Hittite Journal of Science and Engineering, 2022, 9 (3) 183–191
ISSN NUMBER: 2148–4171
DOI: 10.17350/HJSE19030000270

Synthesis and Characterization of New Ferrocenyl and 3-methoxytolyl Dithiophosphonates

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Article History:
Received: 2022/07/04
Accepted: 2022/08/01
Online: 2022/09/28

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ABSTRACT

In this study, perthiophosphonic acid anhydrides which are previously synthesized (2,4-bis(3-methoxytolyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide ([((3-methoxytolyl)P(S)S)$_2$], SAV-B1 reagent and 2,4-bis(ferrocenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide [((ferrocenyl)P(S)S)$_2$], FcLR, Ferrocenyl Lawesson's Reagent) react with alcohols to obtain new dithiophosphonic acids (3-methoxytolyl=$(CH_3)(OCH_3)C_6H_3$- and Xn=Alkyl group (R) for SAV-B1, HXn; R1=3-pentyl-, HX1; R2=2-butyl-, HX2; R3=2-pentyl-, HX3 and Fc=Ferrocenyl- and Yn=Alkyl or aryl group (R') for FcLR, HYn; R'1=4-*tert*-cyclohexyl-, HY1; R'2=2-phenyl-1-propyl-, HY2). These products were later transformed into their ammonium salts ([NH_4][Xn], [NH_4][Yn]). The structures of ammonium salts were characterized by mass, FT-IR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy and elemental analysis.

Keywords:
Ferrocenyl dithiophosphonates; Dithiophosphonates; Dithiophosphonic acid; Dithiadiphosphetanes disulfides; Perthiophosphonic acid anhydrides.

INTRODUCTION

Perthiophosphonic Acid Anhydrides (PTPA) which are known as 1,3-dithia-2,4-diphosphetane 2,4-disulfides are an important starting material in the synthesis of Organo-dithiophosphorus compounds. Some of PTPA can be obtained in the laboratory, such as the Ferrocenyl-Lawesson reagent (FcLR) [1], as well as commercially available [2], such as the Lawesson reagent (LR). LR and FcLR are also among the PTFAs commonly used in the synthesis of Organo-dithiophosphorus compounds [3]. These compounds are suitable for use as additives in industry [4,5], agriculture [6], biochemistry [7] and metallurgy [8].

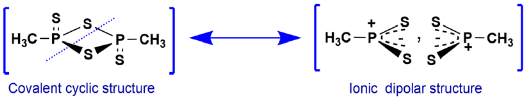

Figure 1. The proposed structures for 1,3-dithia-2,4-diphosphetane 2,4-disulfides.

Based on the ionic dipolar structure, the phosphorus atom has a partial positive charge. The attack of various types of nucleophiles to the electrophilic central phosphorus identifies the class of Organo-dithiophosphorus compound (Figure 2), [9]. If it is to be dithiophosphinic acid, a carbanion [10] as a nucleophile attacks the phosphorus atom. As a nucleophile, for example, an amine onset to the central atom, in this case, amidodithiophonic acid is formed. [11]. Conversely, if dithiophosphonic acids (DTPOA), the reaction of alcohol with PTPA should be preferred. [12].

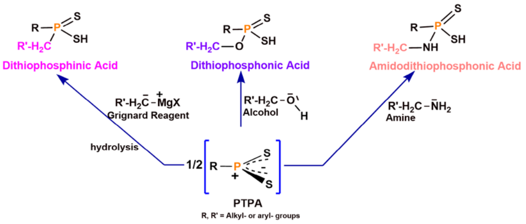

Figure 2. Synthesis reactions of various types of Organo-dithiophosphorus compounds.

DTPOAs bear two sulfur, one alkoxy and alkyl/aryl group that is attached to the phosphorus atom. They are malodorous and not stable, formed by the reaction of PTPA and alcohol. So, the crude acids are converted into odorless derivatives such as salts or complexes. Consequently, these derivatives are stable than the acids [13].

In this study, new dithiophosphonic acids (3-methoxytolyl= $(CH_3)(OCH_3)C_6H_3$- and Xn=alkyl- group, HXn; 3-pentyl-, HX1; 2-butyl-, HX2; 2-pentyl-, HX3 and Fc=Ferrocenyl- and Yn=alkyl- or aryl- group, HYn; 4-*tert*-cyclohexyl-, HY1; 2-phenyl-1-propyl-, HY2) were synthesized. These acids were obtained from direct reactions of two perthiophosphonic acid anhydrides which is previously known ((2,4-bis(3-methoxytolyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, $[((CH_3)C_6H_3(OCH_3)P(S)S)_2]$, SAV-B1, [14] and 2,4-bis(ferrocenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, $[((C_5H_4)P(S)S)_2]$, FcLR, Ferrocenyl Lawesson Reagent, [1]) with various aliphatic/aromatic alcohols. Crude DTPOAs were converted to their salts, namely ligands or dithiophosphonates ($[NH_4][Xn]$, $[NH_4][Yn]$) with ammonia gases in benzene media (Figure 3).

MATERIAL AND METHODS

Reagents

3-methoxytoluene, P_4S_{10}, benzene, 3-pentyl alcohol, 2-butyl alcohol, 2-pentyl alcohol, 2-phenyl-1-propyl alcohol and 4-*tert*-butylcyclohexyl alcohol were supplied from Sigma-Aldrich and ferrocene, xylene, n-hexane and diethyl ether were also supplied from Merck. FcLR [2] and SAV-B1 were synthesized by known procedure [14].

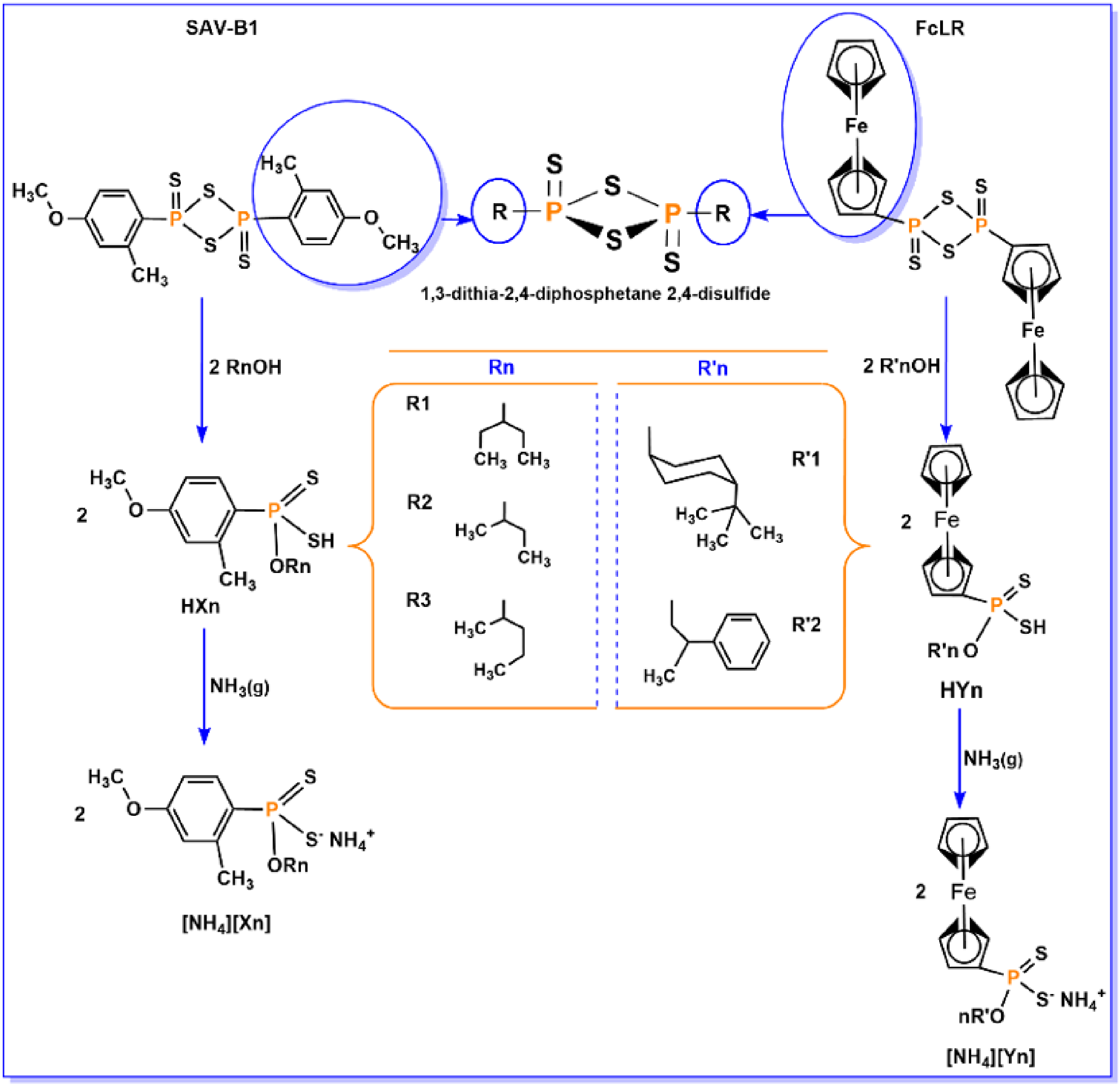

Figure 3. Synthesis reaction of the compounds.

The structural characterization of five alkyl/aryl ammonium dithiophosphonates were mass-(ESI) spectroscopy, FT-IR, ^1H-, ^{13}C- and ^{31}P-NMR spectroscopy as well as elucidated elemental analysis.

Instruments

Melting points (m.p.) of the compounds in BUCHI M-560 device; elemental analysis on LECO 932 CHNS-O

Elemental Analyzer; IR measurements on Perkin Elmer brand Spectrum Two FT-IR model device with ATR module (4000-400cm⁻¹); mass measurements LC/MS system in Waters supplied instrument with a C-18 HPLC column and a Waters Micromass ZQ connected to an ESI ionizer; NMR measurements (^{1}H-, ^{13}C-, ^{31}P-) on a Varian Mercury (Agilent) 400 MHz device were performed.

General Procedure for the ammonium dithiophosphonates, [NH₄][Ln]

2.3 mmol (1.00 g) of the SAV-B1 reagent was placed into with round bottom flask, and onto it, 4.6 mmol of one of the alcohols (0.41 g of 3-pentyl alcohol for HX1; 0.34 g of 2-butyl alcohol for HX2; 0.41 g of 2-pentyl alcohol for HX3) was added dropwise. Similarly, 1.78 mmol (1.00 g) of the FcLR was placed into with round bottom flask, and onto it, 4.6 mmol of one of the alcohols (0.55 g of 4-*tert*-cyclohexyl alcohol for HY1 and 0.48 g of 2-phenyl-1-propyl alcohol for HY2) was mixed dropwise. This mixture was heated until all dissolved (50-60°C) and then cooled to 0°C. The oily viscous product (HXn or HYn) was mixed with 50-60 mL benzene. Through the crude acidic solution, dry NH_3 gas was bubbled. After the salts were precipitated as an amorphous solid (a white for [NH₄][Xn] and white for [NH₄][Yn]) were filtered and purified by washing with benzene. The product is left to dry in a desiccator.

Ammonium O-3-pentyl (3-methoxytolyl)dithiophosphonate, [NH₄][X1]: Yield: 1.12 g (75%). White. m.p. 183°C. LC/MS, MS: m/z 305,6; $[M\text{-}NH_4]^+$; 18% , 235,18; $[M\text{-}(NH_4\text{+}(\text{-}CH(C_2H_5)_2]^+$; 100%. Anal. Calced. For: $C_{13}H_{24}NO_2PS_2$ (321.44 g.mol^{-1}): C, 48.58; H, 7.53; S, 19.95; found: C, 48.12; H, 7.09; S, 19.63 %.

Ammonium O-2-butyl (3-methoxytolyl) dithiophosphonate, [NH₄][X2]: Yield: 0.97 g (68%). White. m.p. 177°C. LC/MS, MS: m/z 289.7, ($[M\text{-}NH_4]^+$, 100%). Anal. Calcd. for: $C_{12}H_{20}NO_2PS_2$ (305.40 g.mol^{-1}): C, 47.20; H, 6.55; S, 21.00; found: C, 47.31; H, 6.62; S, 21.12 %.

Ammonium O-2-pentyl (3-methoxytolyl)dithiophosphonate, [NH₄][X3]: Yield: 1.05 g (70%). White. m.p. 175-176°C. LC/MS, MS (m/z): 303,8, ($[M\text{-}NH_4]^+$, 84%), 608,1, ($[2(M\text{-}NH_4)]^+$, 100%). Anal. Calcd.for: $C_{13}H_{24}NO_2PS_2$ (321.44 g.mol^{-1}): C, 48.58; H, 7.53; S, 19.95; found: C, 48.68; H, 7.64; S, 20.06 %.

Ammonium O-4-*tert*-butylcyclohexyl (ferrocenyl)dithiophosphonate, [NH₄][Y1]: Yield: 1.18 g (73%). Yellow. m.p. 170-172°C. LC/MS, MS: m/z 437,7; $[M\text{-}NH_4]^+$; 28%, 283,5; $[M\text{-}(NH_4\text{+}(\text{-}O(C_3H_5)_2(C_4H_9]^+$; 100%, 421,7; $[M\text{-}(NH_4\text{+}CH_3)]$; 100%. Anal. Calcd.for: $C_{20}H_{32}FeNOPS_2$ (453.42 g.mol^{-1}): C, 52.98 ; H, 7.11; S, 14,14; found: C, 53.06; H, 7,19; S, 14,21 %.

Ammonium O-2-phenyl-1-propyl (ferrocenyl) dithiophosphonate, [NH₄][Y2]: Yield: 1.11 g (72%). Yellow. m.p. 165-167°C. LC/MS, MS: m/z 416,8; $[M\text{-}NH_4]^+$; 100%. Anal. Calcd. for: $C_{19}H_{24}FeNOPS_2$ (433.35 g.mol^{-1}): C, 52.66; H, 5.58; S, 14,80; found: C, 52.72; H, 5.64; S, 14,89 %.

RESULTS AND DISCUSSION

Spectroscopic studies

IR spectra of the [NH₄[Xn] and [NH₄][Yn]

The IR data of the compounds are presented in Table 1.

The characteristic ν(N-H) stretching bands of the [NH₄][Xn] show up at 2926-2965 cm⁻¹; for [NH₄][Yn] appear 2880 cm⁻¹ and 2940 cm⁻¹ on IR. Symmetric and asymmetric phosphorus-sulfur stretching vibrations (ν(PS)sym and ν(PS)asym) are other important peaks. These peaks are shown up at 591-557 cm⁻¹ for ν(PS)sym and 720-652 cm⁻¹ ν(PS)asym of the compounds. Data on IR reported for similar compounds are consistent with our findings [15,16].

Table 1. Some of the characteristic IR bands (cm⁻¹) of the compounds.

Compound	$\nu_{N\text{-}H}$	$\nu_{(PS)sym}$	$\nu_{(PS)asym}$
[NH₄][X1]	2965	591	720
[NH₄][X2]	2926	557	656
[NH₄][X3]	2956	560	652
[NH₄][Y1]	2940	579	669
[NH₄][Y2]	2880	583	667

Mass spectra of the [NH₄][Xn] and [NH₄][Yn]

Mass spectra of the compounds are given in Figures 4-8. The reason why the peaks in the mass spectrum are different from expected is because of the different masses phosphorus and sulfur isotopes [17-20].

In the mass spectrum of the [NH₄][X1], it is seen that

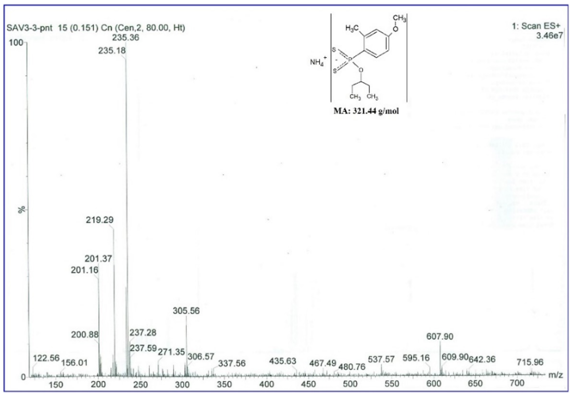

Figure 4. MS spectrum of the [NH₄][X1].

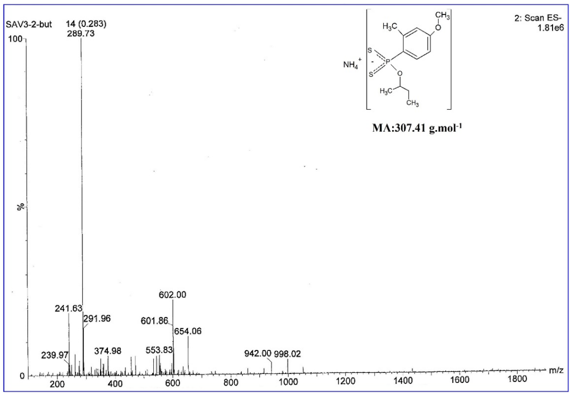

Figure 5. MS spectrum of the $[NH_4][X2]$.

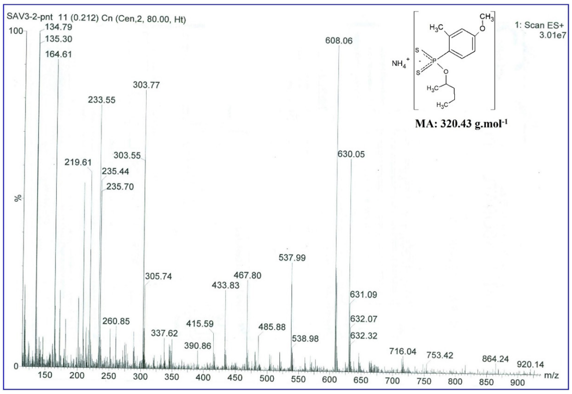

Figure 6. MS spectrum of the $[NH_4][X3]$.

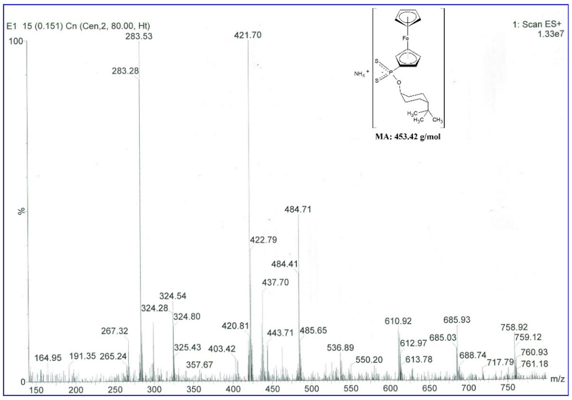

Figure 7. MS spectrum of the $[NH_4][Y1]$.

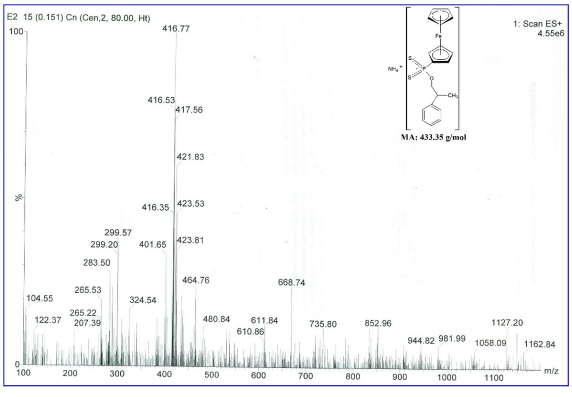

Figure 8. MS spectrum of the $[NH_4][Y2]$.

the principle peak is formed by the removal of the 3-pentyl group from the structure of the molecule, $([M-(NH_4+(-CH(C_2H_5)_2]^+)$. $[NH_4][X2]$ molecular ion peak appeared as the principle peak at 100% relative abundance $([M-NH_4]^+)$. Although the molecular ion peak of the $[NH_4][X2]$ was noticeable $([M-NH_4]^+$; 84%), it was not the main peak.

In the ionization process, different groups can be separated from the molecule, as well as the leaving groups of the molecule can be attached to each other [21-23]. For this reason, during the ionization process, two $[NH_4L3]$ combined with each other $([(M-NH_4)_2]^+)$. Another possible result of such combining in the ionization process for $[NH_4L3]$ compound is that $[(NaPS_2O)]^+$ which is shown up as principle peak.

As seen in the mass spectrum at 283.53 (m/z) of the $[NH_4][Y1]$ compound is relating to the leaving of the 4-*tert*-butylcyclohexanol group from the molecule. On the other hand, the peak observed at 421.70 (m/z) of the same compound belongs to the separation of methyl groups from the molecule. The principle peak of the $[NH_4][Y2]$ is observed in the spectrum as the molecular ion peak.

NMR spectra of the $[NH_4][Xn]$ and $[NH_4][Yn]$

Atom numbering of the compounds for NMR is depicted on the NMR spectra. The ^1H-NMR, ^{13}C-NMR and ^{31}P-NMR data of the compounds are given in Table 2, Table 3 and Table 4, respectively. On the other hand, the NMR spectra are given in Figures at the end of their NMR comments (Figure 9-13 for ^1H-NMR, Figure 14-18 for ^{13}C-NMR and Figure 19-23 for ^{31}P-NMR). D_2O was used as the solvent in the NMR spectrum analysis of ligands. ^{13}C- and ^{31}P-NMR measurements were done as decoupled. The chemical shift values "δ" and the splitting constant "J" are given in ppm and Hz, respectively (s: single; d: doublet; dd: doublet of the doublet; m: multiplet).

The chemical shift values of the C_2-H; C_3-H and C_5-H

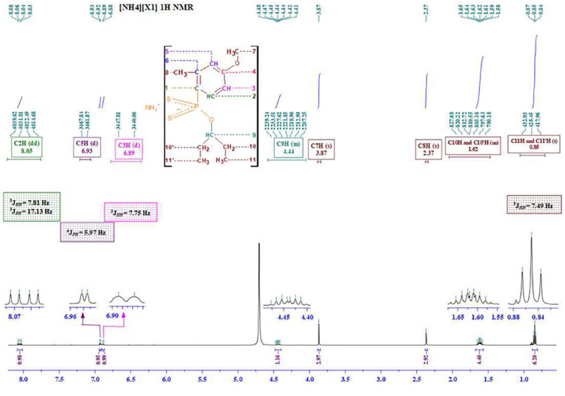

Figure 9. ^1H NMR spectrum of $[NH_4][X1]$.

Table 2. ^{1}H-NMR data of the compounds.

	[NH$_4$][X1]	[NH$_4$][X2]	[NH$_4$][X3]	[NH$_4$][Y1]		[NH$_4$][Y2]
C_2-H	8.1 (dd, H) $^3J_{PH}$= 17.1 $^3J_{HH}$= 7.8	8.0 (dd, H) $^3J_{PH}$= 17.2 $^3J_{HH}$= 7.8	7.9 (dd, H) $^3J_{PH}$= 17.2 $^3J_{HH}$= 7.8	4.6 (s, 2H)	subs-Fc-C_2H, -$C_{2'}$H	4.6 (s, 2H)
C_3-H	6.9 (d, H) $^3J_{HH}$= 7.8	6.8 (d, H) $^3J_{HH}$= 7.7	6.8 (d, H) $^3J_{HH}$= 7.8	-	subs-Fc-C_3H, -$C_{3'}$H	4.4 (s, 2H)
C_5-H	6.9 (d, H) $^4J_{PH}$= 6.0	6.9 (d, H) $^4J_{PH}$= 5.9	6.8 (d, H) $^4J_{PH}$= 5.9	4.3 (m, 7H)	uns-Fc subs-Fc-C_3H, -$C_{3'}$H	4.3 (m, 7H)
C_7-H	3.9 (s, 3H)	3.8 (s, 3H)	3.7 (s, 3H)	-	unsubs-Fc	4.3 (s, 5H)
C_8-H	2.4 (s, 3H)	2.3 (s, 3H)	2.2 (s, 3H)	4.5 (d, H) $^3J_{PH}$= 13.5	C_9-H	4.0 (m, 2H)
C_9-H	4.4 (m, H)	4.4 (m, H)	4.5 (m, H)	2.0 (m, 4H)	C_{10}-H	3.0 (m, H)
C_{10}-H	1.6 (m, 4H)	1.5 (m, 2H)	1.4 (m, 2H)	1.2 (m, 4H)	C_{11}-H	1.2 (d, 3H) $^3J_{HH}$= 6.9
C_{11}-H	0.9 (d, 6H) $^3J_{HH}$= 7.5	1.1 (d, 3H) $^3J_{HH}$= 6.3	1.2 (m, 2H)	0.9 (s, H) $^3J_{HH}$= 6.2	C_{12}-H	-
C_{12}-H	-	0.8 (t, 3H) $^3J_{HH}$= 7.5	1.1 (d, 3H) $^3J_{HH}$= 6.3	0.9 (s, 9H)	C_{14}-H	-
C_{13}-H	-	-	0.7 (t, 3H) $^3J_{HH}$= 7.4	-	Arom-CH	7.4 (m, 5H)

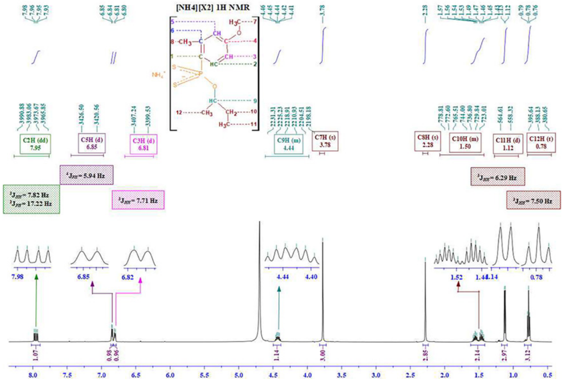

Figure 10. ^{1}H NMR spectrum of [NH$_4$][X2].

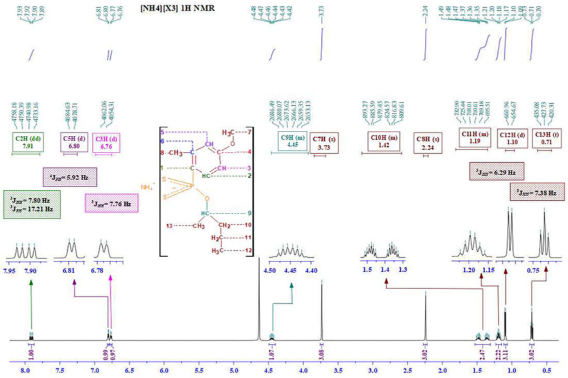

Figure 11. ^{1}H NMR spectrum of [NH$_4$][X3].

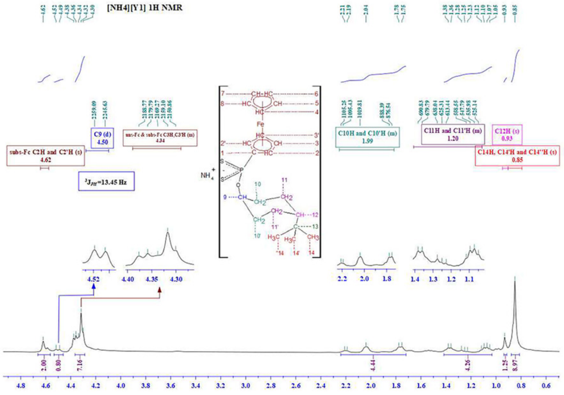

Figure 12. ^{1}H NMR spectrum of [NH$_4$][Y1].

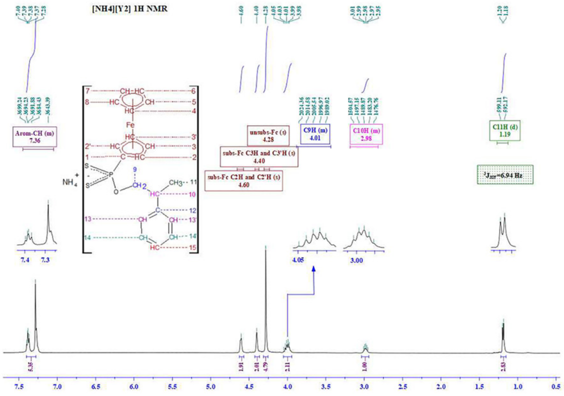

Figure 13. ^{1}H NMR spectrum of [NH$_4$][Y2].

in the aromatic ring in the ^{1}H-NMR spectrum of the [NH$_4$][Xn] series are in the range of 7.8-8.1 ppm; 7.7-7.8 ppm and 5.9-6.0 ppm, respectively. The C_2-H proton in the 3-methoxytolyl ring appears as a doublet of doublets due to splittings by the phosphorous ($^3J_{PH}$= 17.1-17.2 Hz). C_2-H and C_3-H protons display a three-bond coupling to each other in the range of $^3J_{HH}$= 7.7-7.8 Hz for [NH$_4$][Xn]. Although the C_3-H and C_2-H protons have adjacent protons to each other, C_3-H proton could not display a four-bond coupling to phosphorus. It can be concluded that phosphorus atom is substituted in its ortho-position (C_8-H) relative to the methyl group in the aromatic ring.

As for ferrocene-containing salts ([NH$_4$][Yn]), The che-

Table 3. ^{13}C-NMR data of the dithiophosphonates.

	[NH₄][X1]	[NH₄][X2]	[NH₄][X3]	[NH₄][Y1]		[NH₄][Y2]
C₁	126.5 J_{PC}= 111.1	126.5 J_{PC}= 111.1	125.9 J_{PC}= 110.4	70.3	**subs-Fc-C₂ –C₂′**	subs-Fc-C2; 71.6 $^2J_{PC}$= 15.0 subs-Fc-C2′ 72.0, $^2J_{PC}$= 15.3
C₂	133.0 $^2J_{PC}$= 11.0	133.0 $^2J_{PC}$= 11.7	133.0 $^2J_{PC}$= 11.7	-	**subs-Fc-C₃ –C₃′**	subs-Fc-C3; 70.8 $^3J_{PC}$= 11.6 subs-Fc-C3′ 70.9, $^2J_{PC}$= 11.3
C₃	120.4 $^3J_{PC}$= 14.5	120.3 $^3J_{PC}$= 14.5	120.3 $^3J_{PC}$= 14.4	70.4	**uns-Fc&Subs-Fc-C₃ –C₃′**	-
C₄	159.6	159.4 $^4J_{PC}$= 2.6	159.4 $^4J_{PC}$= 2.8	-	**unsubs-Fc**	70.5
C₅	112.8 $^3J_{PC}$= 6.4	112.7 $^3J_{PC}$= 7.4	112.6 $^3J_{PC}$= 7.4	70.0	**C₉**	69.3, $^2J_{PC}$= 7.9
C₆	144.4	144.5 $^2J_{PC}$= 2.6	144.4 $^2J_{PC}$= 2.6	47.0	**C₁₀**	40.3 $^3J_{PC}$= 8.2
C₇	55.2	55.0	55.0	32.3	**C₁₁**	18.5
C₈	20.8	20.7	20.6	27.6	**C₁₂**	-
C₉	80.2 $^2J_{PC}$= 7.8	75.4 $^2J_{PC}$= 7.7	74.1 $^2J_{PC}$= 7.8	27.6	**C₁₃**	-
C₁₀	26.3	30.0 $^3J_{PC}$= 4.7	39.3 $^3J_{PC}$= 4.7	25.7	**C₁₄**	-
C₁₁	8.59	8.9	20.7 $^4J_{PC}$= 3.2	-	**Arom-C**	127.9
C₁₂	-	20.1 $^3J_{PC}$= 3.1	17.9	-	-	-
C₁₃	-	-	13.3	-	-	-

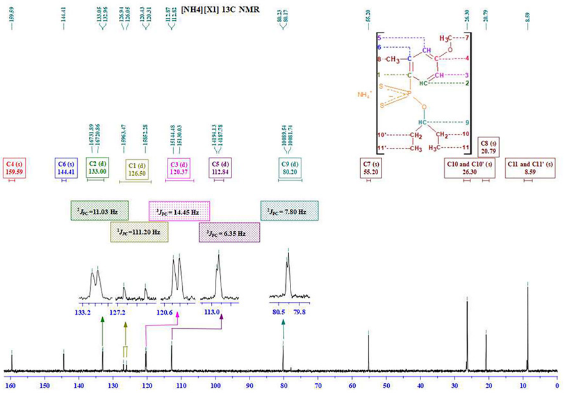

Figure 14. ^{13}C NMR spectrum of [NH$_4$][X1].

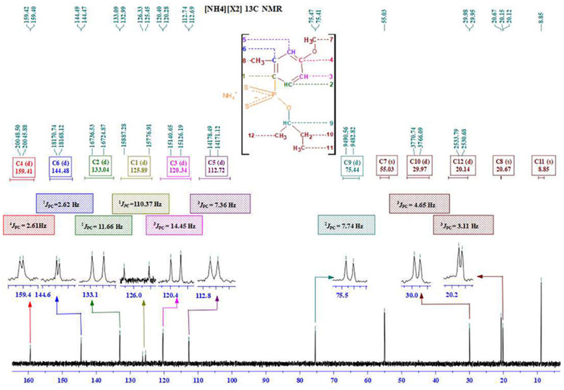

Figure 15. ^{13}C NMR spectrum of [NH$_4$][X2].

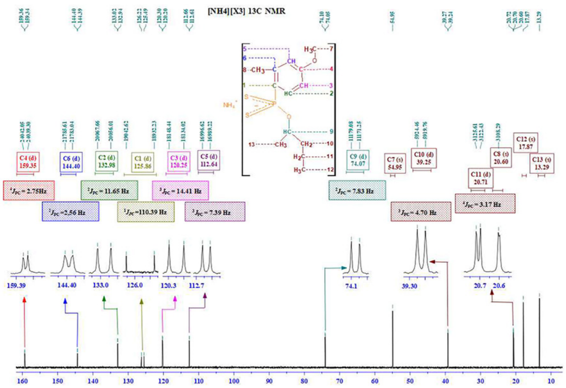

Figure 16. ^{13}C NMR spectrum of [NH$_4$][X3].

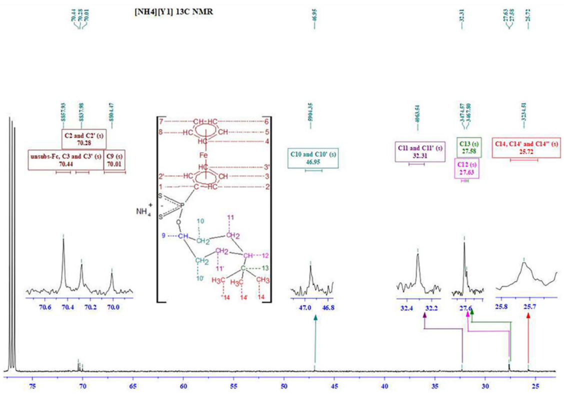

Figure 17. ^{13}C NMR spectrum of [NH$_4$][Y1].

mical shift values of the subs-Fc C₂-H and C₂'-H protons in the ferrocene ring are 4.6 ppm. As seen in Table 2, the un-

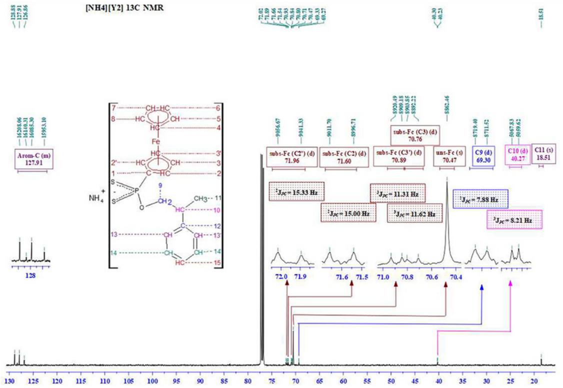

Figure 18. ^{13}C NMR spectrum of $[NH_4][Y2]$.

Table 4. ^{31}P-NMR data of compounds.

SAV-B1	δ (ppm)		FcLR
$[NH_4][X1]$	100.08	103.30	$[NH_4][Y1]$
$[NH_4][X2]$	100.16	106.07	$[NH_4][Y2]$
$[NH_4][X3]$	100.09		

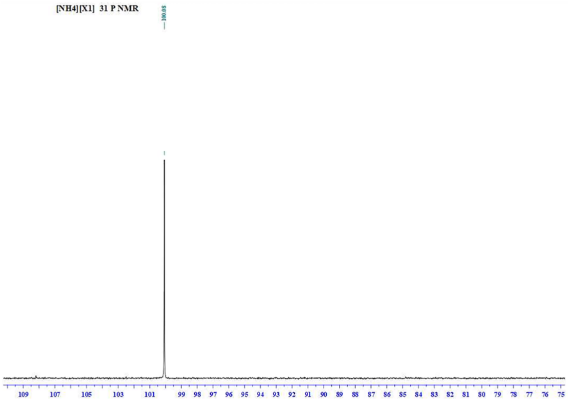

Figure 19. ^{31}P NMR spectrum of $[NH_4][X1]$·

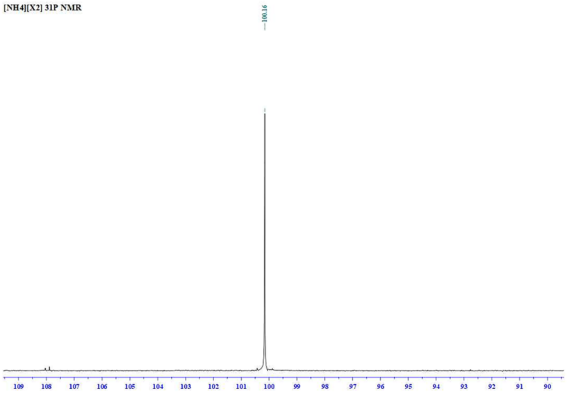

Figure 20. ^{31}P NMR spectrum of $[NH_4][X2]$·

substituted cyclopentadienyl ring (C_3H, uns-Fc) and subs-Fc C_3-H and C_3'-H protons overlap each other in the ferrocenyl ring in the compound $[NH_4][Y1]$ whereas the same protons signals are resonated as different chemical shift values (without overlapping) in $[NH_4][Y2]$.

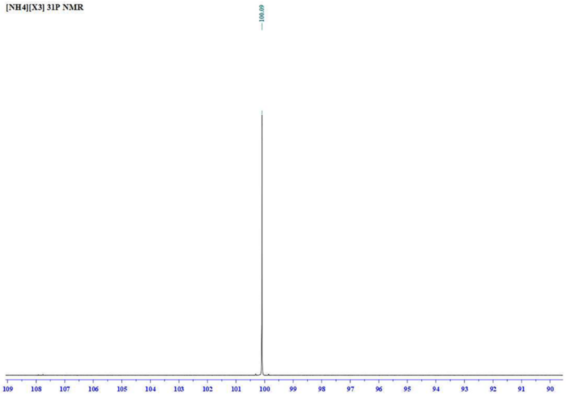

Figure 21. ^{31}P NMR spectrum of $[NH_4][X3]$·

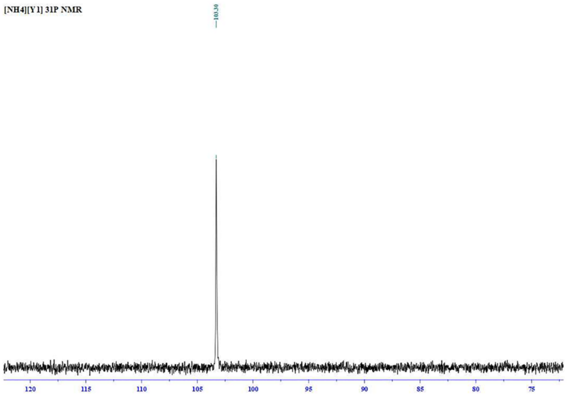

Figure 22. ^{31}P NMR spectrum of $[NH_4][Y1]$·

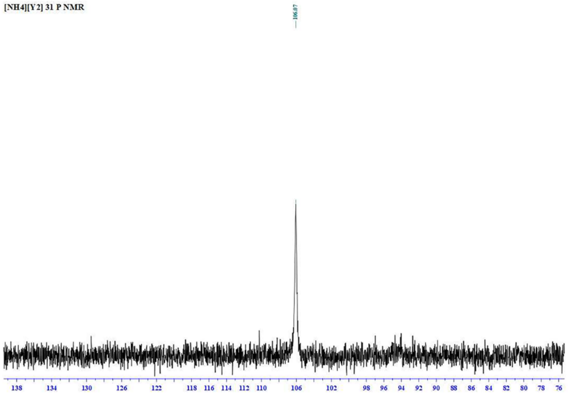

Figure 23. ^{31}P NMR spectrum of $[NH_4][Y2]$·

The ^{1}H-NMR chemical shift and coupling constants values of the dithiophosphonates are good agree well with the literature reports for similar compounds [14,21,22].

In the ^{13}C-NMR spectrum of the $[NH_4][Xn]$ compounds, ipso carbon atom (C_1) coupling constant values are between 110.4 Hz and 111.1 Hz. In the same compounds, the phosphorus atom could not split the carbon atom C_8 three bond coupling, but C_3 and C_5 are split three bond coupling by the phosphorus as doublet of doublet.

Unlike $[NH_4][Xn]$ series, ipso carbon peak (C_1) in the $[NH_4][Yn]$ series could not be observed due to the fact that it was below the solvent peaks. In the $[NH_4][Y1]$, subs-Fc

C_2-H and C_2'-H appeared as a single peak (70.3 ppm) in the spectrum, while the same carbons $[NH_4][Y2]$ resonated in different chemical shift values. Moreover, subs-Fc C_2-H and C_2'-H carbon atoms in the $[NH_4][Y2]$ are split two bond coupling by the phosphorus atom ($^2J_{PC}$= 15.0 Hz for subs-Fc-C_2; $^2J_{PC}$= 15.3 Hz for subs-Fc-C_2'). Similar trends are observed in the subs-Fc-C_3 and C_3'. The ^{13}C-NMR chemical shift data and coupling constants values of ammonium salts are in agreement with similar structures [8, 25].

Since there is only one type of phosphorus atom in the structure of the compounds, the phosphorus peak appeared as a single peak in the proton-decoupled ^{31}P NMR spectra. The ^{31}P-NMR chemical shifts of the dithiophosphonates are located in the range 100.08-106.07 ppm. All the ^{31}P-NMR chemical shift values compare well with the literature reports for similar structures [14,21,22].

CONCLUSIONS

In this study, five new dithiophosphonate salts from perthiophosphonic acid anhydrides (SAV-B1 and FcLR) were studied. The structures of these compounds were characterized by different spectroscopies (mass spectrometry, FT-IR, ^1H-NMR, ^{13}C-NMR, ^{31}P-NMR, elemental analysis).

Symmetrical PS bond (ν(PS)sym) and asymmetrical PS bond (ν(PS)asym) stretching vibration bands were shown up as expected in the IR spectrum [15,16]. Moreover, the suggested structures of the compounds were supported by mass spectroscopic method.

In the $[NH_4][Y1]$ salt, subs-Fc C_2-H and C_2'-H showed up as a single peak (70.3 ppm) in the spectrum, but not for $[NH_4][Y2]$ as the same carbon atoms. Furthermore, subs-Fc C_2-H and C_2'-H carbon atoms in the $[NH_4][Y2]$ are split two bond coupling by the phosphorus atom as a doublet of doublet peaks in the spectrum while the same situation is observed for the subs-Fc C_3-H and C_3'-H carbon atoms in the $[NH_4][Y2]$.

In addition, ^1H-NMR and ^{13}C-NMR spectra indicated that methyl- moiety in 3-methoxytolyl in the compounds is positioned in the *m*-position to the phosphorus whereas the methoxy group in 3-methoxytolyl- in the compounds is located in the *p*-position to phosphorus in the $[NH_4][Xn]$ series.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AUTHOR CONTRIBUTION

Ertugrul Gazi Saglam, Conceptualization, Validation, Preparation, Formal analysis, Investigation, Resources, Supervision, Writing-Original, Writing-Review & Editing, Visualization, Funding acquisition. Elif Bulat, Conceptualization, Visualization, Preparation, Methodology, Formal analysis, Investigation, Writing-Original, Visualization Funding acquisition. Ayşe, Validation, Investigation, Visualization, Writing-Original, Visualization Funding acquisition.

References

1. Foreman MRStJ, Slawin AMZ, Woollins JD. 2,4-Diferrocenyl-1,3,dithiadiphosphetane 2,4 disulfide; structure and reactions with catechols and $[PtCl_2(PR_3)_2]$ (R = Et or Bun). Journal of the Chemical Society, Dalton Transactions, 18 (1996) 3653–3657.
2. Thomsen I, Clausen K, Scheibye S, Lawesson S-O. Thiation with 2,4-bis(4-Methoxyphenyl)-1,3,2,4- Dithiadiphosphetane 2,4-disulfide: N-methylthiopyrrolidone. Organic Syntheses, 7 (1990) 372.
3. Cortés-Santiago A, Navarrete-López AM, Vargas R. Garza J. Dissociation energy for the P_2S_2 ring in a family of thionation reagents and the corresponding chemical reactivity of separated species: a density functional theory analysis. Journal of Physical Organic Chemistry, 30 (5) (2016) 1–9.
4. Ziyatdinova GK, Budnikov GK, Samigullin AI, Gabdullina GT, Sofronov AV, Al'metkina LA, Nizamov IS, Cherkasov RA. Electrochemical Determination of Synthetic Antioxidants of Bisdithiophosphonic Acids. Journal of Analytical Chemistry, 65 (12) (2010) 1273-1279.
5. McCleverty JA, Kowalski RSZ, Bailey NA, Mulvaney R, O'Cleirigh DA. Aspects of the Inorganic Chemistry of Rubber Vulcanisation. Part 4. Dialkyl- and Diaryl-dithiophosphate and –dithiophosphinate Complexes of Zinc: Phosphorus-31 Nuclear Magnetic Resonance Spectral Studies and Structures of $[NMe_4][Zn\{S_2P(OC_6H_4Me\text{-}p)_2\}_3]$ and $[NEt_4][Zn(S_2PPh_2)_3]$. Journal of the Chemical Society, Dalton Transactions, 4 (1983) 627-634.
6. Kabra V, Mitharwal S, Singh S. Synthesis and Insecticidal Activity of Novel Dithiophosphonates. Phosphorus, Sulfur Silicon, 184 (9) (2009) 2431-2442.
7. Banaei A, Saadat A, McArdle P, Goli MM. Crystal structure, antibacterial activity and nanoparticles of Cd(II) complex derived from dithiophosphonate ligand. Phosphorus, Sulfur Silicon, 193 (6) (2018) 369-3674.
8. Xihong H, Guoxin T, Jing C, Linfeng R. Characterization of the extracted complexes of trivalent lanthanides with purified cyanex 301 in comparison with trivalent actinide complexes. Journal of the Chemical Society, Dalton Transactions, 43 (2014) 17352-17357.
9. Wheatley PJ. An X-ray diffraction determination of the crystal and molecular structure of "methyl metadithiophosphonate $[CH_3{\cdot}PS_2]_2$. Journal of the Chemical Society, 0 (1962) 300–302.
10. Dimert K, Kuchen W. Synthesis of Dithiophosphinic Acids by Nucleophilic Fission of Perthiophosphonic Anhydrides. Angewandte Chemie International Edition, 10 (7) (1971) 508–509.

11. Aydemir C, Solak S, Doğanlı GA, Şensoy T, Arar D, Bozbeyoglu N, Dogan NM, Lönnecke P, Hey-Hawkins E, Şekerci M, Karakuş M. Synthesis, Characterization, and Antibacterial Activity of Dithiophosphonates and Amidodithiophosphonates. Phosphorus, Sulfur Silicon, 190 (3) (2015) 300–309.
12. Lecher HZ, Greenwood RA, Whitehouse KC, Chao TH. The Phosphonation of Aromatic compounds with Phosphorus Pentasulfide. Journal of the American Chemical Society, 78 (19) (1956) 5018–5022.
13. Karakuş M, Lönnecke P, Hey-Hawkins E. Zwitterionic ferrocenyldithiophosphonates: the molecular structure of [FcP(S)S(OCH$_2$CH$_2$NH$_2$Me)] [Fc = Fe(η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$)]. Polyhedron, 23 (2004) 2281–2284.
14. Sağlam EG, Bulat E, Yılmaz H. The Syntheses and Characterization of New Dithiophosphonates derived from Novel 2,4-Bis(methoxytolyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfides and Their Ni(II) Complexes. Journal of the Turkish Chemical Society Section A: Chemistry, 7 (3) (2020) 789-800.
15. Sağlam EG, Bulat E, Acar N, Demirel I. New Homodinuclear Alkyl- and Aryl- Dithiophosphonato Cd(II) and Hg(II) complexes: Syntheses and Characterizations. Journal of the Turkish Chemical Society Section A: Chemistry, 7 (1) (2020) 49-64.
16. Aragoni MC, Arca M, Demartin F, Devillanova FA, Graiff C, Isaia F, Lippolis V, Tiripicchio A, Verani G. Reactivity of phosphonodithioato NiII complexes: solution equilibria, solid state studies and theoretical calculations on the adduct formation with some pyridine derivatives. Journal of the Chemical Society, Dalton Transactions, 18 (2001) 2671–2677.
17. Chakravarty M, Pailloux S, Ouizem S, Smith KA, Duesler EN, Paine RT, Williams NJ, Hancock RD. Synthesis and metal coordination chemistry of (phenyl)(pyridine-2-ylmethyl)phosphinodithioic acid, [2-C$_5$H$_4$N]CH$_2$P(S)(SH)(Ph). Polyhedron, 33 (2012) 327-35.
18. Heinz S, Keck H, Kuchen W. Mass spectrometric studies of dithiophosphinato metal complexes. Organic Mass Spectrometry, 19 (1984) 82-86.
19. Karakuş M, Yılmaz H. Synthesis and Characterization of Ni(II), Zn(II), and Cd(II) Complexes with Dithiophosphonate Derivatives. Russian Journal of Coordination Chemistry, 32 (6) (2006) 437–43.
20. Keck H, Kuchen W. Massenspektrometrische Untersuchungen An Organophosphorverbindungen IV. Über den massenspektrometrischen Zerfall von Dithiophosphinsären. Phosphorus, Sulfur Silicon, 14 (1983) 225-228.
21. Sağlam EG, Ebinç A. Syntheses and Spectroscopic Characterization on New [O-3-phenyl-1-propyl-(4-methoxyphenyl) dithiophosphonato] Ni(II), Cd(II) and Hg(II) Complexes. Journal of the Turkish Chemical Society Section A: Chemistry, 5(3) (2018) 1239-1248.
22. Sağlam EG, Acar N. Syntheses and characterization of new dithiophosphinato zinc complexes. Journal of the Turkish Chemical Society Section A: Chemistry, 5 (2) (2018) 931-940.
23. Ernst L. ^{13}C n.m.r. spectroscopy of diethyl alkyl and benzyl-phosphonates. A study of phosphorus– carbon spin–spin coupling constants over one to seven bonds. Organic Magnetic Resonance, 9 (1) (1977) 35-43.