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Ferrocenyl Complexes and Use of their Derivatives for Solving Environmental Problems

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ABSTRACT

Ferrocenylcarbines were used to separate sulfur compounds from oil and oil products. For this purpose, reactions of ferrocenyl carbines with H2S and some mercaptans (1: 1 and 1: 2 ratios) were carried out at the temperature range of 30-4000 C in tetrahydrofuran environment (THF) and thioether derivatives of ferrocene were obtained. The obtained thio-ethers were investigated by IR-spectral method.

Keywords: *ferrocene, ferrocenylcarbines, H2S, mercaptans, etc.*

INTRODUCTION

Recently, the problem of atmospheric pollution is considered to be topical issues of the globe. The damage caused by the transportation to the atmosphere, the annual amount of toxic gases emitted to the atmosphere is much higher than the norm.The presence of sulfur in fractions of oil used in the development of automobile engines ultimately leads to sulfur dioxide emissions into the atmosphere.This indicates that the sulfuric gases are higher than permissible density limit. For this purpose, oils and oil fractions have to be added into the sulfur content so that they can eliminate sulfur compounds. That is why, ferrocenyl carbines have been used as metal-organic complexes [1, 2].

It has been determined that some members of the metal-organic complexes can break down the sulfur content of oil and oil products. Ferrocenylisoproponol has been used for this purpose.During the study of chemical properties of ferrocenyl carbines, their reactions with H_2S and some of the mercaptans were carried out. The process was carried out in THF environment at temperature range 30-40 ^{0}C, with ferrocenylcarbines: H_2S ratio =1: 1 and mono substituted these derivatives of ferrocenyl were obtained.

$$C_5H_5FeC_5H_4\text{-}C(R_1R_2)OH + H_2S \rightarrow C_5H_5FeC_5H_4\text{-}C(R_1R_2)\text{-}SH + H_2O \quad (1)$$

$$2C_5H_5FeC_5H_4\text{-}C(R_1R_2)OH + H_2S \rightarrow (C_5H_5FeC_5H_4\text{-}C(R_1R_2))_2S + 2H_2O \quad (2)$$

$R_1=R_2=CH_3$; $Fc=C_5H_5FeC_5H_4$.

Reactions with organic radical mercaptans (for example, n-C_4H_9SH) were investigated and the corresponding thioephritis were taken [2]

$$C_5H_5FeC_5H_4\text{-}C(R_1R_2)OH + n\text{-}C_4H_9SH \rightarrow C_5H_5FeC_5H_4\text{-}C(R_1R_2)\text{-}S\text{-}C_4H_9\text{-}n + H_2O \quad (3)$$

Research has shown that ferrocenylcarbines are highly sensitive again sulfur compounds. Thus, with the addition of ferrocenylcarbines into different types of oil products (Dagestan oil, etc.) their sharp odor decreases. Considering the fact that, sulfur compounds have a bad smell, the reduction of this smell after the addition of ferrocenylcarbines can be attributed to the fact that sulfur compounds are subjected to chemical transformation.In this regard, ferrocenyl carbines have been used to precipitate sulfur in oil and oil fractions. As they react with hydrogen sulfide and mercaptans at room temperature, they can be used to precipitate the sulfur content of the oil. As a result of the reactions, ferrocenyl carbines were used to precipitate sulfur in the petrol fraction at ordinary room temperature. After a while (20-24

hours), collapse of the sulfur compounds in the petrol fraction were observed [3].

According to these characteristics of ferrocenyl carbohydrates,in the future demercaptanization of mercaptan compounds from oil and oil products can be explored and used more widely.

There have been several ways in which oil refining products could be cleaned from hydrogen sulfide or sulfur compounds with aromatic (mercaptans, mercaptanides), cyclic and heterocyclic (thiophenes and thiophane) structures. These methods include either the completely dispersing of sulfur compounds by chemical extposure, or the method which can not be regenerated into the initial substances by catalytic exposure. Sulfur compounds - mercaptans are subjected to chemical purification in all fractions, which are taken from separation of sulfuric oil products during thermal and catalytic cracking, coking and at the second phase of other processes [3].

In some cases, alkaline in the crude oil is oxidized by solutions or molecule oxygen on the surface of various adsorbents and converted to alkanesulfonolic acids -RSO_2OH.On the other hand, petroleum products are purified from liquid mercaptans by using sodium plumbite, calcium hypochlorite, copper (II) chloride. Hydrotreatment is more effective for the treatment of sulfur compounds - the thiophenes, disulfides, and high-molecular mercaptan compounds with complex structure [3]. Hydrothermal treatment by this method is a process carried out with the participation of aluminum-cobalt-molybdenum and aluminum-nickel-molybdenum catalysts at a temperature of 3 MPa and sometimes more in partial pressure at a temperature not less than 1000^0C.The main purpose of hydrotreating is to provide destructive hydrotreating of sulfuric compounds.

The initial stage of the hydrogenolysis of sulfuric compounds is to provide hydrogen bonding to the splits of sulfur-carbon bonding that results in the formation of corresponding C-H-linked hydrocarbons and S-H-bonded hydrogen sulphide. The process of demer - captanization of separate fractions at light and heavy gases during the initial oil refining is widespread.This method is based on the RSSR principe so that, non-symmetric RSH type mercaptans are transformed into RSOOM salts in the alkaline environment and symmetrical mercaptans into neutral disulfide compounds with the presence of specific catalysts.

Ferrochemical-based manganese and cobalt-containing cluster compounds have been synthesized and their stoichiometric and catalytic potentials have been studied for demercaptanization of some sulfur oil products. These cluster compounds have been studied in both directions with rectablishment of mercaptans.

One of them is to investigate the interaction effects between clusters and some of the mercaptans with stoichiometric reactions, and the other to investigate the possibility of using clusters in the process of demercaptanization of sulfur oil products by catalytic systems with some seolithic carriers.It has been determined that Fe-Mn and Fe-Co based cluster compounds react stoichiometrically with H2S, n-C_4H_9SH compounds to form corresponding mono sulfides.

From this point of view, cleaning of sulfur oil products from mercaptans and and other sulfuric compounds is one of the most important issues that modern fuel and energy complexes have to solve.Purification of sulfur oil products is of great scientific and practical importance.

One of them is a technical problem, so that when using hydrocarbon fuels with sulfur compounds, most of the engine gets damaged faster due to corrosionand the second is that the amount of gases emitted into environment due to non-normal operation of the engine can increase,thereby causing the ecological situation to become worse.

At present, growth in the sulfur content of the atmosphere results in serious complications. Sulfuric gases, which cause greenhouse effect, lead to the increasment of the sour rains, so that, harms living organisms seriously beside to agriculture. As sulfur gases ressolve in water at high level, they convert into the appropriate acids by combining with drops of water in the air and the acidity of the soil increases. It leads to unwanted consequences. Therefore, it is important to find solutions to the minimization of the process of transferring sulfur gases into the atmosphere through transport, chemical companies and mountain-rock mines, so that to protect our ecology.

It has been studied, for example, gasification of petrol is observed while boilingmercaptan oil productcontaining (175mg / l) sulphure (Kazakhstan's flat-rolled petrol) with 1 mmol ferrocenylmethylcarbinol in a tube equipped with refrigerator for several minutes. Mercaptan

organic compounds in its composition were demercaptanizatied and the oil product was cleaned up to 0.03%.

The amount of sulfur in the composition of Azerbaijani oil is relatively seldom compared to other areas.However, this does not mean that the problem is not solved.Because the sulfur content in the atmosphere is not provided in this way alone, the amount of sulfur delivered to the biosphere is greater than normal. As a continuation of the research, chromatographic analysis was carried out by examining the physical and chemical properties of oil samples from many areas of Azerbaijan (Figure 1.2).The crude oil quality analysis was carried out by gas chromatograph equipped with a gas-ionizing GC-FID 6890 (Agilent, USA) and detector ZB-1 (Phenomenex, USA) calender.In the analysis, helium has been used as a gas-bearing agent.

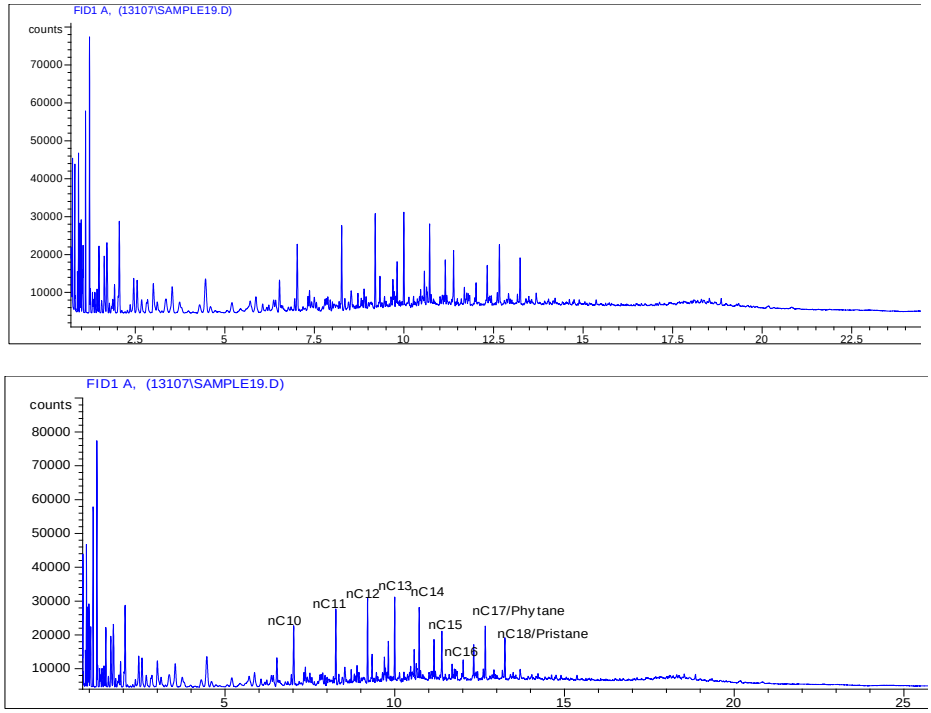

Figure1. *Chromatography of Oil Rocks*

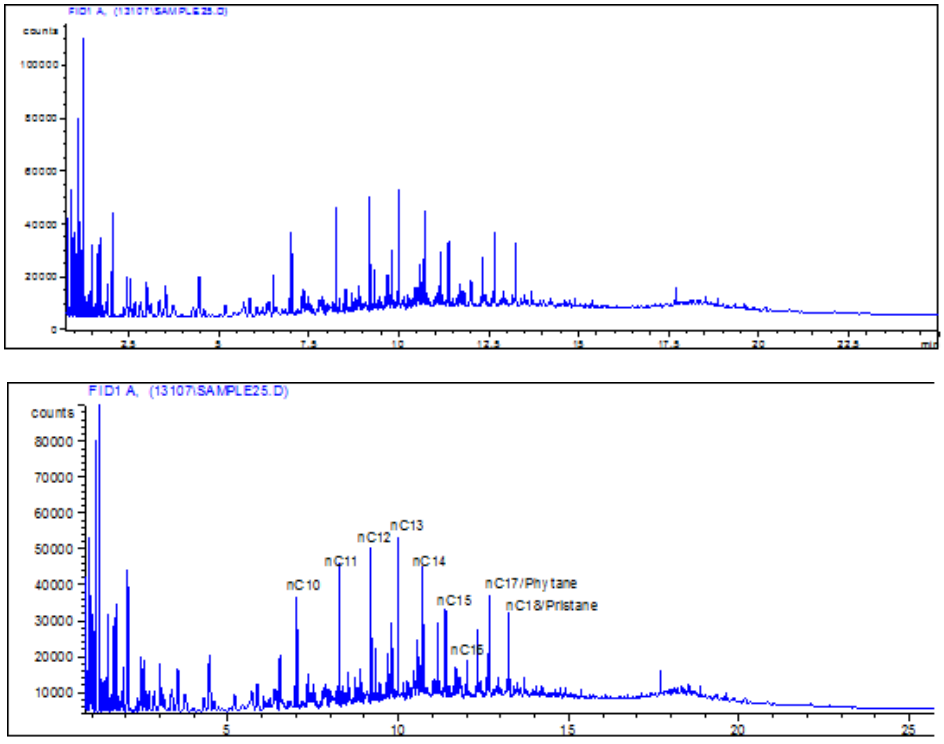

Figure2. *Chromatography of Siyazan oil*

In the initial stage, after the oil processing, the gasoline fraction was heated up to boiling point in laboratory conditions to determine the sulfur content of the gasoline fraction. After boiling, sedimentation were observed at the bottom of the tube, while stored for several days.It indicates that sulfuric products incured to sedimentation after the acquisition.As a result of the investigations it was found that the basis of the sediment is FeS.There is a Fe ... S coordination relationship between Fe and S atoms in the ferrocenylthioethers, which ultimately ensures that FeS is obtained easily [4].

The IR-spectral method was used to study the structures of the corresponding thiohepheres, which were supposed to be obtanied through breaking S-H and C-S communications during the interaction reaction of ferrocenyl carbins with H_2S, as well as n-C_4H_9SH[5].In the IR spectrum the dance frequency corresponding to the OH group is 3620 cm $^{-1}$in the field and the dance frequency corresponding to the S-H group is 2525 cm $^{-1}$in the field.For the corresponding carbuncles and thiohepheres, the absorption strips of dance frequencies are √c-o 1260-1280 cm^{-1} for C-O and √c-s 1135-1152 cm^{-1} for C-D.

Thus, in the preceding article, thio-esters of ferrocenyl carbins (alkyl substituents) have been synthesized with corresponding sulfur compounds. These reactions are of practical importance.Thus, based on the addition of ferrocenylcarbines into oil fractions, tio compounds are obtained that can be used to demercaptanize oil products.

LITERATURE

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