Coordination Polymer of M(II)-Pyrazinamide (M = Co, Cd) with Double End-to-End Thiocyanate Bridge

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Abstract. Pyrazinamide (pza, C₄N₂H₃CONH₂) is a good ligand for coordination polymer. Their transition metal complexes are known to have antibacterial activities, magnetic properties, etc. Coordination polymers of M(II)-pyrazinamide with thiocyanate (M = Co (a), Cd (b)), prepared using bench-top layering technique with M(II):pza:SCN ratio of 1:2:2, is successfully crystallised at room temperature. Single crystal XRD was used to determine the crystal structure. Infrared and melting point determination were also performed. Crystal structure of both complexes, solved in Triclinic P-1, show that each octahedral metal centre is connected to two adjacent metal centres by double end-to-end thiocyanate bridge forming a 1D polymeric structure with M⋯M distances of 5.524 Å (in a) and 5.887 Å (in b). Two monodentate pyrazinamide ligands occupy the rest of the coordination sites on the metal centre in a trans relationship. Only in complex a, one lattice pyrazinamide molecule is involved in the asymmetric unit. Crystal packing of both a and b are also displaying non-covalent networks as a result of hydrogen-bonding involving the pyrazine ring, amide and carbonyl groups between adjacent chains and π⋯π interactions (only occurred in a). In addition, the observed melting points of both a and b are relatively close to each other (around 180°C), and ATR-IR spectra support the presence of the bridging thiocyanate and terminal pyrazinamide.

1. Introduction
Pyrazinamide or pyrazine-2-carboxamide (pza, C₄N₂H₃CONH₂) is a known compound for decades but it was started to be widely used in the 1970s mostly for medical uses, i.e. for tuberculosis treatment [1,2]. In inorganic chemistry, pyrazinamide is also a good ligand for the construction of metal complexes, clusters, and/or coordination polymers due to their versatility to coordinate to the metal centre in mono, bi, or polydentate fashions (Figure 1) [3-5]. Transition metal complexes of pyrazinamide, with or without co-ligand, have been explored since then and their properties, such as antibacterial activity [6], electroluminescence [7], and antiferromagnetic behaviour [8], were reported.

Figure 1. Possible coordination modes of pyrazinamide with metal ion (M)
Metal complexes and/or coordination polymers of M(II)-pza (M = transition metal ions) have been reported many times and to the best of our knowledge, M(II)-pza coordination polymers with double end-to-end thiocyanate bridge were never been published. There are, however, several analogue complexes published with formula of poly-[M(µ-NCS)₂(X)]₂ (X = monodentate terminal ligand), such as poly-[Cd(µ-NCS)₂(pia)]₂ [4], poly-[Cd(µ-NCS)₂(3pica)]₂ [9], poly-[M(µ-NCS)₂(4pica)]₂ (M = Co, Cd) [9]), poly-[M(µ-NCS)₂(py)]₂ (M = Mn [10], Fe [11], Co [11], Cd [12]) and poly-[M(µ-NCS)₂(4pi)]₂ (M = Cu [13], Cd [14]), poly-[Cu(µ-NCS)₂(ambzin)]₂ [15], poly-[Cd(µ-NCS)₂(3ampy)]₂ [16], [Cd(µ-NCS)₂(val)]₂ H₂O [16], etc. The source of the thiocyanate could be from NaSCN, KSCN, or NH₄SCN. In addition, some of these coordination polymers also shows interesting magnetic properties [9, 10, 15].

In this paper, we reported the synthesis and crystal structure of [{Co(µ-NCS)₂(pza)₂}₁ pza]ₙ (a) and [{Cd(µ-NCS)₂(pza)₂}ₖ (b). The melting point and ATR-IR analyses of the complexes are also discussed. Synthesis of M(II)-pza-thiocyanate (M = Mn, Ni) compounds using similar procedure only gives amorphous products and were not included in this paper. Improved procedure to produce better XRD quality-crystalline products are ongoing.

2. Materials and Methods

2.1. Materials and Measurements

Sigma–Aldrich chemicals and solvent (pyrazinamide, NaSCN, Co(NO₃)₂·6H₂O, Cd(ClO₄)₂·6H₂O, and methanol) were used as received. Solid-state IR spectra were recorded by using an Agilent ATR microscope at 1000-600 cm⁻¹. Melting points were measured with an Electrothermal Melting Point Apparatus in open capillaries. Low-temperature single-crystal X-ray diffraction experiments were performed using a Bruker Apex II KAPPA CCD with Mo-Kα radiation (λ, 0.71073 Å) equipped with an Oxford Instruments nitrogen gas cryostream. Single crystals were mounted on nylon loops in viscous hydrocarbon oil. Crystals were quench-cooled to 123(2) K. Analysis of diffraction data collected with the Bruker Apex II KAPPA CCD was performed by using SAINT within the APEX2¹⁷ software package. Empirical absorption corrections were applied to all data by using SADABS.¹⁸ The structures were solved using SHELXS¹⁹ and refined using SHELXL-1³¹⁹ within the graphical interface Olex2.²⁰ All hydrogen atoms were refined using a riding model, while all non-hydrogen atoms were refined using an anisotropic model.

2.2. Synthesis of the Complexes

2.2.1. [{Co(µ-NCS)₂(pza)₂}₁ pza]ₙ (a). A 3-mL methanolic solution of pyrazinamide (50 mg, 0.406 mmol) was carefully layered on top of a 5-mL aqueous solution of Co(NO₃)₂·6H₂O (34.6 mg, 0.203 mmol) and NaSCN (32.9 mg, 0.406 mmol), separated by 5 mL buffer layer of H₂O:CH₃OH (1:1). Two weeks later, a clear homogenous pink solution was formed. Upon slow evaporation at room temperature for 2 months, the solution gives red block crystals. The crystals were then isolated, washed with cold water and then air-dried for overnight (yield = 35 mg, 32%).

2.2.2. [{Cd(µ-NCS)₂(pza)₂}ₖ (b). A 3-mL methanolic solution of pyrazinamide (50 mg, 0.406 mmol) was carefully layered on top of a 5-mL aqueous solution of Cd(ClO₄)₂·6H₂O (85.1 mg, 0.203 mmol) and NaSCN (32.9 mg, 0.406 mmol), separated by 5 mL buffer layer of H₂O:CH₃OH (1:1). A month later, long block colourless crystals were yielded. The crystals were then isolated, washed with cold water and then air-dried for overnight (yield = 45 mg, 47%).

3. Result and Discussion

3.1. Crystal Structure

Crystal structures of both complexes, [{Co(µ-NCS)₂(pza)₂}₁ pza]ₙ (a) and [{Cd(µ-NCS)₂(pza)₂}ₖ (b), were solved in Triclinic P-1 space group with unit cell volumes of 1077.52(10) Å³ and 420.62(8) Å³, respectively. The unit cell volume of a is nearly three times larger than that of b since there is one lattice pyrazinamide molecule, which hydrogen-bonded to one of the pyrazinamide ligand, involved in the asymmetric unit of a (Figure 2). Coordination environment around the metal centre in a and b is similar,
in which each metal centre is surrounded by two monodentate pyrazinamide in a *trans* relationship and four bridging thiocyanate ligands forming an octahedral neutral complex. The pyrazinamide ligands are coordinated through one of the pyrazine nitrogen atom (N5 and N8 in *a*; N3 in *b*). Moreover, two adjacent metal centres are connected by two end-to-end thiocyanate ions with M···M distances of 5.524 Å (in *a*) and 5.887 Å (in *b*), thus the complexes form 1D coordination polymers with a metal centre coordination core of MN$_4$S$_2$ (Figure 3). The M···M distance in this work is slightly shorter to those observed in poly-[$\text{M(µ-NCS)}_2(4\text{pica})_2$] (M = Co, Cd) [9]. 5.581 Å in Co(II) and 5.926 Å in Cd(II) complexes, which is likely due to different size, hydrogen bonding, flexibility or steric effect of the terminal monodentate ligand. Two different M···M distances may also be observed in a 1D M(II)-double thiocyanate chain as reported in poly-[$\text{Cd(µ-NCS)}_2(3\text{ampy})_2$] with Cd···Cd distances of 5.7329(7) Å and 6.0354(8) Å [16].

![Figure 2](image-url)  
**Figure 2.** Asymmetric unit of {[$\text{Co(µ-SCN)}_2(\text{pza})_2$]·pza}$_n$ (*a*, left) and {[$\text{Cd(µ-SCN)}_2(\text{pza})_2$]$_n$ (*b*, bottom right) shown with thermal ellipsoids at 50% probability except hydrogen atoms (note: cyan = cobalt (*a*) or cadmium (*b*), blue = nitrogen, red = oxygen, grey = carbon, yellow = sulphur, white = hydrogen); coordination environment around the metal centre (top right)

![Figure 3](image-url)  
**Figure 3.** Both *a* and *b* forms 1D chains due to double end-to-end thiocyanate bridges with M···M distances of 5.524 Å (in *a*, left) and 5.887 Å (in *b*, right); note: cyan = cobalt (*a*) or cadmium (*b*), blue = nitrogen, red = oxygen, grey = carbon, yellow = sulphur, white = hydrogen.

Selected bond lengths and angles around the metal centres in the complex *a* and complex *b* are presented in Table 1, whereas crystallographic data of both complexes are presented in Table 3. As expected, the coordination bond length around the metal centre in complex *b* is longer than in complex *a* due to Cd(II) has a bigger size than Co(II). The Cd-N/S bond lengths are ranged from 2.2701(14) to 2.6964(5) Å, whereas the Co-N/S bond lengths are ranged from 2.0370(14) to 2.5306(4) Å. The longest coordination bonds in both *a* and *b* occur between the metal ion and the thiocyanate sulphur atoms.
Table 1. Selected bond lengths and angles around the metal centres in a and b

| Complexes | Bond Lengths (Å) | Angles (°) |
|-----------|-----------------|------------|
| a         | Co1-N1         | 2.0370(14) | 180.0 |
|           | Co1-N1#a       | 2.0370(14) | 89.68(4) |
|           | Co1-N5         | 2.2052(15) | 89.68(4) |
|           | Co1-N5#a       | 2.2052(15) | 90.32(4) |
|           | Co1-S2#b       | 2.5352(4)  | 90.32(4) |
|           | Co1-S2#c       | 2.5352(4)  | 179.99(14) |
|           | Co2-N2         | 2.0441(14) | 84.93(4) |
|           | Co2-N2#b       | 2.0441(14) | 95.07(4) |
|           | Co2-N8         | 2.1903(14) | 95.07(4) |
|           | Co2-N8#b       | 2.1903(14) | 92.46(6) |
|           | Co2-S1         | 2.5306(4)  | 87.54(6) |
|           | Co2-S1#b       | 2.5306(4)  | 87.54(6) |
|           | N2,1          | -x, y, 1-z | 92.46(6) |
|           | N1,1          | -x, y, 1-z | 92.46(6) |
|           | N1,1#c         | +x, y, +z  | 92.46(6) |
| b         | Cd1-N1         | 2.2701(14) | 180.0 |
|           | Cd1-N1#d       | 2.2700(14) | 89.77(3) |
|           | Cd1-N3         | 2.4314(14) | 89.77(3) |
|           | Cd1-N3#d       | 2.4313(14) | 90.23(3) |
|           | Cd1-S1#e       | 2.6964(5)  | 90.23(3) |
|           | Cd1-S1#f       | 2.6964(5)  | 90.23(3) |
|           | N2,1           | 2-x, y, 1-z | 91.85(4) |
|           | N1,1           | 2-x, y, 1-z | 91.85(4) |
|           | N1,1#d         | 1-x, y, 1-z | 91.85(4) |
|           | N1,1#e         | 1-x, y, 1-z | 91.85(4) |

As reported in polymeric double end-to-end thiocyanate complexes [9-14], the linear thiocyanate anions bind to the metals have M–N–S angles close to 180° (at the N-bound end) and M–S–N angles close to 90° (at the S-bound end). Accordingly, the M–N–S and M–S–N angles in a are 163.06° (Co1-N1-S1), 162.21° (Co2-N2-S2), and 99.85° (Co2-S2-N2), while the M–N–S and M–S–N angles in b are 163.18° (Cd1-N1-S1), and 99.66° (Cd1-S1-N1). In addition, the double end-to-end thiocyanate bridge in b creates eight-membered Cd$_2$(SCN)$_2$ rings with a chair conformation, whereas in a, the Co$_2$(SCN)$_2$ rings form a flat conformation which probably due to the M–M distance in a is shorter than in b. The lattice pza molecules in a which hydrogen bonded to one of the pza ligands may also affect this conformation.

In both a and b, several hydrogen-bond motifs are observed (Table 2). Each lattice pza molecule in a is hydrogen bonded to two adjacent pza ligand from the same Co-(SCN)$_2$-Co chain. The Co-(SCN)$_2$-Co chain is also hydrogen bonded to two neighbouring chains through the amine and carbonyl groups of the pza ligand resulting 2D hydrogen-bonded sheets with a (Co–pza)$\cdots$(pza–Co) distance of 14.734 Å. The crystal packing of a then grows into a 3D hydrogen-bonded π$\cdots$π stacked networks (Figure 4) due to π$\cdots$π interactions between two closest pyrazine rings with a plane centroid-to-plane centroid of 3.582 Å. Unlike in a where lattice pza is observed, only hydrogen bonds between the pza ligands occurred in b. Each pza ligand is hydrogen-bonded to two neighbouring pza ligand in intramolecular and intermolecular fashion. Each chain in b is also hydrogen bonded to two adjacent chains, thus 2D hydrogen-bonded sheets are formed with a (Cd–pza)$\cdots$(pza–Cd) distance of 11.984 Å. Although there are no π$\cdots$π interactions between two closest pyrazine rings observed, crystal packing of b also forms non-covalent networks due to hydrogen bonding formed between the sheets (Figure 4).
Table 2. Hydrogen bond data of a and b

| Complex | D   | H   | A     | D-H (Å) | H···A (Å) | D···A (Å) | DHA (°) |
|---------|-----|-----|-------|---------|-----------|----------|--------|
| a       | N3  | H3A | O3    | 0.86    | 2.03      | 2.887(2) | 172.5  |
|         | N9  | H9A | O1    | 0.86    | 2.03      | 2.887(2) | 173.2  |
|         | N6  | H6A | O2#g  | 0.86    | 2.05      | 2.905(2) | 178.3  |
|         | N6  | H6A | N10#e | 0.86    | 2.36      | 3.044(2) | 136.8  |
|         | N9  | H9B | N7#e  | 0.86    | 2.54      | 3.274(2) | 143.6  |
| b       | N4  | H4A | O1#h  | 0.86    | 2.01      | 2.862(18) | 168.4  |
|         | N4  | H4B | N2#i  | 0.86    | 2.48      | 3.172(18) | 138.9  |

*Note: #e = 1-x, 1-y, -1-z; #g = -1-x, 1-y, -z; #h = -x, 1-y, -z; #i = 1-x, 2-y, -z*

Table 3. Crystallographic data of [{Co(pza)₂(μ-SCN)₂}·pza]ₙ (a) and [Cd(pza)₂(μ-SCN)₂]ₙ (b)

| Complexes | a                  | b                  |
|-----------|--------------------|--------------------|
| Chemical formula | C₁₇H₁₅CoN₁₁O₃S₂ | C₁₂H₁₀CdN₈O₂S₂     |
| Formula Mass  | 544.45             | 474.80             |
| Crystal system| Triclinic          | Triclinic          |
| Space group   | P-1                | P-1                |
| a/Å           | 6.8711(4)          | 5.8871(6)          |
| b/Å           | 11.0487(6)         | 6.3004(7)          |
| c/Å           | 14.6891(8)         | 11.8296(13)        |
| α/°           | 94.949(2)          | 96.219(4)          |
| β/°           | 103.144(2)         | 102.848(4)         |
| γ/°           | 93.867(2)          | 96.821(4)          |
| Unit cell volume/Å³ | 1077.52(10) | 420.62(8)          |
| Temperature/K | 123(2)             | 123(2)             |
| Z             | 2                  | 1                  |
| μ (mm⁻¹)     | 1.038              | 1.571              |
| Reflections measured | 15710               | 11887              |
| Independent reflections | 5122               | 2107               |
| Observed reflections (I > 2σ(I)) | 4365               | 2075               |
| R_int        | 0.0319             | 0.0383             |
| Final R₁ values (obs. data) | 0.0274             | 0.0180             |
| Final wR(F²) values (obs. data) | 0.0706             | 0.0411             |
| Final R₁ values (all data) | 0.0353             | 0.0184             |
| Final wR(F²) values (all data) | 0.0750             | 0.0412             |
| Goodness of fit on F² | 1.066              | 1.084              |
3.2. ATR-IR and MP analyses

In general, the ATR-IR spectra of both complexes shows characteristic N_{pyrazine}-coordinated pyrazinamide and bridging thiocyanate absorptions as expected which consistent to the X-ray structure analysis (Figure 5). Due to non-coordinated (free) pza molecules in the lattice, there are more bands observed in the complex a than in complex b.

The asymmetric and symmetric stretching mode of NH_{2} in a appeared at 3457 cm\(^{-1}\) (free pza), 3408 cm\(^{-1}\) (coordinated pza), and 3287 cm\(^{-1}\) (both free and coordinated pza), respectively; while in b, they are appeared at 3416 and 3285 cm\(^{-1}\), respectively. These bands are also supported by a sharp peak at 1606 cm\(^{-1}\) (free pza in a), 1590 cm\(^{-1}\) (coordinated pza in a), and 1591 cm\(^{-1}\) (in b), which correspond to scissoring of the NH_{2} group and medium peak at 1590 cm\(^{-1}\) (both in a and b), which belong to the bending of the NH_{2} group. A very sharp peak at 1706 cm\(^{-1}\) (free pza in a), 1686 cm\(^{-1}\) (coordinated pza in a), and 1686 cm\(^{-1}\) (in b), which belongs to a C=O stretch, suggest that the C=O of pza ligand is not coordinated to the metal ions. Coordinated C=O is commonly observed in a lower wavenumber (around 1650-1500 cm\(^{-1}\)). This also means that the pza ligands in both a and b are coordinated to the metal ion in a monodentate fashion through the pyrazine nitrogen atom, as already confirmed by the X-ray structure analysis. The presence of pza in both complexes are also supported by medium peaks around 3100-3000 cm\(^{-1}\) which correspond to the C–H stretch.

In general, the bridging thiocyanate group (M–NCS–M) has the highest \(\nu(CN)\) wavenumber (2165–2065 cm\(^{-1}\)) compare to the \(\nu(CN)\) wavenumber of terminal thiocyanate groups (M–NCS = 2010–2050 cm\(^{-1}\); M–SCN = 2130–2085 cm\(^{-1}\)), while the \(\nu(CS)\) wavenumber of M–NCS (870–820 cm\(^{-1}\), weak) is higher than that of M–NCS–M (800 – 750 cm\(^{-1}\)) and M–SCN (760 – 700 cm\(^{-1}\), broad), respectively, although other factors such as mass, charge, and size of the central atom influences the frequencies of thiocyanate ligand [21]. In these works, the \(\nu(CN)\) band is observed at 2118 cm\(^{-1}\) in a and 2115 cm\(^{-1}\) in
b, while the $\nu$(CS) band appears at 783 cm$^{-1}$ in a and 808 cm$^{-1}$ in b. The slight difference of $\nu$(CN) and $\nu$(CS) frequencies in the complex a and complex b is due to the thiocyanate bridge is coordinated to two different metal centre, which is cobalt(II) in a and cadmium(II) in b. This observed $\nu$(CN) and $\nu$(CS) bands in the complex a and complex b are in line with the bridging thiocyanate ligand.

![ATR-IR spectra of complex a (top) and b (bottom)](image_url)

Figure 5. ATR-IR spectra of complex a (top) and b (bottom)

The melting point of the complex was also determined for further characterisation. The observed melting points of both complexes are relatively close to each other (180°C for a and 185°C for b). Upon heating, complex a colour is gradually changed from red to pink to orange, and finally at 180°C, complex a was changed from dark orange crystal to dark blue liquid, indicating the phase change of the complex at high temperature. Although no further chemical analysis was conducted on the dark blue liquid, this indicates the formation of tetrahedral cobalt(II) complex as commonly observed in cobalt(II) complexes. In complex b, there was no phase change observed throughout the heating as cadmium(II) complexes are usually more stable than cobalt(II) complexes. The crystal remains colourless upon heating and then turn into a light yellowish liquid at 185°C.
4. Conclusion
Two 1D coordination polymers of \([\text{[Co(µ-NCS)}_2\text{(pza)}_2]\] and \([\text{[Cd(µ-NCS)}_2\text{(pza)}_2]\] were made and structurally characterised. In both complexes, double end-to-end thiocyanate ions bridges between two adjacent metal centre and the pza ligand only coordinate to the octahedral metal ion in a monodentate fashion via pyrazine nitrogen atom forming a metal centre coordination core of Mn₃S₂. Crystal packing of both a and b are also displaying non-covalent networks as a result of hydrogen-bonding involving the pyrazine ring, amide and carbonyl groups between adjacent chains and π···π interactions (only occurred in a). In addition, the observed melting points of both complexes are relatively close to each other (around 180°C) and ATR-IR spectra support the presence of the bridging thiocyanate and terminal pyrazinamide.

Acknowledgments
Author thanks Chemistry Department of Brawijaya University, Indonesia for financial support and acknowledges Prof. Stuart Batten and his group member (Monash University, Australia), Assoc. Prof. Jack Clegg (The University of Queensland, Australia), and Australia Award Scholarship–DFAT Australia.

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