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IR SPECTROSCOPIC STUDY OF SULFUR- AND PHOSPHORIC-CONTAINING IMMOBILIZED LIGAND

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ANNOTATION

The article studies the IR spectrum of a covalent immobilized ligand based on in situ covalent attachment by O, O-di- (2-aminoethyl) -dithiophosphate potassium on a urea-formaldehyde matrix. As a result of the carried out IR spectroscopic studies, the structures of the ligand and its coordination compound with copper (II) were determined.

Keywords: IR spectroscopy, covalent immobilized ligand, O,O-di-(2-aminoethyl)-dithiophosphate potassium, coordination compound of copper (II).

INTRODUCTION

Recently, a new direction of synthesis of promising sorbents has been actively developing by modifying various polymeric materials and metal complexes based on them. As a result of the modification, the structure of not only the organic matrix changes, but also the composition of functional groups, which makes it possible to obtain sorbents with increased selective and selective properties and use them for concentration, separation and determination of metals from dilute solutions and their metal complexes as catalysts for heterogeneous catalytic processes [1 , p.7].

The sorbent was obtained by polycondensation of urea, formaldehyde and 2-aminopentanedioic acid, and its sorption properties were also studied [2, P.71], the cellulose surface was functionalized with thiosemicarbazide groups [3, p.393], immobilized metal complexes of some d and f elements with hetarylformazans [4, p.53], studied the concentration of Cu (II), Co (II), Ni (II) and Cd (II) on silica gel with a covalently immobilized azohydrazone group [5, p.13], determined the sorption characteristics of Co (II), Cd (II), Ni (II), Cu (II) and Zn (II) on silica gel with covalently immobilized 1- (2-pyridylazo) -2-naphthol [6, p.57]. A sorbent for the concentration of lanthanum from large-volume water samples has been proposed. The sorbent is stable under dynamic conditions and is based on supercrosslinked polystyrene modified with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one [7, p. 497].

Chelating immobilized ligands are widely used for the concentration and separation of trace elements. Further development of their application is associated with high selectivity and effective effect of concentration of ions of elements from solutions of complex chemical composition. The use of immobilized ligands with high selectivity towards non-ferrous metal ions is one of the promising directions in the practice of wastewater treatment.

The aim of the study is to synthesize a new immobilized ligand based on in situ covalent attachment of O, O-di- (2-aminoethyl) -dithiophosphate of potassium on a urea-formaldehyde matrix, which has a high complexing property to copper and silver cations.

EXPERIMENTAL PART

An immobilized ligand based on covalent attachment was synthesized by the in situ method of O, O-di- (2-aminoethyl) -dithiophosphate potassium on a urea-formaldehyde matrix. The process of covalent immobilization of O, O-di- (2-aminoethyl) -dithiophosphate potassium with urea-formaldehyde resin was carried out in molar ratios 1: 2 of the starting materials at a temperature of 90 ° C, the reaction time was 1 h. Based on the results of elemental analysis, it was found: C – 29,16%, H - 4,98%, N – 16,55%, O – 13,82%, P – 9,46%, S – 18,93%; calculated: C – 29,03%, H - 4,84%, N – 16,29%, O – 14,2%, P – 9,15%, S – 18,31%. $(C_{14}H_{32}N_8O_6P_2S_4K_2)_n$, n=50-70. IR spectrum: ν(NH) 3296 cм$^{-1}$, $\nu_s(CH_2)$ 2917 cм$^{-1}$, $\delta(CH_2)+\delta(CN)$ 1628 cм$^{-1}$, $\delta_{as}(CH_2)$ 1474 cм$^{-1}$, $\delta_s(CH_2)$ 1370 cм$^{-1}$, ν(C-O) 1170 cм$^{-1}$, ν(POC) 1029 cм$^{-1}$, ν(C-C) 895 cм$^{-1}$, ν(P-O) 728 cм$^{-1}$, ν(P=S) 684 cм$^{-1}$, ν(P-S-) 468 cм$^{-1}$ (Fig. 1, table 1.).

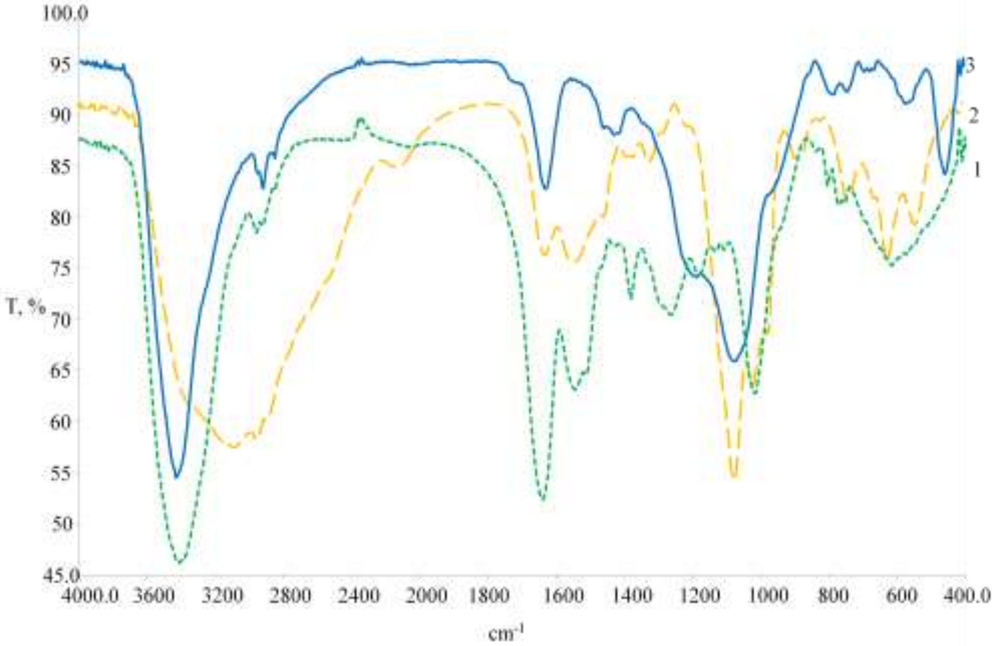


Fig. 1. IR spectra of urea-formaldehyde matrix (1), di- (2-aminoethyl) potassium dithiophosphate (2) and sorbent (3) based on them.

Table №1. Absorption frequencies in the IR spectra of ligand L and its coordination compounds with the Cu (II) ion, cm^{-1}

Absorption frequency, cm^{-1}			**Absorption frequency characteristics**
Potassium di- (2-aminoethyl) - dithiophosphate	L	L+ Cu (II)	
3084	3296	3308	ν(NH)
2952	2917	2923	$\nu_s(CH_2)$
1628	1628	1603	$\delta(CH_2)+\delta(CN)$
1457	1474	1471	$\delta_{as}(CH_2)$
1367	1370	1382	$\delta_s(CH_2)$
1074	1170	1128	ν(C-O)
973	1029	1035	ν(POC)
895	895	893	ν(C-C)
743	728	752	ν(P-O)
625	684	653	ν(P=S)
545	468	445	ν(P-S-)

RESULTS AND ITS DISCUSSION

The structure of the resulting ligand, synthesized on the basis of covalent attachment of O, O-di- (2-aminoethyl) -dithiophosphate potassium on a urea-formaldehyde matrix, is proposed as follows.

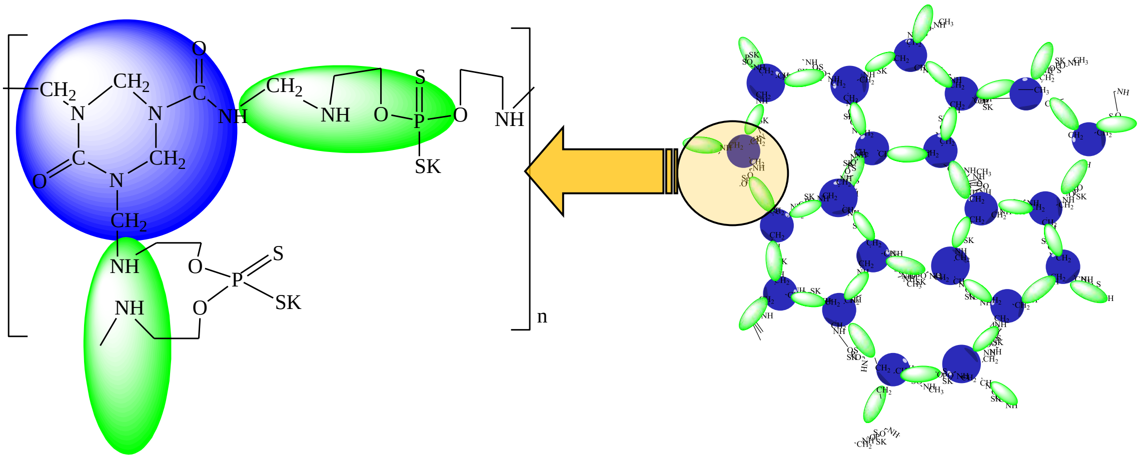
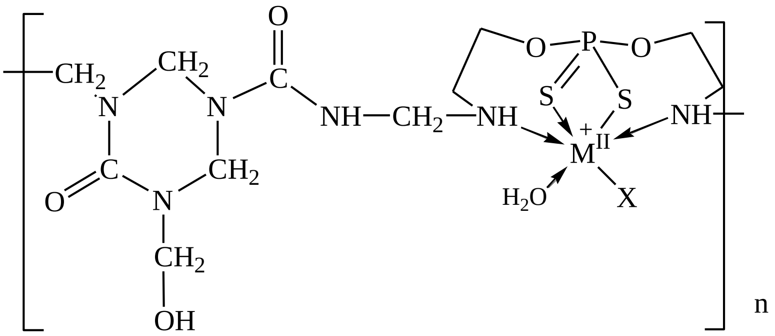


Fig. 2. Model of covalent attachment of O, O-di- (2-aminoethyl) -dithiophosphate potassium on a urea-formaldehyde matrix.

The complexation of metal ions by the obtained macroligand has been studied. For this, 250 ml of a 0.1 N solution of nitrate and chloride salts of the corresponding metals were prepared, of which 10 ml were poured into glass ampoules, 0.03 g of macroligand was added and left for 2 hours.

According to the results of the study, the P = S and P-S-H groups contained in the L ligand molecule form coordination bonds with metal atoms. In this case, the S-H group undergoes deprotonation (the H atom has an effective charge of 1.209 eV), and the sulfur atom forms a bond with the metal atom. The metal ion can bind to the complexing agent of the ligand L through its sulfur atoms to form an internal chelate-type complex. These theoretical conclusions were verified based on the analysis of the IR spectra of the obtained complex compounds. Based on the data of IR spectra, the structure of complex compounds formed as a result of sorption has the following form:



Here, M^{II}-Cu (II), X- Cl^-, NO_3^-.

CONCLUSIONS

A covalent immobilized complexing ligand has been synthesized based on in situ covalent attachment by the O, O-di- (2-aminoethyl) -dithiophosphate potassium method on a urea-formaldehyde matrix. The vibration frequency of the characteristic groups of the obtained ligand was studied by infrared spectroscopic analysis. It was also established by IR spectroscopy that complexation involves the substitution of the protons of the thio group of the ligand with Cu (II) ions and the formation of two seven- and one four-membered strong metal chelate through the amino and thio groups of the ligand.

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