

# Structural Modification of Xanthate Collectors To Enhance the Flotation Selectivity of Chalcopyrite

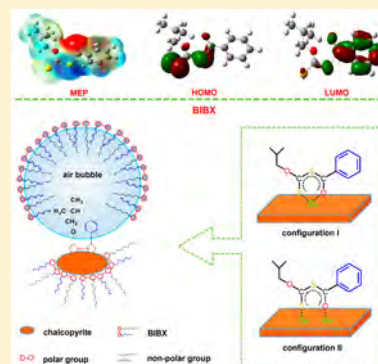
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**S** Supporting Information

**ABSTRACT:** A modified xanthate compound similar to xanthogen formates, *S*-benzoyl *O*-isobutyl xanthate (BIBX), was designed by introducing a carbonyl and a benzyl group into the xanthate structure. The preparation, recovery performance, and mechanism of adsorption of this compound to chalcopyrite is discussed. BIBX was synthesized using a one-pot approach with superior efficiency, which has important commercial implications. BIBX's performance in the recovery of and mechanism of adsorption to chalcopyrite was investigated via flotation tests, adsorption quantity measurements, FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. The results show that BIBX displays a substantially stronger collecting ability toward chalcopyrite than sodium isobutyl xanthate and *O*-isopropyl-*N*-ethylthionocarbamate. Moreover, BIBX displays superior selectivity for chalcopyrite compared to pyrite. The adsorption data indicate that BIBX can be applied under slightly acidic or alkaline conditions. BIBX behaves like a bidentate ligand, bonding with the chalcopyrite copper through the thiol sulfur and carbonyl oxygen atoms. These findings are supported by FTIR and XPS data. DFT calculations predict two distinct adsorption geometries, one with one Cu atom to form a six-membered ring complex and another with two Cu atoms to form an "irregular pentagon"-shaped complex.



## 1. INTRODUCTION

Flotation is the most common process applied in mineral separation to recover valuable minerals. In this process, the surface of a target mineral is rendered hydrophobic by the attachment of a collector by chemical adsorption, van der Waals forces, or electrostatic bonds.<sup>1</sup> Collectors are generally active toward whole mineral classes, e.g., sulfide minerals, rather than toward a specific mineral. Difficulty arises when a particular metallic mineral must be separated from an ore with a complex composition or when the surface properties of the mineral result in a poor flotation response. The limited resources of today's mining industry increase the need to treat ores with lower grades, greater fineness, and greater mineralogical complexity. Current practices involve the development of more efficient collectors.

"Xanthate" refers to any salt with a general formula of  $\text{ROCS}_2\text{M}$ . Xanthates are currently the most important collectors used in the flotation of sulfide minerals and some oxides, including copper, zinc, and lead oxide minerals. The first xanthate compound was discovered and named in 1823; it was first applied in flotation in 1924.<sup>2</sup> Since this discovery, numerous other commercial alkyl xanthates have been developed that see continued use as collectors for base-metal flotation; these xanthates include potassium amyl xanthate (PAX), sodium isopropyl xanthate (SIPX), and sodium isobutyl xanthate (SIBX). From a structural viewpoint, xanthates are a product of carbonic acid, where the two oxygen atoms are replaced by sulfur and one alkyl group replaces a hydrogen

atom. In the presence of moisture, xanthates form unstable xanthic acid ( $\text{ROCS}_2\text{H}$ ), which can be regarded as the acid ester of dithiocarbonic acid [ $\text{ROC}(\text{S})\text{SR}$ ]. Thioamines and thioureas are xanthate- or xanthic acid (acid ester)-related compounds that arise from the reaction of an amine with carbon disulfide. The reaction stoichiometry dictates the formation of dithiocarbamic acids ( $\text{RNHCS}_2\text{H}$ ) or thioureas [ $\text{RSC}(\text{NH}_2)_2$ ].<sup>3</sup>

Many modified dithiocarbamic acids ( $\text{RNHCS}_2\text{H}$ ) and thioureas [ $\text{RSC}(\text{NH}_2)_2$ ] have been described in various patents. These developments have been applied in sulfide mineral flotation. For example, *O*-isopropyl-*N*-ethylthionocarbamate (IPETC) was produced by the Dow Chemical Co. in 1954; it proved to be selective toward copper sulfide flotation and copper-activated sphalerite, particularly against pyrite in alkaline media, as well as being effective in acidic circuits.<sup>4–7</sup> Alkyl thionocarbamates were produced by Cytec (S100 series). Ackerman et al.<sup>8</sup> investigated the influence of different alkyl substituents (including *O*-alkyl and *N*-alkyl) on the performance of thionocarbamates and found that the collecting power increases with increasing chain length of the substituents; they also suggested that *O*-alkyl and *N*-alkyl substituents affect the hydrophobicity and steric accessibility of the thionocarbamates.

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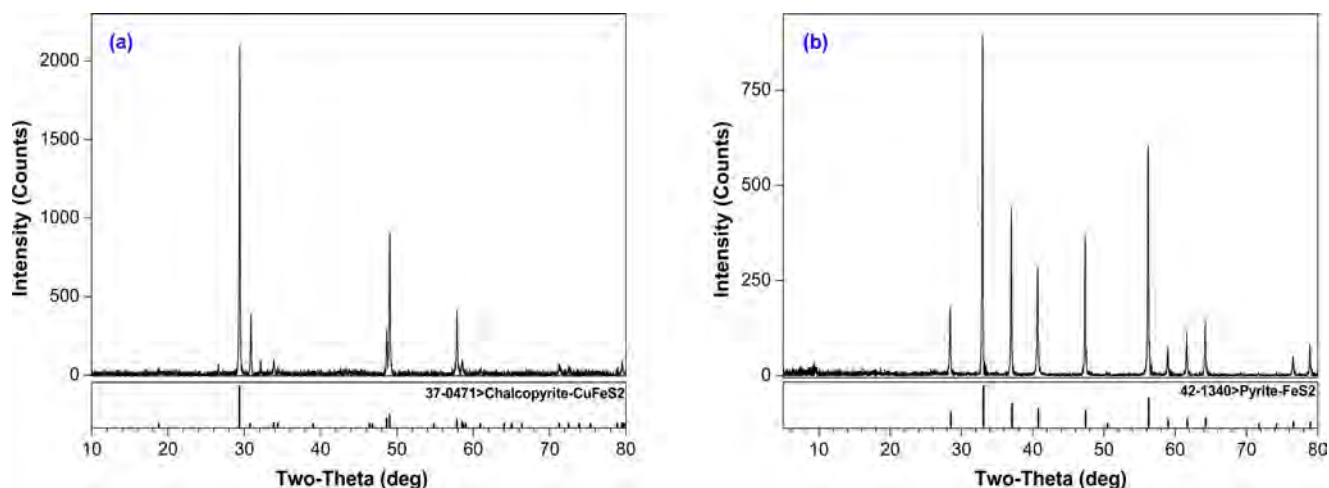


Figure 1. XRD patterns of chalcopyrite (a) and pyrite (b).

In 1997, Nagara<sup>9,10</sup> published a new class of thionocarbamates, *O*-alkyl-*N*-allyl thionocarbamates, that were developed and widely used in the industrial flotation of copper sulfides and copper-activated zinc minerals. More recently, both experimental and theoretical studies on modified thionocarbamates and thioureas have been carried out. These structural modifications provided additional active points or incorporated functional groups on the N donor atom, resulting in xanthate-related compounds that exhibit a high affinity for float copper minerals but also exhibit a high selectivity against the recovery of pyrite.<sup>6,11–14</sup> Our efforts, reported by Liu et al.,<sup>14</sup> involved the introduction of a novel collector; the adsorption thermodynamics and kinetics of this novel collector, *N,N'*-diisopropoxypropyl-*N''*,*N'''*-oxydiethylenedicarbonyl bis-(thiourea), were investigated. He et al.<sup>15</sup> synthesized the novel surfactant *N,N*-diethyl-*N'*-cyclohexylthiourea. They found that, after collector attachment, chalcopyrite exhibited an unprecedented hydrophobicity that resulted in the highest recovery within the pH range from 4 to 8.

Another xanthate-based class of compounds is xanthogen formates, ROC(S)SC(O)OR, which were developed in the early 1960s. Xanthogen formates are the products from the reaction between a xanthate and ethyl chloroformates. Dialkyl dixanthogenates are compounds with a structure similar to that of xanthogen formates and are the product of the reaction of xanthic acid with an oxidant with an ROC(S)S-S(S)COR structure.<sup>2</sup> Ackerman et al.<sup>5</sup> reported that xanthogen formates likely act as a bidentate ligand through the alkoxy carbonyl group, which likely ligates the copper atoms on the copper sulfide surface, explaining their stronger affinity toward copper minerals.

Given the excellent specificity of xanthogen formates for copper minerals, we modified the xanthate structure to make a new surfactant, *S*-benzoyl *O*-isobutyl xanthate (BIBX) with an R<sub>1</sub>OC(S)SC(O)R<sub>2</sub> structure, where R<sub>2</sub> is a benzyl ring, to investigate the chelating ability of this structure. This modification introduces a carbonyl group, which forces the xanthate collectors to function through bivalent sulfur but also allows metal chelates to form through the thiol sulfur and carbonyl oxygen atoms to form a six-membered ring. Moreover, this study provides new insights into the effect of a benzyl ring on the chelating contribution of the carbonyl group.

## 2. MATERIALS AND METHODS

**2.1. Materials and Reagents.** Analytical isobutanol, carbon disulfide, sodium hydroxide, and benzoyl chloride were obtained from Aladdin Industrial Co. (Shanghai, China) and were used to synthesize the BIBX collector. Analytical methylisobutylcarbinol (MIBC) was obtained from Aladdin Industrial Co. and was used as a frother in single flotation tests. IPETC (95%), SIBX (85%), and industrial-grade pine oil frothers were purchased from Hunan Mingzhu Flotation Reagent Ltd. Co. (Zhuzhou, China). Analytical hydrochloric acid and sodium hydroxide, acquired from Aladdin Industrial Co., were used for pH adjustment. Deionized water (DI water) was used in all experiments.

The pure chalcopyrite and pyrite were obtained from the Dexing Copper Mine of Jiangxi Province and the Beijing Geological Museum in China, respectively. They were crushed manually and hand-picked. The isolated high-purity samples were ground in a porcelain mill with agate balls to 100% passage through 74 μm. The mill discharge was subjected to an ultrasonic bath, DI water rinse, filtration, and air drying, and was subsequently stored in a silica gel desiccator. The chemical assay (Table S1, Supporting Information) and X-ray diffraction (XRD; Figure 1) analysis show that the purities of the chalcopyrite and pyrite were 93% and 95%, respectively. The minerals with a size fraction of -74 + 38 μm were used in flotation tests and adsorption measurements. The finer fraction (<38 μm) was used for FTIR measurements. The specific surface area of the minerals was determined by the Brunauer–Emmett–Teller (BET) method through N<sub>2</sub> sorption using a Nova1000 surface area analyzer (Quantachrome Instruments, United States). The BET surface areas of the -74 + 38 μm size fraction of chalcopyrite and pyrite were 0.09 and 0.11 m<sup>2</sup>·g<sup>-1</sup>, respectively.

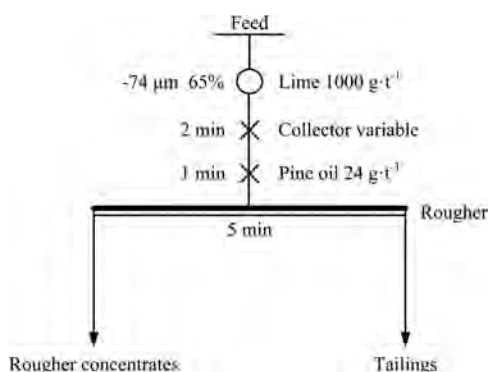
The bench-scale flotation ore was from the Dexing Copper Mine, China. The valuable minerals are chalcopyrite, chalcocite, pyrite, digenite, tetrahedrite, covellite, tennantite, bornite, marcasite, molybdenite, cuprite, and malachite. The dominant gangue minerals are primarily quartz, illite, sericite, biotite, carbonates, and chlorite. The multielement chemical analysis results and the phase analysis results are listed in Tables S2 and S3 (Supporting Information), respectively. The phase analysis results show that the percentage of copper is 23.28% in the

oxidized state. Therefore, the test material is a refractory ore because of its low grade and high oxidation rate.

**2.2. Experimental Methods.** **2.2.1. Synthesis and Characterization of BIBX.** BIBX (a light yellow oil, yield 94.26%) was synthesized via a one-pot reaction of isobutanol, carbon disulfide, sodium hydroxide, and benzoyl chloride using abundant carbon disulfide as a solvent, which does not require the purification of the intermediate chemical compounds. The full synthesis conditions and characterization results are given in the [Supporting Information](#).

**2.2.2. Flotation Tests.** Pure mineral flotation was performed on an XFG5-35 flotation machine (Jilin Prospecting Machinery Factory, China). It was operated at 1650 rpm with a 35 mL Plexiglas cell. Chalcopyrite or pyrite (2 g) was placed into the flotation cell before the cell was filled with 30 mL of DI water. After 1 min of agitation, the pulp pH was first adjusted to the desired value by adding either hydrochloric acid or sodium hydroxide solution. The selected collector was then added with a calculated dosage to obtain a certain concentration in slurry. Afterward, 1 mL of a  $2.25 \times 10^{-3}$  mol·L<sup>-1</sup> MIBC aqueous solution was added, and the mixture was agitated for 1 min. A 10% ethanol (v/v) solution was used instead of water to dissolve BIBX because of its poor solubility in water compared to the solubilities of IPETC and SIBX. Pure mineral flotation was conducted for 5 min. Both the froth stream and tailings were weighed after filtration and air drying. The recovery was calculated on the basis of the mass recovered.

The bench-scale flotation tests were conducted in a self-aeration XFD-63 flotation machine with a volume of 3000 mL. Prior to flotation, 1 kg of crushed ore was ground in a ball mill to ensure 65% mineral passage through 74 μm. The rougher flotation scheme is shown in [Figure 2](#). The Cu recovery was



**Figure 2.** Flow diagram and conditions of bench-scale flotation tests.

calculated on the basis of mass recovery and product head assays. Pure mineral flotation and bench-scale flotation tests were performed in triplicate; the mean values are reported. The maximum relative deviation was less than 5%.

**2.2.3. Adsorption Tests.** Collector adsorption tests were performed in a shaking incubator at a controlled temperature of 25 °C. The pure chalcopyrite or pyrite adsorbents (500 mg) in the size fraction of  $-74$  to  $+38$  μm were placed in contact with the collectors at a concentration between  $8.1 \times 10^{-6}$  and  $4.2 \times 10^{-4}$  mol·L<sup>-1</sup> at various pulp pH values. After 1 h of conditioning, the residual concentration of the collectors was determined using a UV/vis spectrophotometer (UV-1750, Shimadzu Co., Ltd.) in the appropriate concentration range; the absorbance at 284 nm was used to quantify the BIBX concentration in a 30% ethanol solution (v/v), and the

absorbances at 301 and 241 nm were used to quantify the SIBX and IPETC concentrations in water on the basis of the calibration curve shown in [Figure S1 \(Supporting Information\)](#), respectively. The adsorption amount of the collector on a given mineral surface was calculated according to the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{1000mS} \quad (1)$$

where  $Q_e$  is the amount of collector adsorbed onto the minerals (mol·m<sup>-2</sup>),  $C_0$  and  $C_e$  denote the initial and equilibrium collector concentrations (mol·L<sup>-1</sup>), respectively,  $V$  is the volume (mL), and  $S$  and  $m$  represent the specific surface area (m<sup>2</sup>·g<sup>-1</sup>) and mineral mass (g), respectively.

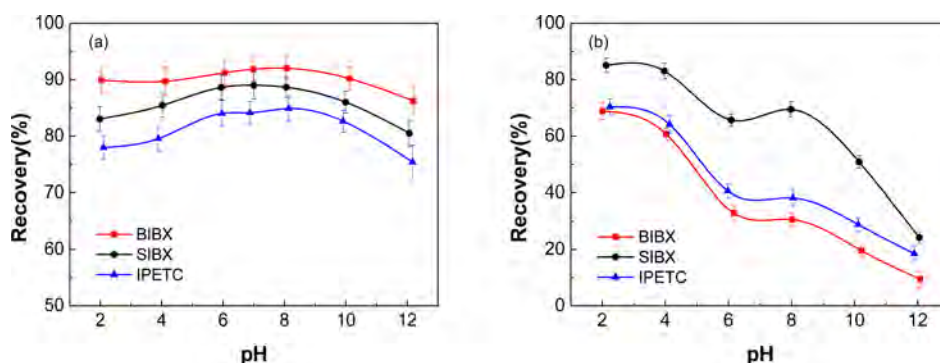
Because BIBX may decompose in an aqueous solution, possibly leading to inaccurate adsorption experiments, the decomposition of BIBX in a 30% ethanol solution (v/v) was investigated ([Figure S2 in the Supporting Information](#)). BIBX is relatively unstable under aqueous conditions, decomposing gradually, although it is more stable under acidic conditions than under alkaline conditions. As shown in [Figure S2d](#), BIBX is degraded by 3.80%, 4.97%, and 9.53% after 1 h under neutral (pH 6.82), acidic (pH 5.36), and alkaline (pH 7.89) conditions, respectively. The data were obtained in our adsorption tests after the collectors had conditioned for 1 h, and the effect of the degradation was relatively small. In addition, the 1 h equilibration time for the collectors adsorbed onto the mineral surface was adequate according to previous reports.<sup>6,16</sup>

**2.2.4. Characterization Techniques.** The FTIR spectra were collected on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific Inc., United States) over the wavenumber range from 400 to 4000 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi system (Thermo Fisher Scientific Inc., United States) with monochromatic Al K $\alpha$  radiation as an excitation source operated at 200 W with a 20 eV pass energy. The pressure of the analysis chamber was approximately 10<sup>-9</sup> Torr, and the takeoff angle of the photoelectrons was 45°. The binding energies were calibrated on the basis of the C 1s peak (284.6 eV). Element atomic percentages were calculated from the peak area corrected by set in the Thermo Avantage software 5.52 (Thermo Fisher Scientific Inc.). Accurate curve-fitting analysis of the high-resolution Cu 2p, S 2p, and O 1s spectra was also carried out using the Thermo Avantage software. A description of the detailed preparation of FTIR and XPS samples is provided in the [Supporting Information](#).

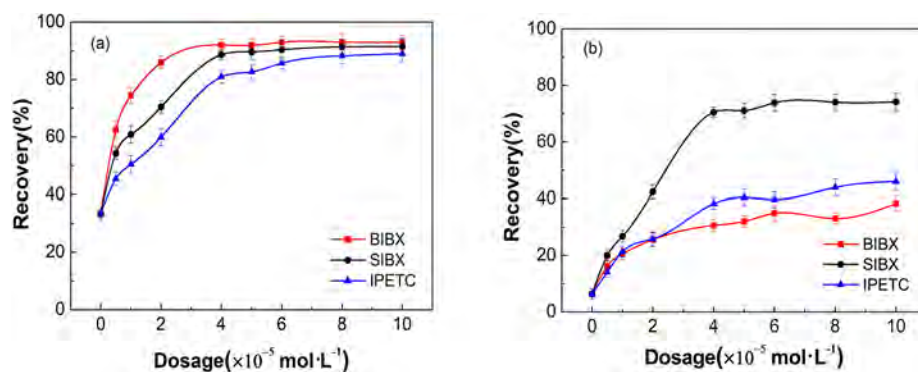
**2.3. Computational Details.** All calculations were performed using the Gaussian 03 program. The molecular structure of BIBX was optimized successively by MM2 force field and PM3 methods and further optimized and analyzed using density functional theory (DFT) methods at the B3LYP/6-311+G(d) level. The integral equation formalism for the polarizable continuum model was used to optimize the molecular structure of this collector in an aqueous solution, and the dielectric constant of water ( $\epsilon = 78.39$ ) was used throughout. The atomic charge was determined to describe the reactivity of the collector molecules and was calculated according to Mulliken population analysis.

### 3. RESULTS AND DISCUSSION

**3.1. Microflotation Tests.** Pure mineral flotation tests were performed using BIBX, SIBX, and IPETC as collectors. [Figures](#)



**Figure 3.** Mass recovery in the flotation of pure chalcopyrite (a) and pyrite (b) as a function of the pulp pH (the collector concentration is  $4 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ).

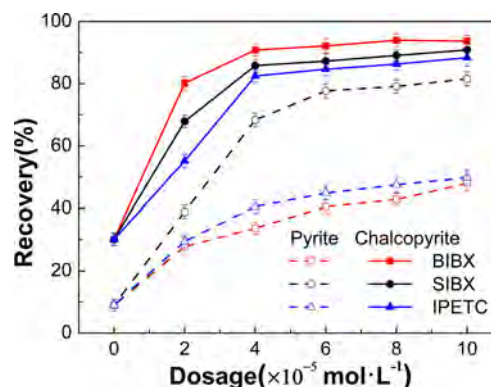


**Figure 4.** Mass recovery in the flotation of pure chalcopyrite (a) and pyrite (b) as a function of the collector dosage at a pulp pH of 8.

3 and 4 show the data corresponding to tests at various pulp pH values and increasing collector doses, respectively. Figure 3a shows that BIBX has a higher recovery for chalcopyrite than the traditional xanthate SIBX and the very common copper collector IPETC. At pH 8, BIBX recovered 92.02% of chalcopyrite, whereas SIBX and IPETC recovered only 88.64% and 80.89%, respectively. Interestingly, the three collectors exhibit the same data distribution for pyrite flotation, as shown in Figure 3b, where increases in the pulp pH result in a dramatic reduction in pyrite recovery. Under alkaline conditions, the floatability of pyrite is extremely low: approximately 20% for BIBX at a pulp pH of 10.0. The substantial disparity between the recoveries of chalcopyrite and pyrite ensures their separation by flotation. If we define a separation index as the ratio between the recovery of chalcopyrite and the recovery of pyrite at pH 8, then a higher index indicates better selectivity against pyrite. The recovery ratios are 3.00, 1.28, and 2.11 for BIBX, SIBX, and IPETC, respectively.

Figure 4a shows that, at the same collector dose, BIBX leads to the highest chalcopyrite recovery, indicating that BIBX is more efficient than SIBX and IPETC at recovering chalcopyrite. By contrast, BIBX exhibits the worst pyrite recovery performance, as shown in Figure 4b. The data from Figure 4 were used to calculate the separation index, as previously defined, revealing that BIBX maintains a higher index than SIBX and IPETC. The results of the microflotation tests are in agreement with the aforementioned results, demonstrating that the new collector structure with contributions from the carbonyl and benzyl groups displays superior chalcopyrite recovery and better selectivity against pyrite than SIBX and IPETC.

**3.2. Flotation of a Synthetic Ore Mixture.** The results of the microflotation studies suggest that chalcopyrite can be selectively floated from pyrite using BIBX as a collector. To further evaluate the flotation performance of BIBX for separating chalcopyrite from pyrite, we conducted experiments using a 1:1 synthetic mixture of chalcopyrite and pyrite; the results are shown in Figure 5. At the same dosage of the three

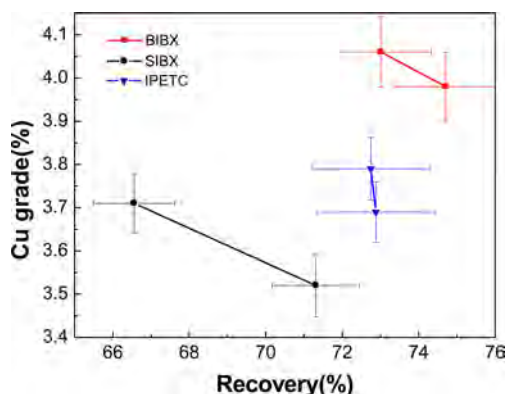


**Figure 5.** Flotation recovery of a chalcopryite–pyrite ore mixture as a function of the collector dosage at a pulp pH of 8.

collectors, BIBX floats more chalcopyrite and less pyrite from a chalcopyrite–pyrite mixture relative to SIBX and IPETC. When the collector concentration was  $4 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ , the recoveries of chalcopyrite were 90.84%, 85.83%, and 82.49%, while those of pyrite were 33.69%, 68.34%, and 40.59% for BIBX, SIBX, and IPETC, respectively. A comparison of Figures 4b and 5 reveals that the recovery of pyrite in the presence of

chalcopyrite is slightly higher than that when pyrite is floated separately. This observed increase is due to the activation of the pyrite surface by the Cu ions released into the solution from the chalcopyrite surface.<sup>17</sup>

**3.3. Batch Flotation Tests.** Figure 6 shows the flotation of copper ore from the Dexing Copper Mine using the three

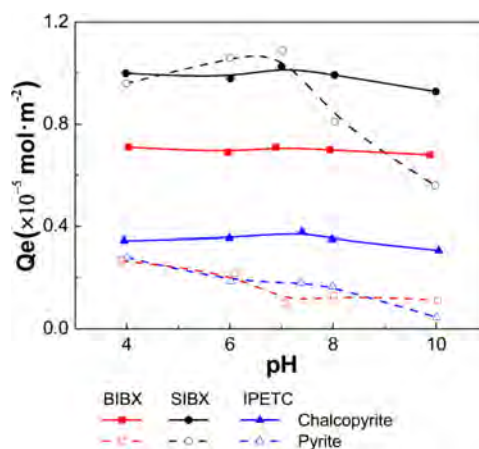


**Figure 6.** Flotation results of copper ore by one roughing flotation process.

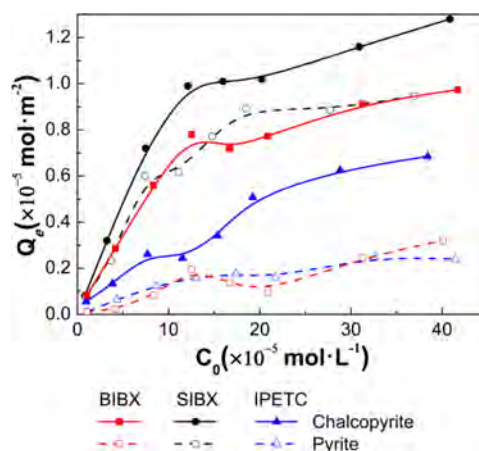
collectors. Tests were performed at 24 and 32 g·t<sup>-1</sup> for each collector. Clearly, the use of BIBX led to a substantial increase in the copper grade, resulting in the highest grade in both tests relative to those for SIBX and IPETC. The grade of Cu in tests using BIBX was greater than 4.0, whereas it was less than 3.8 for the other two collectors. The bench flotation data confirm our conclusion from the pure mineral flotation tests that BIBX promotes the recovery of copper, which makes copper ore flotation more efficient, offering improved selectivity against pyrite.

**3.4. Investigations of the Mechanisms.** The flotation performance of the minerals achieved above is rationalized with emphasis on the interactions between the collector BIBX and the chalcopyrite surfaces. This is investigated in the following sections by adsorption quantity measurements, infrared analysis, XPS, and DFT calculations.

**3.4.1. Adsorption Studies.** The adsorption densities of the collectors used at an initial concentration,  $C_0$ , of  $2.5 \times 10^{-4}$  mol·L<sup>-1</sup> on single mineral (chalcopyrite or pyrite) surfaces at different pH values are shown in Figure 7. The results indicated that, with an increase in the pH from 4 to 10, the amounts of the three collectors adsorbed onto chalcopyrite and pyrite decreased gradually; in addition, the effect of pH on the adsorption of the collectors onto pyrite was more significant than the effect of pH on the adsorption of the collectors onto chalcopyrite. Over the investigated pH range, the amounts of BIBX and IPETC adsorbed onto chalcopyrite were much larger than the amounts adsorbed onto pyrite. However, the adsorption of SIBX onto pyrite was similar to that of chalcopyrite under acidic to weakly alkaline conditions; this result is consistent with the poor selectivity of xanthate in the flotation. The pH-dependent behaviors observed in the adsorption tests are in good agreement with the flotation results. The adsorption of the collectors onto chalcopyrite and pyrite surfaces at pH 8 as a function of their initial concentrations is shown in Figure 8. As the initial concentrations were increased, the amounts of BIBX and IPETC adsorbed onto chalcopyrite increased distinctly, whereas the amounts adsorbed onto pyrite changed only slightly.



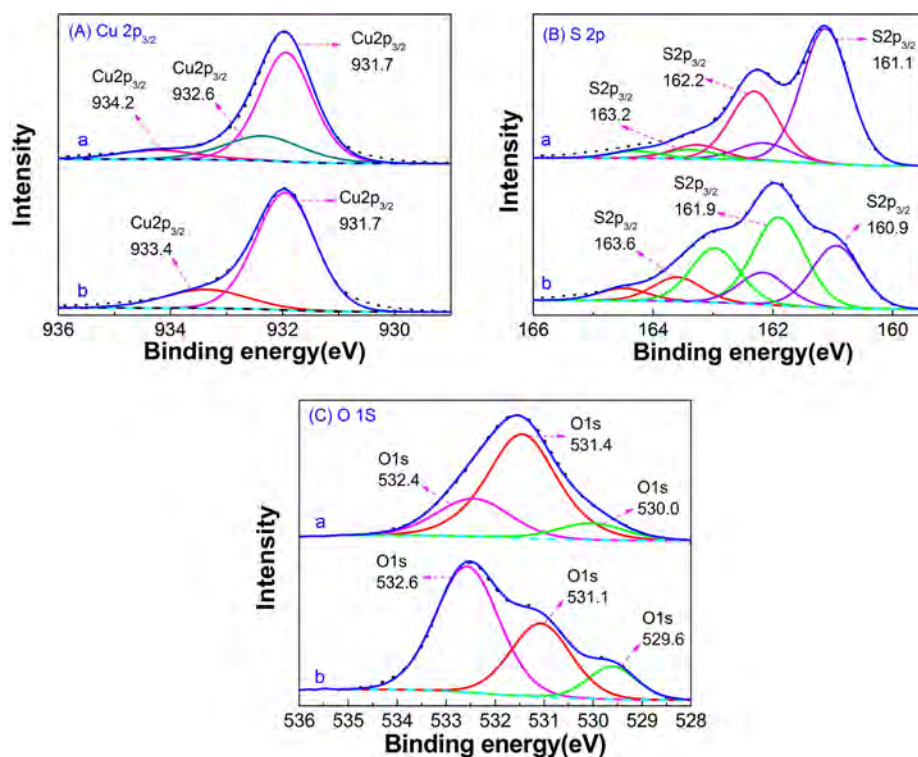
**Figure 7.** Adsorption quantity of collectors on the mineral surfaces with increasing pH and an initial concentration,  $C_0$ , of  $1.6 \times 10^{-4}$  mol·L<sup>-1</sup>.



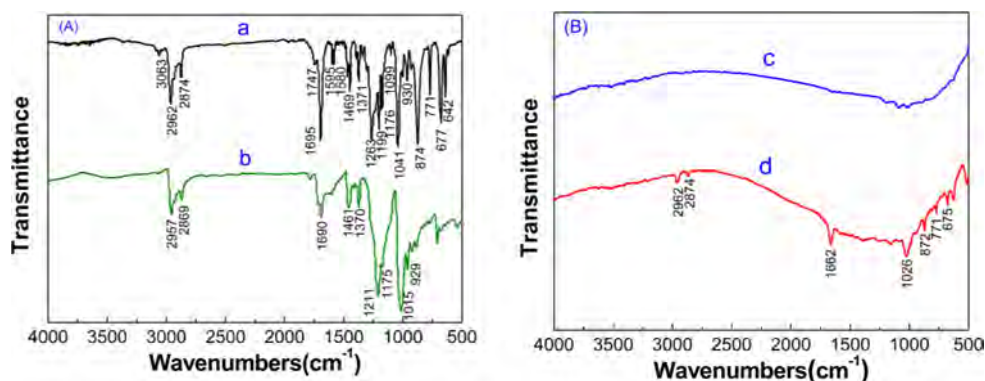
**Figure 8.** Influence of the initial collector concentration on its adsorption capacity at pH 8.

However, the amount of SIBX adsorbed onto chalcopyrite and pyrite increased significantly with increasing concentration of collector added. These results indicate that BIBX and IPETC have a stronger affinity toward chalcopyrite over pyrite than SIBX, which is more apparent for BIBX than IPETC, consistent with the previously discussed flotation results.

**3.4.2. XPS Analysis.** XPS was employed to study the interaction between BIBX and chalcopyrite. Testing was performed on a chalcopyrite surface in the presence and absence of BIBX (Figure 9). XPS analysis reveals each chemical state of the species present, e.g., Cu(II) or Cu(I), which present characteristic and unique electron binding energies. A slight shift in the electron binding energy indicates a change in a species' chemical environment. The atomic concentrations of elements C, S, O, and Cu on the chalcopyrite surface, as determined from the XPS peak intensities, is given in Table S4 (Supporting Information), along with the atomic concentration ratio of these elements to Cu. As shown in Table S4, the S-to-Cu concentration ratio is 1.84, which is lower than the ratio expected on the basis of the chemical formula of chalcopyrite (CuFeS<sub>2</sub>); we expected the S-to-Cu atomic concentration ratio to approach 2 within error. Notably, after the chalcopyrite was immersed in a BIBX solution, the atomic concentrations of C and O on the chalcopyrite surface increased and that of S



**Figure 9.** High-resolution XPS spectra for (A) Cu 2p, (B) S 2p, and (C) O 1s regions of the chalcopyrite surface in the absence (a) and presence (b) of BIBX.



**Figure 10.** FTIR spectra of (A) BIBX and the BIBX–Cu<sup>+</sup> complex and (B) chalcopyrite before and after interaction with BIBX: (a) BIBX, (b) BIBX–Cu<sup>+</sup>, (c) chalcopyrite, and (d) chalcopyrite after treatment.

decreased. This observation confirms that BIBX adsorbed onto the surface of the chalcopyrite.

The Cu 2p regions of the XPS spectra of the two samples are shown in Figure 9A. The peaks at 931.7 and 932.6 eV arise from CuFeS<sub>2</sub> and CuS, respectively, and the peak at 934.2 eV is attributed to copper(II) oxide/hydroxide species, which are easily observed on the chalcopyrite surface.<sup>13,18,19</sup> After the sample was conditioned with BIBX, the Cu 2p<sub>3/2</sub> band at 934.2 eV disappeared, whereas the principal Cu 2p band at 932.6 eV shifted by 0.8 eV to a higher binding energy of 933.4 eV. This shift indicates the electronic density around Cu(I) decreased; this decrease was caused by the donation of electrons to other atoms in BIBX. This observation provides evidence of chemical action between BIBX and chalcopyrite during the adsorption process.

Figure 9B shows the S 2p spectra. The spectrum of untreated chalcopyrite was deconvoluted into three peaks at 161.1, 162.2,

and 163.2 eV, which are associated with metal sulfides (S<sup>2-</sup>), metal-deficient disulfides (S<sub>2</sub><sup>2-</sup>), and polysulfides (S<sub>n</sub><sup>2-</sup>), respectively.<sup>20,21</sup> After the treatment with BIBX, the principal S 2p bands shift to a lower binding energy. Such a shift can be attributed to the alteration of the electrical double layer at the chalcopyrite surface caused by the interaction between the surface and BIBX. Moreover, a broad peak appeared at 163.6 eV accounting for 8.72% of the peak area; this peak may be due to the chemical state of the sulfur atoms on the chalcopyrite surface when the collector is taken up. The new peak is suggested to be due to S–C.<sup>22,23</sup>

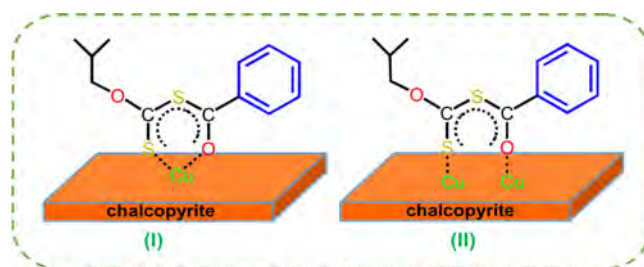
Figure 9C shows the O 1s spectra. The spectrum of the pristine chalcopyrite sample is composed of three peaks at 530.0, 531.4, and 532.4 eV that are assigned to O<sup>2-</sup> and OH<sup>-</sup> from Fe<sub>2</sub>O<sub>3</sub> and FeOOH, which are common on chalcopyrite surfaces.<sup>24,25</sup> After the sample was treated with BIBX, the principal bands in the O 1s spectrum of chalcopyrite shifted by

0.3–0.4 eV to a lower binding energy; such a shift is attributed to the alteration of the electrical double layer at the chalcopryrite surface caused by its interaction with BIBX. Notably, the band at 531.4 eV changes from 66.23% to 31.82%, whereas the peak at approximately 532.6 eV increased by 32.98%, from 23.84% to 56.82%, which may be due to the chemical state of the oxygen atoms on the chalcopryrite surface that change upon the uptake of the collector. This binding energy of approximately 532.6 eV is higher than the reported value for O in a C=O group (531.9 eV) but lower than that for O in C–O (533.2 eV).<sup>26</sup> In a Cu–BIBX complex, copper atoms bind to the S and O atoms in the BIBX molecules to form Cu–S and Cu–O bonds. From an energetics viewpoint, it is a much more electronically stable system because of the conjugated structure of the Cu–S=C–S–C=O–Cu group that forms in the Cu–BIBX complex, and the electrons have the largest delocalization possible. Because the sulfur atom is less electronegative than the oxygen atom, the electrons are attracted from the sulfur atoms to the oxygen atoms, resulting in the organic sulfur atoms possibly having a higher binding energy while the oxygen atoms have a lower binding energy in the Cu–BIBX complex.

**3.4.3. FTIR Analysis.** The FTIR spectra of BIBX, the BIBX–Cu<sup>+</sup> complex, and chalcopryrite before and after conditioning with BIBX are plotted in Figure 10. In the spectrum of BIBX (Figure 10A), the characteristic absorption bands at 1263, 1041, 930, and 1695 cm<sup>-1</sup> are assigned to the C–O–C stretching vibration, C=S stretching vibration, C–S stretching vibration, and C=O stretching vibration of the PhCOS group, respectively.<sup>27–29</sup> The peak at 3063 cm<sup>-1</sup> is attributed to the stretching vibration of C–H in the benzene ring, and the peaks at 874, 771, and 677 cm<sup>-1</sup> are attributed to the C–H out-of-plane bending vibrations of the benzene ring.<sup>29</sup> After the reaction of BIBX with copper ions, the C=O and C=S peaks at approximately 1695 and 1041 cm<sup>-1</sup> shifted to 1690 and 1015 cm<sup>-1</sup>, respectively.<sup>29</sup> The C=O stretching vibration's position is related to the stability constant of the complex: the greater the stability constant, the lower the frequency.<sup>29</sup> The carbon–sulfur bonds therefore may change from C=S to C<sup>-</sup>S, and the carbon–oxygen bonds may change from C=O to C<sup>-</sup>O. This shift also indicates that the sulfur atoms in C=S and the oxygen atoms in C=O are involved in the reaction between BIBX and Cu<sup>+</sup> in aqueous solutions.

A comparison of the spectra of chalcopryrite in the presence and absence of BIBX (Figure 10B) reveals that the absorption bands at approximately 872, 771, and 675 cm<sup>-1</sup> associated with the C–H out-of-plane bending vibrations of the benzene ring clearly appear in the spectrum of the chalcopryrite surface when BIBX is present.<sup>27</sup> These spectral features provide solid evidence that BIBX adsorbs onto the chalcopryrite surface.

More importantly, two new peaks appear at 1662 and 1026 cm<sup>-1</sup> after treatment of the chalcopryrite with BIBX. The peaks in this region were previously discussed and are considered to indicate the change from C=O to C<sup>-</sup>O and from C=S to C<sup>-</sup>S. If this inference is true, we can postulate a possible mechanism of adsorption of BIBX onto the chalcopryrite surface (Figure 11). The BIBX collector possesses two coordination sites (C=S and C=O) that are bonded to Cu atoms on the chalcopryrite. The FTIR and XPS analyses indicated that BIBX acts as a bidentate ligand that coordinates to copper through two functional groups with two distinct geometries. In the first structure (I), the thiol sulfur atom and carbonyl oxygen atoms of BIBX coordinate with the same copper atom to form a coordinated hexatomic ring; in the second structure (II), BIBX



**Figure 11.** Schematic of a possible model of BIBX adsorbed onto chalcopryrite surfaces.

coordinates to different copper atoms to form an “irregular pentagon” complex. Our hypothesis is further supported by previous studies. For example, Ackerman et al.<sup>5</sup> noted that, in the flotation of copper sulfide ores, the thiol sulfur and carbonyl oxygen atoms in the xanthogen formate (R–O–C(=S)–S–C(=O)–O–R') can chelate with the copper on the surface of the mineral to form six-membered-ring chelates. Cu(II) ions are coordinated by two S atoms (C=S) and two O atoms (C=O), as confirmed in a single-crystal X-ray diffraction study by Schwade et al.<sup>30</sup> Similarly, O'Reilly et al.<sup>31,32</sup> reported that the thioureido ligands could coordinate with Cu(II) through the oxygen and sulfur atoms. Arslan et al.<sup>33</sup> revealed two carbonyl oxygen atoms and two thiol sulfur atoms in *N,N*-dialkyl-*N'*-benzoylthioureas reacting with Cu(II) and Ni(II) to form a four-coordinate geometry. Therefore, we believe our hypothesis of the adsorption mechanism is reasonable and can be further supported by DFT calculations.

New peaks were also observed in the chalcopryrite spectra after the BIBX treatment. The bands due to metal coordination complexes occur within the region 1685–1575 cm<sup>-1</sup>. Bands due to C=S and C=O stretching vibrations also appeared at lower frequencies, similar to those in the previously discussed spectra. The shifts in the absorption bands attributed to the C=S and C=O vibrations imply that these species bonded chemically with active atoms on the chalcopryrite surface.<sup>29</sup> The aforementioned results suggest that chemical adsorption could occur when BIBX is adsorbed onto chalcopryrite surfaces.

**3.4.4. DFT Calculation.** Molecular orbital calculations may be helpful in evaluating the potential use of collectors. DFT has been widely used as a cost-effective tool to achieve an atomic-level understanding of the interaction and bond formation between the collector molecules and minerals. To investigate the effect of substitution on the reactivity of xanthate derivatives (*i*-BuOC(S)SC(O)R), the new collector BIBX and *S*-butyl *O*-isobutyl xanthate (BuIBX) were studied using DFT. The optimized geometries of BIBX and BuIBX are shown in Figure 12, and the selected optimized bond lengths and bond angles of BIBX and BuIBX are given in Table S5 (Supporting Information).

The molecular electrostatic potential (MEP) correlates highly with the electron density and is a very useful feature to study reactivity given that an approaching electrophile will be attracted to negative regions.<sup>34</sup> To predict the reactive sites for the investigated molecules, the MEPs of BIBX and BuIBX were calculated at a B3LYP/6-311+G(d)-optimized geometry using DFT. In the contour maps of MEP, the maximum positive region (shaded in blue) is related to the site of nucleophilic attack and the maximum negative region (shaded in red) is related to the site of electrophilic attack. As evident in the MEP maps (Figure 13), the negative electrostatic potential is located

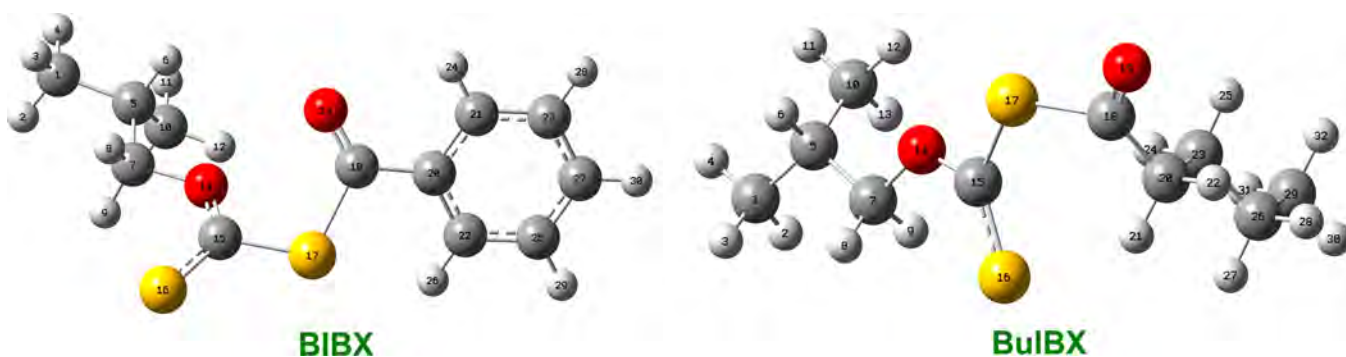


Figure 12. Optimized molecular models of BIBX and BuIBX.

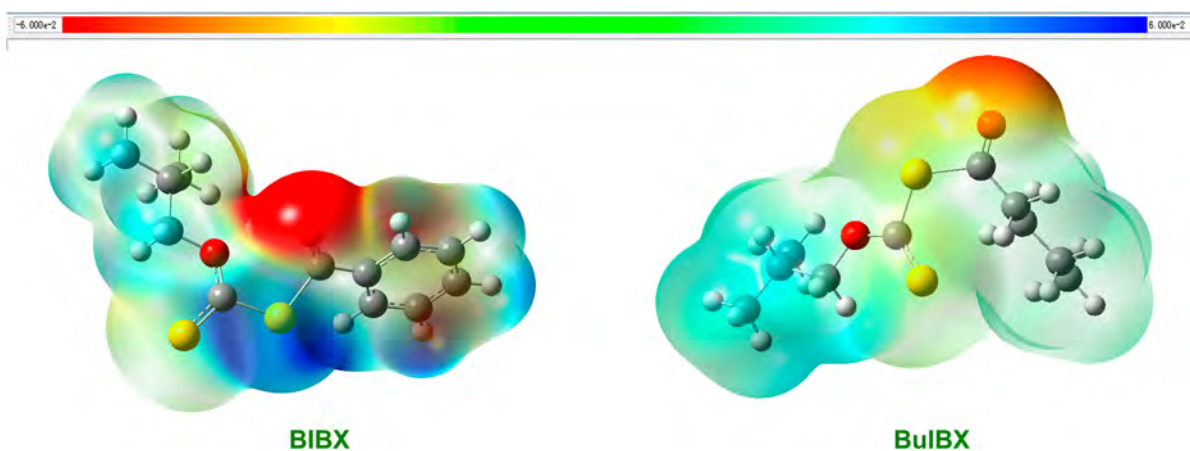


Figure 13. MEPs for BIBX and BuIBX (in au).

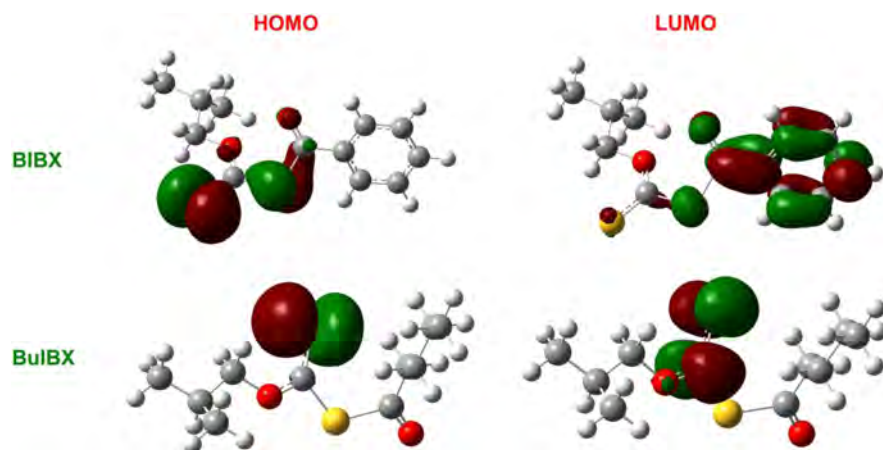


Figure 14. HOMO and LUMO of BIBX and BuIBX at an isosurface value of 0.040 au.

predominantly on the C=O and C=S groups, whereas the positive region is located over the hydrogen atoms on the alkyl group and benzene ring.

The selected atomic charges, dipole moments, and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of BIBX and BuIBX are described in Table S6 (Supporting Information). The HOMO and LUMO compositions obtained by GaussView 3.0 are shown in Figure 14. The chemical reactivity of a molecule is well-known to be determined primarily by the HOMO and LUMO. The HOMO and LUMO are sometimes together termed frontier orbitals because they are molecular orbitals at the energy extremes and most chemical reactions involve them.

The HOMO represents the electron-donating ability, and the LUMO represents the electron-accepting ability. As shown in Figure 14, the HOMO orbitals for BIBX lie predominantly on the S16 and S17 sulfur atoms and the carbonyl oxygen atom (O10) weakly contributes to the HOMO. The sulfur atoms are clearly the electron-donating sites of BIBX, i.e., the reactive sites in the molecule. The results presented here suggest that the BIBX adsorbs onto the mineral surface via the sulfur atoms of the collector transferring electrons to the metal atoms on the mineral surface. Figure 14 also shows that the LUMO is spread over the carbon atoms of the benzyl group and that the S16 and S17 atoms also contribute to the LUMO. In addition, the presence of a benzoyl group in BIBX promotes the contribution



of the LUMO, which can enhance its ability to accept rich d-orbital electrons from metal atoms on the mineral surface to form a back-donation covalent bond.

On the basis of the DFT calculations, we conclude that BIBX binds to the metal atoms through the sulfur (S16) and oxygen (O19) atoms.

#### 4. CONCLUSIONS

A xanthate was structurally modified, resulting in novel collector *S*-benzoyl *O*-isobutyl xanthate (BIBX). BIBX's ability to recover chalcopyrite and its interaction mechanism with Cu were studied. Flotation tests revealed that BIBX is more efficient than conventional sulfide collectors. It has a substantially stronger collecting ability for chalcopyrite. Among BIBX, SIBX, and IPETC, BIBX provided the highest Cu recovery in both microflotation and bench-scale flotation tests. Moreover, it exhibits superior selectivity against pyrite, as observed by the much higher Cu grade obtained for the two rougher concentrates in bench-scale flotation tests. The adsorption data indicate that BIBX exhibits a stronger affinity toward chalcopyrite than pyrite under slightly acidic or alkaline conditions.

Investigations of the mechanism show that BIBX has two dominant chemisorption sites, thiol sulfur and carbonyl oxygen atoms (C=S and C=O, respectively), as indicated by XPS analysis. When the samples were conditioned in a BIBX solution, the S 2p peak of CuFeS<sub>2</sub> at 161.1 eV changed from 47.62% to 22.48% and a new peak that accounts for 8.72% of the peak area appeared at 163.6 eV. The peak area of the O 1s peak at 531.4 eV in the spectrum of CuFeS<sub>2</sub> also decreased from 66.23% to 31.82%, whereas the peak at 532.6 eV accounted for 56.82% of the peak area. FTIR was used as a complementary technique; the FTIR analysis results further supported our findings by the appearance of two additional peaks at 1662 and 1026 cm<sup>-1</sup> after treatment of the surface of chalcopyrite with BIBX. These peaks arose because of changes from C=O to C<sup>-</sup>O and from C=S to C<sup>-</sup>S.

The experimental results and hypothesis were further confirmed by DFT calculations. The negative charge covers the C=S and C=O groups. The HOMO orbital lies predominantly over the S16 and S17 sulfur atoms, which are the electron-donating center of BIBX. The presence of C=O functional groups in the BIBX structure increases the contribution of the LUMO, increasing the possibility of accepting electrons from metals, which results in the formation of a donation covalent bond between BIBX and Cu.

#### ■ ASSOCIATED CONTENT

##### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.6b04566.

Synthesis and characterization of BIBX, preparation procedure of samples for FTIR and XPS analysis, analysis of the mineral composition, atomic concentration of the elements for the chalcopyrite surface, selected optimized bond lengths, bond angles, dipole moments, frontier orbital eigenvalues, and Mulliken charges of the collectors, calibration curves for the collectors, and detailed information on the stability of BIBX (PDF)

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##### Notes

The authors declare no competing financial interest.

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#### ■ REFERENCES

- (1) Leja, J. *Surface Chemistry of Froth Flotation*; Plenum Press: New York, 1982.
- (2) Bulatovic, S. M. *Handbook of Flotation Reagents: Chemistry, Theory and Practice: Volume 1: Flotation of Sulfide Ores*; Elsevier: Amsterdam, 2007.
- (3) Fry, H. S. New Methods of Preparing Thiocarbanilides. *J. Am. Chem. Soc.* **1913**, *35*, 1539.
- (4) Crozier, R. D. *Flotation, Theory, Reagents and Ore Testing*; Pergamon: Oxford, U.K., 1992.
- (5) Ackerman, P. K.; Harris, G. H.; Klimpel, R. R.; Aplan, F. F. Use of Chelating Agents as Collectors in the Flotation of Copper Sulfides and Pyrite. *Miner. Metall. Proc.* **1999**, *16*, 27.
- (6) Fairthorne, G.; Fornasiero, D.; Ralston, J. Interaction of Thionocarbamate and Thiourea Collectors with Sulphide Minerals: A Flotation and Adsorption Study. *Int. J. Miner. Process.* **1997**, *50*, 227.
- (7) Buckley, A. N.; Hope, G. A.; Lee, K. C.; Petrovic, E. A.; Woods, R. Adsorption of *O*-Isopropyl-*N*-ethyl Thionocarbamate on Cu Sulfide Ore Minerals. *Miner. Eng.* **2014**, *69*, 120.
- (8) Ackerman, P. K.; Harris, G. H.; Klimpel, R. R.; Aplan, F. F. Evaluation of Flotation Collectors for Copper Sulfides and Pyrite, I. Common Sulfhydryl Collectors. *Int. J. Miner. Process.* **1987**, *21*, 105.
- (9) Nagaraj, D. R. Development of New Flotation Chemicals. *Trans. Indian Inst. Met.* **1997**, *50*, 355.
- (10) Sheridan, M. S.; Nagaraj, D. R.; Fornasiero, D.; Ralston, J. The Use of a Factorial Experimental Design to Study Collector Properties of *N*-Allyl-*O*-alkyl Thionocarbamate Collector in the Flotation of a Copper Ore. *Miner. Eng.* **2002**, *15*, 333.
- (11) Fairthorne, G.; Fornasiero, D.; Ralston, J. Formation of a Copper-Butyl Ethoxycarbonyl Thiourea Complex. *Anal. Chim. Acta* **1997**, *346*, 237.
- (12) Liu, G. Y.; Zhong, H.; Xia, L. Y.; Wang, S.; Xu, Z. H. Improving Copper Flotation Recovery from a Refractory Copper Porphyry Ore by Using Ethoxycarbonyl Thiourea as a Collector. *Miner. Eng.* **2011**, *24*, 817.
- (13) Liu, G. Y.; Qiu, Z. H.; Wang, J. Y.; Liu, Q. X.; Xiao, J. J.; Zeng, H. B.; Zhong, H.; Xu, Z. H. Study of *N*-Isopropoxypropyl-*N'*-ethoxycarbonyl Thiourea Adsorption on Chalcopyrite Using in Situ SEC, ToF-SIMS and XPS. *J. Colloid Interface Sci.* **2015**, *437*, 42.
- (14) Liu, G. Y.; Xiao, J. J.; Ren, H.; Zhong, H. Adsorption Thermodynamics and Kinetics of *N,N'*-Diisopropoxypropyl-*N''*-oxydiethylenedicarbonyl Bis (thiourea) on Chalcopyrite Surfaces. *J. Ind. Eng. Chem.* **2015**, *21*, 1306.
- (15) He, Z. L.; Liu, G. Y.; Yang, X. L.; Liu, W. A Novel Surfactant, *N,N*-Diethyl-*N'*-cyclohexylthiourea: Synthesis, Flotation and Adsorption on Chalcopyrite. *J. Ind. Eng. Chem.* **2016**, *37*, 107.
- (16) Xie, D. L.; Zhang, X. Y.; Morbidelli, M.; Wu, H. Competitive Adsorption of Xanthates with Different Chain Lengths on Chalcopyrite Particles. *Ind. Eng. Chem. Res.* **2016**, *55*, 1461.

- (17) Chandraprabha, M. N.; Natarajan, K. A.; Modak, J. M. Selective Separation of Pyrite and Chalcopyrite by Biomodulation. *Colloids Surf, B* **2004**, *37*, 93.
- (18) Smart, R. St. C. Surface Layers in Base Metal Sulphide Flotation. *Miner. Eng.* **1991**, *4*, 891.
- (19) McIntyre, N. S.; Cook, M. G. X-Ray Photoelectron Studies on Some Oxides and Hydroxides of Cobalt, Nickel, and Copper. *Anal. Chem.* **1975**, *47*, 2208.
- (20) Acres, R. G.; Harmer, S. L.; Beattie, D. A. Synchrotron XPS, NEXAFS, and ToF-SIMS Studies of Solution Exposed Chalcopyrite and Heterogeneous Chalcopyrite with Pyrite. *Miner. Eng.* **2010**, *23*, 928.
- (21) Fairthorne, G.; Fornasiero, D.; Ralston, J. Effect of Oxidation on the Collectorless Flotation of Chalcopyrite. *Int. J. Miner. Process.* **1997**, *49*, 31.
- (22) Szargan, R.; Schaufuss, A.; Rossbach, P. XPS Investigation of Chemical States in Monolayers: Recent Progress in Adsorbate Redox Chemistry on Sulphides. *J. Electron Spectrosc. Relat. Phenom.* **1999**, *100*, 357.
- (23) Beattie, D. A.; Kempson, I. M.; Fan, L. J.; Skinner, W. M. Synchrotron XPS Studies of Collector Adsorption and Co-adsorption on Gold and Gold: Silver Alloy Surfaces. *Int. J. Miner. Process.* **2009**, *92*, 162.
- (24) Ferris, F. G.; Tazaki, K.; Fyfe, W. S. Iron Oxides in Acid Mine Drainage Environments and Their Association with Bacteria. *Chem. Geol.* **1989**, *74*, 321.
- (25) Mielczarski, J. A.; Cases, J. M.; Alnot, M.; Ehrhardt, J. J. XPS Characterization of Chalcopyrite, Tetrahedrite, and Tennantite Surface Products After Different Conditioning. 1. Aqueous Solution at pH 10. *Langmuir* **1996**, *12*, 2519.
- (26) Ektessabi, A. M.; Hakamata, S. XPS Study of Ion Beam Modified Polyimide Films. *Thin Solid Films* **2000**, *377–378*, 621.
- (27) Woods, R.; Hope, G. A.; Watling, K. A SERS Spectroelectrochemical Investigation of the Interaction of 2-Mercaptobenzothiazole with Copper, Silver and Gold Surfaces. *J. Appl. Electrochem.* **2000**, *30*, 1209.
- (28) Saeed, A.; Erben, M. F.; Bolte, M. Synthesis, Structural and Vibrational Properties of 1-(Adamantane-1-carbonyl)-3-halophenyl Thioureas. *Spectrochim. Acta, Part A* **2013**, *102*, 408.
- (29) Socrates, G. *Infrared and Raman Characteristic Group Frequencies*; John Wiley & Sons: Chichester, U.K., 2004.
- (30) Schwade, V. D.; Kirsten, L.; Hagenbach, A.; Lang, E. S.; Abram, U. Indium (III), Lead (II), Gold (I) and Copper (II) Complexes with Isophthaloylbis (thiourea) Ligands. *Polyhedron* **2013**, *55*, 155.
- (31) O'Reilly, B.; Plutín, A. M.; Pérez, H.; Calderón, O.; Ramos, R.; Martínez, R.; Toscano, R. A.; Duque, J.; Rodríguez-Solla, H.; Martínez-Alvarez, R.; Suárez, M.; Martín, N. Synthesis and Structural Characterization of Cobalt (II) and Copper (II) Complexes with N, N-Disubstituted-N'-acylthioureas. *Polyhedron* **2012**, *36*, 133.
- (32) Pérez, H.; da Silva, C. C. P.; Plutín, A. M.; de Simone, C. A.; Ellena, J. cis-Bis [1,1-dibenzyl-3-(furan-2-ylcarbonyl)thioureato- $\kappa^2$ O,S] copper (II). *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2011**, *67*, m621.
- (33) Arslan, H.; Külcü, N.; Flörke, U. Synthesis and Characterization of Copper (II), Nickel (II) and Cobalt (II) Complexes with Novel Thiourea Derivatives. *Transition Met. Chem.* **2003**, *28*, 816.
- (34) Moro, S.; Bacilieri, M.; Cacciari, B.; Spalluto, G. Autocorrelation of Molecular Electrostatic Potential Surface Properties Combined with Partial Least Squares Analysis as New Strategy for the Prediction of the Activity of Human A3 Adenosine Receptor Antagonists. *J. Med. Chem.* **2005**, *48*, 5698.