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Synthesis and Crystal Structure of {(2-α-Pyridylethyl)tris(phenyl)phosphonium}trichlorozinc(II)

V. A. Starodub and A. Yu. Stoesser

Deparment of Chemistry, Kharkov State University, pl. Svobody 4, Kharkov, 61077 Ukraine
e-mail: starodub@univer.kharkov.ua

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Abstract—The structure of the complex {(2-α-pyridylethyl)tris(phenyl)phosphonium}trichlorozinc(II), which is an unexpected product of the reaction of the Zn^{2+} ion with coordinated 4,5-(2-pyridylethylene)dithio-1,3-dithiol-2-thione, is described. The reaction mechanism is studied by the ESI method of positive and negative ions. The crystals are monoclinic, space group $P2_1/c$, a= 16.129(3) Å, b = 11.167(2) Å, c = 14.874(3) Å, β = 91.77(3)°, Z = 4. The Zn(II) atom has a quasi-tetrahedral environment of three chloride ions and one phosphonium cation coordinated at the nitrogen atom of the pyridyl fragment.

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INTRODUCTION

The 1,3-dithiol-2-thione-4,5-dithiolate complexes ($C_3S_5^{2-}$, **Dmit**) are widely used in modern chemistry in the syntheses of related synthetic metals and superconductors, magnetically ordered structures, and materials of nonlinear optics [1–3]. In recent time, transition metal complexes with 4,5-alkylenedithio-1,3-dithiol-2-thiones, tetrakis(alkylthio)tetrathiofulvalenes, and bis(alkylenedithiotetrathiofulvalenes) attract researchers' attention [4–7]. The method of Dmit functionalization proposed in [8] is of special interest. The authors synthesized alkylpyridyl derivatives of Dmit and demonstrated that they can be used as polyfunctional ligands. In particular, the $[MX_2L]$ complexes were described, where M is Co, Ni, Cu, or Pd; X is Cl or Br; L are alkylpyridyl derivatives of Dmit. The latter can be coordinated at both the nitrogen atom of the pyridyl ligand and the sulfur atoms of the thiol groups.

Note that the functionalization method proposed in [8] gives linear derivatives of Dmit. Using the method described in [9], we synthesized the products of cyclic functionalization of Dmit [10].

In the present report, we describe the synthesis, crystal structure, electrospray–ionization (ESI) data, and IR spectra of a new complex $[ZnCl_3L](MeCN)$ (**I**) (L^+ is the 2-α-pyridylethyl-tris(phenyl)phosphonium cation), which is an unexpected product in the reaction of zinc dichloride with triphenylphosphine and 4,5-(2-pyridylethylene)dithio-1,3-dithiol-2-thione (**II**), whose structure has been determined in [10].

EXPERIMENTAL

All procedures of the synthesis were carried out under dry nitrogen. Triphenylphosphine, $ZnCl_2$, and all solvents (Aldrich and Merck) were used as received. Ligand **II** was synthesized according to a known procedure [10]. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Vario EL instrument (Elementar–Analysesysteme).

Synthesis of complex I. Compound **II** (50 mg, 0.17 mmol) in MeCN (15 ml) was added with stirring to $[ZnCl_2(PPh_3)_2]$ (110 mg) obtained by dissolving $ZnCl_2$ (0.16 mmol) in MeCN (20 ml) containing PPh_3 (0.32 mmol). The reaction proceeds slowly and gives two types of crystals, i.e., red and colorless. The latter were suitable for X-ray diffraction analysis. The yield of the colorless crystals was 30 mg (17%).

For $C_{27}H_{26}Cl_3ZnN_2P$ (M = 581.24)

anal. calcd. (%):	C 55.79	H 4.51,	N 5.40.
Found, (%):	C 55.73,	H 4.42,	N 5.40.

ESI spectra were recorded on an ULTIMA FT-ICR mass spectrometer (Ionspec) with an electrospray source (Analytica). A solution of a mixture of crystals in an isopropyl alcohol–acetone mixed solvent was introduced into the instrument at a rate of 2 μl/min through a high-quality steel capillary with an inner diameter of 100 μm. The solvent was evaporated, and ions got into the region with high vacuum created by a two-step system of pumps (one turbomolecular pump and two cryopumps). The ions were transferred into a hexapole with a skimmer voltage of 20 V through a glass capillary, whose nickel-plated ends were fed with the potential difference from 390 to –140 V. Before detection by the instrument, the ions were accumulated in the hexapole during ~1500 ms. The pressure in this region was 1.33×10^{-4} Pa. The ions got through a qua-

Table 1. Main crystallographic data and experimental details for the structure of complex **I**

Parameter	Value
FW	581.24
Recording temperature, K	173 (2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	16.129(3)
b, Å	11.167(2)
c, Å	14.874(3)
β, deg	91.77(3)
V, Å^3	2677.72
Z	4
ρ(calcd.), g/cm^3	1.442
μ_{Ag}, mm^{-1}	1.72
F(000)	1125
θ range, deg	3.25–63.66
Index range	$-20 \le h \le 19$ $-14 \le k \le 14$ $-10 \le l \le 20$
Number of measured reflections	6302
Number of independent reflections	3347 (R_{int} = 0.0772)
Completeness with respect to θ_{max}, %	91.7
Number of refined parameters	293
R factors ($I > 2\sigma(I)$)	R_1 = 0.0692 wR_2 = 0.2158
R factors (for all data)	R_1 = 0.1010 wR_2 = 0.2370
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	1.86, –1.07

Table 2. Selected bond lengths and bond angles in complex **I**

Bond	d, Å	Bond	d, Å
Zn(1)–N(1)	2.098(3)	P(1)–C(8)	1.803(5)
Zn(1)–Cl(1)	2.267(3)	P(1)–C(14)	1.787(5)
Zn(1)–Cl(3)	2.243(3)	P(1)–C(20)	1.800(5)
Zn(1)–Cl(2)	2.253(3)	C(1)–C(6)	1.502(6)
P(1)–C(7)	1.806(5)	C(6)–C(7)	1.541(7)
Angle	**ω, deg**	**Angle**	**ω, deg**
Cl(1)Zn(1)Cl(2)	110.075(5)	N(1)Zn(1)Cl(1)	111.152(10)
Cl(1)Zn(1)Cl(3)	109.642(5)	N(1)Zn(1)Cl(2)	105.959(10)
Cl(2)Zn(1)Cl(3)	113.002(5)	N(1)Zn(1)Cl(3)	106.934(10)
Zn(1)N(1)C(1)	125.926(3)	P(1)C(7)C(6)	115.388(2)
Zn(1)N(1)C(2)	116.282(3)	C(1)C(6)C(7)	111.525(4)

drupole into an ICR cell (at 1.33 × 10^{-8} Pa), where they were detected.

X-ray diffraction analysis. A STOE STADI4 diffractometer with a planar detector and a graphite monochromator (MoK_α radiation, λ = 0.71073 Å) was used for data collection.

The structure was solved by a direct method (SHELXS97 [11]) and refined by the full-matrix least-squares method for F^2 in the anisotropic approximation (SHELXL97 [12]). Hydrogen atoms were localized geometrically and refined in the riding model with $U_{iso} = 1.2\ U_{eq}$ of the corresponding C atom.

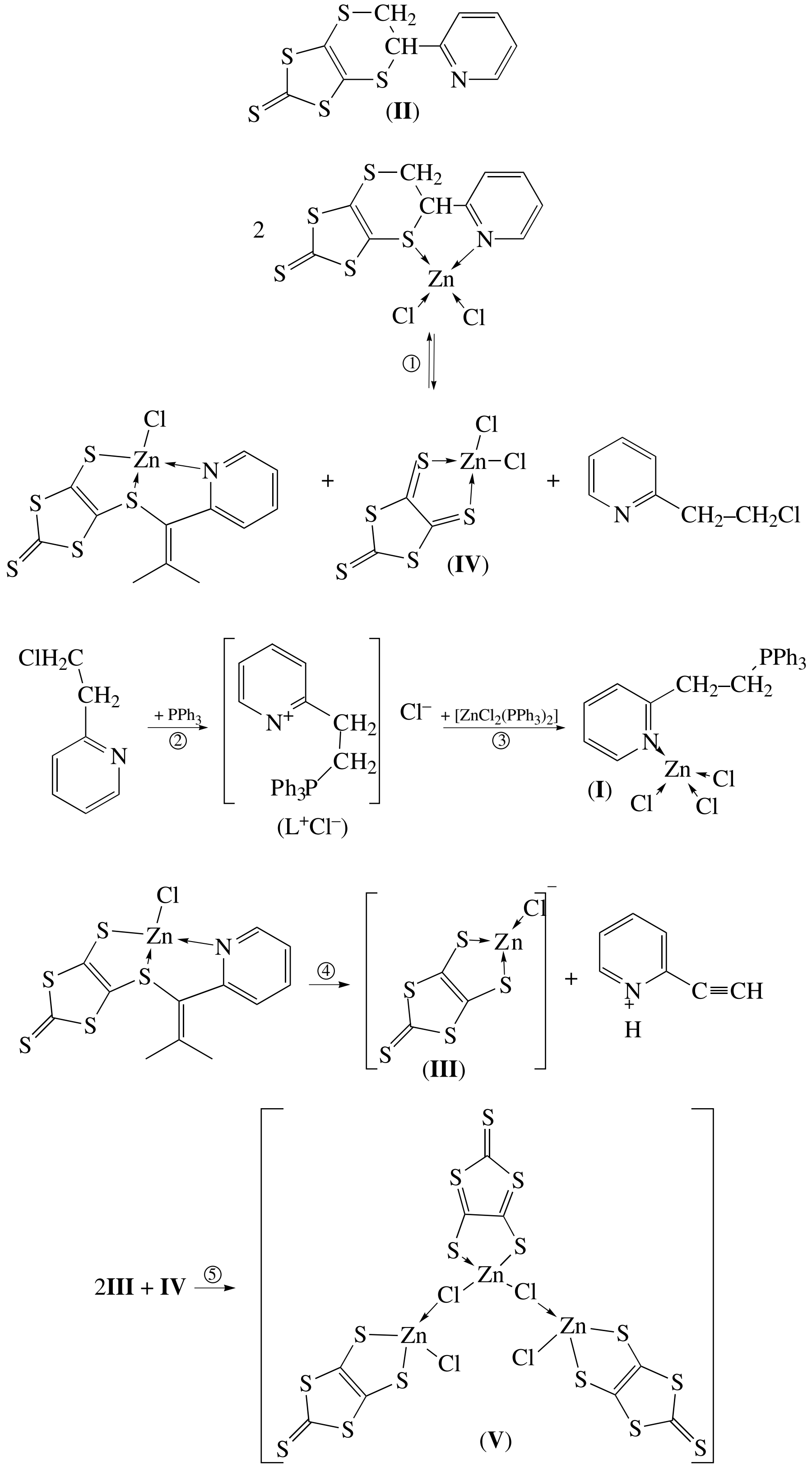
The main crystallographic data for compound **I** are presented in Table 1. The selected bond lengths and bond angles are given in Table 2.

Crystallographic information on the structure of compound **I** is deposited with the Cambridge Structure Database (CSDB no. 294892).

RESULTS AND DISCUSSION

Since the Zn^{2+} ion is classified as boundary Lewis acids, ligand **II** can be coordinated, according to Pearson's concept, to both the sulfur atoms and the nitrogen atom to form the [ZnCl$_2$(II)(PPh$_3$)] complex. However, according to X-ray diffraction data, the reaction of ligand **II** with ZnCl$_2$ and PPh$_3$ affords colorless crystals of complex **I** with the composition [ZnCl$_3$(L)](MeCN). This complex contains coordinated L$^+$ cation formed due to the homolytic cleavage of ligand **II**. A similar phenomenon was observed earlier [13]: the reaction of ligand **II** with mercury(II) halides afforded the [Hg(2PyDT-DTT)$_2$] complex, where 2PyDT-DTT is 5-(1-pyridin-2-yl-vinylsulfanyl)-2-thioxo-[1.3]dithiol-4-thiolate. This complex is formed by the decomposition of binuclear complexes [HgX$_2$(L')]$_2$ with the elimination of hydrogen halide HX. In our case, the formation of the L$^+$ cation can be presented by the following scheme, which also implies the heterolytic cleavage of the C–S bonds to form the Dmit^{2-} anion:

$$[ZnCl_2(PPh_3)_2] + \mathbf{II} \longrightarrow ZnCl_2(II) + 2PPh_3$$



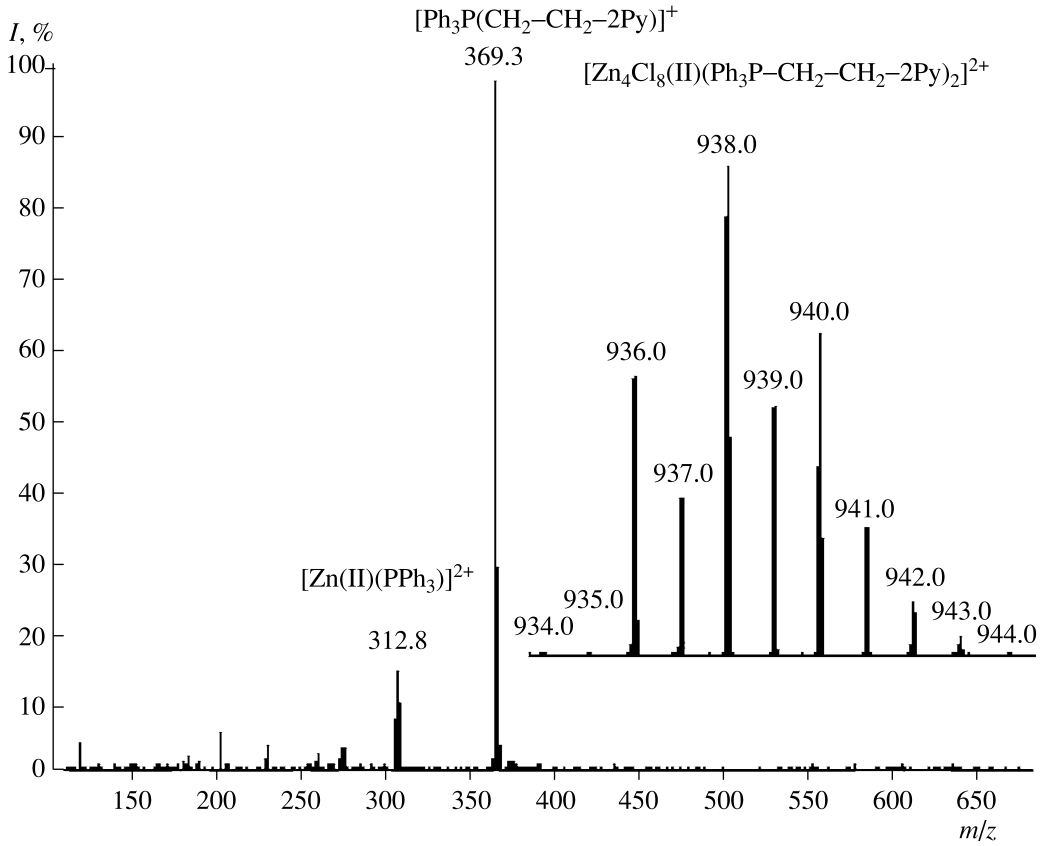


Fig. 1. ESI spectrum of positive ions in a mixture of crystals obtained in the synthesis of complex **I**.

This scheme agrees with the data of the ESI spectra. The most intense peaks in the ESI spectra of positive ions correspond to *m/z* values (I_{rel}, %) of 312.8 (15), 369 (100), and 938 (100). The peak with *m/z* = 369 corresponds to cation L. The peak with *m/z* = 938 is accompanied by lines with *m/z* = 934, 935, 937, 939, 940, 941, 942, and 943 with the intensity ratio corresponding to the content of isotopes ^{64}Zn, ^{66}Zn, ^{68}Zn, ^{32}S and ^{34}S, ^{35}Cl, ^{37}Cl in the doubly charged ion $[Zn_4Cl_8(II)(Ph_3–CH_2–CH_2–2Py)_2]^{2+}$. The less intense group of peaks with *m/z* = 312 (15%) corresponds to the doubly charged ion $[Zn(II)(PPh_3)]^{2+}$ (Fig. 1).

The ESI spectrum of negative ions (Fig. 2) exhibits two series of peaks with *m/z* (I_{rel}, %) at 296–304 (298–100) and 460–468 (46–100). The first of them corresponds to the [ZnCl(Dmit)] anion (**III**) formed by the heterolytic dissociation of the C–S bonds in ligand **II**. The second group of peaks corresponds to the $[Zn_3Cl_4(Dmit)_3]^{2-}$ doubly charged anion (**V**) containing two coordinated $C_3S_5^{2-}$ anions and coordinated isotrithionethiol molecule C_3S_5 (see scheme).

The molecular structure of complex **I** is shown in Fig. 3. The Zn^{2+} ion exists in the center of a distorted tetrahedron and is surrounded by three chloride ions and one ligand L coordinated at the nitrogen atom of the pyridyl fragment. The Zn–N bond length in complex **I** (2.100 Å) lies in a range characteristic of other coordinated heterocyclic amines (average Zn–N 2.056 Å) [3]. The Zn–Cl bond (average 2.254 Å) is

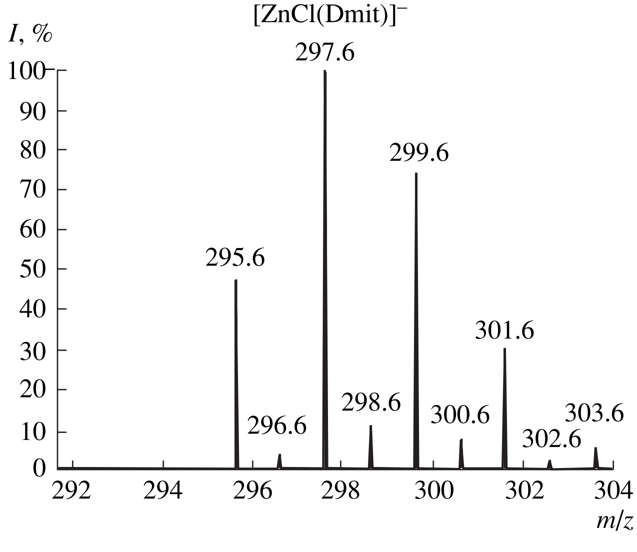


Fig. 2. ESI spectrum of negative ions in a mixture of crystals obtained in the synthesis of complex **I**.

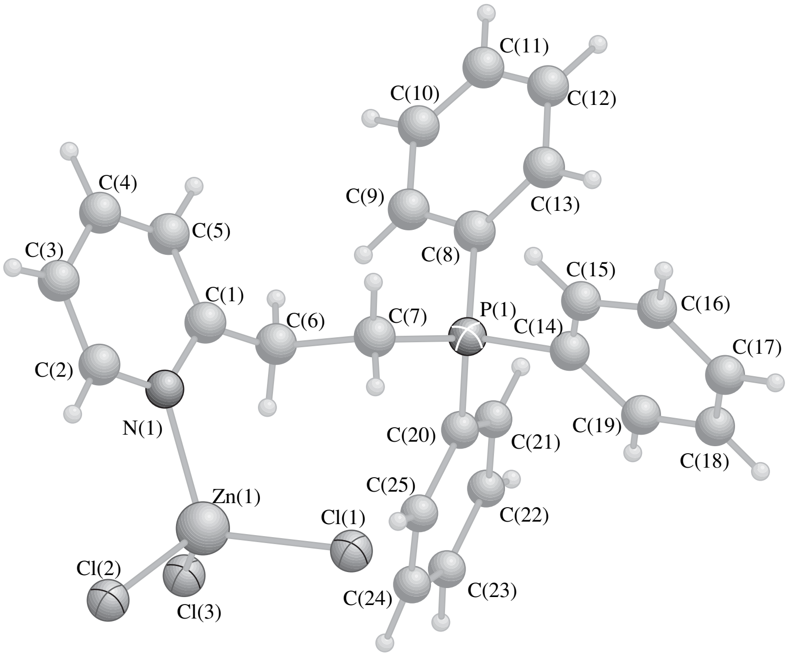


Fig. 3. Molecular structure of complex **I**.

much shorter than the sum of the ionic radii of Zn^{2+} and Cl^- (2.55 Å) [14] and occupies an intermediate position between the Zn–Cl bond length in gaseous $ZnCl_2$ (2.05 Å) and in salt $ZnCl_2 \cdot 1\frac{1}{3}H_2O$ (2.28 Å) built of infinite $(ZnCl_3)_n^{n-}$ chains [14].

The reaction of the Zn^{2+} ion with coordinated 4,5-(2-pyridylethylene)-dithio-1,3-dithiol-2-thione we discovered is unusual and occurs, probably, due to bidentate coordination of the latter, which facilitates cleavage of its C–S bonds.

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