SYNTHESIS AND STRUCTURE OF MIXED-METAL COMPLEX {Na ⊂ [$Fe_2(L)_3$]}(PF_6) DERIVED FROM FURAN-2,5-DICARBONYLBIS(*N*,*N*-DIETHYLTHIOUREA)

Received 10-05-2024

Lê Cảnh Định[1], Vũ Thị Bích Ngọc[2], Triệu Thị Nguyệt[2], Phạm Chiến Thắng[2]*

[1]Bộ môn Hóa học, Khoa Khoa học Tự nhiên, Trường Đại học Quy Nhơn

[2]Bộ môn Hóa học Vô cơ, Khoa Hóa học, Trường Đại học Khoa học Tự nhiên, ĐHQG Hà Nội

* Email: phamchienthang@hus.edu.vn

TÓM TẮT
TỔNG HỢP VÀ NGHIÊN CỨU CẤU TRÚC PHỨC CHẤT HỖN HỢP KIM LOẠI {Na ⊂ [$Fe_2(L)_3$]}(PF_6) TRÊN CƠ SỞ PHỐI TỬ FURAN-2,5-DICARBONYLBIS(*N*,*N*-DIETHYLTHIOUREA)

*Phối tử furan-2,5-dicarbonylbis(N,N-diethylthiourea) (**H_2L**) được tổng hợp từ phản ứng ngưng tụ giữa furan-2,5-dicarbonyl dichloride và N,N-diethylthiourea khi có mặt base hữu cơ Et_3N. Thành phần và đặc điểm cấu tạo của **H_2L** được nghiên cứu bằng các phương pháp phổ như IR, ^1H và $^{13}C\{^1H\}$ NMR. Phản ứng của **H_2L** với hỗn hợp $FeCl_3$ và KCl trong methanol tạo ra phức chất cation. Bằng cách xử lý hỗn hợp phản ứng với (n–Bu_4N)(PF_6), phức chất này kết tủa và tách ra ở dạng muối với anion PF_6^-. Dữ kiện phổ IR, phổ khối lượng và kết quả xác định cấu trúc bằng nhiễu xạ tia X đơn tinh thể chỉ ra sự hình thành phức chất ba nhân chứa đồng thời Fe^{3+} và Na^+ với thành phần {Na ⊂ [$Fe_2(L)_3$]}(PF_6). Phức chất này hình thành từ việc bắt giữ ion Na^+ trong lỗ trống phân tử của phức chất kiểu vòng lớn [$Fe_2(L)_3$] hình thành từ sự phối trí bát diện của ion Fe^{3+} với hợp phần thiourea của phối tử hữu cơ qua các bộ nguyên tử cho (S,O).*

Từ khóa: *aroylbis(thiourea), phức chất hỗn hợp kim loại, phức chất Fe(III)*

1. INTRODUCTION

After the pioneered work of Beyer *et al*. in 1970s [1], the coordination chemistry of aroyl(*N*,*N*-dialkyl thioureas) has manily focused on mononuclear complexes of benzoyl(*N*,*N*-dialkylthioureas) **HL^{ben}** [2-6], and binuclear complexes of the bipodal *iso*-phthaloylbis(*N*,*N*-dialkylthioureas) **H_2L^{iso}** [7-11]. In the coordination compounds structurally determined, the aroylthiourea moieties mainly act as monoanionic, bidentate *S*,*O*-chelators (Figure 1).

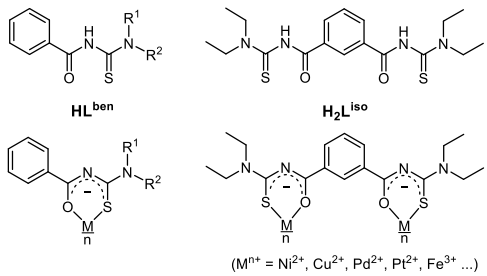


Figure 1. The classical aroyl(N,N-dialkylthioureas) and their major coordination fashions.

The modification of **H_2L^{iso}** by replacement of the phenylene ring by the other building blocks with additional potential atom(s) such as pyrinde in **H_2L^{py}** or catechol in **H_2L^{cat}** (Figure 2) has

led to a new generation of aroylbis(thiourea) with interesting coordination properties.

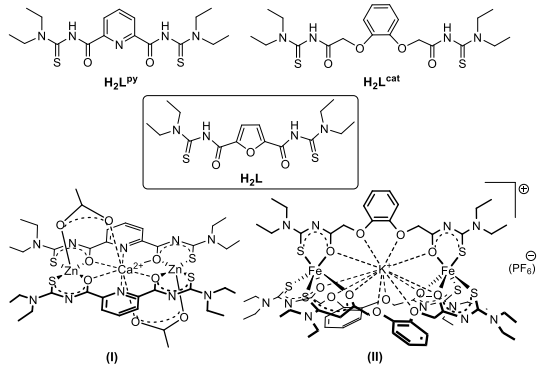


Figure 2. The novel aroylbis(N,N-diethylthioureas) and representative mixed-metal complexes.

In particular, the novel aroylbis(thioureas) are able to bond to metal ions with different Lewis acidity. A series of bimetallic complexes such as **I** and **II** (Figure 2) has been synthsized and characterized [12, 13]. The formation of such trinuclear systems could be considered as the encapsulation of "hard" and large metal ions in the central voids of the macrocycles comprised of the organic ligands and softer transition metal ions. In continuation of this research, herein we report the synthesis and characterization of a new aroylbis(*N*,*N*-diethylthioureas) **H_2L** (Figure 2) derived from furan-2,5-dicarboxylic acid and a mixed-metal complex generated from the self-assembly of such ligand and mixture of Fe^{3+} and Na^+ cations. The outcome of this research could be extened to another alkali metal ions. Furthermore, the corresponding products might have potential applications as cation exchangers due to the specific interactions between the guest cations and the donor atoms of the organic framework.

2. EXPERIMENT

2.1. Materials

All chemicals used in this study were reagent grade and used without further purification. Solvents were distilled before using.

2.2. Physical measurement

IR spectra were measured from KBr pellets on a IRAffinity-1S spectrometer between 400 and 4000 cm^{-1} at Department of Inorganic Chemistry, Faculty of Chemistry, VNU University of Science. NMR spectra were taken with an Ascend^{TM}-500MHz (Bruker) multinuclear spectrometer at Faculty of Chemistry, VNU University of Science. ESI mass spectrum was measured with a LQT Orbitrap XL mass spectrometer at Faculty of Chemistry, VNU University of Science.

2.3 Synthetic procedures

Synthesis of ***H_2L***: **H_2L** was prepared following the procedure reported by Dixon and Taylor with some modifications [14]. A mixture of furan-2,5-dicarboxylic acid (3.122 g, 0.02 mol), $SOCl_2$ (15 mL, 0.2 mol) and two drops of DMF was heated on reflux under a nitrogen atmosphere for 3 h. Subsequently, the residual $SOCl_2$ was removed under reduced pressure. The expected dichloride of the carboxylic acid obtained as an ivory solid was dissolved in dry THF (60 mL) and added dropwise at 0^{o}C (ice bath) to a mixture of *N*,*N*-diethylthiourea (5.28 g, 0.04 mol) and Et_3N (5.7 mL, 0.04 mol) in dry THF (30 mL) under a nitrogen atmosphere. The reaction mixture was warmed up to 45°C and stirred for 2 h. After cooling to room temperature, the colorless precipitate of $Et_3N{\cdot}HCl$ was filtered off and the solvent was removed under reduced pressure. The resulting solid was washed thoroughly with MeOH, which finally gave **H_2L** as a colorless solid. Yield: ~70% (5.383 g). IR (KBr, cm^{-1}): 3262 (m), 3090 (w), 2971 (w), 2932 (w), 2875 (w), 1693 (s), 1659 (s), 1594 (m), 1553 (s), 1519 (s), 1446 (s), 1426 (vs), 1292 (s), 1263 (s), 1218 (vs),

1143 (m), 1111 (s), 1016 (s), 916 (m), 841 (m), 750 (s), 695 (m), 669 (m), 602 (m). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 9.12 (s, 1H, NH); 7.21 (s, 1H, furan); 4.03 (br, q, J = 7.0 Hz, 2H, CH_2); 3.63 (br, q, J = 7.5 Hz, 2H, CH_2); 1.37 (t, J = 7.5 Hz, 3H, CH_3), 1.32 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): 177.8 (C=O); 153.1 (C=S); 147.6, 118.2 (furan); 47.9 (CH_2); 13.4, 11.4 (CH_3).

Synthesis of {Na ⊂ [Fe$_2$(L)$_3$]}(PF$_6$): **H$_2$L** (115 mg, 0.3 mmol) was added to mixture of $FeCl_3 \cdot 6H_2O$ (54.1 mg, 0.2 mmol) and NaCl (58.5 mg, 1.0 mmol) dissolved in few drops of water and 2 mL MeOH. The ligand dissolved quickly and the color of the solution changed immediately to dark. After the addition of 2 drops of Et_3N and stirring at room temperature in 30 min, (n–Bu_4N)(PF_6) (38.7 mg, 0.1 mmol) was added. The reaction mixture had been stirred at 40^{o}C in 2h. Then, the product appearing as a dark brown precipitate was filtered off, washed with MeOH and dried in vacuum. Single crystals for X–ray analysis were obtained by slow evaporation of solution of the complex in CH_2Cl_2/MeOH (2:1 v/v) mixture. Yield: ~75% (107 mg). IR (KBr, cm^{-1}): 2974 (w), 2936 (w), 2876 (w), 1539 (m), 1508 (m), 1408 (s), 1352 (m), 1260 (m), 1150 (w), 1103 (w), 1076 (w), 1011 (m), 972 (w), 843 (s), 758 (m), 669 (w), 557 (m). ESI^{+} MS (m/z): 1296.74 (calcd. 1297.17), 30% {K ⊂ [Fe$_2$(L)$_3$]}$^{+}$; 1280.60 (calcd. 1281.20), 100% {Na ⊂ [Fe$_2$(L)$_3$]}$^{+}$.

2.4. Crystalography

The intensities for the X-ray determinations of the complex were colected on a Bruker D8 QUEST instrument at 293 K with Mo Kα radiation (λ = 0.71073 Å) using a TRIUMPH monochromator. Standard procedures were applied for data reduction and absorption correction [15]. Structure solution and refinement were performed with the SHELXT and SHELXL 2014/7 programs included in the OLEX2-1.5 program package [16-18]. Hydrogen atoms were calculated for idealized positions and treated with the 'riding model' option of SHELXL. Crystal data and structure determination parameters for the complex are given in Table 1.

Table 1. Crystal data and structure refinement for {Na ⊂ [Fe$_2$(L)$_3$]}(PF$_6$) · 0.5 MeOH.

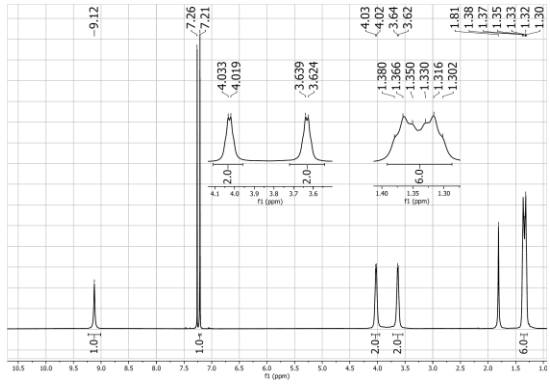
Formula	$C_{48.5}H_{68}O_{9.5}N_{12}S_6Fe_2NaPF_6$
Mw	1443.16
Crystal system	Triclinic
a/Å	14.700(2)
b/Å	15.013(2)
c/Å	17.171(2)
α/^{o}	92.62(2)
β/^{o}	104.720(10)
γ/^{o}	114.030(10)
V/Å^3	3299.4(8)
Space group	P–1
Z	2
D_{calc}/g cm^{-3}	1.453
μ/mm^{-1}	0.737
No. reflect.	86439
No. indep.	11347
R_{int}/R_{sigma}	0.1291/0.1231
No. param.	798
R_1/wR_2	0.0645/0.1121
GOF	1.004
Largest diff. peak/hole (e Å^{-3})	0.57/–0.59

3. RESULTS AND DISCUSSION

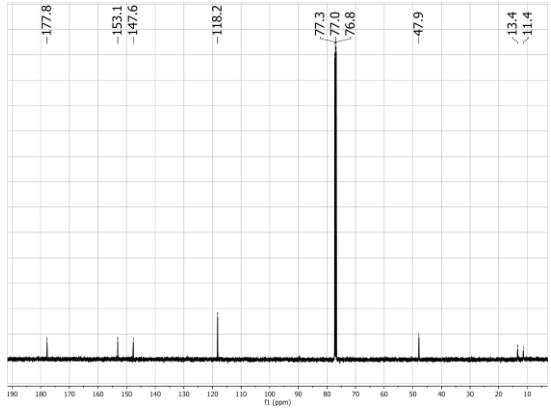
The ligand **H$_2$L** was prepared in good yield from the condensation reaction of furan-2,5-dicarbonyl dichloride and *N*,*N*-diethylthiourea in dry THF with the presence of supporting base Et_3N. Structural features of **H$_2$L** were studied

by spectroscopic methods such as IR, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The IR spectrum of **H_2L** is characterized by a absorption around 1695 cm^{-1} ascribed to the stretching vibration of C=O groups. The presence of NH groups is confirmed not only by the broad band above 3100 cm^{-1} in the IR spectrum but also by the broad signal at 9.12 ppm in the ^{1}H NMR spectrum in $CDCl_3$ (Figure 3a). The resonances of protons in the furan ring are observed as a singlet at 7.21 ppm, while those of aliphatic protons in the ethyl groups appear in upfield region. In particular, two broad quartets at 4.03 ppm and 3.63 ppm are assigned to methylene protons. Whereas, two partially overlapped triplets at 1.37 ppm and 1.31 ppm belong to methyl groups. Furthermore, two separated sets of signals for two ethyl groups demonstrate the hindered rotation around the C(S)–NEt_2 bond, which is well-known for aroyl-*N*,*N*-dialkylthioureas [10, 19-21]. Similar to ^{1}H NMR spectrum, the $^{13}C\{^{1}H\}$ NMR spectrum (Figure 3b) of **H_2L** also strongly support its expected structure. The resonance of CH_3 carbon atoms appears as two separated signals in the most upfield region at 11.3 and 11.4 ppm. The signal at 47.9 ppm corresponds to CH_2 carbon atoms, while the aromatic ones show resonances in the range of 110-150 ppm. The C=O and C=S groups give weak signals at 177.8 and 153.1 ppm, respectively.

Reaction between the ligand **H_2L** and mixture of $FeCl_3$ and NaCl in MeOH with the presence of a supporting base like Et_3N brings about an ionic complex, which could be precipitated by subsequent workup with (n–Bu_4N)(PF_6). Considering the structures of mixed-metal Fe(III)-alkali metal complexes derived from pyridine- and catechol-based aroylbis(thiourea) [12], the resulting complex would have expected composition of {Na ⊂ [$Fe_2(L)_3$]}(PF_6), which is strongly confirmed by X-ray diffraction analysis on the crystals obtained by slowly evaporating solution of the complex in CH_2Cl_2/MeOH. Molecular structure of the compound is introduced in Figure 4. Selected bond lengths and angles are shown in Table 2. X-ray crystallography reveals a trinuclear mixed-metal complex caused by the accommodation of the Na^+ ion in the central cavity of the metallacyclic compound [$Fe_2(L)_3$] consisted of two Fe^{3+} ions and three doubly deprotonated ligands $\{L\}^{2-}$. Each Fe^{3+} ion octahedrally bonds to three (*S*,*O*)-chelating aroylthiourea moieties with the facial arrangement of sulfur atoms.



(a)



(b)

Figure 3. (a) ^{1}H NMR and (b) $^{13}C\{^{1}H\}$ NMR spectra of H_2L in $CDCl_3$.

Table 2. Selected bond lengths (Å) in {Na ⊂ [Fe₂(L)₃]}(PF₆)·0.5MeOH.

Fe1–O10	2.059(4)	Fe2–O20	2.026(4)	Na–O10	2.763(5)
Fe1– O40	2.022(4)	Fe2– O50	1.990(4)	Na–O20	2.891(5)
Fe1–O70	1.994(4)	Fe2–O80	2.044(4)	Na–O40	2.615(5)
Fe1–S10	2.424(6)	Fe2–S20	2.412(7)	Na–O50	2.925(5)
Fe1– S40	2.416(4)	Fe2– S50	2.403(2)	Na–O70	3.125(5)
Fe1–S70	2.391(7)	Fe2–S80	2.394(4)	Na–O80	2.638(5)
Na–O1	2.656(5)	Na–O31	2.580(4)	Na–O61	2.565(4)
C10–O10	1.258(7)	C40–O40	1.287(7)	C70–O70	1.288(7)
C10–N10	1.325(7)	C40–N40	1.308(7)	C70–N70	1.303(7)
N10–C11	1.340(7)	N40–C41	1.350(7)	N70–C71	1.350(7)
C11–S10	1.739(6)	C41–S40	1.736(6)	C71–710	1.741(6)
C20–O20	1.267(7)	C50–O50	1.270(7)	C80–O80	1.272(6)
C20–N20	1.312(7)	C50–N50	1.308(7)	C80–N80	1.305(7)
N20–C21	1.350(7)	N50–C51	1.346(7)	N80–C81	1.342(7)
C21–S20	1.737(6)	C51–S50	1.731(6)	C81–S80	1.740(6)

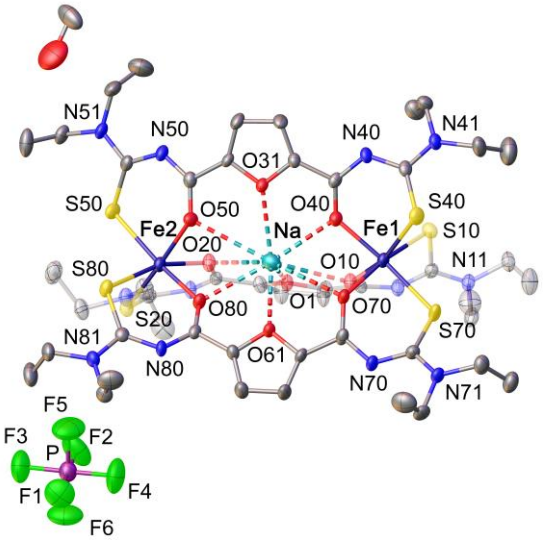


Figure 4. Molecular structure of {Na ⊂ [Fe₂(L)₃]}(PF₆)·0.5MeOH. Hydrogen atoms are omitted for clarity.

The Fe–O and Fe–S bond lengths (Table 2) are similar to those found in trinuclear mixed-metal iron(III) complexes with aroylbis(thioureas) [12, 22]. Adopting an axially truncated trigonal bipyramidal geometry, the Na^+ ion is nine-coordinate with six carbonyl oxygen donors and three furan oxygen donors forming the mutual base of the bipyramid. Such coordination envinroment was previously found in mixed-metal complexes based on 2,6-dipicolinoylbis(*N*,*N*-diethylthiourea) [12]. The partial double bond character of the C–O, C–N and C–S bonds points out the typical delocalization of π-electrons within chelating aroylthiourea moieties [21]. The preceding bonding situations of the complex are validated by experimental data obtained from mass spectrometry and IR spectroscopy.

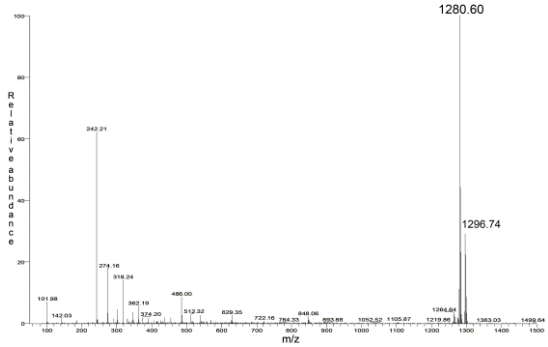


Figure 5. ESI⁺ mass spectrum of the complex.

The mass spectrum (Figure 5) with the based peak corresponding to the expected fragment $\{Na \subset [Fe_2(L)_3]\}^+$ obviously shows that the Na^+ ion is an integral part of the complex. It is interseting that the peak at *m*/*z* = 1296.74 is assigned to the $\{K \subset [Fe_2(L)_3]\}^+$ cation resulting from rapid exchange of the central Na^+ ion by K^+ ion present in the MS matrix. In the IR spectrum, the disappearance of absorptions above 3100 cm^{-1} ascribed to ν_{NH} implies the deprotonation of **H_2L** during complex formation and the presence of the deprotonated ligand $\{L\}^{2-}$ in composition of the complex. Compared to the uncoordinated ligand **H_2L**, the remarkable bathochromic shift (about 120 cm^{-1}) of

absorption assigned to $\nu_{C=O}$ in the complex (Table 3) reveals the formation of *S*,*O*-chelates with the typical extended π-systems. Moreover, the strong absorption band at about 843 cm^{-1} confirms the nature of the coordination compound as PF_6^- salt (Table 3).

*Table 3. Selected absorption bands (cm^{-1}) in IR spectra of **H_2L** and the complex {Na ⊂ $[Fe_2(L)_3]$}(PF_6).*

	ν_{NH}	ν_{CH}	ν_{CO}	ν_{PF}
H_2L	3262 (m, br)	2970 (w), 2932 (w)	1659 (s)	-
{Na⊂$[Fe_2(L)_3]$}(PF_6)	-	2974 (w), 2936 (w)	1539 (s)	843 (s)

4. CONCLUSION

A new benzoylbis(thioureas) derived from furan-2,5-dicarboxylic acid has been synthesized and examined for its potential for serving as a building block in construction of multinuclear coordination compounds. Self-assembled reaction of furan-2,5-dicarbonylbis(*N*,*N*-diethylthiourea), **H_2L**, with a mixture of Fe^{3+} and Na^+ ions brings about a novel mixed-metal complex. The supportive experimental data revealed a trinulcear bimetallic complex resulting from the encapsulation of the Na^+ cation in the central cavity of the macrocycle $[Fe_2(L)_3]$ arised from the facial octahedral coordination of Fe^{3+} ions and (*S*,*O*)-chelating thiourea moieties of the deprotonated ligands $\{L\}^{2-}$.

Acknowledgement: This research was funded by VNU Asia Research Center (ARC) from grants source by CHEY Institute for Advanced Studies, code CA.22.06A.

REFERENCES

[1] Beyer, L.; Hoyer, E.; Hennig, H.; Kirmse, R.; Hartmann, H.; Liebscher, J., (1975). Synthese und Charakterisierung neuartiger Übergangsmetallchelate von 1,1-Dialkyl-3-benzoyl-thioharnstoffen. *J. Prakt. Chem.*, **317(5)**, 829-839.

[2] Fitzl, G.; Beyer, L.; Sieler, J.; Richter, R.; Kaiser, J.; Hoyer, E., (1977). Kristall- und MolekülStruktur von Bis(1,1-diäthyl-3-benzoyl-thioureato)palladium(II). *Z. Anorg. Allg. Chem.*, **433(1)**, 237-241.

[3] Knuuttila, P.; Knuuttila, H.; Hennig, H.; Beyer, L., (1982). The Crystal and Molecular Structure of Bis(1,1-diethyl-3-benzoylthioureato)nickel(II). *Acta Chem. Scand.*, **36(A)**, 541-545.

[4] Bensch, W.; Schuster, M., (1992). Die Kristallstruktur von Tris(*N*,*N*-Diethyl-*N*′-benzoylthioureato) Rhodium(III). *Z. Anorg. Allg. Chem.*, **615(9)**, 93-96.

[5] Bensch, W.; Schuster, M., (1995). Crystal structure of tris(*N*, *N*-diethyl-*N*′-benzoylthioureato)cobalt(III), $Co(C_{12}H_{15}N_2OS)_3$. *Zeitschrift für Kristallographie - Crystalline Materials*, **210(1)**, 68-68.

[6] Pham, C. T.; Pham, T. T.; Nguyen, V. H.; Trieu, T. N.; Nguyen, H. H., (2021). Syntheses, Structures, and Bioactivity Evaluation of some Transition Metal Complexes with Aroylbis(N,N-diethylthioureas) Derived from Natural Compounds. **647(13)**, 1383-1391.

[7] Köhler, R.; Kirmse, R.; Richter, R.; Sieler, J.; Hoyer, E.; Beyer, L., (1986). Zweikernverbrückende Bis-*N*-acylthioharnstoffe–Liganden in Trimetallamacrocyclen und Chelatpolymeren. *Z. Anorg. Allg. Chem.*, **537(6)**, 133-144.

[8] Koch, K. R.; Hallale, O.; Bourne, S. A.; Miller, J.; Bacsa, J., (2001). Self-assembly of 2:2 metallomacrocyclic complexes of Ni^{II} and Pd^{II} with 3,3,3′,3′-tetraalkyl-1,1′-isophthaloylbis(thioureas). Crystal and molecular structures of cis-$[Pd(L^2\text{-}S,O)]_2$ and the adducts of the corresponding Ni^{II} complexes: $[Ni(L^1\text{-}S,O)(pyridine)_2]_2$ and $[Ni(L^1\text{-}S,O)(4\text{-dimethylaminopyridine})_2]_2$. *J. Mol. Struct.*, **561(1–3)**, 185-196.

[9] Rodenstein, A.; Griebel, J.; Richter, R.; Kirmse, R., (2008). Synthese, Struktur und EPR-Untersuchungen von binuklearen Bis(*N*,*N*,*N*‴,*N*‴-tetraisobutyl-*N*′,*N*″-isophthaloylbis(thioureato))-Komplexen des Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II} und Pd^{II}. *Z. Anorg. Allg. Chem.*, **634(5)**, 867-874.

[10] Nguyen, H. H.; Pham, C. T.; Rodenstein, A.; Kirmse, R.; Abram, U., (2011). Bipodal Acylthiourea Ligands as Building Blocks for Bi-, Tetra-, and Polynuclear Oxorhenium(V) Complexes. *Inorg. Chem.*, **50(2)**, 590-596.

[11] Selvakumaran, N.; Bhuvanesh, N. S. P.; Karvembu, R., (2014). Self-assembled Cu(II) and Ni(II) metallamacrocycles formed from 3,3,3',3'-tetrabenzyl-1,1'-aroylbis(thiourea) ligands: DNA and protein binding studies, and cytotoxicity of trinuclear complexes. *Dalton Trans.*, **43(43)**, 16395-16410.

[12] Chien Thang, P.; Hung Huy, N.; Hagenbach, A.; Abram, U., (2017). Iron(III) Metallacryptand and Metallacryptate Assemblies Derived from Aroylbis(*N*,*N*-diethylthioureas). *Inorg. Chem.*, **56**, 11406-11416.

[13] Le, C. D.; Pham, C. T.; Nguyen, H. H., (2019). Zinc(II) {2}-metallacoronates and {2}-metallacryptates based on dipicolinoylbis(*N*,*N*-diethylthiourea): Structures and biological activities. *Polyhedron*, **173**, 114143-114147.

[14] Dixon, A. E.; Taylor, J., (1908). III.-Acylogens and thiocarbamides. *J. Chem. Soc., Trans.*, **93**, 18-30.

[15] Bruker *APEX2*, 2014.

[16] Sheldrick, G., (2015). SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A*, **71(1)**, 3-8.

[17] Sheldrick, G., (2015). Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C*, **71(1)**, 3-8.

[18] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., (2009). OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.*, **42(2)**, 339-341.

[19] Koch, K. R., (2001). New chemistry with old ligands: *N*-alkyl- and *N*,*N*-dialkyl-*N*′-acyl(aroyl)thioureas in co-ordination, analytical and process chemistry of the platinum group metals. *Coord. Chem. Rev.*, **216–217**, 473-488.

[20] Schwade, V. D.; Kirsten, L.; Hagenbach, A.; Lang, E. S.; Abram, U., (2013). Indium(III), lead(II), gold(I) and copper(II) complexes with isophthaloylbis(thiourea) ligands. *Polyhedron*, **55**, 155-161.

[21] Nguyen, H. H.; Jegathesh, J. J.; Takiden, A.; Hauenstein, D.; Pham, C. T.; Le, C. D.; Abram, U., (2016). 2,6-Dipicolinoylbis(*N*,*N*-dialkylthioureas) as versatile building blocks for oligo- and polynuclear architectures. *Dalton Trans.*, **45(26)**, 10771-10779.

[22] Nguyen, H. H.; Abram, U.; Pham, C. T., (2022). Ammonium-Iron(III) metallacryptate inclusion complexes based on Aroylbis(N,N-diethylthioureas): Synthesis and structure. *Vietnam Journal of Chemistry*, **60(5)**, 622-628.