

SYNTHESES AND STRUCTURE OF ALKYL AND DIALKYL
ISOPENTYLDITHIOCARBAMATE THIOETHERSM.S. Mukanova^{1,2*}, L.M. Akhmetova^{1,2}, Ye.S. Sycheva¹¹ A.B. Bekturov Institute of Chemical Sciences, Almaty, Kazakhstan² Kazakh-British Technical University, Almaty, Kazakhstan

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Abstract. *Introduction.* Dithiocarbamates and their derivatives are promising sulfur-containing compounds used as flotation reagents in the flotation enrichment of mineral raw materials. Variations in the structure of the hydrocarbon substituent and the introduction of additional functional fragments make it possible to regulate their surface properties. The *aim* of this study was to synthesize new alkyl and dialkyl thioethers based on isopentylthiocarbamates and to establish their structures using IR and NMR spectral methods. *Results and discussion.* The reaction of isopentylamine with carbon disulfide in an alkaline medium yielded disodium isopentylbis(dithiocarbamate) and sodium isopentylthiocarbamate in 58% and 30% yields, respectively. The subsequent reaction of the salts with hexyl, heptyl, octyl, nonyl, and decyl bromides allowed the synthesis of a series of alkyl and dialkyl thioethers in 75–98% yields. The composition and structure of the synthesized compounds were confirmed by elemental analysis, IR, ¹H, and ¹³C NMR spectroscopy. Spectral characteristics indicate the presence of a dithiocarbamate fragment, an isopentyl substituent, and alkyl substituents of varying lengths. *Conclusion.* Synthetic conditions for a series of new isopentylthiocarbamate thioethers have been developed. The synthesized isopentylthiocarbamate thioethers with variable alkyl fragment lengths are of interest for further study of their flotation properties and the possibility of using them as flotation reagents.

Keywords: isopentylthiocarbamate, alkyl and dialkyl thioether, alkylation reaction, structure, IR, ¹H, and ¹³C NMR spectroscopy

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Citation: Mukanova M.S., Akhmetova L.M., Sycheva Ye.S. Syntheses and structure of alkyl and dialkyl isopentylthiocarbamate thioethers. *Chem. J. Kaz.*, **2026**, 3(95), 173-183. DOI: <https://doi.org/10.51580/2026-3.2710-1185.39>

1. Introduction

Flotation remains one of the most widely used mineral beneficiation methods because it can separate minerals with very close physical characteristics. The problem of searching for new organic collectors, which ensure high recovery of valuable components with separation selectivity, becomes a priority.

Xanthates are the main flotation reagents for sulfide minerals. Although these compounds have been widely used in industry, there have been some limitations regarding selectivity, the possibility of forming toxic decomposition products, and the dependence of the action on environmental parameters. For these reasons, over the last few decades, there has been intensive research into alternative sulfur-containing compounds, among which dithiocarbamates have been considered one of the most promising classes of flotation reagents [1-3].

Dithiocarbamates exhibit high reactivity due to the presence of the $-NCS_2$ functional group, which enables complexation with surface metal ions. Interaction with the mineral surface results in the formation of stable metal-sulfur complexes, which alter the hydrophilicity and surface energy of the particles. This makes them suitable for use as both collectors and depressants in the separation of various types of mineral raw materials [4,5].

Among dithiocarbamine compounds, dithiocarbamates based on aliphatic amines are of particular interest, since they are distinguished by the availability of the starting components and the possibility of regulating the properties by changing the length and structure of the hydrocarbon substituent.

Studies have shown that simple aliphatic dithiocarbamates can effectively modify the surface properties of minerals. For example, sodium dimethyldithiocarbamate has a selective effect on the pyrite surface, reducing its hydrophobicity through the formation of hydrophilic complexes with surface iron cations [5]. In a lead-zinc mineral separation system, the combined use of $ZnSO_4$ and dimethyldithiocarbamate increased the efficiency of sphalerite suppression due to the competitive adsorption of reagents on the mineral surface [6].

Sodium diethyldithiocarbamate has also demonstrated high efficiency in the flotation of oxidized copper minerals. Its use in combination with xanthates was found to promote the formation of a more hydrophobic malachite surface due to the formation of Cu-S compounds and enhanced collector adsorption [7]. In the flotation of smithsonite, the use of a mixture of dodecylamine and diethyldithiocarbamate increased zinc recovery due to the combined physical and chemical adsorption of reagent system components [8]. In recent years, research on modified dithiocarbamate compounds containing additional functional groups has advanced significantly. These reagents possess multiple active sites for interaction with mineral surfaces and demonstrate increased efficiency in the flotation of difficult-to-process minerals. For example, dithiocarbamate-hydroxamate compounds have demonstrated excellent results in the recovery of bastnaesite, cassiterite, galena, chalcopyrite, and wolframite. Their high activity is explained by the formation of stable complexes between the reagent's functional groups and surface metal atoms [9-14].

Despite a significant amount of research devoted to dithiocarbamates, the synthesis and application of dithiocarbamates based on aliphatic amines, particularly their derivatives with a modified thioether structure, remain understudied. However, modification of dithiocarbamates can significantly affect their hydrophobicity, stability, and ability to interact with mineral surfaces.

In this regard, the preparation of new alkyl thioethers based on sodium isopentyl dithiocarbamate is of interest. The introduction of a thioether moiety into the dithiocarbamate structure can alter the electronic and surface properties of the molecule, potentially enabling the production of effective flotation reagents with improved collection properties.

The aim of this work is to synthesize alkyl thioethers based on sodium isopentyl dithiocarbamate as potential flotation reagents.

2. Experimental part

The reaction control and product purity were monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates, with spot visualization performed using iodine vapor. The eluent consisted of a mixture of ethanol and acetone/hexane (1/4). Infrared (IR) spectra were recorded on a Nicolet 5700 FTIR spectrometer using KBr pellets and thin-layer films. Melting points were determined with a Hanon MP450 apparatus. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECA 400 spectrometer (JEOL), operating at 400 MHz for ^1H and 100 MHz for ^{13}C , using deuterated D_2O and CDCl_3 as solvents. Elemental analysis was performed with a THERMO FlashSmart CHNS/O elemental analyzer (USA, 2024).

Disodium isopentyl-bis(dithiocarbamate) (1). A solution of 8.0 g (0.2 mol) of NaOH in 3 mL of water was added to a solution of 8.717 g (0.1 mol) of isopentylamine in 110 mL of ethanol. Then a solution of 15.2 g (0.2 mol) of carbon disulfide was added dropwise at room temperature under stirring. After the complete addition of carbon disulfide, the reaction mixture was stirred at room temperature for four hours. The solvent was removed under reduced pressure using a water-jet vacuum pump and the solid residue was purified by recrystallization from ethanol. Yield 16.44 g (58%), $R_f = 0.84$ (ethanol/benzene, 1/2), $T_m = 296\text{--}297^\circ\text{C}$. Found, %: C, 29.27; H, 4.11; N, 4.69; Na, 16.32; S, 45.55. $\text{C}_7\text{H}_{11}\text{NNa}_2\text{S}_4$. Calculated, %: C, 29.67; H, 3.91; N, 4.94; Na, 16.22; S, 45.25. IR spectra, ν , cm^{-1} : 2931, 2852 (CH_2 , CH_3); 1470, 1421 (CH_2 , CH_3); 1221 ($=\text{C}-\text{N}$); 1109 ($\text{N}-\text{C}(\text{S})=\text{S}$); 966 ($\text{C}=\text{S}$); 883 ($\text{C}-\text{S}$). NMR ^1H spectra (D_2O), δ , ppm: 1.48 (7H, 2CH_3 , CH); 1.54 (2H, CH_2); 4.12 (t, 2H, $\text{N}-\text{CH}_2$). NMR ^{13}C spectra (D_2O), δ , ppm: 25.64 (CH_2 , 2CH_3); 23.78 (CH); 53.06 ($\text{N}-\text{CH}_2$); 205.05 ($2\text{C}=\text{S}$).

Sodium isopentyl dithiocarbamate (2). Yield 5.56 g (30%), $R_f = 0.93$ (ethanol/benzene, 1/2), $T_m = 107\text{--}108^\circ\text{C}$. Found, %: C, 39.05; H, 6.33; N, 7.29; Na, 12.71; S, 34.73. $\text{C}_6\text{H}_{12}\text{NNaS}_2$. Calculated, %: C, 38.90; H, 6.53; N, 7.56; Na, 12.41; S, 34.61. IR spectra, ν , cm^{-1} : 3369 (NH); 2936, 2852 (CH_2 , CH_3); 1470, 1421 (CH_2 , CH_3); 1221 ($=\text{C}-\text{N}$); 1131, 1111 ($\text{N}-\text{C}(\text{S})=\text{S}$); 1003, 967 ($\text{C}=\text{S}$); 883 ($\text{C}-\text{S}$). NMR ^1H spectra (D_2O), δ , ppm: 1.23 (t, 6H, 2CH_3); 1.50 (m, 2H, CH_2);

1.56 (m, 1H, CH); 4.35 (dt, 2H, N-CH₂). NMR ¹³C spectra (D₂O), δ, ppm: 13.63 (2CH₃); 23.80 (CH); 25.66 (CH₂); 53.08 (N-CH₂); 204.28 (C=S).

General procedure for the Synthesis of alkyl and dialkyl thioesters (3-12)

The corresponding alkyl bromide (hexyl, heptyl, octyl, nonyl and decyl) was added dropwise to a solution of dithiocarbamate in acetone. The reaction mixture was stirred at room temperature (22 °C) for five hours. After completion of the reaction, the mixture was filtered through a Schott funnel using a vacuum pump. The resulting solution was concentrated under reduced pressure using a water-jet vacuum pump, and the product was purified by recrystallization from hexane. The synthesis was applied to a series of alkyl bromides. As a result, the corresponding alkyl isopentyldithiocarbamate and dialkyl isopentyl bis(dithiocarbamate) derivatives were obtained.

Dihexyl isopentyl-bis(carbamodithioate) (3). Yield 9.30 g (76%), oil, R_f = 0.64 (acetone/hexane, 1/3), n_D^{20} 1.4031. Found, %: C, 55.64; H, 9.29; N, 3.67; S, 31.75. C₁₉H₃₇NS₄. Calculated, %: C, 55.97; H, 9.15; N, 3.44; S, 31.45. IR spectra, ν, cm⁻¹: 2930, 2856 (CH₂, CH₃); 1473, 1424 (CH₂, CH₃); 1241, 1226 (=C-N); 1133, 1116 (N-C(S)=S); 1006, 979 (C=S); 893, 854 (C-S). NMR ¹H spectra (CDCl₃), δ, ppm: 0.82 (s, 6H, 2CH₃ (hexyl)); 1.26 (s, 6H, 2CH₃ (isopentyl)); 1.36 (s, 1H, CH); 1.63 (s, 18H, 9CH₂); 3.22 (t, 4H, 2(S-CH₂)); 3.84-4.23 (br., d, N-CH₂). NMR ¹³C spectra (CDCl₃), δ, ppm: 14.10 (2CH₃ (hexyl)); 22.60 (2CH₃ (isopentyl)); 24.41 (2CH₂CH₃); 25.99, 25.56 (CH); 28.70, 28.78 (6CH₂); 31.46 (N-CH₂-CH₂); 37.37 (S-CH₂); 51.27, 52.75 (N-CH₂); 196.14 (2C=S).

Diheptyl isopentyl-bis(carbamodithioate) (4). Yield 9.94 g (76%), oil, R_f = 0.75 (acetone/hexane, 1/3), n_D^{20} 1.4032. Found, %: C, 57.45; H, 9.24; N, 3.54; S, 29.71. C₂₁H₄₁NS₄. Calculated, %: C, 57.88; H, 9.48; N, 3.21; S, 29.43. IR spectra, ν, cm⁻¹: 2928, 2855 (CH₂, CH₃); 1472, 1424 (CH₂, CH₃); 1228 (=C-N); 1133, 1116 (N-C(S)=S); 1006, 979 (C=S); 892, 854 (C-S). NMR ¹H spectra (CDCl₃), δ, ppm: 0.80 (s, 6H, 2CH₃ (heptyl)); 1.21 (br. s, 6H, 2CH₃ (isopentyl), CH₂); 1.34 (s, 1H, CH); 1.62 (br. s, 20H, 10CH₂); 3.21 (S-CH₂); 3.8-4.21 (N-CH₂). NMR ¹³C spectra (CDCl₃), δ, ppm: 14.14 (2CH₃ (heptyl)); 22.65 (2CH₃ (isopentyl)); 24.40 (2CH₂CH₃); 25.96, 25.57 (CH); 28.74, 28.94, 29.06 (8CH₂); 31.76 (N-CH₂-CH₂); 37.36 (2S-CH₂); 51.26, 52.72 (N-CH₂); 196.14 (2C=S).

Dioctyl isopentyl-bis(carbamodithioate) (5). Yield 13.64 g (98%), oil, R_f = 0.71 (acetone/hexane, 1/3), n_D^{20} 1.4033. Found, %: C, 59.21; H, 9.67; N, 3.31; S, 27.33. C₂₃H₄₅NS₄. Calculated, %: C, 59.56; H, 9.78; N, 3.02; S, 27.65. IR spectra, ν, cm⁻¹: 2927, 2856 (CH₂, CH₃); 1470, 1424 (CH₂, CH₃); 1238 (=C-N); 1133 (N-C(S)=S); 1007, 980 (C=S); 893, 854 (C-S). NMR ¹H spectra (CDCl₃), δ, ppm: 0.84 (t, 6H, 2CH₃ (octyl)); 1.24 (s, 18H, 2CH₃ (isopentyl), 6CH₂); 1.38 (s, 3H, CH, CH₂); 1.65 (t, 12H, 6CH₂); 3.25 (t, 4H, 2S-CH₂); 3.85, 4.25 (2s, 2H, N-CH₂). NMR ¹³C spectra (CDCl₃), δ, ppm: 14.21 (2CH₃ (octyl)); 22.74 (2CH₃ (isopentyl)); 24.44 (2CH₂CH₃); 25.82 (CH); 28.77, 29.15, 29.28 (10CH₂); 31.90 (N-CH₂-CH₂); 37.40 (2S-CH₂); 51.28, 52.79 (N-CH₂); 196.15 (2C=S).

Dinonyl isopentyl-bis(carbamodithioate) (6). Yield 12.7 g (86 %), oil, $R_f = 0.76$ (acetone:hexane = 1:3). n_D^{20} 1.4034. Found, %: C, 61.17; H, 10.3; N, 2.69; S, 25.74. $C_{25}H_{49}NS_4$. Calculated, %: C, 61.04; H, 10.04; N, 2.85; S, 26.07. IR spectra, ν , cm^{-1} : 2927, 2855 (CH_2 , CH_3); 1456, 1424 (CH_2 , CH_3); 1243, 1226 ($=C-N$); 1133, 1117 ($N-C(S)=S$); 1006, 981 ($C=S$); 893, 854 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 6H, $2CH_3$ (nonyl)); 1.23 (s, 18H, $2CH_3$ (isopentyl), $6CH_2$); 1.38 (s, 3H, CH, CH_2); 1.66 (t, 16H, $8CH_2$); 3.25 (t, 4H, $2S-CH_2$); 3.86, 4.26 (2s, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.21 ($2CH_3$ (nonyl)); 22.76 ($2CH_3$ (isopentyl)); 24.44 ($2\text{---}CH_2CH_3$); 25.57, 26.05 (CH); 28.26, 28.70, 28.87, 29.15, 29.35, 29.56 ($12CH_2$); 31.95 ($N-CH_2\text{---}CH_2$); 37.41 ($2S-CH_2$); 51.27, 52.79 ($N-CH_2$); 196.18 ($2C=S$).

Didecyl isopentyl-bis(carbamodithioate) (7). Yield 13.9 g (89 %), oil, $R_f = 0.74$ (acetone/hexane, 1/3), n_D^{20} 1.4036. Found, %: C, 62.17; H, 10.44; N, 2.85; S, 24.36. $C_{27}H_{53}NS_4$. Calculated, %: C, 62.37; H, 10.27; N, 2.69; S, 24.66. IR spectra, ν , cm^{-1} : 2925, 2854 (CH_2 , CH_3); 1469, 1424 (CH_2 , CH_3); 1227, 1226 ($=C-N$); 1133, 1117 ($N-C(S)=S$); 1007, 981 ($C=S$); 892, 853 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.84 (t, 6H, $2CH_3$); 1.23 (s, 20H, $2CH_3$, $7CH_2$); 1.38 (s 5H, CH, $2CH_2$); 1.65 (t, 16H, $8CH_2$); 3.25 (t, 4H, $2S-CH_2$); 3.86, 4.26 (2s, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.22 ($2CH_3$ (decyl)); 22.77 ($2CH_3$ (isopentyl)); 24.44 ($2\text{---}CH_2CH_3$); 25.59, 26.04 (CH); 28.77, 29.15, 29.32, 29.41, 29.60, 29.65 ($14CH_2$); 31.98 ($N-CH_2\text{---}CH_2$); 37.42 ($2S-CH_2$); 52.81, 51.29 ($N-CH_2$); 196.20 ($2C=S$).

Hexyl isopentylcarbamodithioate (8). Yield 9.3 g (75 %), oil, $R_f = 0.72$ (acetone/hexane, 1/4, n_D^{20} 1.4037. Found, %: C, 58.06; H, 10.32; N, 5.81; S, 25.57. $C_{12}H_{25}NS_2$. Calculated, %: C, 58.24; H, 10.18; N, 5.66; S, 25.91. IR spectra, ν , cm^{-1} : 2928, 2858 (CH_2 , CH_3); 1463, 1425 (CH_2 , CH_3); 1217 ($=C-N$); 1133 ($N-C(S)=S$); 1053 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.86 (t, 6H, $2CH_3$ (hexyl)); 1.28 (t, 7H, $2CH_3$ (isopentyl), CH); 1.39 (t, 6H, $3CH_2$); 1.65 (t, 4H, $N-CH_2\text{---}CH_2$, $S-CH_2\text{---}CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.61 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.11 (CH_3 (hexyl)); 22.60 (CH_3 (isopentyl)); 24.45 (CH); 28.42, 28.67, 28.74, 28.83 ($4CH_2$); 31.39 ($N-CH_2\text{---}CH_2$); 36.00 ($S-CH_2$); 69.82 ($N-CH_2$); 215.32 ($C=S$).

Heptyl isopentylcarbamodithioate (9). Yield 11.51 g (88 %), oil, $R_f = 0.81$ (acetone/hexane, 1/4), n_D^{20} 1.4038. Found, %: C, 59.31; H, 10.27; N, 5.55; S, 24.78. $C_{13}H_{27}NS_2$. Calculated, %: C, 59.71; H, 10.41; N, 5.36; S, 24.52. IR spectra, ν , cm^{-1} : 2927, 2856 (CH_2 , CH_3); 1466, 1425 (CH_2 , CH_3); 1219 ($=C-N$); 1145, 1133 ($N-C(S)=S$); 1054 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 3H, CH_3 (heptyl)); 1.25 (s, 6H, $2CH_3$ (isopentyl)); 1.39 (t, CH); 1.65 (t, 4H, $2CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.61 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.17 (CH_3 (heptyl)); 22.68 ($2CH_3$ (isopentyl)); 24.45 (CH); 28.46, 28.89, 28.95 ($5CH_2$); 31.76 ($N-CH_2\text{---}CH_2$); 36.00 ($S-CH_2$); 69.81 ($N-CH_2$); 215.32 ($C=S$).

Octyl isopentylcarbamodithioate (10). Yield 12.40 g (90 %), oil, $R_f = 0.9$ (acetone/hexane, 1/4), n_D^{20} 1.4040. Found, %: C, 60.76; H, 10.91; N, 5.26; S, 22.97. $C_{14}H_{29}NS_2$. Calculated, %: C, 61.03; H, 10.61; N, 5.08; S, 23.27. IR spectra, ν , cm^{-1} : 2926, 2855 (CH_2 , CH_3); 1468, 1425 (CH_2 , CH_3); 1218 ($=C-N$); 1145, 1133 ($N-C(S)=S$); 1055 ($C=S$); 853 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 3H, CH_3 (octyl)); 1.25 (s, 12H, $2CH_3$ (isopentyl), $3CH_2$); 1.39 (t, 5H, CH, $2CH_2$); 1.65 (m, 4H, $2CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.61 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.21 (CH_3 (octyl)); 22.74 ($2CH_3$ (isopentyl)); 24.45 (CH); 28.45, 28.99, 29.17, 29.23, 29.28 ($6CH_2$); 31.87 ($N-CH_2-CH_2$); 36.01 ($S-CH_2$); 69.86 ($N-CH_2$); 215.41 ($C=S$).

Nonyl isopentylcarbamodithioate (11). Yield 13.2 g (91 %), oil, $R_f = 0.85$ (acetone/hexane, 1/4), n_D^{20} 1.4042. Found, %: C, 61.91; H, 10.93; N, 4.65; S, 21.94. $C_{15}H_{31}NS_2$. Calculated, %: C, 62.22; H, 10.79; N, 4.84; S, 22.15. IR spectra, ν , cm^{-1} : 2926, 2854 (CH_2 , CH_3); 1464, 1425 (CH_2 , CH_3); 1217 ($=C-N$); 1133 ($N-C(S)=S$); 1055 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 3H, CH_3 (nonyl)); 1.24 (s, 14H, $2CH_3$ (isopentyl), $4CH_2$); 1.39 (t, 5H, CH, $2CH_2$); 1.66 (m, 4H, $2CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.62 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.21 (CH_3 (nonyl)); 22.76 ($2CH_3$ (isopentyl)); 24.45 (CH); 28.46, 28.99, 29.16, 29.23, 29.33, 29.57 ($7CH_2$); 31.95 ($N-CH_2-CH_2$); 36.01 ($S-CH_2$); 69.81 ($N-CH_2$); 215.34 ($C=S$).

Decyl isopentylcarbamodithioate (12). Yield 12.8 g (84 %), oil, $R_f = 0.9$ (acetone/hexane, 1/4), n_D^{20} 1.4045. Found, %: C, 63.06; H, 10.82; N, 4.91; S, 21.25. $C_{16}H_{33}NS_2$. Calculated, %: C, 63.31; H, 10.96; N, 4.61; S, 21.12. IR spectra, ν , cm^{-1} : 2926, 2854 (CH_2 , CH_3); 1464, 1425 (CH_2 , CH_3); 1216 ($=C-N$); 1133 ($N-C(S)=S$); 1054 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.86 (t, 3H, CH_3 (decyl)); 1.24 (s, 16H, $2CH_3$ (isopentyl), $5CH_2$); 1.40 (t, 5H, CH, $2CH_2$); 1.66 (m, 4H, $2CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.62 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.22 (CH_3 (decyl)); 22.77 ($2CH_3$ (isopentyl)); 24.45 (CH); 28.46, 28.99, 29.22, 29.40, 29.56, 29.67 ($8CH_2$); 31.98 ($N-CH_2-CH_2$); 36.01 ($S-CH_2$); 69.80 ($N-CH_2$); 215.33 ($C=S$).

3. Results and discussion

The synthesis of disodium isopentyl-bis(dithiocarbamate) and sodium isopentylidithiocarbamate was carried out by the interaction of isopentylamine with carbon disulfide (in a ratio of 1:2) in the presence of an alkali in alcohol at room temperature. As a result of isolation from the reaction mixture, disodium isopentyl-bis(carbamodithioate) (1) and sodium isopentylcarbamodithioate (2) were obtained in individual form with yields of 58 and 30% respectively (Fig. 1).

In order to synthesize potential flotation reagents, the conditions for the synthesis of long-chain alkyl and dialkyl thioesters of isopentylidithiocarbamates were optimized. The synthesis of alkyl and dialkyl thioesters was carried out by the alkylation reaction of disodium isopentyl-bis(dithiocarbamate) (or sodium isopentylidithiocarbamate) with alkyl bromides (hexyl, heptyl, octyl, nonyl and decyl) in acetone at room temperature. As a result, alkyl thioesters of

isopentylcarbamodithioate (yields of 75–91%) and dialkyl thioesters of isopentyl-bis(carbamodithioate) (yields of 76–98%) were synthesized (Fig. 1).

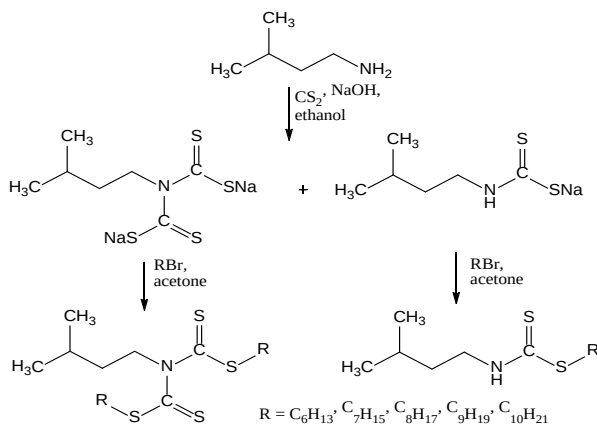


Figure 1 – Synthesis of isopentylthiocarbamates and their alkyl and dialkyl thioesters.

The composition and identity of the synthesized isopentylthiocarbamates (1,2) and their alkyl and dialkyl thioethers (3-12) were confirmed based on elemental analysis and IR spectroscopy.

The IR spectra of isopentylthiocarbamates (1,2) and their alkyl and dialkyl thioethers (3-12) exhibit characteristic absorption bands indicating the formation of dithiocarbamates and their alkyl thioethers. The band at 1216-1241 cm^{-1} corresponds to the stretching vibrations of the N–C= bond. The absorption at 1109-1145 cm^{-1} is due to the characteristic vibrations of the dithiocarbamate group N–C(S)=S. The absorption in the region of 966-1055 cm^{-1} is due to vibrations of the thiocarbonyl bond C=S, while the bands in the range of 853–893 cm^{-1} are characteristic for the C–S bond.

The IR spectrum of the monosubstituted isopentylthiocarbamate (2) contains an absorption band corresponding to the stretching vibrations of the NH group at 3369 cm^{-1} . The observed absorption bands confirm the formation of sodium dithiocarbamates based on isopentylamine.

Furthermore, the presence of long-chain alkyl substituents for alkyl and dialkyl thioethers (3-12) is confirmed by intense bands of stretching vibrations of the CH₂ and CH₃ groups in the region of 2854-2930 cm^{-1} , as well as deformation vibrations of methylene groups at 1425-1468 cm^{-1} .

The structure of isopentylthiocarbamates (1,2) and their alkyl and dialkyl thioethers (3-12) was established using ¹H and ¹³C NMR spectroscopy.

According to the ¹H and ¹³C NMR spectra, the signals of the isopentyl fragment and the dithiocarbamate group were identified for compounds (1) and (2). The N–CH₂ protons appear at δ 4.12 ppm for (1) and 4.35 ppm for (2), the remaining signals of the aliphatic fragment are in the range of δ 1.23–1.56 ppm. In the ¹³C spectra, the N–CH₂ carbon atom is characterized by signals at δ

53.06 and 53.08 ppm, respectively, and the carbons of the isopentyl substituent are in the range of δ 13.63–25.66 ppm. The presence of the dithiocarbamate group is confirmed by the signals of the thiocarbonyl carbon C=S at δ 205.05 ppm. for (1) and 204.28 ppm for (2). Thus, the spectral data confirm the formation of mono- and bis(dithiocarbamate) derivatives of isopentylamine.

Analysis of the ^1H and ^{13}C NMR spectra of the obtained dialkyl and alkyl isopentylthiocarbamate thioesters (3–12) revealed a consistent pattern of signals corresponding to their proposed structure. In the ^1H spectra, the signals of methyl protons of the alkyl radicals are located at δ 0.79–0.86 ppm, while methylene protons appear predominantly in the region of δ 1.20–1.66 ppm. With increasing alkyl chain length, the integrated intensity of these signals' increases. The isopentyl fragment is characterized by signals of methyl protons near δ 1.2–1.3 ppm and methine proton at δ 1.3–1.4 ppm. The signals of the S–CH₂ protons are observed at δ 3.08–3.25 ppm, while the N–CH₂ protons resonate downfield, at approximately δ 3.8–4.6 ppm.

In the ^{13}C spectra, the methyl groups of the alkyl chains give signals at δ 14.1–14.2 ppm, while the carbon atoms of isopentyl substituent methyl and methine groups give signals at approximately δ 22.6–22.8 and 24.5–26.1 ppm, respectively. The chemical shifts of the CH₂ groups of the alkyl chains are found in the δ 28–30 ppm region. The S–CH₂ carbon atom resonated at δ 36–37 ppm, and the N–CH₂ carbon atoms are observed in the δ 51–53 and 69.8 ppm region. The signals for thiocarbonyl carbon C=S are observed in the region of δ 196–215 ppm. The obtained spectral characteristics confirm the formation of alkyl and dialkyl isopentylthiocarbamate thioethers and are consistent with the change in the length of the alkyl substituents.

4. Conclusion

In this study, new dithiocarbamate derivatives based on isopentylamine were synthesized, including disodium isopentyl-bis(carbamodithioate) (1), sodium isopentylcarbamodithioate (2), and their alkyl and dialkyl thioethers (3–12). The mono- and bis-isopentylthiocarbamates were synthesized in the interaction reaction of isopentylamine with carbon disulfide in an alkaline medium.

Using sodium salts (1) and (2), derivatives with linear alkyl substituents at C₆–C₁₀ were synthesized. The isolated compounds are characterized by satisfactory yields, demonstrating the applicability of this method to the preparation of a series of dithiocarbamate thioethers with varying hydrocarbon chain lengths.

The composition and structure of the synthesized compounds were confirmed by a combination of elemental analysis, IR, and NMR spectroscopy data. The spectral data are consistent with the proposed structures and allow the identification of signals from the isopentyl and alkyl fragments, as well as the characteristic N–CH₂, S–CH₂ and C=S signals.

The resulting series of compounds combines the dithiocarbamate functional moiety with alkyl chains of varying lengths, enabling the variation of their

hydrophobic and surface-active properties. Therefore, the synthesized alkyl and dialkyl thioethers are of interest as promising compounds for further study of their flotation activity and selectivity in the flotation enrichment of sulfide and other minerals.

Acknowledgments: This work was funded by the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. BR27101179, «Fundamentals of obtaining innovative, environmentally friendly, multifunctional chemical products and materials»).

Conflict of Interest: All authors declare that they have no conflict of interest.

ИЗОПЕНТИЛДИТИОКАРБАМАТТАРДЫҢ АЛКИЛДІ ЖӘНЕ ДИАЛКИЛДІ ТИОЭФИРЛЕРІНІҢ СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫМЫ

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Түйіндеме. *Kіріспе.* Дитиокарбаматтар және олардың туындылары минералдық шикізатты флотациялық байытудағы флотореагенттер ретінде қолданылатын болашағы зор күкірткүрамды қосылыстар болып табылады. Көмірсутектік орынбасардың құрылымын өзгерту және қосымша функционалдық фрагменттерді енгізу олардың беттік қасиеттерін реттеуге мүмкіндік береді. *Зерттеудің мақсаты* – изопентилдитиокарбаматтар негізіндегі жаңа алкил- және диалкилді тиоэфирлерді синтездеу және олардың құрылымын ИҚ- және ЯМР-спектроскопиялық әдістерімен анықтау. *Нәтижелер және оларды талқылау.* Изопентиламиннің күкірт көміртегімен сілтілік ортада әрекеттесуі нәтижесінде сәйкесінше 58 және 30% шығыммен изопентил-бис(дитиокарбаматтың) динатрий тұзы және натрий изопентилдитиокарбаматы алынды. Тұздардың гексил, гептил, октил, нонил және децил бромидтерімен кейінгі реакциялық әрекеттесуі 75–98% шығыммен алкил- және диалкилді тиоэфирлер қатарын синтездеуге мүмкіндік берді. Синтезделген қосылыстардың құрамы мен құрылымы элементтік талдау, ИҚ-, ¹H және ¹³C ЯМР-спектроскопия әдістерімен дәлелденді. Спектрлік сипаттамалар дитиокарбамат фрагментінің, изопентил орынбасарының және әртүрлі ұзындықтағы алкил орынбасарларының бар екенін дәлелдейді. *Қорытынды.* Жаңа изопентилдитиокарбамат тиоэфирлерінің қатарын синтездеу шарттары жасалынды. Ұзындығы әртүрлі алкил фрагменттерімен синтезделген изопентилдитиокарбамат тиоэфирлері олардың флотациялық қасиеттерін және флотореагенттер ретінде қолдану мүмкіндігін одан әрі зерттеуге қызығушылық тудырады.

Түйінді сөздер: изопентилдитиокарбамат, алкил- және диалкилді тиоэфир, алкилдеу реакциясы, құрылым, ИҚ-спектроскопия, ¹H және ¹³C ЯМР-спектроскопиясы

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СИНТЕЗ И СТРУКТУРА АЛКИЛОВЫХ И ДИАЛКИЛОВЫХ ТИОЭФИРОВ ИЗОПЕНТИЛДИТИОКАРБАМАТОВ

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Резюме. Введение. Дитиокарбаматы и их производные являются перспективными серосодержащими соединениями, применяемыми в качестве флотореагентов при флотационном обогащении минерального сырья. Изменение строения углеводородного заместителя и введение дополнительных функциональных фрагментов позволяют регулировать их поверхностные свойства. Целью данного исследования являлся синтез новых алкиловых и диалкиловых тиоэфиров на основе изопентилдитиокарбаматов, и установление их структуры ИК и ЯМР спектральными методами. Результаты и обсуждение. В результате взаимодействия изопентиламина с сероуглеродом в щелочной среде получены динатриевая соль изопентил-бис(дитиокарбамата) и изопентилдитиокарбамат натрия с выходами 58 и 30%, соответственно. Последующая реакция солей с бромидами гексила, гептила, октила, нонила и децила позволила синтезировать серию алкиловых и диалкиловых тиоэфиров с выходами 75–98%. Состав и структура синтезированных соединений подтверждены методами элементного анализа, ИК-, ^1H и ^{13}C ЯМР-спектроскопии. Спектральные характеристики свидетельствуют о наличии дитиокарбаматного фрагмента, изопентильного заместителя и алкильных заместителей различной длины. Заключение. Разработаны условия синтеза серии новых изопентилдитиокарбаматных тиоэфиров. Синтезированные изопентилдитиокарбаматные тиоэфиры с варьируемой длиной алкильного фрагмента представляют интерес для дальнейшего изучения их флотационных свойств и возможности применения в качестве флотореагентов.

Ключевые слова: изопентилдитиокарбамат, алкил- и диалкиловый тиоэфир, реакция алкилирования, структура, ИК-спектроскопия, спектроскопия ЯМР ^1H и ^{13}C .

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