A COMPARATIVE STUDY OF THE STRUCTURE
OF COPPER AND LEAD XANTHATES

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XPS, PbL_3 and CuK EXAFS, solid state NMR, and EPR techniques are used to study insoluble products formed in the interaction of aqueous solutions of lead(II) nitrate and copper (II) sulfate with potassium *n*-butylxanthate (KX). The XPS spectra of lead xanthates with the composition PbX_2 are similar to those of KX, and interatomic distances of 0.279 nm suggest a nearly ionic character of Pb–S bonds. In copper xanthate precipitating together with dixanthogen (approximately 15 wt.%), the Cu(I)–S bond length is smaller (0.229 nm), and copper coordination number of 2.9 in a composite with dixanthogen increases to 3.3 after its removal by washing with acetone. The XPS spectra indicate the covalent character of the bond and non-equivalence of xanthate radicals. Solid state ^{1}H and ^{13}C NMR spectra as well as the actual absence of metal lines under the measurement conditions demonstrate strong disordering of the structure of xanthates, which is stronger for PbX_2 and weakest in CuX after the removal of dixanthogen. EPR reveals sulfur-containing radicals and Cu^{2+} in CuX, however, their amounts are insignificant and decrease after the washing with acetone. The results of the work are significant for the understanding of the reactivity of xanthates, in particular, under the conditions of flotation of base metal ores.

INTRODUCTION

Xanthic acid salts ROC(S)S$^-$, where R is an alkyl radical (further X$^-$), are used in the production of rayon and pesticides, as additives for lubricating oils and to control rubber polymerization and vulcanization [1-4]; some xanthates exhibit antitumor, anti-inflammatory, fungicide, antioxidant, and antivirus activities [5-7]. Xanthates are applied in the analytical determination, separation, and precipitation of heavy metals in hydrometallurgy and wastewater treatment. Metal xanthates, including copper and lead ones, decompose with the formation of nanosized metal sulfides at relatively low temperatures of 140-160 °C, which allows the use of this method to produce polymeric composites for solar energy conversion, nonlinear optics, sensors, heat sensors, etc. [8-10]. A great amount of alkali metal xanthates is used as collectors in flotation of base and precious metal sulfide ores [11]. Up to date, however, the action mechanism of xanthates has been far

from clear. Copper and lead xanthates that are least soluble among abundant non-ferrous metals and iron are of the greatest interest in the theory and practice of flotation and other processes. There is a number of studies of the structures of bulk xanthates with diverse hydrocarbon radicals [12-21], but low-dimensional and weakly ordered products formed in suspensions and on the surface of minerals under real flotation conditions can be substantially different. Thus, in the direct interaction of aqueous solutions of copper(II) ions

$$Cu^{2+} + 2X^- \rightarrow CuX + 0.5X_2 \tag{1}$$

we obtain a mixture of copper(I) xanthate and oil-like dixanthogen, in fact, in the form of a composite nanosized material [22] whose structure and properties have been scarcely studied. Meanwhile, dixanthogen having strong adhesion to various surfaces and the hydrophobizing action [23] can significantly change the xanthate properties. Lead xanthate is formed by the exchange reaction

$$Pb^{2+} + 2X^- \rightarrow PbX_2. \tag{2}$$

However, for example, a possible formation of basic lead xanthate PbOHX, galenite of "molecular" lead xanthate, and dixanthogen on the surface of galena PbS was reported [12, 24, 25].

The aim of this work was a comparative study of the structural properties of lead and copper *n*-butylxanthates obtained by a simple chemical reaction in an aqueous solution with the use of X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (EXAFS), solid state NMR, and EPR. Much attention was paid to the dixanthogen effect on the features of the structure and properties of copper(I) xanthate, which can be important, in particular for flotation processes.

MATERIALS AND RESEARCH TECHNIQUES

In this work, copper sulfate and lead nitrate (chemically pure), potassium *n*-butylxanthate (~ 95% purity), acetone (high purity grade), deionized water (resistance higher than 10 MOhm·cm) were used. Potassium xanthate was purified by double recrystallization from acetone and stored in the frozen state; aqueous xanthate solutions were prepared directly before the experiment. To obtain copper(I) and lead(II) xanthates at room temperature equal volumes of aqueous solutions of $CuSO_4$ or $Pb(NO_3)_2$ (20 mM) and potassium xanthate (40 mM) were mixed at room temperature. The hydrosols were centrifuged (9000 rpm, 10 min), the precipitate was washed several times by decantation with water, separated from the solution, and dried in the air to the constant weight. The samples obtained had a yellow color typical of xanthic acid salts. Copper xanthate containing about 15 wt.% of dixanthogen had a pasty consistency; to remove dixanthogen the product was five times washed with acetone.

XPS spectra were measured on a SPECS spectrometer with a PHOIBOS 150 MCD 9 energy analyzer at room temperature and a pressure in the analytical chamber of 10^{-9} mbar. To excite the spectrum monochromatized AlK_α radiation (1486.6 eV) of the X-ray tube was applied. The C1*s* line of the xanthate hydrocarbon radical (285.0 eV) was used as the internal standard to take into account electrostatic charging; if necessary, a slow electron gun was utilized to eliminate heterogeneous charging of the samples. The XPS spectra were processed with the CasaXPS program; the spectra were fitted by Gauss-Lorentz peaks after the Shirley background subtraction.

The Cu*K*-edge EXAFS spectra were measured in transmission mode of a VEPP-3 storage ring of the EXAFS station (electron energy 2 GeV, average current 50-100 mA) at the Siberian Center for Synchrotron and Terahertz Radiation (Budker Institute of Nuclear Physics, Novosibirsk, Russia) with the use of a Si(111) slit monochromator and argon-helium ionization detectors. Oscillating parts of the absorption spectra $\chi(k)$ weighted by a k^2 factor were obtained by the standard procedure in the VIPER program [27]. The local environment of metal atoms was found using the fitting procedure implemented in the EXCURV 98 program package [28] for Fourier filtered experimental data ($\Delta R = 1.5\text{-}3.2$ Å). In processing the data the phase and amplitude characteristics were calculated in the von-Bart and Hedin approximation. The normalized oscillating part of the absorption spectra $\chi(k)$ with k^2 weighing were fitted in the photoelectron wave vector range from 3.0 Å^{-1} to 12.0 Å^{-1}.

Because of the absence of the reference compound in the calculations the factor S_0^2 was taken to be 1.0. The spectra were simulated in the single-scattering approximation for the first coordination sphere.

^{1}H and ^{13}C solid state NMR measurements were performed at room temperature on an AVANCE-300 spectrometer (Bruker, Germany) with Larmor frequencies of 300.14 MHz for protons and 75.47 MHz for carbon respectively. The ^{1}H NMR spectra were measured by Fourier transform spectroscopy with a duration of a 90° pulse of about 4 μs. The ^{13}C spectra were measured by cross-polarization with proton decoupling. The crystalline adamantane line with δ of 38.56 ppm relative to tetramethylsilane was used as the external standard for the ^{13}C spectra [29]. The EPR spectra were measured in CW mode on an ELEXSYSE-580 spectrometer (Bruker, Germany) in quartz ampoules at room temperature.

RESULTS AND DISCUSSION

XPS. The XPS study of the samples (Fig. 1, Table 1) shows that the elemental composition of the surface of lead *n*-butylxanthate only insignificantly deviates from the stoichiometry of the $Pb(SSCOR)_2$ compound. Thus, the ratio Pb:S = 3.6 instead of expected 1:4, which seems to be explained by the structural features of the surface; a possible contribution of PbX_2 decomposition in the air or the spectrometer vacuum under X-ray radiation cannot be excluded [30]. In the copper xanthate sample, dixanthogen almost completely evaporated under ultrahigh vacuum conditions, which is evidenced by the ratio Cu:S = 2.0 and the elemental composition as a whole that is close to the stoichiometry of the Cu(SSCOR) compound. After the preliminary removal of dixanthogen with acetone the Cu:S ratio even slightly increases, which is likely to be explained by structure disordering, e.g., outside orientation of hydrocarbon chains near the surface.

In the lead xanthate spectra the Pb4*f* doublet is well described by one component with the binding energy of the Pb4$f_{7/2}$ maximum of 138.1 eV, which is characteristic of lead(II) xanthate [31]. The spectra of copper xanthate before and after the dixanthogen removal with acetone were, in general, identical. The spectrum of copper with the Cu2$p_{3/2}$ peak at 932.9 eV, the absence of shake-up satellites at 944-948 eV, and the position of the maximum of the CuL_3MM Auger spectrum at 916 eV confirms that copper is in the Cu(I) state, and the amount of Cu(II) is lower than the detection limit of the method.
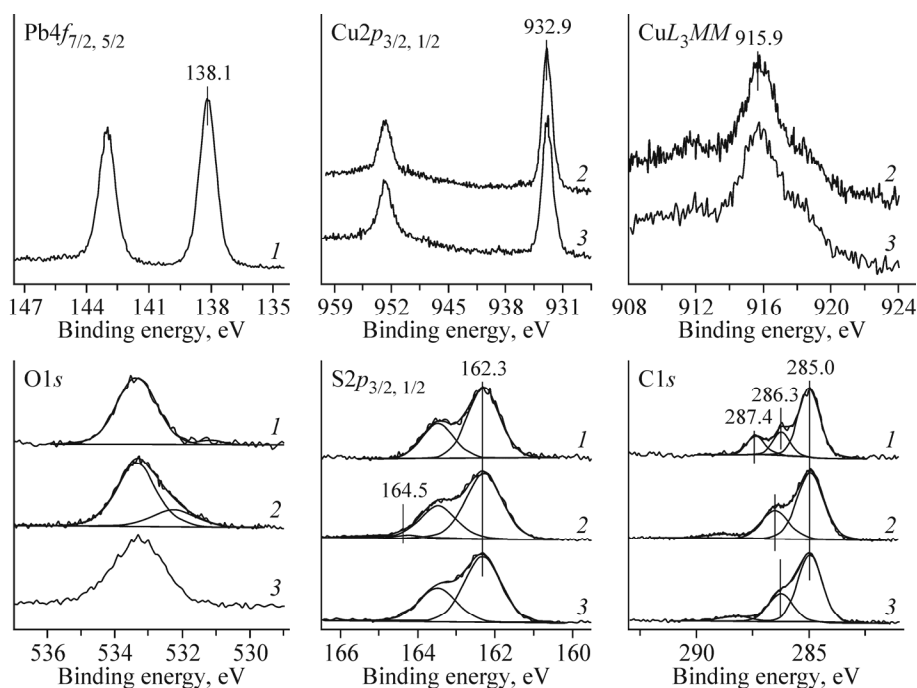

Fig. 1. XPS spectra of lead *n*-butylxanthate (*1*), mixture of copper xanthate with dixanthogen (*2*) and after its removal (*3*).

TABLE 1. Atomic Concentrations of Elements from the XPS Data, %

Sample	M	S	O	C
PbX$_2$	6.5	24.1	9.5	59.9
CuX+X$_2$	8.5	17.0	14.8	59.6
CuX	8.3	19.0	10.9	61.8

The S2p band for lead xanthate can be fitted by the main S2$p_{3/2}$ component with a binding energy of 162.3 eV, which is similar to that in KX and agrees with the data on lead xanthate [24, 25]. In the spectrum of copper xanthate, along with the main doublet, a weak band (5-10%) appears near 164 eV, which can belong to bridging sulfur atoms in residual dixanthogen or xanthate degradation products. Note also that the width of sulfur lines is larger for copper xanthate than for lead xanthate.

The greatest distinction is observed in the spectra of carbon. The C1s spectrum of lead xanthate resembles the spectrum of potassium xanthate and contains aliphatic carbon lines at 285.0 eV and the bands near 286.5 eV (–CH$_2$–O–) and 287.4 eV (–C(S)S$^-$) whose intensity ratio of 4.6:1.3:1.0 is close to 5:1:1 expected for n-butylxanthate. As noted in [14, 24, 25], the bonding of the –C(S)S$^-$ group with the Pb^{2+} ion practically does not affect the binding energies of carbon and sulfur from the respective group. However, in the C1s spectra of copper xanthate the intensity of the 286.5 eV line assigned to the –CH$_2$–O– group is several times higher than that of the –C(S)S$^-$ group, which is, in addition, shifted to a higher binding energy (288 eV). Apparently, the local positive charge of the major part (~75%) of carbon atoms bonded to sulfur decreases and becomes close to that on the carbon atom bonded to the oxygen atom. After washing with acetone for dixanthogen removal, a relative decrease occurs in both signals together with some decrease in the binding energy of the line of carbon bonded to sulfur. In principle, it can be explained by hydrocarbon contamination of the sample during treatment with an organic solvent. However, a change and disorder of the xanthate structure seems to be more probable. Note that long-term (of about half-year) storage of copper xanthate in the air did not cause similar changes, although dixanthogen almost completely evaporated. The O1s line with a binding energy of 533.3 eV corresponds to oxygen in xanthate [12-14] and, probably, some contribution of residual water. In the spectrum of copper xanthate a band at 532.2 eV is also observed (about 20% of the total intensity) whose assignment is ambiguous; sometimes it was ascribed to impurities [25]. On the other hand, it is possible to expect that the electron density shift observed in the spectra of carbon must also affect the spectra of oxygen. Thus, unlike lead xanthate where the ionic type metal–sulfur bond is dominant, in the copper(I) xanthate–dixanthogen composite there is a strong specific Cu–S interaction. It seems to be accompanied by a decrease in the local positive charge on three of four C* carbon atoms bonded to sulfur, whereas in one of the –C–O–C*(S)S$^-$ groups, on the contrary, the positive charge increases and decreases on the neighboring oxygen atom.

EXAFS. Results of the EXAFS study of xanthates are depicted in Fig. 2 and Table 2. Coordination number (c.n.) of 3.7 was obtained for the lead compound, which is close to the stoichiometric one, and the average Pb–S bond length is 2.79 Å; shorter Pb–O bonds are absent. Note also a high Debye–Waller factor. According to the single crystal X-ray diffraction data on monoclinic crystalline lead butylxanthate [18], bond lengths between lead and sulfur atoms of one of the xanthate molecules are 2.82 Å and 2.77 Å, and for another molecule they are 2.76 Å and 3.03 Å, i.e. the average bond length (2.85 Å) is somewhat longer in the crystal, and the coordination of one of sulfur atoms in the pyramidal environment of Pb noticeably differs. Lead ethylxanthate solutions in acetone were studied by EXAFS [19] and the Pb–S distance of 2.73 Å was found, however, the number of bonds was two. From this comparison the conclusion may be drawn that lead xanthogenat that we obtained was in an intermediate, strongly disordered or quasi-liquid state.

For the copper xanthate sample precipitated in a mixture with dixanthogen c.n. 2.9 was obtained and the average Cu–S distance was 2.29 Å. The latter is in the range characteristic of Cu–S bonds in copper(I) compounds with c.n. 3 or 4, e.g., for alkyl dithiophosphates (2.28 Å) [32] and copper sulfides (2.30-2.32 Å) [33]. After the removal of dixanthogen from the composite the bond length remains the same, however, c.n. increases from 2.9 to 3.3. The previous assumption about
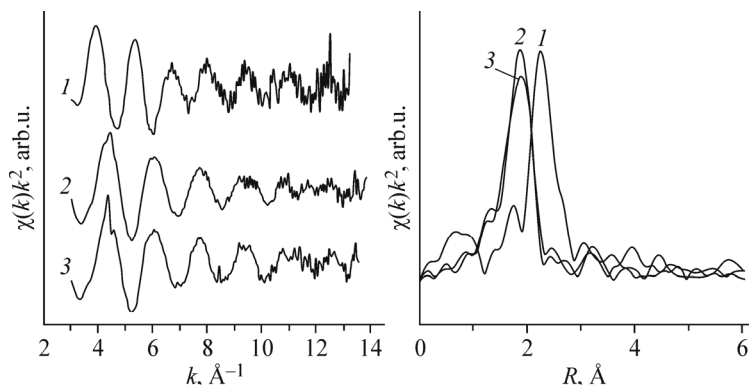
Fig. 2. Experimental EXAFS spectrum $\chi(k)k^2$ and the respective Fourier transform magnitude (without taking into account the phase shift) for lead xanthate (*1*), a mixture of copper xanthate with dixanthogen (*2*) and after dixanthogen removal (*3*).

TABLE 2. Results of Modeling Experimental EXAFS Spectra

Sample	N(S)	R(S)	$2\sigma^2$	E_f	fit
PbX$_2$	3.7	2.79	0.022	–1.4	6.7
CuX+X$_2$	2.9	2.29	0.013	–6.7	6.4
CuX	3.3	2.29	0.017	–7.5	4.4

Note. N is c.n., R is the interatomic distance, σ^2 is the Debye–Waller factor.

copper c.n. 3 and 4 was based on the Cu*K*-edge XANES spectra measured in the ultrahigh vacuum in total photoelectron yield and fluorescence yield modes respectively, i.e. after dixanthogen volatilization. The XANES and transmission electron microscopy results also revealed the heterogeneity of the structure of composite particles [22]. Thus, c.n. is 3 in the presence of dixanthogen and approaches 4 after its removal.

NMR. Fig. 3 depicts solid state NMR spectra of lead and copper xanthates along with the spectra of KXs. The ^{1}H spectra of crystalline potassium *n*-butylxanthate has a complex structure and contains four types of hydrogen atoms [34], with the central sharp peak apparently corresponding to a mobile terminal CH$_3$ group. The ^{1}H spectrum of copper xanthogenat in a mixture with dixanthogen consists of an intense narrow line (70%) and a strongly broadened line (30%) that is well seen in the changed scale in the inset. The broad line corresponds to protons in the solid salt matrix whereas the narrow line corresponds to the mobile phase of dixanthogen. After the removal of dixanthogen the broad component becomes most intense and the line corresponding to protons of the CH$_3$ group is significantly broadened, which can correspond to the frozen conformational state in the position of CH$_3$ groups observed in the crystalline sample [18]. The ^{1}H NMR spectrum of lead xanthate is much narrower and more homogeneous, which implies a high mobility of proton-containing groups in the compound.

Liquid state ^{13}C NMR spectra of potassium *n*-butylxanthate have five lines at 14.3 ppm, 20.2 ppm, 32.0 ppm, 71.8 ppm, and 233.5 ppm for –CH$_3$, –CH$_3$CH$_2$, –CH$_2$, –CH$_2$O, and –C(S)S$^-$ respectively [23]. In the solid state NMR spectra of KX and synthesized Pb and Cu xanthates, broad bands with complex shapes appear (Fig. 3*b*) while the band characteristic of the –C(S)S$^-$ group almost completely disappears (inset). The fact is that the –C(S)S$^-$ group has no own protons and an exchange interaction with hydrogen atoms occurs only in the solvated state, which is manifested as a signal [16]. It was impossible to measure the ^{13}C spectra of a mixture of copper xanthate and dixanthogen because of a high concentration of paramagnetic impurities (radicals, Cu^{2+} ions; see the EPR data). The spectrum of copper xanthate after the removal of dixanthogen is similar to the spectrum of KX. Only in the region of –CH$_2$ groups (32 ppm) some broadening is observed which is due to an increase in the anisotropy of the chemical screening tensor. It can be related to a lower mobility of the
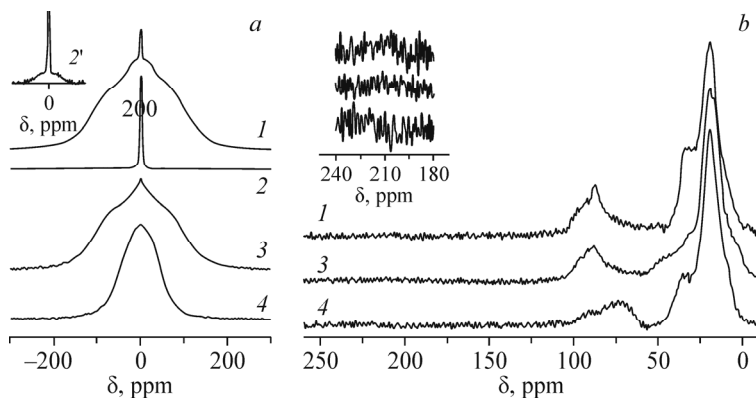
Fig. 3. Solid state ^1H (*a*) and ^{13}C (*b*) NMR spectra of potassium *n*-butylxanthate (*1*), copper xanthate with dixanthogen (*2*) and after its removal (*3*), and lead xanthate (*4*).

groups as compared to the potassium salt. In the spectrum of lead xanthate an appreciable broadening and shift are observed in the region of $-CH_2$ and $-CH_2O$ groups, which is indicative of high disorder of the product [29].

We failed to measure solid state ^{63}Cu and ^{65}Cu spectra, which seemed to be due to a strong quadrupole broadening of NMR lines because of both low-symmetric coordination of copper in the molecule of the compound and strong disorder of the structure. The latter factor also seems to be responsible for the impossibility to measure ^{207}Pb spectra in lead xanthate.

EPR. Generally, copper in compounds with sulfur almost always is in oxidation state 1+, although, e.g., in [35, 36], copper(II) xanthates were stabilized in the matrix of nickel(II) and thallium(I) xanthates. In the obtained samples we managed to detect by EPR the presence of copper(II) compounds and other paramagnetic centers (Fig. 4). In the EPR spectra of the product containing copper xanthate and dixanthogen, a signal with $g_0 = 2.100$ is observed and can be assigned to Cu(II) surrounded by sulfur anions. The *g* factor value can be explained by covalent Cu–S bonds, probably, in the distorted square planar coordination of the complex [35-37], and the isotropic character can be explained by dynamic processes in the nearest environment of copper, which are caused by the quasi-liquid state of the medium of copper complexes or Jahn–Teller type effects. Moreover, weakly anisotropic and relatively narrow transitions from paramagnetic centers with $g_0 = 2.024$ and $g_{II} = 1.971$, $g_\perp = 1.980$ are observed. These transitions are typical of sulfur-containing radicals of the hole and electron origin respectively [38] and arise during copper(II) reduction. The appearance of these radicals is associated with the formation of reaction products.

After treating the sample with acetone, the unstructured signal of Cu(II) at $g_0 = 2.100$ and signals from sulfur-containing radicals disappear and new transitions are observed whose intensity and position coincide with those characteristic of the distorted square planar copper(II) complex with xanthate [35, 36]. However, the concentrations of all detected
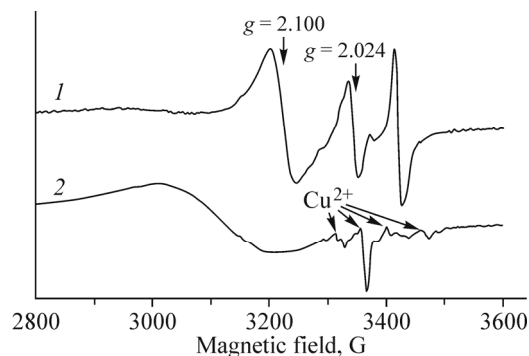

Fig. 4. EPR spectra of a mixture of copper xanthate with dixanthogen (*1*) and after its removal with acetone (*2*).

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paramagnetic centers are low and their role in the structure and properties of the material is limited. In particular, the transitions causing the broadening of copper NMR lines occur between three- and four-coordinated Cu(I) atoms rather than between Cu(I) and Cu(II).

The comparison of XPS, EXAFS, and NMR data provides insight into the structures of insoluble products of the direct interaction of xanthate ions with lead and copper ions in aqueous solutions. The character of the chemical binding in lead xanthate PbX_2 is close to ionic, and according to the XPS and EXAFS data, all four Pb–S bonds, and hence, four sulfur atoms are almost equivalent, unlike the single crystal state. The reason for this seems to be the disorder and distortion of the structure manifested in the high Debye–Waller factor and solid state NMR spectra that indicate high disorder of the structure of the compound. At the same time, we did not observe any signs of the formation of lead hydroxo xanthates or significant deviations from the stoichiometry, including with changes in the reagent ratio towards an excess of lead or xanthate.

Copper xanthate CuX is characterized by a large fraction of the covalent Cu–S interaction, which results in the electron density redistribution in a butyl xanthogene molecule. It is best illustrated by C1s XPS spectra. The shorter Cu–S bond length is likely to enhance the rigidity of the structure than that of lead xanthate despite smaller c.n. even in the composite containing dixanthogen. Acetone treatment removing dixanthogen increases copper c.n. and enhances the structure rigidity. A certain role appears to be played by partial dissolution and recrystallization of CuX in acetone because dixanthogen evaporation in the air or vacuum less modifies xanthate. Nonetheless, in all systems and especially in combination with dixanthogen ("solution in dixanthogen"), copper xanthate is disordered and characterized by a high mobility of copper ions and other structural elements. These effects can decisively affect the reactivity of xanthates, including interactions on the surface of minerals during flotation.

CONCLUSIONS

In the direct interaction of aqueous solutions of copper(II) and lead(II) with potassium n-butylxanthates, lead(II) xanthate of composition PbX_2 and copper(I) xanthate CuX in a mixture with dixanthogen are formed. In lead xanthate the character of four Pb–S bonds is close to ionic, the bonds are practically identical, unlike crystalline xanthate, which seems to be due to disordering and high mobility of Pb ions and other structural elements. In copper xanthate the Cu(I)–S bond length is shorter and copper c.n. is 3 in the composite with dixanthogen and increases after its removal. The XPS spectra of carbon and oxygen indicate a considerable electron density redistribution in ~75% of –C–O–C(S)S⁻ groups in CuX as compared to potassium xanthate and PbX_2. The character of solid state ^{1}H and ^{13}C NMR spectra and also the broadening of metal lines, which in fact prevents their measurement, suggest structural disorder of xanthates (highest for PbX_2 and relatively lower for CuX) especially after treatment with acetone and dixanthogen removal. EPR detects sulfur radicals and Cu^{2+}, but their amounts are insignificant and decrease after the washing with acetone.

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