Synthesis and reaction with metal ions of a new thionocarbamate

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Abstract The synthesis and research of a novel thionocarbamate N,N'-diethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate which contains two ester and two thioamide groups are reported. This compound was characterized by elemental analysis, UV spectrum, infrared spectrum, mass spectrum, and ¹H NMR and ¹³C NMR spectroscopy. Additionally, the metal ion–collector interaction in organic solution was put into practice. The results of UV spectroscopic analysis showed that this dithionocarbamate with a new structure exhibited a stronger complex ability with Cu²⁺ than with Ni²⁺ or Fe³⁺. Furthermore, infrared spectroscopic analysis implicated that this dithionocarbamate binds to Cu²⁺ through both the C=O and C=S groups. Bench-scale flotation tests were also carried out, verifying that it has a higher copper flotation recovery and better selectivity to sulfide ores containing Cu compared with universal collectors.

Keywords Dithionocarbamate · Synthesis · Metal ions · Flotation

Introduction

The thionocarbamates are liquid and their densities are slightly lower than that of water. Thionocarbamates as intermediates in organic synthesis have been described [1-4], and they are excellent collectors in the separation of copper and sulphur [5-8]. Due to their characteristic group of -C(=S)-NH-, they exhibit higher selectivity and less dosage, and have the properties of frothiness. Since industrial ore deposits at present are barren, fine, and complex, and the grade of minerals becomes gradually lower and lower, it is necessary to consider the impact of

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collectors' chemical structure on flotation properties such as selectivity, collecting ability and frothiness.

There are many reports regarding the synthesis of thionocarbamates containing an ester and a thioamide functional group [9–14]. However, the synthesis of thionocarbamates with two ester and two thioamide functional groups has seldom been reported. This kind of compound usually has multiple coordinating atoms and groups. If these compounds could form complexes with metal ions in flotation, they would be a new type of high-efficiency collector for the retrieval of minerals, and their associated noble metal will be intensified. To our best knowledge, there is no report using this kind of compound to retrieve minerals.

In this paper, a new thionocarbamate N,N'-diethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate was synthesized by a two-step method. This synthesized compound was characterized by elemental analysis, UV spectrum, infrared spectrum, mass spectrum, and ¹H NMR and ¹³C NMR spectroscopy. After mixing the compound solution with Cu²⁺ and Fe³⁺ ion solutions, respectively, the changes of absorbance of three solutions via a UV–VIS spectrophotometer were determined. The precipitate of dithionocarbamate reacted with Cu²⁺ ion was analyzed through infrared spectroscopy. In addition, bench-scale flotation tests were carried out.

Experimental

Regents and instruments

Ethyl chloroformate and 1,4-dihydroxybutane were in chemical grade. *N*,*N*-dimethylaniline, sodium thiocyanate, ethanol and acetone were in analytical grade.

The elemental content was measured by Vario EL III elemental analyzer from Elementar, Germany. The UV spectra were gained by a UV-2100 UV–VIS spectrophotometer from UNICO. The infrared spectra were obtained by AVATAR360 infrared spectrophotometer from Nicolet, USA, and solid samples were tested at wavelengths from 400 to 4,000 cm⁻¹ with the KBr pressed disc method. The ¹H NMR and ¹³C NMR spectra were obtained by an ADVANCE III 400 NMR spectrometer from Bruker, Germany, using DMSO- d_6 as solvent. The mass spectrometer from Bruker Daltonics, Germany, equipped with an ESI source in positive ion mode for detection.

Synthesis of dithionocarbamate

Synthesis of N-ethoxylcarbonyl isothiocyanate

N-ethoxylcarbonyl isothiocyanate was synthesized by ethyl chloroformate and sodium thiocyanate. First, 8.11 g (0.1 mol) sodium thiocyanate was dissolved in 20 mL water, to which was added 0.51 mL (0.004 mol) *N*,*N*-dimethylaniline as catalyst and the mixture cooled to -1-5 °C. Next, 9.53 mL (0.1 mol) ethyl chloroformate were dropped into the mixture slowly in 0.5 h which was then held at 3–8 °C for 4 h with constant stirring. After the reaction completed, the mixture

NaSCN +
$$C_1 \xrightarrow{O} C_2H_5 \xrightarrow{N,N-Dimethylaniline} S = C = N \xrightarrow{O} OC_2H_5 \xrightarrow{1,4-Butanediol} C_2H_5 O \xrightarrow{O} N \xrightarrow{N-O} OC_2H_5$$

Scheme 1 Synthetic route of dithionocarbamate

turned into two phases. The product *N*-ethoxylcarbonyl isothiocyanate was in the organic phase with a yield of 76.4%.

Synthesis of N,N'-diethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate

An amount of 4.43 mL (0.05 mol) 1,4-dihydroxybutane was dissolved in acetone with the ratio 1:2 and this solution added into 13.1 g (0.1 mol) *N*-ethoxylcarbonyl isothiocyanate dropwise at 8–15 °C in 0.5 h. After that, the mixtures were heated to 45–55 °C with reflux and stirred for 4 h to obtain the product of yellow cream. The produced cream was washed with ethanol and distilled water, respectively, several times and then dried in vacuum. The obtained white needle-like compound was the target product with a yield of 89.94%. The synthetic route is shown in Scheme 1.

Results and discussion

Characterization of N,N'-diethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate

The elemental content is as follows: Anal. Calcd for $C_{12}H_{20}O_6N_2S_2$ (%): C, 40.91; H, 5.68; N, 7.96; S, 18.18. Found (%): C, 40.94; H, 5.89; N, 7.69; S, 18.01.

UV–VIS (CH₃OH): $\lambda_{\text{max}} = 254$ nm.

Infrared spectrum of *N*,*N'*-diethoxycarbonyl-*O*,*O'*-(1,4-butylidene) dithionocarbamate is shown in Fig. 2. Characteristic peaks appeared as follows: 3,187 cm⁻¹ for N–H stretch vibration; 2,924 and 2,863 cm⁻¹ for C–H stretch vibration; 1,758 cm⁻¹ for C = O stretch vibration; 1,533 cm⁻¹ for –C(= S)–NH– composite vibration; 1,252 cm⁻¹ for C–O and C–N composite vibration; 1,164 cm⁻¹ for O–C(=O)–N–C vibration; 1,085 cm⁻¹ for C=S stretch vibration. These spectral characteristics confirm that this dithionocarbamate contains the functional groups of amidocyanogen, alkoxycarbonyl and thiocarbonyl.

The NMR data are as follow: ¹H NMR (400 MHz, DMSO- d_6 , chemical shift δ): 1.181–1.216 (m, 6H, CH), 1.807 (s, 4H, CH), 4.080–4.133 (m, 4H, CH), 4.452 (s, 4H, CH), 11.504 (s, 2H, NH); ¹³C NMR (400 MHz, DMSO- d_6 , chemical shift δ): 14.56 (s, 2C), 24.81 (s, 2C), 61.84 (s, 2C), 71.23 (s, 2C), 150.60 (s, 2C), 189.57 (s, 2C).

ESI-MS (m/z): 359.4 $(M + Na^+)$.

The characterization above demonstrated that the structure of the prepared compound is in accordance with our prediction.

Reaction with metal ions

UV spectroscopic analysis

spectroscopy was used to monitor the metal ion-collector interaction in organic solution. Solutions (4 \times 10⁻⁵ M, in methanol) of Cu²⁺, Ni²⁺, and Fe³⁺ were prepared from the corresponding chloride salts. Solutions (4 \times 10⁻⁵ M, in methanol) of NNdiethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate were prepared for the following experiments. Mixing 10 mL of one metal ion solution with 10 mL of the dithionocarbamate solution, sufficient oscillation and several hours of standing were required before measuring the absorbance of the supernatant against the metal ion's blank. As presented in Fig. 1, after adding those metal ions solutions, the absorbance of solutions becomes weaker. Moreover, the absorbance at 254 nm was significantly reduced in the presence of Cu^{2+} ions, less weakened for Ni^{2+} ions, and had little weakening for Fe^{3+} ions. These results indicate that this dithionocarbamate possesses good selectivity towards these metal ions. The decrease in absorbance implies that dithionocarbamate reacted with metal ions to form complexes to decrease the concentration of dithionocarbamate in supernatants. Furthermore, it was noteworthy that the dithionocarbamate exhibited stronger complex ability with Cu(II) than with Ni(II) or Fe(III). Thus, we believe that this new form of thionocarbamate can be used in ore flotation fields to collect Cu from copper ore.

Infrared spectroscopic analysis

After adding the solution of this dithionocarbamate into a Cu^{2+} solution dropwise with stirring, a large number of brick-red floc appeared. So, it is necessary to filter the mixture and wash the precipitate more than once, then let it air-dry. Infrared spectra of dithionocarbamate and the copper-dithionocarbamate complex are compared in Fig. 2.

Figure 2 shows that the C–O and C–N composite vibrations at $1,252 \text{ cm}^{-1}$ are the same for each compound, while the C–H stretching bands are at around 2,900 cm⁻¹. The peak shift caused by reaction with Cu²⁺ is observed for the N–H stretching vibration which shifts 49 cm⁻¹ to low energies at around 3,138 cm⁻¹



Fig. 1 UV spectra of solutions before and after the addition of metal ions



Fig. 2 Infrared spectra of a N,N'-diethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate, b copperdithionocarbamate complex

(from 3,187 cm⁻¹), the C=O stretching vibration which shifts 11 cm⁻¹ to high energies at around 1,769 cm⁻¹ (from 1,758 cm⁻¹), the -C(=S)-NH- composite vibration which shifts 19 cm⁻¹ to low energies at around 1,514 cm⁻¹ (from 1,533 cm⁻¹), the O-C(=O)-N-C vibration which shifts 5 cm⁻¹ to high energies at around 1,169 cm⁻¹ (from 1,164 cm⁻¹), and the C=S stretch vibration which shifts 35 cm⁻¹ to low energies at around 1,050 cm⁻¹ (from 1,085 cm⁻¹). The C=O and C=S stretch vibrations in the dithionocarbamate spectrum are significantly sharper after reaction with Cu²⁺. This demonstrates that dithionocarbamate binds to the Cu²⁺ through both the C=O and C=S groups. The present infrared study is supported by the findings of others [15–18]. In addition, the present infrared evidence suggests that the interaction between the oxygen-to-copper bond is stronger than the sulfur-to-copper bond in agreement with literature reports [15, 19].

Flotation test

The test material was fractory copper porphyry ore from the Dexing Copper Mine of Jiangxi Province in China. Among the ore, the copper-bearing minerals were chalcopyrite, chalcocite, digenite, covellite, tetrahedrite, tennantite, and bornite, as well as some oxide copper minerals such as malachite and cuprite. The main iron-bearing minerals were pyrite and marcasite. The molybdenum form was molybdenite and the gold forms were native gold and electrum. The significant amounts of non-sulfide gangue minerals were quartz, sericite, chlorite, illite, and biotite.

The ore (1 kg, crushed to -2 mm during sampling) was ground to 68% passing 74 µm in a closed steel $\Phi 200 \times 400$ mm XMB ball mill at a pulp density of 62.5% by weight. The bench-scale flotation tests were performed in a XFD-63 flotation cell (self-aeration) whose volume for rougher flotation was 3.0 dm³, using 1 kg ore at

Fig. 3 Flow sheet of flotation tests



Rough concentrate

Tailing

Reagent dosage (g t ⁻¹)	Product	Yield (%)	Grade (%)		Recovery (%)	
			Cu	S	Cu	S
Butyl xanthate 50	Rough concentrate	9.86	3.48	23.23	78.87	81.42
2 [#] frothing agent 20	Tailing	90.14	0.102	0.58	21.13	18.58
	Feed	100.00	0.435	2.81	100.00	100.00
Z-200 16	Rough concentrate	6.15	5.58	20.02	79.62	44.13
2 [#] frothing agent 12	Tailing	93.85	0.094	1.66	20.38	55.87
	Feed	100.00	0.431	2.79	100.00	100.00
<i>N,N</i> ′-diethoxycarbonyl- <i>O,O</i> ′-(1,4- butylidene) dithionocarbamate 16	Rough concentrate	5.32	6.45	17.63	80.17	33.26
	Tailing	94.68	0.090	1.99	19.13	66.74
2 [#] frothing agent 12	Feed	100.00	0.428	2.82	100.00	100.00

Table 1 Results of flotation tests

every turn to obtain a Cu/Fe rougher concentrate. The flotation flow sheet is described in Fig. 3. After wet grinding, the pH of the pulp slurry was pre-adjusted to 9.0 by the addition of 1,600 g/t lime. The other reagents dosage and the results of the flotation tesst are presented in Table 1.

The results indicated that the dithionocarbamate reported in this article could obtain a higher copper flotation recovery compared with butyl xanthate and Z-200, the two universal collectors. In addition, it has better selectivity to sulfide ores containing Cu.

Conclusions

In this paper, N,N'-diethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate was synthesized by a two-step method. The intermediate N-ethoxylcarbonyl isothiocyanate was synthesized from ethyl chloroformate and sodium thiocyanate by nucleophilic substitution reaction and isomerization. Using this intermediate reacted with 1,4-dihydroxybutane as raw material, the target product N,N'-diethoxycarbonyl-O,O'-(1,4-butylidene) dithionocarbamate was obtained by a nucleophilic addition reaction.

The metal ion–collector interaction in organic solution was put into practice. The results of UV spectroscopic analysis showed that this dithionocarbamate with a new structure can react with Cu^{2+} and Ni^{2+} separately, and it has the best selectivity to the Fe³⁺ ion. Infrared spectroscopic analysis demonstrated that this dithionocarbamate binds to the Cu^{2+} through both the C=O and C=S groups. Bench-scale flotation tests were also carried out, the results verifying that it has higher copper flotation recovery and better selectivity to sulfide ores containing Cu compared with universal collectors. Thus, the *N*,*N*'-diethoxycarbonyl-*O*,*O*'-(1,4-butylidene) dithionocarbamate reported in this paper displayed excellent floating properties to copper, and it is suggested that it is applied in flotation of sulfur copper as a new collector.

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References

- 1. B.P. Bongar, V.S. Sadavarte, L.S. Uppalla, J. Chem. Res. 450, 9 (2004)
- 2. A.R. Katrizky, S. Singh, P.P. Mahapatra, N. Clemense, K. Kirichenko, ARKIVOC. 9 (2005)
- 3. P. Morf, F. Raimondi, H.G. Nothofer et al., Langmuir. 22 (2006)
- 4. F. Aryanasab, A. Ziyaei Halimehjani, M.R. Saidi, Tetrahedron Lett. 51 (2010)
- 5. M.S. Sheridan, D.R. Nagaraj, D. Fornasiero et al., Miner. Eng. 15 (2002)
- 6. G.Y. Liu, H. Zhong, T.G. Dai et al., Miner. Eng. 21 (2008)
- 7. G.Y. Liu, H. Zhong, T.G. Dai, Miner. Eng. 19 (2006)
- 8. Q. Zhang, Y.H. Hu, J. Xu et al., Trans. Nonferrous Met. Soc. China, 16 (2006)
- 9. L.S. Tang, G.N. Li, Q. Lin, Nonferrous Met. (Miner. Process.), 2000
- 10. J.H. Yu, Nonferrous Mines, 30 (2001)
- 11. X.P. Zhang, S.W. Lu, Chem. J. Chin. Univ. 29 (2008)
- 12. H.P. Hemantha, V.V. Sureshbabu, Tetrahedron Lett. 50 (2009)
- X.P. Zhang, S.W. Lu, S.D. Wang, Process for the preparation of thionocarbamates. 2006-1-18 CN[P]: 1721402A
- H. Zhong, G.Y. Liu, H. Wang et al., A preparation method of N-hydrocarbon oxy carbonyl isothiocyanate and its derivatives. 2005-9-28 CN[P]: 1220678C
- 15. C.I. Basilio, Fundamental studies of thionocarbamate interactions with sulfide minerals [D] (Virginia Polytechnic Institute and State University, Virginia, 1989)
- 16. J.A. Mielczarski, R.H. Yoon, J. Colloid Interface Sci. 131 (1989)
- 17. J.A. Mielczarski, R.H. Yoon, Langmuir, 7 (1991)
- 18. J.O. Leppinen, C.I. Basilio, R.H. Yoon, Colloids Surf. 32 (1988)
- 19. T.J. Lane, A. Yamaguchi, J.A. Quagliano et al., J. Am. Chem. Soc. 81 (1959)