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Synthesis and Study of Complexes of 3,4-Bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene with Mn(II) Salts

V. P. Morgalyuk[a], **O. I. Artyushin**[a], **A. V. Vologzhanina**[a], **P. V. Dorovatovskii**[b], **B. V. Lokshin**[a], **A. G. Buyanovskaya**[a], **R. U. Takazova**[a], **and V. K. Brel**[a, *]

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia*
[b] *National Research Center "Kurchatov Institute," Moscow, Russia*
**e-mail: v_brel@mail.ru*

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Abstract—The coordination properties of 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2) were studied in relation to manganese(II) chloride and perchlorate complexes. Manganese(II) chloride forms 1 : 1 complex with bis-phosphine oxide L^2, while the composition of the manganese(II) perchlorate complex is 2 : 1. The crystal structures of bis-phosphine oxide L^2 complexes with manganese dichloride (CCDC no. 2165179) and manganese perchlorate (CCDC no. 2165180) were determined by X-ray diffraction.

Keywords: phosphine oxides, 1,3-butadienes, complexes, manganese salts, crystal structure

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INTRODUCTION

In recent years, various Mn(II) complexes with organophosphorus ligands have attracted attention owing to their unique photophysical properties, high stability, and low cost [1]. For example, complexes of manganese dihalides with triphenylphosphine oxide demonstrate bright photo- and triboluminescence [2, 3]. The complexes $[Mn(L)_3]Hal_2$ and $[Mn(L)_3]$-$MnHal_4$ (Hal = Cl, Br) with high emission properties were synthesized by reactions of chelating bis(phosphine oxides), $Ph_2P(O)CH_2P(O)Ph_2$, and $Ph_2P(O)CH_2CH2P(O)Ph_2$ with Mn(II) halides [4–6]. Quite recently, manganese dichloride and manganese dibromide complexes with 4,6-bis(diphenylphosphinyl)dibenzofuran were used to prepare promising Mn(II)-based PhOLEDs [7]. A coordination polymer was synthesized from 1,2,4,5-tetrakis(phosphinylbenzene) and manganese(II) perchlorate [8]. Using 2,3-bis(diphenylphosphinyl)-1,3-butadiene (L^1) as the ligand, organic-inorganic hybrid complexes $[Mn(L^1)_3][MnHal_4]$ were obtained. It should be noted that these complexes containing four- and six-coordinate Mn2+ ions exhibit high photophysical properties. It was shown that the Mn^{2+} ion in the $[Mn(L^1)_3]^{2+}$ cation has an octahedral geometry of [MnO6] (Oh), whereas the $[MnHal4]^{2-}$ anion is tetrahedral (Td) [4].

It seemed of interest to continue the study of Mn(II) coordination compounds with other bidentate phosphinyl-containing ligands on an alkadiene platform, in particular, with 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2), which proved useful for studying extraction of U(VI) and Th(IV) from nitric acid solutions [9].

EXPERIMENTAL

Reagent grade acetonitrile used in the work was distilled over P_2O_5 for dehydration and stored above CaH_2. Commercial ethanol was used as received. The ligand L^2 was prepared by a previously described procedure [9].

IR spectra were recorded on a VERTEX 70v Fourier transform IR spectrometer (Germany). Elemental analysis (C, H) was carried out on a CarloErba 1106 automatic analyzer; phosphorus was determined by spectrophotometry on a Cary 100 Scan instrument; chlorine was quantified by titration (0.001 M $AgNO_3$); and manganese content was found from the weight of incombustible residue.

Synthesis of (3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene) dichloride manganese(II) (I). The ligand L^2 (130 mg, 0.25 mmol) was added with stirring to a suspension of finely ground $MnCl_2·4H_2O$ (24 mg, 0.12 mmol) in acetonitrile (5 mL). The mixture was stirred until $MnCl_2·4H_2O$ dissolved, and the solution was concentrated at 20°C at a reduced pressure (14 mm Hg) to a volume of 2 mL. The precipitate that formed in 7 days was collected on a filter, washed with benzene (2 × 4 mL), dried in air, washed with water (2 × 5 mL), and dried at a reduced pressure (14 mm Hg) over P_2O_5 to a constant weight. The yield of complex **I**, formed as a white-colored finely crystalline compound, was was 58 mg (76%). T_{dec} = 180–185°C.

IR (KBr; ν, cm^{-1}): 3059, 2944, 1607, 1607, 1576; 1300–1274, 1128.

For $C_{32}H_{32}O_2P_2Cl_2Mn$

Anal. calcd., %	C, 60.39	H, 5.07	P, 9.73	Cl, 11.14
Found, %	C, 60.07	H, 5.06	P, 9.30	Cl, 10.82

After recrystallization from hot acetonitrile, the yield of complex **I** was 0.046 g (60%), T_{dec} = 190–195°C.

For $C_{32}H_{32}Cl_2O_2P_2Cl_2Mn$

Anal. calcd., %	C, 60.39	H, 5.07	P, 9.73	Cl, 11.14
Found, %	C, 60.02	H, 5.04	P, 9.62	Cl, 11.03

Synthesis of bis[3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene]-manganese(II) diperchlorate (II). A solution of $Mn(ClO_4)_2 \cdot H_2O$ (53.5 mg, 0.196 mL) in acetonitrile (2 mL) was added to a solution of L^2 (200 mg, 0.392 mmol) in acetonitrile (3 mL), the mixture was stirred for 2 h, and then the solvent was evaporated at a reduced pressure (14 mm Hg). The remaining thick oil was triturated with ether (5 mL). The resulting white crystals were collected on a filter and washed with ether (5 mL), dried in air, and recrystallized from boiling ethanol (5 mL). Crystals suitable for X-ray diffraction were selected, and the rest of the crystals were dried in vacuum over P_2O_5 to a constant weight. The yield of complex **II** was 187 mg (75%), T_{dec} = 240–245°C.

IR (KBr; ν, cm^{-1}): 3435, 3059, 3011, 2911, 1611, 1588, 1438, 1381, 1368, 1147, 1114, 1097, 1074.

For $C_{64}H_{64}O_{12}P_4Cl_2Mn$

Anal. calcd., %	C, 60.29	H, 5.06	Cl, 5.56	Mn, 4.31	P, 8.93
Found, %	C, 60.13	H, 5.30	Cl, 5.46	Mn, 4.5	P, 9.07

X-ray diffraction study of complex $[MnCl_2L^2]$ (**I**) was carried out at 100.0(2) K on a Bruker Quest four-circle automated diffractometer equipped with an array detector. The reflection intensities for the complex $[Mn(EtOH)_2(L^2)_2](ClO_4)_2$ (**II**) were measured on the Belok K4.4 station of the Kurchatov synchrotron radiation source (National Research Center "Kurchatov Institute," Moscow, Russia) at a 0.745 Å wavelength at 100.0(2) K. The experimental reflection intensities were corrected for absorption using SADABS (Bruker AXS Inc. Madison (WI, USA)), iMosflm [10], and Scala [11] programs. The structures were solved by the dual space method implemented in the SHELXT program [12] and refined by full-matrix least-squares method of SHELXL-2014 [13] on F^2 for all data in the anisotropic approximation for all non-hydrogen atoms, except for disordered atoms, using the Olex2 program [14]. The perchlorate anion disordered over two positions (0.512 : 0.488 occupancy ratio) and the solvent molecules in the structure of **II** were refined in the isotropic approximation. The hydrogen atoms were placed into geometrically calculated positions and refined in the riding model with isotropic thermal parameters $U_{iso} = 1.5U_{equiv}(C)$ for the methyl groups and $U_{iso} = 1.2U_{equiv}(C)$ for benzene rings, where $U_{equiv}(C)$ are equivalent isotropic thermal parameters of the atoms bonded to the hydrogen atoms. The structure of **II** contains disordered solvation molecules, the contribution of which to the reflection intensity was included using the Solvent-Mask algorithm of Olex2. The crystallographic data and X-ray diffraction experiment and structure refinement details for structures **I** and **II** are summarized in Table 1.

The atom coordinates and thermal parameters are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2165179 (**I**) and 2165180 (**II**); http://www.ccdc.cam.ac.uk/structures).

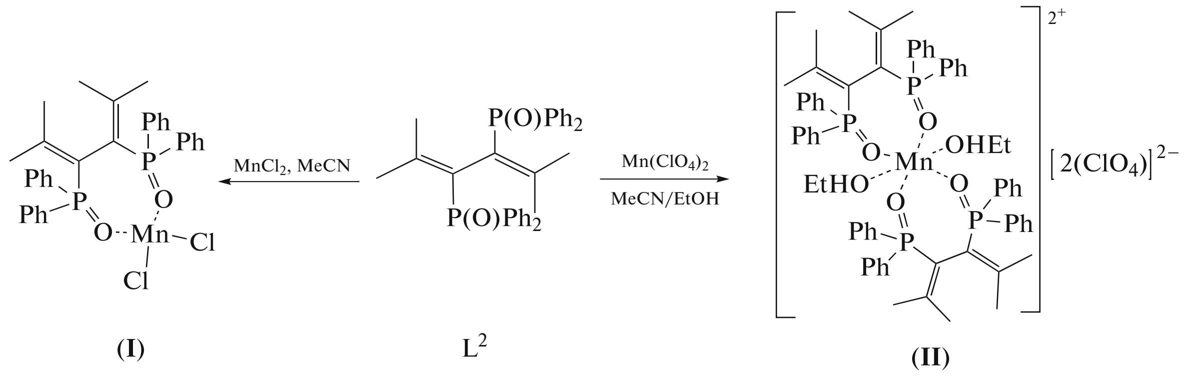
The X-ray diffraction pattern of the $[MnCl_2L^2]$ sample after recrystallization was measured in the reflection mode at room temperature on a Bruker D8 Advance diffractometer equipped with a LynxEye detector and a Ge(111) monochromator. Rietveld analysis was performed using the TOPAS 4.2 program (Bruker AXS GmbH, Karlsruhe (Germany)), with the preferred orientation being included in the spherical harmonics approximation [15].

RESULTS AND DISCUSSION

Complexes **I** and **II** were synthesized by the reaction of 2,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2) with $MnCl_2$ and $Mn(ClO_4)_2$ (Scheme 1).

Table 1. Crystallographic data and X-ray experiment and structure refinement details of structures **I** and **II**

Parameter	Value	
	I	**II**
Molecular formula	$C_{32}H_{32}Cl_2MnO_2P_2$	$C_{68}H_{76}Cl_2MnO_{14}P_4$
M	636.35	1367.00
System	Orthorhombic	Tetragonal
Space group	*Pbca*	$P4_12_12$
a, Å	15.7136(10)	17.941(3)
b, Å	19.2881(12)	17.941(3)
c, Å	20.4240(12)	23.271(5)
V, Å^3	6190.2(7)	7490(3)
Z	8	4
ρ(calcd.), g/cm^3	1.366	1.212
μ, mm^{-1}	0.730	0.430
F(000)	2632	2860
Number of reflections: measured/unique (N_1)/observed (with $I > 2\sigma(I)$, N_2)	65291/9451/7136	29755/6818/4580
R_{int}	0.045	0.074
Number of refined parameters	356	395
R_1 (for N_2)	0.030	0.118
wR_2 (for N_1)	0.081	0.271
GOOF	1.091	1.076
Residual electron density (max/min), e/Å^3	0.391/–0.304	1.753/–1.370



Scheme 1.

The complex of $MnCl_2$ with phosphine oxide L^2 was synthesized by the reaction of $MnCl_2 \cdot 4H_2O$ with L^2 in acetonitrile at 20°C. According to X-ray diffraction, IR spectroscopy, and elemental analysis data, the reaction gave a tetrahedral neutral 1 : 1 complex $[MnL^2Cl_2]$ (**I**). However, by analogy with literature data [4], the formation of a 2 : 1 cation–anion complex ($[Mn(L^2)_2][MnCl_4]$) (**Ia**) with the same elemental composition as complex **I** could not be ruled out either. To verify this assumption, complex **I** was addi-

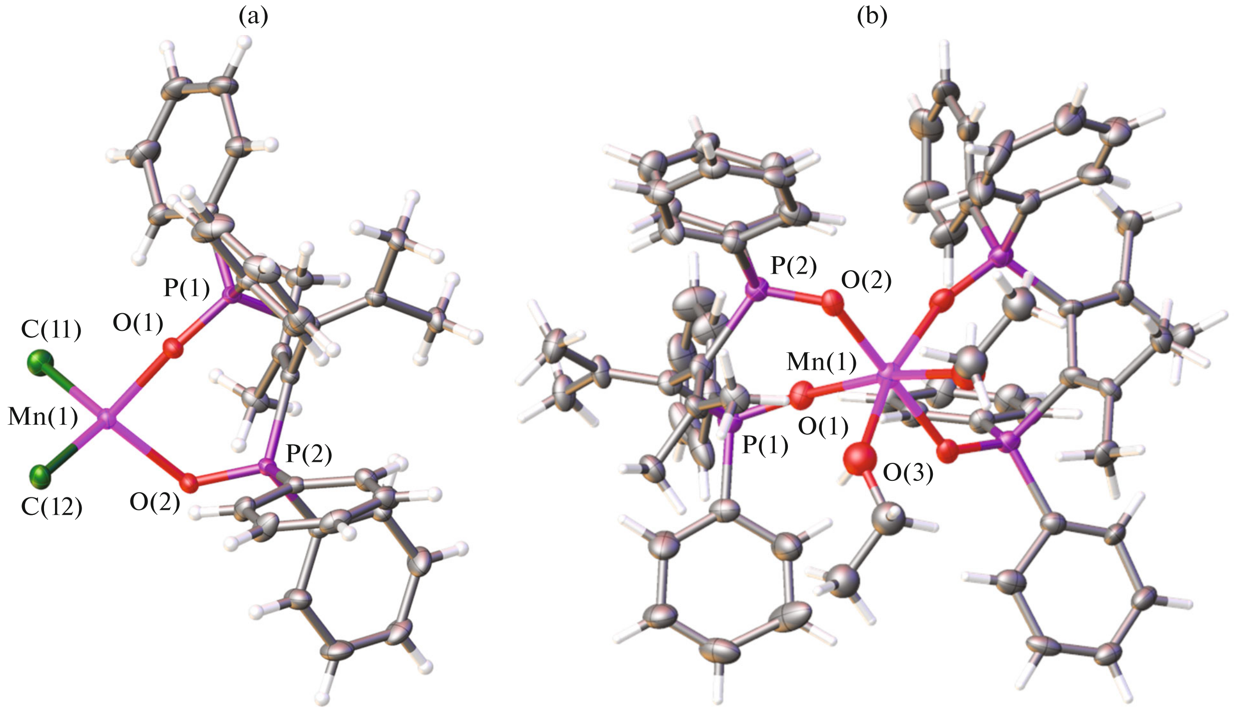


Fig. 1. View of (a) $[MnCl_2L^2]$ and (b) $[Mn(EtOH)_2(L^2)_2]^{2+}$ in thermal ellipsoids.

tionally recrystallized from hot acetonitrile; however, after recrystallization, the composition and structure of the complex did not change, as was confirmed by powder X-ray diffraction and element analysis.

The complex of $Mn(ClO_4)_2$ with bis-phosphine oxide L^2 was synthesized in acetonitrile and recrystallized from ethanol. According to X-ray diffraction data, the reaction gave octahedral cationic 1 : 2 complex $[Mn(L^2)_2(EtOH)_2](ClO_4)_2$ (**II**), which rapidly lost the solvation ethanol on storage. Drying at a reduced pressure of 1–2 mm Hg gave the complex $[Mn(L^2)_2(EtOH)_2](ClO_4)_2$ (**II**), the composition of which was confirmed by IR spectroscopy and elemental analysis.

The composition of complexes **I** and **II** was studied by X-ray diffraction analysis (Fig. 1). Complex **I** has an island structure where the metal atom coordinates one bis-phosphine oxide molecule and two chloride anions. The anions are terminal ligands, while bis-phosphine oxide is a bidentate chelating ligand. Thus, the metal coordination polyhedron is the distorted MnO_2Cl_2 tetrahedron. The independent part of the unit cell of **II** contains a metal atom located on a twofold rotation axis, a bidentate chelating bis-phosphine oxide molecule, a monodentate terminal ethanol molecule, and an outer-sphere perchlorate anion disordered over two positions. Thus, complex **II** also has an island structure, with the metal coordination polyhedron being a distorted MnO_6 octahedron.

The Mn–O bond length is shorter in tetrahedral complex **I** (2.0440(9)–2.06789(9) Å) than in octahedral complex **II** (2.085(9)–2.112(9) and 2.307(12) Å for phosphine oxide and ethanol, respectively). The Mn–Cl bond lengths are 2.3255(4)–2.3295(4) Å. The coordination of the bis-phosphine oxide groups causes elongation of the P=O bonds to 1.494(10)–1.519(10) Å versus 1.475(1)–1.479(1) Å length in the uncoordinated ligand, the structure of which was reported previously [16]. Like complexes of this ligand with the uranyl cation, which were studied by X-ray diffraction [9], the differences between the conformations of the uncoordinated ligand in $L·H_2O$ [16] and the coordinated ligand in the manganese(II) complexes can be attributed to rotation of two $Ph_2P=O$ moieties around the single $P–C_{diene}$ bond. Also, rotation around the $P–C_{Ph}$ bond gives rise to differences in the relative arrangement of the benzene rings. The ligand conformations in the crystals of the complex and in the free state are compared in Fig. 2.

Potentially, the composition of compound **I** allows the formation of halogen bonds and stacking interactions in the crystal. However, actually chlorine atoms are involved in weak C–H...Cl hydrogen bonds with atoms of the methyl and phenyl groups, while C=C bonds are shielded by other groups and are not involved in π...π interactions. As a result, most inter-

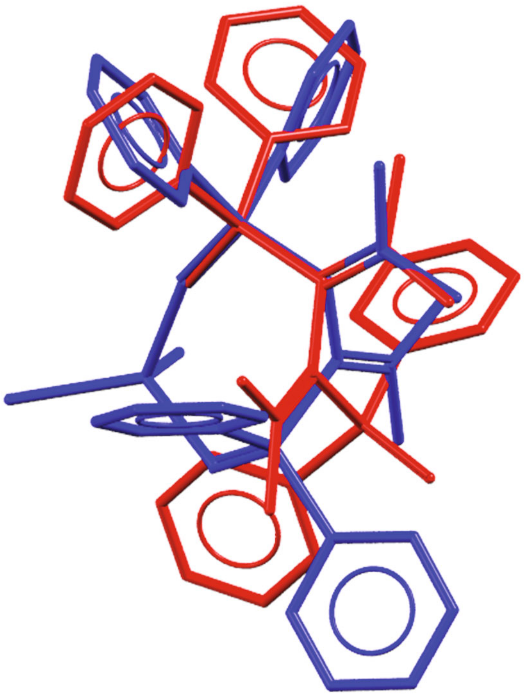


Fig. 2. Comparison of ligand conformations in the crystals of $[MnCl_2L^2]$ (blue) and $L·H_2O$ (red) [16]. The atoms of the POC_3 coordination polyhedra are superimposed onto one another. Hydrogen atoms are omitted.

molecular contacts are hydrophobic H...H and H...C interactions. In the structure of **II**, steric restrictions prevent stacking interactions and intermolecular hydrogen bonds, and molecular packing is due to electrostatic and hydrophobic interactions.

After recrystallization from acetonitrile, the sample of **I** was studied by powder X-ray diffraction. The full-profile Rietveld analysis of the X-ray diffraction patterns confirmed the phase purity of the compound; the sample corresponded to the crystalline phase of $[MnCl_2L^2]$.

The composition and structure of complexes **I** and **II** of manganese salts with 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2) and the previously described complexes of 2,3-bis(diphenylphosphinyl)-1,3-butadiene (L^1) [4] are significantly different. Whereas ligand L^1 gives octahedral 1 : 3 complexes $[Mn(L^1)_3][MnBr_4]$, the complex formation of L^2 gives, depending on the type of the counter-ion, either tetrahedral 1 : 1 complex $[MnL^2Cl_2]$ or octahedral 1 : 2 complex $[Mn(L^2)_2(EtOH)_2](ClO_4)_2$, in which two coordination sites are occupied by ethanol O atoms. This difference in the composition may be attributable to the larger size of ligand L^2 containing four methyl groups. However, another cause is also possible. A comparison of octahedral complexes $[Mn(L^2)_2(EtOH)_2](ClO_4)_2$ and $[Mn(L^1)_3][MnBr_4]$ [4] shows that the Mn–O bonds between Mn^{2+} and phosphinyl groups are markedly shorter in $[Mn(L^2)_2(EtOH)_2](ClO_4)_2$ than in $[Mn(L^1)_3]$-$[MnBr_4]$: 2.085(9)–2.112(9) and 2.140(3)–2.154(3) Å, respectively. Therefore, ligand L^2 is located more closely to the Mn^{2+} ion; this decreases the remaining space around Mn^{2+}, which is thus sufficient to accommodate two ethanol molecules, but not the larger L^2 ligand. Obviously, the same reasoning also applies to the single-ligand complex $[MnL^2Cl_2]$.

Thus, we studied the coordination properties of 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2) towards manganese(II) chloride and manganese(II) perchlorate by X-ray diffraction analysis. It was shown that the introduction of methyl groups into the 1,3-butadiene skeleton of 2,3-bis(diphenylphosphinyl)-buta-1,3-diene (L^1) considerably affects the coordination behavior towards manganese ions. The reaction of ligand L^2 with $MnCl_2$ gives 1 : 1 complex $[MnCl_2L^2]$, while the reaction with $Mn(ClO_4)_2$ affords 1 : 2 complex $[Mn(L^2)_2(EtOH)_2](ClO_4)_2$. Both complexes have island structure.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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