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Synthesis and semi-empirical sparkle PM6 study of substituted dithiophosphoric compounds of gadolinium(III)

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Seven gadolinium(III) derivatives containing dialkyl and alkylene dithiophosphate chelating ligands $[S_2P(OR)_2]_3 \cdot 2CH_3CN$ ($R = Et, n\text{-Pr}, n\text{-Bu}$ and Ph) and $[S_2POR'O]_3 \cdot 2CH_3CN$ ($R' = CH_2CMe_2CH_2, CH_2CEt_2CH_2$ and CMe_2CMe_2) have been synthesized. The metal complexes have been characterized by elemental analyzes, molecular weight determinations, IR, and UV–Visible spectroscopy. Microanalytical data revealed a 1:3 metal–ligand ratio in all complexes. Geometries were fully optimized at the semi-empirical sparkle PM6 level of theory using MOPAC2009 and geometrical structures and electronic properties of the complexes have been evaluated. The optimized geometries were confirmed to be minima on the potential energy surfaces through frequency calculations. Absorption spectra of the complexes have been calculated using ORCA2.9 package utilizing the predicted optimized wave functions. Linear and nonlinear static optical susceptibilities for all complexes were calculated at the same level of theory. The polarizability invariants were, in general, well correlated with the molecular volume and the number of carbons within the alkyl moieties. The largest electric properties were exhibited by the phenyl dithiophosphate complex.

Keywords: Gadolinium; PM6; MOPAC2009; ORCA2.9; Sulfur derivatives

1. Introduction

Lanthanide and actinide complexes to sulfur derivatives of carboxylic and phosphoric acids have been known since the early twentieth century. The first published work mentioning thorium, uranyl, and neodymium dithiocarbamates was reported by Delépine in 1908 [1]. The wide geometric variation of transition [2, 3] and non-transition [4, 5] metal complexes with dialkyl and alkylene dithiophosphates is a consequence of the alternative geometries associated with bidentate bridging, bidentate terminal, and monodentate ligation to the metals.

There are four types of lanthanide dithiophosphate complexes [6] with structures established by X-ray diffraction (figure 1). These adducts may be classified as: (i) neutral tris(dithiophosphato) Ln(III) adducts, $Ln[(OC_2H_5)_2PS_2]_3[(C_6H_5CH_2)SO]_2$, in which the metal is eight-coordinate (distorted-square antiprism or dodecahedral) [7–10]; (ii) anionic

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tetrakis(dithiophosphato) metallates, $\{\text{Ln}[(\text{OC}_2\text{H}_5)_2\text{PS}_2]_4\}\{\text{As}(\text{C}_6\text{H}_5)_4\}$, with dodecahedral geometry, achieved by coordination with eight sulfurs from the four isobidentate ligands [11, 12]; (iii) cationic bis(dithiophosphato) metal complexes, with a non-coordinated dithiophosphate as a counter ion. The central metal of the cationic complex is seven-coordinate in a pentagonal bipyramidal geometry, wherein the four sulfurs of two dithiophosphates and oxygen of one benzamide occupy equatorial positions, while the other two benzamide oxygens are axial. The molecular formula of the complex is $[\text{Ln}\{[(\text{CH}_3)_2\text{CHO}]_2\text{PS}_2\}_2(\text{H}_2\text{NCOC}_6\text{H}_5)_3][[(\text{CH}_3)_2\text{CHO}]_2\text{PS}_2]$ [13]; (iv) The final possibility for lanthanide dithiophosphate complex, composed of both cationic and anionic species, was reported by Okhi *et al.* Metal of the cationic complex is seven-coordinate with pentagonal bipyramidal geometry. However, the metal of the counteranion is eight coordinate with dodecahedral geometry. Okhi's complex has the molecular formula $[\text{Nd}\{(\text{C}_3\text{H}_7\text{O})_2\text{PS}_2\}_2\{(\text{C}_4\text{H}_9)_2\text{SO}\}_3][\text{Ln}\{(\text{C}_3\text{H}_7\text{O})_2\text{PS}_2\}]$ [8, 14].

Lanthanides favor high coordination states, so that not only the intended donor, e.g. dialkyl and alkylene dithiophosphoric acids, but also solvents are often involved in ligation to the metal, saturating the metal coordination sphere. However, for bulky ligands such as cyclohexyl phosphine donors, solvent ligation may not occur.

Trivalent lanthanides are hard metals and readily form complexes with hard ligands; there is extensive coordination chemistry of lanthanides with O-donors such as gadolinium(III) (Gd(III)) acetate [15]. Fewer complexes with N-donors such as acetonitrile [16] have been reported, although the number is still considerable [17].

Most lanthanides can form complexes with high coordination numbers. One such group of complexes, the Gd(III) polyaminopolycarboxylates, are of great medical significance as contrast enhancers in magnetic resonance imaging (MRI) [18–20]. The usefulness of Gd(III) complexes in MRI can be attributed to the high electron spin of the metal and its remarkable ability to enhance the relaxation rate of protons in aqueous media of surrounding tissues [21, 22].

In this work, we report reaction of Gd(III) with dialkyl and alkylene dithiophosphoric acids followed by a theoretical investigation of the corresponding adducts to elucidate the changes in geometrical and electrical parameters which occur during complexation.

2. Experimental

Moisture was carefully excluded throughout all experimental manipulations. Dialkyl and alkylene dithiophosphoric acids were prepared according to reported procedures [23]. Anhydrous Gd(III) chloride was used as received from Aldrich, without further drying. UV spectra were recorded in ethanol from 200–500 nm on a UV-visible spectrophotometer-1601 (Shimadzu, Japan). IR spectra were recorded as Nujol mulls using CsI cells from 200–4000 cm^{-1} on a FTIR 8201 PC spectrometer. Analyzes for carbon, hydrogen, and nitrogen were carried out using EA 1110-CHNS Elemental Analyzer (CE Instrument). Sulfur was determined by Messenger's method [24] as barium sulfate. The gadolinium content in each complex was determined by precipitation from the corresponding complex as Gd_2O_3 and then calculated using the formula:

$$\% \text{Gd} = 0.868 \times \frac{\text{weight of } \text{Gd}_2\text{O}_3 \text{ precipitated}}{\text{weight of complex taken}}$$

The gadolinium complexes were prepared by reacting Gd(III) chloride with dialkyl and alkylene dithiophosphoric acids by dissolving Gd(III) chloride (0.33 g, 1.27 mmol) in 30 ml acetonitrile at 50 °C for 1 h under constant stirring. Each ligand (3.80 mmol), whether HS₂P(OR)₂ or HS₂P(OR')₂, was dissolved in 10 mL acetonitrile and then added dropwise to the gadolinium solution. Each of the reaction mixtures was refluxed for 5 h under constant stirring. To monitor the progress of reactions and to establish the identity and purity of reactants and products, thin layer chromatography was performed on aluminum slides coated with silica gel 60, using appropriate solvent systems; spots were visualized under ultra-violet light. The excess solvents in all reactions were removed *in vacuo*. The obtained adducts were washed with copious amounts of *n*-hexane and then dried under high vacuum for 24 h.

3. Computational details

The molecular structures of the title compounds were constructed using Gabedit [25] and then fully optimized at the semi-empirical sparkle PM6 level of theory [26] using MOPAC2009 [27]. Molecular vibrational frequencies for the optimized structures were calculated at the same level of theory and corrected by means of the scaling factor (1.061) developed by Fekete *et al.* [28]. Linear and nonlinear static optical susceptibilities for all isomers were calculated at the same level of theory utilizing the optimized wave functions. UV–visible absorption spectra of the gadolinium complexes were estimated at the CIS/TD-DFT(BP86)/alrich-VDZ level of theory by means of ORCA2.9 software (an *ab initio*, DFT and semi-empirical SCF-MO package) [29–31]. Optimized structures, vibrational modes of frequency, and UV–visible spectra were depicted using Gabedit graphical user interface software.

4. Results and discussion

4.1. Micro analytical results

Reactions of Gd(III) chloride with dialkyl and alkylene dithiophosphoric acids were carried out in 1:3 stoichiometric ratios in refluxing acetonitrile. Colors of the reaction media changed from colorless to yellow during the reactions and the title adducts were formed according to the following equations:



R = Et, Pr-*n*, Bu-*n* and Ph; R' = –CH₂CMe₂CH₂–, –CH₂CEt₂CH₂– and –CMe₂CMe₂–

Experimental details such as percentage yields, melting points(mp), and molecular weights of the isolated tris (dialkyl and alkylene dithiophosphato) Gd(III) adducts, as well as the elemental analyzes of their sulfur, gadolinium, and nitrogen contents are recorded in table 1. Complexes 1–3 and 7 were isolated as sticky yellow solids, while 4–6 were fine

Table 1. Physical and elemental analyzes data of the prepared gadolinium complexes.

No.	Complexes	mp	Yield (%)	M Found (Calc.)	Elemental analysis			
					S (%)	Gd (%)	N (%)	C (%)
1	$[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2\}_3]$	128–130	68.7	784.5 (795.0)	24.05 (24.20)	19.65 (19.78)	3.48 (3.52)	23.92 (24.17)
2	$[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_3\text{H}_7)_2\}_3]$	133–135	70.4	868.2 (879.2)	21.68 (21.88)	17.69 (17.89)	3.14 (3.18)	29.75 (30.05)
3	$[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_4\text{H}_9)_2\}_3]$	137–139	73.8	950.1 (963.4)	19.73 (19.97)	16.13 (16.32)	2.88 (2.91)	34.58 (34.91)
4	$[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_6\text{H}_{13})_2\}_3]$	129–131	65.6	1069.7 (1083.3)	17.59 (17.76)	14.42 (14.52)	2.56 (2.59)	24.18 (24.39)
5	$[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O})_3\}]$	130–132	50.2	820.2 (830.8)	22.95 (23.16)	18.72 (18.93)	3.34 (3.37)	27.23 (27.47)
6	$[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OCH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{O})_3\}]$	134–137	78.5	905.8 (914.9)	20.86 (21.03)	16.97 (17.19)	3.05 (3.06)	32.48 (32.82)
7	$[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})_3\}]$	126–128	77.1	863.3 (872.9)	21.79 (22.04)	17.85 (18.02)	3.17 (3.21)	29.98 (30.27)

Nomenclature of the complexes:

- 1: Bis(methylisocyanide)tris(*O, O'*-diethyl)dithiophosphato)Gd(III);
- 2: Bis(methylisocyanide)tris(*O, O'*-di-n-propyl)dithiophosphato)Gd(III);
- 3: Bis(methylisocyanide)tris(*O, O'*-di-n-butyl)dithiophosphato)Gd(III);
- 4: Bis(methylisocyanide)tris(*O, O'*-diphenyl)dithiophosphato)Gd(III);
- 5: Bis(methylisocyanide)tris(*O, O'*-(2,2-dimethyl)propyl)dithiophosphato)Gd(III);
- 6: Bis(methylisocyanide)tris(*O, O'*-(2,2-diethyl)propyl)dithiophosphato)Gd(III);
- 7: Bis(methylisocyanide)tris(*O, O'*-(1,1,2,2-tetramethyl)ethyl)dithiophosphato)Gd(III).

yellow powders. All of the complexes were soluble in common organic solvents such as chloroform, dichloromethane, and benzene. The solid compounds are insoluble in n-hexane which was used for washing and purification of the complexes. mp of the complexes, if **6** with aromatic residual substituent is excluded, are in excellent correlation with the molecular weights (M) of the complexes. This melting point correlation can be expressed by the formula:

$$mp = 0.595 M + 80.755, R^2 = 0.9969$$

Molecular weights determination (MWDs) and elemental analyzes of the sulfur and gadolinium contents confirmed the expected monomeric nature of each of these complexes (figure 1). In addition, MWDs provided strong evidence of the presence of two ligating solvent molecules (CH_3CN) in each gadolinium coordination sphere, consistent with elemental analyzes of the nitrogen residues within these adducts. Calculated molecular weights of all complexes deviated by not more than 1.1–1.4% from experimental ones. Sulfur, gadolinium nitrogen, and carbon contents deviated from that of the experimental ones by 0.8–1.2%, 0.7–1.3%, 0.89–1.26%, and 0.86–1.04%, respectively. MWDs and elemental analyzes gave an estimate of the coordination number (CN=8) of the gadolinium metals within these complexes. Estimation of the coordination number of these complexes could be accomplished using the following equation:

$$\text{CN} \approx 2 \left(\frac{M_{\text{complex}} - (M_{\text{Gd}} + 2M_{\text{CH}_3\text{CN}})}{M_{\text{S}_2\text{P}(\text{OR})_2}} \right) + 2$$

4.2. Geometrical structures

The optimized geometrical parameters (bond lengths and bending angles) obtained at the semi-empirical sparkle PM6 level of theory are listed in Supplementary material without comparison with the corresponding crystallographic data, since single crystal X-ray diffraction was not possible due to crystallization difficulty. A schematic presentation of the bonding modes of the ligating atoms around the gadolinium core is depicted in figure 2. The optimized geometrical structures of the title compounds with the numbering schemes are shown in figure 3 for **1**, **2**, **3**, and **4** where hydrogens are omitted for clarity. Optimized geometries for all isolated structures were confirmed to be minima (true stationary points) on the potential surface energy as revealed by inexistence of imaginary frequencies. Thermodynamic stability of the complexes was established through energy calculations, where the total energy of each complex is lower than the energy sum of its constituents.

As shown in the selected figures, the metal of each complex is eight coordinate, with dodecahedral geometry. Each $(\text{OR})_2\text{PS}_2^-$ ligand is chelated to the metal via two sulfurs. Two of the $(\text{OR})_2\text{PS}_2^-$ chelating ligands span m-edges while the other one spans an a-edge as shown in figure 2. The two CH_3CN ligands are ligated via nitrogen at both ends of the base of a trapezium. From the optimized geometries the metal and the ligating atoms form nearly a trapezium plane with slight deviation from planarity (the average deviation is 4.0°). The central Gd–S–S–P ring moieties in all complexes are twisted where the familiar propeller orientations are adopted. The aromatic rings in **4** are in propeller orientations as

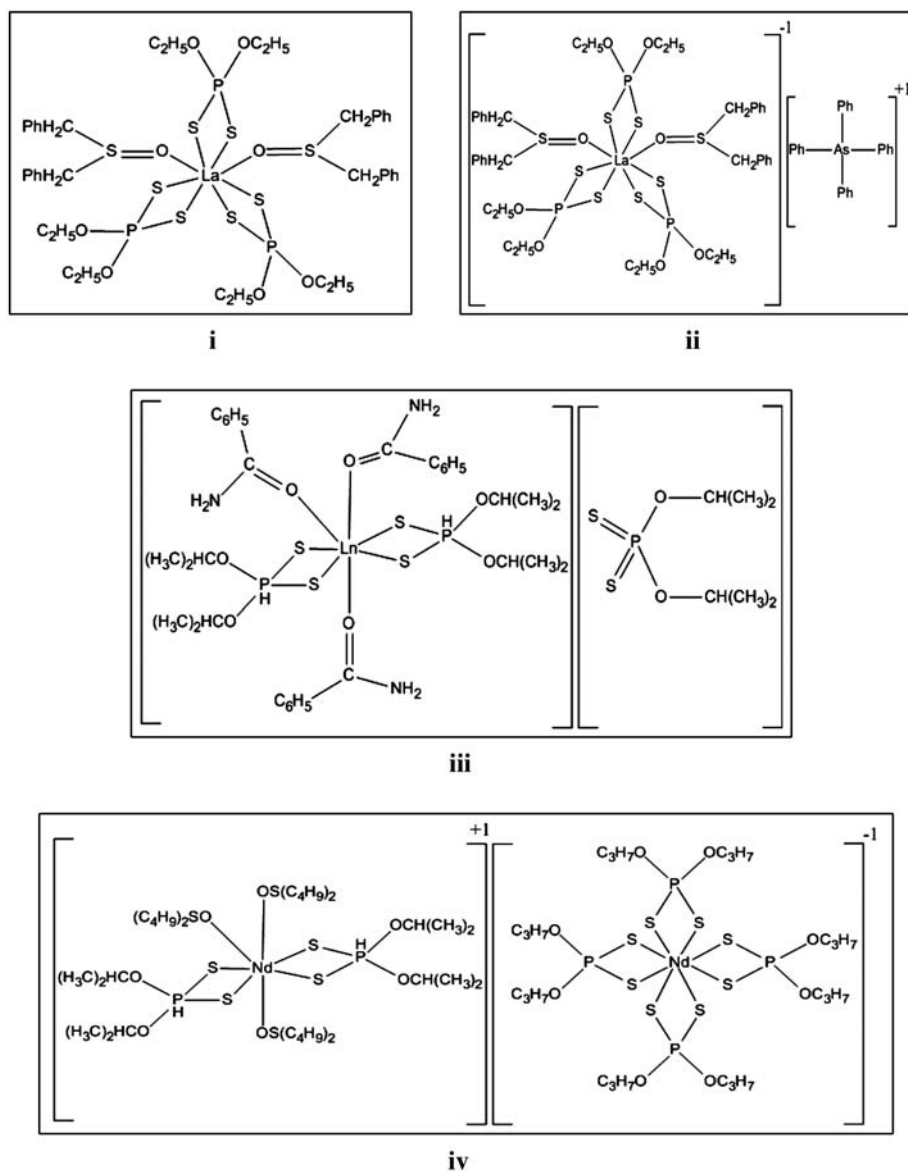


Figure 1. Representative structures of the four types of lanthanide dithiophosphate complexes classified as the following: (i) Neutral tris(dithiophosphato) Ln(III) adducts, (ii) Anionic tetrakis(dithiophosphato) metallates, (iii) Cationic bis(dithiophosphato) metal complex, and (iv) the cationic-anionic lanthanide complex.

well, while the P–O–Pr–O six-member rings in **5** and **6** are all twisted, adopting either chair or half chair conformations.

Two factors are important in favoring eight coordination for these complexes, size and charge of Gd cation. The gadolinium cation is large enough to accommodate eight ligands (two monodentate and three bidentate) without crowding. The eight σ -bonds from the weakly electronegative *S* and moderately electronegative *N* of the ligands would result in

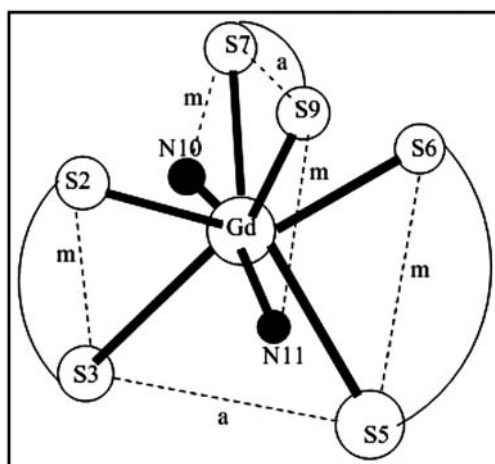


Figure 2. A schematic presentation of the bidentate ligands around the metal.

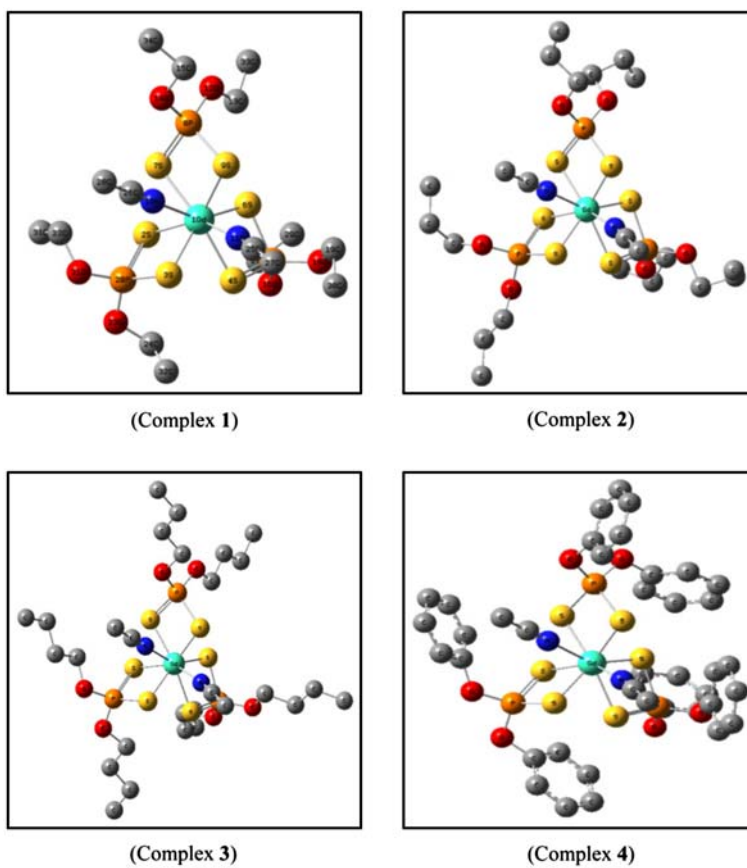


Figure 3. A perspective drawing of 1–4 with the numbering scheme on 1.

accumulation of electron density on the metal and thus the adduct stability would be negatively influenced. The high formal oxidation state (+3) of the metal helps prevent excess build-up of electron density on Gd and thus the complexes are stabilized.

The reliability of semi-empirical PM6 sparkle in predicting geometrical parameters of sulfur-ligated complexes was assessed by simple comparison between PM6 optimized geometries and the corresponding experimental single X-ray diffraction data. The comparison included small organic sulfur-containing ligands as well as large Nd [9] acceptors to simulate the Gd complexes in the study. It was found that bond distances and angles were in reasonable agreement with the corresponding single crystal X-ray diffraction data ($R^2=0.96$ and 0.85 , respectively; $R^2=0.92$ considering Nd–S bond lengths alone). The performance of PM6 proved even better in the case of small organic sulfur-containing compounds, for which $R^2=0.98$ for the bonding distance.

Selected bond distances and angles calculated by PM6 for the respective Gd adducts are presented in Supplementary Material. The two bond distances (d_{S-P}) within the same ring (Gd–S–P–S) are significantly different. One bond is shorter than the other indicating that one of the S–P bonds, the shorter one, would have more double bond character than the other. Therefore, it is likely that the P=S double bonds of the ligands are localized. This result was confirmed experimentally with two different vibrational frequencies recorded for the P–S and P=S bonds.

Bond lengths for the Gd–S pairs of each coordinated ligand are not equal; moreover, differing significantly from one coordinated ligand to another within the same complex. One Gd–N bond was also slightly longer than the other one within the same complex, probably because of steric effect from vicinal coordinated ligands.

Calculations have also shown that the N–Gd–N angle differs remarkably from one adduct to another. The smallest N–Gd–N angle was reported for the phenyl dithiophosphate complex (figure 3, complex (4)), while the largest was attributed to the corresponding 2,2-diethylpropyl dithiophosphate adduct. The dihedral measurements showed that the Gd–S–P–S rings in all structures were slightly twisted, having Gd–S–P–S dihedral angles slightly larger than the zero for planarity, ranging from 1.2° to 5.8° .

4.3. IR spectra

Significant IR bands of the metal complexes with their assignments are listed in table 2. Spectra of the free ligands, dialkyl and alkylene dithiophosphoric acid, show broad medium intensity bands at $2400\text{--}2550\text{ cm}^{-1}$ due to $\nu_{(S-H)}$ [32] which vanish in complexes, confirming complexation. Spectra of the metal complexes exhibit strong bands at $999\text{--}1160\text{ cm}^{-1}$ and $846\text{--}918\text{ cm}^{-1}$, attributed to $\nu_{(P-O-C)}$ and $\nu_{(P-O-(C))}$ stretching vibrations, respectively [33]. Strong bands were assigned to dioxaphospholane and dioxaphosphorinane ring vibrations at $956\text{--}999\text{ cm}^{-1}$, probably coupled with C–C stretching vibrations [34]. Sharp bands present at $667\text{--}691\text{ cm}^{-1}$ were assigned to $\nu_{(P=S)}$ [35]. Bands of medium intensity at $515\text{--}600\text{ cm}^{-1}$ may be assigned to $\nu_{(P-S)}$ asymmetric and symmetric vibrations [36]. The presence of coordinated CH_3CN in the Gd(III) complexes was further confirmed by strong bands at $2250\text{--}2255\text{ cm}^{-1}$ due to $\nu_{(CN)}$ [16]. The bands observed at $340\text{--}350\text{ cm}^{-1}$ were classified $\nu_{(Gd-S)}$ [37] while bands due to Gd–O [38] were found at $340\text{--}350\text{ cm}^{-1}$.

The scaled symmetric stretching frequencies calculated with the sparkle PM6 semi-empirical level of theory are in agreement with the experimental values. For instance, the experimental values for $\nu_{(Gd-S)}$ were $340\text{--}350\text{ cm}^{-1}$. The corresponding theoretical values

Table 2. IR spectral data of Gd(III) dialkyl and alkylene dithiophosphates.

No.	Compound	$\nu_{(P)-O-C}$	$\nu_{P-O-(C)}$	Ring vibration	ν_{P-S}	ν_{P-S}	ν_{C-N}^*	ν_{Gd-S}
1	Gd[S ₂ P(OEt) ₂] ₃ ·2CH ₃ CN	1020.3 s	918.1 s	–	669.0 m	522.6 w	2254.6 s	
2	Gd[S ₂ P(OPr-n) ₂] ₃ ·2CH ₃ CN	999.1 s	846.7 s	–	667.3 m	530.4 m	2254.6 s	341.5 w
3	Gd[S ₂ P(OBu-n) ₂] ₃ ·2CH ₃ CN	1002.9 s	846.7 s	–	678.9 m	550.0 m	2253.6 s	343.2 w
4	Gd[S ₂ P(OPh) ₂] ₃ ·2CH ₃ CN	1159.1 s	900.7 s	–	688.5 s	522.7 m	2251.9 s	349.1 m
5	Gd[S ₂ POCH ₂ CMe ₂ CH ₂ O] ₃ ·2CH ₃ CN	1042.5 s	840.0 s	964.3 s	690.8 s	515.0 s	2252.7 s	346.6 w
6	Gd[S ₂ POCH ₂ CEt ₂ CH ₂ O] ₃ ·2CH ₃ CN	1062.7 s	860 m	991.3 s	689.8 s	540.2 m	2254.6 s	347.7 w
7	Gd[S ₂ POCMe ₂ CMe ₂ O] ₃ ·2CH ₃ CN	1010.6 s	858.3 s	960.0 m	682.8 s	592.0 s	2252.7 s	348.2 m

m=medium, s=strong and w=weak absorption bands.

*This band due to the solvent (acetonitrile).

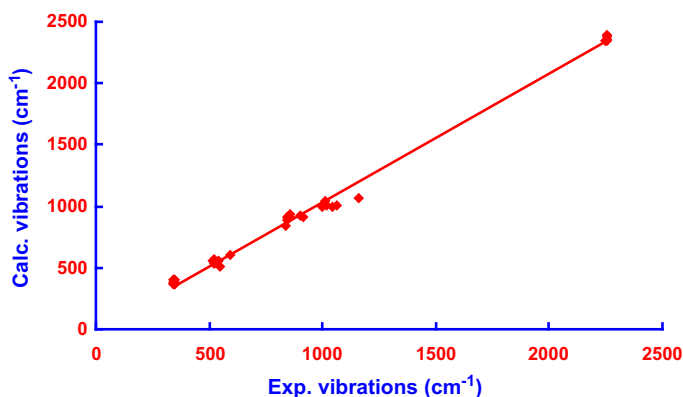


Figure 4. Correlation of experimental vibrational modes of frequencies with the corresponding PM6 sparkle calculated modes.

were 468–407 cm⁻¹. The $\nu_{(CN)}$ bands for the compounds were at 2225–2256 cm⁻¹, while the calculated values were 2300–2350 cm⁻¹. Theoretical $\nu_{(S-P)}$ bands were observed at 514–570 cm⁻¹ while experimental values are 515–600 cm⁻¹. Our theoretical findings for $\nu_{(S-P)}$, $\nu_{(P)-O-(C)}$, and $\nu_{P-O-(C)}$ bands of complexes are 650–675 cm⁻¹, 900–1100 cm⁻¹, and 912–1025 cm⁻¹, while the experimental counterparts are 667–691 cm⁻¹, 999–1160 cm⁻¹, and 846–918 cm⁻¹, respectively. Figure 4 displays plot of the theoretical frequencies vs. the experimental vibrational modes where a very nice correlation factor is obtained; $R^2=0.9959$.

4.4. UV Spectra

UV spectra of tris(neopentylene dithiophosphato) Gd(III) show new bands at $\lambda_{max}=276$ nm (figure 5). The comparison between neopentylene dithiophosphoric acids with the desired complexes reflected a shift in λ_{max} ($\Delta\lambda=19$ nm) indicating formation of new compounds.

Excited states of the metal complexes were modeled using ORCA calculations via CIS/TD-DFT(BP86)/alrich-VDZ level of theory. In CIS [39], we consider every possible single excitation that can be formed by excitation from the electronic ground state of occupied orbital to the virtual orbital. Inner shells are usually frozen for this procedure.

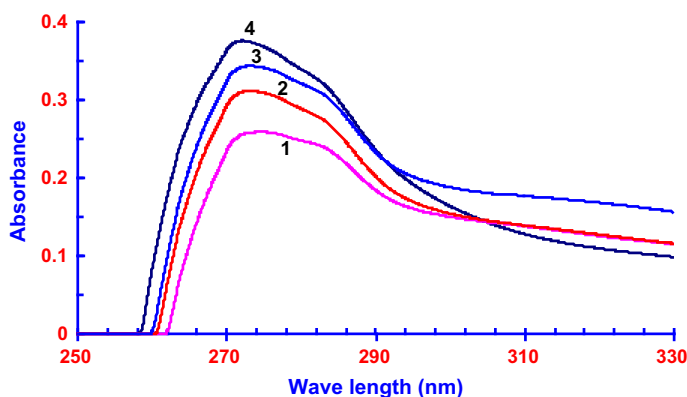


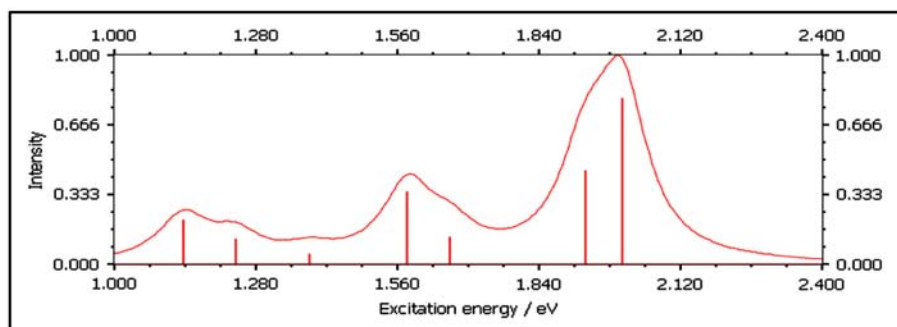
Figure 5. λ_{\max} given in nm for 1–4.

Transition intensity from ground state (g) to excite one (e) is expressed in this work in terms of oscillator strength f_{eg} ; $f_{eg} = \left(\frac{4\pi m_e}{3e^2 \hbar}\right) \nu_{eg} |\mu_{eg}|^2$, where ν_{eg} is the excitation frequency, μ_{eg} is the transition dipole moment such that $\mu_{eg} = \langle e | \mu | g \rangle$, and the remaining components are the usual physical constants. The oscillator strength could be expressed as wavenumber ν_{eg} in cm^{-1} and Debye units in case of transition dipole moment in the form: $f_{eg} = 4.70165 \times 10^{-7} cm D^{-2} \nu_{eg} |\mu_{eg}|^2$ [40].

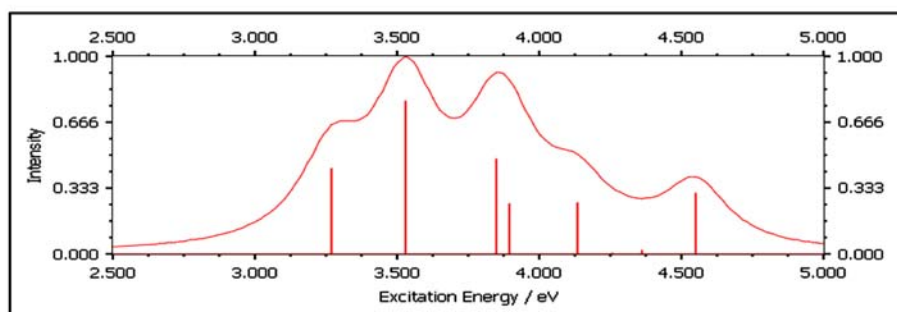
Oscillator strengths in addition to the estimated CIS vertical excitation energies of selected excited states of 1, 2, 3, and 4 are recorded in table 3 while figure 6 represents the corresponding absorption spectra of these complexes.

Table 3. CIS/TD-DFT(BP86)/Alrich-VDZ calculated vertical transition energies (E, eV) and oscillator strengths for 1–4.

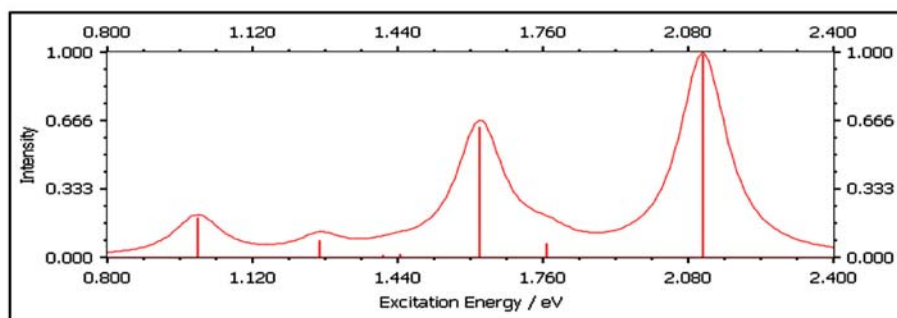
Complex	State	E_{eV}	f_{eg}
1	59a \rightarrow 99a	0.156	0.0006
	83a \rightarrow 99a	1.024	0.0289
	93a \rightarrow 99a	1.271	0.0145
	93a \rightarrow 99a	1.412	0.0014
	79a \rightarrow 99a	1.666	0.0700
2	110a \rightarrow 118a	3.272	0.0111
	114a \rightarrow 118a	3.531	0.0216
	110a \rightarrow 118a	3.849	0.0224
	119a \rightarrow 118a	3.899	0.0207
	109a \rightarrow 129a	1.299	0.0166
3	76a \rightarrow 135a	0.163	0.0007
	107a \rightarrow 135a	1.000	0.0261
	117a \rightarrow 135a	1.41	0.0019
	77a \rightarrow 135a	1.447	0.0025
	104a \rightarrow 135a	1.622	0.0854
4	98b \rightarrow 146b	1.046	0.0147
	98b \rightarrow 147b	1.076	0.0001
	177b \rightarrow 146b	1.179	0.0002
	128a \rightarrow 147a	1.202	0.0027
	119ba \rightarrow 147b	1.315	0.0097



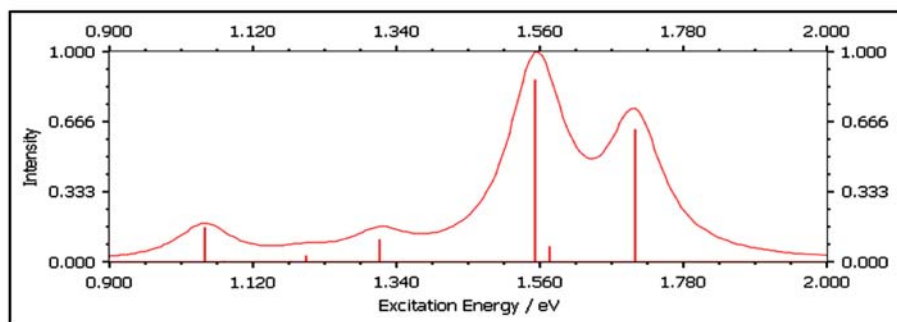
Complex 1



Complex 2



Complex 3



Complex 4

Figure 6. Absorption spectra of 1–4 as predicted by ORCA calculations via CIS configuration interaction.

On the basis of theoretical calculations, spectroscopic data, molecular weights, and comparison with previous work such as $\text{Ln}[\text{S}_2\text{P}(\text{OR})_2]_3 \cdot 2\text{L}$; $\text{Ln} = \text{Nd}$, $\text{R} = \text{Pr-n}$, $\text{L} = \text{PhCONH}_2$ [9], the structures are monomeric eight coordinate, most probably, in dodecahedral geometry where the dithiophosphate moieties are bidentate, occupying six of the coordination sites. The other two sites are occupied by CH_3CN .

4.5. Electronic properties

The electric dipole moment of a molecule plays a crucial role in structural chemistry. This parameter is expected to have different values in different excited states due to possible changes in nuclear rearrangements and redistribution of electron charge density.

When a molecule is subjected to an external electric field E , the molecular charge density may rearrange, hence the dipole moment may change. The influence on the dipole moment could be described mathematically by equation (1) [41]:

$$\mu_{e,j}(E) = \mu_{e,j}(o) + \sum_{j=x}^z \alpha_{ij} E_j + \frac{1}{2!} \sum_{j=x}^z \sum_{k=x}^z \beta_{ijk} E_j E_k + \frac{1}{3!} \sum_{j=x}^z \sum_{k=x}^z \sum_{l=x}^z \gamma_{ijkl} E_j E_k E_l + \dots \quad (1)$$

Here $\mu_{e,j}$ is the j^{th} Cartesian component of the dipole moment, $\mu_{e,j}(o)$ is the dipole in the absence of a field, and $\mu_{e,j}(E)$ is the dipole moment in the presence of a field. The nine independent quantities α_{ij} define the dipole polarizability tensor, and β_{ijk} and γ_{ijkl} are the first and second members of an infinite number of dipole hyperpolarizability tensors. While γ occurs for both centrosymmetric and non-centrosymmetric media, β vanishes for centrosymmetric groups. One would notice a weak component β_μ directed along the applied electric field for systems with $\beta \neq 0$ defined as β_{vec} [42]. The average molecular polarizability $\langle \alpha \rangle$, anisotropy $\Delta \alpha$, and average hyperpolarizabilities β and γ descriptors are calculated utilizing the following expressions:

$$\langle \alpha \rangle = \frac{1}{3} \sum_{i=x}^z \alpha_{ii} \quad (2)$$

$$\Delta \alpha = \frac{1}{\sqrt{2!}} \sum_{\substack{i=x,y \\ j=y,z}} (\alpha_{ii} - \alpha_{jj})^2 \quad (3)$$

$$\langle \beta \rangle_{\text{vec}} = \left(\sum_{i=x}^z \beta_i^2 \right)^{1/2} \quad (4)$$

$$\beta_{i=x,y,z} = \beta_{iii} + \frac{1}{3} \sum_{j \neq i} (\beta_{ijj} + 2\beta_{jji}) \quad (5)$$

$$\gamma = \frac{1}{5} \sum_{\substack{i=x,y,z \\ j=x,y,z}} \gamma_{ijij} = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{zzxx})) \quad (6)$$

Chemical hardness η is defined as the second derivative of the total electronic energy with respect to the number of electrons in the system while external potential is maintained constant [43]; η could be expressed in terms of vertical ionization energy and electron affinity in the form of energy gap between frontier orbitals, the highest occupied molecular

Table 4. Semi empirical PM6 sparkle calculated dipole moments (μ , D), average molecular polarizabilities ($\langle\alpha\rangle$, au), anisotropies ($\Delta\alpha$, au), hyperpolarizabilities (β , au) and ($\bar{\gamma}$, au), molecular global hardnesses (η , eV) and vertical ionization energies (IE , eV).

Electrical invariant	1	2	3	4	5	6
μ/D	5.8718	0.9437	6.1006	8.4769	4.2276	5.2467
α_{xx}	470.9	562.1	625.8	733.6	525.7	552.8
α_{yy}	462.5	493.6	627.0	617.2	529.5	632.5
α_{zz}	482.1	573.5	619.7	809.2	483.5	578.6
$\langle\alpha\rangle$	471.8	543.1	624.2	720.0	512.9	588.0
$\Delta\alpha$	289.0	1270.3	115.1	2843	750.5	1195.4
β_x	154.8	465.63	492.0	779.1	429.0	298.1
β_y	93.9	239.1	242.8	993.6	167.4	172.3
β_z	-630.6	-844.0	-415.0	565.1	-59.7	398.7
$\bar{\beta}$	656.1	993.1	687.9	1383.3	464.4	526.8
$\bar{\beta}/(esu)$	5.7×10^{-30}	8.6×10^{-30}	5.9×10^{-30}	12.0×10^{-30}	12.0×10^{-30}	4.5×10^{-30}
γ_{xxxx}	75737.7	122568.5	78762.3	137393.0	165976.7	95872.6
γ_{yyyy}	49864.3	34761.6	76275.5	37968.0	121658.6	182381.8
γ_{zzzz}	113194.6	150244.7	99516.8	291566.6	78027.3	84729.1
$\bar{\gamma}$	78857.1	88841.5	95622.7	169922.2	118535.3	124970.2
$\bar{\gamma}(esu)$	4.0×10^{-35}	4.5×10^{-35}	4.8×10^{-35}	8.6×10^{-35}	6.0×10^{-30}	6.3×10^{-30}
η/eV	4.303	4.251	4.24	4.097	4.118	4.103
IE/eV	8.913	8.823	8.815	9.044	8.471	8.445

orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), where $\eta = \frac{(\epsilon_{LUMO} - \epsilon_{HOMO})}{2}$ [44]. The PM6 sparkle semi empirical calculated electric parameters using MOPAC 2009 are reported in table 4.

Calculations indicate that the adduct with Ph moieties has the largest dipole moment (8.4769 D), a finding consistent with anisotropy (deviation from spherical symmetry) estimation where this structure has the highest anisotropy value (2843 au) of all the Gd complexes. It also has the largest static linear optical susceptibility $\langle\alpha\rangle$ and static nonlinear first and second-order hyperpolarizabilities $\bar{\beta}$ and $\bar{\gamma}$ (table 4). The polarizability invariants of all complexes are well correlated with their molar volumes (V) and can be represented by the formula $\langle\alpha\rangle = 8.885 V + 93.71$, $R^2 = 0.931$. Furthermore, $\langle\alpha\rangle$ parameters are in good correlation with the number of carbons (n) in the residual substituents represented by the formula $\langle\alpha\rangle = 0.643 n - 33.946$, $R^2 = 0.983$.

An assessment of the hardness and softness invariants for the series of complexes indicates the adduct with Ph moieties has the lowest value of η . One could conclude that this compound would be more available for reaction than the others since the hardness and softness invariants could be utilized to assess the relative reactivities of chemical substances. The estimated vertical ionization potential (IE), which stands for the energy gap between frontier orbitals, would support such conclusion where the compound with Ph moieties has the lowest energy gap between frontier orbitals, *viz.* highest occupied and LUMOs.

5. Conclusion

Seven Gd(III) complexes, $[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2\}_3]$, $[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_3\text{H}_7)_2\}_3]$, $[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_4\text{H}_9)_2\}_3]$, $[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OC}_6\text{H}_5)_2\}_3]$, $[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{O})_3\}]$, $[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}(\text{OCH}_2\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{O})_3\}]$, and $[\text{Gd}(\text{NCCH}_3)_2\{\text{S}_2\text{P}$

(OC(CH₃)₂C(CH₃)₂O)}₃], were synthesized and identified using elemental analyzes, molecular weight determinations, IR, and UV–visible spectroscopy and established as monomers. The geometrical and electrical invariants of the Gd(III) complexes were then theoretically investigated at the parameterized semi-empirical PM6 sparkle level of theory in terms of geometrical and electrical parameters. Absorption spectra of metal complexes were also investigated. The ground state stationary natures of the compounds were confirmed at the potential energy surfaces. Hardnesses, linear, and nonlinear static optical susceptibilities demonstrated that the phenyl dithiophosphosphate complex had the largest values for these invariants. The polarizability invariants are nicely correlated with both molar volumes and number of carbons in alkyl moieties of these complexes.

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References

- [1] M. Delépine. *Bull. Soc. Chim. Fr.*, **3**, 643 (1908).
- [2] R. Abu El Komboz, A.A.S. El. Khaldy, O.S. Nasman, R.M. Baraka. *Phosphorus, Sulfur Silicon Relat. Elem.*, **177**, 567 (2002).
- [3] A.A.S. El. Khaldy, J.R. Durig. *Phosphorus, Sulfur Silicon Relat. Elem.*, **165**, 197 (2000).
- [4] A.M.C. Villegas, R.A. Toscano, M. Hernandez, M.L. Cardoso, P.G.Y. Garcia, R.C. Olivares. *J. Organomet. Chem.*, **690**, 2872 (2005).
- [5] I. Haiduc. *J. Organomet. Chem.*, **29**, 623 (2001).
- [6] I. Haiduc, D.B. Sowerby, S. Fanglu. *Polyhedron*, **14**, 3389 (1995).
- [7] A. Pinkerton, D. Schwarzenbach. *J. Chem. Soc., Dalton Trans.*, **23**, 2466 (1976).
- [8] T. Imai, M. Nakamura, K. Nagai, Y. Ohki, Y. Suzuki, M. Shimoi, A. Ouchi. *Bull. Chem. Soc. Jpn.*, **59**, 2115 (1986).
- [9] R. Nakamura, K. Nagai, M. Shimoi, A. Ouchi. *Bull. Chem. Soc. Jpn.*, **57**, 2919 (1984).
- [10] T. Imai, A. Ouchi. *Bull. Chem. Soc. Jpn.*, **59**, 669 (1986).
- [11] S. Spiliadis, A.A. Pinkerton, D. Schwarzenbach. *Inorg. Chim. Acta*, **75**, 115 (1983).
- [12] A.A. Pinkerton, D. Scharzenbach. *J. Chem. Soc., Dalton Trans.*, 1470 (1981).
- [13] K. Nagai, R. Nakamura, M. Shimoi, A. Ouchi. *Bull. Chem. Soc. Jpn.*, **57**, 2725 (1984).
- [14] Y. Ohki, M. Nakamura, Y. Suzuki, K. Nagai, M. Shimoi, A. Ouchi. *Bull. Chem. Soc. Jpn.*, **58**, 1593 (1985).
- [15] M.B. Inoue, M. Inoue, Q. Fernando. *Inorg. Chim. Acta*, **232**, 203 (1995).
- [16] C. Su, M. Tan, N. Tang, X. Gan, Z. Zhang, Q. Xue, K. Yu. *Polyhedron*, **16**, 1643 (1997).
- [17] H.C. Aspinall, D.C. Bradley, M.B. Hursthouse, K.D. Sales, N.P.C. Walker. *J. Chem. Soc., Chem. Commun.*, **22**, 1585 (1985).
- [18] C. Ferroud, H. Borderies, E. Lasri, A. Guy, M. Port. *Tetrahedron Lett.*, **49**, 5972 (2008).
- [19] D. Kasala, T.S. Lin, C.Y. Chen, G.C. Liu, C.L. Kao, T.L. Cheng, Y.M. Wang. *Dalton Trans.*, **40**, 5018 (2011).
- [20] C.L. Kahakachchi, D.A. Moore. *Metalomics*, **2**, 490 (2010).
- [21] M. Holz. *Magn. Reson. Chem.*, **31**, S154 (1993).
- [22] L. Lattuada, G. Lux. *Tetrahedron Lett.*, **44**, 3893 (2003).
- [23] H.P.S. Chauhan, C.P. Bhasin, G. Srivastava, R.C. Mehrotra. *Phosphorus and Sulfur*, **15**, 99 (1983).
- [24] A.I. Vogel. *A Text Book of Quantitative Inorganic Analysis*, ELBS IV Edition, London (1973).
- [25] A.R. Allouche. *J. Comput. Chem.*, **32**, 174 (2011).
- [26] R.O. Freiro, A.M. Simas. *J. Chem. Theory Comput.*, **6**, 2019 (2010).
- [27] MOPAC2009, James J. P. Stewart, Stewart Computational Chemistry, Version 10.124W <http://OpenMOPAC.net>.
- [28] Z.A. Fekete, E.A. Hoffmann, T. Koertvelyesi, B. Penke. *Mol. Phys.*, **105**, 19 (2007).
- [29] F. Neese. *The ORCA program system. WIREs Comput Mol Sci*, **2**, 73 doi: 10.1002/wcms.81 (2012).
- [30] A.D. Becke. *Phys. Rev. A*, **38**, 3098 (1988).
- [31] J.P. Perdew. *Phys. Rev. B*, **33**, 8822 (1986).

- [32] D.L. Pavia, G.M. Lampman, G.S. Kriz, J.A. Vyvyan. *Introduction to Spectroscopy*, 4th Edn, p. 29, Cengage Learning, Belmont, CA (2009).
- [33] H.P.S. Chauhan, G. Srivastava, R.C. Mehrotra. *Phosphorus and Sulfur*, **17**, 161 (1983).
- [34] J. Casdeon, W.N. Baxter, W. De Acetis. *J. Organomet. Chem.*, **24**, 247 (1959).
- [35] J.S. Yadav, R.C. Mehrotra, G. Srivastava. *Phosphorus. Sulfur*, **34**, 21 (1987).
- [36] J.R. Wasson, G.M. Waltherman, H.J. Stocklosa. *Top. Curr. Chem.*, **35**, 65 (1973).
- [37] D. Perry, R.A. Geanangel. *Inorg. Chim. Acta*, **13**, 185 (1975).
- [38] W. Brzyska, W. Ozga. *Thermochim. Acta*, **273**, 205 (1996).
- [39] J.B. Foresman, M. Head-Gordon, J.A. Pople, M.J. Frisch. *J. Phys. Chem.*, **96**, 135 (1992).
- [40] T.W. Robinson, D.P. Schofield, H.G. Kjaergaard. *J. Chem. Phys.*, **118**, 7226 (2003).
- [41] H. Soscún, J. Hernández, R. Escobar, C. Toro-Mendoza, Y. Alvarado, A. Hinchliffe. *Int. J. Quant. Chem.*, **90**, 497 (2002).
- [42] P.P. Korambath, S.P. Karna. *J. Phys. Chem.*, **104**, 4801 (2000).
- [43] R.G. Parr, R.G. Pearson. *J. Am. Chem. Soc.*, **105**, 7512 (1983).
- [44] P.K. Chattaraj, P. Fuentealba, B. Gomez, R. Contreras. *J. Am. Chem. Soc.*, **122**, 348 (2000).