Ars Separatoria Acta 9-10 (2012-2013) 95-102
www.arsseparatoriaacta.com

NEW COLORANT METAL COMPLEXES, DERIVATIVES OF 1,2–DIAZOXY–4–NAPHTHALENESULFONIC ACID AND PENTANE-2,4-DIONE. PART I. PREPARATION AND PROPERTIES.

Agnieszka WASILEWSKA[1], Ewa MAĆKOWSKA[1], Włodzimierz URBANIAK[1,2]

[1]Faculty of Chemical Technology and Engineering
University of Technology and Life Sciences
Seminaryjna 3, 85-326 Bydgoszcz, Poland
52 374 9048, ema@utp.edu.pl

[2]Faculty of Chemistry, Adam Mickiewicz University
Umultowska 89b, 61-614 Poznań, Poland
61 829 1257, Wlodzimierz.Urbaniak@amu.edu.pl

ABSTRACT

A vast array of colorants used in various industries include metal complex colorants, which are useful mainly in the textile industry. Substances to be used in fiber dyeing are expected to have optimum properties, therefore, such compounds remain to be of interest to researchers. The results of studies on the possible modifications of known colorants are presented in this paper.

Keywords: colorants, asymmetric metal complexes, heteroleptic complexes, resistance to UV radiation, acetylacetone

INTRODUCTION

Colorants belong to a number of many groups of compounds, which are usually derived from nahpthalene, benzene, anthracene, as well as heterocyclic compounds having chromophore groups such as azo, nitroso, carbonyl or nitro group and auxochrome substitutes, for instance amino, hydroxy, sulfonic, and carboxy groups. Widely manufactured and used are also colorants in the form of metal complex compounds such as manganese, cobalt, nickel, copper, zinc, and iron [1, 2] which contain one or two coloring ligands. A compound in which

two chelating ligands are bonded to a single metal atom is type 1:2 and is symmetrical in the case of same ligands or asymmetric for different ligands. Compounds in which a single chelating ligand falls on a single metal atom are referred to as being type 1:1. The use of type 1:1 complex compounds or type 1:2 asymmetric compounds results in colorations of same purity and brightness.

Derivatives of 1,2-diazoxy-4-naphthalenesulfonic acid are one of the groups of type 1:2 symmetrical colorant metal complexes, used in the textile industry. Their general formula is shown below:

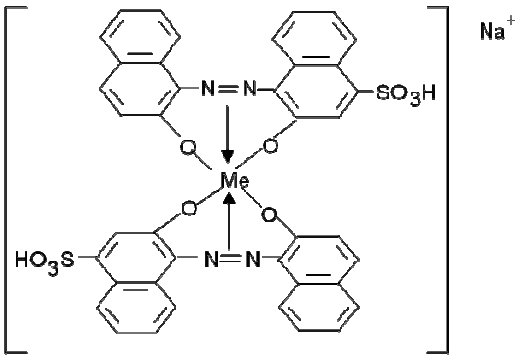

Fig. 1. The general formula of metal complexes, derived from 1,2-diazoxy-4- naphthalenesulfonic acid

Being very well soluble in water, the compounds are used for dyeing wool products, leatherware, and polyamide fibers. The resulting colours depend on the concentration and on the central atom that forms the complex [3, 4].

β-Diketones, especially pentane-2,4-dione and its aryl derivatives, are another group of the compounds of interest. Their essential property is their excellent ability to absorb UV radiation, both the UVA and UVB ranges [5]. Their good solubility in alcohols and fats, combined with low toxicity, makes them useful in cosmetics for making protective filters [6] for use both in the hair [7] and skin protection products [8-10].

The impact of sunlight exposes human skin to UV radiation. UV radiation is divided in three ranges: UVA (400 – 315 nm), UVB (315 – 280 nm) and UVC (280 – 100 nm). A straight majority of UVC radiation is absorbed by the ozone layer, therefore, its negligible portion only gets through to the Earth. The use of radiation absorbers with various chemical structures, which absorb radiation in the range 290-400 nm was proposed, in addition to cosmetic products, to protect human skin from the adverse effect of UV radiation [11]. Such absorbers include, for instance, the compound proposed by the present authors: it has the structure of a direct colorant and absorbs radiation at a wavelength of 309 nm.

Considering the properties of known colorant metal complexes which are derived from 1,2-diazoxy-4-naphthalenesulfonic acid as well as complexes of acetylacetone and its aryl derivatives, it is safe to assume that a combination of the two groups resulting in a heteroleptic type 1:2 complex will provide a colorant compound with a very high potential to absorb UV radiation.

In this paper were presented synthesis and properties of the products as a mixture containing a major proportion of heteroleptic complexes, thereby having properties of the new compounds.

EXPERIMENTAL

It was the purpose of the present study to obtain asymmetric complex compounds of cobalt or nickel such that one ligand in their molecule is derived from 1,2-diazoxy-4-naphthalenesulfonic acid and the other ligand is a β-diketone.

In the first step, type 1:2 asymmetric complexes were obtained by direct synthesis. The following compounds were used in the synthesis reaction:

– metal salts – cobalt(II) chloride hexahydrate or nickel(II) chloride hexahydrate;
– a ligand resulting from the coupling of 2-naphthol with 1,2-diazoxy-4-naphthalenesulfonic acid in an alkaline environment at 70ºC (DAO);
– a ligand representing the acetylacetone derivatives group: acetylacetone (ACAC), benzoylacetone (BZ-ACAC), 3-benzylacetylacetone (BN-ACAC) or dibenzoylmethane (DBM).

The reaction was carried out in a methanolic solution because of the virtually zero solubility of acetylacetone and its derivatives in water. The metal salts were introduced in the form of an aqueous solution

The synthesis consisted in dissolving equimolar quantities of the ligands in methanol, heating the solution to 60°C, adding a solution of salt (in an amount corresponding to the ratio 1:1) to each ligand and maintaining the set temperature while stirring for 1 hour.

As a result of synthesis, mixtures were obtained which can be used in industry as commercial products.

The first step of the study on the stability of the resulting compounds was to evaluate their resistance to the impact of UV radiation. Aqueous solutions of the resulting complexes at same concentrations were prepared for the purpose. The solutions were then subjected to radiation for 3 hours using a lamp that emits radiation at two wavelengths: 254 and 366 nm for 3 hours. Decomposition was assessed spectrophotometrically at 1 hr intervals.

RESULTS AND DISCUSSION

The reaction described above provided a series of compounds whose the general formula is shown below.

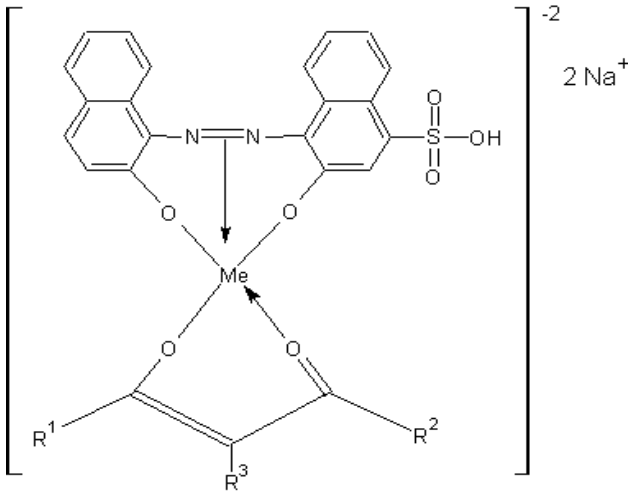

Fig. 2. The general formula of the resulting compounds, where R^1, R^2, R^3 are methyl or phenyl groups, and Me is cobalt or nickel

The result of the synthesis was obtaining mixtures of the sought asymmetric compounds with the corresponding symmetric compounds. The following spectra of aqueous solutions of the resulting mixtures were obtained.

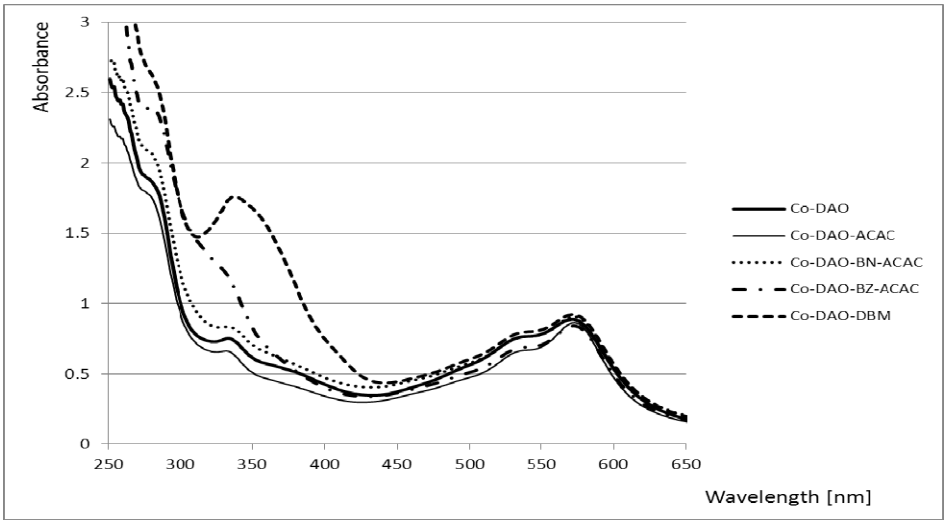

Fig. 3. Absorption spectra of asymmetric cobalt compounds

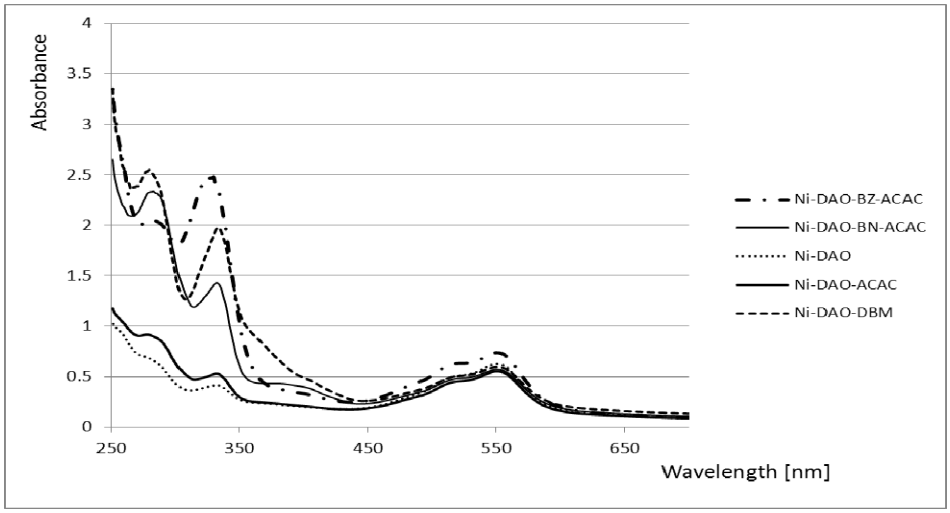

Fig. 4. Absorption spectra of asymmetric nickel compounds

The spectra indicate a significant increase in absorption in the range of UV radiation. Considering the fact that both the β-diketones used and their complexes are practically non-soluble in water, peaks in the range 250-350 nm come from derivatives of acetylacetone which are one of the ligands in the resulting complex. The other ligand is a derivative of 1,2-diazoxy-4--naphthalenesulfonic acid, as shown by the presence of the peak in the visible light range (554 nm).

The isolation and complete identification of a pure heteroleptic compounds is a complex problem and will be discussed in a separate publication [12].

Decomposition, carried out with the use of UV radiation, resulted in the following degrees of discoloration for the respective complexes.

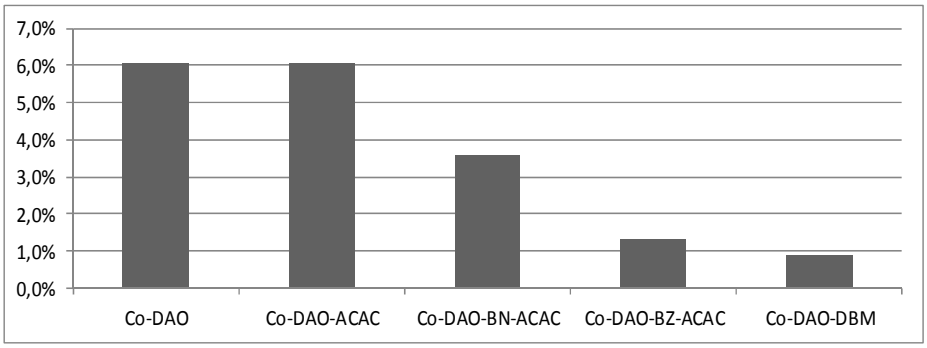

Fig. 5. Degree of decomposition (%) of the cobalt complexes

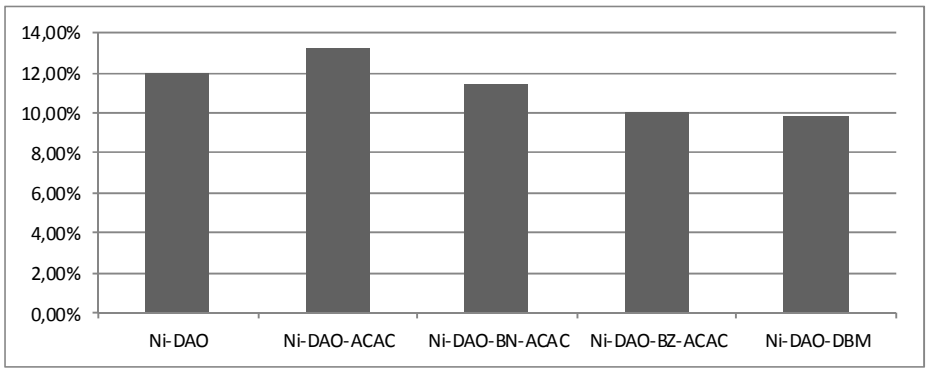

Fig. 6. Degree of decomposition (%) of the nickel complexes

The diagrams indicate, in a majority of cases, that asymmetric complexes have a lesser tendency to decompose due to the influence of UV radiation. In all of the complexes tested which have two different ligands in a molecule, stability was the higher the higher was the number of aryl substitutes in the ligand, derived from penta-2,4-dione. This suggests the conclusion that introduction, to the complex molecule, of a ligand which is an aryl derivative of acetylacetone improves its resistance to UV radiation.

The results obtained were presented in the 39th International Conference of the Slovak Society of Chemical Engineering [13], and a patent application has been filed in the Patent Office of the Republic of Poland [14-17].

CONCLUSIONS

Summing up, a direct synthesis enables preparation of type 1:2 asymmetric metal complexes which are soluble in water and in lower aliphatic alcohols. In addition to being colorants, the compounds obtained show higher absorption of UV radiation, both in the UVA and the UVB ranges, compared with known dyes. Owing to such higher absorption, the colorant complexes show an improved resistance to UV radiation and, hence, to color fading.

Acknowledgements

Financial support from the Ministry of Science and Higher Education (Poland) (project N N204 025338) is gratefully acknowledged.

Symbols

Co-DAO – a complex of cobalt with 1,2-diazoxy-4-naphthalenesulfonic acid;
Co-DAO-ACAC – a complex of cobalt with 1,2-diazoxy-4-naphthalenesulfonic acid and acetylacetone;

Co-DAO-BN-ACAC – a complex of cobalt with 1,2-diaooxy-4-naphthalenesulfonic acid and 3-benzylacetylacetone;
Co-DAO-BZ-ACAC – a complex of cobalt with 1,2-diazoxy-4-naphthalenesulfonic acid and benzoylacetone;
Co-DAO-DBM – a complex of cobalt with 1,2-diazoxy-4-naphthalenesulfonic acid and dibenzoylmethane;
Ni-DAO – a complex of nickel with 1,2-diazoxy-4-naphthalenesulfonic acid;
Ni-DAO-ACAC – a complex of nickel with 1,2-diazoxy-4-naphthalenesulfonic acid and acetylacetone;
Ni-DAO-BN-ACAC – a complex of nickel with 1,2-diazoxy-4-naphthalenesulfonic acid and 3-benzylacetylacetone;
Ni-DAO-BZ-ACAC – a complex of nickel with 1,2-diazoxy-4-naphthalenesulfonic acid and benzoylacetone;
Ni-DAO-DBM – a complex of nickel with 1,2-diazoxy-4-naphthalenesulfonic acid and dibenzoylmethane.

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