Investigation of 8-mercaptoquinoline (thiooxine) and its derivatives 114. Inner complex compounds of 6-methyl-5-sulfo-
-8-mercaptoquinoline

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The interaction of 6-methyl-5-sulfo-8-mercaptoquinoline with Zn(II), Cd(II), Hg(II), Ga(III), In(III), Pb(II), Sn(II, IV), Sb(III), Bi(III), Ag(I), Cu(II), V(IV), Fe(II, III), Co(II), Mo(VI), W(VI), Ni(II), Pd(II), Pt(II), Rh(III), Ir(III), Ru(III), Os(IV) in aqueous solutions has been investigated. Absorption spectra have been studied, composition, the dependence of formation of inner complex compounds of 6-methyl-5-sulfo-8-mercaptoquinoline on hydrogen ion concentration, and stability constants have been determined. At ionic strength $I = 0.1$ mol dm^{-3} and $\theta = 20\,°C$ the following values of the stability constants lg K_1 and (lg β_n) have been found: VO$^+$R $- 8.0$; Ni$^+$R $- 8.7$; ZnR$_2$ $- 9.2$ (17.8); CdR$_2$ $- 9.55$ (18.3); PbR$_2$ $- 10.0$ (16.45); Ga$^+$R$_2$ $- 10.4$ (20.3); InR$_3$ $- 11.3$ (29.5); Sb$^+$R$_2$ $- 14.25$ (25.9); BiR$_3$ $- 14.5$ (31.1); Sn$^+$R$_3$ $-$ (35.0). According to the values of lg K_1, the stability of the complexes of 6-methyl-5-sulfo-8-mercaptoquinoline decreases in the order Bi, Sb, In, Ga, Pb, Cd, Zn, Ni, V.

Исследовано взаимодействие 6-метил-5-сульфо-8-меркаптохинолина с Zn(II), Cd(II), Hg(II), Ga(III), In(III), Pb(II), Sn(II, IV), Sb(III), Bi(III), Ag(I), Cu(II), V(IV), Fe(II, III), Co(II), Mo(VI), W(VI), Ni(II), Pd(II), Pt(II), Rh(III), Ir(III), Ru(III), Os(IV) в водном растворе. Изучены спектры поглощения, определен состав, зависимость образования от концентрации ионов водорода и константы устойчивости внутрикомплексных соединений 6-метил-5-сульфо-8-меркаптохинолина. При ионной силе $I =$ 0,1 моль дм$^{-3}$ и $\theta = 20\,°C$ найдены следующие величины констант устой- чивости lg K_1 и (lg β_n): VO$^+$R $- 8,0$; Ni$^+$R $- 8,7$; ZnR$_2$ $- 9,2$ (17,8); CdR$_2$ $-$ 9,55 (18,3); PbR$_2$ $- 10,0$ (16,45); Ga$^+$R$_2$ $- 10,4$ (20,3); InR$_3$ $- 11,3$ (29,5);

$Sb^+R_2 - 14{,}25\ (25{,}9)$; $BiR_3 - 14{,}5\ (31{,}1)$; $Sn^+R_3 - (35{,}0)$. Из величины lg K_1 составлен ряд устойчивости 6-метил-5-сульфо-8-меркаптохинолинатов: $Bi > Sb > In > Ga > Pb > Cd > Zn > Ni > V$.

Inner complex compounds of 5-sulfo-8-mercaptoquinoline were studied previously [1]. In order to determine the influence of methyl group in the 6th position of quinoline ring, the study of physicochemical properties of inner complex compounds of 6-methyl-5-sulfo-8-mercaptoquinoline (6-methyl-5-sulfothiooxine) is relevant.

This reagent with heavy metal ions forms inner complex compounds soluble in water but insoluble in slightly polar organic solvents. 6-Methyl-5-sulfo-8-mercaptoquinoline can be used for determination and masking of heavy metals in aqueous solutions.

Synthesis [2], absorption spectra, and ionization constants [3] of 6-methyl-5-sulfo-8-mercaptoquinoline were described previously. As for the less acidic properties of mercapto group and the more basic properties of nitrogen atom of the quinoline ring of 6-methyl-5-sulfo-8-mercaptoquinoline, if compared to those of 5-sulfo-8-mercaptoquinoline, an increase of stability of inner complex compounds of the first reagent can be expected.

The results of the investigation of composition, absorption spectra, dependence of formation of the complexes on pH, and their stability constants are described in the present communication.

Experimental

6-Methyl-5-sulfo-8-mercaptoquinoline was used in the form of disodium salt (*I*).

$$\text{H}_3\text{C} - \underset{\text{SNa}}{\overset{\text{SO}_3\text{Na}}{\boxed{}\!\!\boxed{}_{\text{N}}}} \cdot 4\text{H}_2\text{O}$$

I
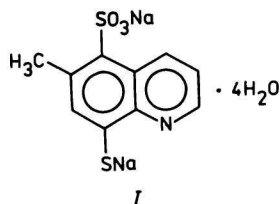
Solutions of metal salts were prepared from chemically pure and highly pure salts or from highly pure metals. Hydrogen ion concentration was measured with pH-meter pH-121. Absorbance of the solutions was measured using a spectrophotometer SFD-1, absorption spectra were recorded on an automatic spectrophotometer Specord UV VIS (Zeiss, Jena).

In spectrophotometric measurements two moles of the reagent were usually taken in excess for complete binding of the metal ion in the complex and were placed into a control cuvette. Cationic inner complex compounds Ga^+R_2, In^+R_2, Sb^+R_2, Bi^+R_2 were studied at

metal:reagent ratio $x(M):x(RH) = 1:2$, in the case of Sn^+R_3 at the ratio $x(Sn(II, IV)):x(RH) = 1:5$, VO^+R — at $x(VO^{2+}):x(RH) = 2:1$, Ni^+R — at $x(Ni^{2+}):x(RH) = 200:1$, Cu^+R — at $x(Cu^{2+}):x(RH) = 10:1$, Pd^+R — at $x(Pd^{2+}):x(RH) = 1:1$. Composition of inner complex compounds was determined by the molar ratio method but in some cases (Mo, W) from the value of molar absorption coefficient.

Because of the existence of platinum metal complexes in aqueous solutions in stable anionic form, heating of the reaction mixture upon a water bath (Pt(II) — 4 min, Rh(III) — 25 min, Ir(III) — 40 min, Ru(III) — 5 min, Os(IV) — 1 min) is required for their quantitative interaction with 6-methyl-5-sulfo-8-mercaptoquinoline. Using the below-mentioned methods crystalline inner complex compounds have been obtained.

Zinc 6-methyl-5-sulfo-8-mercaptoquinolinate

0.3 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ dissolved in 3 cm³ of water are added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 10 cm³ of water. After several minutes yellow crystalline precipitate was obtained. The precipitate is filtered off and washed with 10 cm³ of ethanol and 10 cm³ of acetone. Yield of the product = 0.82 g.

Cadmium 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.34 g of $Cd(CH_3COO)_2 \cdot 2H_2O$ in 30 cm³ of water is added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 50 cm³ of water. 400 cm³ of ethanol are added to the obtained yellow precipitate. The fine crystalline yellow precipitate is filtered off and washed with 50 cm³ of ethanol and 50 cm³ of acetone. Yield of the product = 0.8 g.

Mercury 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.39 g of $Hg(CH_3COO)_2$ in 5 cm³ of water is added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 10 cm³ of water. The yellow crystalline precipitate is filtered off and washed with 50 cm³ of ethanol and 50 cm³ of acetone. Yield of the product = 0.81 g.

Gallium 6-methyl-5-sulfo-8-mercaptoquinolinate

1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt is suspended in 2 cm³ of water, solution of 0.21 g of $Ga(NO_3)_3$ in 2 cm³ of water is added and pH is adjusted to 7.0 with 6 M-hydrochloric acid. 50 cm³ of acetone are added into the obtained red solution. The yellow precipitate is filtered off and washed with 20 cm³ of acetone. Yield of the product = 0.64 g.

Indium 6-methyl-5-sulfo-8-mercaptoquinolinate

1 g of 6-methyl-5-sulfo-8-mercaptoquinolinate disodium salt is suspended in 2 cm³ of water, neutralized with 6 M-hydrochloric acid to pH = 7 and solution of 0.21 g of $In_2(SO_4)_3$ in 2 cm³ of water is added to it. 50 cm³ of acetone are added into the obtained solution. The yellow precipitate is filtered off and washed with 20 cm³ of acetone. Yield of the product = 0.8 g.

Antimony 6-methyl-5-sulfo-8-mercaptoquinolinate

6 M-hydrochloric acid is added to solution of 1 g of 6-methyl-5-sulfo-8-mercapto-quinoline disodium salt in 10 cm³ of water to pH = 2.5 and subsequently solution of 0.41 g of $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$ in 10 cm³ of water and after that 100 cm³ of ethanol are added. The yellow precipitate is filtered off and washed with 20 cm³ of acetone. Yield of the product = 0.63 g.

Bismuth 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.41 g of $Bi(NO_3)_3 \cdot 5H_2O$ in 10 cm³ of 20 % $HClO_4$ was added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 8 cm³ of water. Then 50 cm³ of saturated solution of sodium acetate are added. The yellow precipitate is filtered off and washed with 5 cm³ of ethanol, 5 cm³ of acetone, and 25 cm³ of ether. Yield of the product = 0.77 g.

Lead 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.41 g of $Pb(NO_3)_2$ in 3 cm³ of water is added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 4 cm³ of water, then 20 cm³ of ethanol are added. The yellow precipitate is filtered off and washed with 10 cm³ of ethanol and 10 cm³ of acetone. Yield of the product = 0.72 g.

Tin 6-methyl-5-sulfo-8-mercaptoquinolinate

1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt is suspended in 2 cm³ of water. 6 M-hydrochloric acid is added dropwise to the suspension until pH = 2.5. Then solution of 0.27 g of $SnCl_2 \cdot 2H_2O$ in 1 cm³ of 0.2 M-hydrochloric acid is added and subsequently 50 cm³ of ethanol and 10 cm³ of acetone. Yield of the product = 0.8 g.

Nickel 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.31 g of $Ni(CH_3COO)_2 \cdot 4H_2O$ in 3 cm³ of water is added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 8 cm³ of water. The red precipitate

is filtered off and washed with 25 cm³ of ethanol and 25 cm³ of acetone. Yield of the product = 0.77 g.

Palladium 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.22 g of $PdCl_2$ in 2 cm³ of 1 M-hydrochloric acid that has been adjusted with saturated solution of sodium acetate to pH = 4.5 is added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 8 cm³ of water. The red precipitate is filtered off and washed with 20 cm³ of ethanol and 20 cm³ of acetone. Yield of the product = 0.71 g.

Platinum 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.51 g of K_2PtCl_4 in 5 cm³ of water is added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 8 cm³ of water, and heated in a boiling water bath. After cooling to room temperature the violet precipitate is filtered off and washed with 20 cm³ of ethanol and 20 cm³ of acetone. Yield of the product = 1.0 g.

Copper 6-methyl-5-sulfo-8-mercaptoquinolinate

Solution of 0.25 g of $Cu(CH_3COO)_2 \cdot H_2O$ in 5 cm³ of water is added to solution of 1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt in 10 cm³ of water and then 50 cm³ of ethanol are added. The brown precipitate is filtered off and washed with 20 cm³ of ethanol and 20 cm³ of acetone. Yield of the product = 0.6 g.

Cobalt 6-methyl-5-sulfo-8-mercaptoquinolinate

1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt is suspended in 2 cm³ of water and solution of 0.39 g of $CoCl_2 \cdot 6H_2O$ in 1 cm³ of water is added and subsequently 50 cm³ of acetone. The yellow precipitate is filtered off and washed with 20 cm³ of acetone. Yield of the product = 0.64 g.

Iron 6-methyl-5-sulfo-8-mercaptoquinolinate

1 g of 6-methyl-5-sulfo-8-mercaptoquinoline disodium salt is suspended in 2 cm³ of water, and the suspension is adjusted with concentrated acetic acid to pH = 5. To suspension a solution of 0.39 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ in 1 cm³ of water and 10 cm³ of acetone are added. Greyish-brown solution is formed and colourless precipitate of sodium sulfate crystallizes. Sodium sulfate is filtered off and 500 cm³ of acetone are added to the filtrate. The brown precipitate of iron 6-methyl-5-sulfo-8-mercaptoquinolinate is filtered off and washed with 20 cm³ of acetone. Yield of the product = 0.65 g.

Analytical data for inner complex compounds are summarized in Table 1.

Table 1

Crystalline inner complex compounds of 6-methyl-5-sulfo-8-mercaptoquinoline

Composition Colour	pH of precipitation	Yield %	w_i(calc.)/% w_i(found)/%				
			C	H	N	S	H_2O
$Zn(C_{10}H_7NO_3S_2Na)_2 \cdot 10H_2O$	8.0	90	30.10	4.29	3.51	16.07	22.58
Yellow			30.14	4.29	3.48	15.88	22.40
$Cd(C_{10}H_7NO_3S_2Na)_2 \cdot 4H_2O$	8.0	91	32.59	3.01	3.80	17.40	9.78
Yellow			32.62	2.95	3.70	17.35	9.95
$Hg(C_{10}H_7NO_3S_2Na)_2 \cdot 10H_2O$	8.0	77	25.74	3.67	3.00	13.74	19.31
Yellow			25.81	3.60	3.10	13.62	19.25
$GaOH(C_{10}H_7NO_3S_2Na)_2 \cdot 6H_2O$	7.0	78	35.79	3.30	4.17	19.11	10.74
Yellow			35.28	3.08	4.03	19.37	10.97
$In(C_{10}H_7NO_3S_2Na)_3 \cdot 5H_2O$	7.0	80	34.85	3.02	4.06	18.61	8.72
Yellow			35.24	2.97	3.91	18.09	9.27
$SbOH(C_{10}H_7NO_3S_2Na)_2 \cdot 3H_2O$	2.5	70	32.22	2.84	3.78	17.21	7.25
Yellow			32.26	2.95	3.84	17.13	7.32
$Bi(C_{10}H_7NO_3S_2Na)_3 \cdot 5.5H_2O$	6.0	83	31.69	2.84	3.70	16.92	8.78
Yellow			32.00	2.88	3.82	16.83	8.68
$Pb(C_{10}H_7NO_3S_2Na)_2 \cdot 5H_2O$	8.0	70	28.26	2.85	3.30	15.09	10.60
Yellow			28.10	2.65	2.86	15.15	10.45
$Sn(C_{10}H_7NO_3S_2Na)_2 \cdot 3H_2O$	2.5	94	33.12	2.78	3.86	17.68	7.45
Red			32.69	2.76	3.67	17.35	7.58
$Ni(C_{10}H_7NO_3S_2Na)_2 \cdot 6H_2O$	8.0	88	33.39	3.64	3.89	17.83	15.03
Dark red			33.25	3.61	3.81	17.90	14.95
$Pd(C_{10}H_7NO_3S_2Na)_2 \cdot 9H_2O$	4.5	84	29.25	3.93	3.41	15.62	19.75
Red			28.70	4.01	3.26	15.41	20.51

Table 1 (Continued)

Composition Colour	pH of precipitation	Yield	w_i(calc.)/% w_i(found)/%				
		%	C	H	N	S	H_2O
$Pt(C_{10}H_7NO_3S_2Na)_2 \cdot 9H_2O$	8.0	89	26.40	3.55	3.08	14.10	17.82
Violet			26.43	3.50	2.95	14.03	17.76
$Cu(C_{10}H_7NO_3S_2Na)_2 \cdot 4H_2O$	8.0	70	34.90	3.22	4.07	18.64	10.47
Brown			34.75	3.20	4.02	18.57	10.20
$Co(C_{10}H_7NO_3S_2Na)_3 \cdot 7.5H_2O$	8.0	76	35.22	3.55	4.11	18.81	13.21
Brown			35.10	3.61	4.07	18.75	13.38
$Fe(C_{10}H_7NO_3S_2Na)_3 \cdot 3H_2O$	5.0	83	38.38	2.90	4.48	20.49	5.76
Brown			37.76	2.90	4.70	19.82	6.17

Results and discussion

In most cases 6-methyl-5-sulfo-8-mercaptoquinoline forms inner complex compounds with the number of molecules of the reagent corresponding to the charge of the central atom (Table 2). In some 8-mercaptoquinolinates (Mn, Sb, Bi) coordination capacity of the central atom is saturated with additional molecules of the reagent [4], however, in 6-methyl-5-sulfo-8-mercaptoquinolinates, as well as in the previously investigated 5-sulfo-8-mercaptoquinolinates [1] in aqueous solution coordination capacity of the central atoms is saturated by water molecules. Therefore, only 6-methyl-5-sulfo-8-mercaptoquinolinate of nickel adds an additional molecule of the reagent.

Ga(III) and Sb(III) form only cationic complexes of the composition Ga^+R_2 and Sb^+R_2, but Sn(II) and Sn(IV) the complex Sn^+R_3. At a sufficient amount of the reagent the following ions In^{3+}, Bi^{3+}, Pb^{2+}, VO^{2+}, Ni^{2+}, Cu^{2+}, Pd^{2+} form neutral complexes with the number of molecules of the reagent in the molecule corresponding to the charge of the central atom, but at the excess of metal ions cationic singly charged complexes are formed of the following composition: In^+R_2, Bi^+R_2, Pb^+R, VO^+R, Ni^+R, Cu^+R, Pd^+R. In the case of trivalent iron the composition of the complex with the ratio $x(Fe(III)):x(RH) = 1:3.5$ has been found using the molar ratio method, but in the case of divalent iron the ratio has been found to be $x(Fe(II)):x(RH) = 1:4$. However, absorption spectra in both cases coincide. Using proportionality between the value of molar absorption coefficient of the complex and the number of reagent molecules bound to the central atom [4], it can be concluded from the value of molar absorption coefficient of 6-methyl-5-sulfo--8-mercaptoquinolinate of iron that a complex of the composition FeR_3, is formed. In the presence of air oxygen a conjugated oxidation of Fe(II) to Fe(III) and of the reagent to disulfide takes place. Therefore excess amounts of the reagent are required for complete formation of the complex. Divalent mercury at the ratio $x(Hg(II)):x(RH) = 1:2$ forms a complex of the composition HgR_2, but at the ratio $x(Hg(II)):x(RH) = 1:1$ and in the presence of chloride ions it forms a complex of the composition HgClR. In alkaline medium at the ratio $x(Hg(II)):x(RH) = 1:1$ a complex of the composition HgOHR is formed. Divalent cobalt ions form a complex of the composition CoR_3. In the presence of air oxygen Co(II) is oxidized to Co(III) that is bound with 6-methyl-5-sulfo-8-mercaptoquinoline to a stable complex, which shifts oxidation reaction. Molybdenyl ions in weakly acid medium in the presence of excess of the reagent $x(MoO_2^{2+}):x(RH) = 1:4$ form a complex of the composition MoO_2R_2. Tungstenyl ions quantitatively interact with 6-methyl-5-sulfo-8-mercaptoquinoline in weakly acid medium, $x(WO_2^{2+}):x(RH)$ ratio being 1:8. Judging by the small molar absorption coefficient of the complex $(\varepsilon_{386} = 6000 \ dm^3 \ mol^{-1} \ cm^{-1})$ it can be pressumed that tungsten adds only one molecule of the reagent and the complex evidently has the composition WO_2OHR.

Dependence of formation of inner complex compounds of 6-methyl-5-sulfo-8-mercaptoquinoline on hydrogen ion concentration is shown in Fig. 1. In more acidic medium cationic complexes Pd^+R, $Pd_2^+R_3$, $AgRH^+$, Sb^+R_2, Bi^+R_2 are formed.
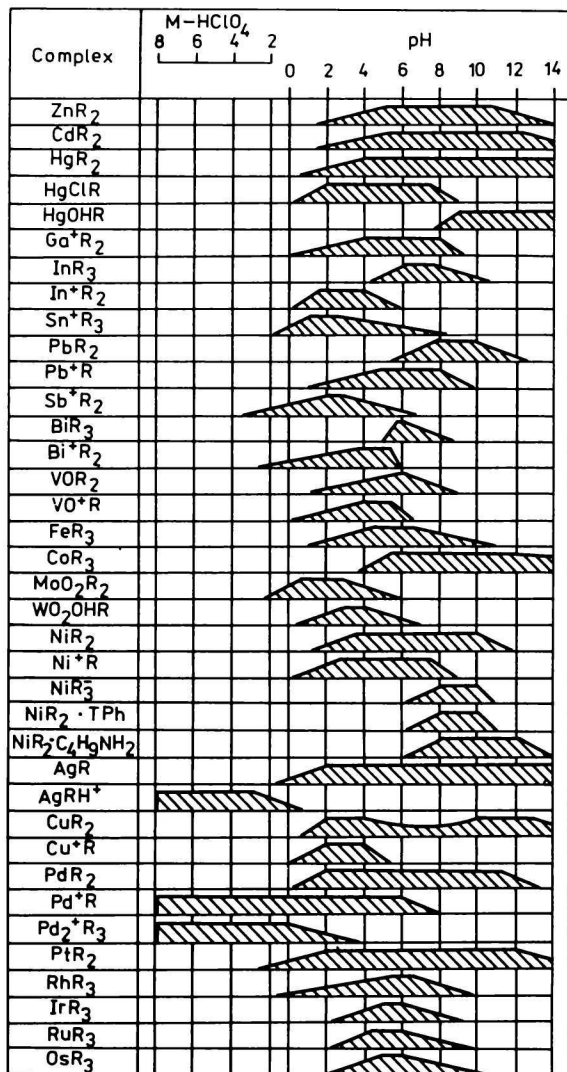

Fig. 1. Dependence of formation of inner complex compounds of 6-methyl-5-sulfo-8-mercapto-quinoline in aqueous solution on hydrogen ion concentration.

Table 2

Composition, pH intervals of maximum formation, absorption maxima, and molar absorption coefficients of 6-methyl-5-sulfo-8-mercaptoquinolinates in aqueous solution

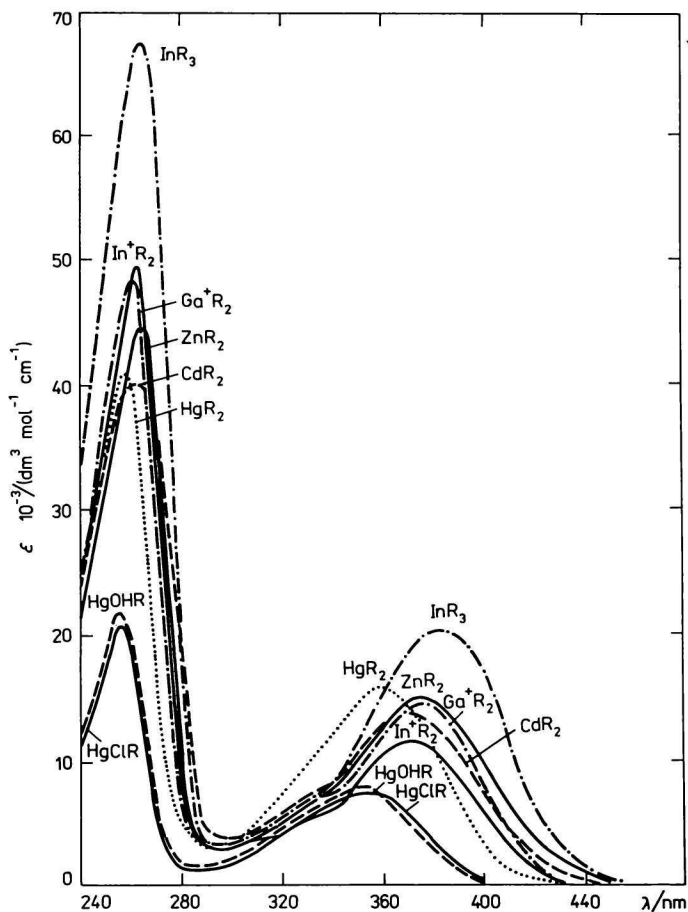| Composition of the complex	pH interval of maximum formation	$\lambda_{1\ max}$ nm	$\varepsilon_{1\ max}$ $dm^3\ mol^{-1}\ cm^{-1}$	$\lambda_{2\ max}$ nm	$\varepsilon_{2\ max}$ $dm^3\ mol^{-1}\ cm^{-1}$
ZnR_2	5.0—10.5	264	44 700	375	14 900
CdR_2	5.0—12.5	262	40 100	371	13 600
HgR_2	4.0—14	259	40 700	359	15 600
$HgClR$	2.0— 7.5	256	20 700	354	7 500
$HgOHR$	9.0—14	256	21 700	352	7 900
Ga^+R_2	3.8— 8.0	260	48 500	374	14 450
InR_3	6.0— 8.0	264	67 500	383	20 100
In^+R_2	1.5— 4.0	262	48 700	370	11 600
Sn^+R_3	1.0— 2.8	262	60 900	372	19 300
PbR_2	7.5—10.0	264	38 200	386	17 000
Pb^+R	5.0— 8.0	260	20 800	376	6 000
Sb^+R_2	2.0— 3.0	260	37 300	385	14 400
BiR_3	5.8— 6.3	258	56 600	381	22 500
Bi^+R_2	3.5— 5.5	257	38 800	381	16 000
VOR_2	6.2— 6.4	259	32 500	406	10 600
VO^+R	4.2— 5.5	268	17 000	398	4 500
FeR_3	4.5— 6.6	257	59 200	409	12 800
CoR_3	5.5—11.0	281	45 700	433	19 100
MoO_2R_2	0.5— 2.8			435	8 100
WO_2OHR	3.0— 4.0			386	6 000
NiR_2	3.5—10.0	248	35 300	494	6 700
Ni^+R	2.5— 7.5	268	21 600	388	6 000
NiR_3^-	8.0—10.0	275	50 000	411	21 000
$NiR_2 \cdot Butam$	8.0—12.0	272	35 000	402	14 800
$NiR_2 \cdot TPh$	8.0—10.0			412	10 000
AgR	2.0—14	242	16 300	380	5 200
$AgRH^+$	$3M—8M-HClO_4$	259	18 750	394	3 830
CuR_2	2.0— 4.0	253	32 300	404	12 700
	10.5—12.8	272	35 000		
Cu^+R	2.0— 4.0	267	14 800	389	5 000
PdR_2	2.0—11.0	286	37 500	462	8 300
Pd^+R	$8M-HClO_4—6.0$	285	9 200	349	12 300
$Pd_2^+R_3$	$1M—8M-HClO_4$	245	57 400	366	22 100
PtR_2	2.0—12.0	297	21 400	529	7 300
RhR_3	5.5— 6.5	277	50 300	429	18 500
IrR_3	5.0— 6.0	280	52 750	445	13 800
RuR_3	4.5— 5.5			516	7 000
OsR_3	5.0— 5.5			523	11 900

Fig. 2. Absorption spectra of aqueous solutions of 6-methyl-5-sulfo-8-mercaptoquinolinates of zinc, cadmium, mercury, gallium, and indium.

Absorption maxima (Table 2, Figs. 2—6) of 6-methyl-5-sulfo-8-mercapto-quinolinates of metals with completed d-electron orbitals in aqueous solution are within the region of 359—380 nm, but those of inner complex compounds with noncompleted d-electron orbitals within the region of 406—529 nm. According to the previous suggestions [5], 6-methyl-5-sulfo-8-mercaptoquinolinates of metals with completed d-electron orbitals can be presented as derivatives of thiolic form of the reagent and their structure can be expressed by the formula *II*, while inner complex compounds of metals with noncompleted d-electron orbitals — as

derivatives of zwitterionic form of the reagent and their structure can be expressed by the formula *III*.
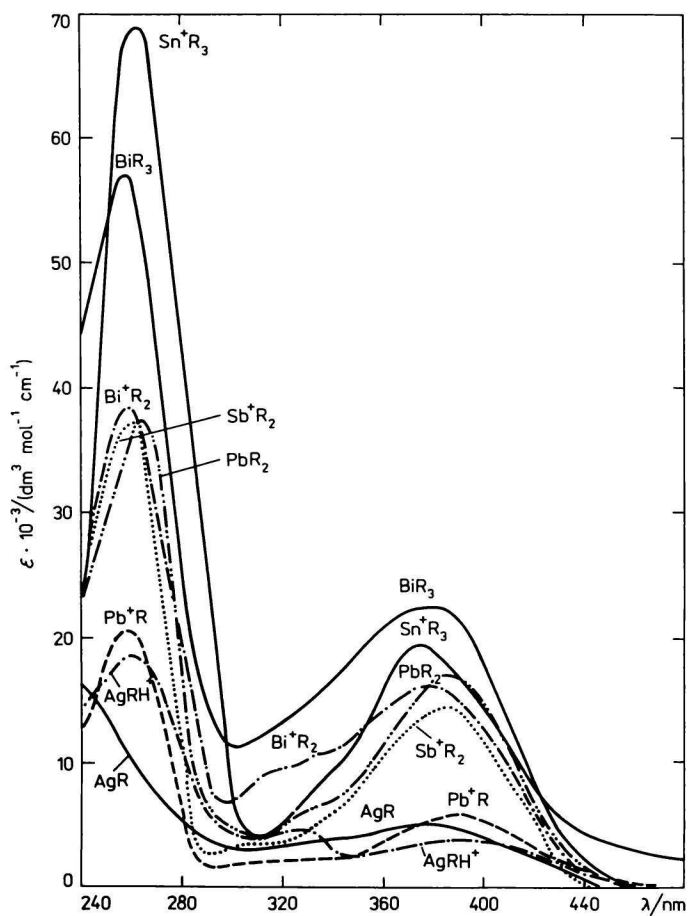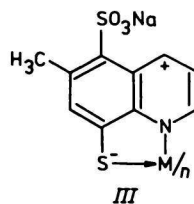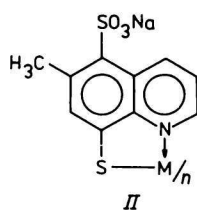

Fig. 3. Absorption spectra of aqueous solutions of 6-methyl-5-sulfo-8-mercaptoquinolinates of antimony, bismuth, lead, tin, and silver.
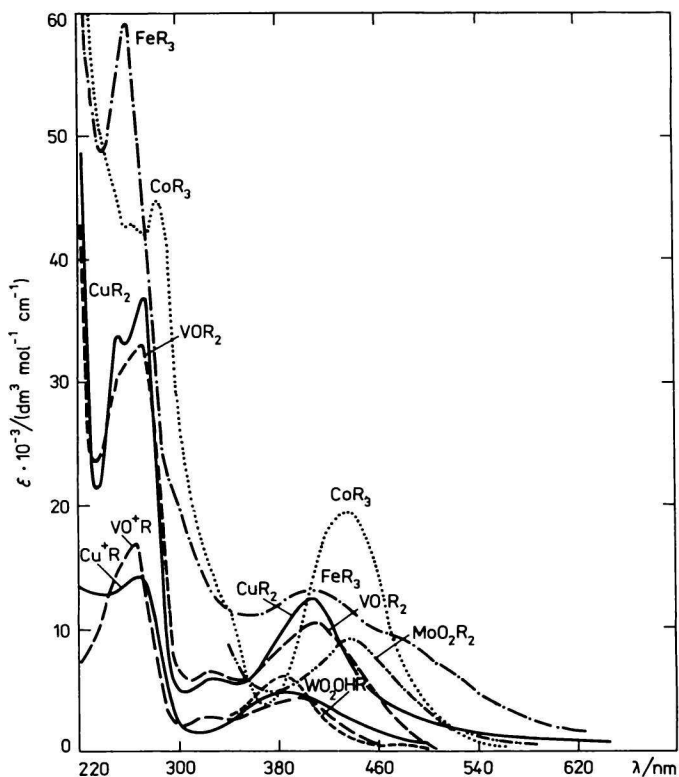
Fig. 4. Absorption spectra of aqueous solutions of 6-methyl-5-sulfo-8-mercaptoquinolinates of iron, cobalt, copper, vanadium, molybdenum, and tungsten.

6-Methyl-5-sulfo-8-mercaptoquinolinates cannot be extracted into inert organic solvents. However, in the form of tetraphenylarsonium and other onium associates the complexes can be extracted into chloroform and other organic solvents. Absorption maxima of onium associates in chloroform practically coincide with absorption maxima of 6-methyl-8-mercaptoquinolinate complexes. On interaction with molecules of coordinatively active solvents hypsochromic shift of absorption maxima occurs, parallelly to the increase of coordination activity of solvent molecules. This is exemplified with the nickel complex. Transferring nickel complex from chloroform (*IV*) to aqueous solution (*V*), hypsochromic shift of absorption maximum from 528 nm to 494 nm takes place. Adding n-butylamine (by the method of equilibrium shift it has been established that 6-methyl-5-sulfo-8-mercaptoquinolinate of nickel adds one molecule of n-butylamine), a further
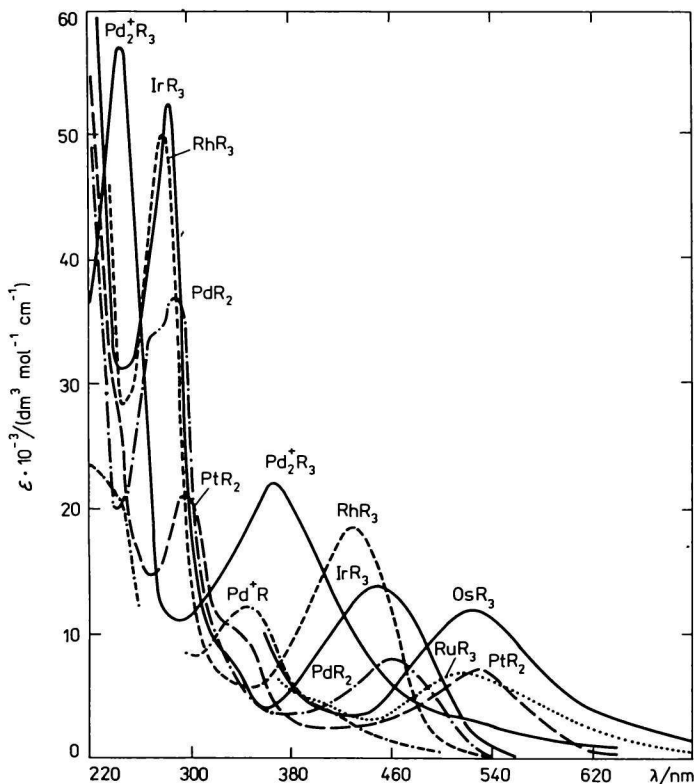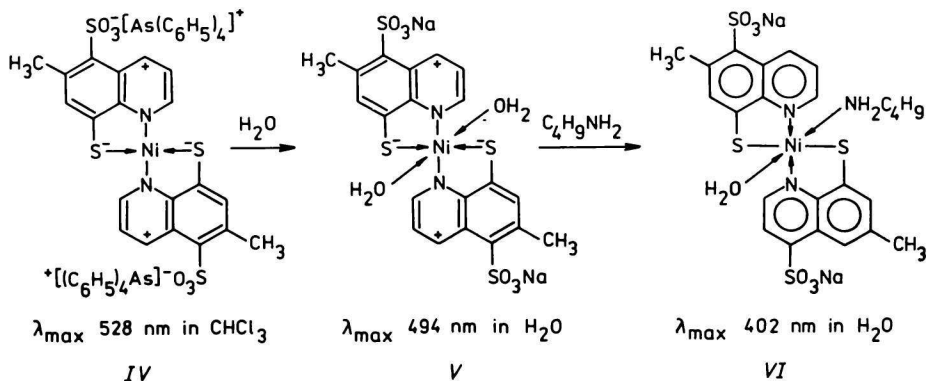
Fig. 5. Absorption spectra of aqueous solutions of 6-methyl-5-sulfo-8-mercaptoquinolinates of palladium, platinum, rhodium, iridium, ruthenium, and osmium.

hypsochromic shift of absorption maximum to 402 nm (*VI*) occurs. The gradual hypsochromic shift of absorption maximum indicates an increase of coordination saturation of the central atom and weakening of mesoionic structure of the complex (Scheme 1).

In alkaline medium (pH = 8—10) composition of 6-methyl-5-sulfo-8-mercaptoquinolinate of nickel corresponding to the ratio $x(\text{Ni}) : x(\text{R}) = 1 : 3$ has been found by the molar ratio method (Table 2). Absorption maximum of the complex (411 nm) (Table 2, Fig. 6) is considerably shifted hypsochromically in comparison with the normal complex NiR_2 (494 nm). In alkaline medium in the presence of thiophenol the absorption maximum of 6-methyl-5-sulfo-8-mercaptoquinolinate of nickel (Fig. 6) also undergoes considerable hypsochromic shift and

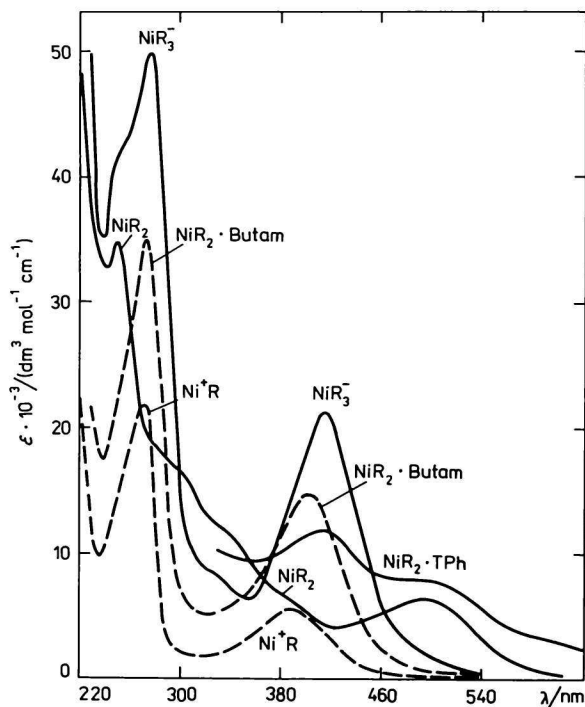λ_{max} 528 nm in CHCl₃ ... λ_{max} 494 nm in H₂O ... λ_{max} 402 nm in H₂O

IV ... V ... VI

Scheme 1

Fig. 6. Absorption spectra of aqueous solutions of 6-methyl-5-sulfo-8-mercaptoquinolinates of nickel: neutral complex (NiR₂), cationic complex (Ni⁺R), nickel complex with an excess molecule of the reagent (NiR₃⁻), nickel complex in the presence of thiophenol (NiR₂ · TPh), and nickel complex in the presence of n-butylamine (NiR₂ · Butam).

is situated approximately at 412 nm, *i.e.* practically coinciding with absorption maximum of the complex NiR_3^-. This means that the additional molecule of the reagent is coordinated to nickel atom *via* negatively charged sulfur atom. The structure of the complex can be expressed by the formula *VII*.
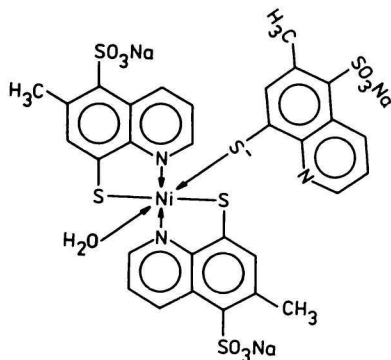
VII

The shift of absorption maximum in the region of the spectrum where absorption maxima of complexes of nontransition metals are located (Table 2) testifies to the nonmesoionic structure of the yellow adducts formed by amines (*VI*), additional molecule of 6-methyl-5-sulfo-8-mercaptoquinoline or thiophenol.

In a number of cases when there is an excess of metal ions 6-methyl-5-sulfo-8-mercaptoquinoline forms cationic complexes (Table 2) the absorption maxima of which are hypsochromically shifted in comparison with absorption maxima of the neutral complexes. In the case of cationic inner complex compounds of metals with completed *d*-electron orbitals the hypsochromic shift of absorption maxima is equal to approximately 10 nm but for the cationic inner complex compounds of metals with noncompleted *d*-electron orbitals it reaches 100 nm. For example, on breaking away one ligand the red mesoionic 6-methyl-5-sulfo-8-mercaptoquinolinate of nickel (*V*, absorption maximum 494 nm) changes into a yellow cationic complex (*VIII*, absorption maximum 388 nm).
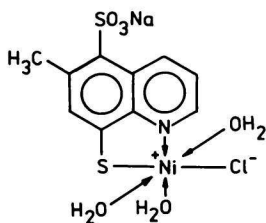

λ_{max} 388 nm in H_2O

VIII

It can be presumed that in hydrated cationic complexes the central atoms are coordinatively saturated and similarly to ions of nontransition metals, form with 6-methyl-5-sulfo-8-mercaptoquinoline inner complex compounds of nonmesoionic structure.

Absorption maximum of 6-methyl-5-sulfo-8-mercaptoquinolinate of silver in strongly acid medium (3—8 M-HClO₄) is shifted bathochromically by 14 nm in comparison with absorption maximum of this complex in pH range 2—14. It is possible that in this case under the influence of high hydrogen ion concentration there occurs breaking of the metal—nitrogen coordination bond and a protonated mercaptide *IX* is formed.

IX
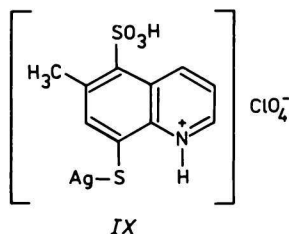
Using the spectrophotometric method, which was also applied to 5-sulfo-8--mercaptoquinolinates [6], stability constants of 6-methyl-5-sulfo-8-mercaptoquinolinates have been determined. The results are presented in Table 3.

6-Methyl-5-sulfo-8-mercaptoquinolinates are by 0.3—1.1 orders more stable than the corresponding 5-sulfo-8-mercaptoquinolinates. This can be explained by the increase of the covalence of the metal atom—sulfur atom bond and of the metal

Table 3

Stability constants of inner complex compounds of 6-methyl-5-sulfo-8-mercaptoquinoline at ionic strength $I = 0.1$ mol dm^{-3} and $\theta = 20$ °C

Composition	lg K_1	lg K_2	lg K_3	lg β_n
VO$^+$R	8.0			
Ni$^+$R	8.7			
ZnR$_2$	9.2	8.6		17.8
CdR$_2$	9.55	8.75		18.3
PbR$_2$	10.0	6.45		16.45
Ga$^+$R$_2$	10.4	9.9		20.3
InR$_3$	11.3	11.1	7.10	29.5
Sb$^+$R$_2$	14.25	11.65		25.9
BiR$_3$	14.5	9.7	6.9	31.1
Sn$^+$R$_3$				35.0

atom—nitrogen atom donor—acceptor bond resulting from the positive contribution of methyl group.

As seen from the values of lg K_1, the stability of 6-methyl-5-sulfo-8-mercapto-quinolinates decreases in the order Bi, Sb, In, Ga, Pb, Cd, Zn, Ni, V. This order coincides with that for 5-sulfo-8-mercaptoquinolinates [6], with the exception of antimony and bismuth which have exchanged their places.

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