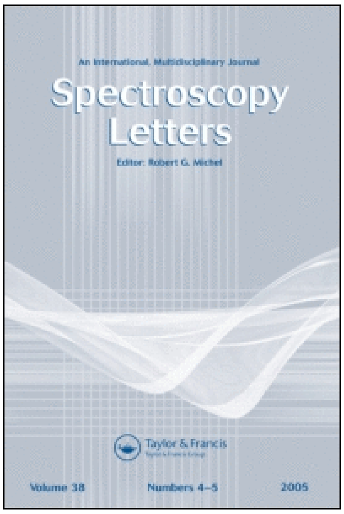

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Spectral Studies on Cyclic Chromotropic Acid Tetramers and Their Interaction with Metal Ions

J. Duda[a]; A. Łacka[a]
[a] Institute of General Food Chemistry, Technical University of Lodz, Lodz, Poland

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SPECTRAL STUDIES ON CYCLIC CHROMOTROPIC ACID TETRAMERS AND THEIR INTERACTION WITH METAL IONS

Key words: chromotropic acid, formaldehyde, glyoxylic acid, titanium (IV) complexes, cyclotetrachromotropylene derivatives

J.Duda and A.Łącka

Institute of General Food Chemistry, Technical University of Lodz, 90-924 Lodz, Poland

ABSTRACT

With comparable molar quantities, chromotropic acid reacts with compounds containing aldehyde groups -CHO e.g. with formadehyde or glyoxylic acid to form cyclic compounds with rings containing four chromotropic acid fragments – cyclotetrachromotropylene derivatives. The cyclic compounds, due to the presence of a cavity in the molecule, can play the part of host and complex smaller molecules, which has been confirmed on the basis of triethylamine by the ^{1}H-NMR measurements. Using spectrophotometric method the stability constant of 1:1 complex formed between Ti(IV) and cyclic compound chromotropic acid with formaldehyde has been determined - $K = (9{,}0 \pm 0{,}1) \cdot 10^4$.

INTRODUCTION

The reaction between chromotropic acid and formaldehyde has been known since 1937[1] and used to determine trace quantities of formaldehyde, but the nature

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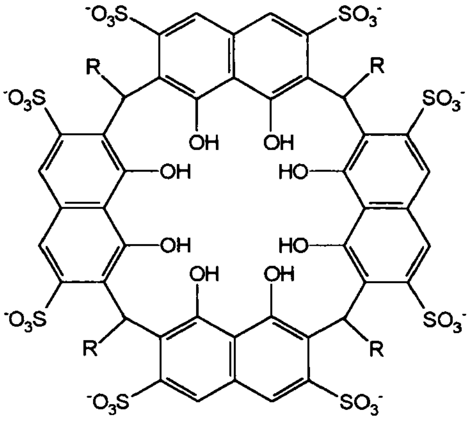
of the coloured compound resulted from this process has not been unmistakably recognised as yet, various structures being ascribed to this compound. Georghiu[2] has found a stepwise reaction of molecule addition resulted in a compound with polymeric structure, while Poh[3] has ascribed a structure of a cyclic tetramer to the resultant compound if the reaction takes place in excess formaldehyde. Next papers by this author described the reaction of the obtained tetramer as a host in complexing metal ions and compounds such as amines and sugars playing the part of guest[4-6].

The process between chromotropic acid and formaldehyde is characteristic of compounds possessing aldehyde groups -CHO. Thus, it is possible to obtain products of this reaction with other organic compounds containing this group, e.g., glyoxalic acid CHOCOOH.

In this study, a derivative of cyclic chromotropic acid tetramer with glyoxylic acid was obtained.



1. R = H
2. R = COOH

The properties of this tetramer **2** and of the tetramer with formaldehyde **1** were examined and compared in complexation reactions with amines and metal ions.

EXPERIMENTAL

Preparation of Cyclic Derivatives of Chromotropic Acid

Aqueous solutions of chromotropic acid and formaldehyde or glyoxylic acid were mixed in proportion 1:5. After about 7 days, red-brown products in the form of plastic amorphous precipitate were obtained. The raw products were practically pure, which was verified by thin layer chromatography, using the following developing systems: water:methanol:acetone (3:2:1) and methanol:n-butanol (2:3). The resultant chromatograms showed no traces of fluorescence of free chromotropic acid, while the compounds under investigation appeared on the chromatograms in the form of elongated spots, which was due to the multi-step dissociation of the compounds obtained.

The raw products were crystallised from a water-ethanol solution. Samples with glyoxalic acid were dried under vacuum over P_2O_5, while those with formaldehyde in an oven at a temperature of 105°C.

Spectra

NMR spectra were recorded by means of a Bruker apparatus and UV-VIS spectra were taken with a Hewlett Pacard HP 8453 spectrophotometer.

RESULTS AND DISCUSSION

Figs 1 and 2 show changes in the UV-VIS spectra of chromotropic acid after addition of formaldehyde and glyoxalic acid. The changes appear immediately after mixing the solutions, but after a longer time they become more intensified, resulting in the formation of final solid compounds. Aqueous solutions of these compounds alter their colour many times depending on changes in the medium acidity, which points to a multi-step dissociation of subsequent acidic groups of these derivatives. The values of dissociation constants pK_i were calculated from the analysis of the UV-VIS spectra obtained with various pH values (Figs 3 and 4). The results are given in Table 1.

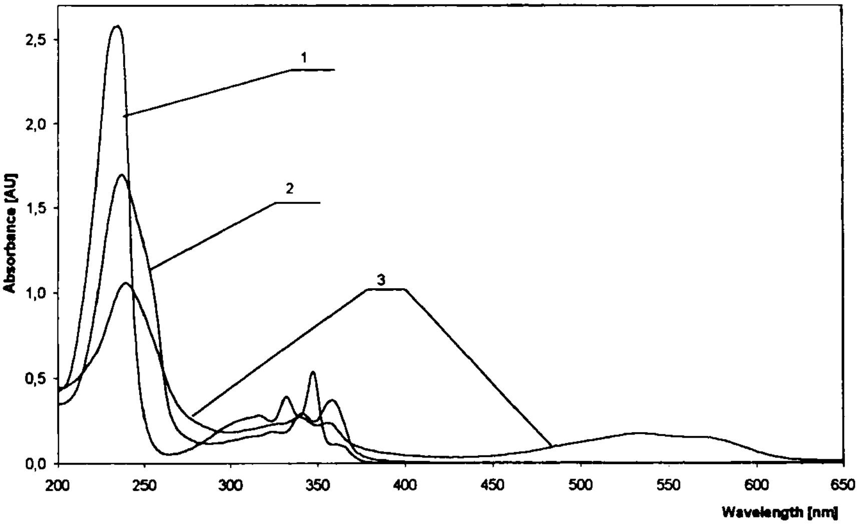


FIG. 1. UV-VIS spectra (1 – chromotropic acid, 2 – chromotropic acid + formaldehyde after 60 min., 3 – chromotropic acid + formaldehyde after 150 hours).

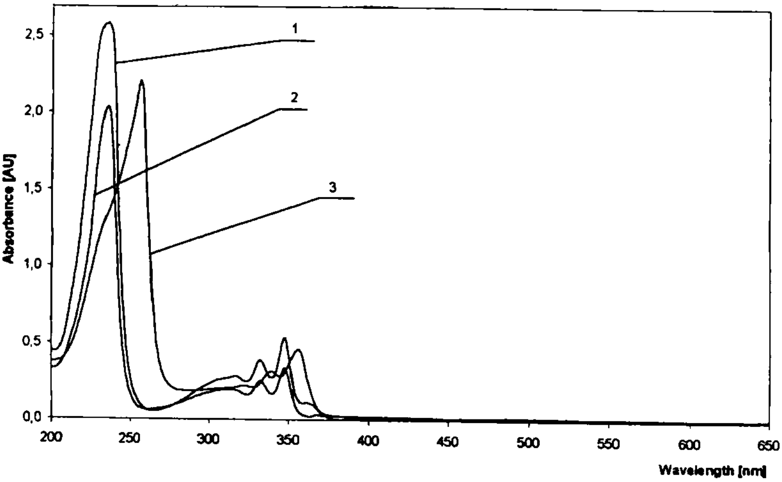


FIG. 2. UV-VIS spectra (1 – chromotropic acid, 2 – chromotropic acid + glyoxylic acid after 60 min., 3 – chromotropic acid + glyoxalic acid after 160 hours).

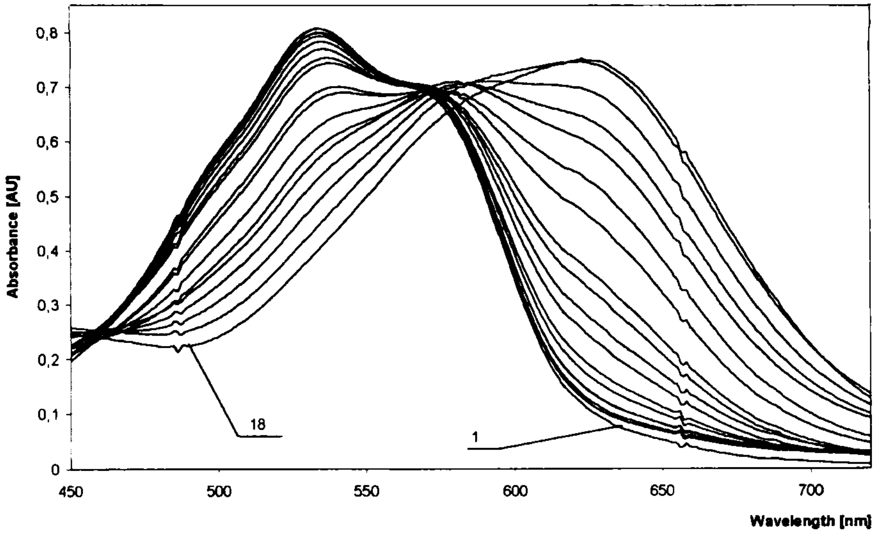


FIG.3. UV-VIS spectra of cyclotetrachromotropyle solution (**1**) with a concentration of 4 · 10^{-5} mol·dm^{-3} with various pH of the solution (1 - 3.8, 2 - 5.2, 3 - 6.0, 4 - 6.6, 5 - 6.8, 6 - 7.2, 7 - 7.7, 8 - 8.1, 9 - 8.3, 10 - 8.9, 11 - 9.2, 12 - 9.8, 13 - 10.3, 14 - 10.8, 15 - 11.1, 16 - 11.5, 17 - 12.1, 18 - 12.4)

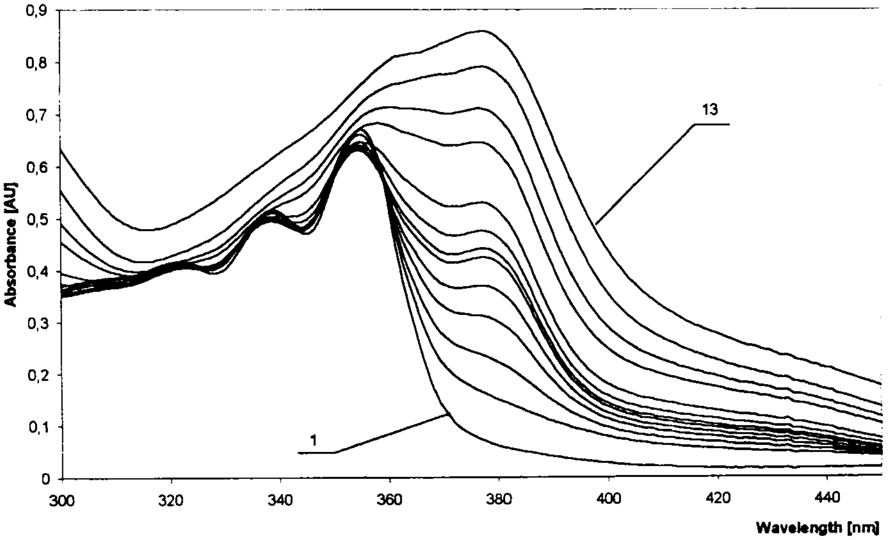


FIG.4. UV-VIS spectra of cyclotetrachromotropyle solution (**2**) with a concentration of 4 · 10^{-5} mol·dm^{-3} with various pH of the solution (1 - 3.4, 2 - 4.2, 3 - 4.9, 4 - 5.4, 5 - 6.0, 6 - 6.6, 7 - 7.0, 8 - 7.7, 9 - 8.2, 10 - 9.3, 11 - 10.0, 12 - 10.9, 13 - 12.1)

TABLE 1. Dissociation constants determined from the changes in absorption

Compound	pK_1	pK_2	pK_3	pK_4	pK_5
cyclotetrachromotropylene (1)	6.5	8.4	10.3	11.3	
cyclotetrachromotropylene (1)*	6.5	8.8	10.5	11.5	
cyclotetrachromotropylene (2)	4.5	6.3	8.5	10.1	>12

* determined by Poh[4]

Four dissociation constants of compound **1** suggest that only one of -OH groups is dissociated in each naphthalene ring. The dissociation of the second group due to the intramolecular hydrogen bond takes place at a higher pH (for chromotropic acid $pK_2 > 13$[7]).

The first dissociation constant of compound **2** illustrates the dissociation of carboxyl groups, while the others refer to subsequent dissociations of hydroxyl groups, similarly as in the case of compound **1**.

The interactions between triethylamine and derivatives **1** and **2** are illustrated by ^{1}H-NMR spectra shown in Fig. 5. The shift effects of protons in CH_2 and CH_3 groups of amine are given in Table 2.

The product resulted from the reaction between chromotropic acid and formaldehyde **1** is a weaker acid than the second examined compound **2**. The effect of amine protonation by acid **1** is unnoticeable and the spectrum shows proton signal broadening resulting from the dominating effect of proton shielding in CH_2 and CH_3 due to the amine penetration into the cyclic compound cavity.

In the case of the product resulted from the reaction between chromotropic acid and glyoxylic acid **2**, there is a shift of signals towards negative values (protonation effect) and noticeable band broadening due to amine complexation within the cavity of the compound under investigation. The results obtained confirm the cyclic structure of the obtained products.

FIG.5. NMR spectra : 1 – $N(C_2H_5)_3$ amine, 2 – amine + 1, 3 – amine + 2.

Chromotropic acid is best characterised by its capability to form complexes with Fe^{3+} and Ti(IV) ions[8, 9] and the obtained cyclic derivatives of this acid should possess a similar feature. Complex formation between compound 1 and metal ions was also examined. The complex formation is associated with a clear change in colour of solutions from pink to lilac for complexes with Ti(IV) ions or gray-blue

TABLE 2. The shift effects of protons in CH_2 and CH_3 groups of amine

Compound	Protons δ [ppm] CH₃	Δδ *	CH₂	Δδ *
amine $N(C_2H_5)_3$	1.005 1.034 1.063		2.600 2.630	
1	0.786 0.815 0.845	+0.221 +0.219 +0.218	2.614 2.642	-0.014 -0.012
2	1.064 1.094 1.123	-0.059 -0.060 -0.060	2.968 2.996	-0.368 -0.366

*- Δδ = δ(amine) - δ(complexed amine)

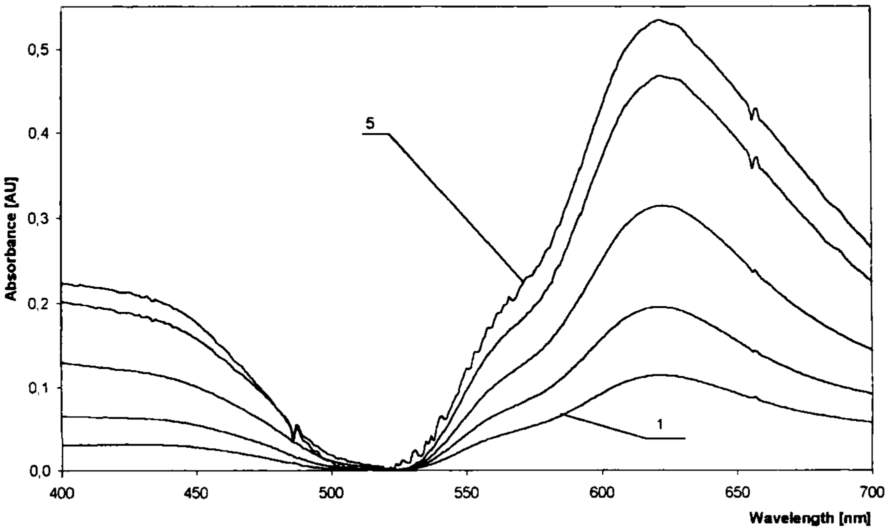


FIG.6.VIS spectra of Ti(IV) complexes with a concetration of 1.0 · 10^{-5} mol·dm^{-3} with cyclotetrachromotropylene (1) with a concetration of : 1) 0.5 · 10^{-5} mol·dm^{-3}, 2) 1·10^{-5} mol·dm^{-3}, 3) 2·10^{-5} mol·dm^{-3}, 4) 5·10^{-5} mol·dm^{-3}, 5) 10·10^{-5} mol·dm^{-3}.

for complexes with Fe(III) ions. This is connected with the combination of metal ions by -OH end of the molecule.

Since the band of the Ti(IV) complex is partly overlapped by the band of ligand **1**, the independent spectrum of complexes (Fig.6) was obtained by substracting the free ligand spectrum from the spectrum obtained. From the relationship shown in Fig.6 it follows that there is formed a complex of 1:1 type, the calculated value of stability constant being $K = (9.0 \pm 0.1) \cdot 10^4$. As could be expected, the Ti(IV) complex is at least by one order of magnitude more stable than complexes with other metal ions[5].

REFERENCES

1. Eegriwe E. Reactions and Reagents for the Detection of Organic Compounds. Z. Anal. Chem. 1937; 110: 22-25.
2. Georghiou P.E., Ho Chi K. The Chemistry of the Chromotropic Acid Method for the Analysis of Formaldehyde. Can. J. Chem. 1989; 67: 871-876.
3. Poh B.L., Lim C.S., Khoo K.S. A Water-Soluble Tetramer from Reacting Chromotropic Acid with Formaldehyde. Tetrahedron Letters 1989; 30: 1005-1008.
4. Poh B.L., Lim C.S. Complexation of Amines with Water-Soluble Cyclotetrachromotropylene. Tetrahedron 1990; 46: 3651-3658.
5. Poh B.L., Seah L.H., Lim C.S. Complexations of Metal Cations with Cyclotetrachromotropylene in Water and Methanol. Tetrahedron 1990; 46: 4379-4386.
6. Poh B.L., Tan C.M. Contribution of Guest-Host CH-π Interaction to the Stability of Complexes Formed from Cyclotetrachromotropylene as Host and Alcohols and Sugars as Guests in Water. Tetrahedron 1993; 49: 9581-9592.
7. Banerjee A., Dey A.K. Metal Chelates of Uranium(VI) and Thorium(IV) with Disodium 1,8-Dihydroxynaphthalene-3,6-disulfonate. A Potentiometric Study. J. Inorg. Nucl. Chem. 1968; 30: 995-1003.
8. Rosotte R., Jaudon E. Colorimetric Determination of Titanium in Steel in the Presence of Vanadium by Chromotropic Acid. Anal. Chim. Acta 1952; 6: 149-165.

9. Purohit R., Devi S. Spectrophotometric Determination of Titanium(IV) Using Chromotropic Acid and a Flow Injection. Analyst. 1992; 117: 1175-1177.

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