

Synthesis, Structural Elucidation and Anion Binding Studies of Isophthalamide Derivatives as Potential Receptor for Chromate Anions

(Kajian Sintesis, Penentuan Struktur dan Pengikatan Anion Terbitan Isoptalamida Berpotensi sebagai Reseptor untuk Anion Kromat)

MAISARA ABDUL KADIR*, SYAHIRAH OMAR, NUR SHUHAILA HARYANI ABD HARIS & RAMIZAH RAMLI

ABSTRACT

This study highlights the synthesis and structural elucidation of two new isophthalamide isomers namely N,N'-1,3-bis(4-methylpyridin-2-yl)isophthalamide (4-MPI) and N,N'-1,3-bis(5-methylpyridin-2-yl)isophthalamide (5-MPI), prepared from reaction between isophthaloyl chloride with 2-amino-4-methylpyridine and 2-amino-5-methylpyridine, respectively. Their potential studies as anion receptors for chromate anions are also include in this paper. Characterization of these compounds were accomplished using common spectroscopic techniques such as Fourier Transform Infrared (FT-IR), ¹H and ¹³C Nuclear Magnetic Resonance (NMR), UV-Vis spectrometer and mass spectrometry. FTIR analysis showed the presence of four significant peaks comprising $\nu(N-H)$, $\nu(C-H)$, $\nu(C=O)$ and $\delta(N-H)$ at range 3256-3274 cm⁻¹, 2812-2928 cm⁻¹, 1662-1686 cm⁻¹ and 1533-1537 cm⁻¹, respectively. Meanwhile, ¹H NMR confirmed the presence of methyl, aromatic carbon and amide resonances at δ_H 2.983-2.994 ppm, 6.860-8.974 and 10.138-11.300 ppm, respectively. In the ¹³C NMR spectra, the appearance of methyl, aromatic and carbonyl carbon signals were determined at δ_C 18.45-20.59 ppm, 108.42-159.22 ppm and 167.04-167.20 ppm, respectively. UV-Vis study showed that 4-MPI and 5-MPI shows promising potential as anion receptors for chromate anions.

Keywords: Anion; chromate; isophthalamide; receptor

ABSTRAK

Kajian ini menekankan sintesis dan penentuan struktur dua sebatian isomer baharu terbitan isoptalamida, iaitu N,N'-1,3-bis(4-metilpiridina-2-il)isoptalamida (4-MPI) dan N,N'-1,3-bis(5-metilpiridina-2-il)isoptalamida (5-MPI) yang disediakan melalui tindak balas antara isoptaloil klorida masing-masing dengan 2-amino-4-metilpiridina and 2-amino-5-metilpiridina. Pencirian terhadap sebatian ini dilakukan melalui gabungan beberapa teknik spektroskopi seperti Transformasi Fourier inframerah (FT-IR), ¹H dan ¹³C Resonans Magnetik Nukleus (NMR), UV-Vis dan spektrometer jisim. Spektrum FTIR menunjukkan kehadiran lima puncak penting mengandungi $\nu(N-H)$, $\nu(C-H)$, $\nu(C=O)$ dan $\delta(N-H)$ masing-masing pada julat 3256-3274 cm⁻¹, 2812-2928 cm⁻¹, 1662-1686 cm⁻¹ dan 1533-1537 cm⁻¹. Keputusan data ¹H RMN mengesahkan kehadiran resonans metil, aromatik dan amida masing-masing pada julat δ_H 2.983-2.994 ppm, 6.860-8.974 dan 10.138-11.300 ppm. Manakala, spektra ¹³C RMN menunjukkan kehadiran signal metil, aromatik dan karbonil masing-masing pada δ_C 18.45-20.59 ppm, 108.42-159.22 ppm dan 167.04-167.20 ppm. Analisis UV-Vis menunjukkan bahawa sebatian 4-MPI dan 5-MPI mempunyai potensi sebagai reseptor untuk anion kromat.

Kata kunci: Anion; isoptalamida; kromat; reseptor

INTRODUCTION

The field of anion coordination chemistry has become of a topical interest due to the impacts anions have in nature (Dong et al. 2012; Gale 2000; Ranjan & Pradyut 2014; Zhao et al. 2018) Fertilizer run-off, metallo-toxic anions and oxoanions, such as phosphate and chromate which were sourced from agricultural and industrial waste have widely cause to water pollutant (Cametti & Rissanen 2013, 2009; Gao et al. 2018). High level of phosphate is detrimental to the environment, which disrupts aquatic life cycles. Meanwhile, chromate, which has been classified as carcinogenic to humans by The International Agency for Research on Cancer (IARC) cause to eutrophication (Hsu et al. 2019).

Realizing the crucial need of anion receptors, various efforts have been devoted to produce synthetic anion receptors that can efficiently bind with these anions. This involve development of anion receptors from hydrogen bonds donor molecules such as amide, thiourea and imidazolium (Kai et al. 2015; Zhao et al. 2018). It is well known that resins and zeolites have been conventionally used to treat anions in water but these materials are effective in separating anions with higher valence, greater atomic weights and smaller radii such as I⁻, NO₃⁻, CN⁻, HSO₄⁻, NO₂⁻, Cl⁻ and HCO₃⁻ (Bezerra et al. 2019). Thus, lower valence and large radii such as chromate is possibly remained or recovered in drinking water during water treatment phase.

To date, employment of amide molecules such as bis pyridyl bis amide ligands has become of interest due to their ability to form interactions with oxoanions, either in discrete molecules or in the form of coordination polymers (Kadir & Sumbly 2018, Lin et al. 2018). Many of the anion receptors molecule were designed with specific scaffold like a U-shaped structure, to promote anion binding through amine NH moieties. Realizing the need to remove chromate anions due to their high toxicity to human health and environment, herein we have designed and synthesized two new isophthalamide derivatives namely *N,N'*-1,3-*bis*(4-methylpyridin-2-yl)isophthalamide and *N,N'*-1,3-*bis*(5-methylpyridin-2-yl)isophthalamide as potential anion receptors candidate (Figure 1).

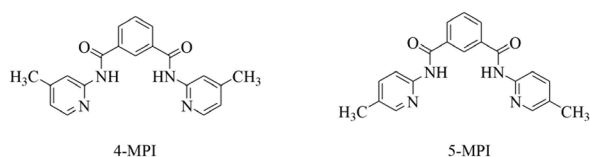


FIGURE 1. Molecular structure of 4-MPI and 5-MPI

By having the inward pointed N-H fragments such as amine as the binding site, an *in situ* anion's pocket will naturally acts as anion binding host, through hydrogen bonding as shown in Figure 2.

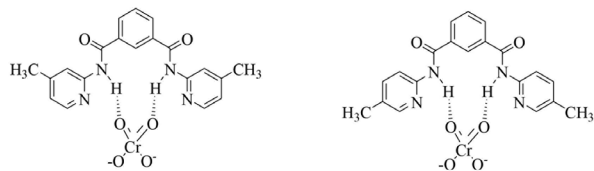


FIGURE 2. Expected hydrogen bond interactions between 4-MPI and 5-MPI with chromate anions (CrO_4^{2-})

This paper describes in details the structure elucidation of two new synthesized isophthalamide compounds from various spectroscopic methods, along with the chemistry of isomeric effects that cause from methyl at meta and para positions. As a final approach, a preliminary anion binding is used to identify their potential as anion receptors, before further anion recognition investigation is carried out in future.

MATERIALS AND METHODS

NMR spectra of ^1H and ^{13}C NMR were recorded using Bruker Advance III 400 spectrometer with deuterated dimethylsulfoxide (DMSO-d_6) as solvent. Melting points were measured using Melting Point Stuart SMP3 while CHNS elemental analyses were recorded by CHNS Flashes 1112 series. Infrared spectra were collected on a Perkin Elmer Spectrum BX Infrared spectrometer as KBr disks.

Electrospray (ES) mass spectra were recorded using a Finnigan LCQ mass spectrometer by preparing serial dilutions of a 1 mg/mL solution of the compound. For UV-Vis analysis, all compounds were recorded by using Spectrophotometer Shimadzu UV-1601PC in 1 cm^3 cuvette in methanolic solution for absorbance analysis. All chemicals were used without further purification.

PREPARATION OF *N,N'*-1,3-*bis*(4-METHYLPYRIDIN-2-YL) ISOPHTHALAMIDE (4-MPI)

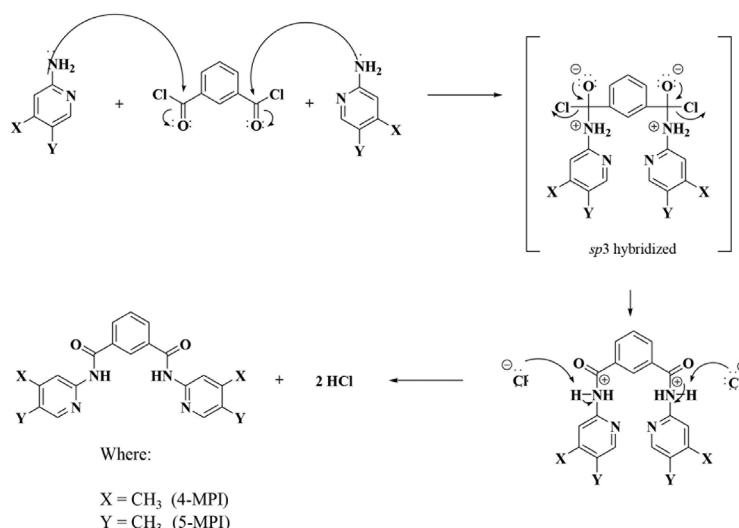
Isophthaloyl chloride (2.03 g, 10.1 mmol) was dissolved in dichloromethane (100 mL). 2-amino-4-methylpyridine (2.1 mL 20.6 mmol) and trimethylamine was added slowly and the resulting solution was stirred for 48 h to give diamide as a white solid. Thin layer chromatography (TLC) technique was used to monitor the reaction till completion. After the reflux process was completed, the solvent (dichloromethane) was removed by using rotary evaporator (111°C at 77 mbar). The residue obtained after rotary evaporation was triturated with 10 mL of hot ethyl acetate for three times to produce pale yellow solid (0.6759 g, 83.95%). The residue was collected through filtration and let dried in silica gel. The melting point obtained was 200°C.

PREPARATION OF *N,N'*-1,3-*bis*(5-METHYLPYRIDIN-2-YL) ISOPHTHALAMIDE (5-MPI)

Isophthaloyl chloride (2.03 g, 10.1 mmol) was dissolved in dichloromethane (100 mL). 2-amino-5-methylpyridine (2.1 mL, 20.6 mmol) and trimethylamine was added slowly and the resulting solution was stirred for 48 h to give diamide as a white solid. Thin layer chromatography (TLC) technique was used to monitor the reaction till completion. After the reflux process was completed, the solvent (dichloromethane) was removed by using rotary evaporator (111°C at 77 mbar). The residue obtained after rotary evaporation was triturated with 10 mL of hot ethyl acetate for three times to produce pale yellow solid (0.7680 g, 65 %). The residue was collected through filtration and let dried in silica gel. The melting point obtained was 205°C.

RESULTS AND DISCUSSION

In this study, two types of isophthalamide isomers namely *N,N'*-1,3-*bis*(4-methylpyridin-2-yl)isophthalamide (4-MPI) and *N,N'*-1,3-*bis*(5-methylpyridin-2-yl)isophthalamide (5-MPI) were synthesized using acyl chloride method. One mol of isophthaloyl chloride was dissolved in dry dichloromethane before being charged with two mol of substituted aminopyridine. Trimethylamine was added to increase the basicity of the reaction and continued to reflux for several hours until completion and gave product as white solids. The mechanism of formation is illustrated in Scheme 1. The reaction started with the nucleophilic attack from nitrogen atom on aminomethylpyridine towards the electrophilic carbon carbonyl of isophthaloyl chloride



SCHEME 1. Mechanism formation of 4-MPI and 5-MPI

to form sp^3 hybridized intermediate. This intermediate consists of electronegative chlorine atom which is well known as a good leaving group. As the lone pair on oxygen atom reforms the π bond, this has led to the removal of chlorine atom. The forming compound is not yet stable as nitrogen of amide has one extra bond, makes it positively charge. The previously removed chlorine atom then abstracts the proton from amide group to finally stabilize the compound and afforded the products as 4-MPI and 5-MPI, respectively.

Compounds 4-MPI and 5-MPI were obtained as pale white solids with melting points of 200°C and 205°C, respectively. According to Katrizky et al. (1997), amino-substituted benzaldehyde and methoxy-substituted acetanilide displayed different melting points based on the attachment of substituents at the ortho-, meta- and para-positions. To note, these two compounds exhibited higher values of melting points when the substituents were placed in the para- position compared to meta- position. This is probably due to the effect of amino and methoxy groups which were known as electron donating substituents. These results were in accordance with the one we obtained in our previous study (Kadir et al. 2017), where compound 5-MPI with methyl group placed in para- position outnumbered the melting point of compound 4-MPI by 5°C.

Among the factors that influence the melting points are the position isomerism of the substituent and also the type of substituent itself, whether it belongs to electron donating group or electron withdrawing group. To elaborate on the positional isomerism, Rao and Sunkada (2007) have stated that in term of disubstituted benzene derivatives, the melting points of symmetrical para- isomers were found higher than those of ortho- and meta- isomers compounds. Being more symmetrical in structure will add more values in the melting point readings. Besides, they added that the geometry of a compound also played an important role in affecting the melting point reading. Steric crowding produced due to the effect of molecular geometry of a

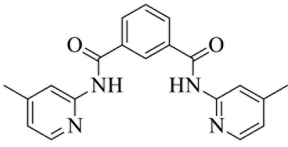
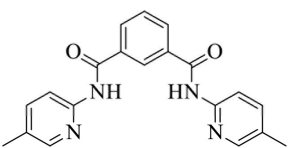
compound will causes the packing coefficient in crystals to decrease, which finally results in the decrease of melting point too. To relate these findings with our study, compound 4-MPI with the methyl group substituted at meta- position was affected more by steric crowding, hence causing it to end up with a slightly lower melting point than compound 5-MPI. The molecular structures and physical properties of the synthesized compounds are shown in Table 1.

INFRA-RED SPECTROSCOPIC ANALYSIS

Four main absorption bands, which are $\nu(\text{N-H})$, $\nu(\text{C-H})$, $\nu(\text{C=O})$ and $\delta(\text{N-H})$ were determined from the FT-IR spectra of the synthesized compounds. An example of infra-red spectrum for compound 4-MPI is given in Figure 3. Based on the spectrum, $\nu(\text{N-H})$ was observed at wavenumber 3274 cm^{-1} (Ameram & Yamin 2013). Medium intensity absorption band represented by $\nu(\text{C-H})$ was determined at 2812 cm^{-1} . Meanwhile, a strong intensity absorption band was observed at 1686 cm^{-1} , which proven the existence of carbonyl group in the synthesized compound (Zhao et al. 2013). The signal for $\nu(\text{C=O})$ has shifted to a slightly lower wavenumber from the normal stretching value at around $\sim 1700 \text{ cm}^{-1}$, which may be due to the formation of intramolecular hydrogen bonding which occurred at pendant pyridyl group and between both of the amide NH moieties (Sunkari et al. 2015). Besides, Kurt and Mercimek, (2009) and Yusof et al. (2010) reached unanimity as they agreed that resonance effect with benzene ring and intramolecular hydrogen bonding formation with amide group may have been responsible for the lower wavenumber recorded. On the other hand, the $\delta(\text{N-H})$ was assigned to the strong intensity band appeared at 1537 cm^{-1} .

The IR spectrum obtained for compound 5-MPI closely resembles the one of 4-MPI in term of the absorption pattern. However, the wavenumbers recorded for $\nu(\text{N-H})$ and $\nu(\text{C=O})$ of both compounds showed notable difference

TABLE 1. Molecular structures, elemental results and physical properties of the synthesized compounds

Compound	Molecular structure	Physical appearance & Yield (%)	CHN (%) Calculated (experimental)
4-MPI	 N,N' -1,3-bis(4-methylpyridin-2-yl)isophthalamide	Pale yellow solid (83.95 %)	C:69.35 (68.21) H: 5.24 (5.29) N:16.17 (17.02)
5-MPI	 N,N' -1,3-bis(5-methylpyridin-2-yl)isophthalamide	Pale yellow solid (65.0 %)	C:69.35 (69.11) H: 5.24 (5.26) N:16.17 (15.99)

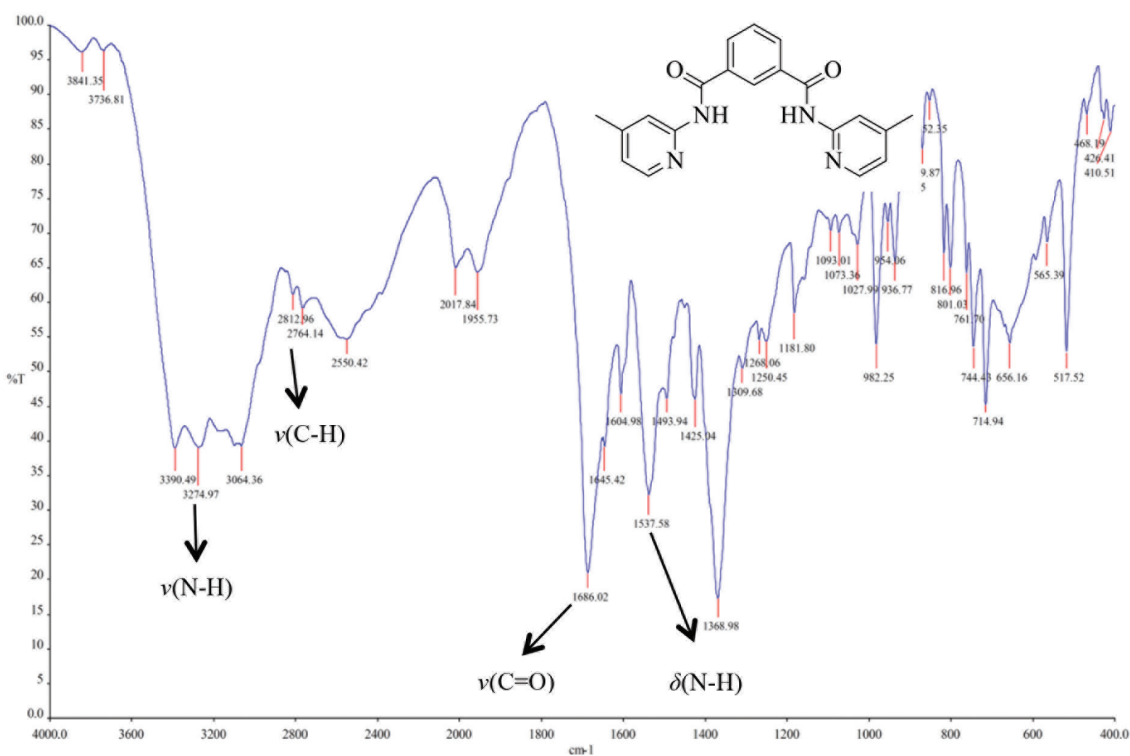


FIGURE 3. The infrared spectrum of 4-MPI

in values. Compound 5-MPI recorded the appearance of amide stretching at 3256 cm^{-1} which was 18 cm^{-1} lesser from the wavenumber of 4-MPI (3274 cm^{-1}). On the other hand, the carbonyl stretching for 5-MPI appeared in strong intensity at 1662 cm^{-1} . However, the wavenumber was also a bit lower when compared to the wavenumber of 4-MPI, with a value difference of 24 cm^{-1} . Hereby, understanding

the role played by methyl substituent is crucial in order to resolve the issue. Methyl group has a role as electron donating substituent. Based on Pavia et al. (2015), resonance effect exerted by methyl group can conjugated with phenyl ring and carbonyl group. This will results in increasing of the single bond character of carbonyl group, which finally led to the lower wavenumber obtained.

In this present study, it was shown that wavenumbers of the amide stretching and carbonyl stretching for compound 4-MPI were found higher in comparison to the values recorded for compound 5-MPI. We believe that combination of resonance effect and also steric effect might have contributed to such results. As compound 5-MPI consisted of para- substituted methyl substituent, it experienced weaker steric effect than compound 4-MPI (meta- substituted methyl substituent) which in turn resulted in much lower wavenumber recorded. Steric effect certainly has direct correlation with positional isomerism, which deals with different attachment of methyl group. Therefore, the changes in positional isomerism will also determine the degree of steric effect and will eventually influencing the wavenumber of each compounds. The FT-IR spectral data of both the 4-MPI and 5-MPI are presented in Table 2.

¹H AND ¹³C NMR SPECTROSCOPIC ANALYSIS

¹H NMR spectra of compounds 4-MPI and 5-MPI were recorded in DMSO-*d*₆ with the solvent resonance appeared at approximately ~2.5 ppm. Figure 4 shows the ¹H NMR spectrum of 4-MPI as the reference in this section.

The methyl proton signals of 4-MPI and 5-MPI were observed at slightly downfield from the normal values at δ_{H} 2.983 ppm and 2.994 ppm, respectively. Theoretically, the methyl group donates electron to the pyridine ring which activating the pyridine ring. At the same time, this has causes the methyl protons to

be left with lesser electron density and resulted in the shifted to the downfield at ~2.9 ppm. Interestingly, the two methyl protons showed different peak splitting. As the methyl protons of compound 4-MPI were not affected by the adjacent protons, thus, it appeared as a singlet. Meanwhile, methyl protons of 5-MPI showed triplet splitting. This is interpreted as the result of the three methyl protons being all equivalent and led to the coupling with the two protons attached to the adjacent carbon.

The aromatic proton resonances (combination of phenyl and pyridine protons) of both compounds were believed to be deshielded by the diamagnetic anisotropy of the ring and caused a great shift in values at around δ_{H} 6.860-8.974 ppm, respectively (Yalçın et al. 2015). The N-H proton signals were observed as a singlet resonance appeared at the downfield region at δ_{H} 10.138 ppm (4-MPI) and 11.300 ppm (5-MPI). The shifted might has been affected by the electron-withdrawing effect of the electronegative nitrogen in the pyridine ring (Barakat et al. 2015). To highlight, amide proton resonance of 5-MPI was seen at much higher frequency region as compared to the one of 4-MPI due to the attachment of methyl group at the para- position which has triggered lesser steric effect towards amino proton (Movassaghi & Hill 2006). The overall ¹H NMR data are given in Table 3.

The ¹³C NMR spectra of the synthesized compounds showed the presence of all important signals at the expected chemical shift. Figure 5 displays the ¹³C NMR spectrum for compound 4-MPI.

TABLE 2. IR data of 4-MPI and 5-MPI

Compound	$\nu(\text{N-H})$, cm^{-1}	$\nu(\text{C-H})$, cm^{-1}	$\nu(\text{C=O})$, cm^{-1}	$\delta(\text{N-H})$, cm^{-1}
4-MPI	3274 (m)	2812 (m)	1686 (s)	1537 (s)
5-MPI	3256 (m)	2928 (m)	1662 (s)	1533 (s)

*s = strong intensity, m = medium intensity

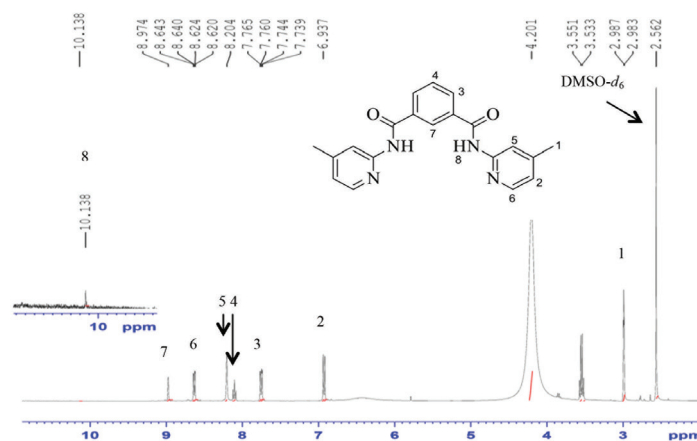
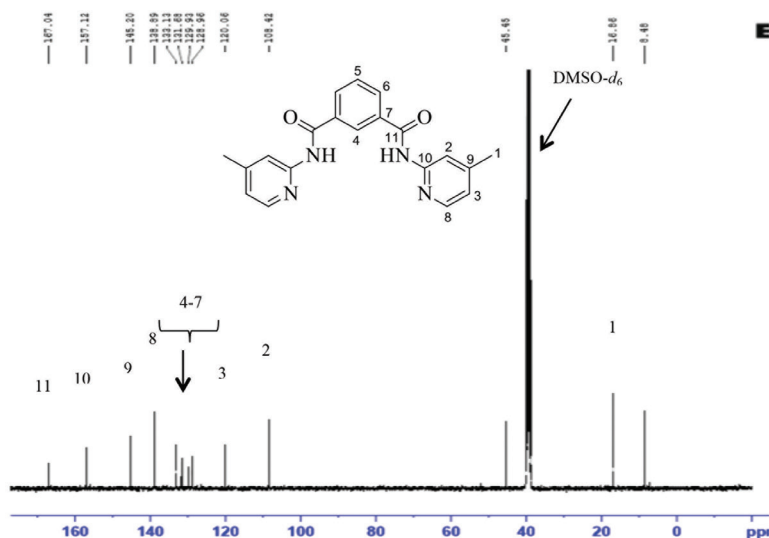


FIGURE 4. The ¹H NMR spectrum of compound 4-MPI

TABLE 3. The ^1H NMR data of 4-MPI and 5-MPI

Proton	4-MPI δ_{H} , ppm	5-MPI δ_{H} , ppm
DMSO- d_6	2.562	2.560
H1 (CH_3)	2.983 (s)	2.994 (t)
H2 (CH)	6.937 (d)	6.860 (d)
H3 (CH)	7.739 (d)	7.679 (d)
H4(CH)	8.101 (t)	8.010 (t)
H5 (CH)	8.204 (s)	8.203 (s)
H6 (CH)	8.620 (d)	8.534 (d)
H7 (CH)	8.974 (s)	8.965 (s)
H8 (NH)	10.138 (s)	11.300 (s)

*s = singlet, d = doublet, t = triplet

FIGURE 5. The ^{13}C NMR spectrum of compound 4-MPI

Based on the results obtained, the methyl resonances for 4-MPI and 5-MPI were found at upfield region at δ_{C} 18.45 ppm and 20.59 ppm, respectively (Adam et al. 2016; Kadir et al. 2017; Rabiatur et al. 2011). The resonance signals for aromatic carbons for both compounds were indicated at δ_{C} 108.42-159.22 ppm. The presence of carbonyl group, amide group and as well as nitrogen atom in the pyridine moieties have caused the aromatic carbons signals to be slightly shifted to the downfield. Meanwhile, the signals for C=O resonance were found mostly deshielded compared to the other resonances observed at δ_{C} 167.04 (4-MPI) and 167.20 ppm (5-MPI), respectively (Hassan et al. 2015; Shoaib et al. 2014). The carbonyl carbons were assigned at the low field due to the electronegativity effect of oxygen atom from C=O group. The results showed that compounds 4-MPI and 5-MPI portrayed similar data as reported by previous studies (Kadir et al. 2017; Schmuck & Machon 2005; Sumbly & Hanton 2009). The ^{13}C NMR data for the synthesized compounds are shown in Table 4. Further confirmation by mass spectrometry also agreed with the formation of protonated symmetrical compounds appeared in low abundance at m/z 347.15, respectively.

ULTRAVIOLET-VISIBLE SPECTROSCOPY

Ultraviolet-Visible analysis is used to observe the electronic transitions of the compound based on the absorbance values. The electronic absorption spectra were recorded in methanol ($1 \times 10^{-5}\text{M}$) with cut-off point of 205 nm. On the other hand, by using UV-vis spectra, the presence of chromophore groups such as carbonyl (C=O) and pyridine groups can be detected.

The UV-Vis spectrum of the synthesized ligands is shown in Figure 6. From the spectrum, it shows that the C=O group of ligand 4-MPI undergoes $n \rightarrow \pi^*$ transition at λ_{max} 240 nm and the pyridine group undergoes $\pi \rightarrow \pi^*$ at λ_{max} 270 nm. While the molar absorptivity for C=O and pyridine groups were found for $48000 \text{ cm}^{-1} \text{ M}^{-1}$ and $20000 \text{ cm}^{-1} \text{ M}^{-1}$. The UV-Vis spectroscopy analyses for 5-MPI, two main absorption peaks representing carbonyl and pyridine had also been observed at λ_{max} 256 nm and 278 nm, each represents $n \rightarrow \pi^*$ transition and $\pi \rightarrow \pi^*$ transition. The molar absorptivity $47000 \text{ cm}^{-1} \text{ M}^{-1}$ and $60000 \text{ cm}^{-1} \text{ M}^{-1}$ is higher. The electron transition in pyridine was caused by electrons transfer from the benzene ring π -system to the C=O group. The data obtained is depicted in Table 5.

TABLE 4. The ^{13}C NMR data of 4-MPI and 5-MPI

Carbon	4-MPI δ_{C} , ppm	5-MPI δ_{C} , ppm
C1 (CH_3)	18.45	20.59
C2 (C aromatic)	108.42	108.44
C3 (C aromatic)	120.06	113.40
C4 (C aromatic)	128.95	128.87
C5 (C aromatic)	129.93	129.94
C6 (C aromatic)	131.58	132.00
C7 (C aromatic)	133.13	133.03
C8 (C aromatic)	138.89	145.95
C9 (C aromatic)	145.20	148.11
C10 (C aromatic)	157.12	159.22
C11 (C=O)	167.04	167.20

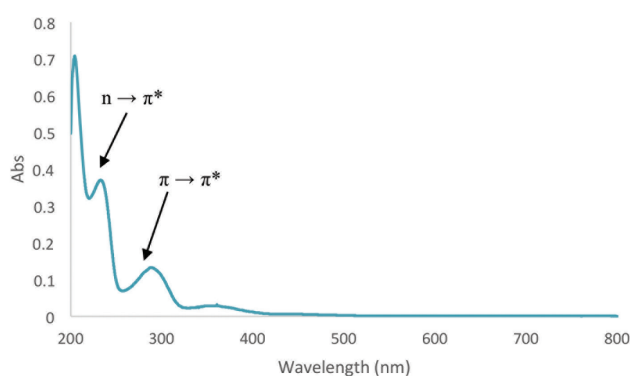


FIGURE 6. UV-Vis spectrum of 4-MPI

From the data obtained for both ligands, it can be concluded that 5-MPI have higher molar absorptivity value than 4-MPI.

PRELIMINARY ANION BINDING STUDIES

The investigation for anion binding study was done following the literature procedure by Shi et al. (2012) and Shao et al. (2009). These study were conducted by using chromate anion which representing tetrahedral geometries such as phosphate and perchlorate anion species. The time interval study was conducted by combining 4-MPI and 5-MPI with chromate anion with concentration 2.5×10^{-5} M and analyzed every half and hour for three hours. The study shows that the absorbance of the 4-MPI at 205.5 nm increased when the receptor is exposed to the chromate (analyte) much longer. Complex 4-MPI-Chromate shows the increasing of binding ability as the time extended from 0 to 3 h. In stark

contrast to that, the absorbance of chromate (at 215 nm) is reduced from 0.403 to 0.350 showing the decreased in concentration of chromate in solution, as expected. This type of result was also observed in 5-MPI analysis, in similar to the finding reported by Shi et al. (2012) in their anion binding study. As conclusion, 4-MPI and 5-MPI have good responses towards chromate anions as receptors molecule (Figures 7 & 8).

CONCLUSION

Structure of N,N' -1,3-bis(4-methylpyridin-2-yl)isophthalamide (4-MPI) and N,N' -1,3-bis(5-methylpyridin-2-yl)isophthalamide (5-MPI) have been successfully elucidated by typical spectroscopic techniques such Fourier Transform Infrared (FT-IR) and Nuclear Magnetic Resonance (NMR). There were notable difference in the

TABLE 5. The UV-Vis data of 4-MPI and 5-MPI

Compounds	Chromophores	Transition	λ_{max} (nm)	ϵ , $\text{cm}^{-1} \text{M}^{-1}$
4-MPI	C=O	$n \rightarrow \pi^*$	240	48000
	Pyridine	$\pi \rightarrow \pi^*$	270	20000
5-MPI	C=O	$n \rightarrow \pi^*$	256	47000
	Pyridine	$\pi \rightarrow \pi^*$	278	60000

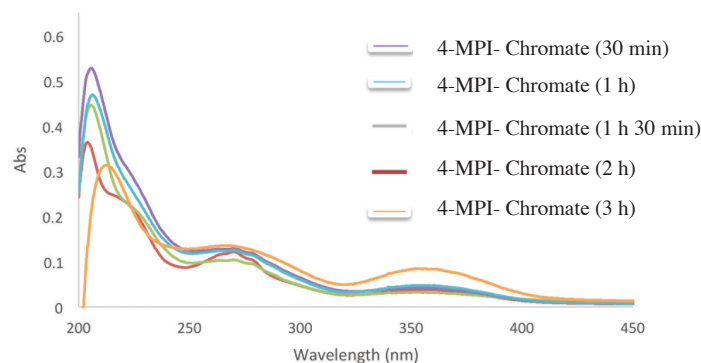


FIGURE 7. UV-Visible spectra of 4-MPI-Chromate from time interval study

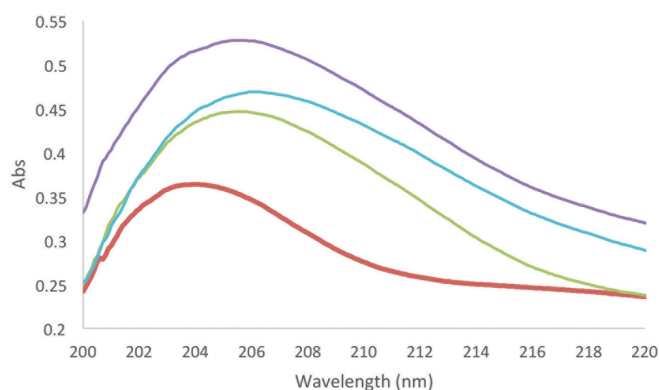


FIGURE 8. Enlargement of 4-MP I-Chromate UV-Vis spectra at range 200-220 nm

melting point readings, FTIR wavenumbers and NMR chemical shifts obtained for compounds 4-MPI and 5-MPI. Such differences was mainly contributed by the different attachment of methyl substituent at the pyridine ring that has led to the resonance effect, steric effect and formation of intramolecular hydrogen bonding. Preliminary binding studies using UV-Vis spectroscopy shows promising potential for 4-MPI and 5-MPI to be used as reseptor for chromate anions. However, futher investigation involving kinetic studies is needed to complete this study in future.

ACKNOWLEDGEMENTS

The authors greatly acknowledge the scientific and financial support from University Malaysia Terengganu through Talent and Publication-Enhancement Research Grant (TAPE), vote number 55128.

REFERENCES

- Adam, F., Fatihah, N.N., Ameram, N., Subramaniam, S. & Mubarrakh, S.A. 2016. The synthesis and characterisation of 2-methyl-N-((4-methylpyridine-2-yl) carbamothiol) benzamide: Its preparation with antibacterial study. *Journal of Physical Science* 27(2): 83-101.
- Ameram, N. & Yamin, B.M. 2013. Synthesis and characterization o-, m-and para-toluyl thiourea substituted para-pyridine and ethyl pyridine as a chromoionophore. *IOSR Journal of Applied Chemistry* 4(6): 59-67.
- Barakat, A., Al-Najjar, H.J., Al-Majid, A.M., Soliman, S.M., Mabkhot, Y.N., Ghabbour, H.A. & Fun, H.K. 2015. Synthesis and molecular characterization of 5,5'-((2,4-dichlorophenyl) methylene)bis(1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione). *Journal of Molecular Structure* 1084: 207-215.
- Bezerra, B.G.P., Parodia, A., da Silva, D.R. & Pergher, S.B.C. 2019. Cleaning produced water: A study of cation and anion removal using different adsorbents. *Journal of Environmental Chemical Engineering* 7(2): 103006.
- Cametti, M. & Rissanen K. 2013. Highlights on contemporary recognition and sensing of fluoride anion in solution and in the solid state. *Chemical Society Review*. 42: 2016-2038.
- Cametti, M. & Rissanen, K. 2009. Recognition and sensing of fluoride. *Chemical Communication* 20: 2809-2829.
- Dong, Z.Y., Yang, Y., Zhang, L.F., Xue, Y.R., Feng, M.Y. & Gao, G.H. 2012. Ionic liquids containing the urea moiety for recognition of halides and complex anions. *Chinese Science Bulletin* 57: 473-478.
- Gale, P.A. 2000. Anion coordination and anion-directed assembly: Highlights from 1997 and 1998. *Coordination Chemistry Reviews* 199: 181-233.
- Gao, Q., Xu, J. & Bu, X.H. 2018. Recent advances about metal-organic frameworks in the removal of pollutants from wastewater. *Coordination Chemistry Reviews* 378: 17-31.
- Hassan, I.N., Rahim, F., Hanifah, S.A., Tarawneh, M.A. & Yamin, B.M. 2015. Synthesis, characterization, spectroscopic and X-ray diffraction studies of novel pair of thiourea derivatives of 2-morpholine-4-yl-ethylamine. *Asian Journal of Chemistry* 27(10): 3711-3715.

- Hsu, L.C., Tzou, Y.M., Chiang, P.N., Fu, W.M., Wang, M.K., Teah, H.Y. & Liu, Y.T. 2019. Adsorption mechanisms of chromate and phosphate on hydrotalcite: A combination of macroscopic and spectroscopic studies. *Environmental Pollution* 247: 180-187.
- Kadir, M.A. & Sumbly, C.J. 2018. Synthesis, characterization and crystal structure of coordination polymers developed as anion receptor. *Solid State Phenomena* 273: 134-139.
- Kadir, M.A., Mansor, N. & Osman, U.M. 2017. Synthesis and structural characterization of 6-(*N*-methyl-pyridin-2-ylcarbonyl)-pyridine-2-carboxylic acid methyl ester isomers. *Sains Malaysiana* 46(5): 725-731.
- Kai, C.C., Shih, S.S., Maurice, O.O. & Alistair, J.L. 2015. Anion recognition and sensing by transition-metal complexes with polarized N-H recognition motifs. *Coordination Chemistry Reviews* 284: 111-123.
- Katritzky, A.R., Maran, U., Karelson, M. & Lobanov, V.S. 1997. Prediction of melting points for the substituted benzenes: A QSPR approach. *Journal of Chemical Information and Computer Sciences* 37(5): 913-919.
- Kurt, G. & Mercimek, B. 2009. Preparation of new benzoylthiourea-functionalized PVC resin and investigation on the complexation properties. *Journal of Inorganic and Organometallic Polymers and Materials* 19: 367-373.
- Lin, H., Cui, Z., Tian, Y., Wang, X. & Liu, G. 2018. Assembly, fluorescent and adsorption properties of two cadmium(ii)/cobalt(ii) coordination complexes functionalized by the flexible bis(pyridyl)-bis(amide) ligand. *Journal of Inorganic and Organometallic Polymers and Materials* 28: 1810.
- Movassaghi, M. & Hill, M.D. 2006. Single-step synthesis of pyrimidine derivatives. *Journal of the American Chemical Society* 128(44): 14254-14255.
- Pavia, D.L., Lampman, G.M., Kriz, G.S. & Vyvyan, J.R. 2015. *Introduction to Spectroscopy*. 5th ed. Washington: Cengage Learning Asia.
- Rabiatun, H.J., Wan, M.K., Mohd, S.M.Y., Maisara, A.K. & Bohari, M.Y. 2011. Structural and spectroscopic studies of novel methylbenzoyl thiourea derivatives. *Malaysian Journal of Analytical Sciences* 15(1): 70-80.
- Ranjan, D. & Pradyut, G. 2014. Recent developments in anion induced capsular self-assemblies. *Chemical Communication* 50: 10538-10554.
- Rao, S.P. & Sunkada, S. 2007. Making sense of boiling points and melting points. *Resonance* 12(6): 43-57.
- Schmuck, C. & Machon, U. 2005. Amino acid binding by 2-(guanidiniocarbonyl) pyridines in aqueous solvents: A comparative binding study correlating complex stability with stereoelectronic factors. *Chemistry-A European Journal* 11(4): 1109-1118.
- Shi et al. (2012) and Shao et al. (2009) – author, kindly assist to provide full details. Thank you.
- Shoaib, M., Shafiullah, Ul-Bari, A., Tahir, M.N. & Shah, S.W.A. 2014. Acute toxicity, brine shrimp cytotoxic, antioxidant and analgesic activities of synthesized 1-benzoyl-3-methyl thiourea. *Pharmacology Online* 3: 91-99.
- Sumbly, C.J. & Hanton, L.R. 2009. Syntheses and studies of flexible amide ligands: A toolkit for studying metallo-supramolecular assemblies for anion binding. *Tetrahedron* 65(24): 4681-4691.
- Sunkari, J., Kundha, S., Gundapaneni, R.R., Reddy, A., Pola, S., Kodumuru, S. & Sreedasyam, J.S. 2015. Supramolecular interactions between a diamine-diamide ligand and anions, trigonal planar NO³⁻ and spherical Cl⁻: Multiple hydrogen bond cooperativity through water molecules. *Indian Journal of Chemistry* 54(A): 596-606.
- Yalçın, Ş.P., Ceylan, Ü., Sarioğlu, A.O., Sönmez, M. & Aygün, M. 2015. Synthesis, structural, spectral (FT-IR, ¹H and ¹³C NMR and UV-Vis), NBO and first order hyperpolarizability analysis of *N*-(4-nitrophenyl)-2,2-dibenzoylacetamide by density functional theory. *Journal of Molecular Structure* 1098: 400-407.
- Yusof, M.S.M., Jusoh, R.H., Khairul, W.M. & Yamin, B.M. 2010. Synthesis and characterisation of *N*-(3,4-dichlorophenyl)-*N'*-(2,3 and 4-methylbenzoyl)thiourea derivatives. *Journal of Molecular Structure* 975: 280-284.
- Zhao, M.M., Dong, X.Y., Li, G., Yang, Y.H., Zhang, Y.J. & Yang, X.Q. 2013. Antituberculosis and antifungal activities of synthesized benzoylthiourea derivatives. *Asian Journal of Chemistry* 25(13): 7548-7550.
- Zhao, J., Yang, D., Yang, X.J. & Wu, B. 2018. Anion coordination chemistry: From recognition to supramolecular assembly. *Coordination Chemistry Reviews* 378: 415-444.

Maisara Abdul Kadir*, Syahirah Omar, Nur Shuhaila Haryani
Abd Haris & Ramizah Ramli
Faculty of Science and Marine Environment
Universiti Malaysia Terengganu
21030 Kuala Nerus, Terengganu Darul Iman
Malaysia

Maisara Abdul Kadir*
Advanced Nano Materials (ANoMa) Research Groups
Faculty of Science and Marine Environment
Universiti Malaysia Terengganu
21030 Kuala Nerus, Terengganu Darul Iman
Malaysia

*Corresponding author: maisara@umt.edu.my

Received: 15 December 2018

Accepted: 28 March 2019