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Comparison of crystal structure and DFT calculation of triferrocenyl trithiophosphite's conformation

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Abstract

A multiferrocene triferrocenyltrithiophosphite was studied by X-ray single-crystal diffraction. Triferrocenyl trithiophosphite has nine axes of internal rotation: three P-S bonds, three C-S bonds and three Fe – cyclopentadienyl axes. Rotation around the P-S bonds results in a totally asymmetric structure with three ferrocenylthio-groups exhibiting different orientations towards the phosphorus lone electron pair (LEP). A comparison of DFT calculations and X-ray diffraction data is presented, in which we show which conformations are preferred for a given ligand.

Keywords

multi-ferrocenyl compounds, phosphorus thioesters, DFT calculations, trithiophosphite, X-ray

Introduction

Design of novel “stimuli-responsive” molecules is very attractive area in modern chemistry due to a number of various practical applications of such compounds [1-6]. Multi(ferrocenyl) compounds with a strong metal−metal coupling are of particular interest owing to their multiredox, magnetic coupling, and unpaired electron density migration properties. From a practical point of view, such switchable arrays were intensely studied because conjugated organic chains containing Fe^{II}/Fe^{III} couples of the ferrocenyl group can be potentially used in molecular electronics, quantum cellular automata, optoelectronic materials, and biochemistry for application in redox or photonic devices [6].

A promising approach is the coordination self-assembly of multiferrocene ensembles from ferrocene-containing ligands and metal ions or clusters. This makes it possible to realize an almost infinite number of multiferrocene compounds, to select leading compounds for the successful creation of molecular electronics devices. It should be noted that with the exception of tertiary phosphines, a relatively small number of trivalent phosphorus derivatives have been used to construct multiferrocene compounds. The use of ferrocene derivatives containing a phosphorus-sulfur bond is a promising direction, since coordination with a metal atom can occur both at the phosphorus and sulfur atoms [7]. To obtain such complexes it is important to know the conformational capabilities of the ligand [8-11].

However, to date, XRD data on phosphorus derivatives containing a ferrocenyl substituent at the sulfur atom are presented only in acidified and sulfurized forms. Trithiophosphite has not been studied by X-ray structural analysis, although it is of the greatest interest for the construction of complexes of multiferrocene systems. Here we present a comparison of DFT calculations and X-ray diffraction data, in which we show which conformations are preferred for a given ligand.

MATERIALS AND METHOD

Source of material

To a suspension of white phosphorus (0.08 g, 0.645 mmol) in acetone (30 mL) were added diferrocenyldisulfide (1.68 g, 3.8 mmol) and 0.2 mL 15N solution of potassium hydroxide. The reaction mixture was stirred for 12 h at room temperature and then the solvent was evaporated in a vacuum. The product was extracted with benzene (3*30 mL) and after evaporation of the solvent triferrocenyltrithiophosphite (1.34 g, 76%) was obtained as yellow-orange powder. Single crystals suitable for X-ray diffraction were obtained from a mixture of benzene/hexane (1:1) in a fridge.

General

All reactions and manipulations were carried out under dry pure N_2 using standard Schlenk apparatus. All solvents were distilled from sodium/benzophenone and stored under nitrogen before use. The NMR spectra were recorded on a Bruker MSL-400 (^1H 400 MHz, ^{31}P 161.7 MHz, ^{13}C 100.6 MHz). $SiMe_4$ was used as internal reference for ^1H and ^{13}C NMR chemical shifts, and 85% H_3PO_4 as external reference for ^{31}P. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrometer. The elemental analyses were carried out at the microanalysis laboratory of the Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences.

Experimental section

Data set for single crystals of triferrocenyltrithiophosphite was collected on a Rigaku XtaLab Synergy S instrument with a HyPix detector and a PhotonJet microfocus X-ray tube using Cu Kα (1.54184 Å) radiation at 100 K. Images were indexed and integrated using the CrysAlisPro data reduction package. Data were corrected for systematic errors and absorption using the ABSPACK module. The GRAL module was used for analysis of systematic absences and space group determination. Using Olex2 [11], structure was solved by direct methods with SHELXT [12] and refined by the full-matrix least-squares on F^2 using SHELXL [13]. Non-hydrogen atoms were refined anisotropically. The figures were generated using Mercury 4.1 program [14].

$C_{30}H_{27}S_3PFe_3$.

Crystal Data for $C_{30}H_{27}Fe_3PS_3$ (M =682.21 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.49490(10) Å, b = 19.8932(3) Å, c = 18.4291(3) Å, β = 99.792(2)°, V = 2707.70(7) Å^3, Z = 4, T = 100.0(5) K, μ(CuKα) = 15.586 mm^{-1}, $Dcalc$ = 1.674 g/cm^3, 17211 reflections measured (6.59° ≤ 2Θ ≤ 153.132°), 5496 unique (R_{int} = 0.0570, R_{sigma} = 0.0467) which were used in all calculations. The final R_1 was 0.0496 (I > 2σ(I)) and wR_2 was 0.1349 (all data). CCDC number 2201898.

Results and Discussion

Previously electrochemical properties of triferrocenyltrithiophosphite was studied and three reversible one-electron peaks corresponding to the stepwise oxidation of three ferrocene fragments in the cyclic voltammograms of oxidation of triferrocenyltrithiophosphite was observed. It should be noted that the first oxidation potential is almost identical to free ferrocene [6]. Here in we report the crystal structure of triferrocenyltrithiophosphite.

For triferrocenyltrithiophosphite *trans*, *gauche*, *gauche*-configuration with torsion angles –34, -40, 173° respectively has been observed, although propeller-like *gauche*, *gauche*,

gauche-configuration of alkyl(aryl)thio groups has been observed for free trithiophosphites even in solid state [7] or in gas phase [8-10].

Triferrocenyl trithiophosphite has nine axes of internal rotation: three P-S bonds, three C-S bonds and three Fe – cyclopentadienyl axes. Rotation around the P-S bonds results in a totally asymmetric structure with three ferrocenylthio-groups exhibiting different orientations towards the phosphorus lone electron pair (Figure 1).

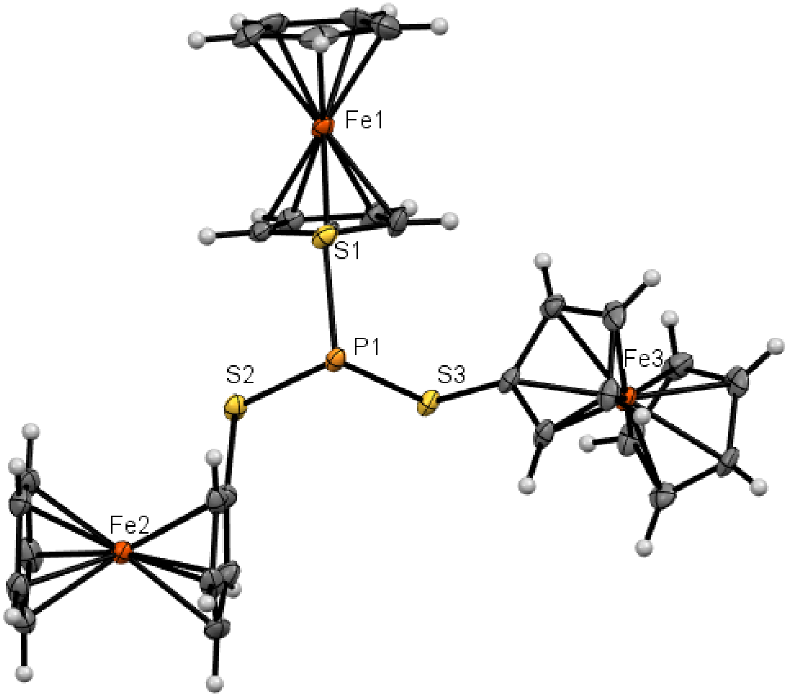

Figure 1. ORTEP representation of triferrocenyltrithiophosphite showing 50% probability thermal ellipsoids.

Several possible conformations of triferrocenyltrithiophosphite have been considered quantum-chemically (Figure 2, Table 1): *trans-trans-trans* (*ttt*), *gauche-trans-trans* (*gtt*), *gauche-gauche-trans* (*ggt*), and *gauche-gauche-gauche* (*ggg*). During optimization *ggt* conformer adopted *cis-gauche-trans* conformation with Fc(C)-S-P-lone pair dihedral angles 8°, -60° and 173° respectively (Table 1). The lowest energy has been predicted for *ttg* conformer, nevertheless the energy differences between *gtt* and *cgt* conformers is negligible (0.23 kcal/mol). Interestingly, that *cgt* conformation has been found previously for tricymantrenyl trithiophosphite with lone electron pair at phosphorus atom [15]. The highest relative energy is predicted for *ggg* conformer (1.7 kcal/mol). The ferrocene adopt almost eclipsed conformation in the all models with the dihedral angle between to Cp ring ~10°. Our previous work indicates that Cp can rotate at room temperature [16]. The Fc(C)-S-P-lone pair dihedral angle for *ttt* conformer is ~150°, and for *ggg* conformer is ~-35°. For the *gtt* / *cgt* conformers *trans* S-Fc bonds are almost antiparallel to phosphorus lone pair (LP): 175°, -161° / 173°. The dihedral angle for *gauche* S-Fc bond in *gtt* conformer is -56°, and close value is predicted for one of the *gauche* S-Fc bond in *tgg* conformer (-60°), whereas second one is almost parallel to LEP (8°).

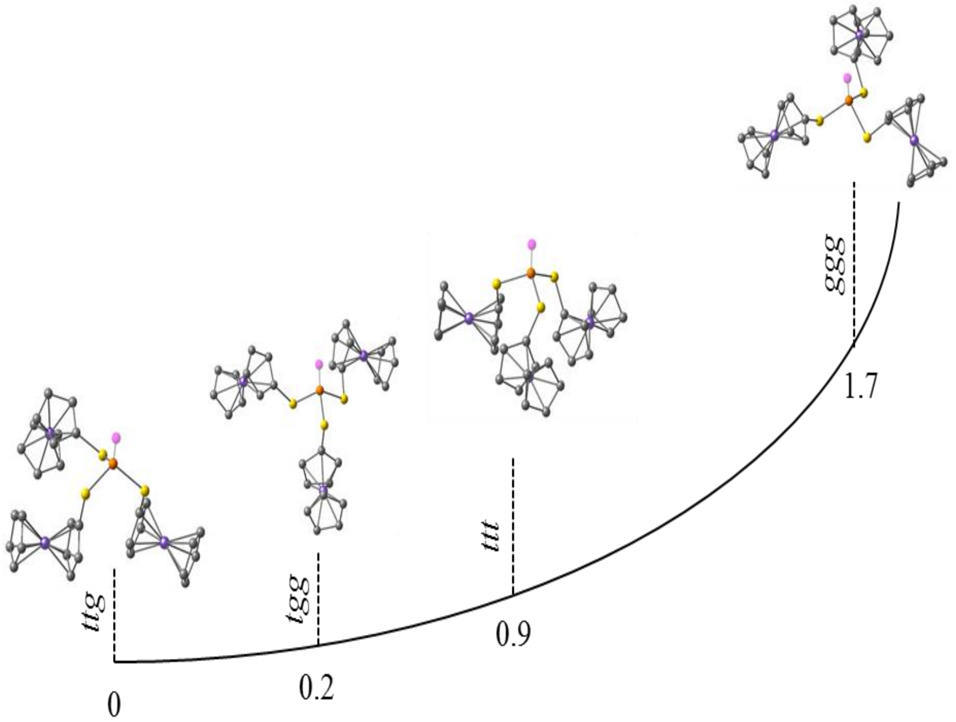

Figure 2. Optimized conformations and relative energies of four possible conformers of triferrocenyltrithiophosphite.

Table 1. Calculated relative energies and dihedral angles Fc(C)-S-P=X (°) (X=LEP, O, S) of four possible conformers of $(FcS)_3P$, $(FcS)_3PO$ and $(FcS)_3PS$

	$(FcS)_3P$	**$(FcS)_3PO$**	**$(FcS)_3PS$**
ttt	0.91	**0**	0.04
	149/151/151	149/149/149	149/149/149
gtt	**0**	0.23	0.20
	-56/175/-161	-56/-173/-135	47/174/135
ggt/cgt	0.23	0.52	0.36
	8/-60/173	-62/-47/165	46/45/176
ggg	1.73	0.55	**0**
	-37/-35/-36	-52/-34/-53	42/44/44

Interestingly, that previously for compounds triferrocenyltrithiophosphate and triferrocenyltetrathiophosphate with P=O and P=S bonds propeller-like *ggg* conformations have been found by X-Ray analysis. Indeed, computations predict *ggg* conformer to be the most energetically advantageous for P=S molecule, however with very close energies of *ttt* and *ggg* conformers (Table 1). For P=O the *ttt* conformer is predicted to have the lowest energy. Nevertheless for both P=X compounds computations predict very small energy differences between all four conformers, lower 0.6 kcal/mol. Thus one can conclude that in these cases crystal packing influence the conformation. Comparison of the crystal packings P_{LEP}, P=O and P=S compounds clearly confirms this conclusion experimentally (Figure 3).

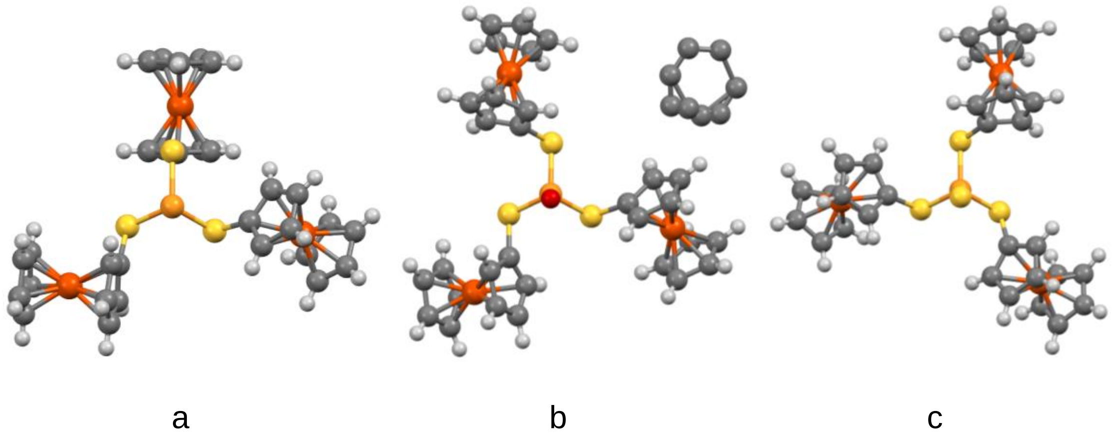

Figure 3. Geometry of a) $(FcS)_3P$, b) $(FcS)_3PO$ [15] and c) $(FcS)_3PS$ [7] in the crystal by X-Ray data. C atoms – grey, Fe atoms – brown, O atoms – red, P atoms – orange, S atoms - yellow.

We compared the crystal packings of three similar compounds: $(FcS)_3P$, $(FcS)_3PO$ [15] and $(FcS)_3PS$ [7] (Fig. 3). All three compounds form crystals belonging to the monoclinic syngony. In all three cases, the molecules in the crystals form a herringbone motif. In $(FcS)_3P$ crystals, C-H…π interactions dominate, while in $(FcS)_3PS$ and $(FcS)_3PO$ crystals, in addition to C-H…π interactions, interactions appear: one C-H…S and two C-H…O, respectively. It should be noted that $(FcS)_3PO$ crystals contain a solvent molecule that participates in intermolecular interactions. Thus, despite the similarity of the molecular structure of the three compounds and some crystal parameters, the intermolecular interactions differ noticeably from each other.

Conclusions

A multiferrocene triferrocenyltrithiophosphite $(FcS)_3P$ was studied by X-ray single-crystal diffraction for the first time. DFT calculations and X-ray diffraction data were compared, and prefered conformations were shown. Despite the similarity of the molecular structures and some crystal parameters of $(FcS)_3P$, $(FcS)_3PO$ and $(FcS)_3PS$, the intermolecular interactions differ noticeably from each other.

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