

## STUDIES OF ACTIVATION OF GALENA BY COPPER AND XANTHATE (PIPX) SYNTHESIZED COLLECTORS ADSORPTION

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### Abstract

In this study, we suggest proceeding to an experimental study concerning the synthesis of new organo metallic product xanthate (PIPX) by intermittent method and their use in the processes of sulphides flotation. Flotation of sulphide minerals and their activation and modification have been investigated for many years. In this work the influence of sulphite on xanthate-induced flotation of copper-activated galena has been studied been investigated. The adsorption of potassium isopropyl xanthate (PIPX  $3 \cdot 10^{-3} \text{M}$ ) on galena has been also studied using electrochemical potential, FTIR spectra and SEM. Galena activated with copper sulfate ( $10^{-4} \text{M}$ ) have been investigated at  $\text{pH} = 9$ . Surface species have been identified and correlated with SEM. After copper sulfate activation, copper xanthate exists on all of the minerals studied. Basic pH is most favorable for potassium isopropyl xanthate adsorption on activated minerals.

Keywords: Xanthate (PIPX), Galena, Activation, Adsorption.

### 1. Introduction

Although copper sulfate has been used as an activator many years before xanthate were adopted to flotation, it is believed that copper activation of galena was accidentally introduced to galena flotation in 1914 [1].

Since then, large amount of experiments have been conducted to study the activation process and the subsequent xanthate adsorption in order to achieve better selectivity and recovery in galena flotation. The past eight decades has seen a lot of improvement on galena flotation thanks to the better understanding of the activation and xanthate adsorption process.

It is generally accepted today that galena floats poorly with short chain xanthate

**Nomenclatures**

$K_s$	Solubility product
pH	Potential hydrogen
PbS	Galena
PIPX	Potassium isopropyl xanthate
Wt	Weight percent
X	Ion Xanthathique

**Abbreviations**

FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope

collectors. This has been clearly established by Gaudin [2], who resolved earlier uncertainty by his demonstration that with pure unactivated galena no recovery was obtained with ethyl xanthate, a moderate recovery with amyl xanthate, and complete recovery with hexyl xanthate. Similarly, Wark and Cox [3] were able to measure the critical  $pH$  values for galena flotation with amyl xanthate but not with ethyl xanthate. There are several explanations for the relatively weak interaction between galena and short chain xanthate.

Klassen and Mokrousov [4] suggested that zinc xanthate is so soluble that they would dissolve from the mineral surface, while Dixon [5] and Maust and Richardson [6] suggested that the high band gap of galena makes it kinetically inert towards the adsorption of anions such as xanthate. Proposed that the electron-to-hole ratio at the surface is too high to permit the lower xanthates to chemisorb.

Due to the reasons described above, an activation process is required prior to the flotation via Reaction (1). The activation product (CuS-like species) can then react with xanthate to form insoluble copper xanthate species through an electrochemical reaction such as Reaction (2). The insoluble CuX species will render the mineral surface hydrophobic.



The interaction between collectors and surfaces plays an important role and the understanding of the interaction mechanisms of different reagents with mineral surface is significant in achieving selective flotation.

It is now widely accepted that there are two separate mechanisms by which collectors adsorb on sulphide minerals. Firstly, there is the chemisorptions mechanism where the adsorbed xanthate molecule forms a chemical bond with metal atoms at the sulphide surface. The other mechanism is electrochemical, and involves the electrochemical oxidation of the adsorbed collector molecules to give Oxidation product species, which renders the sulphide surface hydrophobic [7].

Much of the research was focused on the action of hydrophobic xanthate type surfactants on sulphide minerals. Different possibilities have been suggested in literature to explain how xanthates can render hydrophobic the surface of minerals [8-13].

A distinct progress in identifying the structure of the surface products formed on the mineral surface after the sorption of the collector has been achieved with

the aid of the spectroscopic methods, especially infrared (IR) spectroscopy correlated with scanning electron micrograph (SEM) [14].

The most commonly used thiol collectors are xanthates, which are alkali metal (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ) salts of mono alkyl esters of dithiocarbonic acid (e.g. Potassium isopropyl xanthate :  $\text{C}_3\text{H}_7\text{OCS}_2\text{K}$ ). They are used as flotation agents in the recovery of metal sulphids (e.g.,  $\text{MeS}$ :  $\text{PbS}$  *galena*) [15].

The activating effect of sodium sulphide is strongly time dependent. An increase in sulphidisation leads to an increase in the hydrophobicity of the mineral surface. Excess of copper sulfate acts as a depressant for oxidized lead and metal minerals because the adsorption of divalent sulphide ion on the surface of lead oxide minerals increases the negative charge which prevents the adsorption of collector. FTIR and SEM have been found to be useful techniques for elucidating the surface properties of solids, which may be relevant in applied aspects of mineral processing [16].

In the present investigation, the adsorption behavior effects of various amounts of anionic collectors on pure galena surfaces was verified using diffuse reflectance FT-IR and SEM studies.

## 2. Materials and Methods

### 2.1. Materials and reagents

The galena sample was obtained from the Cheabet Elhamra mine, Algeria. The elemental composition of galena is shown in Table 1. The galena sample was crushed and the selected grains ground in an agate mortar. The galena fraction of  $-208+108\mu\text{m}$  was used in adsorption tests. The final grinding product ( $-208+108\mu\text{m}$ ) was used for the SEM microscopy examination. The pH was adjusted using HCl and NaOH. Xanthate (PIPX) solution prepared by dissolving the chemical grade PIPX collector in purified water. The purification of xanthate includes dissolving commercial grade xanthate in acetone and its crystallization. Copper sulfate was used to introduce copper ions during the conditioning time. Galena was activated by copper at pH basic).

### 2.2. Methods

Mineral suspensions of 5g galena  $0.377\text{ mm}$  in size [17] in  $50\text{ cm}^3$  of the solution were conditioned at the desired pH for 5 min after each reagent addition in the presence of various activators.  $50\text{ cm}^3$  of copper sulfate ( $10^{-4}\text{ M}$ ) were used in xanthate (PIPX  $3.10^{-3}\text{ M}$ ). It was conditioned in distilled water for 8 min and conditioned in copper solution at pH 9, pH was regulated with NaOH ( $10^{-1}\text{ M}$ ) and HCl ( $10^{-1}\text{ M}$ ).

**Table 1. Chemical Analysis of Galena Pure and Galena Activated by Copper Sulfate  $10^{-4}\text{ M}$  Treated with PIPX  $3.10^{-3}\text{ M}$  at Conditioned in Water for 8min.**

Mineral Elements	Chemical elements present (wt. %)					
	Pb	S	Fe	O	Cu	C
Wt. % (Galena pure)	83.32	9.97	2.39	3.58	0.74	00.00
Wt. % ( Galena treated with PIPX)	75.91	19.51	00.00	04.34	00.21	00.03

The scanning electron micrograph (SEM) type JSM-6390 is a high-performance device with a resolution of 3.0 nm. The customized GUI interface allows the instrument to be intuitively operated, and Smile Shot™ software ensures optimum operation settings. The JSM-6390 specimen chamber can accommodate a specimen of up to 152 mm in diameter. Standard automated features include auto focus/auto stigmator, autogun (saturation, bias and alignment), and automatic contrast and brightness.

FT-IR measurements were recorded on a SHIMADZU 8400S FTIR spectrometer in the region of 400-4000  $\text{cm}^{-1}$  supplied with OMNIC software. The tablets were prepared by grinding 2mg of the solid sample with 50 mg of KBr. Before every analysis, the background was collected and subtracted from the spectrum of the sample. Two hundred scans at a resolution of 4  $\text{cm}^{-1}$  were recorded for each sample.

### 3. Results and Discussions

#### 3.1. Studies of activation of galena by copper sulfate

Figure 1 show the rest potential measurements of the galena in a  $10^{-4}$  M  $\text{CuSO}_4$  solution at pH 9 as a function of the activating time. It can be seen that the rest potential of the galena increases sharply upon the addition the copper solution, indicating that a new phase (copper (II) sulfide) is formed on the surface of galena. The potential reaches a plateau value of +51 mV as shown in Fig. 1 after approximately 8 minutes. The new phase (activation product) is probably CuS.

The initial positive potential can be attributed to the adsorption of  $\text{Cu}(\text{OH})^+$  on PbS surface. Some of  $\text{Cu}(\text{OH})^+$  is transferred into CuS via reaction:



#### 3.2. Potassium isopropyl xanthate adsorption on copper-activated galena

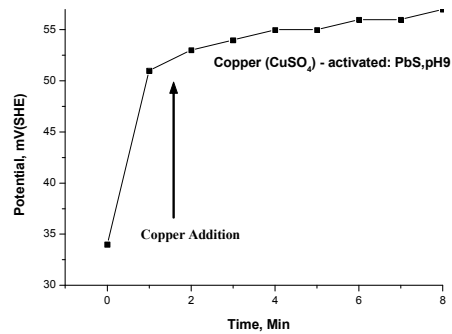
The interaction between collectors and surfaces plays an important role in understanding of interaction mechanisms of different reagents with the mineral surface. It is now widely accepted that there are two separate mechanisms by which collectors adsorb on the sulfide minerals. Firstly, there is the chemisorption mechanism where the adsorbed xanthate molecule forms chemical bond with metal atoms (Pb) at the sulfide (PbS) surface.

The other mechanism is electrochemical and involves electrochemical oxidation of the adsorbed collector molecules to give oxidation product species, which renders the galena surface hydrophobic [18].

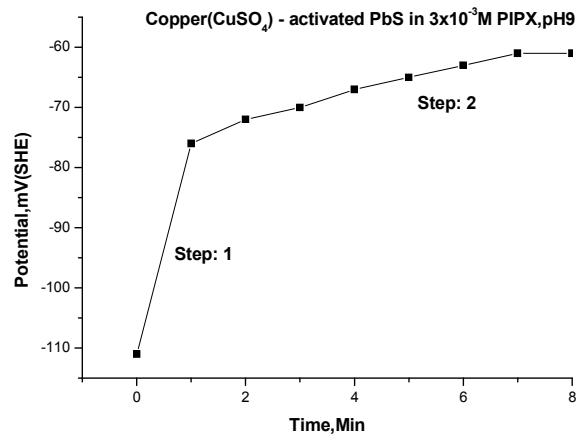
Results of galena surface oxidation to form hydrophobic and hydrophilic species depends strongly on potential. The rest potential measurement of galena activated with  $\text{CuSO}_4 10^{-4}\text{M}$  in  $3.10^{-3}\text{M}$  PIPX at pH 9 are shown in Fig. 2.

The rest potential measurement changes from: -115 mV to -55mV as shown in Fig. 2. As is known the solubility of Pb-AX ( $K_s = 1.20 \cdot 10^{-11}$ ) is considerably higher than that of  $\text{Pb}(\text{OH})_2$  ( $K_s = 1.35 \cdot 10^{-19}$ ) and therefore xanthate (PIPX) is not adsorbed on galena [19]. Therefore, copper activation is essential for flotation of

galena. As is shown in Fig. 2 galena can easily be activated with copper ions at pH 9. Addition of  $3 \cdot 10^{-3}$  M PIPX resulted in formation of strongly hydrophobic Cu-IPX, and very high adsorption [20].

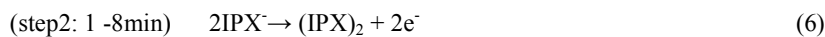
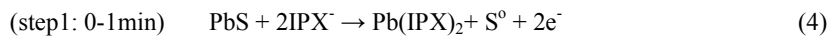


**Fig. 1. Rest Potential Measurement of Galena in a  $10^{-4}$  M  $\text{CuSO}_4$  Solution at pH 9.**



**Fig. 2. Rest Potential Measurement of Galena in a  $10^{-4}$  M  $\text{CuSO}_4$  and  $3 \cdot 10^{-3}$  M PIPX Solution at pH 9.**

The mechanism is:

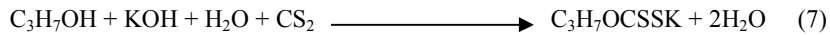


The expectation is that any of these species ( $\text{Pb}(\text{IPX})_2$ ,  $\text{S}^0$ ,  $(\text{IPX})_2$ ) constitutes entities contributing to the hydrophobicity of the surface.

### 3.3. Studies of potassium isopropyl xanthate (PIPX) adsorption on copper activated galena using FTIR technique and SEM

#### 3.3.1. Synthesis of potassium iso propyl xanthate (PIPX) by the discontinuous method

During the intermittent method, in the basic solution of alcohol, consisted of 0.5 mole of isopropyl alcohol, 0.5 mole of water, 0.5 mole of potassium hydroxide and 0.5 mole of disulfure of carbon ( $\text{CS}_2$ ) were slowly added. After that, we separate the deposit of xanthate, which after addition of all the portion of disulfure of carbon representing constituent formed crystals. This method allows of obtaining of the high quality xanthates, they are obtained using Eq. (7). (Superior activity of xanthate has 90%).



#### 3.3.2. Characterization of pure galena and xanthate (PIPX) using FTIR technique and SEM

Several surface sensitive techniques, capable of analysing the first few atomic layers of the mineral surface, have been used for more than ten years in a variety of studies related to the mechanisms of oxidation and adsorption in sulfide mineral flotation. The significance of these techniques is that they provide not only a compositional analysis of the surface but also information on chemical states (oxidation, bonding) and spatial distribution of adsorbed species on individual particles and complex mixtures of minerals as a function of depth through the surface layers [21].

The characteristics and operating condition of the SEM technique have been fully described in other publications [18]. It is well established that all metal sulfide minerals exhibit oxide and hydroxide species on their surface after exposure to air or aqueous solution. They have been observed in studies of galena [20].

The surface oxidation of galena has been less systematically studied than those of other sulfide minerals but the pattern of reaction appears to be similar. It has been suggested that galena oxidizes considerably more slowly than the other sulfide minerals under these conditions. Further studies of PbS oxidation using SEM are still required. The physical nature of the oxidized layer formed initially on these surfaces can be seen in Fig. 3 where a galena sample, ground initially in distilled water and allowed to condition for 8 minutes, was reground at that time and examined immediately using high resolution field emission SEM without coating at 15 KV, 2  $\mu\text{m}$ .

#### a) Characterization of galena by SEM

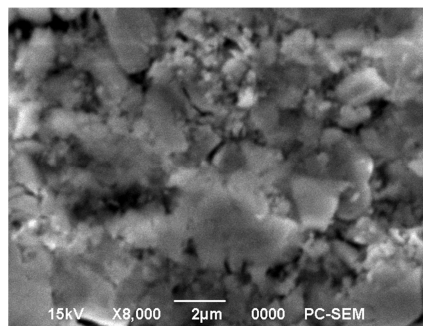


Fig. 3. Field Emission Scanning Electron Micrograph of Ground Galena.

### b) Characterization of galena by RX

This method is used to identify the nature and structure of the crystallized products. According to Fig. 4, there is the diameter  $d_1=3.31$  and  $d_2=4.23$ ; the angle  $(2^\circ\theta)_1=26.94$  and  $(2^\circ\theta)_2=20.94$ .

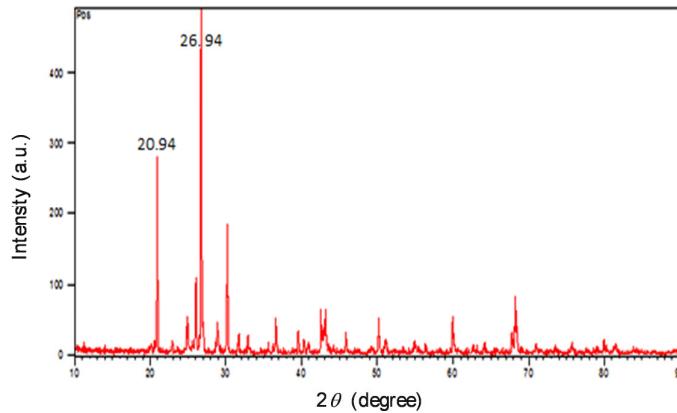


Fig. 4. RX Spectra of Galena.

### c) Characterization of galena by FTIR

FTIR spectroscopic studies were carried out on galena samples both before and after adsorption. The assignments of the various bands and peaks made in this study are in reasonable agreement with those reported in the literature for similar functional groups. Figure 5 shows the FTIR spectra, where the characteristic bands of galena in  $669.058\text{--}842.885\text{cm}^{-1}$  and  $1616.06\text{--}1637.27\text{cm}^{-1}$  corresponding to the carbonate  $\text{CO}_3^{2-}$  ion group are found to be active. The strong bands related to the presence of bound water ( $-\text{OH}$ ) stretching is around  $3552.24\text{ cm}^{-1}$ .

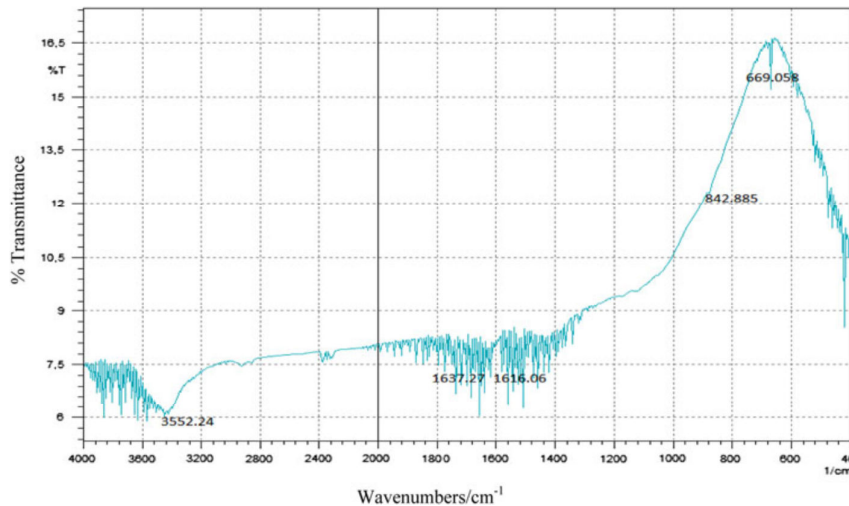


Fig. 5. IR Spectra of Galena.

#### d) Characterization of potassium isopropyl xanthate (PIPX) by FTIR

The FTIR spectra of xanthate (PIPX) Fig. 6 the absorption band at  $1060.4\text{ cm}^{-1}$  is related to (C=S) bands and two bands at  $1384.7$  and  $1668.5\text{ cm}^{-1}$  is assigned to the bending vibration of (O-CS), the band at  $2450\text{ cm}^{-1}$  which are characteristic of the hydrocarbon chain, the band at  $3250\text{ cm}^{-1}$  is characteristic of (O-H) stretching [19].

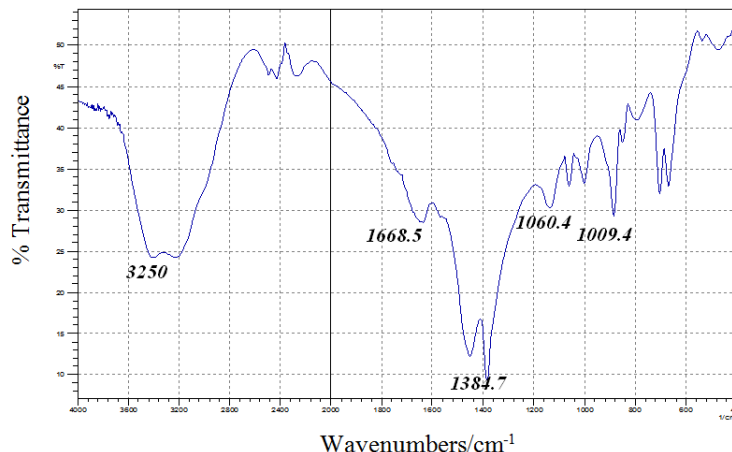


Fig. 6. IR Spectra of PIPX.

#### e) Characterization of potassium isopropyl xanthate (PIPX) by SEM

The characteristics and operating condition of the SEM technique have been fully described in other publications [22]. Further studies of PIPX surface using SEM are still required. The physical nature of the oxidized layer formed initially on these surfaces can be seen in Fig. 7, where a PIPX sample was reground and examined immediately using high resolution field emission SEM without coating at 15 kV.

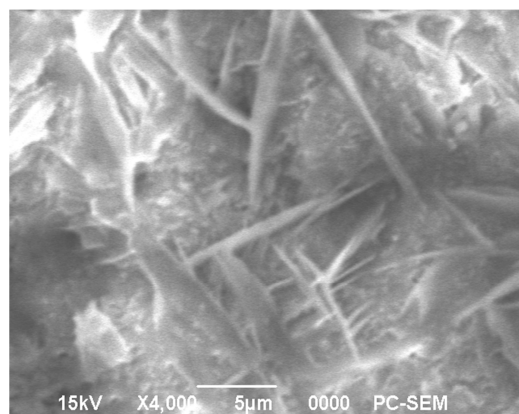


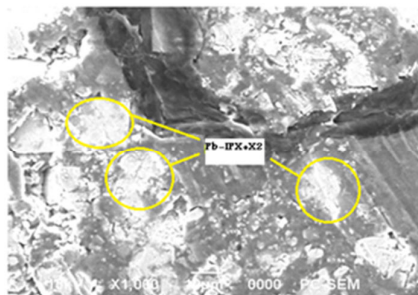
Fig. 7. Field Emission Scanning Electron Micrograph of Ground Xanthate PIPX Surface.



### 3.3.3. Improving of potassium isopropyl xanthate (PIPX) adsorption on galena

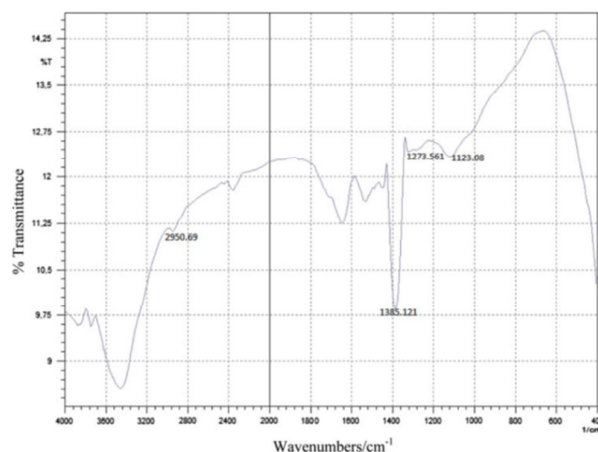
On copper-activated galena surfaces [23] at low copper (II) additions and high affinity adsorption behavior, copper (I) isopropyl xanthate is the predominant surface species. The rate and extent of xanthate adsorption are, however, decreased by extended conditioning periods apparently due to penetration of copper ions into the plumb sulfide lattice confirmed by SEM. Time dependence of  $3 \cdot 10^{-3}$  M PIPX adsorption is then related to the subsequent back diffusion to the galena aqueous solution interface. A thigh copper sulphate ( $10^{-4}$  M) addition at pH 9, both dioxanthogen and copper (I) isopropyl xanthate are detected on the galena surface.

Figure 8 displays SEM of typical galena particle surface after for 8 min in the presence of  $3 \cdot 10^{-3}$  M PIPX. There appears to be evidence of the colloidal precipitates observed before copper sulfate and copper nitrate is present. The surface compositional information is summarized in Table 1 (wt. Cu: 00.21%).



**Fig.8. Field Emission Scanning Electron Micrograph of Ground Galena Surface activated by Copper Sulfate  $10^{-4}$  M Treated with PIPX  $3 \cdot 10^{-3}$  M at Conditioned in Water for 8 min.**

The infrared bands observed in Fig. 9 at  $1123.08 \text{ cm}^{-1}$  are characteristic of (Pb-IPX) and  $1273.561 \text{ cm}^{-1}$  are characteristic of dioxanthogene (IPX)<sub>2</sub> forms oxidized with the molecule of isopropyl xanthate) [24].



**Fig. 9. IR Spectra of Galena Activated by Copper Sulfate  $10^{-4}$  M Treated with PIPX  $3 \cdot 10^{-3}$  M at Conditioned in Water for 8 min.**

#### 4. Conclusions

The following conclusions were drawn:

- The potassium isopropyl xanthate (PIPX) has good collector ability on a sulphide mineral galena.
- Activation of galena at lower potentials increases the copper uptake by the mineral.
- Oxidation of galena at potential of +51mV forms CuS product on galena in water for 8 min.
- Using the SEM technique action of  $3.10^{-3}$ M potassium isopropyl xanthate has been identified (adsorption to specific surface sites and colloidal precipitation from solution).
- The FTIR spectra revealed the presence of copper on the surface of galena and this is confirmed the adsorption of PIPX onto surface (Pb-PIX,  $1123.08\text{ cm}^{-1}$ ,  $(\text{IPX})_2$ ,  $1273.56\text{ cm}^{-1}$ ).

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