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ORIGINAL ARTICLE **OPEN ACCESS**

Effect of The Substitute On The Structure of The Complex Compounds of Paraaminosalicylates of The Lead (Ii) And Synthesis And Physical-Chemical Studies Of Coordination Compounds Of Oktaakvabispara- Aminosalisilat Ion of The Lead (II)

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ABSTRACT
Synthesized nanostructured coordination lead compounds (II) with paraaminosalicylic acid are of interest for inorganic biochemistry. According to X-ray diffraction, element, infrared spectroscopic and derivatographic analysis, the individuality and chemical formula, as well as the process of thermal destruction of the complex are determined. It was found out that the structure of the complex compound consists of eight water molecules which are uncoordinated with the central atom. The proposed schematic structure of the complex is given on the basis of the results of the research.
Key words: *Crystalline structure, complex, element composition, IR spectroscopy, paraaminosalicylic acid, lead acetate, thermogravimetric analysis.*

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INTRODUCTION

Possible interactions of the lead with metabolites, the importance of which for life processes is the subject of dispute of many articles [1-4], in particular, with paraaminosalicylic acid (PAS) are of great interest for inorganic biochemistry. Crystalline structures of lead (II) complexes with paraaminobenzoic acid [5, 6] were synthesized and decoded. In various synthesis conditions complex compounds with different chemical formula were obtained– $[Pb(p\text{-}H_2NC_6H_4COO)_2]_n$ (I) и $[Pb(p\text{-}H_2NC_6H_4COO)_2NO_3]_n$ (II).

The crystalline structure of the complex compound (I) is constructed from one-dimensional polymer chains parallel to the axis (Fig. 1) and a carboxyl group of one of crystallographically nonequivalent anions of paraaminobenzoic acid (PABA) forms a chelate with the metal atom and simultaneously as a bridge links two other neighboring Pb atom.

Second PABA anion forms a chelate with only one atom of Pb. Atoms of N of aminogroup of PABA does not enter to the coordination sphere of Pb atom. The nitrogen atoms of the bridging anion PABA form hydrogen bonds with neighboring atoms of oxygen from the COO- group of a another chain. The structure of the complex compound II can be represented as a three-dimensional coordination polymer. But amid all the structure of patterns and compactness, the chains consisting of Pb atoms and fixed together by COO- PABA groups are standing out.

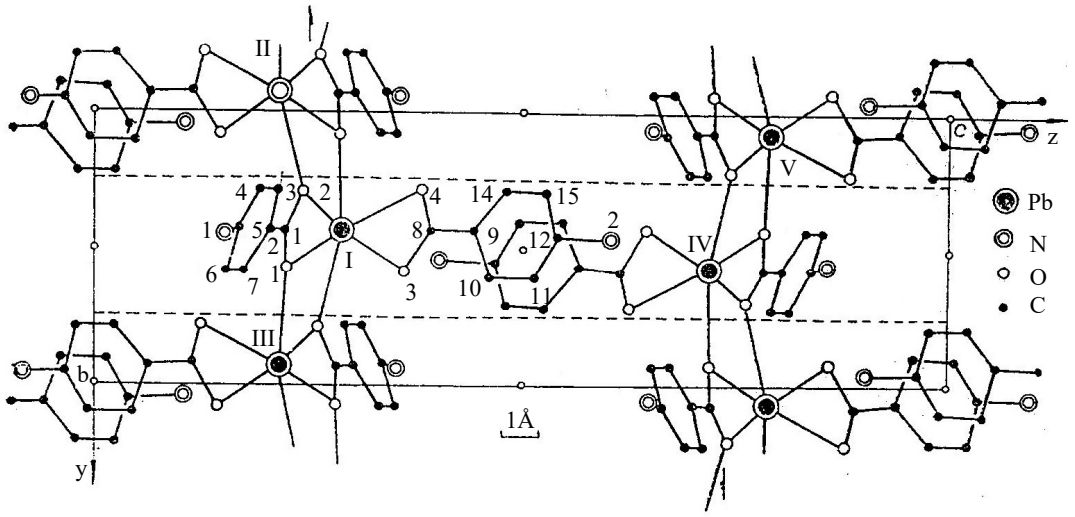

Fig.1. The crystalline structure of the complex compound – $[Pb(p\text{-}H_2NC_6H_4COO)_2]$.

In contrast to the complex (I), the nitrogen atom of NH_2 groups of PABA is included in the coordination sphere of the Pb atom.

As seen from the above, depending on the starting materials and the synthesis conditions with the same ligand, the lead (II) forms the complex compounds of various composition and structure. This article focuses on the synthesis and physical-chemical studies of the complex compound of Pb (II) with PASA - which differs from the above-mentioned ligand functional - OH group in the ortho - position. The aim of this study is to investigate the influence of the OH group on the composition and structure of the complex.

EXPERIMENTAL SECTION

The element composition of the obtained compound was defined by a gas chromatography method by means of an analyzer CHN30E Carlo ERBA. The content of the metal was calculated on the basis of the weight loss curve by the quantity of oxide obtained after being heated on derivatograph up to >827^{0}C. XRD analysis was performed on the Commander Sample ID (Coupled Two Theta/Theta WL=1,54060) IR spectra were recorded on SPECORD-M80 in 400-4000 sm^{-1} area. Derivatograms were recorded on NETZSCH STA 449 F3 STA 449 F3A-0836-M (range 23/10.0 (k/min)/1000).

Synthesis of complex. The starting materials were p-$NH_2C_6H_3(OH)COOH$, $Pb(CH_3COO)_2$ of qualification (GOST 3759-75). The complex is prepared by interaction of paraaminosalicylic acid with lead acetate at a stoichiometric ratio of 2:1. The solution was refluxed until disappearance of the odor of acetic acid, filtered while hot and cooled to room temperature.

Upon cooling small transparent single crystals dropped from the solution which were filtered and washed for several times with warm distilled water, and were left to dry on filter paper at room temperature. Chemical composition of the complex compound was defined on the basis of the data obtained from phase XRD, element, IR spectroscopic and thermogravimetric analysis.

RESULTS AND DISCUSSION

XRD of synthesized complex. XRD of complex compounds of lead (II) Shows the figure 2.

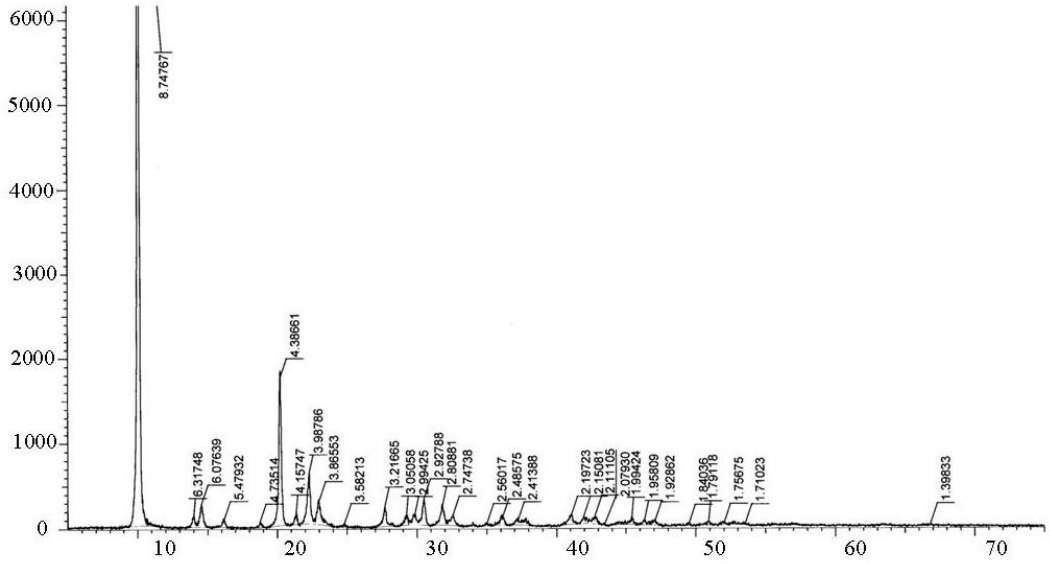

Fig.2. XRD of complex compound of leaf (II).

By the identification of X-ray the parameters of the unit cell of the complex compound: a=8.748; в=7.876; c=22.54 Å, were determined, two its parameters differ slightly, the third parameter differ significantly (0.22 Å) from the parameters of the unit cell of complex compound in I: a=8.766 (4); в=7.505 (4); c=22.758 Å.

To our opinion, this is due to the fact that the NH_2 – anion group unlike aminobenzoic complex of the lead (II) is included in the coordination of lead, but OH groups form intramolecular and intermolecular hydrogen bonds in the complex through a water molecule and due to this the polymer layers approach to each other and therefore the parameter "c" of the cell that is perpendicular to the layers, is shortened by 0.22 Å. Thus, the results of X-ray analysis make it possible to assume that the newly formed complex compound form two-dimensional polymeric structure along the axis b and c.

Element analysis of the complex. The results of element analysis of synthesized complex shows the table 1.

Table 1. The results of element analysis of synthesized complex.

Found, %				Formula	Calculated, %			
N	H	C	Pb		Pb	C	H	N
4.30	3.73	27.74	31.65	Pb $C_{14}H_{22}N_2O_{14}$	31.62	25.64	3.63	4.27

On the basis of the results of the element analysis, the chemical formula of the complex compound has been formed - $[Pb(p\text{-}NH_2C_6H_3(OH)COO)_2(H_2O)_8]$.

IR spectra of synthesized complex. Figure 3 shows the IR spectra of the complex compound Comparison of the IR spectra of the complex compound and the acid showed that the absorption band at 1659 and 1615 cm^{-1} in the acid which relates to the valent vibrations of the carboxyl group in a complex, shifts to low-frequency region 1625 and 1583 cm^{-1} (ν_{BS}) and symmetrical absorption bands appear (ν_S) at 1377 and 1321 cm^{-1}.

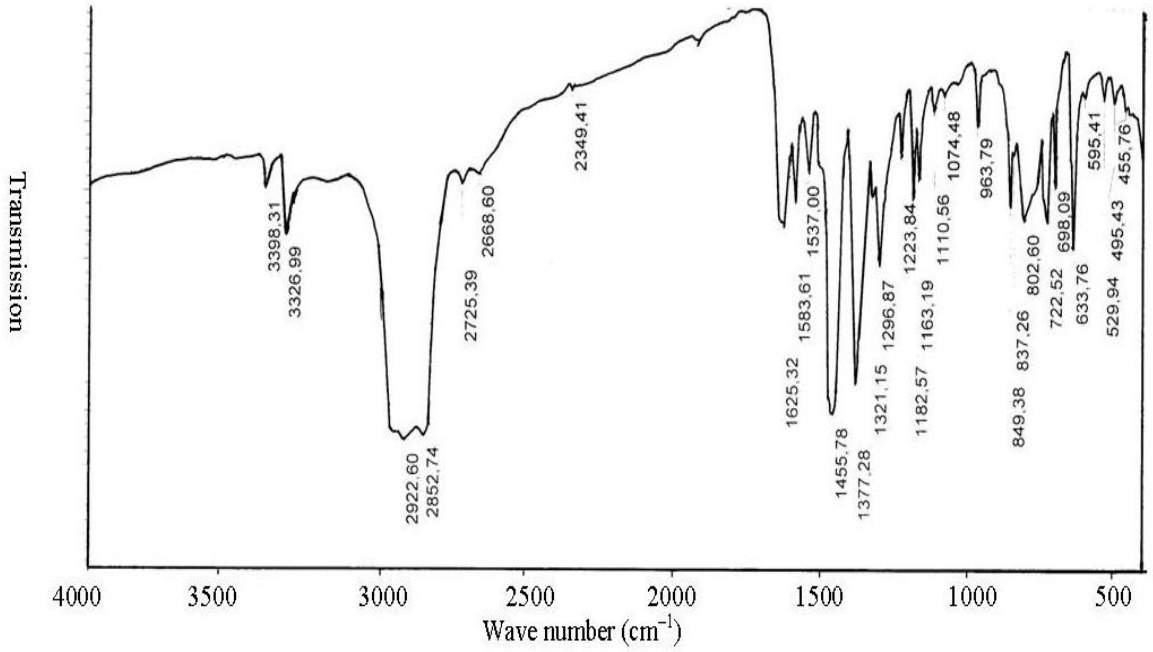

Fig.3. IR spectra of complex compound of lead (II).

This means that complex formation with paraaminosalicylic acid, unlike paraaminobenzoic acid, forms a chelate with the central atom bidentate complex. Value of difference ν_α и ν_S COO- groups of the ligands is 248 and 262 cm^{-1} which shows that the paraaminosalicylic acid anions are associated identically with the same central atom.

From the IR spectra of the complex compound and the acid can also be seen that the absorption bands at 3494 and 3386 cm^{-1} in an acid which refer to NH_2 group in the complex are shifted to lower frequency region 3398 and 3326 sm^{-1}, which clearly shows the co-ordination of NH_2 groups with the lead (II) [7, 8]. IR spectroscopy results show that at the formation of complex compounds of the lead (II) with paraaminosalicylic acid denticity of carboxyl groups, unlike p-aminobenzoic complex of lead (II) is identical - chelate. Thus, the results of IR spectroscopy also confirm the structure obtained by data of X-ray analysis.

Thermogravimetric analysis of the complex. Thermogravigram of the complex compound is shown in Fig. 4. Decomposition of the complex compound $[Pb(p\text{-}NH_2C_6H_3COO(OH))_2\cdot(H_2O)_8]$ starts at 197^{0}C and is accompanied by a shallow, but a clear endothermic effect with the maximum at 207,6^{0}C and corresponds to the removal of eight water molecules.

Experimental mass loss value is 21.09% (calculated 21.97%). As seen from the thermogravigram, water molecules leave the crystal lattice at a high temperature and with high speed. This indicates that the molecules are bonded to OH group and to each other by strong hydrogen bonds. Then, in 225-700^{0}C temperature range, gradually decomposition of anhydrous intermediate of the complex compound and burning down of the organic part of the molecule takes place. Experimental mass loss in this case is 38.15% without one carbon atom and three atoms of oxygen (calculated 37.24%). $PbCO_3$ is formed as an intermediate product of thermolysis after burning down of the organic part of the complex. Net weight is 40.76% (calculated 40.78%). $PbCO_3$ is stable up to 827^{0}C. Then a weight loss is observed on the thermogram which corresponds to the decomposition of the lead carbonate with removal of a carbon dioxide which is equal experimentally 0.18% (calculated 0.17%). The PbO is an final product of thermolysis.

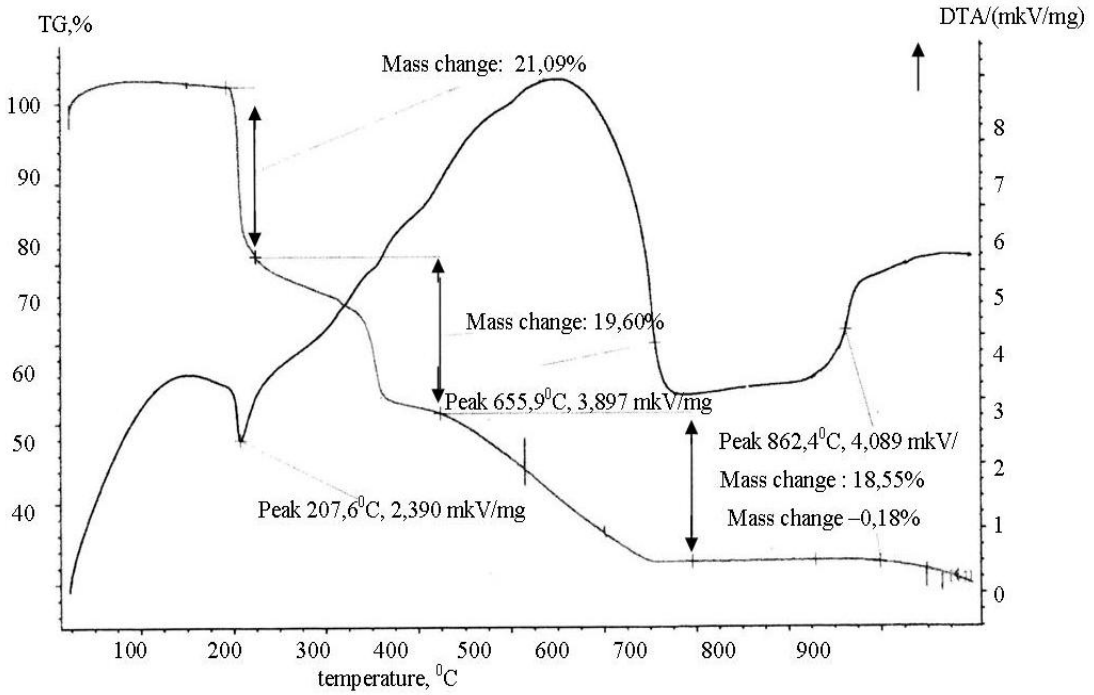

Fig.4. Thermogramm of complex compound of lead (II).

Below is a diagram of a solid phase transformation of the complex compound.

$$[Pb(p\text{-}NH_2C_6H_3(OH)COO)_2(H_2O)_8] \xrightarrow[-\,8H_2O]{197\text{-}225\ (207{,}6^0C)} [Pb(p\text{-}NH_2C_6H_3(OH)COO)_2]$$

$$\xrightarrow[\text{- organic part}]{225\text{-}700\ (550^0C)} PbCO_3 \xrightarrow[-\,CO_2]{>\,827^0C} PbO.$$

Thus, the results of thermogravimetric studies also confirm the results of X-ray, element analysis and infrared spectroscopy, i.e. the complex compound has the chemical formula of $[Pb(p\text{-}NH_2C_6H_3(OH)COO)_2(H_2O)_8]$. As we have already mentioned paraaminobenzoic complex of the lead (II) lacks water. Taking into consideration that paraaminosalicylic acid differs from paraaminobenzoic acid only for OH group located in the ortho–position, due to OH group paraaminosalicylate of lead (II) involves in itself 8 molecules of water. As a result of this the crystalline structure of the complex compound is also radically different from the structure of the complex compound of anhydrous paraaminobenzoate of the lead (II).

Thus, in the complex of paraaminosalicylate of the lead (II), carboxylic acid groups form a chelate with a metal and an amino group of anion in the axial position enters to a coordination of a central atom. As a result, parallel two-dimensional checkered polymer layers that are bound together by hydrogen bonds via the crystalline water molecules are formed and 3D structure is established. Estimated schematic structure of the complex compound of the paraaminosalicylate of the lead (II) is shown in Fig. 5. The coordination number of the lead is 6 and coordination polyhedron is octahedron. All eight water molecules are crystalline and they are found in carcass and interpolymeric spaces.

CONCLUSIONS

The carrying out experiments show that the presence of paraaminosalisilate anions OH^- group in ortho position leads to the significant change of complex compound structure. Unlike of Pb paraaminobenzoate anions of this complex show the monodensitity and N atoms of NH_2 groups are included into the coordination sphere of central atom. Therefore the polymeric structure of this complex compound is provided.

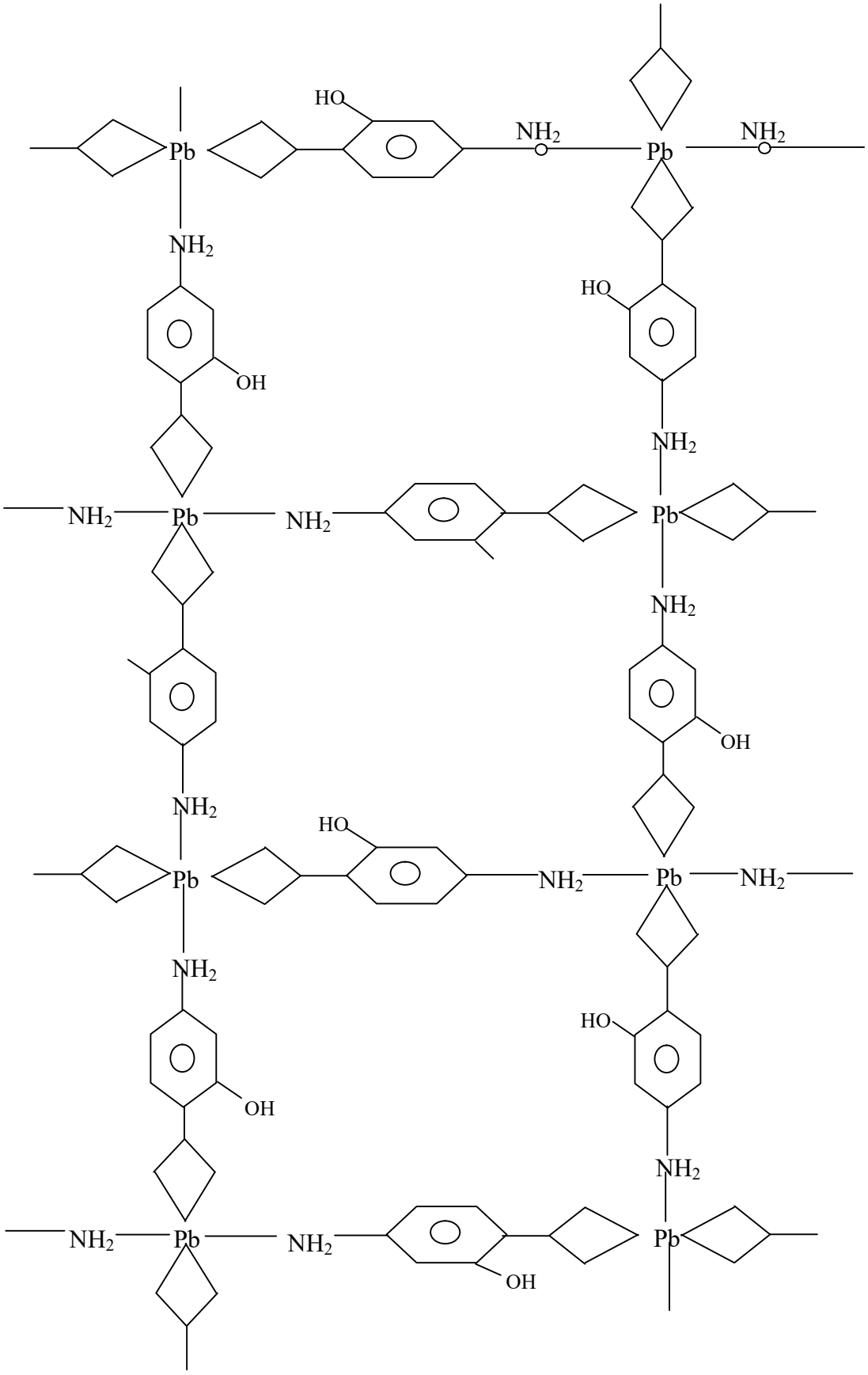

Fig.5. Proposed schematic structure of the complex compound.

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