Synthesis and optical properties of some 3D metal complexes based on β-dicarbonyl ferrocene derivatives

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Abstract

We obtained β-diketone – 1-ferrocenylbutanedione-1,3 by Claisen condensation. Ligands - hydrazones of monocarboxylic acids 1-ferrocenylbutanedione-1,3 (H_2L) were synthesized by the interaction of carboxylic acid hydrazides with ferrocenoylacetone. The optical properties of all compounds synthesized in the work have been studied; based on the absorption spectra data, the values of the optical band gap were determined; it was shown that all the synthesized compounds are d-π type chromophores and have a band gap of 1,39–2,26 eV, i.e. they belong to narrow-gap semiconductors.

Introduction

A great interest of chemists to ferrocene arose immediately after its discovery. Over time, interest in ferrocene and its derivatives only grew, this is due to the wide practical application of the latter in such areas of science and technology as medicine and pharmacology, biotechnology, technology of polymer composite materials, in the fuel and energy complex. The most promising of ferrocene derivatives are carbonyl derivatives, they have a wide raw material base and optimal production technology. Due to the presence of several reaction centers, carbonyl derivatives of ferrocene are transitional compounds in many chemical reactions. This opens up wide opportunities for their modification and development of new methods of synthesis based on carbonyl compounds. Of great importance is the production of ferrocene derivatives of biosensors, redox-active DNA markers, redox labels, “smart glasses”, “smart watches”, structural materials for

magnetic and random access memory, materials with liquid crystal properties, turnstiles, molecular magnets, solar batteries, in medicine: anti-cancer, antimicrobial and anti-anemic agents, electrochemical glucometers, liquid–crystal indicators, etc. At present, ferrocene-containing complex compounds are often included in the composition of materials used in photonics and nonlinear optics, they are used as ligands in the creation of chemosensors, are being investigated as molecular tweezers, rotors, shuttles, brakes, turnstiles [1], [2], [3]. Diversity properties of ferrocene-containing hydrazones is, in particular, a consequence of the mutual influence of ferrocene and hydrazone fragments. In addition, on properties of the resulting ferrocene-containing systems are also influenced by other substituents located in the hydrazone fragment. Analysis of the accumulated material allows you to purposefully introduce into the structure of the synthesized compound completely certain acyl and aroyl groups, leaving the constant presence of a ferrocene fragment in the synthesized. In this regard, obtaining and studying systems containing simultaneously ferrocene and hydrazone fragments is of undoubted interest.

At the first stage of the synthesis, a condensation reaction of monoacetylferrocene (MAF) with ethyl acetate was carried out. To carry out this reaction, metal sodium was added in small portions to a solution of acetylferrocene in ethyl acetate, constantly stirring with a magnetic stirrer. The reaction mixture was kept for 5–6 h at a temperature of 40–45 °C. The resulting precipitate of the sodium salt of the ferrocenoylacetone derivative was placed in a separating funnel, cooled with ice, added with ether and treated with a 10% solution of HCl. The decomposition product was dried with $MgSO_4$. After removal of the solvent during cooling, a black mass precipitates from the mother liquor, which was treated with double ethyl ether, resulting in a red finely crystalline precipitate. The resulting precipitate was filtered off, washed with water, dried and recrystallized from hexane. Dark brown crystals were obtained with a yield of 82% and T_m 95–96.5 °C.

1-Ferrocenylbutanedione-1,3 (**I**) was synthesized according to the following reaction scheme:

To a solution of 13.5 g (0.05 mol) of ferrocenylacetone in 60 ml of absolute alcohol 3.75 g (0.05 mol) of acetylhydrazide in 100 ml of ethanol was gradually added with stirring. The reaction mixture was heated in a round-bottom flask with a reflux condenser for 2 h, the reaction mixture was left at room temperature, then 1/3 of the solvent

was distilled off and the mother liquor was left for 3 days, the precipitated crystals were filtered off washed with ethyl alcohol and dried in air. Product yield H_2L^1 7.97 g, brown fine crystalline powder. Interaction of alcoholic solutions of ferpocenoylacetone with hydrazides of monocarboxylic acids were carried out similar reactions too btain hydrazones H_2L^2 - H_2L^7. The ligands were synthesized according to the following reaction scheme:
To a hot solution of 1.73 g (0.005 mol) of benzoylhydrazon monoacetylferrocene in 30 ml of absolute ethyl alcohol was mixed 0.455 g (0.0025 mol) of hot aqueous ammonia solution of copper(II) acetate. The reaction mixture was heated for 3 h until a precipitate formed. The brick-brown precipitate that formed was filtered off and washed several times with absolute ethyl alcohol. The yield is 79%.

In a similar way mixing alcohol solutions of the ligands H_2L^2- H_2L^7 and an aqueous ammonia solution of $M(CH_3COO)_2$ (where M = Cu(II), Ni(II) and Zn(II)), complex compounds of the composition $ML{\cdot}NH_3$ were obtained in an equimolar ratio [8], [9]:

Section snippets

Results and discussions

For the synthesis of ligands, monoacetylferrocene, carboxylic acid hydrazides, metallic sodium, chemically pure ethyl acetate were used as starting reagents. For the synthesis of complex compounds the following salts of qualification pure for analysis were used as initial reagents: nickel(II), copper(II) and zinc(II) acetates. The electronic absorption spectra were recorded on a UV-1900 spectrophotometer (Shimadzu, Japan) in the wavelength range from 190 to 1000 nm, cuvette length 10 mm,

Conclusion

Based on the acquired values of the red boundary of the absorption region, the values of E_g^{opt} calculated by show, that the compounds studied in this work can be attributed to narrow-gap semiconductors, for which the band gap is smaller or about 2 eV.

CRediT authorship contribution statement

Z.A. Sulaymanova: Visualization, Writing – original draft. **L.R. Radjabova:** Investigation. **N.A. Sharifova:** Investigation. **S.A. Karomatov:** Conceptualization, Methodology.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Sulaymonova Zilola Abduraxmonovna reports article publishing charges was provided by Bukhara State University. Sulaymonova Zilola Abduraxmonovna reports a relationship with Bukhara State University that includes: employment, non-financial support, and speaking and lecture fees.].

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