European Journal of Chemistry 5 (2) (2014) 339-342

European Journal of Chemistry

Journal homepage: www.eurjchem.com

Cation binding by some pyranopyridothiazole derivatives

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ARTICLE INFORMATION

DOI: 10.5155/eurjchem.5.2.339-342.1003

Received: 15 December 2013
Received in revised form: 23 February 2014
Accepted: 25 February 2014
Online: 30 June 2014

KEYWORDS

Thiazole
Extraction
Stoichiometry
Complexation
Stability constants
Inclusion properties

ABSTRACT

The binding properties of a cyanopyranopyridothiazole (L1), aminothiazole (L2), iminothiazole (L3) and phenyliminothiazole (L4) derivatives toward some transition metal and heavy metal cations, have been investigated in methanol, followed by UV spectrophotometry absorption and conductivity determination. The stoichiometries of the formed complexes and their stability constants were determined by a digital data processing. The study of extraction properties from water into dichloromethane shows a lower extraction affinity for the metal picrates with L1, unlike L2-L4 which are better extracted and specially Fe(III) with L4.

1. Introduction

The pyranopyridothiazole derivatives are biologically interesting molecules which have established utility in the pharmaceutical compounds. These ring systems have a wide application range in the biological activities and the pharmacological actions [1-5], such as antibacterial [6,7] and inhibitory activities [8-10]. Otherwise, the pyranopyrido thiazole derivatives found a wide uses in the industry compounds and the chemistry of dyes and pigments such as laser technologies [11,12], colour and non-colour photographic processes [13], optical disk as recording media [14] and inks [15]. Recently, a different heterocyclic cyanine dyes have been reported as high sensitivity and low fogging information recording media of high reflectivity and carrier-to-noise ratio, laser disc media, laser-sensitive optical recording material. Besides their use as colorants [16], they have considerable potential for application in energy conversion [17]. Moreover, the structure activity studies revealed that the synthesized compounds are also important in many other fields. Referring to our previous work [18], attempts have been made in order to synthesize a new fused and isolated heterocyclic compounds, as well as some compounds of cyanine dyes like apocyanine and monomethine cyanine dyes [19].

2. Experimental

2.1. Instruments and materials

The UV spectra have been recorded on a Perkin Elmer Lambda 11 spectrophotometer. Methanol (Riedel-deHaën for HPLC), acetonitrile (SDS for HPLC, 0.03% water content) and dichloromethane (Fluka, purum) are commercial and used without further purification. The supporting electrolyte used in the determination of the stability constant is NEt_4Cl and NEt_4ClO_4 (Acros Organics). The chosen metal salts have been chlorides or perchlorates (Fluka, purum). The picrate salts employed in the extraction have been prepared as described in the literature [20,21].

2.2. Synthesis of thiazole derivatives (L1, L2, L3 and L4)

The synthesis of thiazole derivatives **L1**, **L2**, **L3** and **L4** have been achieved via interaction of 4,5-dihydro-2-ehylacetate-4-oxothiazole **L1** with benzilidenemalononitrile **L2**, amido acrylonitrile **L3** and amido cinnamonitrile **L4** according to Al-Ayed *et al.* [19] (Figure 1).

ISSN 2153-2249 (Print) / ISSN 2153-2257 (Online) © 2014 Eurjchem Publishing - Printed in the USA
http://dx.doi.org/10.5155/eurjchem.5.2.339-342.1003

Table 1. Stability constants log β_{xy} of the complexes of **L1**, **L2**, **L3** and **L4** with some transition metal cations in methanol at 25 °C, I = 10^{-2} M, ($0.01 \leq \sigma_{n-1} \leq 0.14$).

Ligands	M:L	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cr(II)	Mn(II)	Fe(III)	Pb(II)	Sn(II)
L1	1:1	- *	3.42	3.03	3.09	4.10	4.40	4.07	4.01	3.04
L2	1:1	4.10	3.30	3.19	-	-	-	3.20	-	-
L3	1:1	2.90	3.12	3.03	3.09	-	-	3.16	-	-
L4	1:1	2.10	3.85	3.19	3.65	-	3.01	3.50	-	4.05

* -: Absorbance changes too small to enable satisfactory fitting.

L1: Cyanopyranopyridothiazole **L2:** Aminothiazole

L3: Iminothiazole **L4:** Phenyliminothiazole

Figure 1. Chemical structure of ligand.

2.3. Stability constant measurements

The stability constants β_{xy} are the concentration ratios $[M_xL_y^{xn+}]/[M^{n+}]^x[L]^y$ following the general equilibrium:

$$yL + xM^{n+} \leftrightharpoons M_xL_y^{xn+} \qquad (1)$$

where M^{n+}: metal ion, L: ligand have been determined in acetonitrile and methanol by UV-absorption spectrophotometry at 25 °C.

The ionic strength has been maintained at 0.01 mol/L using Et_4NClO_4. The spectra of ligand solutions of concentrations ranging between 1×10^{-4} and 2×10^{-4} mol/L and increasing the metal ion concentration has been recorded between 220 and 400 nm. Generally the metal to ligand ratio R at the end of the titration did not exceed 20 and the equilibriums were quasi-instantaneous for all the systems. Adding the metal salts to the ligand has induced large spectra changes which were enough to allow the analysis of the resulting data using the program "Letagrop" [22]. The best values of the formation constants β_{xy} of the various complex species and their molar absorptivity coefficients for various wavelengths are deduced from the best fit between the experimental and the calculated UV spectra.

The best fit is reflected by the lowest value of U (the sum of U values for all given lambda) corresponding to the square sum of the difference between the experimental and the calculated absorbances ($U = \sum (A_{cal} - A_{exp})^2$). The β_{xy} values correspond to the arithmetic means of at least three independent experiments.

2.4. Conductimetric studies

While the complexation by a neutral ligand is not expected to dramatically alter the molar conductivity of a cationic species, the differences can usually be detected and so the conductance measurement of a ligand solution in to which a metal ion is added can be a useful rapid means of establishing the stoichiometry of a complex ion species. Thus, this procedure was followed to obtain preliminary estimations of the metal ligand ratio in the complexes formed by the heterocyclic amine in methanol solution [23,24].

2.5. Extraction studies

The extraction experiments of alkali metal picrates from water into dichloromethane is performed according to a literature procedure [23]. Equal volumes (5 mL) of neutral aqueous solutions of metal picrate (2.5×10^{-4} mol/L) and CH_2Cl_2 solution (5 mL) of ligand (2.5×10^{-4} mol/L) have been mixed under magnetic agitation for 24 hours and then left standing for 1 hour in order to obtain a complete separation of the two phases.

The concentration of metal picrate remaining in the aqueous phase has been determined from the absorbance A at 355 nm. The percentage extraction (%E) was derived from the following expression in which A_0represents the absorbance of the aqueous solution of a blank experiment without ligand:

$$\%E = 100(A_0 - A)/A_0 \qquad (2)$$

3. Results and discussion

3.1. Complexation of metal cations in methanol

The complexation study of alkali and alkaline earth cations with **L1**-**L4** shows no affinity toward these cations. However, the mononuclear complexes (1:1) could be shown with the transition metal cations. The logarithms of the stability constants log β_{xy} and the stoichiometries for the different complexes formed by the ligand with some transition metals in methanol are given in Table 1.

The transitions metal cations studied in this work show affinities of complexation with the **L1**, **L2**, **L3** and **L4** despite of its total absence with the monovalent and divalent cations (alkaline and alkaline earth cations). This is likely due to the difference in hardness of the considered cations.

The selectivity profile of the ligand **L1** in the transition metal series shows an affinity in case of iron and chromium complexing in methanol, while this becomes an affinity for cobalt in methanol with the ligand **L2**. In the other hand, the stability of the complexes formed with **L3** are at the same order of magnitude, which shows that this complexation is not affected by the effect of the size in the case of the studied transition metal cations (Figure 2).

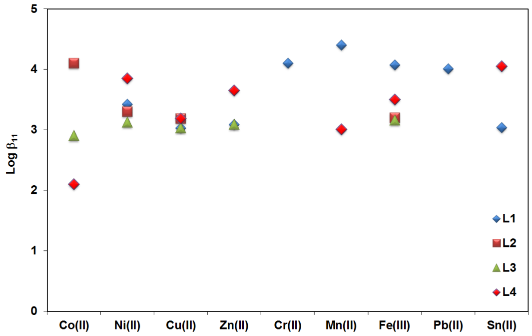

Figure 2. Stability constants log β_{11} (determined in methanol) for some transition metal and heavy metal cations with **L1**-**L4**.

Similarly ligand **L4** for stability of the complexes formed with Ni(II) shows an improved stability in methanol and lower complexation with Cu(II). It is worth to note that the passage from **L2** to **L4** decreases dramatically the Co(II) complexation (100 times). Moreover, the variation of the selectivity profiles suggests that a non-dominant cation size in the complexation phenomenon would be also an interesting factor. The basic pattern of the **L1** ligand has an affinity for complexing transition metal cations such as chromium and lead and shows the formation of mononuclear complex. The transition to cyanopyranopyridothiazole **L2** shows the formation of 1:1 complexes with Ni(II), Cu(II), Co(II), and Fe(III), while it has no affinity for Zn(II), Mn(II), Sn(II), Cr(II) and Pb(II) (Figures 3-5).

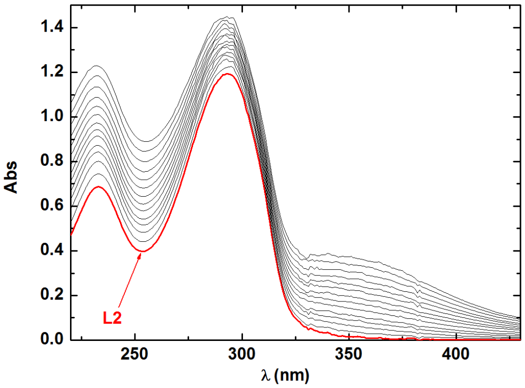

Figure 3. UV absorption spectra on complexation of Fe(III) with **L2** in methanol ($0 \leq R_{M/L} \leq 2$) at 25 °C.

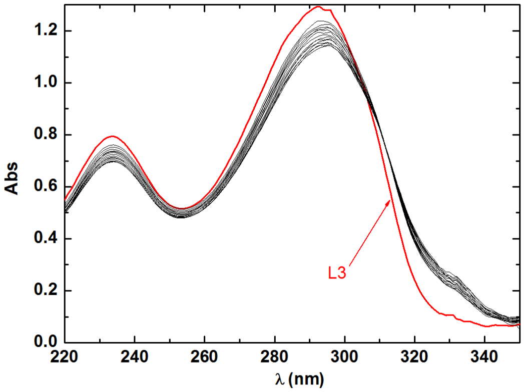

Figure 4. UV absorption spectra on complexation of Zn(II) with **L3** in methanol ($0 \leq R_{M/L} \leq 3$) at 25 °C.

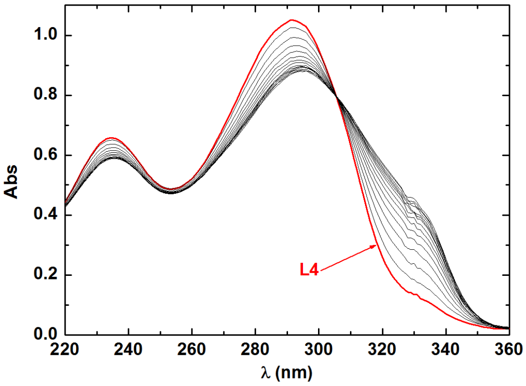

Figure 5. UV absorption spectra on complexation of Ni(II) with **L4** in methanol ($0 \leq R_{M/L} \leq 5$) at 25 °C.

By going against the imine function and oxidation of the ligand **L3** nitrile function, is accompanied by a decreased affinity of complexing with metal cations include Sn(II) and Mn(II).

However, **L4** shows affinity for the Sn(II) and theMn(II), this is probably due to the geometry of more flexible ligand in absence of the phenyl groups. It is noteworthy that the oxidation of the nitrile function of the ligand **L2** to the amide function of ligand **L3** increases the affinity of the Zn(II) cation complexing. On the other hand, the amide appears to decrease the ligand**L3** affinity complexation with the Cr(II), Pb(II), Sn(II) and Mn(II) comparing to the ligand **L1**. Furthermore, the stoichiometries of 1:1 complexes with **L1**-**L4** were confirmed by the conductimetric studies (Figure 6).

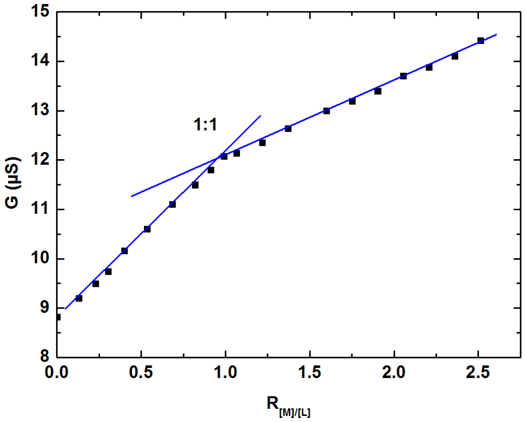

Figure 6. Conductometric titration in the case of **L4** with Cu(II).

Indeed, the stoichiometries determined by the conductometric study of **L1**-**L4** with the cations Ni(II) and Cu(II) have clearly confirmed those derived from the study by the UV spectrophotometry.

3.2. Extraction of metal picrates

A preliminary evaluation of the binding efficiency of pyranopyridothiazole derivatives has been carried out through by solvent extraction of metal picrates into dichloromethane at 20 °C under neutral conditions. The extraction percentages (%E) of some transition metal picrates by **L1**, **L2**, **L3** and **L4** from water into dichloromethane are given in Table 2.

In the series of the metal cations studied, the %E obtained with **L1** is lower (<10%), but for **L2**-**L4** the %E varies between 18 and 53%.

Table 2. Extraction percentages (%E) of some transition metal picrates by **L1**, **L2**, **L3** and **L4** from water into dichloromethane, at 25 °C (CL = CM = 2.5×10^{-4} mol/L).

Ligands	Co(II)	Ni(II)	Cu(II)	Zn(II)	Mn(II)	Fe(III)	Pb(II)
L1	9	6	5	≤1	≤1	4	≤1
L2	23	25	35	22	18	37	29
L3	36	28	32	27	24	46	35
L4	47	34	39	27	30	53	37

However, **L4** is a better extractant than **L2** and **L3** in the series of ligands studied. Looking at the series of cations considered, Fe(III) is a better extract then M(II) cations studied. So, the pyranopyridothiazole derivatives studied do not hexibe meaning selectivity (Figure 7).

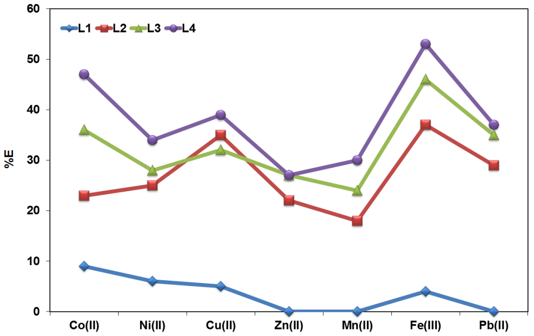

Figure 7. Trends of the extraction percentages (%E) for some transition metal and heavy metal picrates from water into dichloromethane with **L1-L4**.

4. Conclusion

The formation of mononuclear species to a ligand **L1**, **L2**, **L3** and **L4** complex with transition metals and heavy metals has been established in this work. The conductimetric titration confirmed mainly the stoichiometries of complexes formed in solution with **L1**, **L2**, **L3** and **L4** determined by the UV spectrophotometric study. However, the extraction study shows a lower extraction affinity for the metal picrates with **L1**, while **L2**-**L4** are better extracted and specially Fe(III) with **L4**.

Acknowledgement

Special thanks go to Prof. Dr. MalikaTrabelsi Ayadi (LACReSNE-Bizerte) for her invaluable support.

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