

COORDINATION COMPOUNDS OF OXOVANADIUM(IV) BASED ON S-METHYLISOTHIOSEMICARBAZIDE AS DYES FOR THERMOPLASTIC POLYMERS

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Abstract. The colouring properties of two coordination compounds previously synthesized by us: 8-(1',2'-naphthyl)-1-R-3-methyl-6-thiomethyl-4,5,7-triazanona-1,3,5,7-tetraenato-1,1'-diolato(-)-O¹, O^{1'}, N⁴, N⁷-vanadyl, where R=CH₃ (**1**), C₆H₅ (**2**) have been investigated. These compounds meet the requirements to be used as dyes for thermoplastic polymers. Colouring complexes have a high photostability (7 points), thermostability (>250 °C) and an intensity of colour, which give a low consumption (0.006 to 0.015 g medium tone, 0.020-0.100 g to 100 g polystyrene intense tone and 0.005 to 0.010 g medium tone and 0.015-0.035 g intense tone for 100 g polyethylene). The investigated compounds stained polystyrene and polyethylene in claret-brick. Compound **2** has a higher thermostability (365 °C) than compound **1** (285 °C).

Keywords: coordination compounds, oxovanadium(IV), dyes, thermoplastic polymer.

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Introduction

Colour is an integral part of the plastic material and it should not be considered as an afterthought. The colorants that are used in the plastics industries can be both dyes and pigments. Dyes must be very strong, transparent and show good heat stability. In the plastics industry dyes are limited in use; therefore they can only be used for a selected number of resins.

Aromatic azo compounds have found a broad spectrum of applications, such as dyes, pigments, food additives, indicators, radical reaction initiators and therapeutic agents [1]. These compounds are mainly used as dyes for textile fibers, wood, wool, leather, metal foil and plastic, also exhibiting a variety of useful properties for biomedical applications [2].

Recently, considerable effort has been dedicated to the synthesis of azo coordination compounds based on Schiff-base ligands, due to their mixed soft-hard donor character (O, N and S donor sites), versatile coordination behaviour [3] and diverse pharmacological properties [4], optical and thermal properties [5], biological properties [6] and their possibility of being used as dyes [7].

The most widely used metal-complex dyes are derived from azo compounds. Although they deliver a multitude of shades, only a few basic components are necessary to produce metal-complex azo dyes.

The template method, where the central ion guides the assembly of polydentate ligands, has an important role in the synthesis of coordination compounds [8]. A number of complex compounds, primarily of transition metals, involving thiosemicarbazones of different denticity, have been prepared and investigated [9]. The condensation of salicylaldehyde thiosemicarbazone with salicylaldehyde in the presence of 3d- elements has changed the thiosemicarbazide functionalized synthetic possibilities (with a coordinating node MN₂O₂). Previously, 3d - element compounds containing thiosemicarbazide (seleno-semicarbazidic) block and anthranilic aldehyde [8, 9], acetylacetone S-alchilzotiosemicarbazone and anthranilic aldehyde [10], acetyl(benzoyl) acetone S-alchilzotiosemicarbazones and 1-hydroxy-2- naphthaldehyde were studied [11]. The use of these blocks lead to the diverse sets of coordinated atoms: N₄ [8], N₅ [12], N₄O [9], N₂O₄ [13], N₂O₂ [14] and N₃O [15]. The coordination mode of thiosemicarbazidic fragment depends on the geometry of the assembling species and is governed by stereochemical preferences of central ion.

In view of the foregoing discussion and continuing interest in coordination chemistry, our present work describes the colouring properties of two mononuclear open-chain complexes, containing N₂O₂ set of donor atoms, previously obtained by us *via* condensation of acetyl(benzoyl)acetone S-methylisothiosemicarbazone with 1-hydroxy-2-naphthaldehyde on the matrix of oxovanadium (VOSO₄•3H₂O): 8-(1',2'-naphthyl)-1-R-3-methyl-6-thiomethyl-4,5,7-triazaocta-1,3,5,7-tetraenato-1,1'-diolato(-)-O¹, O^{1'}, N⁴, N⁷-vanadyl(II) [16], where R=CH₃ **1**, C₆H₅ **2** (Figure 1).

Structures of complexes **1** and **2** were characterized by elemental analyses, IR, UV-Vis, ¹H and ¹³C NMR spectroscopies and mass spectrometry. Complexes were obtained as fine dark-brown crystalline powder, insoluble in water, methanol, slightly soluble in chloroform, soluble in dimethylsulfoxide and dimethylformamide [11].

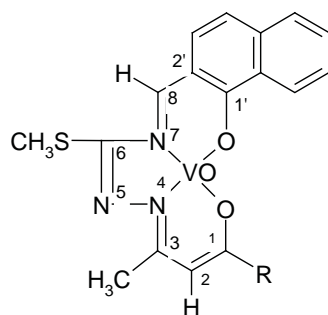
Study of some practical properties of these compounds showed, that they can be used in various fields. The influence of compounds **1** and **2** on the biosynthesis of pectolytic enzymes by *Penicillium viride* fungus has been studied, through the variation of their concentration in the nutrient medium. The obtained results indicated that the presence of tested compounds induces the biomass accumulation and increases the enzymatic activity. It was established, that by

adding the compounds at a concentration of 5 mg/L to the culture medium, the pectolytic activity increases with *cca* 14 %, in comparison with the control solution [11].

Results and discussion

A series of compounds with the above-mentioned formula, which differ only by the metal nature, have been studied as dyeing agents for plastics [13]. It was established, that the colour tone is greatly influenced by the metal atom and is insignificantly influenced by the nature of radical R: nickel(II) compounds colour polystyrene and polyethylene in claret, cobalt(II) compounds - in green with yellow tint, copper(II) compounds - in deep red with yellow tint [17].

The produced compounds have a high thermostability (>250°C), photostability (7 points), migration luminescence, stability and physical-mechanical processing. Given the mentioned properties and both the diversity and intensity of colour [18], they can be used as plastics dyes.



where R=CH₃ (**1**), R=C₆H₅ (**2**)

Figure 1. Structure of compounds 1 and 2.

Current article presents the results of our investigations regarding the colouring properties of compounds **1** and **2**. These compounds were tested as dyes for colouring polystyrene block, suspension, emulsion and both high and low density polyethylene. The carried out under laboratory conditions experiments are promising for the use of these compounds as dyes for colouring polystyrene and polyethylene.

Coordination compounds **1** and **2** colour polystyrene and polyethylene in claret-brick. The influence of the radical R on the colour change of plastic parts is not visually observed, but analysis of the absorption spectra in the visible region suggests an insignificant influence (for complex **1**: $\lambda(\text{nm}) = 334; 281; 242$, respectively $\lg\epsilon = 4.37; 4.50; 4.26$, for complex **2**: $\lambda(\text{nm}) = 335; 282; 244$, respectively $\lg\epsilon = 4.29; 4.53; 4.33$).

It should be noted, that one of the advantages of the investigated dyes is their very low consumption for colouring polystyrene (block, emulsion or suspension) and low or high density polyethylene (0.006 to 0.015 g medium tone, 0.020 to 0.100 g intense tone to 100 g polystyrene and 0.005 - 0.010 g medium tone, 0.015 - 0.035 g intense tone to 100g polyethylene), as shown in Table 1.

Table 1

Characteristics of dyes 1 and 2.

Dye		Thermostability, °C	Photostability, points	Color of polystyrene	Color of polyethylene	Uniformity of color	Consumption dyes, g/100 g polymer							
No	R						Polystyrene				Polyethylene			
							Block type		Emulsion, suspension		High density		Low density	
							Middle tone	Intense tone	Middle tone	Intense tone	Middle tone	Intense tone	Middle tone	Intense tone
1	CH ₃	285	7	Claret - brick	Uniformly	0.006 - 0.010	0.050 - 0.100	0.010 - 0.015	0.020 - 0.080	0.005 - 0.010	0.015 - 0.035	0.008 - 0.010	0.015 - 0.035	
2	C ₆ H ₅	365	7											

It should be noted, that changing the concentration of dye, transparent plastic parts with different shades or uniformly coloured non-transparent ones were obtained. Thus, on the basis of their high photostability, the stability towards physico-mechanical processing, the reported complexes may potentially be good choices as dyes for thermoplastic masses. Due to the adhesion of compounds **1** and **2** to polystyrene, their use as dyes for thermoplastic masses does not require additional agents for grain processing. In this case the dye consumption is reduced significantly.

Conclusion

Due to their colouring capacities, along with the other useful properties, such as high thermo- and photo stability and very simple and inexpensive methods of synthesis, the proposed complexes can be used as dyes for colouring thermoplastic polymers.

Experimental

Polystyrene in block, emulsion or granulated suspension is mixed with the dye in a reactor supplied with a thermometer, a stirrer and a tap to release the obtained content from the reactor into the form. The mixture in the reactor is stirred and heated up until components melt; afterwards they are fused in the required form. When colouring polyethylene, a more intense stirring is required, since the adherence of the dye to polyethylene is lower than to polystyrene.

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