forms, **1a** and **1b**. The different packing in the unit cell is caused by the slight differences in their molecular structures.

The compound **1a** crystallizes in the space group *P*2<sub>1</sub>/*c*. The crystal structure of bis(picolinamide-*N,O*)-bis(thiocyanato-*N*)zinc(II) consists of discrete octahedral complex molecules. An octahedral polyhedron is achieved through [4N + 2O] coordination of the zinc atom, where two nitrogen atoms originate from picolinamides and two from *cis*-positioned NCS-groups (Fig. 1a). The octahedron is almost regular with the two smallest angles being 75.06(5)° and 75.69(5)° for N3–Zn1–O1 and N5–Zn1–O2, respectively. All other angles around the zinc atom are in the range 87.44(5)–96.59(6)°, while all the opposite atoms in the coordination sphere form angles in the range 162.89(5)–171.51(5)°. The sums of four angles around the zinc atom closed by coordinating atoms lying in a plane are very close to 360° [359.06°, 359.44°, 361.35°], indicating the planarity of the planes containing the zinc(II) ion and thus also supporting the almost regular octahedral coordination of the central metal atom.

The Zn–N distances are in the range between 2.058(2) and 2.106(2) Å, with the Zn–NCS bonds [2.053(2) and 2.087(2) Å] being shorter than the Zn–N(pia) bonds [2.103(2) and 2.106(2) Å]. The Zn–O distances [2.258(1) Å and 2.218(1) Å] are somewhat longer than in other octahedral zinc complexes with picolinamide or its derivatives: 2.073(2) Å in [Zn(picolinamide)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>I<sub>2</sub>] [15] and

Table 2  
Selected bond distances (Å) and angles (°) for complexes 1–3

| <b>Complex 1a</b>                     |           |                              |           |
|---------------------------------------|-----------|------------------------------|-----------|
| <i>In the coordination polyhedron</i> |           |                              |           |
| Zn(1)–N(1)                            | 2.058(2)  | Zn(1)–O(1)                   | 2.258(1)  |
| Zn(1)–N(2)                            | 2.087(2)  | Zn(1)–O(2)                   | 2.218(1)  |
| Zn(1)–N(3)                            | 2.106(2)  |                              |           |
| Zn(1)–N(5)                            | 2.103(2)  |                              |           |
| N(1)–Zn(1)–N(2)                       | 93.22(7)  | N(1)–Zn(1)–O(2)              | 171.51(5) |
| N(1)–Zn(1)–N(5)                       | 95.98(6)  | N(2)–Zn(1)–O(2)              | 89.44(6)  |
| N(2)–Zn(1)–N(5)                       | 96.59(6)  | N(5)–Zn(1)–O(2)              | 75.69(5)  |
| N(1)–Zn(1)–N(3)                       | 95.41(6)  | N(3)–Zn(1)–O(2)              | 92.36(5)  |
| N(2)–Zn(1)–N(3)                       | 95.47(6)  | N(1)–Zn(1)–O(1)              | 91.25(6)  |
| N(5)–Zn(1)–N(3)                       | 162.89(5) | N(2)–Zn(1)–O(1)              | 169.88(5) |
| O(2)–Zn(1)–O(1)                       | 87.44(5)  | N(5)–Zn(1)–O(1)              | 91.96(5)  |
|                                       |           | N(3)–Zn(1)–O(1)              | 75.06(5)  |
| <i>In the thiocyanate</i>             |           |                              |           |
| N(1)–C(1)                             | 1.152(2)  | C(1)–S(1)                    | 1.629(2)  |
| N(2)–C(2)                             | 1.147(2)  | C(2)–S(2a)                   | 1.631(4)  |
|                                       |           | C(2)–S(2b)                   | 1.623(6)  |
| N(1)–C(1)–S(1)                        | 178.2(2)  |                              |           |
| N(2)–C(2)–S(2a)                       | 172.0(4)  |                              |           |
| N(2)–C(2)–S(2b)                       | 167.0(5)  |                              |           |
| Zn(1)–N(1)–C(1)                       | 154.3(2)  |                              |           |
| Zn(2)–N(2)–C(2)                       | 147.9(2)  |                              |           |
| <b>Complex 1b</b>                     |           |                              |           |
| <i>In the coordination polyhedron</i> |           |                              |           |
| Zn(1)–N(1)                            | 2.069(2)  | Zn(1)–O(1)                   | 2.197(2)  |
| Zn(1)–N(1) <sup>a</sup>               | 2.069(2)  | Zn(1)–O(1) <sup>a</sup>      | 2.197(2)  |
| Zn(1)–N(2)                            | 2.117(2)  |                              |           |
| Zn(1)–N(2) <sup>a</sup>               | 2.117(2)  |                              |           |
| N(1)–Zn(1)–N(2)                       | 97.87(6)  | N(1)–Zn(1)–O(1)              | 88.05(6)  |
| N(1)–Zn(1)–N(2) <sup>a</sup>          | 95.82(6)  | N(1)–Zn(1)–O(1) <sup>a</sup> | 170.09(6) |
| N(1)–Zn(1)–N(1) <sup>a</sup>          | 97.45(7)  | N(2)–Zn(1)–O(1)              | 75.19(5)  |
| N(2)–Zn(1)–N(2) <sup>a</sup>          | 159.19(6) | N(2)–Zn(1)–O(1) <sup>1</sup> | 89.73(5)  |
| O(1)–Zn(1)–O(1) <sup>a</sup>          | 87.76(5)  |                              |           |
| <i>In the thiocyanate</i>             |           |                              |           |
| N(1)–C(1)                             | 1.153(3)  | C(1)–S(1)                    | 1.628(2)  |
| N(1)–C(1)–S(1)                        | 178.5(2)  |                              |           |
| Zn(1)–N(1)–C(1)                       | 171.9(2)  |                              |           |
| <b>Complex 2</b>                      |           |                              |           |
| <i>In the coordination polyhedron</i> |           |                              |           |
| Cd(1)–N(1)                            | 2.333(2)  | Cd(1)–O(1)                   | 2.369(1)  |
| Cd(1)–N(2)                            | 2.312(2)  | Cd(1)–S(1)                   | 2.6519(6) |
| Cd(1)–N(5)                            | 2.333(2)  | Cd(1)–S(2)                   | 2.6328(6) |
| Cd(2)–N(3)                            | 2.271(1)  | Cd(2)–O(2)                   | 2.373(1)  |
| Cd(2)–N(4)                            | 2.346(2)  | Cd(2)–S(3)                   | 2.7831(6) |
| Cd(2)–N(7)                            | 2.352(2)  | Cd(2)–S(4)                   | 2.6154(6) |
| N(1)–Cd(1)–N(2)                       | 176.65(7) | N(1)–Cd(1)–S(1)              | 96.10(5)  |
| N(1)–Cd(1)–N(5)                       | 91.17(7)  | N(2)–Cd(1)–S(1)              | 86.65(6)  |
| N(2)–Cd(1)–N(5)                       | 90.30(7)  | N(5)–Cd(1)–S(1)              | 98.41(4)  |
| N(1)–Cd(1)–O(1)                       | 95.29(6)  | N(1)–Cd(1)–S(2)              | 84.63(5)  |
| N(2)–Cd(1)–O(1)                       | 82.40(7)  | N(2)–Cd(1)–S(2)              | 92.93(5)  |
| N(5)–Cd(1)–O(1)                       | 69.77(5)  | N(5)–Cd(1)–S(2)              | 159.02(5) |
| O(1)–Cd(1)–S(1)                       | 163.74(4) |                              |           |
| S(1)–Cd(1)–S(2)                       | 102.46(2) |                              |           |
| N(1)–Cd(2)–N(2)                       | 176.65(7) | N(1)–Cd(2)–S(1)              | 96.10(5)  |
| N(1)–Cd(2)–N(5)                       | 91.17(7)  | N(2)–Cd(2)–S(1)              | 86.65(6)  |
| N(2)–Cd(2)–N(5)                       | 90.30(7)  | N(5)–Cd(2)–S(1)              | 98.41(4)  |
| N(1)–Cd(2)–O(1)                       | 95.29(6)  | N(1)–Cd(2)–S(2)              | 84.63(5)  |
| N(2)–Cd(2)–O(1)                       | 82.40(7)  | N(2)–Cd(2)–S(2)              | 92.93(5)  |
| N(5)–Cd(2)–O(1)                       | 69.77(5)  | N(5)–Cd(2)–S(2)              | 159.02(5) |

Table 2 (continued)

|                                       |           |   |          |
|---------------------------------------|-----------|---|----------|
| O(1)–Cd(2)–S(1)                       | 163.74(4) |   |          |
| S(1)–Cd(2)–S(2)                       | 102.46(2) |   |          |
| <i>In the thiocyanate</i>             |           |   |          |
| N(1)–C(1)                             | 1.149(3)  | C(1)–S(1) <sup>b</sup>                    | 1.649(2) |
| N(2)–C(2)                             | 1.148(3)  | C(2)–S(2) <sup>c</sup>                    | 1.641(2) |
| N(3) <sup>d</sup> –C(3)               | 1.148(3)  | C(3)–S(3)                                 | 1.654(2) |
| N(4)–C(4)                             | 1.150(3)  | C(4)–S(4) <sup>e</sup>                    | 1.650(2) |
| N(1)–C(1)–S(1) <sup>b</sup>           | 178.4(2)  | N(3)–C(3) <sup>d</sup> –S(3) <sup>d</sup> | 179.2(2) |
| N(2)–C(2)–S(2) <sup>c</sup>           | 177.3(2)  | N(4)–C(4)–S(4) <sup>e</sup>               | 177.3(2) |
| Cd(1)–N(1)–C(1)                       | 140.2(2)  | Cd(2)–S(3)–C(3)                           | 96.72(8) |
| Cd(1)–S(1)–C(1) <sup>b</sup>          | 96.60(7)  | Cd(2)–N(3)–C(3) <sup>e</sup>              | 156.6(2) |
| Cd(1)–N(2)–C(2)                       | 150.2(2)  | Cd(2)–S(4)–C(4) <sup>d</sup>              | 97.55(7) |
| Cd(1)–S(2)–C(2) <sup>c</sup>          | 97.81(7)  | Cd(2)–N(4)–C(4)                           | 138.6(2) |
| <b>Complex 3</b>                      |           |   |          |
| <i>In the coordination polyhedron</i> |           |   |          |
| Hg(1)–S(1)                            | 2.612(1)  | Hg(1)–O(1)                                | 2.493(3) |
| Hg(1)–S(1) <sup>f</sup>               | 2.874(2)  |   |          |
| Hg(1)–S(2)                            | 2.482(1)  |   |          |
| Hg(1)–N(3)                            | 2.239(3)  |   |          |
| S(1)–Hg(1)–S(1) <sup>f</sup>          | 88.17(3)  | N(3)–Hg(1)–S(1)                           | 136.1(1) |
| S(1)–Hg(1)–S(2)                       | 96.08(4)  | N(3)–Hg(1)–S(2)                           | 126.1(1) |
| S(2)–Hg(1)–S(1) <sup>f</sup>          | 99.58(4)  | N(3)–Hg(1)–S(1) <sup>f</sup>              | 95.40(9) |
| O(1)–Hg(1)–S(1)                       | 89.91(8)  | N(3)–Hg(1)–O(1)                           | 69.4(1)  |
| O(1)–Hg(1)–S(1) <sup>f</sup>          | 155.17(9) |   |          |
| O(1)–Hg(1)–S(2)                       | 105.25(9) |   |          |
| <i>In the thiocyanate</i>             |           |   |          |
| N(1)–C(1)                             | 1.151(7)  | C(1)–S(1)                                 | 1.679(5) |
| N(2)–C(2)                             | 1.144(6)  | C(2)–S(2)                                 | 1.668(5) |
| N(1)–C(1)–S(1)                        | 176.7(4)  |   |          |
| N(2)–C(2)–S(2)                        | 179.1(5)  |   |          |
| Hg(1)–N(1)–C(1)                       | 106.0(2)  | Hg(1)–N(2)–C(2)                           | 96.5(2)  |
| Hg(1) <sup>f</sup> –N(1)–C(1)         | 102.2(2)  |   |          |

<sup>a</sup> 1 – x, y, 1/2 – z.<sup>b</sup> –x + 2, –y + 1, –z.<sup>c</sup> –x + 1, –y + 1, –z.<sup>d</sup> –x + 1, –y + 2, –z + 1.<sup>e</sup> –x + 2, –y + 2, –z + 1.<sup>f</sup> –x + 1, –y, 1 – z.

2.110(3) Å in [Zn(3-hydroxypicolinamide)<sub>2</sub>(OH)<sub>2</sub>] [16]. The set of bond lengths around zinc in **1a** indicates that the Zn–N bond involving the thiocyanate anion is stronger than that originating from picolinamide.

The NCS ligand, labelled as 1, (N(1)–C(1)–S(1)), shows a very small distortion from linearity (178.2(2)°), while the isothiocyanate ligand with a disordered sulfur atom deviates significantly [167.0(5)° and 172.0(4)°] and both NCS ligands bind to the metal in a non-linear mode with Zn–N–CS angles of 154.3(2)° and 147.9(2)°, which is generally usual for thiocyanates. The M–N–CS angle for zinc thiocyanate has been found to be in the range 132–180°, but is usually between 150° and 180° [17,18]. The pyridine rings are almost planar [torsion angles are 0.83(1)° and 1.27(1)°] while the chelate rings deviate from planarity [torsion angles 5.32(7)° and 8.36(7)°].

The crystal structure is predominantly determined by hydrogen bonding – there are N–H···O, N–H···S and

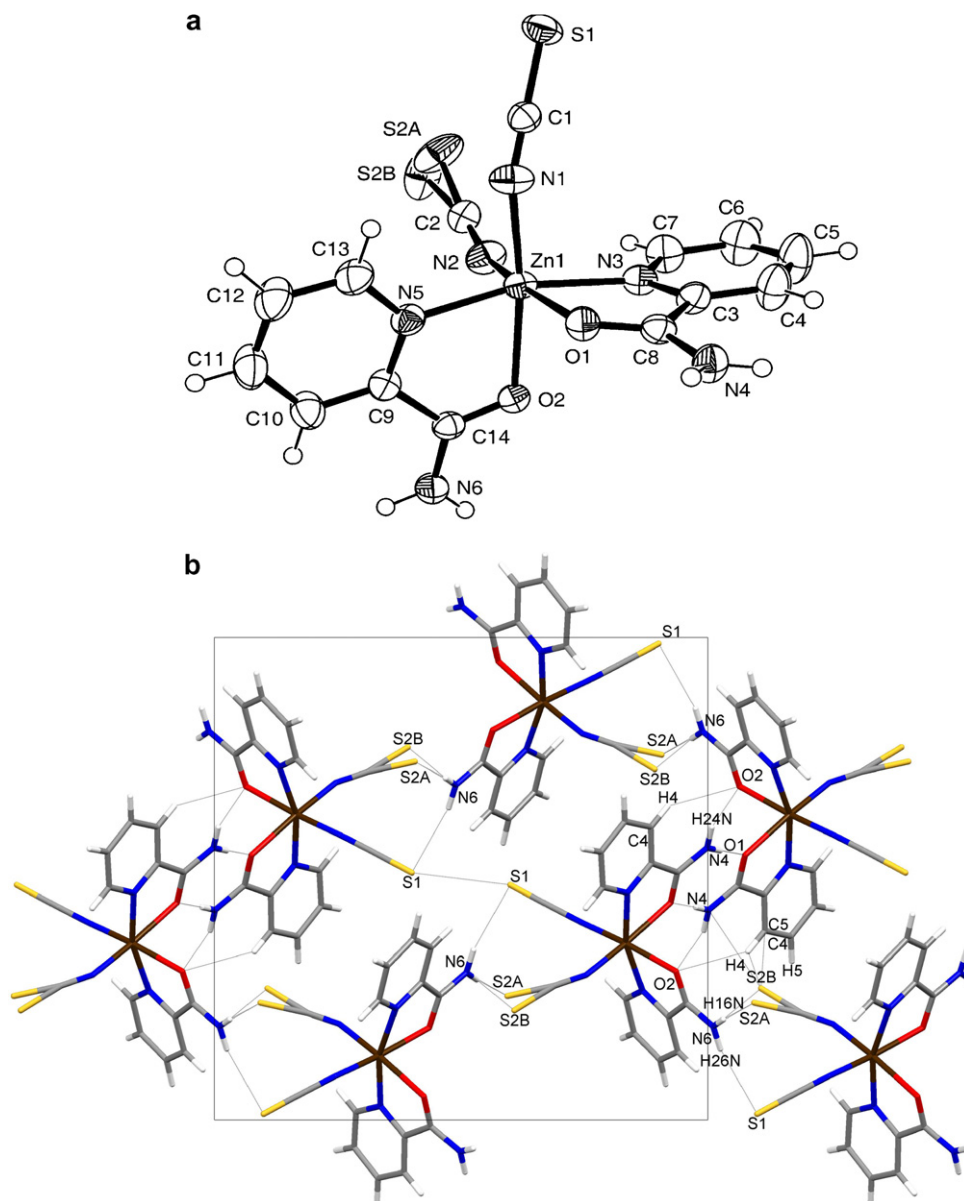


Fig. 1. (a) ORTEP3 drawing of the structural unit of complex **1a**; (b) perspective view along the *a*-axis; hydrogen bonds and contacts are drawn as dotted lines.

C–H···O types of hydrogen bonds. The geometric parameters of these bonds are given in Table 5. The amide nitrogen atoms from both picolinamide ligands, N(4) and N(6), are involved in two hydrogen bonds to two oxygen and two sulfur atoms, respectively (N(4)–H···O and N(6)–H···S). As a consequence of these two different hydrogen bondings the two carboxamide groups have different twist angles (13.0(1)° and 2.06(6)°). The amide nitrogen atom N(4) participates in a centrosymmetric head-to-head hydrogen bond of the  $R_2^2$  (8) type with the amide oxygen atom O(1) from the neighbouring molecule (symmetry code:  $-x, -y, 1 - z$ ). The same amide nitrogen atom N(4) also forms a hydrogen bond with the amide oxygen atom from the neighbouring molecule along the *a*-axis, O(2), which also acts as a bifurcated acceptor in the C(4)–H(4)···O(2) hydrogen bond. The amide nitrogen atom from the other

picolinamide ligand, N(6), also participates in two hydrogen bonds, but of the N–H···S type. Thus each complex molecule bridges adjacent molecules forming chains along the *a*-axis. As shown in Fig. 1b, the molecules are further stabilized through short S···S contacts of the NCS ligands (3.392 Å).

The sulfur atom S(2), is found to be disordered. The same disorder is also observed in space groups of lower symmetries,  $P2_1$  and  $Pc$ . It could, probably, be the consequence of the few short contacts resulting from the vicinity of neighbouring molecules: C(4)–H(4)···S(2b), C(4)···S(2b) and N(4)···S(2b), symmetry code:  $x, 1/2 - y, -1/2 + z$ , and N(6)–H(16N)···S(2b), symmetry code:  $1 - x, 1/2 + y, 1/2 - z$ , as designated in Fig. 1b.

In addition to hydrogen bonds there are also weak  $\pi$ ··· $\pi$  interactions with a short distance between the centroids of

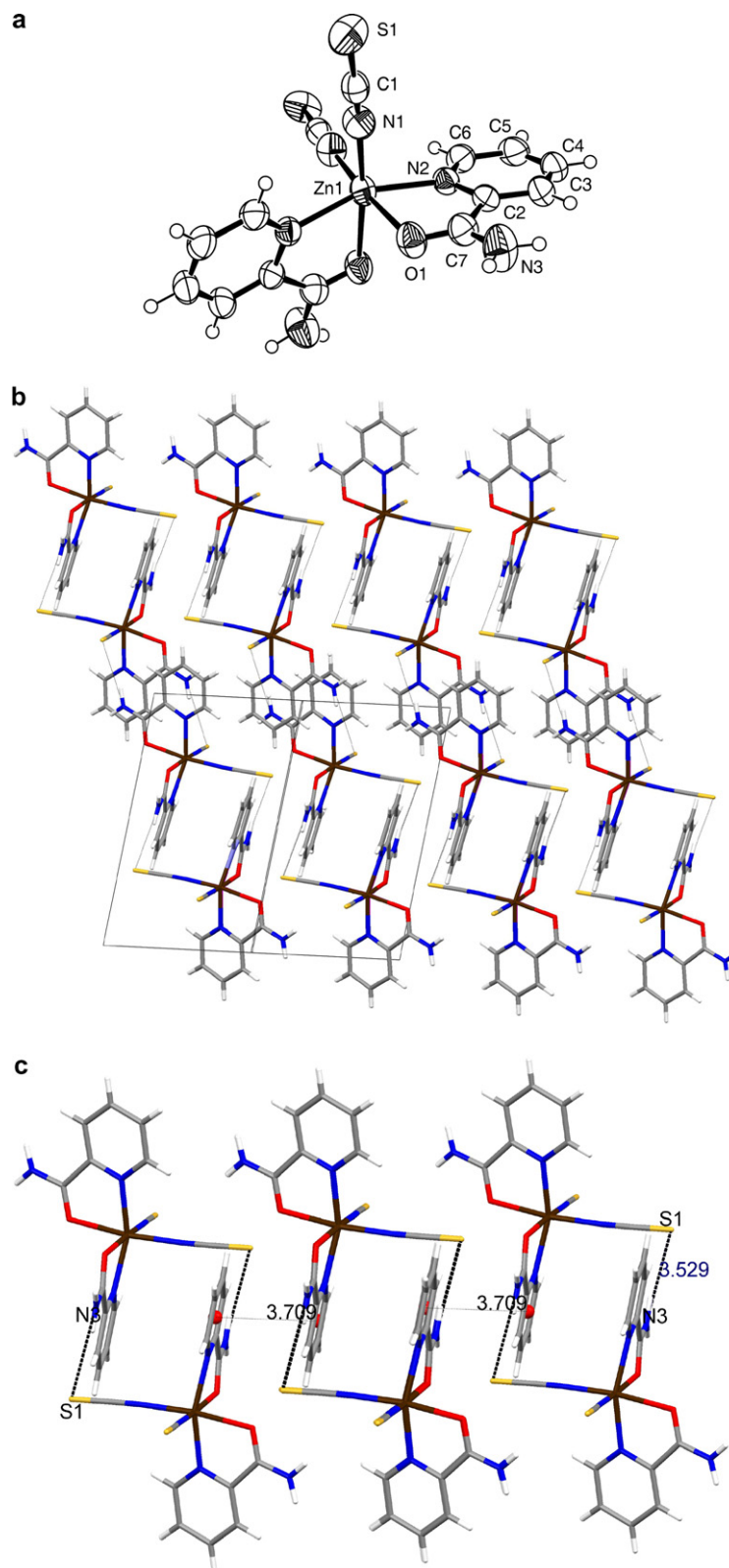


Fig. 2. (a) ORTEP3 drawing of the structural unit of complex **1b** with the atomic numbering scheme of asymmetric unit; (b) perspective view of the crystal packing of compound **1b** along the [101] direction; (c)  $\pi \cdots \pi$  and N–H $\cdots$ S contacts are drawn as dotted lines.

the two aromatic rings N3,C3  $\rightarrow$  C7 and N5,C9  $\rightarrow$  C13, 4.434(2) Å (Table 5).

**1b**, the polymorph of **1a**, crystallizes in space group  $C2/c$  with a central metal ion in a special position. The octahe-

dral coordination polyhedra of the zinc(II) ion was found in both polymorphs. Apart from deviations in the crystal packing of the two polymorphs, there are also some other discrepancies in the molecular geometry.

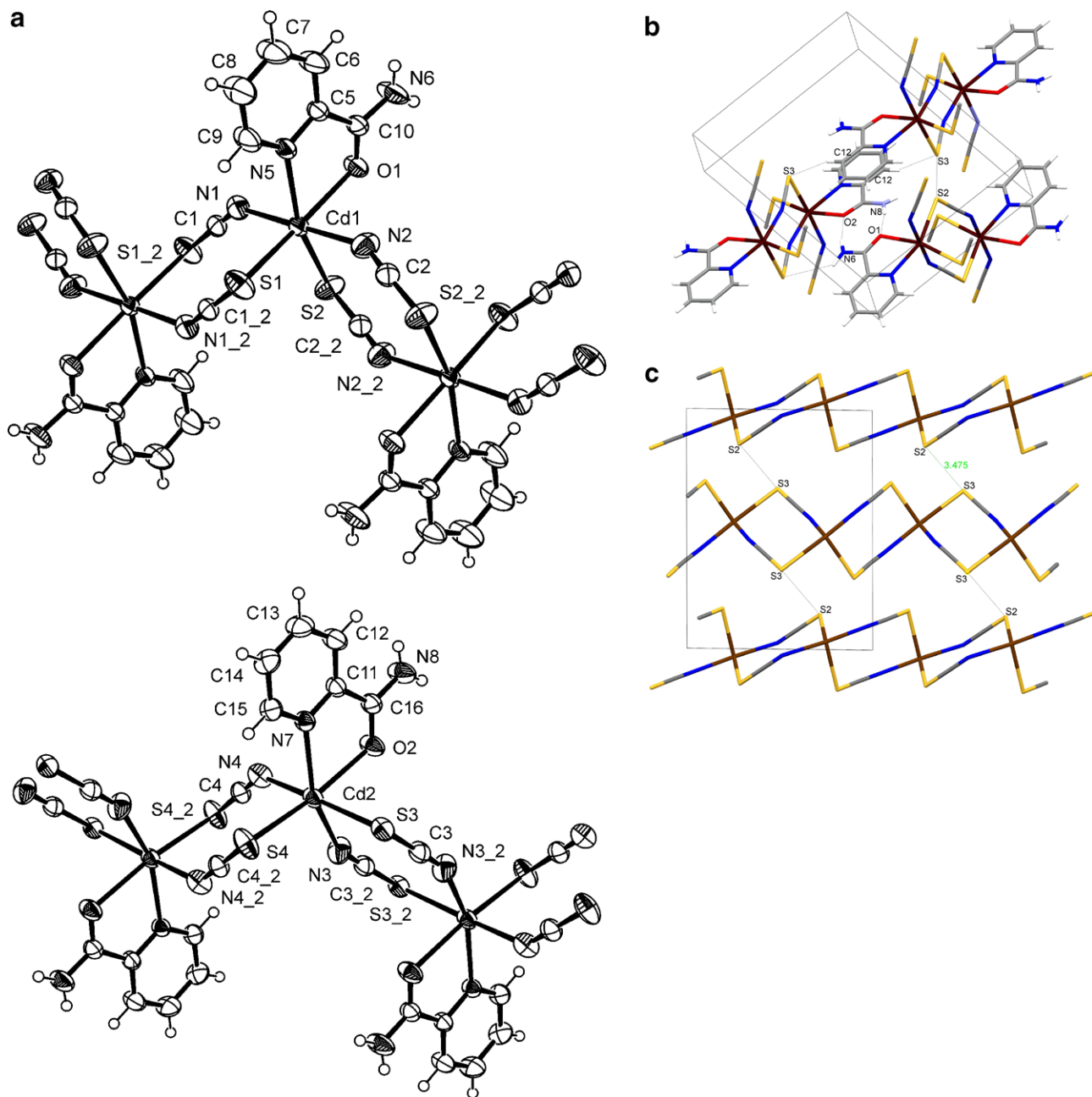


Fig. 3. (a) ORTEP3 drawing of the two crystallographically independent chains of complex **2** with the atomic numbering scheme of the asymmetric unit; (b) perspective view of intermolecular hydrogen bonds and S...S contacts between adjacent polymer chains; (c) a view of the Cd(SCN)<sub>2</sub> chains along the *b*-axis. The picolinamide ligands are omitted for clarity.

The bite angles of the chelate picolinamide ligands are retained in both polymorphs, while significant deviations in bond distances toward the zinc(II) ions are observed. The Zn–O(pia) bond length in polymorph **1b** is shorter than it is in polymorph **1a** [2.197(2) Å, **1b**; 2.258(1) Å and 2.218(1) Å, **1a**]. Further, the Zn–N(py) bond length is elongated to a somewhat smaller extend [2.117(2) Å, **1b**; 2.106(2) Å and 2.103(2) Å, **1a**]. But it is still the case, as in polymorph **1a**, that the thiocyanato ligand is bound to the central zinc(II) ion more tightly than the picolinamide ligand.

The isothiocyanato ligand is more tilted towards the carboxamide group in **1b** than in **1a**. Smaller N(NCS)–Zn–O [88.05(6)° **1a**; 89.44(6)° and 91.25(6)° **1b**] and larger N(NCS)–Zn–N(py) [97.89(6)° **1b**; 95.41(6)–96.59(6)° **1a**] angles in **1b** than in **1a** are established. The chelate ring also deviates more from planarity in polymorph **1b** than in **1a** (Table 3).

There are other differences in the crystal than in the molecular structures of both polymorphs. In crystal structure of **1b** hydrogen bonds are not pronounced. There is just one weak intermolecular interaction of the N–H...S





Table 3  
Selected torsion and dihedral angles (°)

|                               | (1a)     | (1b)    | (2)     | (3)     |
|-------------------------------|----------|---------|---------|---------|
| Py ring (I)                   | 0.83(1)  | 0.7(1)  | 0.4(2)  | 1.2(3)  |
| Py ring (II)                  | 1.27(1)  |         | 0.7(1)  |         |
| Chelate ring (I)              | 5.32(7)  | 11.4(8) | 5.52(8) | 12.7(2) |
| Chelate ring (II)             | 8.36(7)  |         | 2.21(9) |         |
| Py ring (I)–amido group (I)   | 13.0(1)  | 7.51(8) | 3.5(1)  | 2.2(2)  |
| Py ring (II)–amido group (II) | 2.06(6)  |         | 2.3(1)  |         |
| Py (I)–Py (II)                | 85.47(9) |         |         |         |

morphs are also affirmed by different melting temperatures, 169.0(5) °C for **1a** and 167.1(5) °C for **1b**.

### 3.2.2. Crystal structure of $[Cd(SCN)_2(pia)]_n$ (2)

The molecular structure of *catena*-[bis( $\mu$ -thiocyanato-*S,N*)-picolinamide-*N,O*-cadmium(II)] comprises of two crystallographically independent chains along the *a*-axis (Fig. 3a). In both chains the cadmium atom shows a distorted octahedral environment with  $[3N + O + 2S]$  coordination. Two adjacent cadmium atoms are bridged by two inversely related  $\mu$ -SCN<sup>−</sup>-*N,S* and the remaining coordination sites are occupied by the chelate picolinamide ligand, resulting in a structure comprising of eight-membered (N–C–S–Cd)<sub>2</sub> rings. These chains differ in the *cis*- and *trans*-orientation of the two bridging thiocyanato-*N* groups resulting in different chair conformations of the Cd–NCS skeleton, as illustrated in Fig. 3c. The intra-chain Cd···Cd distances from two crystallographically independent chains also differ: 5.743 Å and 5.847 Å for chains containing Cd(1) and Cd(2), respectively, the values are close to those already found for structures with two bridged thiocyanato ligands [19]. The Cd–N(NCS) (2.271(1)–2.346(2) Å) and Cd–S (2.6154(6)–2.7831(6) Å) distances are also very close to those ones reported for complexes containing eight-membered  $[Cd_2(SCN)_2]$  rings [20,21]. The crystal structure

is realized through various non-covalent interactions: (a) N–H···O (between two amido groups) head-to-head double hydrogen bonds of the R<sub>2</sub><sup>2</sup> (8) type (originated from the amide group of two picolinamide ligands coordinated on two symmetrically independent cadmium(II) atoms from adjacent chains, Cd(1) and Cd(2)), (b) N–H···S and (c) C–H···S interactions (Table 4), as well as (d)  $\pi$ – $\pi$  stacking interactions (Table 6). The nitrogen atoms from each amide group are involved in N–H···O hydrogen bonds (N···O 2.948(3) Å and 2.983(3) Å) but the nitrogen atom from the amide group coordinated to Cd(1) also participates in a N–H···S interaction with a N···S distance of 3.456 Å, acting as a bifurcated donor. The weak intermolecular interaction C–H···S between two symmetrically related chains involves aromatic C(12)–H(12) and thiocyanate S(3) (Table 4). As shown in Fig. 3b, the layers are further packed into a three-dimensional framework also through weak S···S interactions of the NCS<sup>−</sup> ligands (3.475(8) Å). The observed interaction is slightly shorter than in comparable cadmium complexes already reported [19]. In the present structure the pyridyl rings from each one-dimensional polymer chain  $\pi$ – $\pi$  stack in an offset face to face arrangement with adjacent chains (3.817(1) Å) contributing to the stability of the crystal structure and resulting in the highest decomposition temperature of all three isolated complexes.

### 3.2.3. Crystal structure of $[Hg(SCN)_2(pia)]_2$ (3)

Bis( $\mu_2$ -thiocyanato-*S*-thiocyanato-*S*-picolinamide-*N,O*)-mercury(II) crystallizes in space group *P* $\bar{1}$  and the crystal lattice (molecular structure) consists of a neutral centrosymmetric dinuclear unit  $[Hg_2(L)_2(SCN)_4]$ , Fig. 4a. The coordination polyhedron around the mercury is best described as a distorted tetragonal pyramid. The metal ion is ligated by three sulfur atoms from thiocyanate, and an amide oxygen and an endocyclic nitrogen from the pic-

Table 4  
Hydrogen bonds and contacts (Å and °) **1–3**

| D–H···A             | D–H     | H···A   | D···A    | $\angle$ DHA | Symmetry code        |
|---------------------|---------|---------|----------|--------------|----------------------|
| <b>Compound 1a</b>  |         |         |          |              |                      |
| N(4)–H(14N)···O(1)  | 0.90(3) | 2.07(3) | 2.962(2) | 175(2)       | $-x, -y, 1-z$        |
| N(4)–H(24N)···O(2)  | 0.84(2) | 2.53(3) | 3.124(2) | 161(2)       | $1-x, -y, 1-z$       |
| N(6)–H(16N)···S(2a) | 0.82(3) | 2.53(3) | 3.347(6) | 176(2)       | $1-x, -1/2+y, 1/2-z$ |
| N(6)–H(26N)···S(1)  | 0.88(2) | 2.54(2) | 3.356(2) | 155.8(2)     | $-x, -1/2+y, 1/2-z$  |
| C(4)–H(4)···O(2)    | 0.95    | 2.53    | 3.300(2) | 138          | $1-x, -y, 1-z$       |
| <b>Compound 1b</b>  |         |         |          |              |                      |
| N(3)–H(13N)···S(1)  | 0.89(3) | 2.65(3) | 3.530(3) | 167(3)       | $1/2-x, 1/2-y, -z$   |
| <b>Compound 2</b>   |         |         |          |              |                      |
| N(8)–H(18N)···O(1)  | 0.84(3) | 2.11(3) | 2.948(3) | 170(3)       |                      |
| N(6)–H(16N)···O(2)  | 0.80(4) | 2.20(4) | 2.983(3) | 166(4)       |                      |
| N(6)–H(26N)···S(3)  | 0.83(3) | 2.77(3) | 3.456(2) | 141(2)       | $1-x, -y, 1-z$       |
| C(12)–H(12)···S(3)  | 0.95    | 2.81    | 3.698(2) | 160          | $1-x, 1-y, 1-z$      |
| <b>Compound 3</b>   |         |         |          |              |                      |
| N(4)–H(14N)···N(2)  | 0.86(7) | 2.10(7) | 2.955(6) | 169(7)       | $x, y, -1+z$         |
| N(4)–H(24N)···O(1)  | 0.75(6) | 2.22(7) | 2.957(6) | 173(7)       | $-x, -y, -z$         |
| C(4)–H(4)···N(2)    | 0.95    | 2.53    | 3.437(6) | 164          | $x, y, -1+z$         |
| C(5)–H(5)···N(1)    | 0.95    | 2.54    | 3.292(7) | 138          | $1-x, -y, -z$        |

Table 5  
 $\pi \cdots \pi$  interactions

| $\pi \cdots \pi$ contacts  | Cg $\cdots$ Cg (Å) | $\alpha$ (°) | $\beta$ (°) | Cg $\cdots$ plane (Cg2) |
|--|--------------------|--------------|-------------|-------------------------|
| <b>Compound 1a</b>   |                    |              |             |                         |
| Cg(N3,C3 $\rightarrow$ C7) $\cdots$ Cg(N3, C3 $\rightarrow$ C7) <sup>a</sup>     | 5.823(2)           | 0.00         | 52.53       | 3.542                   |
| Cg(N3,C3 $\rightarrow$ C7) $\cdots$ Cg(N5, C9 $\rightarrow$ C13) <sup>b</sup>    | 4.434(2)           | 12.41        | 39.56       | 3.419                   |
| <b>Compound 1b</b>   |                    |              |             |                         |
| Cg(N2,C2 $\rightarrow$ C6) $\cdots$ Cg(N2, C2 $\rightarrow$ C6) <sup>c</sup>     | 3.709(1)           | 0.00         | 23.06       | 3.413                   |
| <b>Compound 2</b>  |                    |              |             |                         |
| Cg(N7, C11 $\rightarrow$ C15) $\cdots$ Cg(N7,C11 $\rightarrow$ C15) <sup>d</sup> | 3.817(1)           | 0.00         | 25.99       | 3.431                   |
| <b>Compound 3</b>  |                    |              |             |                         |
| Cg(N3, C3 $\rightarrow$ C7) $\cdots$ Cg(N3, C3 $\rightarrow$ C7) <sup>e</sup>    | 4.713(3)           | 0.02         | 42.80       | 3.458                   |

<sup>a</sup> 1 - x, -y, 1 - z.

<sup>b</sup> 1 + x, 1/2 - y, 1/2 + z.

<sup>c</sup> 1 - x, 1 - y, -z.

<sup>d</sup> - x, 1 - y, 1 - z.

<sup>e</sup> 1 - x, -y, -z.

olinamide ligand. One thiocyanate ligand is terminal, while the other bridges two mercuric ions in an end-on fashion.

The distances in the thiocyanato ligands are 1.151(7) and 1.144(6) Å for N–C bonds, and 1.679(5) and 1.668(5) Å for C–S bonds, in the bridging and terminal ligand, respectively, as expected for *S*-coordination of thiocyanates [22]. The thiocyanates are coordinated in a linear fashion as can be seen from the N1–C1–S1 and N2–C2–S2 angles [176.7(4)° and 179.1(5)°], as evident, the bridging SCN-ligand deviates more from linearity than the terminal one.

The pyridyl and chelate rings deviate the most from planarity as compared with structures of **1** and **2** (Table 3) but the amide group, at the same time, closes the smallest torsion angle with the pyridyl ring.

Two dimers are connected together by a N–H $\cdots$ O hydrogen bond of the R<sub>2</sub><sup>2</sup>(8) type (Fig. 4b) forming infinite one-dimensional chains in the [101] direction (N(4)–H(24 N) $\cdots$ O(1), Table 4). The well known tendency of the mercury(II) ion towards soft basis, in this case the sulfur atom of the ambidentate thiocyanate ion, releases the thiocyanate nitrogen atom to participate in hydrogen bonding. So, both thiocyanate nitrogens, N(1) and N(2), from one chain of dimers participate in hydrogen bonds holding together two such adjacent chains. While N(1) participates in C–H $\cdots$ N bonding, N(2) acts as a bifurcated acceptor for C–H $\cdots$ N and N–H $\cdots$ N chelate hydrogen bonds. In such a way infinite two-dimensional sheets of channels, closed by two adjacent chains of dimers, are formed. These 2D sheets are probably held together by weak C $\cdots$ S contacts, C(1) $\cdots$ S(2) 3.293 Å and C(7) $\cdots$ S(2) 3.400 Å.

### 3.3. Spectroscopic properties

#### 3.3.1. IR spectra

In general, C–N stretching frequencies,  $\nu$ (CN), of thiocyanates are lower in *N*-bonded complexes (near or below 2050 cm<sup>-1</sup>) than *S*-bonded complexes (near 2100 cm<sup>-1</sup>).

For bridging complexes (M–SCN–M) the CN stretching frequency is above 2100 cm<sup>-1</sup> [23]. The stretching CN frequencies observed at 2096 cm<sup>-1</sup> for **1a** and **1b**, at 2118 and 2094 cm<sup>-1</sup> for **2** and at 2130 cm<sup>-1</sup> for **3** clearly indicate a different coordination mode of the SCN-ligand. The thiocyanate is coordinated to zinc through the nitrogen atom, and to mercury through the sulfur atom, while cadmium is coordinated *via* both, *N*- and *S*- atoms. All above mentioned frequencies are significantly higher than the corresponding one found in the IR spectrum of KSCN (2048 cm<sup>-1</sup> [24]). The SCN group is a good electron supplier and the electron transfer from SCN<sup>-</sup> to Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> ions cause the significant increase of the CN stretching frequency [25]. It is worth emphasising that in **1** the  $\nu$ (CN) frequency is significantly higher (2096 cm<sup>-1</sup>) than that in the reported zinc *N*-bonded thiocyanate complexes (2077 cm<sup>-1</sup>, 2073 cm<sup>-1</sup>) [26,27].

The position of the C–S stretching frequencies in the region 860–690 cm<sup>-1</sup> is usually employed for differentiating *S*- from *N*-bonded terminal thiocyanates;  $\nu$ (CS) bands that are observed in the range 860–780 cm<sup>-1</sup> and 720–690 cm<sup>-1</sup> indicate the *N*- and *S*-coordination mode of the SCN-ligand, respectively [28]. However, the  $\nu$ (CS) modes in the IR spectra of compounds **1–3**, are overlapped by selected bands of the ligand in this region and make the assignment quite uncertain.

#### 3.3.2. NMR spectra

The <sup>1</sup>H and <sup>13</sup>C NMR data of the parent picolinamide (pia) molecule together with the data of its zinc(II), cadmium(II) and mercury(II) thiocyanato complexes **1**, **2** and **3** are presented in Tables 6 and 7, respectively, while the Scheme 1 shows the labelling of the atoms. Complexation <sup>1</sup>H and <sup>13</sup>C NMR shifts are defined as the difference of proton and carbon shifts, respectively, in the complexes and the free ligand molecule. The <sup>1</sup>H NMR data of the free picolinamide in DMSO-*d*<sub>6</sub> are cited from the literature [29], and all other measurements are also performed in DMSO-*d*<sub>6</sub>.

Table 6  
<sup>1</sup>H NMR chemical shifts ( $\delta$ /ppm)<sup>a</sup>, complexation shifts ( $\Delta\delta$ /ppm)<sup>b,d</sup> and H–H coupling constants ( $J_{\text{HH}}$ /Hz)<sup>e</sup> in the ligand molecule, picolinamide, and its complexes with zinc(II), cadmium(II) and mercury(II) thiocyanate, **1**, **2** and **3**

| Compound              |                 | pic <sup>c</sup> | <b>1</b>  | <b>2</b>  | <b>3</b>  |
|-----------------------|-----------------|------------------|-----------|-----------|-----------|
| H-3                   | $\delta$        | 8.43             | 8.24      | 8.14      | 8.13      |
|                       | $J_{\text{HH}}$ | 8.1 (d)          | 7.64 (d)  | 7.77 (d)  | 7.59 (d)  |
|                       | $\Delta\delta$  |                  | −0.19     | −0.29     | −0.30     |
| H-4                   | $\delta$        | 8.22             | 8.15      | 8.07      | 8.06      |
|                       | $J_{\text{HH}}$ | (m)              | (m)       | (m)       | (m)       |
|                       | $\Delta\delta$  |                  | −0.07     | −0.15     | −0.16     |
| H-5                   | $\delta$        | 7.81             | 7.75      | 7.68      | 7.68      |
|                       | $J_{\text{HH}}$ | (m)              | (m)       | (m)       | (m)       |
|                       | $\Delta\delta$  |                  | −0.06     | −0.13     | −0.14     |
| H-6                   | $\delta$        | 8.89             | 8.70      | 8.66      | 8.70      |
|                       | $J_{\text{HH}}$ | 4.5 (d)          | 4.63 (d)  | 4.47 (d)  | 4.84 (d)  |
|                       | $\Delta\delta$  |                  | −0.19     | −0.23     | −0.19     |
| H-1(NH <sub>2</sub> ) | $\delta$        | 8.1              | 8.09      | 7.94      | 7.86      |
|                       | $J_{\text{HH}}$ | broadened        | broadened | broadened | broadened |
|                       | $\Delta\delta$  |                  | −0.01     | −1.16     | −0.24     |
| H-2(NH <sub>2</sub> ) | $\delta$        | 8.5              | 8.64      | 8.38      | 8.31      |
|                       | $J_{\text{HH}}$ | broadened        | broadened | broadened | broadened |
|                       | $\Delta\delta$  |                  | 0.14      | −0.12     | −0.19     |

<sup>a</sup> Referred to TMS in DMSO solutions.

<sup>b</sup> Complexation shift is defined as the <sup>1</sup>H chemical shift difference of corresponding nuclei in the complex and free picolinamide molecule.

<sup>c</sup> Taken from Ref. [29].

<sup>d</sup> Sign (+) denotes deshielding effect, while (−) denotes shielding effect.

<sup>e</sup> Digital resolution  $\pm 0.30$  Hz: (s) singlet, (d) doublet, (m) multiplet.

Table 7  
<sup>13</sup>C NMR chemical shifts ( $\delta$ /ppm)<sup>a</sup> and complexation shifts ( $\Delta\delta$ /ppm)<sup>b,c</sup> in the ligand molecule, picolinamide, and its complexes with zinc(II), cadmium(II) and mercury(II) thiocyanate, **1**, **2** and **3**

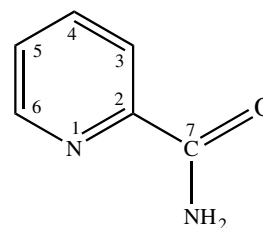
| Compound |                | pic <sup>a</sup> | <b>1</b> | <b>2</b> | <b>3</b> |
|----------|----------------|------------------|----------|----------|----------|
| C-2      | $\delta$       | 150.75           | 148.39   | 149.06   | 149.33   |
|          | $\Delta\delta$ |                  | −2.36    | −1.69    | −1.42    |
| C-3      | $\delta$       | 122.35           | 122.49   | 122.32   | 122.38   |
|          | $\Delta\delta$ |                  | 0.14     | −0.03    | 0.03     |
| C-4      | $\delta$       | 138.08           | 139.02   | 138.36   | 138.32   |
|          | $\Delta\delta$ |                  | 0.94     | 0.28     | 0.24     |
| C-5      | $\delta$       | 126.89           | 127.46   | 127.00   | 126.87   |
|          | $\Delta\delta$ |                  | 0.57     | 0.11     | −0.02    |
| C-6      | $\delta$       | 148.90           | 147.87   | 148.55   | 148.80   |
|          | $\Delta\delta$ |                  | −1.03    | −0.35    | −0.1     |
| C-7      | $\delta$       | 166.51           | 166.02   | 166.05   | 165.95   |
|          | $\Delta\delta$ |                  | −0.49    | −0.46    | −0.56    |
| C(SCN)   | $\delta$       |                  | 134.65   | 133.35   | 115.97   |

<sup>a</sup> Referred to TMS in DMSO solutions.

<sup>b</sup> Complexation shift is defined as the <sup>13</sup>C chemical shift difference of corresponding nuclei in complex and free picolinamide molecule.

<sup>c</sup> Sign (+) denotes deshielding effect, while (−) denotes shielding effect.

In the <sup>1</sup>H NMR spectra of all three complexes shielding of all protons is established. The only one exception found is the proton of the amido group of the zinc complex, which is deshielded. It is probably caused by different H-



Scheme 1.

bonding in the Zn complex than in the free ligand. The greatest complexation shifts ( $\Delta\delta$ ) are observed for the H-6 and H-3 protons, which are three or four bonds remote from the metal centers.

In the <sup>13</sup>C NMR spectra of all the complexes, in general, the greatest changes upon complexation were observed for the chemical shifts in the zinc complex (**1**), and the smallest changes were for the mercury complex (**3**). In all three complexes carbon atom C-2 is found to be the most shielded (−1.42 to −2.36 ppm). The carboxamido carbon atom is also greatly influenced by coordination to the metal centers and is the only C atom for which the greatest complexation shift is found for mercury in comparison with the other complexes. The C-4 carbon atom, which is *para* to the pyridine nitrogen atom, is found to be deshielded in all complexes due to delocalisation of  $\pi$ -electrons through the pyridine ring.

The formation of thiocyanate and isothiocyanate complexes can be easily detected by the characteristic  $^{13}\text{C}$  signal for  $-\text{SCN}$  and  $-\text{NCS}$  groups that are usually found at  $\sim 111$  and  $\sim 145$  ppm, respectively [30]. In the  $^{13}\text{C}$  spectra of the investigated thiocyanato complexes there are signals at 135, 133 and 116 ppm in the zinc, cadmium and mercury complexes respectively, indicating coordination of the thiocyanato ligands to the metal centers through  $N$ - in the cases of Zn (**1**) and Cd (**2**) and through  $S$ - in the case of Hg (**3**).

### 3.4. Thermal analysis

Thermal decomposition of the complex **1** is shown in Fig. 5. At normal temperature and pressure the crystals possess good stability and do not show any hygroscopic effect. The analysis of the TGA and DTA curves shows that the thermal decomposition of **1** starts around  $160^\circ\text{C}$ . The first step is the decomposition of **1** to  $\text{Zn}(\text{SCN})_2$ , corresponding to the endothermic DTA peaks at  $172.9^\circ\text{C}$ . In the temperature range  $270$ – $700^\circ\text{C}$  two endothermic peaks (a main large one at  $273^\circ\text{C}$ , and a second small around  $350^\circ\text{C}$ ) were observed.

The TGA curve of **2** (Fig. 6) shows a large weight loss in the range  $200$ – $350^\circ\text{C}$  followed by an endothermic DTA peak with a minimum at  $251.6^\circ\text{C}$ , and subsequently continues with a weight loss in range up to  $350^\circ\text{C}$  without any peak in the DTA curve. The decomposition process suggests that the loss of picolinamide and thiocyanate groups occurs almost simultaneously. The final product after  $700^\circ\text{C}$  should mainly be  $\text{CdS}$ .

The thermal analysis of **3** reveals that the thermal decomposition of the complex involves three processes, two endothermal and one exothermal process (Fig. 7). The first step is the decomposition of **3** to  $\text{Hg}(\text{SCN})_2$  (minimum at  $145.9^\circ\text{C}$ ), and the second one is the decomposition of  $\text{Hg}(\text{SCN})_2$  due to elimination of  $\text{CS}_2$ ,  $(\text{CN})_2$  and  $\text{N}_2$  gases (maximum at  $200.8^\circ\text{C}$ ) The last one is the sublimation of  $\text{HgS}$ , corresponding to the endothermic peak in the temperature range  $350$ – $450^\circ\text{C}$ .

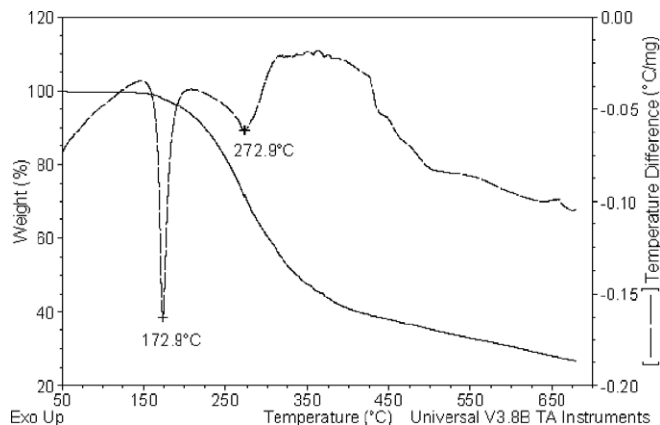


Fig. 5. TGA and DTA curve of **1**.

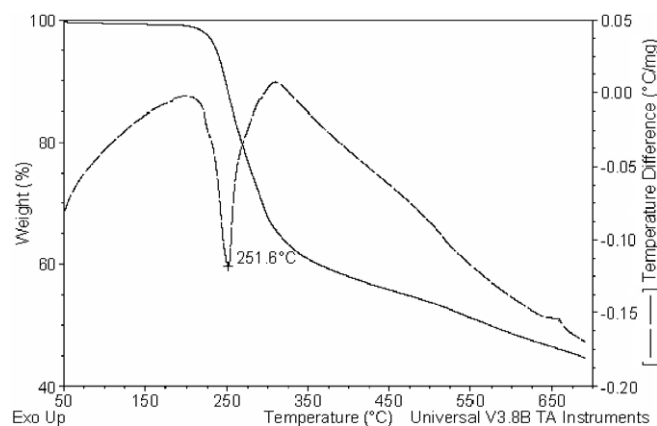


Fig. 6. TGA and DTA curve of **2**.

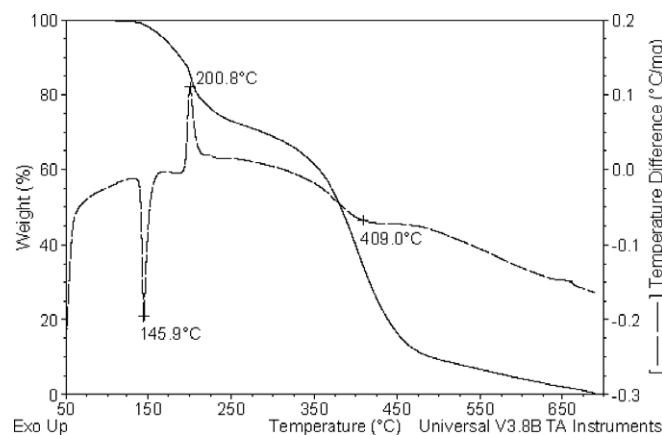


Fig. 7. TGA and DTA curve of **3**.

## 4. Conclusion

Three new heteroleptic complexes of the group 12 metals with picolinamide and thiocyanate have been synthesized. The zinc and cadmium complex have been readily prepared by the *in situ* reaction from water solution, while the mercury complex has been prepared by prior isolation of mercury(II) thiocyanate. The isolated title compounds were investigated by X-ray analysis, spectroscopic and thermal methods.

Having the amide group in a *para* position to the endocyclic nitrogen atom, picolinamide acts as a chelating  $N,O$ -ligand towards all three metals of group 12, leaving the amido  $N$ -atom for participation in hydrogen bonding and contacts. The thiocyanate ion acts as  $N$ - for the zinc complex **1**,  $S$ -/ $\mu$ - $S$ - for the mercury complex **3** and a  $\mu$ - $N,S$ -donor ligand for the cadmium thiocyanato complex **2**. Compound **1** is comprised of monomeric units and compound **3** dimeric units, while compound **2** is comprised of polymeric units. The thiocyanate shows a great variety of bonding modes with the group 12 metals, as a terminal as well as a bridging ligand. As a terminal ligand it is bound to metal ion from almost linear in **1b** [ $\text{M}-\text{N}-$

C = 171.9(2)°] to almost perpendicular bonding mode in **3** [ $\angle\text{M-S-C} = 96.5(2)^\circ$ ]. It is also noticed that there is elongation of the C–S bond lengths for the *S*-coordination in **3** in comparison to the *N*-coordination of the terminal thiocyanate ligand in **1**, while as a bridging  $\mu$ -*N,S*-ligand in **2** the C–S bond length is somewhere in between the values for **1** and **3**. Although Zn and Cd have the same coordination number and Hg a smaller one, the bite angle in the case of Cd and Hg is the same, and in the case of Zn it is somewhat larger.

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### Appendix A. Supplementary material

CCDC 644422, 645305, 645306 and 646561 contain the supplementary crystallographic data for **1a**, **1b**, **2** and **3**. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)]. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2007.09.014](https://doi.org/10.1016/j.poly.2007.09.014).

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