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Complex Compounds of Trivalent Thallium with 7-iodo-8-hydroxyquinoline-5-Sulphonic and 8-hydroxyquinoline-7-Sulphonic Acids.

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This paper deals with the complex compounds of trivalent thallium with 7–iodo–8–hydroxyquinoline–5–sulphonic and 8–hydroxyquinoline–7–sulphonic acids.

From spectrophotometric studies and elementary analyses the combination ratio between metal: ligand has been established as being 1:3. The i.r. spectra have been measured and they support the formation of these compounds.

Introduction

The complex compounds of Tl^{III} with 8–hydroxyquinoline and some of its derivatives have been studied by several authors.

Thus, Feigl[1-2] has precipitated Tl^{III} with 8–hyroxyquinoline and 2,5–dibromo–8–hydroxyquinoline. The same metal was precipitated by means of 2–methyl–8–hydroxyquinoline and 5–nitroso–8–hydroxyquinoline.[3]

Moeller[4] dealt with the spectrophotometric detection of Tl^{III} with 8–hydroxiquinoline in $CHCl_3$, pointing out that the sensitivity of the method is 1.5-5 γ/ml of Tl. By means of thermogravimetric analyses,[5-6] it has been established that the complex compounds presented above contain a molecule of water, at 120 °C.

The derivatives of 8–hydroxyquinoline were employed by Busev[7] as indicators for complexometric determination of trivalent thallium. Stary[8] used some solvents for the extraction of thallium oxinate, while Faraglia[9] obtained different organothallic compounds with 8–hydroxyquinoline.

In this paper, the formation of complex compounds of Tl^{III} with 7–iodo–8–hydroxyquinoline–5–sulphonic and 8–hydroxyquinoline–7–sulphonic acids were investigated.

Experimental Section

All of the reagents used were analytical pure. Tl^{III} was obtained by chlorine oxidation of the monovalent state in HNO_3 (1:1) medium, at 60-70°C. The trivalent state of oxidation was precipitated as $Tl(OH)_3$, filtered and dried to 180°C, obtaining hydrated thallic oxide. An arbitrary amount of this oxide (2-3 g) was dissolved in 25 ml HNO_3 (63 per cent) and, after addition of water, a stock solution in a glass vessel of 500 ml was obtained. The exact concentration of the metal was established gravimetrically.[10]

The u.v. and visible spectra were measured with a « Specord u.v.-vis » spectrophotometer, while the i.r. spectra were obtained by means of a « Perkin-Elmer 337 » apparatus.

Results and Discussion

1. *Spectrophotometric Studies in the u.v. and visible region.* At the beginning, the absorption spectra of the metal, ligands and resulting complex compounds in the u.v. and visible region were measured (Figure 1). Then, the combination ratio between the metal and ligand was determined by means of the Job[11-12] and mole ratio[13-15] methods. During the study, two absorption maxima, which are salient features for the resulting compounds, were exploited. Thus, for the first complex compound (Tl^{III}–7–iodo–8–hydroxyquinoline 5 sulphonic acid) $\lambda = 385$ nm and for the second (Tl^{III}–8–hydroxyquinoline–7–sulphonic acid) $\lambda = 370$ nm.

Several equimolar aqueous solutions of ligand and metal (as $Tl(NO_3)_3$) having the concentrations 3.02×10^{-3} and 4.98×10^{-3} M, for the first and the second compound, were made. Different amounts of these solutions were taken according the methods applied.

Before each spectrophotometric measurement, the final volume which was reached by water addition, was 100 ml. The experimental results are set out in the Figures 2 and 3. From these plots, is drawn the conclusion that the combination ratio between the

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(1) F. Feigl, *Nature*, *161*, 436 (1948).
(2) F. Feigl and L. Baumfeld, *Analyt. Chim. Acta*, 3, 83 (1949).
(3) R.G.W. Hollingshed, *Analyt. Chim. Acta*, *12*, 401 (1955).
(4) T. Moeller and A.J. Gohen, *Analyt. Chem.*, *22*, 686 (1950).
(5) M. Borrel and R. Paros, *Analyt. Chim. Acta*, *4*, 267 (1950).
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(10) A.I. Busev and V.G. Tiptsova, *Zhur. analit. Khim*, *XIV*, 28 (1959).
(11) P. Job, *Ann. Chim.* (*France*), (*10*)9, 113 (1928).
(12) P. Job, *Ann. Chim.* (*France*), (*11*)6, 97 (1936).
(13) J.A. Yoe and A. Jones, *Ind. Eng. Chem. Anal. Ed*, *16*, 11 (1944).
(14) A.S. Meyer Jr and G.H. Ayres, *J. Amer. Chem. Soc.*, *77*, 2671 (1955).
(15) A.S. Meyer jr. and G.H. Ayres, *J. Amer. Chem. Soc.*, *79*, 49 (1957).

metal and ligand, for both complex compounds, is 1:3.

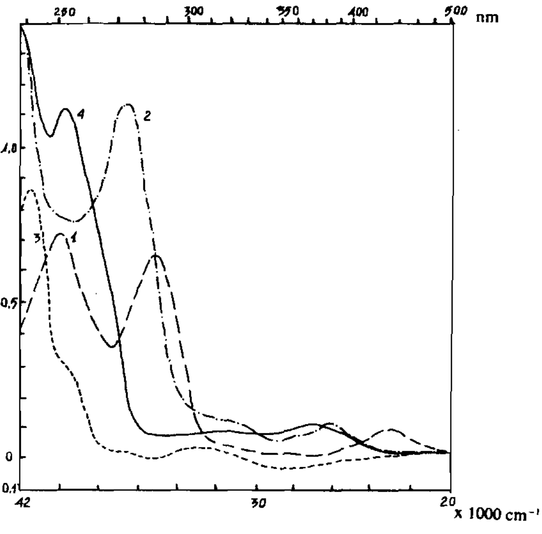

Figure 1. Absorption spectra of the ligands and chelate compounds:

1. 7-iodo-8-hydroxyquinoline-5-sulphonic acid (1.52×10^{-5} M).
2. Tl^{III}-7-iodo-8-hydroxyquinoline-5-sulphonic acid (complex concn. 2.49×10^{-5} M).
3. 8-hydroxyquinoline-7-sulphonic acid (1.52×10^{-5} M).
4. Tl^{III}-8-hydroxyquinoline-7-sulphonic acid (complex concn. 2.49×10^{-5} M).

The absorption maximum for Tl^{3+} (2.49×10^{-5} g.ion/l) is at 207 nm.

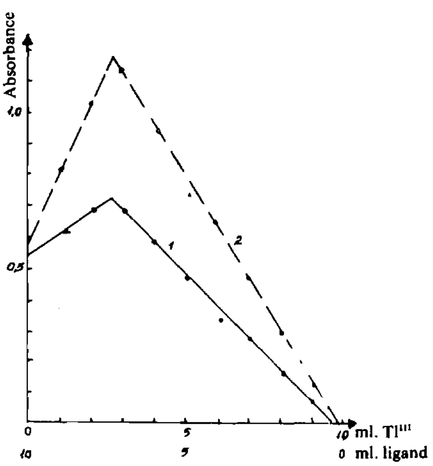

Figure 2. Job's method applied to the complex compounds studied.

1. Tl^{III}-7-iodo-8-hydroxyquinoline-5-sulphonic acid.
2. Tl^{III}-8-hydroxyquinoline-7-sulphonic acid.

To calculate the constants of stability, characterizing the two compounds, the Nagakura method[16-17] was used.

Two different solutions of $Tl(NO_3)_3$ having the concentrations 4.98×10^{-3} and 4.98×10^{-4} g.ion/l (as Tl^{3+}) and only one solution for each organic ligand with the concentration of 1.66×10^{-3} M, were made.

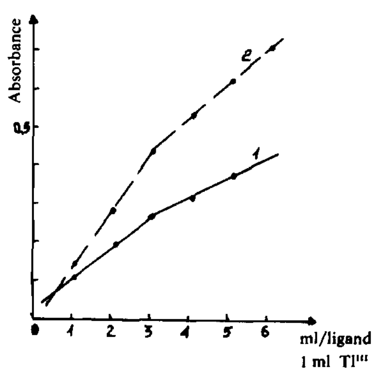

Figure 3. The mole ratio method used for the given complex compounds:

1. Tl^{III}-7-iodio-8-hydroxyquinoline-5-sulphonic acid.
2. Tl^{III}-8-hydroxyquinoline-7-sulphonic acid.

Then, the following separate solutions were utilized for the sectrophotometric measurements:

$A_1 = 5$ ml ligand A+95 ml water
$A_2 = 5$ ml ligand A+5 ml $Tl^{3+}(4.98\times10^{-3})$+90 ml water
$A_3 = 5$ ml ligand A+5 ml $Tl^{3+}(4.98\times10^{-4})$+90 ml water
$B_1 = 5$ ml ligand B+95 ml water
$B_2 = 5$ ml ligand B+5 ml $Tl^{3+}(4.98\times10^{-3})$+90 ml water
$B_3 = 5$ ml ligand B+5 ml $Tl^{3+}(4.98\times10^{-4})$+90 ml water

where A is 7–iodo–8–hydroxyquinoline 5 sulphonic and B is 8–hydroxyquinoline–7–sulphonic acid.

The absorptions of each separate solution, for different temperatures, were determined, and the data obtained are presented in Table I. The calculated constants of stability (K_{stab}) are shown in Table II.

Table I. The dependence of absorbance on teh composition of solutions.

Solution	Absorbance 23.2°C	32.0°C	38.8°C
A_1	0.145	0.136	0.132
A_2	0.788	0.778	0.770
A_3	0.775	0.762	0.750
B_1	0.240	0.238	0.235
B_3	0.685	0.680	0.672
B_3	0.648	0.640	0.630

Table II. Average values of the constants of stability corresponding to the compounds studied.

Compound	K_{stab}(l/mole) 23.2°C	32.0°C	38.8°C
$(C_9H_5NO_4SI)_3Tl$	1.641×10^7	1.287×10^7	1.060×10^7
$(C_9H_6NO_4S)_3Tl$	3.810×10^6	3.408×10^6	3.171×10^6

By means of the constants of stability, the thermodynamic parameters free energy (ΔF), enthalpy (ΔH)

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(16) S. Nagakura, *J. Amer. Chem. Soc.*, *76*, 3070 (1954).
(17) S. Nagakura, *J. Amer. Chem. Soc.*, *80*, 520 (1958).

Table III. Thermodynamic parameters calculated for the two complex compounds.

Compound	$-\Delta F$(cal/mole) 23.2°C	32.0°C	38.8°C	$-\Delta H$(cal/mole)	$-\Delta S$(cal/deg.mole)
$(C_9H_5NO_4SI)_3Tl$	9823.349	9981.123	10089.455	9435	15.143
$(C_9H_6NO_4S)_3Tl$	8960.730	9145.405	9328.804	8445	20.388

and entropy (ΔS) were estimated. Thus, for the estimation of ΔF, the following relations were employed:

$$\Delta F = RTlnK_{stab} \qquad (1)$$

while ΔH and ΔS were obtaining by plotting ΔF versus T, in accordance with the equation:

$$\Delta F = \Delta H - T\Delta S \qquad (2)$$

The results are presented in Table III.

2. *Elemental Analyses.* To confirm the combination ratio between the metal and ligand determined spectrophotometrically, elemental analyses for metal and nitrogen were carried out.

The respective complex compounds have been prepared in the solid state by evaporation of equimolar solutions (metal: ligand = 1: 3) on a water bath followed by drying at 130°C. The experimental data are shown in Table IV. These values confirm the existence of the presumed compounds with the combination ratio between metal and ligand, 1: 3.

Table IV. Elemental Analyses.

Compound	% Tl calc.	% Tl obs.	% N calc.	% N obs
$(C_9H_5NO_4SI)_3Tl$	16.15	16.27	4.31	4.32
$(C_9H_6NO_4S)_3Tl$	23.22	23.32	6.16	6.18

3. *Infrared Spectra.* The i.r. spectra for the organic ligands and the corresponding complex compounds, in a solid state, are shown in Figure 4.

As can be observed from these spectra, the positions of the vibration bands are not much different between the ligands and the complex compounds. There are some differences from the point of view of their magnitude.[18-20]

The characteristic bond vibrations C–O (1190 cm^{-1}) and C–N, in aromatic ring (1360-1310 cm^{-1}) are shifted a little to lower frequencies. This may be explained by the fact that the C–O and C–N bonds become a little longer, because, after formation, of the complex the oxygen and nitrogen atoms come somewhat nearer to the thallium ion, due to the new interactions between their electronic orbitals.

It was not possible to observe the disappearence of the O–H group vibration from hydroxyquinoline after formation of the metal-oxygen bond, because the O–H from the sulphonic group remains in the new molecule. The new O–Tl and N–Tl bonds which appear after the formation of the chelate compounds are not reflected in these spectra, because the characteristic vibrations are appear below 400 cm^{-1}.

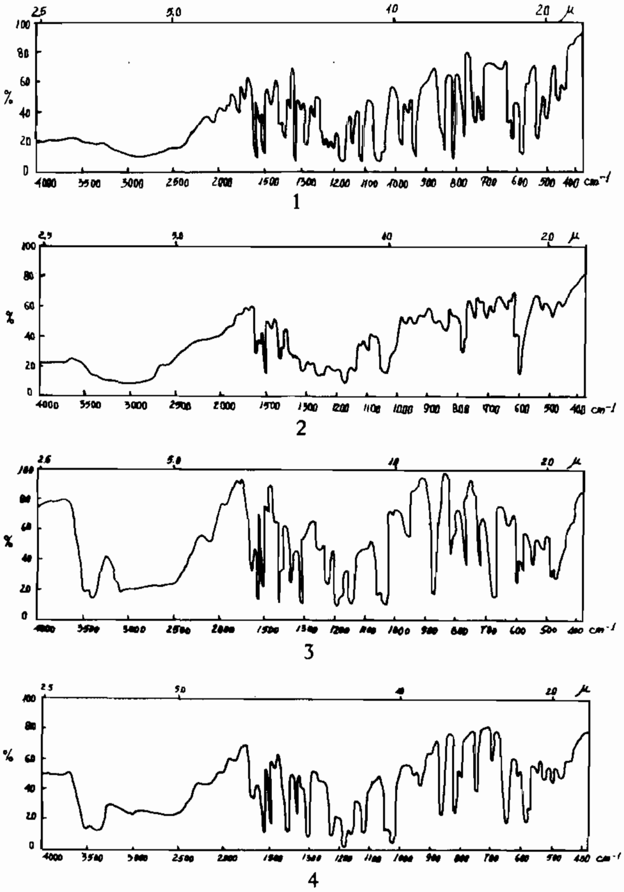

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Figure 4. The i.r. spectra for:

1. 7-iodo-8-hydroxyquinoline-5-sulphonic acid.
2. Tl^{III}-7-iodo-8-hydroxyquinoline-5-sulphonic acid.
3. 8-hydroxyquinoline-7-sulphonic acid.
4. Tl^{III}-8-hydroxyquinoline-7-sulphonica acid.

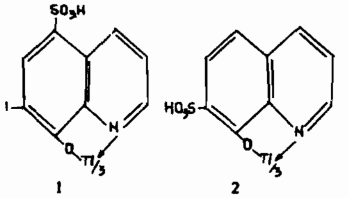

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Figure 5. The structural formulas for the chelate compounds investigated:

1. Tl^{III}-7-iodo-8-hydroxyquinoline-5-sulphonic acid.
2. Tl^{III}-8-hydroxyquinoline-7-sulphonic acid.

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(18) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », J. Wiley and Sons, New York, London.

(19) K.G. Stone, *J. Amer. Chem. Soc.*, *76*, 4997 (1954).

(20) R.G. Charles, H. Freiser, R. Friedel, L.E. Hilliard, and WM.D. Johnston, *Spectrochim. Acta*, *8*, 1 (1956).

Taking into account all of the above arguments, we can conclude that the complex compounds between Tl^{III} and 7–iodo–8–hydroxyquinoline–5–sulphonic and 8–hydroxyquinoline–7–sulphonic acids were formed, having the structural formula given in Figure 5. The compounds described above are not obtained directly in the solid state, as in the case of other oxinates, because the sulphonic group renders these compounds soluble. Nevertheless, following the method above, these chelate compounds may be prepared in the solid state.

These complex compounds may be used for the direct spectrophotometric detection of trivalent thallium. In contrast with the other oxine derivatives (which with the same ion give precipitates which must be rendered soluble by means of several organic solvents for spectrophotometric measurements) in this case these operations are not necessary, because these measurements are achieved directly in the initial solutions at the established molc ratio.