

Investigation of 8-mercaptoquinoline (thiooxine) and its derivatives

111. Interaction with metal ions and properties of inner complex compounds of 2-propyl-8-mercaptoquinoline

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Interaction of 2-propyl-8-mercaptoquinoline with Cu(II), Ag(I), Zn(II), Cd(II), Hg(II), Ga(III), In(III), Tl(I), Pb(II), Sb(III), Bi(III), Fe(II), Co(II), Ni(II), Pd(II), Pt(II), Ru(III), Rh(III), and Os(III) ions in the system chloroform—water has been investigated. Absorption spectra have been studied, pH intervals of extraction of the complexes, their composition in extracts, their solubility in chloroform and stability in the two-phase system chloroform—water have been determined. The difference in the properties of 2-propyl-8-mercaptoquinolinates in comparison to complexes of other alkyl derivatives is explained by steric hindrance in the molecules of complexes executed by the propyl group in the position 2 of the ligand.

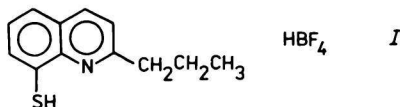
Изучено взаимодействие 2-пропил-8-меркаптохинолина с ионами Cu(II), Ag(I), Zn(II), Cd(II), Hg(II), Ga(III), In(III), Tl(I), Pb(II), Sb(III), Bi(III), Fe(II), Co(II), Ni(II), Pd(II), Pt(II), Ru(III), Rh(III), и Os(III) в системе вода—хлороформ. Изучены спектры поглощения, определены интервалы pH максимальной экстракции комплексов, их состав в экстрактах, растворимость в хлороформе и устойчивость в двухфазной системе вода—хлороформ. Отличие свойств 2-пропил-8-меркаптохинолинатов от комплексов других алкильных производных 8-меркаптохинолина объясняется пространственными препятствиями в молекулах комплексов со стороны пропильной группы в молекуле 2-пропил-8-меркаптохинолина.

The investigation of alkyl derivatives of 8-mercaptoquinoline showed that the strongest effect on the properties of inner complex compounds was exerted by alkyl substituents in 2nd position of the molecule of the reagent [1]. In the series of mono alkyl derivatives containing a substituent in *ortho* position at nitrogen atom,

2-methyl- and 2-isopropyl-8-mercaptoquinolines and their complexes have been investigated previously [2, 3]. In the case of 2-isopropyl-8-mercaptoquinoline considerable increase of solubility of inner complex compounds in organic solvents if compared to 8-mercaptoquinolines was determined [1]. The study of the effect of *n*-propyl group in the 2nd position in the molecule of 8-mercaptoquinoline on the properties of inner complex compounds is of great interest. Interaction of 2-propyl-8-mercaptoquinoline with metal ions and the properties of inner complex compounds of this reagent have been studied in the present investigation.

Experimental

Tetrafluoroboric acid salt of 2-propyl-8-mercaptoquinoline (*I*) which hydrolyzes in aqueous solutions forming free oily 2-propyl-8-mercaptoquinoline, was used in the present work.

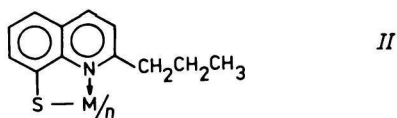


Solutions of the reagent were prepared by dissolving *I* in 0.1 M-hydrochloric acid. Solutions of metal salts were prepared from highly pure metals or from respective standard substances. Chloroform was used as an extracting agent. Absorption spectra were recorded on a Zeiss (Jena) Specord UV VIS spectrophotometer. Molar absorption coefficients were obtained employing Model C-16 spectrophotometer. Hydrogen ion concentration in solutions was determined on either Model 4 or Model 25 pH-meter, calibrated with the precision of 0.02 pH. pH intervals of maximum extraction were determined at stoichiometric ratio of the reagent (RH) and metal ion, in the case of Ga, Tl, Ru, Os, Rh at the excess of the reagent ($[M]:[RH] = 1:10$).

For complete formation of the complexes of platinum metals it is necessary to heat the solutions on a water bath (10–15 min). The composition of the complexes was determined by the mole ratio method and by the shift of the equilibrium. Stability constants of the complexes in the system chloroform–water were determined by spectrophotometric method [4]. Solubility of the complexes in chloroform was determined spectrophotometrically by extracting complexes into insufficient amount of chloroform for their complete dissolution (15 min). Precipitates of the complexes were obtained in the presence of a small excess of the reagent if compared to that stoichiometrically necessary for the formation of the complex.

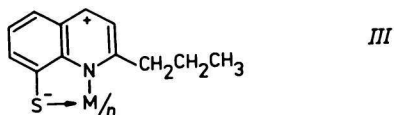
Results and discussion

2-Propyl-8-mercaptoquinoline with metal ions containing completely filled *d*-orbitals, analogously to 8-mercaptoquinoline [1] forms inner complex compounds of the following general structure *II*



Inner complex compounds of these elements (Ag, Zn, Cd, Hg, Ga, In, Tl, Pb, Sb, Bi) are pale yellow or colourless in chloroform solutions, and they may be considered to be derivatives of the colourless thiolic form of the reagent.

For inner complex compounds of metal ions containing incompletely filled *d*-orbitals the canonical electronic structure III is important.



Inner complex compounds of typical transition metals (Pd, Pt, Os, Ru, Rh, Ni, Co, Fe) correspond to this structure, they are characterized by intensive colour, *i.e.*, considerable bathochromic shift of absorption maxima in the visible region of spectrum (Table 1). This refers particularly to complexes of transition metals (with the exception of iron(II) complex). Hypsochromic shift of absorption maxima takes place also in the case of 2-methyl- and 2-isopropyl-8-mercaptoquinolines [2, 3]. This evidently can be explained by inner coplanar hindrance on part of alkyl substituent in *ortho* position to nitrogen atom in the molecule of ligand.

X-ray structural studies of complexes of typical transition metals Ni(II) and Pt(II) with 8-mercaptoquinoline, 2-methyl- and 2-isopropyl-8-mercaptoquinoline show that the above-mentioned 2-alkyl-8-mercaptoquinolines form complexes not of square-planar (as it was in the case of 8-mercaptoquinoline) but distorted tetrahedral coordination geometry [5—8]. As the central atom and ligand molecules are not on one plane, strain in molecules of the complex diminishes, which leads to hypsochromic shift of absorption maxima. In regard to 2-methyl- and 2-isopropyl-8-mercaptoquinolines, 2-propyl-8-mercaptoquinolines are characterized only by insignificant hypsochromic shift of absorption maxima. This testifies to identical effect of the above-mentioned alkyl groups on spectral properties of the complexes.

2-Propyl-8-mercaptoquinolines are not soluble in water but readily extracted into chloroform in wide pH ranges (Table 1). A characteristic distinctive feature of 8-mercaptoquinoline the cadmium and silver complexes of which cannot be extracted into organic solvents is good solubility of cadmium and silver 2-propyl-8-mercaptoquinolines (0.13 mol dm^{-3} and 0.43 mol dm^{-3} , respectively) in chloroform. It has been established that cadmium readily extracted also in the form of 2-methyl-8-mercaptoquinolate [2]. The good solubility of cadmium complexes with 2-alkyl-substituted 8-mercaptoquinolines is evidently due to their tetrahe-

Table 1

Physicochemical properties of inner complex compounds of 2-propyl-8-mercaptoquinoline dissolved in chloroform

Element	Composition of the extracted complex	Colour of the extract	pH intervals of maximum extraction	λ_{\max} nm	$\frac{\epsilon_{\max}}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	$\Delta\lambda_{\max}$ nm
Ag(I)	AgR	colourless	1.0—14.0	361	5 800	— 4
Zn(II)	ZnR ₂	pale yellow	3.5—14.0	400	8 700	— 6
Cd(II)	CdR ₂	pale yellow	4.0— 8.0	394	8 450	
Hg(II)	HgR ₂	colourless	2M-HCl—14.0	367	10 200	— 6
In(III)	InR ₂ Cl	pale yellow	3.0— 5.5	375	8 400	—33
Ga(III)	GaR ₂ OH	pale yellow	3.7— 6.5*	378	8 400	—13
Tl(I)	TlR	yellow	9.8—14.0*	403	4 400	— 1
Pb(II)	PbR ₂	pale yellow	5.0 14.0	398	11 250	—14
Sb(III)	SbR ₃ ·HR	colourless	3.0—10.0	373	16 300	— 8
Bi(III)	BiR ₃ ·HR	colourless	3.5—14.0	384	16 750	—12
Cu(II)	CuR	yellow	0.5—14.0	402	4 100	—32
Fe(II)	FeR ₂	brown	6.5— 8.5	460	5 250	+12
Co(II)	CoR ₂	greenish-yellow	4.5—14.0	449	7 500	—21
Ni(II)	NiR ₂	light brown	5.5—11.0	376	4 800	
				472	6 300	—66
Pd(II)	PdR ₂	dark yellow	1.5—11.0	456	8 400	—29
Pt(II)	PtR ₂	pink	1.8— 7.8	427	4 300	
				531	5 800	—36
Ru(III)		green	3.5— 5.5*	590	3 000	
				680	3 750	
Rh(III)		orange-yellow	4.5— 5.7*	454	8 550	—11
Os(III)		brown	3.5— 6.7*			

* Determined at the excess of the reagent [M]: [RH] = 1:10.

 $\Delta\lambda_{\max}$ — Difference in nm between position of maximum absorption of 2-propyl-8-mercaptoquinolinates and 8-mercaptoquinolinates [1] in the long-wave region of spectrum.

dral configuration. It was shown by X-ray studies that 2-methyl-8-mercaptoquinolate of cadmium has a distorted tetrahedral configuration [9] and consequently less dense packing of molecules in crystal structure.

The existence of steric hindrance in the molecules of complexes can be also explained by the fact that in some 2-propyl-8-mercaptoquinolates a tendency to add small number of ligand molecules to the central atom is observed.

In contrast to 8-mercaptoquinolates of the composition CuR_2 , FeR_3 , CoR_3 , InR_3 , 2-propyl-8-mercaptoquinoline forms in extracts complexes of the composition CuR , FeR_2 , CoR_2 , In^+R_2 . As it was mentioned previously, 2-alkyl derivatives of 8-mercaptoquinoline display the tendency to form inner complex compounds with divalent metal ions of tetrahedral structure. However, this configuration is not characteristic of Cu(II). The existence of propyl group in the 2nd position in the molecule of the ligand evidently excludes the possibility of forming planar configuration, therefore the second molecule of the ligand is not added to the central ion. An easily occurring oxidation-reduction process leads to the formation of 2-propyl-8-mercaptoquinolate of Cu(I) and to oxidation of the ligand to 8,8'-(2,2'-dipropyl)-diquinolyl disulfide. It should be noted that 8-mercaptoquinoline, when interacting both with Cu(II) and Cu(I), forms in the extract 8-mercaptoquinolate CuR_2 .

With Fe(III) ions 2-propyl-8-mercaptoquinoline does not form a stable complex. It has been shown previously that both Fe(II) and Fe(III) form with 8-mercaptoquinoline derivatives which are not substituted in the 2nd position only complexes of composition FeR_3 . In the given case the small size of Fe^{3+} ion (radius 67 pm) evidently hinders the adding of three molecules because of steric hindrances on part of the propyl group.

Attempts to obtain stable complexes with Mn(II), Ir(III), Mo(VI), W(VI), V(IV) were unsuccessful. Under the action of Mn(II), VO^{2+} , MoO_4^{2-} , WO_4^{2-} , 2-propyl-8-mercaptoquinoline is oxidized to 8,8'-(2,2'-dipropyl)-diquinolyl disulfide. From the solutions of In(III) in the presence of chloride ions indium(III) chloro-2-propyl-8-mercaptoquinolate InR_2Cl is extracted. In general, the number of molecules of the ligand linked with the central ion corresponds to its charge, however, in case of Sb(III) and Bi(III) adding of further molecules of the reagent is observed and complexes with the composition of $\text{MR}_3 \cdot \text{HR}$ are extracted.

Molar absorption coefficient at maximum absorption is approximately proportional to the number of molecules of the ligand linked with the central atom and is expressed by the equation [1] $\epsilon_K \approx n\epsilon_{\text{RH}}$, where ϵ_K is molar absorption coefficient of the complex and ϵ_{RH} is molar absorption coefficient of the extract of the reagent in chloroform. ϵ_{RH} for 2-propyl-8-mercaptoquinoline in chloroform is equal to $4600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

2-Propyl-8-mercaptoquinolates are characterized by better solubility in chloroform in comparison to 8-mercaptoquinolates (10—100 times) with the excep-

tion of iron(II) complex (Table 2). Better solubility of 2-alkyl-8-mercaptoquinolines can also be explained by steric hindrances in the molecules of complexes on part of the propyl group. The resulting tetrahedral complexes have smaller lattice energy because of less dense packing of molecules in crystal structure and consequently they are easier destroyed under the impact of the solvent. For 2-alkyl-8-mercaptoquinolines (2-R.tox) solubility S in chloroform increases in the order (Tables 1 and 2)

$$S(\text{tox}) < S(2\text{-methyl-tox}) < S(2\text{-propyl-tox}) < S(2\text{-isopropyl-tox})$$

Inner complex compounds of 2-propyl-8-mercaptoquinoline are insoluble in water, therefore their two-phase stability constants in the system chloroform—water have been determined. These constants characterize the completeness of metal ion extraction from aqueous solution by the given reagent and can be used only for comparative estimation of solubility. Comparison of two-phase stability constants

Table 2

Solubility in chloroform $S_{MR_n}^0$, two-phase stability constants $\log \beta'_{MR_n}$, solubility product pL , equilibrium concentration of metal ions over 1 M-solution of the complex in chloroform $p [M^{n+}]$, and equilibrium concentration of metal ions over precipitate $p' [M^{n+}]$ of inner complex compounds of 2-propyl-8-mercaptoquinoline

MR_n	$\frac{S_{MR_n}^0}{\text{mol dm}^{-3}}$	$\log \beta'_{MR_n}$	pL	$p [M^{n+}]$	$p' [M^{n+}]$
ZnR ₂	9.2×10^{-2}	29.0	30.0	9.7	10.0
CdR ₂	1.3×10^{-1}	27.2	28.1	9.1	9.4
HgR ₂	1.5×10^{-1}	58.0	58.8	19.3	19.6
GaR ₂ OH	9.2×10^{-2}	27.7	28.7	9.2	9.6
InR ₂ Cl	9.6×10^{-3}	30.4	32.4	10.1	10.8
TlR	1.4×10^{-2}	7.9	9.8	4.0	4.9
PbR ₂	2.8×10^{-3}	26.4	29.0	8.8	9.7
BiR ₃		56.2		14.1	
BiR ₃ ·HR	6.0×10^{-2}				
SbR ₃ ·HR	7.0×10^{-2}				
CuR	6.3×10^{-2}	13.5	14.7	6.8	7.4
CoR ₂	8.2×10^{-2}	27.2	28.3	9.1	9.4
FeR ₂	3.9×10^{-3}	22.2	24.6	7.4	8.2
NiR ₂	8.1×10^{-2}	24.8	25.9	8.3	8.6
AgR	4.3×10^{-1}				
PdR ₂	1.2×10^{-1}				
PtR ₂	7.5×10^{-2}				
Rh	2.3×10^{-2}				
Os	1.1×10^{-2}				
Ru	3.5×10^{-2}				

shows that alkyl-8-mercaptoquinolinates are characterized by large value of $\log \beta'_{MR_n}$. Substitution of hydrogen ion for electron-donor alkyl group in the molecule of 8-mercaptoquinoline leads to the increase of the basic properties of nitrogen atom and to decrease of acidic properties of mercapto group. On account to this, covalence character of the metal—ligand bond is increased and as a result of this increases also the stability of complexes. Higher values of $\log \beta'_{MR_n}$ of 2-alkyl-8-mercaptoquinolinates in comparison to 8-mercaptoquinolinates can be explained also by their better solubility in chloroform and consequently by larger values of distribution coefficients in the system chloroform—water.

In the series of the investigated 2-alkyl-8-mercaptoquinolinates the values of two-phase stability constants in general increase in the following way

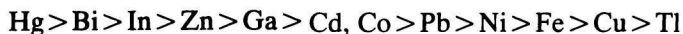


As it was mentioned above, solubility of complexes in chloroform increases in this order.

From concentration of metal ions in equilibrium with 1 M-solution of the complex in chloroform (Table 2) calculated by the formula

$$p[M^{n+}] = \frac{\log \beta'_{MR_n}}{n+1}$$

extraction order of metals with 2-propyl-8-mercaptoquinoline can be determined



The order of solubility of 2-propyl-8-mercaptoquinolinates determined according to equilibrium concentration of metal ions over precipitate of the complex (Table 2) and calculated from the expression

$$p'[M^{n+}] = \frac{pL}{n+1}$$

is as follows



These orders are related to those of 2-methyl- and 2-isopropyl-8-mercaptoquinolinates.

References

1. Bankovskii, Yu. A., *Khimiya vnutrikompleksnykh soedinenii merkaptokhinolina i ego proizvodnykh.* (Chemistry of the Inner Complex Compounds of Mercaptoquinoline and Its Derivatives.) Izd. Zinatne, Riga, 1978.
2. Bankovskii, Yu. A. and Sturis, A. P., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1970, 729.

3. Sturis, A. P., Bankovskii, Yu. A., and Sturis, A. K., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1976, 650.
4. Bankovskii, Yu. A., Chera, L. M., and Ievin'sh, A. F., *Zh. Anal. Khim.* 23, 1284 (1968).
5. Pech, L. Ya. and Sturis, A. P., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1978, 493.
6. Pech, L. Ya., Ozols, Ya. K., Kemme, A. A., Bleydelis, Ya. Ya., and Sturis, A. P., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1980, 549.
7. Pech, L. Ya., Ozols, Ya. K., and Sturis, A. P., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1979, 623.
8. Pech, L. Ya., Ozols, Ya. K., Sturis, A. P., and Ievin'sh, A. F., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1977, 18.
9. Pech, L. Ya., Ozols, Ya. K., Kemme, A. A., Bleydelis, Ya. Ya., and Sturis, A. P., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 1979, 259.