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# Tribologically Active Azomethine Metal Complexes

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**Abstract—**Oil-soluble bis(salicylideneiminates) were prepared chemically (from acetates of 3*d*-metals) and electrochemically (by anodic dissolution of complex forming agents) from *o*-hydroxybenzylideneimines of higher aliphatic amines. The structure of the ligands and complexes was established by the methods of IR and NMR spectroscopy. Lubricant compositions prepared with the use of the salicylideneiminate-modified high-temperature silicon liquids cause the formation of a tribopolymer metal-containing film. Its investigation by the method of the X-ray spectral analysis proved the presence of carbon, silicon, and nickel in the films.

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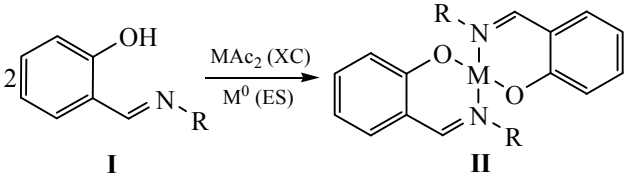
Polyfunctional materials prepared on the basis of metal complexes of azomethines [1–5] are represented by luminescent [6–8] and magnetoactive [9, 10] compounds, catalysts [11], sensors [12–14], metal-containing polymers [15].

An important place among practically useful metallocomplex azomethine structures is occupied by additives to lubricant compositions related to the field named tribocoordination chemistry (tribology) [16–28]. In continuation of this field of research, taking into account refs. [18, 29–32], we have prepared oil-soluble coordination compounds of the type **II** ($L_2M$, LH–ligand systems) by the methods of chemical synthesis (CS) [33, 34] and electrochemical synthesis (ES) [33–35], based on salicylideneimines of higher ($C_6$–$C_{18}$) amines (**I**, LH):




**I** **II**

R = $C_6H_{13}$ (**a**), $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{16}H_{33}$, $C_{18}H_{37}$; M = Co, Ni, Cu, Zn; Ac = $OCOCH_3$.

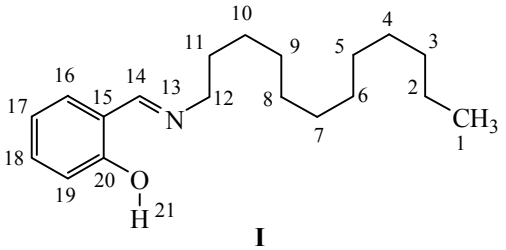
Bis(alkyliminates) **II** were studied as components of high-temperature lubricant compositions we prepared on the basis of polymethylsiloxane (PMS-200A) and polyphenylmethylsiloxane (PPMS) with addition of dioctyl phthalate (DOP) and alkyl ethers of pentaerythritol (B-3-V).

Imines **I** were synthesized by conventional method using the reaction of salicylic aldehyde and alkylamines [3]. As other hydroxyazomethines [1, 3, 36], salicylidenealkylimines **I** exist in the enolimine tautomeric form, as proved by the data of $^1H$, $^{13}C$ and $^{15}N$ NMR spectroscopy of **I** (R = $C_{12}H_{25}$) in the $CDCl_3$ solution.

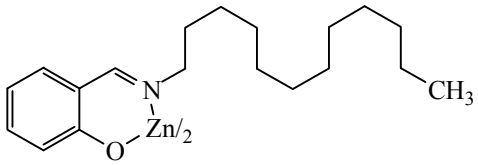
Full assignment of the signals in the $^1H$ NMR spectrum was made by the use of the 2D techniques: COSY (Correlation Spectroscopy) and NOESY (Nuclear Overhouser Effect SpectroscopY) [37]. The assignment is confirmed by the presence of cross peaks in the NOESY spectrum between the methine proton ($H_{14}$) and the protons of the hydroxyl group ($H_{21}$) and the aromatic ring ($H_{16}$) in compounds **I** and **II** (Table 1).

Full assignment in the $^{13}C$ and $^{15}N$ NMR spectra was made by the use of the 2D techniques HSQC

**Table 1.** $^{1}H$, $^{13}C$ and $^{15}N$ chemical shifts of compounds **I** and **II** in $CDCl_3$




**I**




**II**

| Comp. no. | Nucleus | Numbers of magnetic nuclei of carbon atoms, the attached hydrogen atoms and nitrogen atom | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4–9 | 10 | 11 | 12 | 13($^{15}$N)* | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 |
| **I** | $^{1}H$ | 0.9 | 1.28 | 1.28 | 1.28 | 1.38 | 1.68 | 3.55 | | 8.29 | | 7.21 | 6.84 | 7.27 | 6.95 | | 13.57 |
| | $^{13}C$ | 14.01 | 22.60 | 31.84 | 29.50 | 27.12 | 30.81 | 59.43 | –8.34 | 164.32 | 118.76 | 130.95 | 118.21 | 131.86 | 161.93 | 161.37 | |
| **II** | $^{1}H$ | 0.86 | 1.27 | 1.27 | 1.23 | 1.27 | 1.57 | 3.50 | | 8.13 | | 7.07 | 6.56 | 7.25 | 6.82 | | |
| | $^{13}C$ | 14.04 | 22.62 | 30.49 | 29.40 | 26.73 | 31.85 | 61.21 | –72.00 | 170.95 | 117.88 | 135.51 | 114.27 | 134.73 | 123.12 | 170.60 | |

(Heteronuclear one-Quantum Correlation Spectroscopy) and HMBC (Heteronuclear Multiple Bond Correlation spectroscopy) [38].

The structure of tautomer **I** is proved by the signals of the HC=N ($^{1}H$ 8.29 ppm; $^{13}C$ 164.32 ppm; $^{15}N$ –8.34 ppm) and OH (13.57 ppm) groups.

Complex compounds **II**, by analogy with the results of [26], were prepared by direct reaction of ligands **I** with metal acetates (CS) and by electrochemical synthesis (ES) using the metals in the zero oxidation state [33–35].

To prove the structure of complexes of the type **II** the results of heteronuclear NMR spectroscopy were employed based on the achievements of the method in coordination chemistry [39, 40].

The formation of complex (compound **II**, Table 1) is proved by disappearance of the signal of the OH group of compound **I** in the $^{1}H$ NMR spectrum at 13.57 ppm (Table 1)and by upfield shift of the signal of the methine $H_{14}$ by 0.16 ppm (δ = 8.13 ppm for compound **II** and δ = 8.29 ppm for compound **I**, Table 1).

Characteristic changes of the chemical shifts of the signals in the $^{13}C$ NMR spectrum also confirm the formation of complex. The chemical shift of the $C_{20}$ carbon atom of the aromatic ring suffers downfield shift by 9.23 ppm (δ = 170.60 ppm for compound **II** and δ = 161.37 ppm for compound **I**, Table 1) due to the ation of the bond between the metal (Zn) and oxygen atoms. Besides, the chemical shift of the $C_{14}$ carbon atom of the methine group HC=N is also shifted downfield by 6.63 ppm (δ = 170.95 ppm for compound **II** and δ = 164.32 ppm for compound **I**, Table 1) which is in agreement with coordination of the zinc atom to nitrogen atom.

In the $^{15}N$ NMR spectrum, the formation of complex causes an upfield shift of the nitrogen atom signal by 63.66 ppm (δ = –72.00 ppm for compound **II** and δ = –8.34 ppm for compound **I,** Table 1).

In the IR spectra a decrease in the stretching vibration frequencies of the C=N bond of complexes **II** (1620–1625 $cm^{-1}$) is observed as compared with the similar frequencies of the ligands **I** (1637–1639 $cm^{-1}$), which is indicative of the chelates formation [26].

The obtained results, taking into account the data of [1–4, 26], unequivocally prove the formation of chelate structures **II** both in the crystalline phase and in solutions.

Earlier, tribological properties [15–26] of the metal complex additives were investigated for lubricant compositions obtained mainly on the basis of mineral and synthetic oils.

In this work, we have studied tribochemical characteristics of high-temperature polyorganylsiloxanes modified with chelates of the type **II**. The results are presented in Table 2.

The data of Table 1 show that, judged from the loading characteristics ($P_{max}$), the effectiveness of coordination compounds as additives increases in the

**Table 2.** Results of tribochemical tests of salicylaliminates of 3*d* metals in polyorganyl siloxanes compounded with ester

| Base | $M^{2+}$ $ML_2$ | Concentration of $ML_2$, wt % | $P_{max}$, MPa | $F_{fr}$ | Friction pair wear, mg |
|---|---|---|---|---|---|
| 50%PMS-200A 50% DOP | – | – | 10.4 | 0.0429 | 159 |
| ″ | Ni | 0.5 | 17.2 | 0.008 | 38 |
| ″ | Zn | 0.5 | 18.2 | 0.0153 | –10 |
| ″ | Cu | 0.5 | 18.8 | 0.0069 | –12 |
| ″ | Co | 0.5 | 21.2 | 0.0115 | –7.5 |
| 50% PPMS 50% B3V | Ni | 2.0 | 14.2 | 0.029 | 2.0 |
| ″ | Cu | 3.0 | 18.4 | 0.018 | –6 |

order Ni < Zn < Cu < Co. The assessment of the anti-wear properties of the additives showed that the nickel complex decreases the friction pair wear four times, whereas for the Zn, Cu and Co complexes a negative wear is observed, that is, after friction, their weight is increased. The observed effect is explained by the fact that the weight of the film formed on the friction surfaces is larger than the wear of the metal surfaces.

The use of the method of IR spectroscopy for investigation of tribopolymer films after friction of the lubricant compositions containing coordination compounds of Cu, Ni, Co and Zn in the medium of dioctyl phthalate and polymethylsiloxane revealed the presence in the films predominantly the Si–O (1036, 1071 $cm^{-1}$), Si–C (1252, 1262 $cm^{-1}$), C–H (2858, 2924, 2925 $cm^{-1}$) [41, 42] and a small amount of the C=O groups (1721 $cm^{-1}$) [43]. This allows a conclusion that the tribopolymer belongs to the class of polysiloxanes rather than polyesters, as was suggested on the basis of previous studies [44]. At the same time, the presence of an ester is necessary since without it the effect of selective transfer is not observed and a characteristic film on the surfaces of friction is not formed. The ester and the coordination compounds contribute to the enhancement of the strength of the linkage of the tribopolymer with the metal support due to coordination compounds chemically bound with the metal and polymer.

In this connection, significant results were obtained by the use of an electron ion raster scanning microscope Nova NanoLab 600, which allowed to detect the presence of a film on the friction surfaces of ca. 1 μm thickness. The use of the X-ray spectral method for analysis of the surface showed the presence of carbon, silicon, and nickel in the film.

Nickel, apparently, forms a protective metal film on the surface of iron, similar to the earlier studied film of metal copper in nanooils with the size of the metal particles of 25 and 60 nm [32], which are formed even at room temperature in the absence of pronounced reducing agents [45].

The performed studies allows a preparation of plastic lubricants containing coordination compounds of nickel and copper with patented composition [27, 28].

## EXPERIMENTAL

IR spectra were obtained on a Varian 3100-FT-IR Excalibur instrument using the method of frustrated total internal reflection. $^{1}H$, $^{13}C$, $^{15}N$ NMR spectra were taken on a AVANCE-600 instrument (Bruker) in the regime of internal stabilization of the polar-resonance line of $^{2}H$.

Chemical shifts in the $^{1}H$ and $^{13}C$ NMR spectra are given relative to the signals of the deuterated solvent ($CDCl_3$): 7.24 ppm for protons and 77.00 ppm for carbons (Table 1). Chemical shifts in the $^{15}N$ NMR spectrum are given relative to the signal of $^{15}N$ in nitromethane (Table 1).

Tribochemical measurements were conducted on an end friction machine (AE-5).

Electron microscopy studies were performed on a electron-ion scanning microscope Nova NanoLab 600 (FEI Company, Netherlands).

Ligands **I** were synthesized by reflux of equimolar amounts of salicylic aldehyde and the corresponding amines in benzene. Complex compounds were obtained by the procedures described in [26], where the data of elemental analysis of ligands **I** and bis-chelates **II** are also given.

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