

**SYNTHESES, CRYSTAL STRUCTURES AND
ANION EXCHANGE STUDIES OF
COORDINATION POLYMERS CONTAINING
N,N-2,6-BIS(4-PYRIDYLMETHYL)PYRIDINE
DICARBOXAMIDE WITH CHROMATE ANION**

NUR SYAZWANI BINTI KASSIM

**MASTER OF SCIENCE
UNIVERSITI MALAYSIA TERENGGANU**

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**Thesis Submitted in Fulfillment of the
Requirement for the Degree of Master of Science
in the School of Fundamental Science
Universiti Malaysia Terengganu
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Dedicated this thesis to:

My super fantabulous and dedicated supervisor, Dr Maisara Abdul Kadir

My beloved parents (abah and ma) and siblings

My fiance in my life Hisyam Zulkefli

Thanks for the endless loves and support

Indeed we have granted you a clear victory (1)

And grant you a might victory (3)

[Surah Al- Fath]

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfillment of the requirement for the degree of Master of Science

SYNTHESES, CRYSTAL STRUCTURES AND ANION EXCHANGE STUDIES OF COORDINATION POLYMERS CONTAINING *N,N*-2,6-BIS(4-PYRIDYLMETHYL)PYRIDINE DICARBOXAMIDE WITH CHROMATE ANION

NUR SYAZWANI BINTI KASSIM

SEPTEMBER 2016

Main Supervisor : Maisara Abdul Kadir, PhD

Co-Supervisor : Associate Professor Mohd Sukeri Mohd Yusof, PhD

School : School of Fundamental Science

The release of hazardous anions such as chromate, nitrate and perchlorate into the waterways system has cause a destructive effect on human and the aquatic environment. To overcome this problem, many techniques utilizing amide compounds as anion receptors have been reported. New trend of using coordination polymers as anion receptors has attracted a lot of attention due to their large surface area and high selectivity. Therefore, in this study, a flexible U-shaped ligand with potential to bind anion, namely *N,N*-2,6-bis(4-pyridylmethyl)pyridine dicarboxamide (**L1**) has been successfully synthesized. This ligand was used as an organic linker in the construction of coordination polymers ($\{[\text{Zn}(\text{L1})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}\}_n$ (**MC1**), $\{[\text{Cd}(\text{L1})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}\}_n$ (**MC2**) and $\{[\text{Cd}(\text{L1})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}\}_n$ (**MC3**) which was purposely designed to selectively bind and separate anions, particularly chromate. All compounds were characterized using a combination of Fourier transform infrared (FTIR), ^1H and ^{13}C Nuclear magnetic resonances (NMR) while the structure of the coordination polymers were confirmed by X-ray

crystallography and elemental analysis. The FTIR spectra for ligand **L1** shows three important peaks which were assigned to $\nu(\text{N-H})$ stretching asymmetry at 3256 cm^{-1} , $\nu(\text{C=O})$ at 1650 cm^{-1} and $\nu(\text{N-H})$ bending at 1535 cm^{-1} . The $\nu(\text{N-H})$ stretching for all coordination polymers were shifted to the lower frequency compared to their organic linkers, **L1** due to the coordination of the nitrogen at the pendant pyridine to the metal ion. In ^1H NMR spectrum of the ligand (**L1**), the signals for protons of methylene, pyridine and amide group were indicated at range 4.5 ppm, 7.1-8.3 ppm and 8.7 ppm, respectively. In ^{13}C NMR, the resonances for carbon of methylene, pyridine and carbonyl group were found at range 42.2 ppm, 122.6-149.2 ppm and 163.94 ppm, respectively. The crystals of coordination polymers **MC1** and **MC2** crystallize in triclinic space group *P*-1 with the cell dimension almost identical to each other. Meanwhile, complex **MC3** crystallizes as a 2-D coordination polymer in monoclinic space group *C2/c*. A solid state anion exchange experiment was attempted to investigate the potential of **MC1-MC3** to exchange their counter anions with chromate. The FTIR spectra show that the intensity of the nitrate peak decreased by 82% and 81% respectively. The presence of strong chromate peak was also observed for FTIR spectrum of **MC3**. Meanwhile, the perchlorate anion was indicated to fully replaced chromate anion. Further investigation on anion exchange potential of these coordination polymers with chromate anions were calculated using Gaussian 09 software package at theoretical level of DFT/B3LYP with GEN (6-31G (d,p) for all compounds and LANL2DZ for Zn, Cd, and Cr) as basis set. The calculation shows that the energy interaction of nitrate (-350.2181 KJ/mol) is higher than energy interaction of chromate (-325.7500 KJ/mol) in **MC2**. The results obtained from theoretical and experimental show that coordination polymers **MC1** and **MC2** have limited binding to chromate anions due to their high stability with

nitrate. Complex **MC3** has shown promising potential to be applied as anion receptors for chromate but the theoretical study cannot be carried out due to problems in the limitation and incompatible Gaussian software.

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**SINTESIS, STRUKTUR-STRUKTUR HABLUR DAN KAJIAN POTENSI
PERTUKARAN ANION OLEH POLIMER KOORDINATAN YANG
MENGANDUNGI *N,N*-2,6-BIS (4-PIRIDILMETIL)PIRIDINA
DIKARBOKSAMIDA DENGAN KROMAT ANION**

NUR SYAZWANI BINTI KASSIM

SEPTEMBER 2016

Penyelia Utama : Maisara Abdul Kadir, PhD
Penyelia Bersama : Profesor Madya Mohd Sukeri Mohd Yusof, PhD
Pusat Pengajian : Pusat Pengajian Sains Asas

Pembebasan anion berbahaya seperti kromat, nitrat dan perklorat ke dalam sistem perairan memberikan kesan buruk kepada manusia dan persekitaran akuatik. Untuk mengatasi masalah ini, banyak teknik menggunakan sebatian amida sebagai reseptor anion telah dilaporkan. Pendekatan terkini menggunakan polimer koordinatan sebagai reseptor anion telah menarik perhatian ramai di atas kelebihanannya yang mempunyai luas permukaan yang tinggi dan sangat selektif. Oleh itu, dalam kajian ini, satu ligan yang fleksibel dan berbentuk U telah berjaya disintesis dan diberi nama sebagai *N,N*-2,6-bis(4-piridilmetil)piridina dikarboksamida (**L1**). **L1** ini digunakan sebagai penghubung organik dalam pembentukan polimer koordinatan, $\{[\text{Zn}(\mathbf{L1})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}\}_n$ (**MC1**), $\{[\text{Cd}(\mathbf{L1})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}\}_n$ (**MC2**) dan $\{[\text{Cd}(\mathbf{L1})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}\}_n$ (**MC3**) yang direka khas untuk mengikat dan mengasingkan anion secara terpilih, terutamanya kromat. Sebatian yang berjaya disintesis telah dicirikan dengan menggunakan instrumentasi seperti Inframerah transformasi fourier (FTIR) dan kaedah spektroskopi seperti proton (^1H) dan karbon (^{13}C) resonans magnetik nukleus (NMR), manakala struktur bagi polimer

koordinatan disahkan menggunakan kristalografi sinar-X dan analisis unsur (CHNS). FTIR spektra bagi **L1** menunjukkan tiga puncak yang penting iaitu puncak $\nu(\text{N-H})$ regangan pada 3256, $\nu(\text{C=O})$ pada 1650 dan $\nu(\text{N-H})$ pada 1535 cm^{-1} . Manakala, $\nu(\text{N-H})$ regangan bagi semua polimer koordinatan pula teranjak ke arah frekuensi yang lebih rendah, disebabkan oleh koordinatan oleh atom nitrogen pada gelang piridina kepada ion logam. Bagi spektra proton (^1H) NMR, isyarat proton bagi kumpulan metilena, piridina dan amida berada pada julat 4.5 ppm, 7.1-8.3 ppm dan 8.7 ppm. Manakala bagi spektra karbon (^{13}C) NMR pula, resonans karbon untuk kumpulan metilena, piridina dan karbonil berada pada julat 42.2 ppm, 122.6-149.2 ppm dan 163.94 ppm. Polimer koordinatan **MC1** dan **MC2** menghablur dalam sistem hablur monoklinik, *P-1*. Manakala, kompleks **MC3** menghablur sebagai polimer koordinatan 2 dimensi dalam sistem hablur monoklinik, *C2/c*. Potensi **MC1-MC3** terhadap pertukaran anion dengan kromat telah dijalankan menggunakan kaedah pertukaran anion keadaan pepejal. Keputusan dari spektra FTIR menunjukkan munculnya puncak baru iaitu puncak kromat dan pengurangan puncak nitrat berlaku sebanyak 82% dan 81%. Puncak berintensiti tinggi mewakili kromat dikenalpasti dalam FTIR **MC3**. Kajian lanjut terhadap potensi pertukaran anion bagi sebatian koordinasi polimer terhadap kromat telah dijalankan dengan menggunakan pakej perisian Gaussian 09 pada tahap teori DFT/B3LYP dan GEN (6-31G(d,p) untuk semua sebatian, dan LANL2DZ untuk Zn, Cd, dan Cr) sebagai set basis. Pengiraan menunjukkan tenaga interaksi nitrat anion (-350.2181 KJ/mol) adalah lebih besar daripada tenaga interaksi kromat anion (-325.7500 KJ/mol) bagi **MC2**. Kajian yang diperolehi dari teori dan eksperimen menunjukkan bahawa interaksi antara polimer koordinatan **MC1** dan **MC2** dengan anion kromat adalah terhad manakala ikatan dengan nitrat adalah lebih stabil. Kompleks **MC3** mempunyai potensi yang tinggi

sebagai anion reseptor bagi kromat namun kajian teori tidak dapat dijalankan kerana masalah limitasi dan ketidaksesuaian perisian Gaussian.