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METAL COMPLEX COMPOUNDS AS EFFECTIVE ADDITIVES TO CUTTING FLUIDS

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Among the numerous classes of organic compounds used as additives, transition metal complexes with aromatic azomethines, Schiff bases have proven their worth. Note that Azomethins and their various functionally substituted derivatives exhibit high biological activity. These compounds effectively inhibit the growth of various microorganisms and can be used in microbiology, pharmacology, food and manufacturing industries, as well as additives to lubricating oils. The paper describes the synthesis and study of azomethine compounds based on benzaldehyde and amines (aniline, benzylamine), as well as their transition metals complexes. The antimicrobial and antiwear properties of the original azomethines and their complexes with transition metals (Cu^{2+}, Ni^{2+}, Co^{2+}) were studied. It found that they show effective antiwear properties in lubricating oil AK-15, high bactericidal and fungicidal efficiency in emulsion cutting fluid Azerol-5.

Keywords: *azomethine, Schiff bases, metal complexes, cutting fluid, antimicrobial efficiency, antiwear property, lubricating oil, multifunctional additive.*
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INTRODUCTION

In recent years there has been an intensified search for new compounds, including metal-organic ones simultaneously possessing different functional properties. Exhibiting high biological activity, these compounds [1-5] are widely used as additives to fuels and lubricating oils, polymer stabilizers, metal corrosion inhibitors [6] and can also serve as a source for the synthesis of other compounds. All things considered, the synthesis and study of coordination compounds of transition metals with aromatic azomethines are problems of today both from scientific and practical points of view.

The purpose of the research was to synthesize and study effective complexes of Cu^{2+}, Ni^{2+}, Co^{2+} with Schiff bases obtained through the condensation of benzaldehyde with aniline and benzylamine used as additives to CF.

EXPERIMENTAL PART

Benzylidenaniline (L_1). 21.2 g (0.2 mol) of benzaldehyde and 18.7 g (0.2 mol) of aniline, separately dissolved in a minimum amount of methanol were placed into a reaction flask with a magnetic stirrer and reflux condenser. The reaction mass was stirred for 2 hours. After completion of the reaction, the mixture was filtered and left to crystallize. Precipitated beige crystals were re-crystallized from hexane as follows: MP (melting point) = 92-94^{0}C, yield 17 g (47%), $C_{13}H_{11}N$; IR spectrum (νcm^{-1}), 1629 (CH = N); 1312 (N-C_6H_5)

Benzylidenebenzylamine (L_2) was synthesized in a similar manner. The resulting crystals were re-crystallized from benzene as follows: MP = 115^{0}C, yield 62%; $C_{14}H_{13}N$; IR spectrum (νcm^{-1}), 1625 (CH = N); 1312 (N-C_6H_5)

4-dimethylamino-1-benzilidenaniline (L_3). MP=100^{0}C, yield 84.7% ; $C_{15}H_{16}N_2$;

Benzylideneaniline complex with copper $(L_1)_2Cu$. A mixture of methanol solutions of 3.62 g (0.02 mol) of benzylideneaniline and 1.8 g (0.01 mol) of copper acetate was heated at 65^{0}C in a reaction flask equipped with a reflux condenser for 2.5 hours. The obtained dark crystals were re-crystallized from methanol as follows: MP = 220^{0}C, yield 37.7%; $C_{26}H_{22}N_2Cu$; IR spectrum (νcm^{-1}), 1627.6 (CH = N); 1313, 1578 (CH_3COO^-)

L_1Me, L_2Me and L_3Me were obtained in a similar manner:

Benzylideneaniline complex with nickel $(L_1)_2Ni$. MP = 235^{0}C, yield 46.4%; $C_{26}H_{22}N_2Ni$;

Benzylideneaniline complex with cobalt $(L_1)_2Co$. MP = 242^{0}C, yield 48.4%; $C_{26}H_{22}N_2Co$;

4-dimethylamino-1-benzilidenaniline complex with copper $(L_3)_2Cu$. MP = 185^{0}C, yield 72%; $C_{15}H_{16}N_2Cu$;

4-dimethylamino-1-benzilidenaniline complex with nickel $(L_3)_2Ni$. MP = 130^{0}C, yield 59.1%; $C_{15}H_{16}N_2Ni$;

4-dimethylamino-1-benzilidenaniline complex with cobalt $(L_3)_2Co$. MP = 155^0 C, yield 74.9% ; $C_{15}H_{16}N_2Co$.

The investigated compounds were studied as antimicrobial and anti-wear additives to CF and oils.

Antimicrobial efficiency of the samples was determined by the method of zonal diffusion according to ГОСТ 9.052-88 and ГОСТ 9.082-77 (tab.1). Pure cultures of the following types of bacteria and fungi as aggressive destroyers of oil products were used for testing: Bacteria: *Mycobacterium lacticolium, Pseudomonas aeruginosa*; Fungi: *Aspergillus niger, Cladosporium-resinae, Penicillium chrosegenum, Chactomium globosum, Trichoderma viride.*

These microorganisms were grown at a temperature of 28 ± 2^{0}C in a special thermostat with 90-100% humidity: fungi for 3-4 days, and bacteria for 2-3 days. Meat-peptone agar (MPA) was used for the cultivation of bacterial cultures, and suslo-agar (SA) - for fungi.

The studied compounds and the standard were added to CF Azerol-5 in mass (1.0-0.25%) percents.

The effectiveness of the antimicrobial effect of the compounds was determined by the diameter of the zone of inhibition of the microorganism' growth around the hole with/without additive: the larger it is, the more effective is the antimicrobial action. The analyzed oil and CF are not biostable.

The anti-wear properties of the tested compounds were determined on a four-ball friction machine ЧШМ -3.2 through the use of balls made of SH-15 grade steel with a diameter of 12.7 m at a constant load of 137 N within 4 hours and 392 N within 1 hour; the speed of rotation of the upper ball was 1500 rev /min and evaluated by the diameter of the wear spot (D_w) according to ГОСТ 9490-75 (tab.).

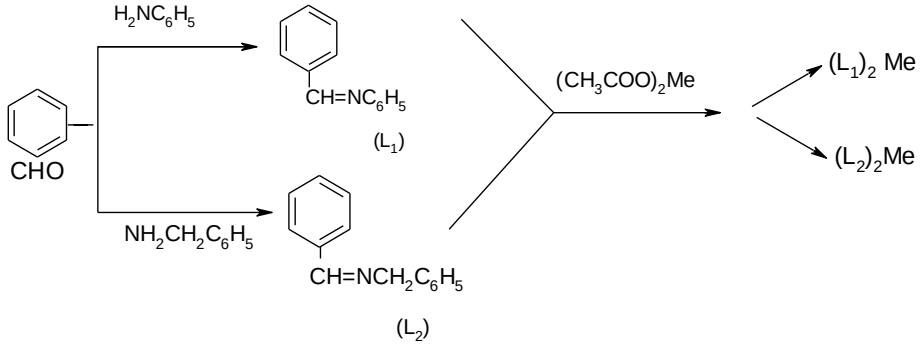
IR spectra were recorded on UR-20 spectrometer in the range of 400-4000 cm^{-1}.

RESULTS AND DISCUSSION

Schiff bases were synthesized through the interaction of benzaldehyde with aniline and benzylamine in the 1:1 ratio in methanol together with their transition metal complexes obtained. The reaction was carried out at the boiling point of alcohol for 2 hours.

The structure of the synthesized compounds was confirmed by IR spectra. The bands of the stretching vibrations of azomethine (C = N) bonds, deformation (= CH) and stretching (C = C) bonds of aromatic fragments of the obtained ligands and stretching vibrations of (Me – N) bond were identified. As follows from the analysis of the spectral characteristics of the original Schiff bases (L_1 and L_2) and their complexes with Cu^{2+}, Ni^{2+}, Co^{2+} the position of the main analytical absorption bands, except for the C = N bond remains practically unchanged. In the IR spectra of complexes (3-5,7-9) the C = N band is observed in the region 1627 cm^{-1} and, as compared with its position in the spectrum of the ligand (1629 cm^{-1}), it slightly shifted (2 cm^{-1}) toward the low frequency region of the aromatic absorption fragments. Such a character of changes in the

position of the C = N bond is interpreted in the literature as coordination of the metal with the nitrogen atom of C = N bond [7].



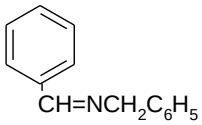
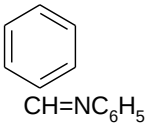
Me = Cu^{2+}, Ni^{2+}, Co^{2+}

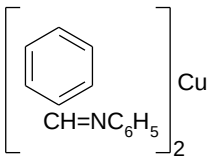
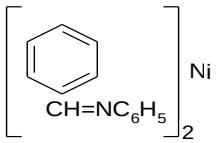
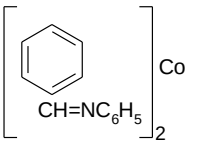
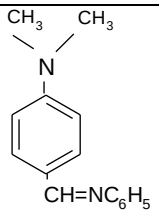
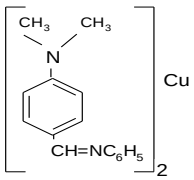
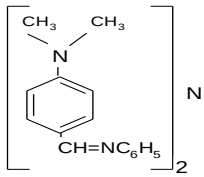
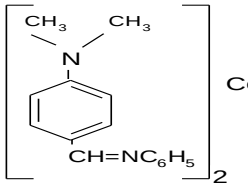
Earlier, it was noted that in the most cases complex compounds are biologically active [3] and have antimicrobial properties. It was interesting to study the influence of the structure of the investigated compounds on the bio-stability of CF.

As mentioned above, the antimicrobial properties were determined in the emulsion composition CF Azerol-5 [8,9] at concentrations of 0.25-1.0%. For comparison, Schiff bases previously derived from dimethylaminobenzaldehyde and their metal complexes [10] were tested. As follows from the test results (table), the Schiff bases and their metal complexes with their antimicrobial properties in terms of their efficiency are at the level of the selected standard – biocide, and in some cases (4,7-9) they surpass it. It should be noted that 4-dimethylamino-1-benzilidenaniline and its complexes with Cu^{2+}, Ni^{2+}, Co^{2+} (6-9) even at low concentrations (0.25-0.5%) possess both bactericidal and fungicidal properties in CF which is due to the presence of additional dimethylamine fragment in the molecule.

The results of the study of anti-wear properties indicate that in the studied friction mode the synthesized Schiff bases are effective at 1.5% concentration both with a load of 137H within 4 h (0.40-0.62) and with a load of 392 N within 1 h (0.43-0.67).

Table 1. Physicochemical and antimicrobial properties of the synthesized compounds

№	Compound	Concen-tration, %	Zone of inhibition of microorganisms growth, cm		Anti-wear properties	
			Mixed bacteria (MPA)	Mixed fungi (SA)	137 N 4 h	392 N 1 h
1		1 0.5 0.25	1.6-1.8 1.0-1.2 1.7-1.7	2.5-2.7 2.4-2.4 2.0-2.2	0.62	0.67
2		1 0.5 0.25	1.2-1.4 1.0-1.0 0.8-1.0	1.6-1.6 1.2-1.4 + +	0.58	0.60

3		1 0.5 0.25	1.8-1.8 1.4-1.5 1.2-1.2	1.2-1.3 1.0-1.0 + +	0.50	0.53
4		1 0.5 0.25	1.6-1.7 1.5-1.6 1.2-1.4	1.2-1.2 0.8-1.0 + +	0.56	0.66
5		1 0.5 0.25	1.4-1.4 1.0-1.0 + +	1.0-1,0 + + + +	0.53	0.60
6		1 0.5 0.25	3.0-3.0 2.6-2.8 1.6-1.8	2.4-2.4 2.0-2.2 1.7-1.7	0.48	0.55
7		1 0.5 0.5	3.3-3.5 3.0-3.0 2.8-2.8	2.6-2.8 2.0-2.2 1.6-1.6	0.40	0.43
8		1 0.5 0.25	3.2-3.2 1.4-1.6 1.0-1.0	2.2-2.4 1.8-2.6 1.4-1.6	0.42	0.45
9		1 0.5 0.25	2.4-2.4 2.0-2.0 1.7-1.8	2.0-2.0 1.2-1.2 + +	0.45	0.47
	Sodium pentachlorofenolate (standard)	1.0 0.5 0.25	1.3 0.7 +	1.4 0.8 +		
	CF Azerol-5	-	+ +	+ +		
	Tricresyl phosphate				0.65	0.68

+ + full microorganism growth around a hole in the Petri dish

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METAL-KOMPLEKS BİRLƏŞMƏLƏR YAĞLAYICI-SOYUDUCU MAYELƏRƏ EFFEKTİV AŞQAR KİMİ

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Keçid metallarının aromatik azometinlərlə - Şiff əsasları ilə kompleks birləşmələri aşqar kimi istifadə olunan çoxsaylı üzvi birləşmə sinifləri arasında perspektiv hesab olunur. Azometinlər və onların müxtəlif funksionaləvəzli törəmələri yüksək bioloji aktivliyə malikdir. Bu cür birləşmələr müxtəlif mikroorqanizmlərin inkişafını effektiv şəkildə inhibirləşdirir və mikrobiologiya, farmakologiya, yeyinti və emal sənayesində, eləcə də sürtkü yağlarına aşqar kimi istifadə edilə bilər. Məqalədə aromatic sıra azin birləşmələrin (benzaldehid, N-dimetilbenzaldehid), eləcə də onların keçid metallarla komplekslərinin sintezi və yağlayıcı-soyuducu mayelərə effektiv çoxfunksiyalı, o cümlədən antimikrob aşqar kimi tədqiqi təsvir olunmuşdur. İlkin maddə olan azometinlər və onların keçid metallarla komplekslərinin mikroba və yeyilməyə qarşı xassələri tədqiq edilmişdir. Onların AK-15 yağında effektiv yeyilməyə qarşı, emulsiya yağlayıcı-soyuducu maye Azerol-5-də yüksək bakterisid və fungisid xassələrə malik olması aşkar edilmişdir.

Açar sözlər: *azometin, Şiff əsasları, metal-komplekslər, yağlayıcı-soyuducu maye, antimikrob effektliliyi, yeyilməyə qarşı xassə, sürtkü yağı, çoxfunksiyalı aşqar.*

МЕТАЛЛОКОМПЛЕКСНЫЕ СОЕДИНЕНИЯ В КАЧЕСТВЕ ЭФФЕКТИВНЫХ ПРИСАДОК К СМАЗОЧНО-ОХЛАЖДАЮЩИМ ЖИДКОСТЯМ

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Среди многочисленных классов органических соединений, используемых в качестве присадок, перспективными зарекомендовали себя комплексные соединения переходных металлов с ароматическими азометинами - основаниями Шиффа. Азометины и их различные функциональнозамещенные производные обладают высокой биологической активностью. Подобные соединения эффективно ингибируют рост различных микроорганизмов и могут быть использованы в микробиологии, фармакологии, пищевой и обрабатывающей промышленностях, а также как присадки к смазочным маслам. В работе описаны синтез и исследование азометиновых соединений, полученных на основе бензальдегида и аминов (анилин, бензиламин), а также их комплексов с переходными металлами (Cu^{2+}, Ni^{2+}, Co^{2+}). Изучены антимикробные и противоизносные свойства исходных азометинов и их комплексов с переходными металлами. Показано, что в масле АК-15 они проявляют эффективные противоизносные, а в эмульсионной СОЖ Азерол-5 - высокую бактерицидную и фунгицидную эффективность.

Ключевые слова: *азометины, основания Шиффа, металлокомплексы, смазочно-охлаждающая жидкость, антимикробная эффективность, противоизносное свойство, смазочное масло, многофункциональная присадка*