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Tribochemically Active Chelate Complexes of Salicylideneimines

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Abstract—N-Alkylsalicylideneimines and their complexes with 3*d* metals were obtained by chemical (from metal salts) and electrochemical methods (from metals in the zero oxidation state). The compounds obtained were characterized by IR and ^{1}H NMR spectroscopy and X-ray diffraction analysis. According to crystallographic data, nickel bis(chelate) exists in the *trans*-planar configuration. A friction test revealed that the tribotechnical characteristics of lubricating formulations are substantially enhanced in the presence of N-alkylsalicylideneiminates.

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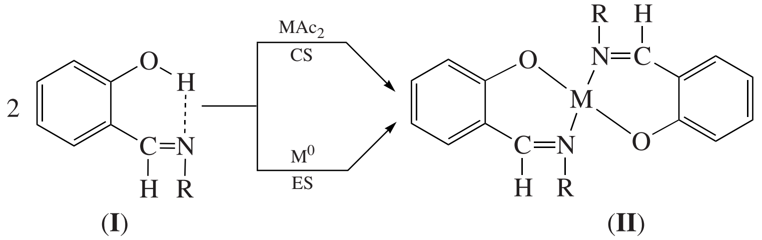
Complexes of salicylaldehyde azomethines occupy an important place in modern coordination chemistry [1–6]. Interest in these metal complexes is due to the possibility of widely varying their structures [2–4] and obtaining from them polyfunctional materials: magnetically active [7–11] and luminescent metal complexes [12], chemical sensors [13], catalysts [14, 15], and synthetic models of bioinorganic objects [16, 17]. Azomethine complexes are employed as effective additives to lubricants [18–21]. Starting from azomethines (**I**), here we obtained complexes **II** by reaction (1) and studied their structures and tribochemical properties.



(1)

R = (a) CH_3, (b) C_2H_5, (c) C_3H_7, (d) C_4H_9, (e) C_5H_{11}, (f) C_6H_{13}, (g) $C_{10}H_{21}$, (h) $C_{12}H_{25}$, (i) $C_{16}H_{33}$, and (j) $C_{18}H_{37}$; M = Cu, Ni, and Zn; CS and ES denote chemical and electrochemical synthesis, respectively.

EXPERIMENTAL

Synthesis of azomethines. The starting azomethines **I** were prepared as follows. Equimolar amounts of salicylaldehyde and an appropriate amine were refluxed in benzene on a water bath with a Dean–Stark trap until the water released during the reaction was completely removed.

Then the reaction mixture was concentrated on a rotary evaporator. The yields of azomethines were 90–95% (yellow oils).

Elemental analysis data for azomethines **I** are given in Table 1; their IR and ^{1}H NMR spectra are presented in Table 2.

Complexes **II** were synthesized in two ways.

Chemical synthesis. A solution of an appropriate metal acetate hydrate (0.001 mol) in ethanol (5 ml) was added to a solution of salicylidene(alkyl)amine (0.002 mol) in ethanol (10 ml). The reaction mixture was refluxed for 2 h. On cooling, a solution of CH_3ONa (0.002 mol) in ethanol was added. The precipitate of the

Table 1. Elemental analysis data for azomethines **I** and their complexes **II**

Compound	Empirical formula	Content (found/calculated), %			
		C	H	N	M
I‡	C_8H_9NO	71.18/71.09	6.92/6.71	10.49/10.49	
Cu-IIa	$C_{16}H_{16}N_2O_2Cu$	CS 58.05/57.76 ES 57.21/57.76	4.96/5.43 5.45/5.43	8.50/8.39 8.40/8.39	19.36/19.03 19.45/19.03
Ni-IIa	$C_{16}H_{16}N_2O_2Ni$	CS 58.79/58.05 ES 58.13/58.05	4.85/4.86 4.73/4.86	8.47/8.45 8.33/8.45	18.10/18.15 18.45/18.15
Zn-IIa	$C_{16}H_{16}N_2O_2Zn$	CS 57.61/57.59 ES 57.57/57.59	4.72/4.83 4.74/4.83	8.35/8.40 8.28/8.40	19.64/19.59 19.57/19.59
Ib	$C_9H_{11}NO$	72.42/72.45	7.50/7.43	9.41/9.39	
Cu-IIb	$C_{18}H_{20}N_2O_2Cu$	CS 60.17/60.07 ES 60.21/60.07	5.71/5.60 5.75/5.60	7.80/7.78 7.87/7.78	17.68/17.66 17.96/17.66
Ni-IIb	$C_{18}H_{20}N_2O_2Ni$	CS 60.98/60.89 ES 61.07/60.89	5.78/5.68 5.73/5.68	7.76/7.89 7.85/7.89	16.62/16.53 16.49/16.53
Zn-IIb	$C_{18}H_{20}N_2O_2Zn$	CS 59.81/59.76 ES 59.93/59.76	5.63/5.57 5.45/5.57	7.82/7.75 7.76/7.75	17.98/18.07 17.92/18.07
Ic	$C_{10}H_{13}NO$	73.48/73.59	8.15/8.03	8.49/8.58	
Cu-IIc	$C_{20}H_{24}N_2O_2Cu$	CS 61.82/61.92 ES 61.45/61.92	6.15/6.23 5.98/6.23	7.20/7.22 7.35/7.22	16.42/16.38 16.15/16.38
Ni-IIc	$C_{20}H_{24}N_2O_2Ni$	CS 62.61/62.70 ES 62.53/62.70	6.42/6.31 6.33/6.31	7.44/7.31 7.50/7.31	16.32/16.59 16.66/16.59
Zn-IIc	$C_{20}H_{24}N_2O_2Zn$	CS 61.71/61.62 ES 61.61/61.62	6.20/6.21 6.14/6.21	7.15/7.19 7.22/7.19	16.89/16.77 16.45/16.77
Id	$C_{11}H_{15}NO$	74.57/74.54	8.40/8.53	7.95/8.90	
Cu-IId	$C_{22}H_{28}N_2O_2Cu$	CS 63.42/63.52 ES 63.29/63.52	6.80/6.78 6.43/6.78	6.65/6.73 6.69/6.73	15.39/15.27 15.48/15.27
Ni-IId	$C_{22}H_{28}N_2O_2Ni$	CS 64.40/64.27 ES 64.42/64.27	6.84/6.86 6.86/6.86	6.82/6.81 6.90/6.81	14.39/14.27 14.35/14.27
Zn-IId	$C_{22}H_{28}N_2O_2Zn$	CS 63.29/63.23 ES 63.31/63.23	6.92/6.75 6.81/6.75	6.75/6.71 6.69/6.71	15.83/15.65 15.42/15.65
Ie	$C_{12}H_{17}NO$	75.47/75.35	8.89/8.96	7.39/7.32	
Cu-IIe	$C_{24}H_{32}N_2O_2Cu$	CS 64.81/64.41 ES 64.34/64.41	7.36/7.26 6.98/7.26	6.42/6.31 6.53/6.31	14.37/14.31 14.30/14.31
Ni-IIe	$C_{24}H_{32}N_2O_2Ni$	CS 65.74/65.63 ES 65.75/65.63	7.39/7.34 7.29/7.34	6.45/6.38 6.30/6.38	13.49/13.36 13.23/13.36
Zn-IIe	$C_{24}H_{32}N_2O_2Zn$	CS 64.70/64.65 ES 64.73/64.65	7.35/7.23 7.37/7.23	6.32/6.28 6.29/6.28	14.56/14.66 14.60/14.66
If	$C_{13}H_{19}NO$	76.18/76.07	9.45/9.33	6. 98/6.82	

Table 1. (Contd.)

Compound	Empirical formula	Content (found/calculated), %			
		C	H	N	M
Cu-IIf	$C_{26}H_{36}N_2O_2Cu$	CS 66.24/66.14 ES 66.03/66.14	7.71/7.69 7.62/7.69	5.93/5.93 6.05/5.93	13.52/13.46 13.15/13.46
Ni-IIf	$C_{26}H_{36}N_2O_2Ni$	CS 66.92/66.83 ES 66.81/66.83	7.75/7.77 7.71/7.77	6.12/6.00 6.18/6.00	12.40/12.56 12.73/12.56
Zn-IIf	$C_{26}H_{36}N_2O_2Zn$	CS 65.78/65.89 ES 66.00/65.89	7.69/7.66 7.67/7.66	6.11/5.91 5.95/5.91	13.84/13.79 13.83/13.79
Ig	$C_{17}H_{27}NO$	78.25/78.11	10.50/10.41	5.47/5.36	
Cu-IIg	$C_{34}H_{42}N_2O_2Cu$	CS 71.29/71.11 ES 71.20/71.11	7.49/7.37 7.32/7.37	4.92/4.88 5.03/4.88	11.27/11.07 11.10/11.07
Ni-IIg	$C_{34}H_{42}N_2O_2Ni$	CS 71.84/71.72 ES 71.79/71.72	7.51/7.43 7.65/7.43	4.98/4.92 4.89/4.92	11.34/11.31 11.14/11.31
Zn-IIg	$C_{34}H_{42}N_2O_2Zn$	CS 70.95/70.89 ES 71.13/70.89	7.42/7.35 7.31/7.35	4.78/4.86 4.83/4.86	11.45/11.35 11.51/11.35
Ih	$C_{19}H_{31}NO$	78.92/78.84	10.75/10.80	4.75/4.54	
Cu-IIh	$C_{38}H_{60}N_2O_2Cu$	CS 71.36/71.26 ES 71.19/71.26	9.52/9.44 9.47/9.44	4.47/4.37 4.83/4.37	9.95/9.92 10.01/9.92
Ni-IIh	$C_{38}H_{60}N_2O_2Ni$	CS 71.92/71.81 ES 71.84/71.81	9.42/9.52 9.20/9.52	4.49/4.41 4.63/4.41	9.34/9.23 9.16/9.23
Zn-IIh	$C_{38}H_{60}N_2O_2Zn$	CS 71.18/71.06 ES 71.13/71.06	9.48/9.42 9.56/9.42	4.44/4.36 4.59/4.36	10.28/10.18 10.51/10.18
Ii	$C_{23}H_{39}NO$	79.92/79.94	11.57/11.38	4.54/4.05	
Cu-IIi	$C_{46}H_{78}N_2O_2Cu$	CS 73.33/73.21 ES 73.37/73.21	9.95/10.42 10.47/10.42	3.61/3.71 3.85/3.71	8.35/8.42 8.41/8.42
Ni-IIi	$C_{46}H_{78}N_2O_2Ni$	CS73.86/73.68 ES 73.53/73.68	10.50/10.48 10.24/10.48	4.00/3.74 3.55/3.74	7.18/7.83 7.32/7.83
Zn-IIi	$C_{46}H_{78}N_2O_2Zn$	CS 72.88/73.03 ES 73.16/73.03	10.31/10.39 10.65/10.39	3.94/3.70 3.84/3.70	8.50/8.64 8.69/8.64
Ij	$C_{25}H_{43}NO$	78.89/79.73	11.64/11.51	3.85/3.72	
Cu-IIj	$C_{50}H_{84}N_2O_2Cu$	CS 74.32/74.25 ES 74.19/74.25	10.59/10.47 10.48/10.47	3.57/3.46 3.83/3.46	7.89/7.85 7.87/7.85
Ni-IIj	$C_{50}H_{84}N_2O_2Ni$	CS 71.79/74.70 ES 71.48/74.70	10.64/10.53 10.59/10.53	3.59/3.49 3.71/3.49	7.42/7.30 7.65/7.30
Zn-IIj	$C_{50}H_{84}N_2O_2Zn$	CS 74.18/74.09 ES 74.13/74.09	10.66/10.44 10.34/10.44	3.54/3.46 3.28/3.46	8.24/8.07 8.01/8.07

Table 2. IR and ^{1}H NMR spectra and selected physical properties of azomethines **I** and their complexes **II**

Compound;	Color	T_m, °ë	IR (ν, cm^{-1})			*^{1}H NMR ($CDCl_3$, δ, ppm)
			OH	C=N	Ph–O	
Ia R = CH_3	Yellow	228–229**	3100–3400	1634	1276	0.86 (3H, t, CH_3, ^3J = 6.6 Hz), 6.80–7.30 (4H, m, C_{Ar}–H), 8.01 (1H, s, CH=N), 13.26 (1H, s, OH)
Cu–IIa	Green	158–159		1620 (1618)	1324 (1321)	
Ni–IIa	Green	206–207		1621 (1619)	1325 (1324)	
Zn–IIa	Yellow	258–259		1625 (1621)	1326 (1324)	0.86 (6H, t, CH_3, ^3J = 6.7 Hz), 6.70–7.28 (8H, m, C_{Ar}–H), 8.14 (2H, s, CH=N)
Ie R = C_5H_{11}	Yellow		3100–3400	1638	1277	0.9 (3H, t, CH_3, ^3J = 6.68 Hz), 1.24 (4H, s, CH_2), 1.67 (2H, m, CH_2), 3.56 (2H, m, CH_2), 6.84–6.95 (2H, m, C_{Ar}–H), 7.20–7.28 (2H, m, C_{Ar}–H), 8.31 (1H, s, CH=N), 13.69 (1H, br.s, OH)
Cu–IIe	Brownish green	96–97		1627 (1625)	1321 (1324)	
Ni–IIe	Olive	141–142		1618 (1620)	1324 (1329)	
Zn–IIe	Yellow	89–90		1624 (1623)	1325 (1320)	0.87 (6H, t, CH_3, ^3J = 6.7 Hz), 1.24 (8H, m, CH_2), 1.54 (4H, m, CH_2), 3.52 (4H, m, CH_2), 6.57–7.27 (8H, m, C_{Ar}–H), 8.15 (2H, s, CH=N)
Ig R = $C_{10}H_{21}$	Yellow		3100–3400	1639	1274	89 (3H, t, CH_3, ^3J = 6.7 Hz), 1.23 (14H, s, CH_2), 1.67 (2H, m, CH_2), 3.54 (2H, m, CH_2), 6.84–6.73 (2H, m, C_{Ar}–H), 7.21–7.28 (2H, m, C_{Ar}–H), 8.32 (1H, s, CH=N), 13.70 (1H, br.s, OH)
Cu–IIg	Light brown	61–62		1624 (1623)	1324 (1326)	
Ni–IIg	Olive	90–91		1621 (1617)	1325 (1326)	
Zn–IIg	Yellow	82–83		1619 (1619)	1324 (1319)	0.88 (6H, t, CH_3, ^3J = 6.7 Hz), 1.15–1.25 (18ç, m, ëç$_2$), 1.57 (4ç, m, ëç$_2$), 3.54 (4ç, m, ëç$_2$), 6.577.28 (8H, m, C_{Ar}–H), 8.14 (2H, s, CH=N)
Ij R = $C_{18}H_{37}$	Yellow		3100–3400	1637	1276	0.87 (3H, t, CH_3, ^3J = 6.67 Hz), 1.25 (30H, s, CH_2), 1.66 (2H, m, CH_2), 3.57 (2H, m, CH_2), 6.85–6.95 (2H, m, C_{Ar}–H), 7.21–7.28 (2H, m, C_{Ar}–H), 8.32 (1H, s, CH=N), 13.69 (1H, br.s, OH)
Cu–IIj	Brown	64–65		1624 (1621)	1327 (1324)	
Ni–IIj	Olive	88–89		1622 (1621)	1317 (1321)	
Zn–IIj	Yellow	69–70		1619 (1622)	1318 (1324)	0.87 (6H, t, CH_3, ^3J = 6.6 Hz), 1.18–1.29 (60H, m, CH_2), 1.57 (4H, m, CH_2), 3.53 (4H, m, CH_2), 6.58–7.29 (8H, m, C_{Ar}–H), 8.15 (2H, s, CH=N)

Notes: * The IR and ^{1}H NMR spectra of the rest of the complexes studied can be made available from the authors upon request.
** T_b of the azomethine.

complex that formed was filtered off and recrystallized from ethanol.

Electrochemical synthesis followed a standard procedure (by reactions of salicylidene(alkyl)amines with the cations dissolving from the anode during electrolysis). The working solution in methanol (10 ml) contained salicylidene(alkyl)amine (0.002 mol) and $[Et_4N]ClO_4$ (0.01 g) as a conducting additive. Electrochemical synthesis was carried out for 1 h (current strength **I** = 40 mA, voltage **V** = 15 V). The precipitate of the complex was filtered off, recrystallized from ethanol, and dried in a vacuum desiccator.

Elemental analysis data for complexes **II** are given in Table 1; their selected physical properties and IR and ^{1}H NMR spectra are given in Table 2.

^{1}H NMR spectra were recorded on Varian Unity-300 instrument (300 MHz) with internal stabilization of the ^{2}H polar resonance line in $CDCl_3$.

IR spectra were recorded on a Nicolet Impact-400 instrument (Nujol).

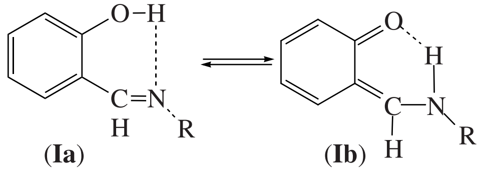
X-ray diffraction analysis. Crystals of the complex Ni-**IIh** are monoclinic, space group $P2_1/c$; at $T = 100$ K $a = 21.141(7)$, $b = 4.9359(17)$, $c = 17.095(6)$ Å, $\beta = 90.828(9)°$, $V = 1783.7(10)$ Å^3, $Z(Z') = 2$ (0.5), $F(000) = 692$, ρcalcd = 1.183 g/cm^3, $\mu = 5.77$ mm^{-1}.

The intensities of 9242 reflections were measured on a Bruker SMART APEX II CCD automated diffractometer ($T = 100$ K, λMoK_α radiation, graphite monochromator, φ- and ω scan modes, $\theta_{max} = 55°$). Further calculations were performed for 4099 independent reflections ($R_{int} = 0.0903$). An absorption correction was applied with the SADABS program [22]. The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located geometrically and refined isotropically with fixed coordinates (rider model) and thermal parameters. Final residuals are $R_1 = 0.0586$ for 2419 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1441$ and GOOF = 0.961 for all independent reflections. All calculations were performed with the SHELXTL PLUS program package (version 5.10) [23].

The tribotechnical characteristics of lubricating formulations [24] were examined on an end-face friction machine (modified AU-5). Mobile specimens (pins 6 mm in diameter) were made of BrOF-0.25 bronze; stationary nibs were made of steel 45. Loading was increased in steps (sliding velocity 0.8 m/s, test duration 5 h). Specimens were worked to $R_a = 0.25–0.32$ μm and degreased with diethyl ether and acetone. The maximum load $\boldsymbol{P}_{\mathbf{max}}$ above which the friction mode is unsteady was determined. Wear $\boldsymbol{I_g}$ was estimated gravimetrically from the difference between the weights of the specimens before and after the tests.

RESULTS AND DISCUSSION

o-Hydroxyazomethines of the type **I** (LH) used as ligands mainly exist in the tautomeric enol–imine form **Ia** [1, 4, 25, 26].



(**Ia**) (**Ib**) (2)

$R = CH_3$.

This tautomerization (2) was revealed by ^{1}H NMR spectroscopy for $R = CH_3$ (see Experimental) and for *o*-hydroxyazomethines with alkyl substituents C_nH_{2n+1} ($n = 2–18$). The ^{1}H NMR spectra show signals for the HC=N (δ 8.31–8.34 ppm) and OH protons (δ 13.69–13.71 ppm), which indicate the presence of tautomer **Ia**.

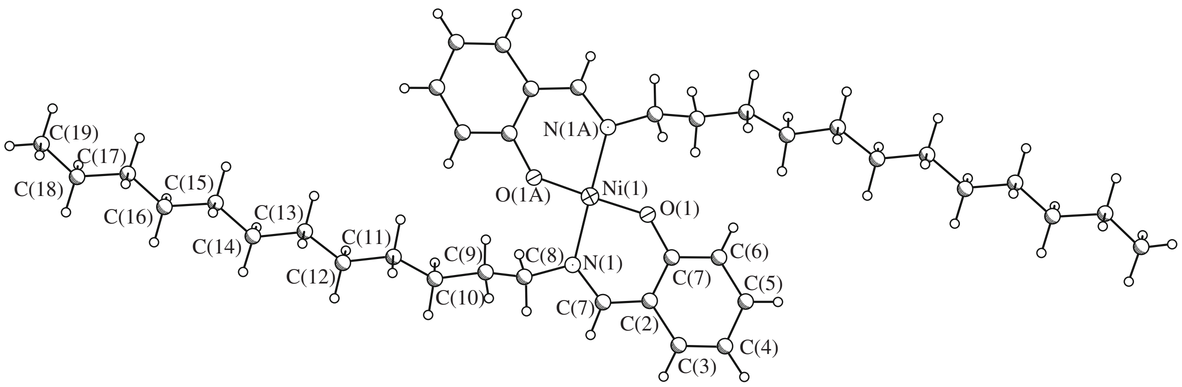
Chelate complexes **II** were synthesized not only in a standard way (direct reaction of azomethine ligands **I** with metal salts (acetates) [2, 27]) but also by a direct electrochemical method [2, 27–31]. The latter involves dissolution of metals in the zero oxidation state (anode) in an electrolytic cell (platinum cathode) in acetonitrile or methanol in the presence of a conducting additive (usually, quaternary ammonium salts). Electrochemical synthesis (3) of complexes of monoproton-donating *o*-hydroxyazomethines **I** consists of the following transformations:

$$\begin{aligned} &\text{Cathode: } LH + n\bar{e} \longrightarrow nL^- + (n/2)H_2, \\ &\text{Anode: } M - n\bar{e} \longrightarrow M^{n+}, \qquad (3) \\ &\text{Solution: } ML_2 \end{aligned}$$

The electrochemical method allows room-temperature reactions giving pure final products (complexes ML_2 (**II**)) in sufficiently high yields. This advantage should be taken into account since the chemical synthesis from metal salts at high temperatures (usually in boiling alcohols) is often accompanied by the formation of the complexes MLA (A = OCOMe, Hal, or NO_3) or metal hydroxides.

The compositions and chelate structures of complexes **II** were proved by ^{1}H NMR spectroscopy for Zn-(**IIa–IIj**) and IR spectroscopy for Cu(Ni, Zn)-(**IIa–IIj**), as well as by X-ray diffraction analysis of Ni-**IIh**.

The IR spectra show no bands at 3200–3400 cm^{-1} (ν(OH) stretching vibrations), which is typical of chelate complexes [32]; the azomethine group absorbs at the lower frequencies (1619–1628 cm^{-1} for the complexes against 1635–1642 cm^{-1} for the ligands). The formation of complexes **II** was confirmed by ^{1}H NMR data for zinc complexes [33]: the signals for the HC=N proton are shifted upfield and the signal for the OH proton disappears.



Structure of the complex Ni-**IIh**. Selected bond lengths are Ni(1)–O(1) 1.828(2) Å, Ni(1)–N(1) 1.925(3) Å, O(1)–C(1) 1.313(4) Å, N(1)–C(7) 1.304(4) Å, N(1)–C(8) 1.486(4) Å, and C(1)–C(2) 1.409(5) Å. Selected bond angles are O(1)Ni(1)N(1) 93.04(10)°, C(1)O(1)Ni(1) 129.6(2)°, C(7)N(1)C(8) 114.7(3)°, and C(7)N(1)Ni(1) 124.6(2)°.

A piece of direct evidence for the formation of chelate complexes **II** from *o*-hydroxyazomethines **I** was obtained from X-ray diffraction data for the complex Ni-**IIh**. According to data in [34, 35], this complex was found to exist in the *trans*-planar configuration (figure).

In the centrosymmetric molecule of Ni-**IIh**, the Ni atom has a square planar coordination. The six-membered chelate ring exists in the sofa conformation; the O atom deviates by 0.19 Å. The average deviation of the other five coplanar atoms from their plane is ±0.02 Å.

The conformation of the alkyl substituent is close to *trans*. The corresponding torsion angles vary from 159.5° to –179.1°. The largest deviation is found for the atoms bound to the chelate ring, which is probably due to an interaction of the methylene atoms with the π-system of the chelate ring. Indeed, an analysis of the crystal packing showed that the molecules in the crystal are involved in a number of shortened molecular contacts: stacking (shortest distances are C(3)···C(6) 3.279(2) Å and C(7)···O(1) 3.147(2) Å) and the contacts C–H···π (H···C 2.73–2.74 Å, angles C–H···C 163°–169°).

The aforesaid selection of alkylamines and testing of alkylamines **Ia**–**Ij** and complexes **IIa**–**IIi** for tribochemical activity were effected because of their high solubilities in aprotic low-polarity solvents (including lubricants). We proceeded from the fact that under the boundary friction conditions, the resulting complexes (version of the direct synthesis [30, 31]) are tribochemically effective [18–21, 24].

Earlier, it has been shown that tribochemical processes in steel–bronze friction couples give copper complexes via a reaction of surface copper (from bronze) with ligands added to a lubricating formulation [18]. Then the copper complex reacts with iron to form a thin film of metallic copper on the steel surface and “selective transfer” occurs [24].

Here we demonstrated that tribochemical processes in steel–steel friction couples in the presence of transition metal complexes result in transcomplexation giving thin films of metallic copper and the other complexing transition metal on both rubbing surfaces. Selective transfer is accompanied by substantial enhancement of the tribotechnical characteristics [24].

According to our data (Table 3), the length ***n*** of the alkyl radical in the complex largely influences its lubricating properties. The lubricating characteristics become appreciably enhanced with an increase in *n* from 1 to 12–16 but then slightly worsen to *n* = 18.

The observed effect can be explained by the formation of a tribopolymer film on the metal surface as comb polymer gels containing complexes that tend to form mesophases at optimum lengths of the alkyl radical (*n* = 8–16). The mesomorphous state of a lubricating formulation lowers the friction coefficient [36].

Complexes **II** seem to be promising as additives to synthetic oils and lubricants based on polyorganosiloxane liquids with low tribometric characteristics.

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Table 3. Influence of the chemical structures of the salicylidene(alkyl)amine complexes on the tribometric properties of oil

Base material	Ester name	Type of the complex	Concentration, wt %			$P_{\max}$, MPa	F_{fr}	I_g, g/cm^3 × 10^{-11}
			ester	ligand I	complex II			
I-50A						36.5	0.098	31.8
I-50A	DOP					66.0	0.065	18.3
I-50A	DOP	IIa M = Cu	20	0.1	0.1	71.5	0.055	5.8
		M = Ni	20	0.1	0.1	74.0	0.052	5.5
		M = Zn	20	0.1	0.1	76.0	0.048	5.3
		M = Zn	20	0.2	0.2	79.0	0.045	5.2
I-50A	DOP	IIb M = Cu	20	0.1	0.1	71.0	0.052	6.1
		M = Ni	20	0.1	0.1	72.5	0.048	5.9
		M = Zn	20	0.1	0.2	74.5	0.045	5.8
I-50A	DOP	IIc M = Cu	20	0.1	0.1	71.0	0.048	5.7
		M = Ni	20	0.1	0.1	73.0	0.045	5.6
		M = Zn	20	0.1	0.2	75.0	0.043	5.4
		M = Zn	20	0.2	0.2	76.5	0.040	4.8
I-50A	DOP	IId M = Cu	20	0.1	0.1	75.5	0.044	5.1
		M = Ni	20	0.1	0.1	76.0	0.042	4.8
		M = Zn	20	0.1	0.1	78.0	0.040	4.5
		M = Zn	20	0.2	0.2	80.5	0.036	4.3
I-50A	DOP	IIe M = Cu	20	0.1	0.1	72.0	0.043	5.4
		M = Ni	20	0.2	0.2	73.5	0.040	5.1
		M = Zn	20	0.1	0.1	76.0	0.038	4.8
		M = Zn	20	0.2	0.2	78.0	0.037	4.7
I-50A	DOP	IIf M = Cu	20	0.1	0.1	83.5	0.045	4.5
		M = Cu	20	0.2	0.2	85.0	0.043	4.3
		M = Ni	20	0.2	0.2	86.0	0.042	3.9
		M = Ni	20	0.3	0.3	88.5	0.041	3.8
		M = Zn	20	0.2	0.2	90.0	0.038	3.6
		M = Zn	20	0.3	0.3	94.0	0.036	3.4
I-50A	DOP	IIg M = Cu	20	0.2	0.2	93.5	0.031	4.1
		M = Cu	20	0.3	0.3	98.0	0.028	3.8
		M = Ni	20	0.3	0.3	102.5	0.026	3.5
		M = Zn	20	0.3	0.3	105.2	0.023	3.4
		M = Zn	20	0.4	0.4	106.0	0.022	3.2
I-50A	DOP	IIh M = Cu	20	0.1	0.1	95.5	0.032	4.2
		M = Cu	20	0.3	0.3	105.0	0.028	3.7
		M = Ni	20	0.2	0.2	108.0	0.027	3.4
		M = Ni	20	0.4	0.4	110.0	0.026	3.4
		M = Zn	20	0.3	0.3	112.0	0.024	3.2
		M = Zn	20	0.5	0.5	114.0	0.023	3.1
I-50A	DOP	IIi M = Cu	20	0.2	0.2	96.5	0.031	4.3
		M = Cu	20	0.3	0.3	103.5	0.027	4.2
		M = Ni	20	0.2	0.2	108.0	0.025	4.1
		M = Ni	20	0.3	0.3	110.0	0.024	3.8
		M = Zn	20	0.2	0.2	110.0	0.023	3.5
		M = Zn	20	0.4	0.4	112.0	0.022	3.5
I-50A	DOP	IIj M = Cu	20	0.2	0.2	93.5	0.033	4.5
		M = Cu	20	0.3	0.3	96.0	0.031	4.4
		M = Ni	20	0.2	0.2	98.0	0.030	4.3
		M = Ni	20	0.4	0.4	110.0	0.028	4.3
		M = Zn	20	0.3	0.3	110.0	0.028	4.2
		M = Zn	20	0.5	0.5	108.0	0.029	4.2

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