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Syntheses and characterization of new dithiophosphinato zinc complexes

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Abstract : Four known dithiophosphinic acids, DTPA, were synthesized and their zinc complexes were newly prepared. The complexes have been proven to have the structures $[Zn(\mu\text{-}DTPA^n)_2(DTPA^n)_2]$, ($[DTPA^n]= R^n(R)P(S)H$, R= 4-$CH_3O$-$C_6H_4$-; R^1= *iso*-amyl-, $DTPA^1$; R^2= *iso*-butyl-, $DTPA^2$; R^3= *sec*-butyl-, $DTPA^3$; R^4= *iso*-propyl-, $DTPA^4$). The DTPAs were prepared by the reaction of the Lawesson reagent, [2,4–bis(4-methoxyphenyl)–1,3,2,4–dithiodiphosphetane–2,4–disulfide] (LR), with the corresponding Grignard compounds. The acids formed are viscous liquids difficult to purify and so they were converted to ammonium salts, $[DTPA^n][NH_4]$, which are easy to obtain as pure crystals. The complexes were identified to have dimeric structures on the basis of mass spectroscopic data.

Keywords: Dithiophosphinic Acid, Dithiophosphinate, Phosphinodithioic Acid, Dithiophosphinato Zinc Complex, Lawesson's Reagent.

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INTRODUCTION

Acidic organodithiophosphorus compounds like dithiophosphoric, dithiophosphonic and dithiophosphinic acids (Figure 1) and the coordination compounds thereof have some industrial interest because of their use as a rubber vulcanizing agent (1,2), lubricating oil additives (3-5), metal flotation mediators (6-8), and pesticides (9-11). Potential uses as chemotherapeutic agents (12), clinical imaging aids (13) and antibiotic synergists are also investigated (14).

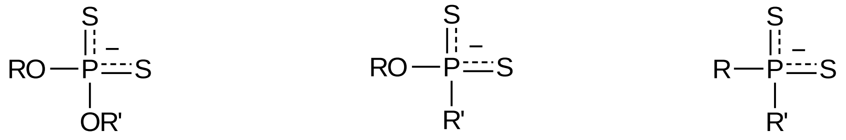
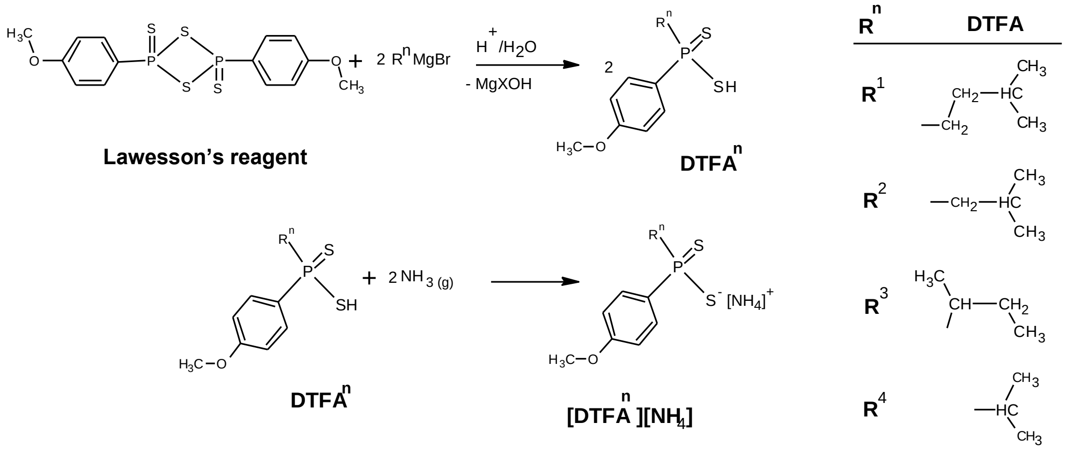

Dithiophosphoric acid Dithiophosphonic acid Dithiophosphinic acid
R, R'= Alkyl- or aryl- groups

Figure 1. Different types of organodithiophosphorus compounds

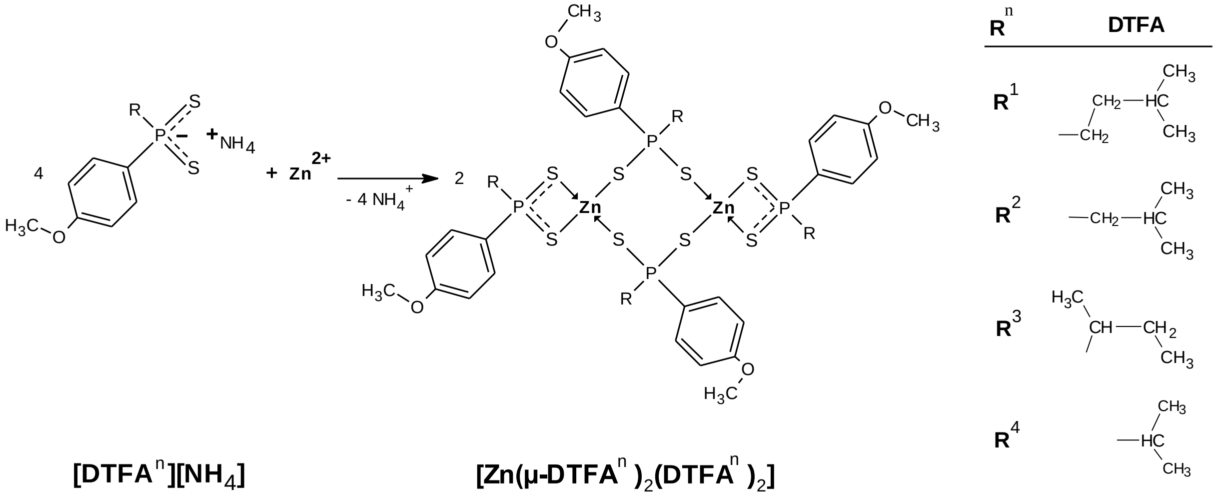
DTPA metal complexes are mostly classified as four-coordination number. The nickel(II)-DTPA complexes are mono-nucleic and as a square-planar (15), on the other hand Zn(II)- or Cd(II)-DTPA complexes are shown to be four coordinated, dimeric structures (16,17). Here, we present the preparation and characterization of the zinc complexes of four different dithiophosphinic acids, $[DTPA^n]$, 4-methoxyphenyl(3-methylbutyl) dithiophosphinic acid, $[DTPA^1]$; 4-methoxyphenyl(2-methylpropyl) dithiophosphihinic acid, $[DTPA^2]$;

4-methoxyphenyl(1-methylpropyl) dithiophosphinic acid, [DTPA^3]; 4-methoxyphenyl(1-methylpropyl) dithiophosphinic acid, [DTPA^4]. The synthesis of the dithiophosphinato ligand was described elsewhere (18-20). As it is general for the related compounds the Lawesson reagent, 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (LR) was reacted with the appropriate Grignard reagent to obtain the corresponding dithiophosphinic acid and the product was neutralized with dry ammonia to yield a crystallizable ammonium salt for purification, [DTPA^n][NH$_4$]. The reactions and the products are summarized in Scheme 1.



Scheme 1. Synthesis of [DTPA^n] and [DTPA^n][NH$_4$].

Zinc complexes of the four dithiophosphinic acids described above were obtained by the treatment of the corresponding ammonium-ligand salt with zinc(II)chloride in ethanolic medium, [Zn(μ-DTPA^n)$_2$(DTPA^n)$_2$], (Scheme 2).



Scheme 2. Synthesis of [Zn(μ-DTPA^n)$_2$(DTPA^n)$_2$].

EXPERIMENTAL

General

Analytical-grade LR, *iso*-amyl bromide, *iso*-butyl bromide, *sec*-butyl bromide and *iso*-propyl bromide were purchased from Merck and used directly without further purification. Benzene, chloroform, ethanol, diethyl ether and ZnCl$_2$ were purchased from Merck. Benzene and diethyl ether were distilled and dried before use. [DTPA^1][NH$_4$], [DTPA^2][NH$_4$], [DTPA^3][NH$_4$] and [DTPA^4][NH$_4$] were prepared according to the literature (21).

The LC/MS system was supplied by Waters with a C-18 HPLC column and a Waters Micromass ZQ connected to an ESI ionizer. Melting point determinations were performed on a Gallenkamp apparatus with a glass capillary. ^{1}H, proton-coupled ^{13}C and ^{31}P NMR spectra were recorded on a Varian Mercury (Agilent) 400 MHz FT spectrometer. CDCl$_3$ was the solvent of preferences for zinc complexes. Internal standards were SiMe$_4$ for the ^{1}H-, ^{13}C-NMR and 85% H$_3$PO$_4$ for ^{31}P-NMR. IR spectra were recorded on a Perkin Elmer Spectrum 400 FTIR instrument (200–4000 cm^{-1}) with wavenumbers in cm^{-1} units. Elemental analyses were performed on a LECO CHNS-932 C instrument.

General procedure for the zinc complexes

To pure ethyl alcoholic solution of 2 mmol (0.04 g) of ZnCl$_2$ in a beaker (40-50 mL) were added 4 mmoles of the ligand of interest (0.34 g of

[DTFA^1][NH$_4$]; 0.31 g of [DTFA^2][NH$_4$]; 0.31 g of [DTFA^3][NH$_4$] and 0.28 g of [DTFA^4][NH$_4$];). After mixing the cation with the ligand, the colorless complex was formed. Upon waiting for 2 days, fine crystals of the complex were formed at the bottom. These crystals were filtered and recrystallized from ethanol or chloroform.

Bis-{bis-[4-methoxyphenyl(3-methylbutyl)dithiophosphinato]zinc(II)} [Zn(μ-DTPA^1)$_2$(DTPA^1)$_2$]. Yield: 1.83 g, 74%. Colorless. M.P. 221-222^{o}C. ^{1}H NMR (δ:ppm, CDCl$_3$): δ= 0.85 (dd, $^3J_{HH}$= 6.51 Hz, 24H, -CH-(C$\underline{\text{H}}_3$)$_2$), 1.47 (m, 8H, -C$\underline{\text{H}}$-), 1.55 (m, 4H, -C$\underline{\text{H}}_2$-CH), 2.28 (m, 8H, -C$\underline{\text{H}}_2$-CH$_2$), 3.84 (s, 12H, OC$\underline{\text{H}}_3$), 6.95 (A-part of AA′MM′X, $^4J_{PH}$= 2.30 Hz (J_{AX}), *N*= 8.70 Hz, 8H, *m*-H), 7.86 M-part of AA′MM′X, $^3J_{PH}$= 13.36 Hz (J_{MX}), *N*= 8.70 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 22.1 (s, -($\underline{\text{C}}$H$_3$)$_2$), 32.0 (d, $^3J_{P\text{-}C}$= 4.4 Hz, -$\underline{\text{C}}$H-(CH$_3$)$_2$)), 28.6 (d, $^2J_{P\text{-}C}$= 17.5 Hz, -C$\underline{\text{H}}_2$-CH), 40.2 (d, $J_{P\text{-}C}$= 50.9 Hz, P-C$\underline{\text{H}}_2$-), 55.4 (s, $\underline{\text{C}}$H$_3$O-), 113.3 (d, $^3J_{P\text{-}C}$= 14.2 Hz, Ar-C$_{meta}$), 126.5 (d, $J_{P\text{-}C}$= 88.9 Hz, P-C$_{\text{arom}}$) 132.3 (d, $^2J_{P\text{-}C}$ = 11.9 Hz, Ar-C$_{ortho}$), 162.1 (s, CH$_3$O-$\underline{\text{C}}$). ^{31}P-NMR (CdCl$_3$): δ= 68.1. LC/MS: *m/z* 647.3 ([[M/2+CH$_3$CN)]$^+$, 100%), 1222.9 ([M]$^+$, 4%), 883.3 ([M-DTPA^1]$^+$, 4%), 614.3 ([M/2-H]$^+$, 6%). Anal. Calcd. for $C_{48}H_{72}Zn_2O_4P_4S_8$ (1224.3 g.mol^{-1}): C, 47.1; H, 5.9; S, 21.0. Found: C, 47.2; H, 5.7; S, 20.8%.

Bis-{bis-[4-methoxyphenyl(2-methylpropyl)dithiophosphinato]zinc(II)} [Zn(μ-DTPA^2)$_2$(DTPA^2)$_2$]. Yield: 2.54 g, 85%. Colorless. M.P. 167-168^{o}C. ^{1}H NMR (CDCl$_3$): δ= 0.88 (t, $^3J_{HH}$= 6.67 Hz, 24H, -CH$_2$-C$\underline{\text{H}}_3$), 2.11 (m, 4H, -C$\underline{\text{H}}$-CH$_3$), 2.28 (m, 8H, $^2J_{PH}$= 11.90 Hz, $^3J_{PH}$= 6.10 Hz P-C$\underline{\text{H}}_2$), 3.84 (s, 12H, OC$\underline{\text{H}}_3$), 6.92 (A-part of AA′MM′X, $^4J_{PH}$= 2.46 Hz (J_{AX}), *N*= 8.50 Hz, 8H, *m*-H), 7.91 M-part of AA′MM′X, $^3J_{PH}$= 13.44 Hz (J_{MX}), *N*= 8.50 Hz, 8H, *o*-H). ^{13}C-NMR (CDCl$_3$): δ= 25.5 (d, $^3J_{P\text{-}C}$= 3.9 Hz, -($\underline{\text{C}}$H$_3$)$_2$), 24.3 (d, $^2J_{P\text{-}C}$= 10.0 Hz, -$\underline{\text{C}}$H-(CH$_3$)$_2$)), 42.9 (d, $J_{P\text{-}C}$= 51.4 Hz, P-C$\underline{\text{H}}_2$-), 55.4 (s, $\underline{\text{C}}$H$_3$O-), 113.7 (d, $^3J_{P\text{-}C}$= 14.1 Hz, Ar-C$_{meta}$), 127.8 (d, $J_{P\text{-}C}$= 80.3 Hz, P-C$_{\text{arom}}$) 132.6 (d, $^2J_{P\text{-}C}$ = 13.1 Hz, Ar-C$_{ortho}$), 161.9 (d, $^4J_{P\text{-}C}$= 3.0 Hz, CH$_3$O-$\underline{\text{C}}$). ^{31}P-NMR (CDCl$_3$): δ= 60,7. LC/MS: *m/z* 1190.3 ([M+Na]$^+$, 2%), 845.2 ([M-(Zn(DTPA^2)]$^+$, 4%), 619.3 ([M/2+CH$_3$CN]$^+$, 92%), 607.2 ([M/2+Na]$^+$, 35%). Anal. Calcd. for $C_{44}H_{64}Zn_2O_4P_4S_8$ (1168.2 g mol^{-1}): C,45.2; H, 5.5; S, 22.0. Found: C, 45.4; H, 5.5; S, 22.2%.

Bis-{bis-[4-methoxyphenyl(1-methylpropyl)dithiophosphinato]zinc(II)} [Zn(μ-DTPA^3)$_2$(DTPA^3)$_2$]. Yield: 2.33 g, 78%. Colorless. M.P. 187-188^{o}C. ^{1}H NMR (CDCl$_3$): δ= 0.92 (t, $^3J_{HH}$= 7.30 Hz, 12H, -CH$_2$-C$\underline{\text{H}}_3$), 1.98 (m, 8H, -C$\underline{\text{H}_2\text{-}}CH_3$), 1.16 (m, -C$\underline{\text{H}}_3$-CH- adjacent with -CH$_3$-C$\underline{\text{H-}}$, 16H), 1.16 (dd, -C$\underline{\text{H}}_3$-CH- ve -CH$_3$-C$\underline{\text{H-}}$ adjacent, $^2J_{PH}$= 21.94 Hz, $^3J_{PH}$= 6.86 Hz, 16H), 3.84 (s, 12H, OC$\underline{\text{H}}_3$), 6.95 (A-part of AA′MM′X, $^4J_{PH}$= 2.32 Hz (J_{AX}), *N*= 8.80 Hz, 8H, *m*-H), 7.83 M-part of AA′MM′X, $^3J_{PH}$ = 12.95 Hz (J_{MX}), *N* =8.80 Hz, 4H, *o*-H). ^{13}C-NMR (ppm, CDCl$_3$): δ =16.26 (d, ^{2}J$_{P\text{-}C}$ = 1.0 Hz, -($\underline{\text{C}}$H$_3$)$_2$), 38.19 (d, J$_{P\text{-}C}$ = 49.6 Hz, P-$\underline{\text{C}}$H-), 55.37 (s, $\underline{\text{C}}$H$_3$O-), 113.6 (d, ^{3}J$_{P\text{-}C}$ = 13.9 Hz, Ar-C$_{meta}$), δ= 124.85 (d, J$_{P\text{-}C}$ = 78.1 Hz, P-C$_{\text{arom}}$) 132.97 (d, ^{2}J$_{P\text{-}C}$ = 12.5 Hz, Ar-C$_{ortho}$), 162.05 (d, ^{4}J$_{P\text{-}C}$ = 2.8 Hz, CH$_3$O-$\underline{\text{C}}$). ^{31}P-NMR (ppm, CDCl$_3$): δ = 82.9. LC/MS: *m/z* 1191.1 ([M+Na]$^+$, 31.2 %); 909.1 ([(M-(Zn(DTPA^3)]$^+$, 89.0 %); 583.2 ([M/2-H]$^+$, 78,5 %). Anal. Calcd. for $C_{44}H_{64}Zn_2O_4P_4S_8$ (1168.2 g mol^{-1}): C,45.2; H, 5.5; S, 22.0. Found: C, 45.6; H, 5.8; S, 22.6%.

Bis-{bis-[4-methoxyphenyl(2-propyl)dithiophosphinato]zinc(II)} [Zn(μ-DTFA^4)$_2$(DTFA^4)$_2$]. Yield: 2.00 g (81 %). Colorless. M.P. 209-210^{o}C. ^{1}H NMR (CDCl$_3$): δ =1.16 (dd, ^{3}J$_{PH}$= 21. 5 Hz, ^{3}J$_{HH}$ = 6.9 Hz, 12H, -CH-(C$\underline{\text{H}}_3$)$_2$), 2.3 (m, 4H, -C$\underline{\text{H}}$-), 3.84 (s, 6H, OC$\underline{\text{H}}_3$), 6.94 (A-part of AA′MM′X, $^4J_{PH}$ = 2.35 Hz (J_{AX}), *N* =8.80 Hz, 4H, *m*-H), 7.83 M-part of AA′MM′X, $^3J_{PH}$ = 12.95 Hz (J_{MX}), *N* =8.80 Hz, 4H, *o*-H). ^{13}C-NMR (ppm, CDCl$_3$): δ =16.26 (d, ^{2}J$_{P\text{-}C}$ = 1.0 Hz, -($\underline{\text{C}}$H$_3$)$_2$), 38.19 (d, J$_{P\text{-}C}$ = 49.6 Hz, P-$\underline{\text{C}}$H-), 55.37 (s, $\underline{\text{C}}$H$_3$O-), 113.6 (d, ^{3}J$_{P\text{-}C}$ = 13.9 Hz, Ar-C$_{meta}$), δ= 124.85 (d, J$_{P\text{-}C}$ = 78.1 Hz, P-C$_{\text{arom}}$) 132.97 (d, ^{2}J$_{P\text{-}C}$ = 12.5 Hz, Ar-C$_{ortho}$), 162.05 (d, ^{4}J$_{P\text{-}C}$ = 2.8 Hz, CH$_3$O-$\underline{\text{C}}$). ^{31}P-NMR (ppm, CDCl$_3$): δ = 82.9. LC/MS: *m/z* 1133.8 ([M+Na]$^+$, 31.2 %); 864.9 ([(M-(Zn(DTFA^4)]$^+$, 100.0 %); 576.9 ([M/2]$^+$+Na]$^+$, 78,5 %); 308.8 ([Zn(DTFA^4]$^+$, 12,3 %). Anal. Calcd. for $C_{40}H_{56}Zn_2O_4P_4S_8$ (1112.1 g mol^{-1}): C,43.2; H, 5.1; S, 23.1. Found: C, 43.2; H, 4.9; S, 23.3%.

RESULT AND DISCUSSION

The data relating to the percent yields, physical appearance, and elemental analyses of the complexes as well as IR-, mass- and NMR (^{1}H-, ^{13}C-, ^{31}P-) spectra are given in the section "Experimental". The major spectroscopic features are as follows:

IR Spectra

The prominent IR bands of the complexes, [Zn(μ-DTPA^1)$_2$(DTPA^1)$_2$], [Zn(μ-DTPA^2)$_2$(DTPA^2)$_2$], [Zn(μ-DTPA^3)$_2$(DTPA^3)$_2$] and [Zn(μ-DTPA^4)$_2$(DTPA^4)$_2$], are summarized in Table 1. The asymmetrical and symmetrical PS stretching vibrations, ν_{asym} and ν_{sym}, show up in the ranges 610–588 cm^{-1} and 492–549 cm^{-1}, respectively. The bands in the range 282–311 cm^{-1} were assigned to Zn-S stretching bands, $\nu_{Zn\text{-}S}$. These values agree well with those reported in the literature for analogous compounds (22-24).

Table 1: Selected FTIR (R) data (cm^{-1}) assignment of significant bands for [Zn(μ-DTPA^n)$_2$(DTPA^n)$_2$]

Compounds	ν_{Zn-S}	ν_{asym} **(PS)**	ν_{sym} **(PS)**
	IR	**IR**	**IR**
[Zn(μ-DTFA^1)$_2$(DTFA^1)$_2$]	308	610;599	518;534
[Zn(μ-DTFA^2)$_2$(DTFA^2)$_2$]	282	589	517;542
[Zn(μ-DTFA^3)$_2$(DTFA^3)$_2$]	297	588	492
[Zn(μ-DTFA^4)$_2$(DTFA^4)$_2$]	311	611	523; 550

Mass Spectra

The mass signals of the complexes reflect the isotopical multitudes of zinc and sulfur. Some of the mass peaks indicate the attachment of an CH_3CN or a Na^+ cation to the species responsible for the signal. CH_3CN or Na^+ ions are likely to be originated from the buffer solution used in the ionization chamber and similar cases were reported in the literature (25). The disintegration pattern of the complexes are also comparable to the literature data reported for analogous structures (26-29). Molecular peaks corresponding to the dimeric structures of the complexes are discernable for all the compounds, but [Zn(μ-DTPA^1)$_2$(DTPA^1)$_2$]. The complexes display Mass-peaks corresponding to the mono-nuclear [Zn(DTPA^n)$_2$] moieties. In the Mass spectrum of all the [Zn(μ-DTPA^n)$_2$(DTPA^n)$_2$] complexes display peaks indicating removal of a DTPA^n leaving back a sort of the formula [Zn$_2$(DTPA^n)$_3$].

^{1}H–NMR Spectra

^{1}H–NMR data are summarized in Table 2. For all the structures investigated the four anisole-ring protons and the phosphorus atom constitute an AA′MM′X system. The AA′MM′ part display practically an AMX pattern (30). This is obviously because $J_{AM'}$ and $J_{A'M}$ are virtually zero. The aromatic protons were assigned on the basis of the magnitudes of the coupling constants to phosphorus. In all the compounds, the protons in *ortho*- position to phosphorus display a $^3J_{PH}$ of ~13 Hz and those *meta*- to phosphorus a $^4J_{PH}$ of ~2.3 Hz.

The peak area integrals of all the signals confirm the assignments of the peaks. Chemical shift and coupling data are in compliance with the literature (31,32).

^{13}C-NMR Spectra

^{13}C–NMR data are given in Table 3. The contact ^{31}P-^{13}C coupling of the *ipso*- carbons varies between 76.3 Hz and 88.8 Hz whereas the one-bond coupling for the aliphatic carbons, C6, lies in the range 48.1 Hz-51.4 Hz. The δ and *J* values are in agreement with those given in the literature (33-35).

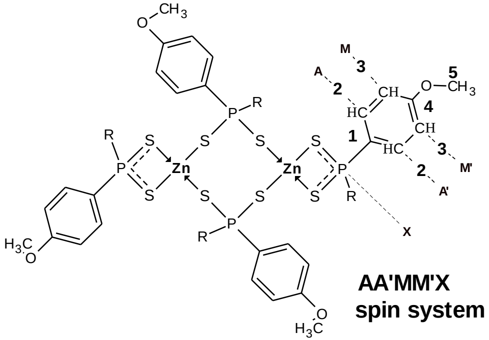
^{31}P–NMR Spectra

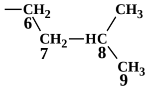
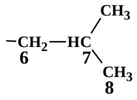
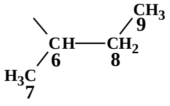
Proton-decoupled ^{31}P–NMR signals of the compounds, [Zn(μ-DTPA^1)$_2$(DTPA^1)$_2$], [Zn(μ-DTPA^2)$_2$(DTPA^2)$_2$], [Zn(μ-DTPA^3)$_2$(DTPA^3)$_2$] and [Zn(μ-DTPA^4)$_2$(DTPA^4)$_2$], appear at 68.1, 60.1, 79.4 and 82.9 ppm, respectively. The fact that each compound displays only one singlet indicate that the phosphorus atoms are in an equivalent environment within the molecule except for [Zn(μ-DTPA^2)$_2$(DTPA^2)$_2$]. These data comply with those reported in the literature (31).

CONCLUSION

In this work four new dithiophosphinato zinc complexes were synthesized and characterized. The characteristic ν_{N-H} stretching bands of the ligands appear at ~3000-3100 cm^{-1} on IR (18-20). These bands disappear on the IR spectra of the complexes proving the substitution of the ammonium group by metal cations. All the complexes are of dimeric structures. The one-bond ^{13}C-^{31}P coupling constants for the aromatic *ipso*- carbons were found to be 30-40 Hz greater than that of the aliphatic carbons (76.3-88.8 Hz and 48.1-51.4 Hz, respectively). Due to the equivalent chemical environment of the phosphorus in the complexes except for [Zn(μ-DTPA^2)$_2$(DTPA^2)$_2$], a single peak appeared in the ^{31}P-NMR spectrum. The structures of the complexes were elucidated on the basis of elemental analysis as well as mas-, FTIR- and NMR- spectra.

Table 2: ^{1}H NMR spectral data of complexes.



[Zn(μ-DTFA^1)$_2$(DTFA^1)$_2$] R^1= *iso*-amyl-	**AA'MM'X spin system, (*N*= J_{AM} + $J_{\text{AM'}}$)**		-OC**H**$_3$	-C6-**H**	-C7-**H**	-C8-**H**	-C9-**H**
	δ= 7.86 (dd, 8H) $^3J_{\text{P-H}}$= 13.36, (J_{MX}) N= 8.70	δ= 6.95 (dd, 8H) $^4J_{\text{P-H}}$= 2.30, (J_{AX}) N = 8.70	δ= 3.84 (s, 12H)	δ= 2.28 (m, 8H)	δ= 1.55 (m, 8H)	δ= 1.47 (m, 4H)	δ= 0.85 (d, 24H) $^3J_{\text{HH}}$ = 6.51
[Zn(μ-DTFA^2)$_2$(DTFA^2)$_2$] **R^2= *iso*-butyl-** 	δ= 7.91 (dd, 8H) $^3J_{\text{P-H}}$= 13.44, (J_{MX}) N= 8.50	δ= 6.92 (dd 8H) $^4J_{\text{P-H}}$= 2.46, (J_{AX}) N= 8.50	δ= 3.84 (s, 12H)	δ= 2.28 (dd, 8H) $^2J_{\text{P-H}}$= 11.90 $^3J_{\text{HH}}$ = 6.10	δ= 2.11 (m, 24H)	δ= 0.88 (d, 24H) $^3J_{\text{HH}}$ = 6.67	-
[Zn(μ-DTFA^3)$_2$(DTFA^3)$_2$] **R^3= *sec*- butyl-** 	δ= 7.83 (dd, 8H) $^3J_{\text{P-H}}$= 12.94, (J_{MX}) N= 8.80	δ = 6.92 (dd 8H) $^4J_{\text{P-H}}$= 2.32, (J_{AX}) N= 8.80	δ= 3.84 (s, 12H)	δ= 1.16 (dd, C6-H and C7-H adjacent, 16H) $^2J_{\text{P-H}}$= 21.94 $^3J_{\text{HH}}$ = 6.86	δ= 1.16 (m, C6-H and C7-H adjacent, 16H)	δ= 1.98 (m, 8H)	δ= 0.92 (t, 12H) $^3J_{\text{HH}}$ = 7.30
[Zn(μ-DTFA^4)$_2$(DTFA^4)$_2$] **R^4= *iso*-propyl-**							

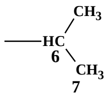
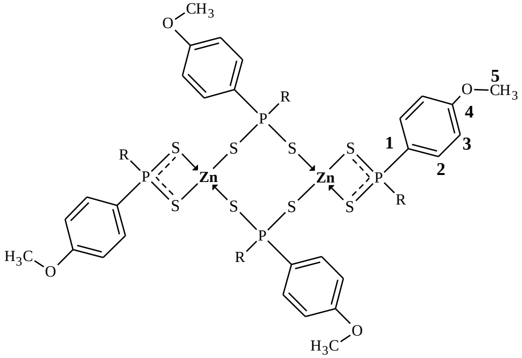
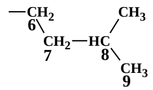
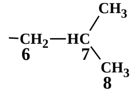
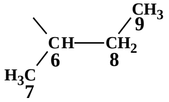
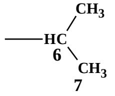
	δ= 7.83, (dd, 8H) $^{3}J_{P\text{-}H}$= 12.95, (J_{MX}) N= 8.80	δ = 6.94 (dd 8H) $^{4}J_{P\text{-}H}$= 2.35, (J_{AX}) N= 8.80	δ= 3.84 (s, 12H)	δ= 2.28 (m, 4H)	δ= 1.16 (dd 12H) $^{3}J_{P\text{-}H}$= 21.5 $^{3}J_{HH}$ = 6.9	-	-

Table 3: ^{13}C-NMR spectral data of complexes.



		-C4	Ar-C_{ortho}	-C1	Ar-C_{meta}	-OCH_3	-C6	-C7	-C8	-C9
[Zn(μ-DTFA¹)₂(DTFA¹)₂]	**R¹= *iso*-amyl-** 	δ= 162.1 (s)	δ= 132.3 (d) $^{2}J_{P\text{-}C}$ = 11.9	δ= 126.5 (d) $J_{P\text{-}C}$ = 88.9	δ= 113.3 (d) $^{3}J_{P\text{-}C}$ = 14.2	δ= 55.4 (s)	δ= 40.2 (d) $J_{P\text{-}C}$ = 50.9	δ= 28.6 (d) $^{2}J_{P\text{-}C}$ = 17.5	δ= 32.0 (d) $^{3}J_{P\text{-}C}$ = 4.4	δ= 22.1 (s)
[Zn(μ-DTFA²)₂(DTFA²)₂]	**R²= *iso*-butyl-** 	δ= 161.9 (d) $^{4}J_{P\text{-}C}$ = 3.0	δ= 132.6 (d) $^{2}J_{P\text{-}C}$ = 13.1	δ= 127.8 (d) $J_{P\text{-}C}$ = 80.3	δ= 113.7 (d) $^{3}J_{P\text{-}C}$ = 14.1	δ= 55.4 (s)	δ= 42.9 (d) $J_{P\text{-}C}$ = 51.4	δ= 24.3 (d) $^{2}J_{P\text{-}C}$ = 10.0	δ= 25.5 (d) $^{3}J_{P\text{-}C}$ = 3.9	**-**
[Zn(μ-DTFA³)₂(DTFA³)₂]	**R³= *sec*-butyl-** 	δ= 162.0 (d) $^{4}J_{P\text{-}C}$ = 2.9	δ= 132.9 (d) $^{2}J_{P\text{-}C}$ = 12.1	δ= 125.1 (d) $J_{P\text{-}C}$ = 76.3	δ= 113.6 (d) $^{3}J_{P\text{-}C}$ = 13.9	δ= 55.4 (s)	δ= 45.6 (d) $J_{P\text{-}C}$ = 48.1	δ= 12.4 (d) $^{2}J_{P\text{-}C}$ = 16.8	δ= 22.8 (s)	δ= 12.4 (s)
[Zn(μ-DTFA⁴)₂(DTFA⁴)₂]	**R⁴= *iso*-propyl-** 	δ= 162.1 (d) $^{4}J_{P\text{-}C}$ = 2.8	δ= 133.0 (d) $^{2}J_{P\text{-}C}$ = 12.5	δ= 125.9 (d) $J_{P\text{-}C}$ = 78.1	δ= 113.6 (d) $^{3}J_{P\text{-}C}$ = 13.9	δ= 55.4 (s)	δ= 38.9 (d) $J_{P\text{-}C}$ = 49.6	δ= 16.3 (d) $^{2}J_{P\text{-}C}$ = 1.0	-	-

Chemical shifts (δ) are reported in ppm. *J* values are reported in Hz. s: singlet; d: doublet; t: triplet; dd: doublet of doublets; m: multiplet.

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REFERENCES

1. Mc.Cleverty J A, Rick S Z, Kowalski N, Bailey A, Mulvaney R, O'Cleirigh D A. Aspects of the Inorganic Chemistry of Rubber Vulcanisation. Part 4.1 Dialkyl- and Diaryl-dithiophosphate and –dithiophosphinate Complexes of Zinc: Phosphorus-31 Nuclear Magnetic Resonance Spectral Studies and Structures of [NMe4][Zn{S,P(OC6H4Me-p)$_2$}$_3$] and [Et4][Zn(S$_2$PPh$_2$)$_3$]. J. Chem. Soc. Dalton Trans. 1983; 627-34. DOI 10.1039/DT9830000627.

2. Satake Y, Kashiwadate K, Iizuka Y, Kouyama T, Katto T, Shiiki Z. Poly(arylene thioether-ketone) compositions improved in both melt stability and crystallinity. 1989: may 2; US 4,826,906.

3. Pradip K G, Deba P P, Neeiotpal S. Di(2-methyl- 5-chlorophenyl) dithiophosphinate and its copper(II) derivative as antioxidant lubricating oil additive. Indian J. Chem. Technol. 1995; 2(1): 46-8. http://nopr.niscair.res.in/handle/123456789/31090.

4. Ziyatdinova G K, Budnikov G K, Samigullin A I, Gabdullina G T, Sofronov A V, Al′metkina, L. A., Nizamov, I. S., Cherkasov, R. A.: Electrochemical determination of synthetic antioxidants of bisdithiophosphonic acids. J. Anal. Chem. 2010; 65: 1273–1279. DOI: 10.1134/S1061934810120129.

5. Yagishita K, Konishi S. Lubricating oil additive and lubricating oil composition. 2013; US 8,481,467.

6. Grigorieva N A, Pashkov G L, Fleitlikh I Yu, Nikiforova L K, Pleshkov M A. Nickel extraction from sulfate media with Cyanex 301 in the presence of electron donor additives. Hydrometallurgy 2010; 105: 82–8. DOI 10.1016/hydromet.2010.08.001.

7. Xihong H, Guoxin T, Jing C, Linfeng R, Characterization of the extracted complexes of trivalent lanthanides with purified cyanex 301 incomparison with trivalent actinide complexes. Dalton Trans. 2014; 43: 17352–17357. DOI**:**10.1039/C4DT02553A.

8. Jing C, Meng W, Xuegang L, Jianchen W. Back-end of nuclear fuel cycle in China. Progr. in Nucl. Energy, 2012; 54: 46-8, DOI:10.1016/j.pnucene.2011.09.003

9. Artem'ev A V, Malysheva S F, Gusarova N K, Belogorlova N A, Fedorov S V, Timokhin B V, Smirnov V I, Trofimov B A. Novel Quinine, Lupinine, And Anabasine Derivatives Containing Dithiophosphinate Groups. Chem. Heterocycl. Compd. 2012 Jun; 48(3): 448-52. DOI:10.1007/s10593-012-1013-3.

10. Michalski J, Potrzebowski M, Lopusinski A. Preparation of S-brom-dithiophosphoric, dithiophosphonic and dithiophosphinic acid derivatives, 1984; US 4,470,933.

11. Kabra V, Mitharwal S, Singh S. Synthesis and Insecticidal Activity of Novel Dithiophosphonates. Phosphorus, Sulfur Silicon Relat. Elem. 2009;184: 2431–42. DOI: 10.1080/10426500802487748

12. Bara A C, Silvestru C, Haiduc I. Antitumor organometallics. I. Activity of some diphenyltin(IV) and diphenylantimony(III) derivatives on in vitro and in vivo Ehrlich ascites tumor. Anticancer Res. 11, 1651-1656, 1991.

13. Bellande E, Comazzi V, Laine J, Lecayon M, Pasqualini R, Duatti A, Hoffschir D, Synthesis and Biodistribution of Nitrido Technetium-99m Radiopharmaceuticals with Dithiophosphinate Ligands:a Class of Brain Imaging Agents. Nucl. Med. and Biol. 1995; 22(3):315-20. DOI: 10.1016/0969-8051(94)00107-U.

14. Durckheimer W, Bormann D, Ehlers E, Schrinner E, Heymes R. Cephem Derivates. 1988; US 4758556.

15. Yordanov, N D, Gochev G, Angelova O, Macicek J. EPR Investigations on bis(dithiophosphinato)copper(II) complexes magnetically diluted in the corresponding nickel(II) single crystals and X-ray crystal structure of bis(di-n-propyldithiophosphinato)nickel(II). Polyhedron 1990; 9: 2597-2602. https://doi.org/10.1016/S0277-5387(00)86834-5.

16. Byrom C, Malik M A, O'Brien P, White A J P, Williams D J. Synthesis and X-ray single crystal structures of bis(diisobutyldithiophosphinato)cadmium(II) or zinc(II): Potential single-source precursors for II/VI materials. Polyhedron, 2000; 19: 211-15. https://doi.org/10.1016/S0277-5387(99)00352-6.

17. Calligaris M, Nardin G, Ripamonti A. Crystal and Molecular Structure of Zinc(II) and Cobalt(II) Diethyldithiophosphinates, J.

Chem. Soc. A, 714-22, 1970. DOI: 10.1039/J19700000714.

18. Sağlam E G, Çelik Ö, Yılmaz H, İde S. Synthesis, spectroscopic characterization and X-ray single crystal structures of *trans*–Bis [4–methoxyphenyl (3-methylbutyl) dithiophosphinato]nickel(II) and Bis[4-methoxyphenyl(3-methylbutyl)dithiophosphinato]cobalt(II) complexes. Transition Met. Chem. 2010; 35: 399-405. DOI:10.1007/s11243-010-9341-6.

19. Sağlam E G, Yılmaz H, Dal H, Hökelek T, Synthesis and Spectroscopic Characterizations of Novel Ni(II) and Co(II) Dithiophosphinate Complexes, and X-Ray Studies on the Ni(II) Complex Phosphorus, Sulfur Silicon Relat. Elem. 2012; (2)187: 213-24. DOI: 10.1080/10426507.2011.601239.

20. Hoffmann H, Schumacher G, Umsetzungen mit p-methoxyphenyl-dithio-phosphonsäure-anhydrid, Tetrahedron Lett. 1967; 31:2963-6. DOI:10.1016/50040-4039(00)90895-5.

21. Diemert K, Kuchen W. "Zur Kenntnis der Organophosphorverbindungen XVII, Dithiophosphinsauren RR'P(S)SH, Ihre Synthese, Derivate und MetallKomlexe", Phosphorus, Sulfur Silicon Relat. Elem. 1977; (2): 131-6. DOI: 10.1080/03086647708077702.

22. Casas J S, García-Tasende M S, Sánchez A, Sordo J, Castellano E E, Zukerman-Schpector J. Synthesis, crystal structure and spectroscopik properties of bis (diphenylditihiophosphinato)cadmium(II). Inorg. Chim. Acta 1994; 219: 115-9. DOI:10.1016/0020-1693(94)03822-8.

23. Sunder S, Hanlan L, Bernstein J. Resonance Raman Spectra of Metal Complexes of Substituted Dithiophospinic Acids., J. Inorg. Chem. 1975;14: 2012-3, DOI: 10.1021/ic50150a058.

24. Czernuszewicz R, Maslowsky E, Jr Nakamoto K, Infrared and Raman Spectra of Bis(imidotetraphenyldithiodiphosphino-S,S') Complexes with Cu(II), Co(II) and Fe(II), Inorg. Chim. Acta, 1980; 40: 199-202. DOI: 10.1016/S0020-1693(00)92004-8.

25. Chakravarty M, Pailloux S, Ouizem S, Smith K A, Duesler E N, Paine R T, Williams N J, Hancock R D. Synthesis and metal coordination chemistry of (phenyl)(pyridin-2-ylmethyl)phosphinodithioic acid, [2-C_5H_4N]CH_2P(S)(SH)(Ph). 2012: 33: 327-35. DOI:10.1016/j.poly.2011.11.041.

26. Keck H, Kuchen W. Massenspektrometrische Untersuchungen An Organophosphorverbindungen IV. Über den massenspektrometrischen Zerfall von Dithiophosphinsären, Phosphorus, Sulfur Silicon Relat. Elem., 1983; 14: 225-8. DOI:10.1080/03086648308075944.

27. Heinz S, Keck H, Kuchen W. Mass spectrometric studies of dithiophosphinato metal complexes. Org. Mass Spoctrom. 1984; 19: 82-6.DOI:10.1002/oms.120190207.

28. Christoph D, Keck H, Kuchen W, Mathow J, Wunderlich H. Synthesis, properties and structure of bis(dialkyldithiophosphinato)manganese(II) complexes. Inorg. Chim. Acta 1987; 132,: 213-5. DOI:10.1016/S0020-1693(00)81744-2.

29. Mohan P N, Keck H, Kuchen W, Haegele G. Metal complexes of phosphinic acids—XII: Praseodymium(III), neodymium(III) and europium(III) complexes of dimethyldithiophosphinic acid. J. Inorg. & Nuclear Chem. 1977; 39: 833-5. DOI:10.1016/0022-1902(77)80164-4.

30. Sağlam E G, Nurcan A, Berline M-S, Hakan D, Tuncer H. Syntheses and Structural Characterizations of a New Benzyl(4-Methoxyphenyl)Dithiophosphinic Acid and Its Ni(II), Co(II), Zn(II), Cd(II) and Ni-Pyridino Complexes. Phosphorus, Sulfur Silicon Relat. Elem. 2016; 191(1): 22-9. DOI;10.1080/10426507.2015.1067206.

31. Karakuş M, Yılmaz H, Bulak E, Lonnecke, P. Bis{μ-[O-cyclopentyl(4-methoxyphenyl) dithiophosphonato]1κ: S,2κ: S-[O-cyclopentyl (4- methoxyphenyl) dithiophosphonato] 1κ2S,S } dizinc (II). Appl. Organometal. Chem. 2005; 19: 396-7. DOI:10.1002/aoc.850.

32. Karakuş M, Yılmaz H, Özcan Y, S İde. Appl. Crystallographic report: Bis{μ-[O-cyclopentyl (4-methoxyphenyl) dithiophosphonato] 1κ:S,2κ: S-[O-cyclopentyl(4-methoxyphenyl) dithiophosphonato]-1κ2S,S'}dicadmium(II). Organometal. Chem. 2004; 18: 141-142.DOI: 10.1002/aoc.588.

33. Ramirez R G, Toscano R A, Silverstu C, Haiduc I. Studies on inorganic tin diphenyldithiophosphinates. Crystal and molecular structure of CIS-dichlorobis(diphenyldithiophosphinato)tin(IV). Polyhedron 1996; 15(21): 3857–67.DOI:10.1016/0277-5387(96)00100-3.

34. Karakuş M, Yılmaz H. Synthesis and Characterization of Ni(II), Zn(II), and Cd(II) Complexes with Dithiophosphonate Derivatives. Rus. J. Coord Chem 2006; 32(6): 437–43. DOI: 10.1134/S1070328406060078.

35. Przychodzen W. New Products of Reaction of Lawesson's Reagent With Diols. Phosphorus, Sulfur Silicon Relat. Elem. 2004; 179: 1621–33. DOI:10.1080/10426500490466175.