COORDINATION COMPOUNDS OF NICKEL(II), COPPER(II) AND COBALT(II) BASED ON S-METHYLISOTHIOSEMICARBAZIDE AS DYES FOR THERMOPLASTIC POLYMERS

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Abstract: We have researched the color properties of coordination compounds synthesized by us previously [1] (8-(1′,2′-naphthyl)-1-R3-methyl-6-thiomethyl-4,5,7-triazaocta-1,3,5,7-tetraenato-1,1′-diolato(-)O, O′, N^4, N^7-M(II), where R=CH_3, C_6H_5, M=Ni, Co, Cu), which can be used for coloring thermoplastic masses. They meet the requirements for use as a pigment for coloring thermoplastic masses [2]. Colors of colored products have a high photostability (7 points), thermostability (>250 °C) and intensity of color that give a low consumption (0.004 to 0.008 g medium tone, a 0.040-0.080 g to 100 g polystyrene intense tone and 0.002 to 0.008 g medium tone and 0.010-0.030 g intense tone for 100 g polyethylene). Compounds of nickel (II) stained polystyrene and polyethylene in red, cobalt (II) - in green with a yellow tinge, copper (II) - in deep red with a yellow tint.

Keywords: coordination compounds, transition metals, dyes, thermoplastic polymers.

Introduction

Synthesis of coordination compounds containing active functional groups capable of forming chelate compounds remains a current problem of preparative chemistry. The interest in the synthesis of compounds with such properties is stimulated by both theoretical and practical issues. They possess biological properties [3], catalytic properties [4], and can be used as dyes [5-10].

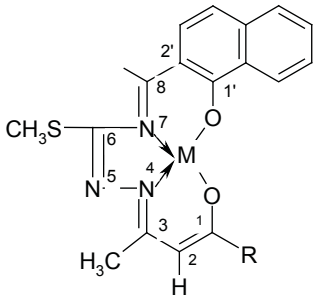
A special role in the synthesis of coordination compounds has the template method, where the central ion guides the assembly of polydentate ligands [11]. Authors [12-17] have shown that thiosemicarbazide and their derivatives easily condense with polydentate organic ligands, polyfunctional possessing different types of coordination especially with transition metals. Metal organizes the assembly of ligands.

For example, 2,2-difluor-9-alkylthio-5,6-di(α-furyl)-12-methyl-1,3-dioxa-4,7,8,10,11,14-hexaaza-2-boracyclotetradeca-4,6,8,11,13-pentaenato-N^4,N^7,N^{10},N^{14}-nickel(II) with coordination node to the central atom N_4, which has a dark brown color, stained polyethylene and polystyrene in green color with brown tint [5]. In [6], where the fragment >BF_2 is replaced with H, it is demonstrated that mentioned polymers don't change their color when used for coloring. In the study of color properties of polymer (9-(1′,2′-naphthyl)-4-methyl-7-alkylthio-5,6,8-triazanon-2,4,6,8-tetraenato(-)-1′,2-diolato-O^1, O^2, N^5, N^8-nickel(II), where the coordinative node is N_2O_2, a color change of coordination polymers has been observed from green with brown tint [5, 6] to bordeaux. In this case, like in those previously mentioned, no visible influence of alkyl radical on the color of polymers is observed.

Of great interest is the influence of metal in this type of compounds at coloring of plastics masses.

Results and discussion

Using these methods, we proceeded to the synthesis of new compounds of this type. As a result of the interaction of methanol solutions of acetyl(benzoyl)acetone S-methylisothiosemicarbazone with 1-hydroxy-2-naphthaldehyde and $M(CH_3COO)_2 \cdot XH_2O$ were obtained coordination compounds: 8-(1′,2′-naphthyl)-1-R-3-methyl-6-thiomethyl-4,5,7-triazaocta-1,3,5,7-tetraenato-1,1′-diolato(-)O, O', N^4, N^7-M(II), where R=CH_3, C_6H_5, M=Ni, Co, Cu, with general formula:



Where R=CH_3, M=Ni (1), Co(2), Cu(3)
R=C_6H_5, M=Ni (4), Co(5), Cu(6) (table 1).

Composition of substances and their structures have been established and confirmed by physico-chemical methods of analysis (IR spectroscopy, UV-Vis, ^{1}H, ^{13}C NMR, mass spectrometry, magnetochemistry and X-ray crystallography) [1].

Compounds are in the form of fine dark-brown crystalline powder, insoluble in water, alcohol, slightly soluble in chloroform, soluble in dimethylsulphoxide. Some practical properties of the mentioned compounds have been studied, which proved to be promising. For example, compounds of nickel(II) and copper(II) activate biological processes which is manifested by stimulating the biosynthesis of pectolytic enzymes of fungal strain (~ 50%) and increased biomass accumulation (10-15%) compared to the control [14].

Table 1

Characteristics of dyes 1-6

Dye			Thermostability, °C	Color of polystyrene	Color of polyethylene	Photostability, points	Uniformity of color	Consumption dyes, g /100 g polymer							
								Polystyrene				Polyethylene			
								Block type		Emulsion, suspension		High density		Low density	
M	R	No.						Middle tone	Intense tone	Middle tone	Intense tone	Middle tone	Intense tone	Middle tone	Intense tone
Ni	CH_3	1	250	Claret	Claret	7	Uniformly	0.004 - 0.008	0.040 – 0.080	0.008 – 0.010	0.020 – 0.050	0.002 - 0.004	0.010 - 0.030	0.002 - 0.004	0.010 – 0.030
Ni	C_6H_5	2	320	Claret	Claret										
Co	CH_3	3	250	Green with yellow tint	Green with yellow tint										
Co	C_6H_5	4	365	Green with yellow tint	Green with yellow tint										
Cu	CH_3	5	250	Claret with yellow tint	Claret with yellow tint										
Cu	C_6H_5	6	360	Claret with yellow tint	Claret with yellow tint										

Bearing a high thermostability (>250 ° C), photostability (7 points), migration luminescence, stability and physical-mechanical processing, given the diversity and intensity of color, the produced compounds meet the requirements [2] for use as plastics dyes.

We tried testing these compounds as pigments for coloring polystyrene block, suspension, emulsion and high and low density polyethylene. Experiments conducted under laboratory conditions received promising results.

Coordination compounds 1 and 2 color polystyrene and polyethylene in claret, compounds 3 and 4 - green with yellow tint, compounds 5 and 6 - deep red with yellow tint. Thus, the metal bears a decisive influence on the color of plastic parts. The influence of the radical R on the color change of plastic parts is not visually observed, but analysis data of the absorption spectra from the visible region suggests a insignificant influence.

It should be noted, that the amount of dyes used for coloring polystyrene (block, emulsion or suspension) and low or high density polyethylene is very low (0.004 to 0.008 g medium tone, 0.040 to 0.080 g intense tone to 100 g polystyrene and 0.002 - 0.008 g medium tone, 0.010-0.030 g intense tone to 100 g polyethylene) (Table 1).

Varying the dye concentration, transparent plastic parts with different shades or non-transparent ones can be obtained. The obtained pieces are colored evenly, possess a high photostability, and stable towards physico-mechanical processing.

Due to the accession of compounds 1-6 to polystyrene, their use as dyes for thermoplastic masses does not require additional staff to process grain, in this case the dye consumption is reduced significantly.

Conclusions

Polystyrene and polyethylene colored with products of condensation of acetyl(benzoyl)acetone S-alkylisothiosemicarbazones and organic polydentate ligands usually have a high thermostability, migration luminescence, stabilized photostability at physical and mechanical processing and pronounced color intensity. Polymers are color-enteritis due to metal, S-alkylisothiosemicarbazone and polydentate aducts, but no alkyl radical influence is observed.

Experimental

Prior to coloring, polystyrene in block, emulsion or suspension granulated is mixed in a reactor supplied with a thermometer, a stirrer and a tap to release the reactor content into the mold. At stirring, the mixture in the reactor is heated up until the components melt; afterwards they are fused as required. In the case of coloring polyethylene, a more intense stirring is required, as the adherence of the dye to polyethylene is lower than for polystyrene.

References

[1]. Cocu, M. Sinteza templata si studiul compusilor coordinativi ai unor 3d-elemente cu liganzi tetradentati in baza tiosemicarbazidei alchilate. PhD thesis abstract. Chişinău 2007, 24 p. (in romanian).
[2]. Gordon, P.; Gregori, P. Organicescaia himia crasitelei. Moscow, Mir, 1986, p. 158 (in russian).
[3]. Dugas, H. Bioorganic chemistry. New York, 1996, pp. 338-460 (ISBN 0-387-94494-X (hardcover), ISBN 0-387-98910-2 (softcover)).
[4]. Bush, D. Uspehi Khim., 1969, v. 38, № 6, p.822-853 (in russian).
[5]. Patent MD 1206 G2, 30.04.1999.
[6]. Patent SU 1808845 A1.
[7]. Patent MD 2881 G2, 10.31.2005.
[8]. Khatirinejad-Fard, S.; Khanlou, M. New method of synthesis for the substituted aromatic di-carbonyl pigments. Abstracts of Papers, 234th ACS National Meeting, Boston, MA, United States, August 19-23, 2007.
[9]. Alexandrescu, G. Industria Usoara. Bucharest, 1965, 12, pp. 7-11(in romanian).
[10]. Patent DE2728864 A1.
[11]. Gerbeleu, N. V., Arion, V. B.; Burgess, John. Template Synthesis of Macrocyclic Compounds. Wiley-VCH, 1999 ISBN: 3527295593, 567 p.
[12]. Gărbălău, N.V.; Revenco, M.D. J. Neorg. Khim., 1971, v. 16, p. 1046; 1972, v. 17, p. 2126; 1973, v. 18, p. 2397 (Russian Journal of Inorganic Chemistry, in russian).
[13]. Iampoliskaia, M.A.; Shova, S.G.; Gărbălău, N.V. and all. J. Neorg. Khim., 1982, v. 27, p. 2551 (Russian Journal of Inorganic Chemistry, in russian).
[14]. Arion, V. B.; Gărbălău, N.V.; Indricean, C.M. J. Neorg. Khim., 1986, v. 31, p. 126 (Russian Journal of Inorganic Chemistry, in russian).
[15]. Cocu, M.A.; Grădinaru, J.I.; Revenco, M.D.; Rybak-Akimova, E.; Gărbălău, N.V. Chem. J. of Moldova, 2008, 3(2), pp. 38-46.
[16]. Bourosh, P.N.; Simonov, Yu.A.; Arion, V.B.; Sobolev, A.N.; Gărbălău, N.V.; Pahopol, V.S. Kristallographiya, 1989, v. 34, p. 637-641 (Crystallography Reports (Kristallografiya), in russian).
[17]. Cocu, M.A.; Clapco, S.; Gărbălău, N.V.; Grădinaru, J.I. Romanian International Conference on Chemistry and Chemical Engineering- RICCCE XIV. Bucharest, Romania, September 22nd – 24th, 2005, p. S01-51 - S01-53.