

**SPECTROPHOTOMETRIC STUDY ON THE BINARY SYSTEM
RHODIUM(III)-1,2,3-CYCLOHEXANETRIONEDIOXIME.
SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM(III).**

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Abstract

The paper presents an optical study of the binary system Rh(III)-1,2,3-cyclohexanetrionedioxi-me. The formation conditions and the analytical application of the formed complex for spectrophotometric determination of Rh(III) were studied. The composition of the Rh(III) complex with this particular α -dioxime was determined by the continuous variation method. Its instability constant is $K_{\text{inst}} = 3.70 \cdot 10^{-10} \text{ mol}^2 \text{ L}^{-2}$.

Introduction

Various α -substituted dioximes as dimethylglyoxime, α -benzyldioxime and furyldioxime were previously used for preparative purposes, as well as for the spectrophotometric determination of Rh(III).¹⁻⁵ However, the alicyclic α -substituted dioximes, such as 1,2,3-cyclohexanetrionedioxi-me were less used in the analytical chemistry of Rh(III) than the other platinic metals.

The present paper reports the study on the formation, the optical properties and the structure of the Rh(III) chelate with 1,2,3-cyclohexanetrionedioxi-me (LH₂). This chelate was proposed for spectrophotometric determination of Rh(III).

Results and discussion

Rh(III) reacts with 1,2,3-cyclohexanetrionedioxi-me at high temperature to form yellow complex compound.

The factors influencing the formation of the new compound are:

- the time period in which the colour of the new product stabilizes is about 10 minutes;
- the optimum pH for the formation is 5. The other pH values do not certify the formation in the studied system of the other more stable coloured compounds.

The electronic spectrum of the complex compound is presented in Figure 1. From

the obtained data one can see that the most favourable wavelength is 470 nm (corresponding to 21270 cm^{-1}).

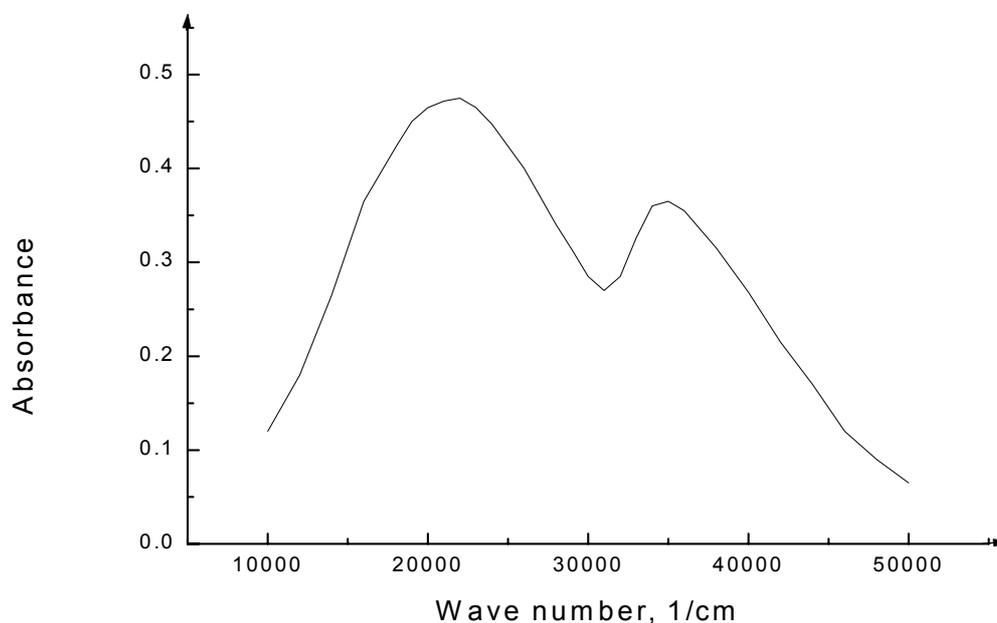


Figure 1. Electronic spectrum of the $\text{RhCl}_3\text{-LH}_2$ system at $\text{pH}=5$

The composition of the Rh(III) chelate was determined by the continuous variation method.

Figure 2 presents the results of the Job's method application for the three isomolar solution series ($1\cdot 10^{-3}\text{ M}$, $1/2\cdot 10^{-3}\text{ M}$, $1/3\cdot 10^{-3}\text{ M}$) at $\text{pH} = 5$ and $\lambda = 470\text{ nm}$. One can notice that each of the three curves reaches a single maximum value corresponding to the same molar ratio, which proves that a single complex compound was formed in the binary system and that its molar ratio is $\text{Rh:LH}_2 = 1:2$.

To calculate the instability constant of the complex compound the Job's method has been used for two nonisomolar solutions series ($\text{RhCl}_3\ 1/3\cdot 10^{-3}\text{ M}$; $\text{LH}_2\cdot 10^{-3}\text{ M}$ and $\text{RhCl}_3\ 1/2\cdot 10^{-3}\text{ M}$; $\text{LH}_2\cdot 1\cdot 10^{-3}\text{ M}$).

The results concerning the instability constant K_{instab} , which are presented in Table 1, show that the new complex compound is stable under the experimental conditions that were used.

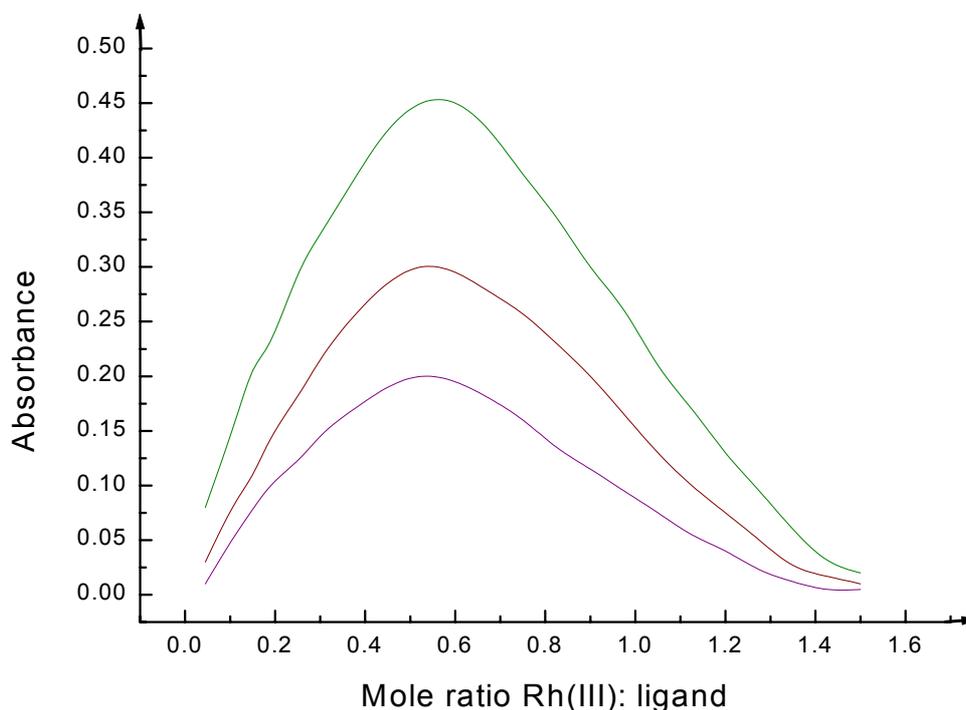


Figure 2. Variation of the absorbance for isomolar series: $1 \cdot 10^{-3}$ M (the upper curve),

$1/2 \cdot 10^{-3}$ M (the curve in the middle) and $1/3 \cdot 10^{-3}$ M (the lower curve)

In Table 1, C is the molar concentration of RhCl_3 , p is the molar concentration ratio of LH_2 and RhCl_3 , x is the LH_2 mole ratio corresponding to minimum absorbance and $K_{\text{instab.}}$ is the instability constant of the complex compound according to the Job's formula:

$$K_{\text{instab.}} = C^{m+n-1} p^{n-1} [(pm+n)x-n]^{m+n} / [m^{n-1} n^{m-1} (p-1)^{m+n-1}] [n-(m+n)x],$$

m and n being the molar indices of Rh(III) and LH_2 respectively.

The charge determination for the complex ion has been achieved by means of the electrophoretic migration method in presence of a weak solution of potassium nitrate. A small quantity of urea was introduced into the solution containing the complex compound corresponding to the molar ratio 1:2. After 15 minutes the displacement of the coloured complex ion towards the anode could be observed, thus proving the existence of its negative charge.

Table 1. Values of the instability constant

C (mol·L ⁻¹)	p	x	K _{instab.} (mol ² ·L ⁻²)	K _{m, instab} (mol ² ·L ⁻²)
1/3·10 ⁻³	3	0.43	1.58·10 ⁻¹⁰	3.70·10 ⁻¹⁰
1/2·10 ⁻³	2	0.52	5.82·10 ⁻¹⁰	

These results prove the following formula: [Rh(LH)₂Cl₂]⁻, in which LH acts as a bidentate ligand, using the nitrogen atoms as donor atoms in the coordination.

In order to establish the coordination geometry and the symmetry for the new complex compound, a spectral analysis in the visible and UV range has been done.

The correspondence between the absorption bands occurring at 21270 cm⁻¹ (470 nm) and 34480 cm⁻¹ (290nm) in the investigated complex [Rh(LH)₂Cl₂]⁻ (Figure 1) and the ones found for the trans octahedral complexes⁶ such as [Rh(NH₃)₄Cl₂]⁺,⁷ [Rhen₂Cl₂]⁺,⁸ [Rh(DH)₂Cl₂]⁻,⁹ leads us to the conclusions that the coordinative compound that appears from the binary system Rh(III)-1,2,3-cyclohexanetrionedioxime is stabilized by short strong intramolecular O-H...O hydrogen bridges and the monodentate Cl⁻ ligands are situated in trans to each other, so that [Rh(LH)₂Cl₂]⁻ has an octahedral coordination geometry and a tetragonal symmetry, belonging to the D_{4h} point group¹⁰ consequently (actually, the point group is either C_{2h} or C_{2v}, but the internal structure of the ligand may be neglected).

Taking into account the results of the study above, which confirm high enough stability of this complex compound, it has been used for analytical purposes, namely for establishing a method of spectrophotometric determination of Rh(III).

The experimental results of the absorbance variation versus Rh(III) concentration is presented in Figure 3. The Beer's law was respected over the concentration range 0.2 – 12.4 mg/L.

In order to test the validity of the method, the experimental data were statistically interpreted. The error corresponding to eight determinations ($t_{0.95} = 2.447$) is $m = (28.213 \pm 0.2772) \cdot 10^{-4}$, meaning that the proposed method is reproducible and accurate and it is not affected by systematic errors, so that [Rh(LH)₂Cl₂]⁻ can be used

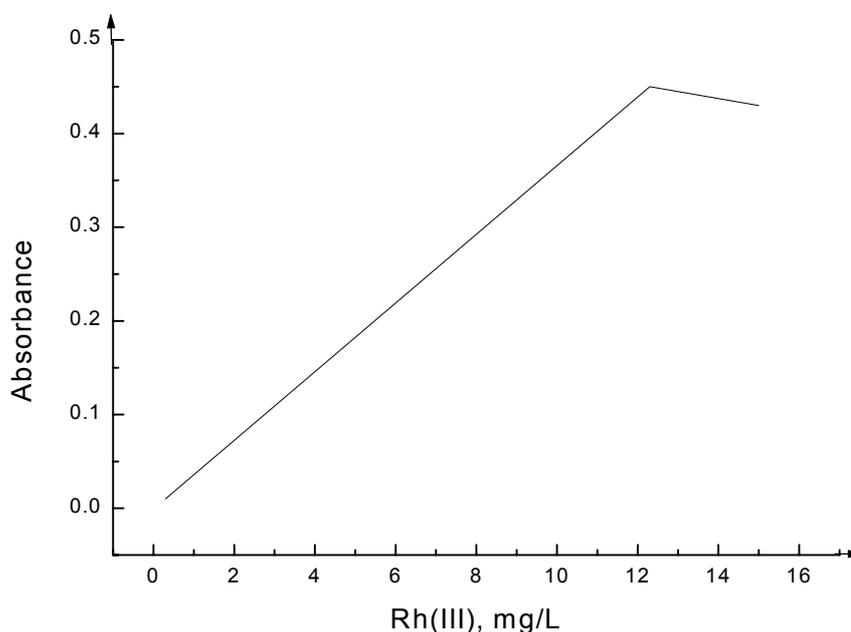


Figure 3. Variation of the absorbance versus Rh(III) concentration

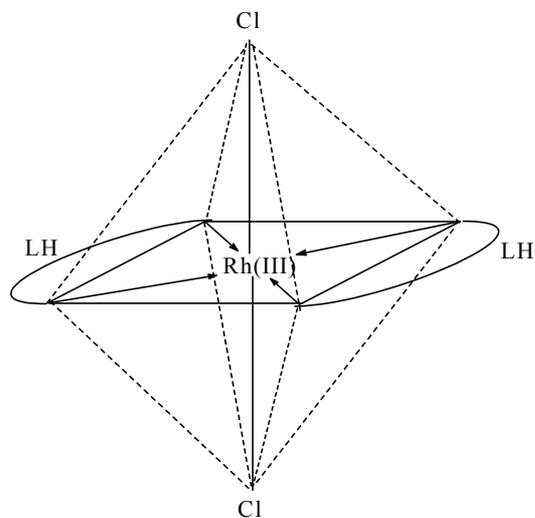
indeed for the spectrophotometric determination of Rh(III).

Other platinum metals ($M = Pd, Pt$), which form sparingly soluble $[M(\text{DioximeH})_2]$ complexes do not interfere in the spectrophotometric determination of rhodium in the $[\text{Rh}(\text{LH})_2\text{Cl}_2]^-$ form. From the reaction's feature between Rh(III) and LH_2 it has been ascertained that it is possible to recognize the Rh(III) in ruthenium's presence up to the ratio $\text{Rh(III):Ru(III)} = 1:20$ and in gold's presence up to the ratio $\text{Rh(III):Au(III)} = 1:28$.

Conclusions

On the basis of all the results obtained by the optical study of the binary system Rh(III)-1,2,3-cyclohexanetrionedioxime, the structure presented below was proposed for the new complex compound, $\text{trans-}[\text{Rh}(\text{LH})_2\text{Cl}_2]^-$.

It also has been proved that $\text{trans-}[\text{Rh}(\text{LH})_2\text{Cl}_2]^-$ may be used for analytical purposes, namely for establishing a reproducible and accurate method of spectrophotometric determination of Rh(III).



Experimental

All the chemicals we used were of analytical grade: RhCl_3 (Merck p.a.), α -1,2,3-cyclohexanetrionedioxiime (LH_2) was obtained by isonitrosation of the cyclohexanone with gaseous ethyl nitrite and it was double recrystallized from alcohol, m. p. 224 °C (decomp.). The electronic spectra were performed in aqueous solutions using an Ocean Optics spectrophotometer.

General procedure: Experiments were done with an aqueous solution of RhCl_3 ($1 \cdot 10^{-3}$ M, $1/2 \cdot 10^{-3}$ M, $1/3 \cdot 10^{-3}$ M) with the aqueous solution of LH_2 ($1 \cdot 10^{-3}$ M, $1/2 \cdot 10^{-3}$ M, $1/3 \cdot 10^{-3}$ M) by solving the ligand. As a consequence of the reaction taking place between Rh(III) and the ligand LH_2 , yellow coloured complex compound was obtained, then the samples were heated for 10 minutes. The solutions were cooled and brought to 25 mL in calibrated flasks.

References and Notes

1. N. Gupta, D. N. Patkar *J. Ind. Chem. Soc.* **1979**, 56, 839–842.
2. A. Wassay, R. K. Bansal, M. K. Satake, B. K. Puri *Bull. Chem. Soc. Jpn.* **1983**, 56, 3603–3609.
3. K. Shrivah, S. K. Sindhwani *Bull. Soc. Chim. Fr.* **1986**, 5, 737–742.
4. K. Shrivah, S. K. Sindhwani *Bull. Chem. Soc. Jpn.* **1985**, 58, 3560–3566.
5. C. Varhelyi, F. Makkay, A. Benko, E. Kazinczy *Chem. Analit.* **1992**, 37, 21–226.
6. A. B. P. Lever *Inorganic Electronic Spectra*, Elsevier, N. Y., **1984**, pp. 458–480.
7. W. D. Blanchard, W. R. Mason *Inorg. Chim. Acta* **1978**, 28, 159–164.
8. S. A. Johnson, F. Basolo *Inorg. Chim.* **1962**, 4, 925–932.
9. N. A. P. Kane-Maguire, P. K. Miller, L.S. Trzupcek *Inorg. Chim. Acta* **1983**, 76, 179–184.
10. A. Vincent *Molecular symmetry and group theory*, John Willey, N. Y., **1992**, pp. 100–111.

Povzetek

Delo prikazuje optične raziskave v binarnem sistemu rodij(III)-1,2,3-cikloheksantriondioksim. Na osnovi vseh rezultatov te študije je predlagana nova kompleksna spojina *trans*-[Rh(LH)₂Cl₂]⁻, struktura z oktaedrično koordinacijsko geometrijo in **D**_{4h} tetragonalno simetrijo. Dokazano je, da ta kelat lahko služi za spektrofotometrično določanje Rh(III).