

Investigation of 8-mercaptoquinoline (thiooxine) and its derivatives

109. Inner complex compounds of 2-phenyl- and 4-phenyl-8-mercaptoquinolines

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The interaction of 2-phenyl- and 4-phenyl-8-mercaptoquinoline with Zn(II), Cd(II), Hg(II), Ga(III), In(III), Tl(I), Tl(III), Pb(II), Sn(II), Sn(IV), As(III), Sb(III), Bi(III), Mo(VI), W(VI), Mn(II), Re(VII), Cr(III), Ni(II), Co(II), Fe(II), Fe(III), V(IV), Cu(I), Cu(II), Ag(I), Au(I, III), Pd(II), Pt(II), Rh(III), Ir(III), Ru(III), and Os(IV) compounds in the system water—chloroform has been studied. Absorption spectra have been studied, composition and solubility of inner complex compounds in chloroform, the dependence of extraction of complexes with chloroform on hydrogen ion concentration in aqueous phase and stability constant of complexes in the system chloroform—water have been determined.

Изучено взаимодействие 2-фенил- и 4-фенил-8-меркаптохинолинов с Zn(II), Cd(II), Hg(II), Ga(III), In(III), Tl(I), Tl(III), Pb(II), Sn(II), Sn(IV), As(III), Sb(III), Bi(III), Mo(VI), W(VI), Mn(II), Re(VII), Cr(III), Ni(II), Co(II), Fe(II), Fe(III), V(IV), Cu(I), Cu(II), Ag(I), Au(I, III), Pd(II), Pt(II), Rh(III), Ir(III), Ru(III) и Os(IV) в системе вода—хлороформ. Изучены спектры поглощения, определен состав и растворимость внутрикомплексных соединений в хлороформе, зависимость экстракции комплексов с хлороформом от концентрации ионов водорода в водной фазе и константы устойчивости комплексов в системе хлороформ—вода.

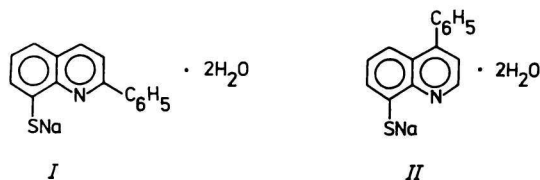
With the phenyl derivatives of 8-mercaptoquinoline the influence of phenyl groups in the position 2 and 4 of the molecules of 8-mercaptoquinoline on physicochemical properties of their inner complex compounds was investigated. The increase of hydrophobicity of molecules was anticipated and consequently also the increase of solubility of inner complex compounds in inert organic solvents. The

study of 2-phenyl-8-mercaptoquinoline is interesting also with regard to steric hindrance executed by the phenyl group in the position 2 on the complex formation.

Absorption spectra, ionization constants, and distribution of 2-phenyl- and 4-phenyl-8-mercaptoquinolines were studied previously [1—2]. In the present investigation the interaction of the reagents with metal ions was studied.

Experimental

Solutions of reagents were prepared from sodium salts of 2-phenyl-8-mercaptoquinoline (*I*) and 4-phenyl-8-mercaptoquinoline (*II*).



Since sodium salts of the reagents in aqueous solutions are easily hydrolyzed and the free reagent easily separates in an oily form, the reagent was dissolved in an 0.01 M solution of sodium hydroxide.

Solutions of metals were prepared either from highly pure metals or from highly pure salts. The inner complex compounds were extracted from the aqueous phase with chloroform. The absorbance of chloroform extracts was measured using the spectrophotometer Specord UV VIS and the concentration of hydrogen ions in aqueous phase was measured using pH-meter type M-25 (Radiometer), calibrated to the accuracy of ± 0.02 pH. For measuring the absorption spectra and for determination of the dependence of extraction of inner complex compounds on hydrogen ion concentration, one gram-equivalent of the reagent in excess of the stoichiometrically necessary amount was taken. An analogously obtained extract, but without the cation of the investigated metal was placed into a control cuvette. However, for quantitative interaction of 4-phenyl-8-mercaptoquinoline with W(VI), Re(VII), and Cr(III) the excess of the reagent (M:RH = 1:10) was necessary.

For quantitative complex formation with 2-phenyl-8-mercaptoquinoline, heating of the reaction mixture in water bath was necessary: Pt(II) — 3 min, Rh(III) — 20 min, Ir(III) — 20 min, Ru(III) — 15 min, Os(IV) — 2 min, and with 4-phenyl-8-mercaptoquinoline: Pt(II) — 5 min, Rh(III) — 20 min, Ir(III) — 30 min, Ru(III) — 10 min, Os(IV) — 3 min, Sn(II) — 3 min, Re(VII) — 10 min, Cr(III) — 15 min.

Composition of the inner complex compounds in extracts was determined using the methods of molar ratio and isomolar series. Two-phase stability constants in the system chloroform—water were determined using the spectrophotometric method [3].

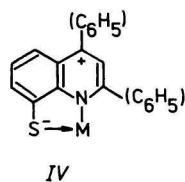
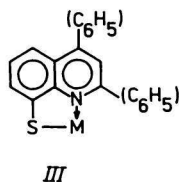
The solubility of the inner complex compounds in chloroform was determined after shaking for 15 min the precipitate of the complex obtained in aqueous phase with an

insufficient amount of chloroform for its solution. The concentration of the complex in chloroform extract was determined spectrophotometrically, using the value of molar absorption coefficient of the complex.

Results and discussion

Phenyl derivatives, similarly to 8-mercaptoquinoline, form inner complex compounds in aqueous media only with transition and nontransition *d* elements (Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi, V, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt and also obviously with Ge, Tc, and Se).

Similarly to the inner complex compounds of 8-mercaptoquinoline and its other derivatives [4], the complexes of phenyl derivatives with nontransition elements (yellow complexes of Ag, Zn, Cd, Hg, Ga, In, Tl, Sb, Bi) are derivatives of the colourless thiolic form of the reagent and their electronic structure may be expressed by the formula *III* but complexes of transition metals (anomalously coloured complexes of Pt, Pd, Ru, Os, Ir, Rh, Ni, Co, Fe, Mn, Re, Mo, W, V, Cr) are derivatives of the coloured zwitterionic form of the reagent and their electronic structure may be expressed by the formula *IV*



The absorption maxima of the mesoionic inner complex compounds of 2-phenyl-8-mercaptoquinoline are hypsochromically shifted in the average by 20 nm, in comparison to the inner complex compounds of 4-phenyl-8-mercaptoquinoline (Tables 1 and 2). This can be explained like in the case of 2-methyl-8-mercaptoquinolinates [5] by decrease of the contribution of mesoionic structure in electronic composition of these complexes resulting from the steric effect of the substitute, which leads to disturbance of coplanarity of the molecule.

4-Phenyl-8-mercaptoquinolinates have absorption spectra with well pronounced absorption maxima in the visible region of the spectrum (Figs. 1—5).

2-Phenyl-8-mercaptoquinolinates in most cases have absorption spectra similar to those of 4-phenyl-8-mercaptoquinolinates (Figs. 6 and 7). However, clearly pronounced absorption maxima are absent in the absorption spectra of 2-phenyl-8-mercaptoquinolinates of trivalent platinum metals (Rh(III), Ir(III), Ru(III), Os(III)) (Fig. 8). It can be assumed that because of the little ionic

Table 1

Physicochemical properties of inner complex compounds of 2-phenyl-8-mercaptoquinoline

Element	Composition of the complex in extract	Colour of the complex in chloroform	pH Interval of maximum extraction	λ_{\max}/nm	$\frac{\epsilon_{\max}}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	$S \cdot 10^4/\text{mol dm}^{-3}$
Zn(II)	ZnR ₂	Yellow	3.5—14.0	429	5 300	300
Cd(II)	CdR ₂	Yellow	4.5—14.0	418	5 700	130
Hg(II)	HgR ₂	Yellow	2 M-HCl—pH 14.0	389	5 700	100
	HgRCl	Yellow	1.5— 8.4	369	3 500	
Tl(I)	TlR	Yellow	11.0—14.0	421	4 000	44
Tl(III)	TlR ₃	Yellow	5.7— 6.3	386	10 000	120
In(III)	InR ₃	Yellow	5.4— 6.0	398	9 300	500
Sb(III)	SbR ₃ · RH	Yellow	6.0—11.0	391	13 300	50
	SbR ₂ Cl	Yellow	0.8— 2.8	382	6 500	
Bi(III)	BiR ₃ · RH	Yellow	1.5—7.0; 10.0—14.0	403	13 200	21
Pb(II)	PbR ₂	Yellow	6.0—9.8; 11.0—14.0	422	9 800	> 10 000
Cu(II)	CuR ₂	Brown	8.5—14.0	443	5 000	
Cu(I)	CuR	Yellow	1.5— 7.2	432	3 270	> 5 000
Ag(I)	AgR	Yellow	1.5 M-H ₂ SO ₄ —pH 14.0	383	3 700	25
Fe(II)	FeR ₂	Brown	7.5	437	5 450	770
Co(II)	CoR ₂	Brown	6.0—12.0	468	5 500	440
Ni(II)	NiR ₂	Red	6.0— 9.5	528	5 660	480

Table 1 (Continued)

Element	Composition of the complex in extract	Colour of the complex in chloroform	pH Interval of maximum extraction	λ_{\max}/nm	$\frac{\epsilon_{\max}}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	$S \cdot 10^4/\text{mol dm}^{-3}$
Pd(II)	PdR ₂	Orange	0.4— 2.5	474	6 500	1 650
Pt(II)	PtR ₂	Red	1.5— 4.5	451	3 700	1 400
				558	3 600	
Rh(III)	RhR ₃	Orange	4.5— 6.8			40
			9.5—13.0			
Ir(III)	IrR ₃	Dark brown	6.0— 9.0			140
Ru(III)	RuR ₃	Dark brown	4.0— 6.0			
			9.4—13.0			760
Os(IV)	OsR ₃	Blue- -dark brownish	4.0— 6.8			680

Table 2

Physicochemical properties of inner complex compounds of 4-phenyl-8-mercaptoquinoline

Element	Composition of the complex in extract	Colour of the complex in chloroform	pH Interval of maximum extraction	λ_{\max}/nm	$\frac{\epsilon_{\max}}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	$S \cdot 10^4/\text{mol dm}^{-3}$
Zn(II)	ZnR ₂	Yellow	3.0—14.0	416	11 600	620
Cd(II)	CdR ₂	Yellow	4.0—13.0	405	12 000	3
Hg(II)	HgR ₂	Yellow	0 —14.0	385	14 400	200
	HgRCl	Yellow	1.0— 6.5	374	6 300	
Ga(III)	GaR ₂ OH	Yellow	2.5— 9.5	405	12 000	> 5000
In(III)	InR ₃	Yellow	4.5—14.0	423	16 400	> 5000
	InR ₂ Cl	Yellow	1.0	410	12 200	
Tl(I)	TlR	Yellow	10.0—14.0	425	5 200	66
Tl(III)	TlR ₃	Yellow	1.5— 6.0	405	18 000	> 5000
	TlR ₂ Cl	Yellow	1.0— 6.5	392	12 200	
Pb(II)	PbR ₂	Yellow	5.5—14.0	427	14 800	8
Sn(II)	SnR ₂	Yellow	0 — 9.5	400	10 000	4800
Sn(IV)	SnR ₂ Cl ₂	Yellow	0 — 9.0	396	9 800	810
As(III)	AsR ₃	Yellow	2.8—5.7 M-HCl	407	13 500	650
Sb(III)	SbR ₃ · RH	Yellow	6.0—11.0	395	22 000	400
	SbR ₂ Cl	Yellow	2.0—3.0 M-HCl	390	12 000	
Bi(III)	BiR ₃ · RH	Yellow	5.5—13.0	410	23 600	26
Mo(VI)	MoO ₂ R ₂	Greenish-yellow	1.0— 6.2	429	10 200	> 5000
W(VI)	WO ₂ R ₂	Greenish-yellow	5.0	405	11 400	2300

Table 2 (Continued)

Element	Composition of the complex in extract	Colour of the complex in chloroform	pH Interval of maximum extraction	λ_{\max}/nm	$\frac{\epsilon_{\max}}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	$S \cdot 10^4/\text{mol dm}^{-3}$
Mn(II)	MnR ₂ · 2RH	Brown	7.0—10.0	420	18 750	> 5000
Re(VII)	Re ₂ O ₇ R ₄	Brown	10.0—11.5 M-HCl	452	11 000	
Cr(III)	CrR ₃	Orange	3.5— 4.5	457	15 800	100
Ni(II)	NiR ₂	Crimson	4.0—14.0	400	13 200	64
				550	8 160	
Co(II)	CoR ₃	Brown	4.5—14.0	480	16 000	1100
Fe(II)	FeR ₃	Reddish-brown	5.0— 8.3	465	13 700	
Fe(III)	FeR ₃	Reddish-brown	3.5— 7.0	465	13 900	1300
V(IV)	VOR ₂	Greenish-yellow	4.0— 6.7	418	11 200	150
				460	8 200	
Cu(II)	CuR ₂	Reddish-brown	0 —14.0	447	11 800	140
Ag(I)	AgR	Yellow	2.0—14.0	378	6 600	4
Au(I, III)	AuR · RH	Orange	2.5—5.0 M-HCl	394	4 600	
				487	3 400	
Pd(II)	PdR ₂	Rosy	8.0 M-HCl—pH 11.0	496	8 840	9
Pt(II)	PtR ₂	Violet-blue	2.0— 8.5	368	18 400	10
				582	9 600	
Rh(III)	RhR ₃	Orange	5.0— 6.5	485	16 000	200
Ir(III)	IrR ₃	Red	7.0— 8.0	505	12 600	1100
Ru(III)	RuR ₃	Violet-blue	3.0— 5.5	550	9 400	720
Os(IV)	OsR ₃	Violet-blue	3.5—11.0	485	10 400	1400
				575	12 800	

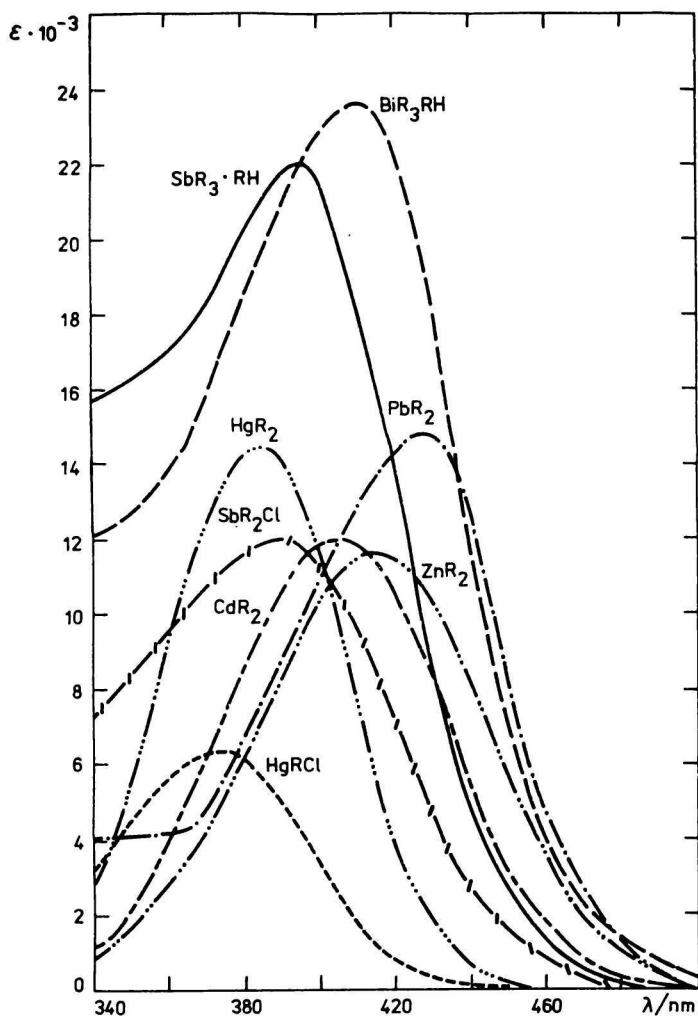


Fig. 1. Absorption spectra of chloroform extracts of 4-phenyl-8-mercaptoquinolinates of zinc, cadmium, mercury, lead, antimony, and bismuth.

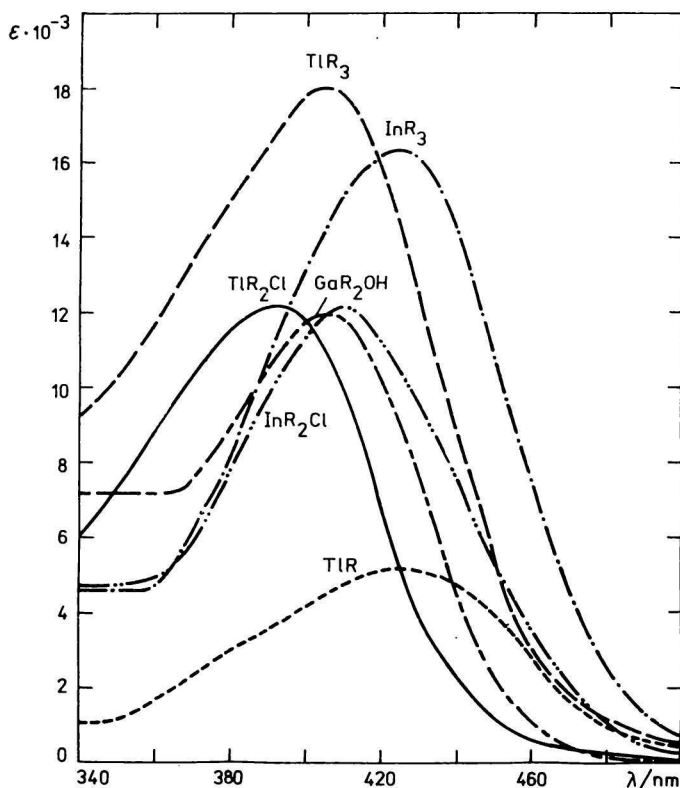


Fig. 2. Absorption spectra of chloroform extracts of 4-phenyl-8-mercaptoquinolinates of gallium, indium, and thallium.

radii of the above-mentioned trivalent platinum metals (74–81 pm) and steric hindrance on the part of phenyl group in the position 2 of the molecule of the reagent, the formation of coordination bond $M-N$ is hampered, and as a result simple mercaptides are partly formed. Judging by the existence of overlapped maxima in absorption spectra (Fig. 8) in the case of the trivalent ruthenium, iridium, osmium, and rhodium a mixture of complexes is formed.

As a consequence of steric effects of the phenyl group in the position 2 the 2-phenyl-8-mercaptoquinoline does not form complexes with metal ions which have a small radius: Ga(III) (62 pm), As(III) (69 pm), Fe(III) (67 pm), Co(III) (64 pm), but interacts with Fe(II) (80 pm) and Co(II) (78 pm) and also with trivalent metal ions which have ionic radii more than 90 pm: Sb(III), Bi(III),

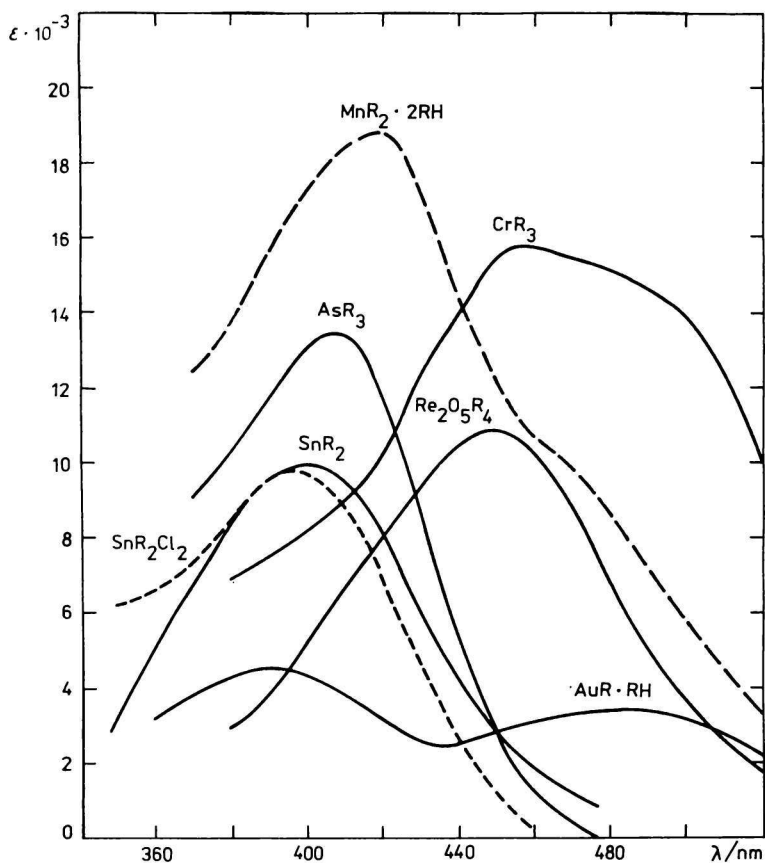


Fig. 3. Absorption spectra of chloroform extracts of 4-phenyl-8-mercaptoquinolates of arsenic, manganese, rhenium, chromium, gold, and tin.

In(III), Tl(III). 2-Phenyl-8-mercaptoquinoline does not interact either with metal ions that are bound to oxygen ions: MoO_2^{2+} , WO_2^{2+} , VO^{2+} , ReO_4^- . This can also be explained by steric effects of the phenyl group in the position 2 in the molecule of the reagent. The reagent lacks space to coordinate with metal ions which are already bounded to oxygen atoms. With copper the 2-phenyl-8-mercaptoquinoline forms two types of inner complex compounds, Cu(II)R_2 and Cu(I)R . The complex CuR_2 is formed with 8-mercaptoquinoline in both cases. The formation of the complex CuR with 2-phenyl-8-mercaptoquinoline can be explained by the difficulties of adding the second molecule of the reagent to copper ion.

2-Phenyl-8-mercaptoquinoline does not form inner complex compounds either with the ions Mn(II) , Au(III) , Cr(III) , Sn(II) , Sn(IV) ; in the presence of these ions, more rapid oxidation of the reagent was observed.

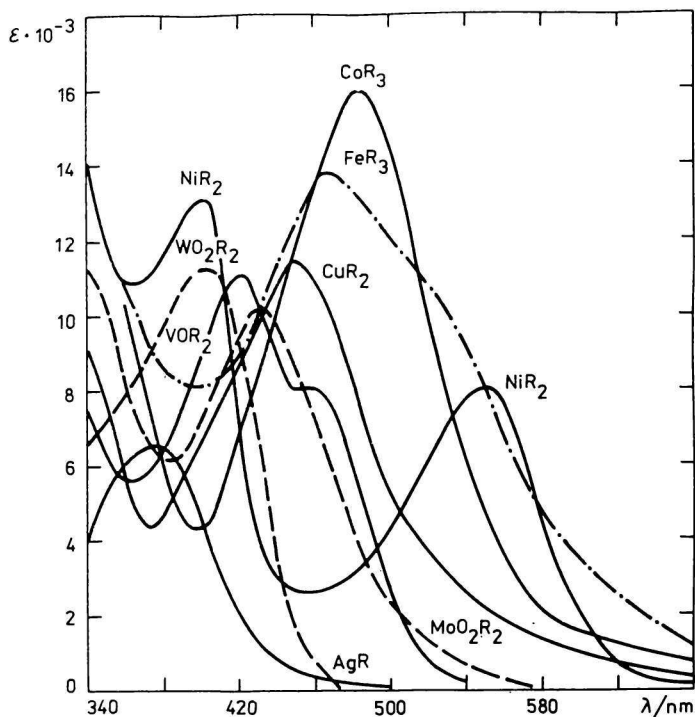


Fig. 4. Absorption spectra of chloroform extracts of 4-phenyl-8-mercaptoquinolinates of nickel, cobalt, iron, copper, vanadium, molybdenum, tungsten, and silver.

The composition of the inner complex compounds usually corresponds to the charge of the central atom, however, 2-phenyl-8-mercaptoquinolinates of antimony and bismuth and 4-phenyl-8-mercaptoquinolinates of antimony, bismuth, manganese, and gold bind additional molecules of the reagent. In acid medium in the presence of excess of metal ions, with 2-phenyl-8-mercaptoquinoline complexes HgRCl , SbR_2Cl are formed, but with 4-phenyl-8-mercaptoquinoline the complexes HgRCl , InR_2Cl , TlR_2Cl , SnR_2Cl arise.

2-Phenyl-8-mercaptoquinolinates and 4-phenyl-8-mercaptoquinolinates do not dissolve in water, but they are easily extracted with organic solvents, the best one being chloroform. With the exception of zinc and mercury complexes and also 4-phenyl-8-mercaptoquinolinates of platinum and palladium, 2-phenyl- and 4-phenyl-8-mercaptoquinolinates are considerably better soluble in chloroform (10–100 times) than the corresponding 8-mercaptoquinolinates because of the hydrophobic nature of the phenyl group. Especially good solubility (more than 0.5 mol dm^{-3}) show 2-phenyl-8-mercaptoquinolinates of lead and copper(I) and

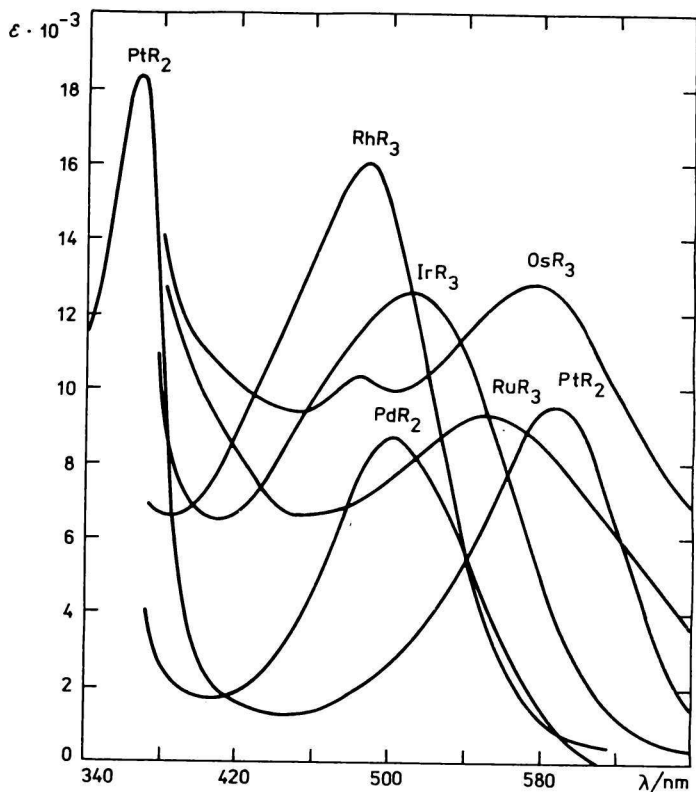


Fig. 5. Absorption spectra of chloroform extracts of 4-phenyl-8-mercaptoquinolinates of palladium, platinum, rhodium, iridium, ruthenium, and osmium.

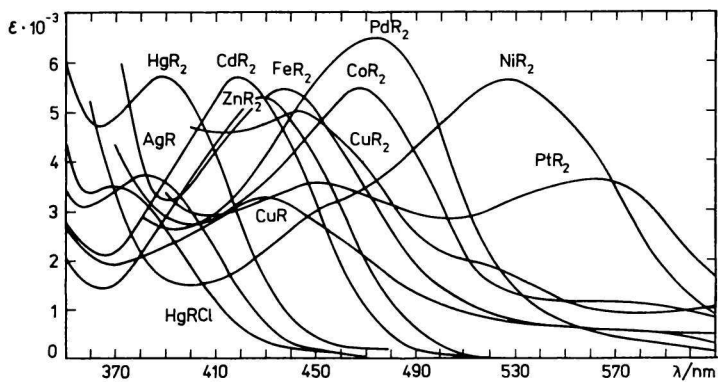


Fig. 6. Absorption spectra of chloroform extracts of 2-phenyl-8-mercaptoquinolinates of zinc, nickel, palladium, platinum, cadmium, mercury, silver, copper, iron, and cobalt.

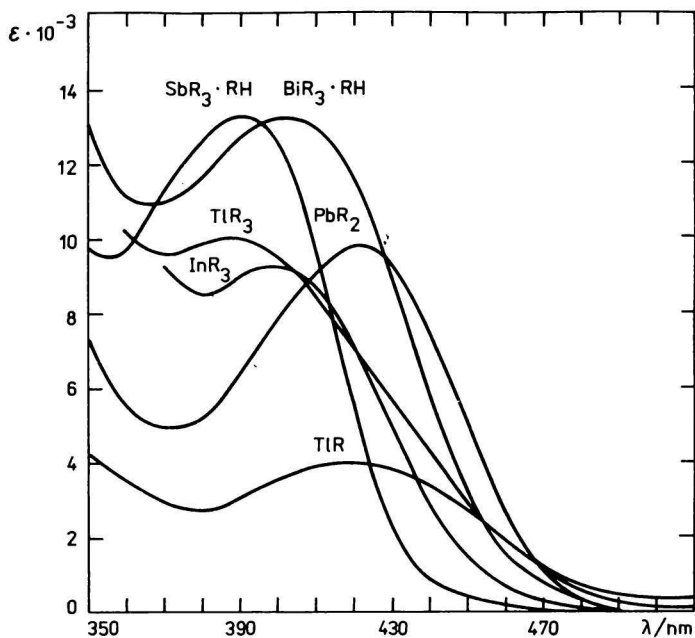


Fig. 7. Absorption spectra of chloroform extracts of 2-phenyl-8-mercaptoquinolinates of antimony, bismuth, thallium, indium, and lead.

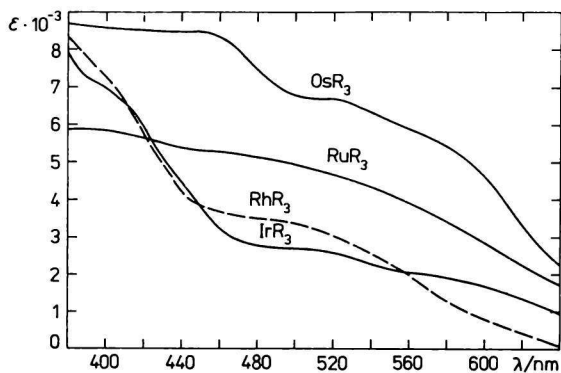


Fig. 8. Absorption spectra of chloroform extracts of 2-phenyl-8-mercaptoquinolinates of osmium, ruthenium, rhodium, and iridium.

4-phenyl-8-mercaptoquinolinates of gallium, indium, thallium(III), molybdenum and manganese (Tables 1 and 2).

The solubility in chloroform of 2-phenyl-8-mercaptoquinolinates of nickel, palladium, and platinum is approximately 100 times higher than that of the corresponding 8-mercaptoquinolinates. This can be explained by the fact that 2-phenyl-8-mercaptoquinolinates in distinction to 8-mercaptoquinolinates of the above-mentioned elements, cannot form tightly packed crystal structures due to steric effects of the phenyl group. The smaller lattice energy is responsible for the

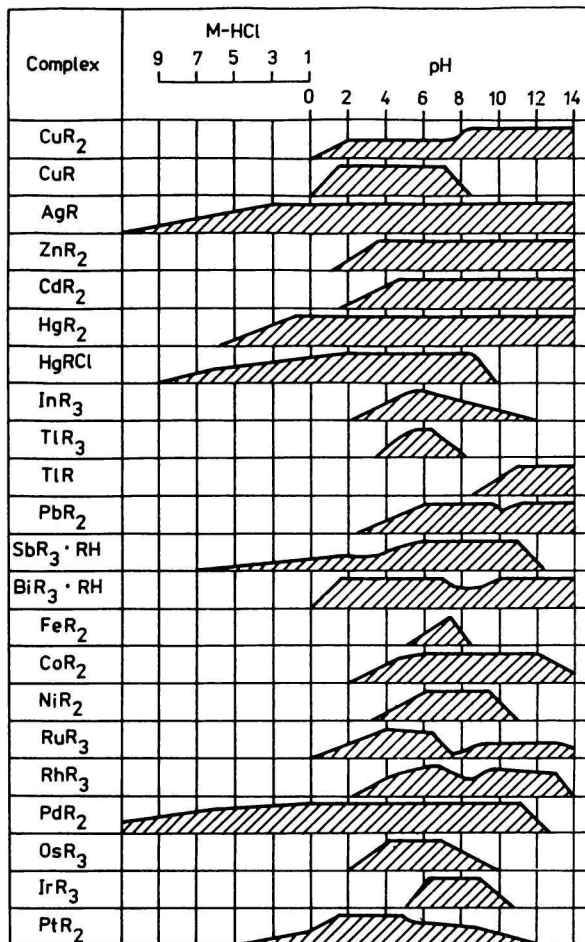


Fig. 9. Dependence of extraction of 2-phenyl-8-mercaptoquinolinates with chloroform on hydrogen ion concentration in aqueous phase.

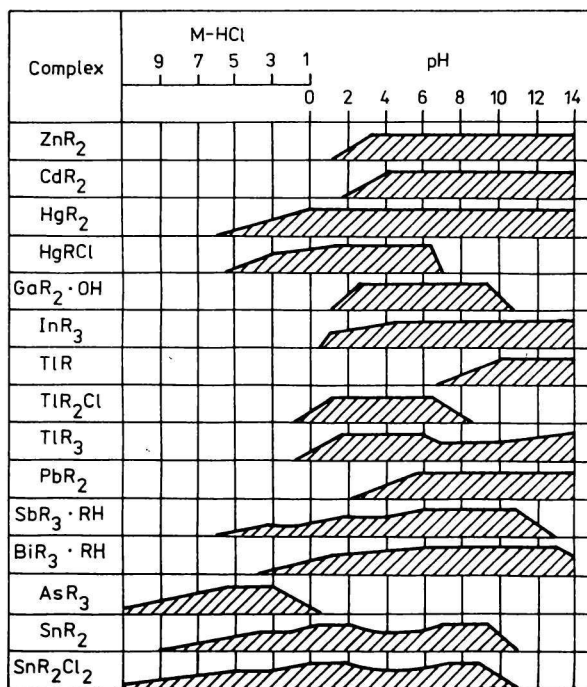


Fig. 10. Dependence of extraction of 4-phenyl-8-mercaptoquinolinates of nontransition metals with chloroform on hydrogen ion concentration in aqueous phase.

better solubility of the complexes in chloroform. This explains why 2-phenyl- and 4-phenyl-8-mercaptoquinolinates of silver and cadmium are extracted with chloroform, and why their 8-mercaptoquinolinates do not dissolve in chloroform.

Owing to their better solubility in chloroform 2-phenyl- and 4-phenyl-8-mercaptoquinolinates are extracted in a wider pH range (Figs. 9—11) than the corresponding 8-mercaptoquinolinates.

4-Phenyl-8-mercaptoquinolinates are a bit more stable in the system aqueous phase—chloroform than the corresponding 2-phenyl-8-mercaptoquinolinates (Table 3). The two-phase stability constants of 2-phenyl- and 4-phenyl-8-mercaptoquinolinates are by several degrees higher than those of the corresponding 8-mercaptoquinolinates [3]. This can be explained mainly by higher distribution constants of the complexes of phenyl derivatives, which is indicated by their better solubility in chloroform.

In accordance with the equilibrium metal ion concentration in aqueous phase which is in contact with 1 M solution of inner complex compounds in chloroform, the order of stability of 2-phenyl-8-mercaptoquinolinates was determined as follows: $\text{Hg} > \text{Sb} > \text{Bi} > \text{Cu} > \text{Zn} > \text{Cd} > \text{In} > \text{Co} > \text{Ni} > \text{Pb} > \text{Fe} > \text{Tl}$ and that of 4-phenyl-8-mercaptoquinolinates: $\text{Hg} > \text{Sb} > \text{Bi} > \text{Cu} > \text{In} > \text{Fe} > \text{Mo} > \text{Ga} > \text{Zn} > \text{Cd} > \text{Ni} > \text{V} > \text{Pb} > \text{Mn} > \text{Tl}$. In general, the line of stability of 4-phenyl-8-mercaptoquinolinates coincides with that of 8-mercaptoquinolinates (the exception is 4-phenyl-8-mercaptoquinolinates of antimony and iron). There is a great difference between the line of stability of 2-phenyl-8-mercaptoquinolinates and that of 8-mercaptoquinolinates resulting from steric effects of the phenyl group in the position 2.

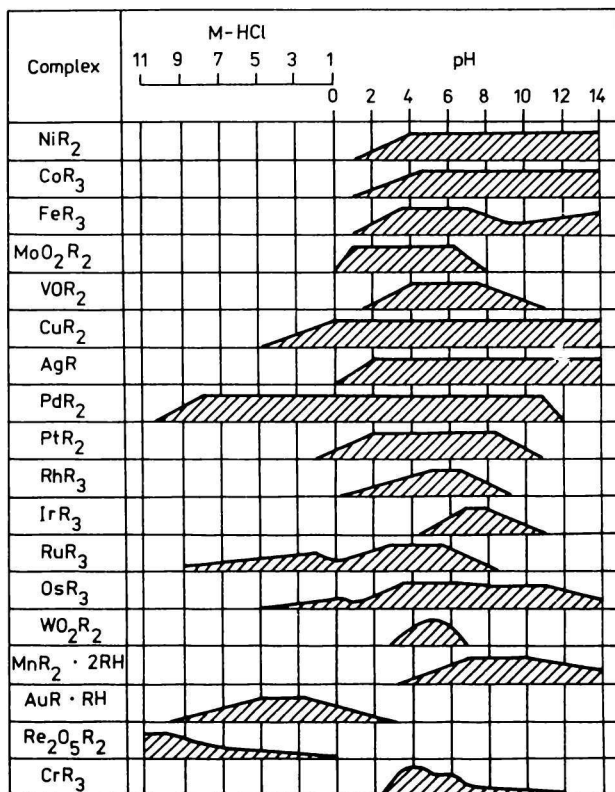


Fig. 11. Dependence of extraction of 4-phenyl-8-mercaptoquinolinates of transition metals with chloroform on hydrogen ion concentration in aqueous phase.

Table 3

Two-phase stability constants $\log \beta'_{MR_n}$ (at ionic strength 0.1 mol dm^{-3} and 20°C) and concentration of metal ions $[M^{n+}]$ in aqueous phase in contact with 1 M solution of inner complex 2-phenyl- and 4-phenyl-8-mercaptoquinolinates in chloroform

Composition of the complex	2-Phenyl-8-mercaptoquinoline		4-Phenyl-8-mercaptoquinoline	
	$\log \beta'_{MR_n}$	$p[M^{n+}]$	$\log \beta'_{MR_n}$	$p[M^{n+}]$
HgR ₂	54.6	18.2	55.3	18.4
SbR ₂ Cl	45.4	15.3	46.2	15.4
BiR ₃	53.6	13.4	59.6	14.9
CuR ₂	33.0	11.0	36.9	12.3
InR ₂ Cl			35.2	11.7
InR ₃	37.4	9.4		
FeR ₂	22.4	7.5		
FeR ₃			46.3	11.6
MoO ₂ R ₂			34.2	11.4
GaR ₂ OH			31.8	10.6
ZnR ₂	31.0	10.3	31.4	10.5
CdR ₂	29.5	9.8	29.9	10.0
NiR ₂	26.6	8.9	29.3	9.8
CoR ₂	27.7	9.2		
VOR ₂			29.0	9.7
PbR ₂	25.6	8.5	27.7	9.2
MnR ₂ ·2RH			42.2	8.4
TlR	8.0	4.0	8.8	4.4

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