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# 3a,6a-Diaza-1,4-Diphosphapentalene Complexes with Lewis Acids $InI_3$ and $SbCl_3$

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**Abstract**—3a,6a-Diaza-1,4-diphosphapentalene (DDP) with indium triiodide forms the $[In(DDP)I_3]$ complex (**I**) with the ratio In : DDP = 1 : 1. The DDP ligand reacts with antimony(III) chloride to form a coordination polymer, the treatment of which with pyridine in the presence of pyridine hydrochloride affords the $[PyH]^+[Sb(DDP)Cl_4)]^-$ complex (**II**) (CIF files CCDC nos. 1937822 (**I**) and 1937823 (**II**)). The metal is coordinated to the phosphorus atom at an angle to the plane of the heteropentalene cycle (101.9(1)° and 106.0(1)° for In and Sb, respectively). This indicates that the coordination occurs due to electrons of the heteroaromatic π system.

*Keywords:* heterophospholes, heteropentalenes, Lewis acids, indium complexes, antimony(III) complexes, coordination polymers, X-ray structure analysis

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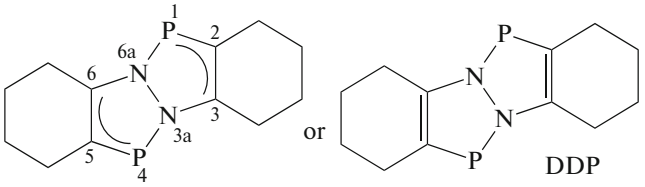
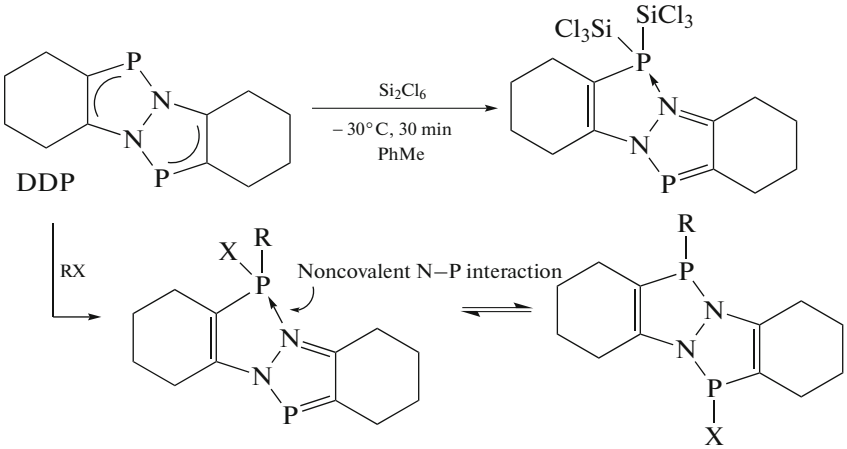
## INTRODUCTION

Although 3a,6a-diaza-1,4-diphosphapentalene (DDP) [1] is classified as annelated azaphosphole [2], this compound exhibits the chemical properties different from those of classical azaphospholes.




It is shown that DDP is very easily involved in addition reactions to the phosphorus atom. In particular, hexachlorodisilane adds to the two-coordinated phosphorus atom at −30°C with the Si–Si bond cleavage to form the bis(trichlorosilyl) derivative [3] (Scheme 1). The reactions of the DDP ligand with organyl halides gave the 1,1-addition products without changing the oxidation state of phosphorus [4, 5] (Scheme 1), whereas addition reactions to the phosphorus atom for usual aromatic azaphospholes are unknown.

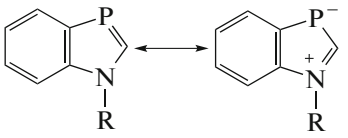



R is alkyl, aryl; X is halogen

**Scheme 1.**

As shown by the quantum chemical calculations [1], the lone electron pair of the phosphorus atoms of DDP lies in the heterocycle plane and, hence, the latter should also lie in the heterocycle plane upon its coordination with the Lewis center. However, the experiments with tin(II) and mercury(II) chlorides showed [1] that the metal atoms were coordinated to the phosphorus atom of DDP at an angle of 104.6° (Hg) and 108.7° (Sn) rather than in the plane of the heteropentalene cycle. This indicates that the lone electron pair on the phosphorus atom is not involved in coordination.

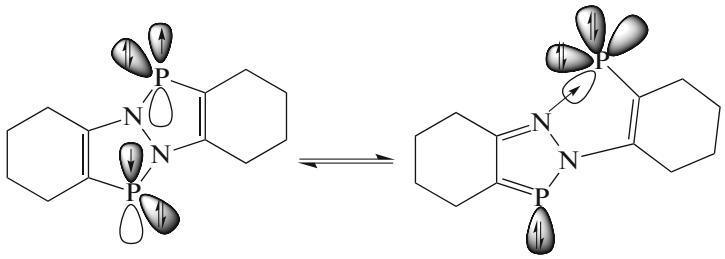
It is known that representatives of the azaphosphole class used as ligands coordinate to metals rather reluctantly [2]. The exceptions are 1,3-benzazaphospholes having an excessive π-electron density on the phosphorus atom due to the partial charge redistribution upon complex formation [6, 7].




R = H, Me, $CH_2CMe_3$

The coordination mode of 1,3-benzazaphospholes depends on the metal nature. When the efficient back π donation from the metal (Cr, Mo, W) to the 1,3-benzazaphosphole ligand is possible, the phosphorus atom coordinates to the metal in the heterocycle plane. In other cases, coordination at an angle to the heterocycle takes place [6, 7]. Note that the strength of the coordination bond of metals with 1,3-benzazaphospholes is lower, as a rule, than that with related six-membered phosphinine cycles [7].

The high coordination activity of DDP is also caused by the intramolecular donation of the electron density to one of the phosphorus atoms. However, in this case, one should speak about the equilibrium between the centrosymmetric form (10-electron aromatic heteropentalene π system) and the stabilized phosphinidene form in which the centrosymmetric character of the molecule is violated and one of the N–P bonds is elongated rather than about tautomeric canonical forms.




In this report, we present the data on the synthesis and structural features of the DDP complexes with the Lewis acids: $InI_3$ and $SbCl_3$. Indium and antimony belong to the fifth row of the periodic table of elements and have three and five valent *p* electrons, respectively. They are prone to form hypervalent compounds.

## EXPERIMENTAL

The compounds were synthesized in vacuum and in an atmosphere of high-purity argon. Tetrahydrofuran (THF) was purified by reflux and distillation over sodium in the presence of sodium benzophenone ketyl. Pyridine was refluxed and distilled over KOH. The DDP ligand was synthesized using the described procedure [1].

**Synthesis of $[In(DDP)I_3]$ (I).** A solution of DDP (0.13 g, 0.5 mmol) in THF (15 mL) was added to a solution of $InI_3$ (0.25 g, 0.5 mmol) in THF (20 mL), and the mixture was kept at room temperature for 8 h. A yellow-brown finely crystalline precipitate was formed within this time. The crystals were washed with THF and dried in vacuo. The yield of compound **I** was 0.30 g (79%).

For $C_{16}H_{24}N_2OP_2I_3In$ (*FW* = 817.85)

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 23.50 | H, 2.96 | I, 46.55 |
| Found, % | C, 23.46 | H, 3.01 | I, 46.50 |

IR (Nujol), ν, $cm^{-1}$: 1601 m, 1345 m, 1335 w, 1281 m, 1224 w, 1161 w, 1130 m, 1071 m, 1037 w, 1020 m, 957 m, 907 m, 949 m, 813 m, 796 m, 773 w, 726 m, 684 w, 593 w, 542 w. $T_{decomp}$ = 100°C.

**Synthesis of $[PyH]^+[Sb(DDP)Cl_4)]^-$ (II).** A solution of DDP (0.25 g, 1.0 mmol) in THF (15 mL) was added to a solution of $SbCl_3$ (0.23 g, 1.0 mmol) in THF (20 mL). The precipitate was filtered off, dried in vacuo, and refluxed in pyridine (20 mL) in the presence of pyridine hydrochloride (0.12 g, 1.0 mmol) for 3 h. The hot solution was filtered. A finely crystalline precipitate of complex **I** was formed as the filtrate was

slowly cooled down to room temperature. The yield of complex **I** was 0.26 g (45%).

| For $C_{17}H_{22}N_3P_2Cl_4Sb$ ($FW$ = 593.90) | | | |
|---|---|---|---|
| Anal. calcd., % | C, 34.38 | H, 3.73 | Cl, 23.88 |
| Found, % | C, 34.42 | H, 3.69 | Cl, 23.91 |

IR (Nujol), ν, $cm^{-1}$: 1601 m, 1524 m, 1341 w, 1281 w, 1265 w, 1243 m, 1225 w, 1195 w, 1147 w, 1136 w, 1076 w, 1040 w, 1020 w, 999 w, 961 w, 904 m, 849 m, 794 m, 770 s, 686 s, 632 w, 606 w, 563 w, 545 w, 470 w.

IR spectra were recorded on a Perkin-Elmer 577 instrument in a range of 4000–400 $cm^{-1}$ in Nujol or on a Perkin-Elmer FT-IR 2000 instrument.

**X-ray structure analyses of complexes I and II.** The crystallographic data were collected on an Agilent Xcalibur E automated diffractometer (ω scan mode, Mo$K_\alpha$ radiation, λ = 0.71073 Å). Experimental sets of intensities were integrated using the CrysAlisPro program [8]. The structures were solved by the "dual-space" method in the SHELXT program [9] and refined by full-matrix least squares for $F^2_{hkl}$ in the anisotropic approximation for all non-hydrogen atoms using the SHELXTL program package [10, 11]. Hydrogen atoms were placed in the geometrically calculated positions and refined in the riding mode. Absorption corrections were applied using the SCALE3 ABSPACK program [12]. The solvate THF molecule in the general position was found in the crystal of complex **II**. The anionic moiety of complex **I** was disordered over two positions. The diagrams of the structures were obtained using the Olex2 program [13]. The main crystallographic characteristics and structure refinement parameters for complexes **I** and **II** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The crystallographic data on the studied structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1937822 (**I**) and 1937823 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The complex of indium triiodide with annelated DDP can easily be synthesized by the interaction of equimolar solutions of the reactants. However, when the reaction is carried out in toluene, a finely crystalline precipitate insoluble in organic solvents is formed. The use of THF as the solvent made it possible to retard the growth of the crystals and isolate product **I** as single crystals. The molecular structure of complex **I** is shown in Fig. 1a.

The crystal cell of complex **I** contains two enantiomers and two solvate THF molecules. The length of the coordination P(1)–In(1) bond is 2.592(2) Å. This value exceeds the sum of covalent radii of the elements (2.47 Å [14]) but is considerably lower than the sum of their van der Waals radii (3.73 Å). The geometry of the five-membered heterocycles in the molecule of complex **I** is close to the planar one, and the maximum deviation of the atoms from the plane is 0.044(2) Å. The angle formed by the line of the In(1)–P(1) bond with the plane of the five-membered heterocycle is 101.9(1)°. The three-coordinate phosphorus atom has a pyramidal geometry with the sum of bond angles 280.4°.

In the heteropentalene fragment, the five-membered heterocycles are nonequivalent, which is observed by the difference in bond lengths. The C(7)–C(8) bond (1.376(7) Å) has a more pronounced aromatic character than C(1)–C(2) (1.344(7) Å), which partially shifts from conjugation. The shortening of the P(2)–N(2) bond (1.694(4) Å) occurs similarly, whereas the P(1)–N(1) bond elongates (1.778(4) Å) upon the formation of the coordination compound.

The indium atom in compound **I** exists in the tetrahedral environment. A slight distortion of the tetrahedral geometry is evidently caused by noncovalent interactions in the crystal. The short contacts are found, in particular, for the I(2)···I(2), P(1)···I(1), and I(1)···C(2) interactions (Fig. 2).

Complex **I** is a coordination polymer. The solubility of complex **I** in organic solvents turned out to be very low, which prevented to study its state in a solution by the NMR method.

Note that indium triiodide can also form trigonal bipyramidal complexes with two molecules of tertiary phosphine [15]. The experiments with DDP showed that the same complex [In(DDP)$I_3$] (**I**) was formed under the conditions of a twofold excess of the ligand.

Unlike the classical Lewis acids, antimony trichloride enters into complex formation with electron pair donors via another mechanism to form the hypervalent derivatives [16]. Several types of complexes with tertiary phosphines are known: neutral $(R_3P)_nSbCl_3$ ($n$ = 1, 2), cationic $[Cl_2(R_3P)_nSb]^+$ ($n$ = 1, 2), and anionic $[Cl_4(R_3P)Sb]^-$ ($R_3P$ = $Me_3P$, $Ph_3P$, $(C_6H_{11})_3P$) [16]. In all cases, antimony is characterized by the pyramidal geometry.

The interaction of solutions of DDP and $SbCl_3$ is accompanied by the precipitation of an ample amorphous substance being, most likely, a coordination polymer of irregular structure. The precipitate was partially dissolved after reflux in pyridine for 3 h. Filtration from the mother liquor gave yellow-green crystals of the compound being, according to the X-ray structure data, the anionic complex $[PyH]^+$-$[Sb(DDP)Cl_4)]^-$ (**II**). The molecular structure of complex **II** is presented in Fig. 1b.

The crystal cell of complex **II** contains two enantiomers in which the anionic moiety is disordered over general positions. The anionic moiety of complex **II** contains the square fragment $SbCl_4$, which is the base

**Table 1.** Crystallographic data and structure refinement parameters for compounds **I** and **II**

| Parameter | Value | |
|---|---|---|
| | **I** | **II** |
| Temperature, K | 100(2) | 100(2) |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1$ |
| $a$, Å | 8.1547(2) | 8.8596(4) |
| $b$, Å | 12.2389(3) | 13.6610(5) |
| $c$, Å | 12.9680(3) | 8.9729(4) |
| α, deg | 64.662(2) | 90 |
| β, deg | 86.231(2) | 91.090(4) |
| γ, deg | 86.571(2) | 90 |
| $V$, Å$^{-3}$ | 1166.51(5) | 1085.80(8) |
| $Z$ | 2 | 2 |
| $\rho_{calc}$, mg m$^{-3}$ | 2.328 | 1.816 |
| μ, mm$^{-1}$ | 5.128 | 1.919 |
| $F$(000) | 760 | 588 |
| Crystal size, mm | 0.70 × 0.30 × 0.20 | 0.25 × 0.17 × 0.10 |
| Range of data collection over θ, deg | 3.04–26.00 | 3.20–28.68 |
| Ranges of reflection indices | $-10 \le h \le 10$, $-15 \le k \le 15$, $-15 \le l \le 15$ | $-11 \le h \le 11$, $-18 \le k \le 18$, $-12 \le l \le 12$ |
| Measured reflections | 16076 | 24972 |
| Independent reflections | 4562 | 5578 |
| Reflections with $I > 2\sigma(I)$ | 4454 | 5385 |
| $R_{int}$ | 0.0383 | 0.0107 |
| Number of refinement parameters | 226 | 312 |
| GOOF ($F^2$) | 1.164 | 1.046 |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$) | 0.0292, 0.0706 | 0.0400, 0.0898 |
| $R_1$, $wR_2$ (for $F^2$ for all reflections) | 0.0301, 0.0712 | 0.0428, 0.0914 |
| Residual electron density ($\Delta\rho_{max}/\Delta\rho_{min}$), e Å$^{-3}$ | 1.239/–1.065 | 0.904/–1.228 |

of the tetragonal pyramid, whose vertex is occupied by the phosphorus atom of diazadiphosphapentalene. The Sb(1)–P(1) bond length (2.624(2) Å) is in the range typical of the complexes with tertiary phosphines ($Cl_3SbPMe_3$ 2.5951(9), $Cl_3SbPPh_3$ 2.7576(5), and $Cl_3SbPCy_3$ 2.6516(14) Å [16]).

The geometry of the diazadiphosphapentalene framework in the molecule of compound **II** is planar, and the maximum deviation of the atoms from the plane is 0.069(6) Å. The angle formed by the line of the Sb(1)–P(1) bond with the heterocycle plane is 106.0(1)°.

The coordination of the antimony atom with phosphorus results in the violation of the symmetry of the heteropentalene framework, as in the case of complex **I**, which is observed from the difference in bond lengths. The C(7)–C(8) bond (1.388(11) Å) is more aromatic in character than the C(1)–C(2) bond (1.334(11) Å), which partially shifts from conjugation. The P(2)–N(2) bond is shortened similarly (1.715(7) Å), whereas the P(1)–N(1) bond is elongated (1.770(7) Å) upon the formation of the coordination compound.

The cationic fragment of compound **II** is the pyridinium cation linked by the hydrogen bond (N(1S)–H···Cl(2) 2.352(3) Å) with the nearest chlorine atom of the $SbCl_4$ fragment and having the short CH···Cl contacts (2.71–2.83 Å) with the adjacent molecules. The crystal structure also contains the short P(2)···Cl(2) contacts (3.430(3) Å) and multiple contacts of the chlorine atoms with the hydrogen atoms of the cyclohexyl fragments (2.79–2.86 Å).

**Table 2.** Selected bond lengths (Å) and bond angles (deg) in complexes **I** and **II**

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| | | **I** | |
| In(1)–P(1) | 2.592(2) | P(1)In(1)I(1) | 112.73(3) |
| In(1)–I(1) | 2.7213(4) | P(1)In(1)I(2) | 103.57(3) |
| In(1)–I(2) | 2.7224(4) | P(1)In(1)I(3) | 112.27(3) |
| In(1)–I(3) | 2.7008(4) | I(1)In(1)I(2) | 108.29(2) |
| P(1)–N(1) | 1.778(4) | I(1)In(1)I(3) | 112.32(2) |
| P(1)–C(1) | 1.805(5) | I(2)In(1)I(3) | 107.04(2) |
| P(2)–N(2) | 1.694(4) | N(1)P(1)C(1) | 86.8(2) |
| P(2)–C(7) | 1.738(5) | N(1)P(1)In(1) | 95.8(2) |
| N(1)–C(8) | 1.341(6) | C(1)P(1)In(1) | 97.7(2) |
| N(1)–N(2) | 1.357(5) | C(7)P(2)N(2) | 88.8(2) |
| N(2)–C(2) | 1.408(6) | C(8)N(1)N(2) | 112.0(4) |
| C(1)–C(2) | 1.344(7) | C(8)N(1)P(1) | 133.6(3) |
| C(7)–C(8) | 1.376(7) | N(2)N(1)P(1) | 114.3(3) |
| | | **II** | |
| Sb(1)–Cl(1) | 2.569(2) | Cl(1)Sb(1)Cl(2) | 88.90(7) |
| Sb(1)–Cl(2) | 2.674(2) | Cl(1)Sb(1)Cl(3) | 166.02(9) |
| Sb(1)–Cl(3) | 2.634(3) | Cl(1)Sb(1)Cl(4) | 91.37(7) |
| Sb(1)–Cl(4) | 2.566(2) | Cl(2)Sb(1)Cl(3) | 88.20(7) |
| Sb(1)–P(1) | 2.624(2) | Cl(2)Sb(1)Cl(4) | 174.53(8) |
| P(1)–N(1) | 1.770(7) | Cl(3)Sb(1)Cl(4) | 90.23(7) |
| P(1)–C(1) | 1.818(7) | Cl(1)Sb(1)P(1) | 91.86(9) |
| P(2)–N(2) | 1.715(7) | Cl(4)Sb(1)P(1) | 82.33(7) |
| P(2)–C(7) | 1.746(8) | P(1)Sb(1)Cl(2) | 92.21(7) |
| N(1)–C(8) | 1.35(1) | P(1)Sb(1)Cl(3) | 74.59(8) |
| N(1)–N(2) | 1.361(9) | N(1)P(1)Sb(1) | 102.6(2) |
| N(2)–C(2) | 1.404(10) | N(1)P(1)C(1) | 86.7(4) |
| C(1)–C(2) | 1.334(11) | C(1)P(1)Sb(1) | 103.3(3) |
| C(7)–C(8) | 1.388(11) | | |

Compound **II** is ionic and loses solubility in organic solvents after the first crystallization from the mother liquor thus preventing the NMR study of the solutions.

We showed that the yield of compound **II** can be increased from 10 to 45% by adding pyridine hydrochloride to the reaction mixture (DDP–$SbCl_3$) on reflux in pyridine.

We studied the complex formation of annelated DDP with antimony trifluoride. In this case, when the reaction occurs in THF, $SbF_3$ is partially reduced to metallic antimony to form a mixture of organophosphorus compounds with P–F bonds, which is indicated by the characteristic $^{31}P$ NMR spectrum with the spin-spin coupling constants $J_{P,F} \sim 840$ Hz.

To conclude, the complexes of annelated 3a,6a-diaza-1,4-diphosphapentalene with indium and anti-

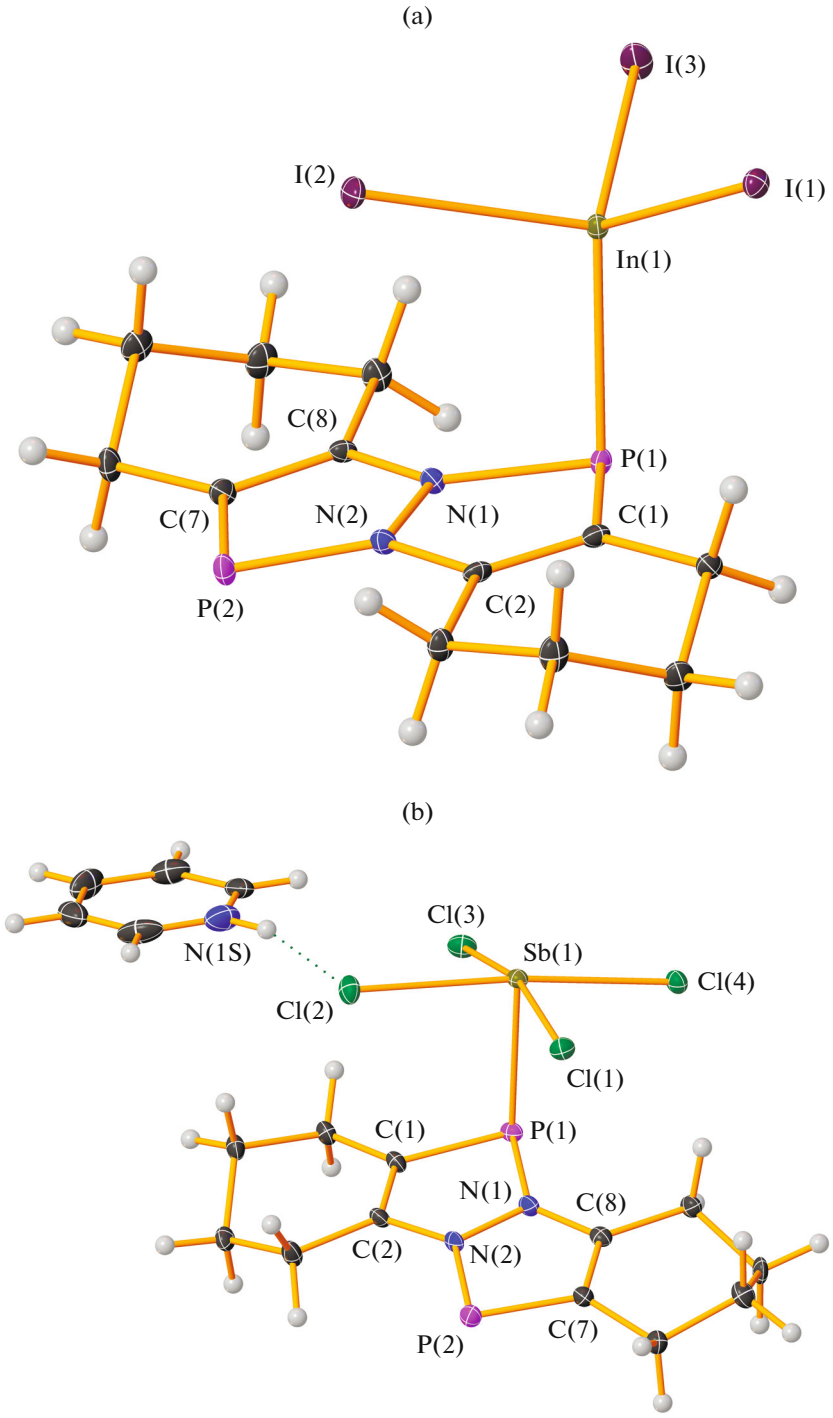



**Fig. 1.** Molecular structures of complexes (a) **I** and (b) **II** with thermal ellipsoids of 30% probability.

mony halides, $[In(DDP)I_3]$ (**I**) and $[PyH]^+[Sb(DDP)Cl_4)]^-$ (**II**), were synthesized and characterized. Complexes **I** and **II** demonstrate the coordination of the metal to the phosphorus atom at an angle of 101.9(1)° and 106.0(1)°, respectively, to the plane of the heteropentalene cycle. This indicates that the coordination is mainly performed due to the electrons of the heteroaromatic π system.

## FUNDING

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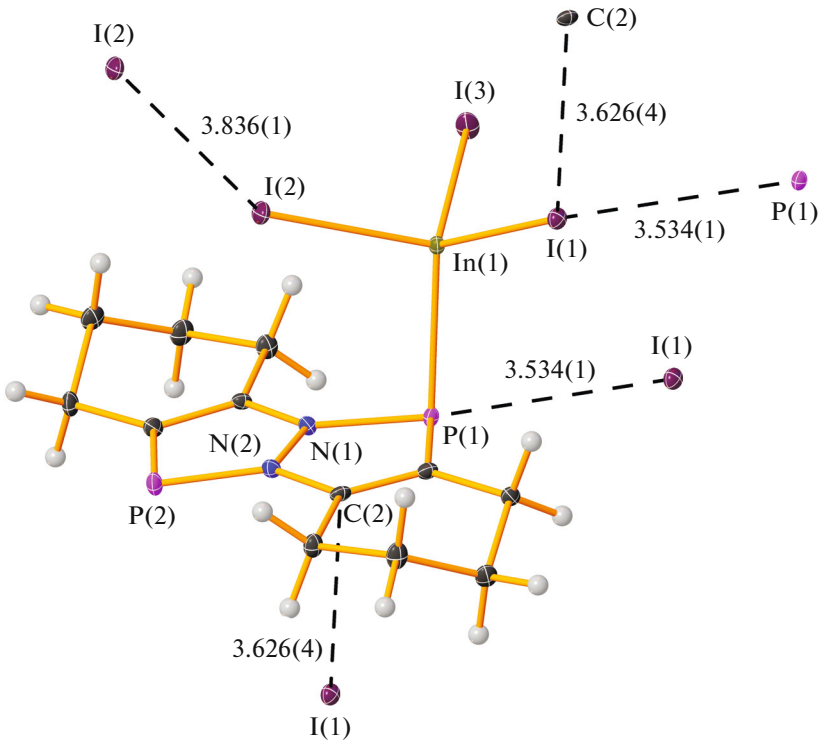


**Fig. 2.** Intermolecular short contacts in the crystal structure of complex **I**. Thermal ellipsoids are presented with 30% probability. The distances are given in Å.

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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