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Coumarin phthalonitriles: Synthesis and cation binding properties

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ABSTRACT

In this study, novel coumarin phtalonitriles derivatives **1-3** were synthesized and characterized via spectroscopic techniques IR, ^{1}H NMR, ^{13}C NMR, mass spectra and elemental analysis.The synthesis of these coumarin phtalonitriles was resulting from a nucleophilic aromatic substitution reaction between 4-nitrophtalonitrile and coumarins derivatives. The complexing properties of the coumarin derivatives toward alkali metal, alkaline earth metal, some transition metals and some heavy metal cations have been investigated in acetonitrile by means of UV spectrophotometry absorption and conductivity methods. Thus, the stoichiometry of the complexes formed and their stability constants were determined.

Indexing terms/Keywords

Synthesis of coumarin phtalonitriles, Stability constants, UV spectrophotometry, Cation binding properties

Academic Discipline And Sub-Disciplines

Organic and organometallic chemistry

SUBJECT CLASSIFICATION

Organic chemistry

1. Introduction

Coumarins are an extremely important family of heterocyclic compounds owing to their presence in a large variety of biologically active substances and their use as valuable agents for pharmaceuticals and fine chemicals. **[1,8]** Over the past several decades, synthesis and screening of coumarin compounds for drug discovery has been a vital subject of constant interest in organic and medicinal chemistry. **[9,11]** The extraction and complexation properties of the synthesized coumarin phtalonitriles towards alkali and alkaline earth metal cations have been investigated in acetonitrile by means of UV spectrophotometry and ^{1}HNMR spectroscopy. The results show the formation of ML and/or ML_2 species depending on the ligand and the cation. **[12, 19]** In this work, novel coumarin phtalonitriles derivatives have been synthesized. Their complexation of alkali metal, alkaline earth metal and transition metal cations, and the liquid liquid extraction of metallic picrate salts by coumarin phtalonitrile derivatives **1-3** were investigated, also. Efforts to quantify the complexation equilibrium were based on the use of UV spectrophotometry, although conductometric measurements were also used to obtain preliminary estimates of the stoichiometry of complexes formed.

2. EXPERIMENTAL

1. General

Melting points were determined using an Electrothermal apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were carried on a Varian Gemini 300 (300 MHz) spectrometer using TMS as internal standard (δ = 0 ppm). IR spectra were recorded on a Perkin-Elmer 398 Spectrophotometer. MS were recorded on a LC-MS-MS 8030 Shimadzu. Elemental analyses were performed on Perkin-Elmer 2400 elemental analyzer, and the values found were within ±0.3% of the theoretical values. The UV spectra were recorded on a Perkin Elmer Lambda 11 spectrophotometer. Acetonitrile (SDS for HPLC, 0.03% water content) and dichloromethane (Fluka, purum) were commercial and used without further purification. The supporting electrolyte used in the stability constant determinations was NEt_4ClO_4 (Acros Organics). The metal salts chosen were perchlorides (Fluka, purum).

2. Stability Constant Measurements

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

$$yL + xM^{n+} \rightleftharpoons M_xL_y{}^{xn+}$$

(Where M^{n+} = metal ion, L = ligand) were determined in acetonitrile by UV-absorption spectrophotometry at 25°C.

The ionic strength was been maintained at 0.01 mol.L^{-1} using Et_4NClO_4. The spectra of ligand solutions of concentrations ranging between 10^{-5} and 2×10^{-5} mol.L^{-1} and increasing concentration of metal ion were recorded between 220 nm and 460 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. Addition of the metal salts to the ligand induced spectra changes large enough to allow the analysis of the resulting data using the program “Letagrop”. **[20]** Best values for 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 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 a differences between experimental and calculated absorbances ($U = \sum (A_{cal} - A_{exp})^2$). The β_{xy} values correspond to the arithmetic means of at least three independent experiments. **[15, 16]**

3. Conductimetric studies

While 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 measurement of conductance of a solution of a ligand into 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 estimates of the metal:ligand ratio in the complexes formed by the heterocyclic. **[17-19, 21]**

4.Synthesis of 4-(2-Oxo-2H-chromen-7-yloxy)-phthalonitrile 1

4-Nitrophthalonitrile (2.25 g, 12.34 mmol) was dissolved in dry DMF (15 mL) under argon and 7-Hydroxycoumarin (2.00 g, 12.34 mmol) was added. After stirring for 15 min at room temperature, finely ground anhydrous potassium carbonate (3.67 g, 26.6 mmol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under argon atmosphere at room temperature for 24 h after which time, the ensuing mixture was poured into 100 mL iced water and the precipitate filtered off, washed with methanol and then dried. The crude product was chromatographered over a silica gel column using a mixture of $CHCl_3$: MeOH (100:5 (v:v)) as eluent, giving a powder of 4-(2-Oxo-2H-chromen-7-yloxy)-phthalonitrile 1. Finally, the pure powder was dried in a vacuum. Yield: (65%). IR spectrum (cm^{-1}): 3061 (Ar-CH), 2225 (CN), 1587 (C=C), 1726 (C=O, lactone and ester), 1483 (C-O-C). ^{1}H NMR (DMSO-d_6): 6.50-8.18(m, 8H, Ar-H+$H_{2,3}$). ^{13}C-NMR (DMSO-d_6): δ 160.1,159. 9, 157.4, 155.4, 144.1, 136.7, 130.8, 124.1, 123.9, 117.3, 116.5, 116.0, 115.5, 109.9, 108.0

Calcd for $C_{17}H_8O_3N_2$: C, 70.83; H, 2.79; N, 9.71. Found: C, 70.80; H, 2.7; N, 9.7; MS (LCMS-MS) m/z: Calc. 287.2; Found: 287.2

5.Synthesis of 4-(4-Methyl-2-oxo-2H-chromen-7-yloxy)-phthalonitrile 2

The synthesis of 2 was similar to that of **1**, except 7-hydroxy-4-methylcoumarin (1.232 g, 7 mmol) was employed instead of 7-hydroxycoumarin. The amounts of the other reagents were: 4-nitrophthalonitrile, 0.865 g (5 mmol) and anhydrous potassium carbonate, 1.035 g (7.55 mmol). Yield: (75%). IR spectrum (cm^{-1}): 3068 (Ar-CH), 2227 (CN), 1587 (C=C), 1724 (C=O, lactone and ester), 1487 (C-O-C). ^{1}H NMR (DMSO-d$_6$): 2.40(s, 3H, CH$_3$), 7.42-8.30(m, 7H, Ar-H+H$_3$). ^{13}C-NMR (DMSO-d$_6$): δ 161.7, 159. 8, 153.2, 150.8, 149.8, 136.6, 125.0, 122.5, 122.2, 121.5, 119.1, 117.7, 117.0, 116.2, 115.7, 115.4, 108.6, 18.5

Calcd for $C_{18}H_{10}O_3N_2$: C, 71.52; H, 3.33; N, 9.26. Found: C, 71.5; H, 3.3; N, 9.2

MS (LCMS-MS) m/z: Calc. 302.284; Found: 301.2: m/z 301.2 [M-H+].

6.Synthesis of 4-(4-Methyl-2-oxo-2H-chromen-6-yloxy)-phthalonitrile 3

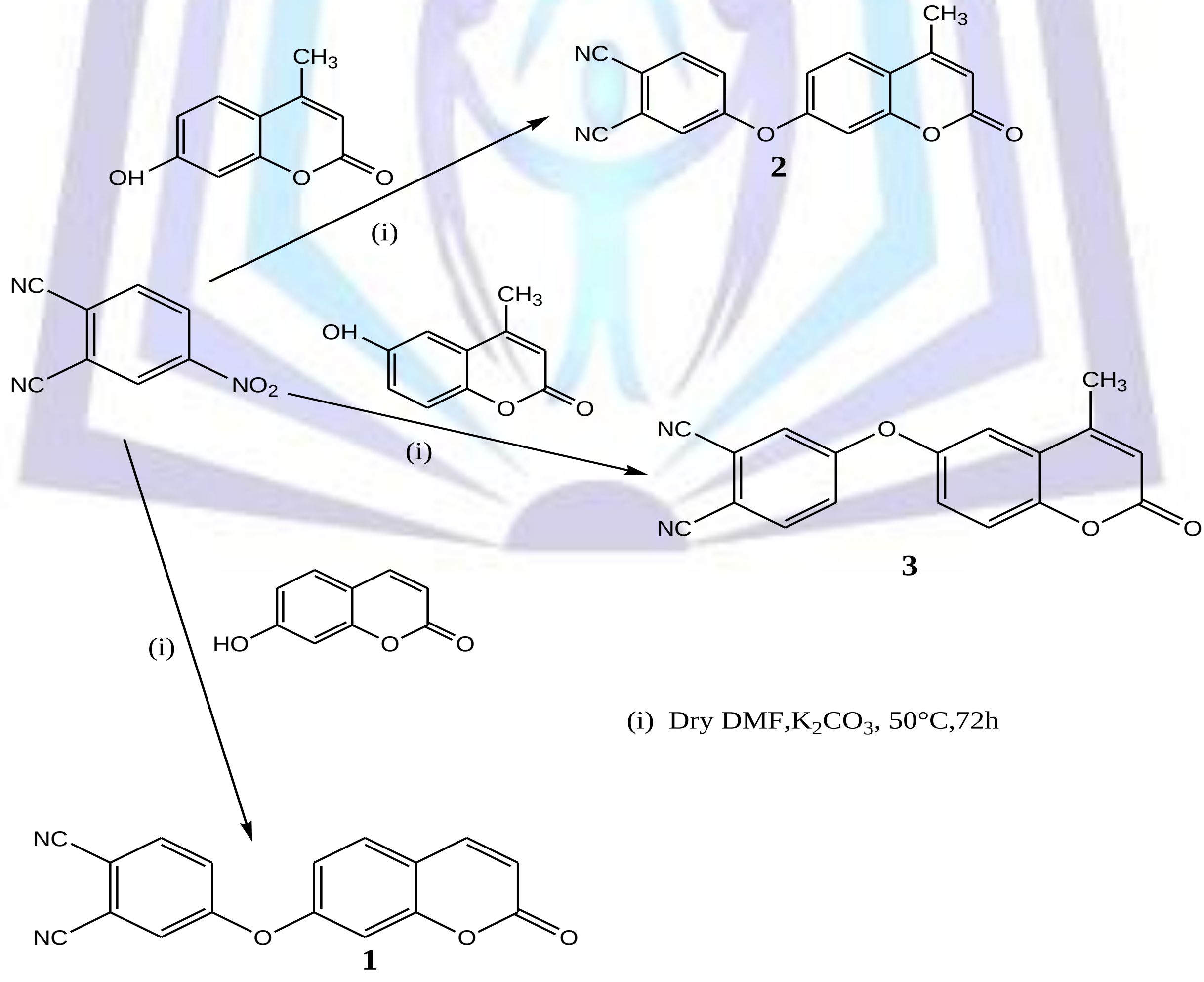
The synthesis of **3** was similar to that of **1**, except 6-hydroxy-4-methylcoumarin (1.232 g, 7 mmol) was employed instead of 7-hydroxycoumarin. The amounts of the other reagents were: 4-nitrophthalonitrile, 0.865 g (5 mmol) and anhydrous potassium carbonate, 1.035 g (7.55 mmol).Yield: (70%). IR spectrum (cm^{-1}): 3059 (Ar-CH), 2229 (CN), 1577 (C=C), 1720 (C=O, lactone and ester), 1435 (C-O-C). ^{1}H NMR (CDCl$_3$): 2.41(s, 3H, CH$_3$),6.48-8.12(m, 8H, Ar-H). ^{13}C-NMR (DMSO-d$_6$): δ 161.7, 159. 8, 153.2, 150.9, 150.0, 136.7, 125.0, 122.6, 122.4, 121.6, 119.1, 117.7, 117.1, 116.2, 115.7, 115.5, 108.7.

Calcd for $C_{18}H_{10}N_2O_3$: C, 71.52; H, 3.33; N, 9.26, Found: C, 71.5; H, 3.3; N, 9.2

MS (LCMS-MS) m/z: Calc. 302.284; Found: 301.2: m/z 301.2 [M-H+].

7. Results and Discussion

The target coumarin phtalonitriles derivatives **1-3** were prepared by a nucleophilic aromatic substitution reaction between 4-nitrophthalonitrile and 7-hydroxycoumarin and 7-hydroxy-4-methylcoumarin and 6-hydroxy-4-methylcoumarin respectively in dry DMF and in the presence of dry K_2CO_3 as base, at 50 °C in 72 h in a good yields (65%, 75% and 70% respectively). **scheme 1**



Scheme 1: protocol synthesis of coumarin phtalonitriles derivatives **1-3**

All the new coumarin phtalonitriles derivatives were characterized by IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis.

In the IR spectrum, the formation of dinitrile derivative **3** was clearly confirmed by the disappearance of the phenolic OH and NO_2 band respectively at 3448 and 1538–1355 cm^{-1} and appearance of the CN band at 2229 cm^{-1} as expected .

In the ^{1}H NMR spectrum of compound **3**, the signal corresponding to the O–H group of 6-Hydroxy-4-methyl coumarin disappeared as expected. Also, ^{1}H NMR spectrum of **3** exhibited signals at δ = 2.3 (s, 3H,CH_3), 7.54–7.35 (m, 6H, Ar–H) belonging to aromatic proton. The ^{13}C NMR data are accord with the expected structure. Also nitrile carbon atoms were observed 117.49 and 113.31 ppm in the ^{13}C NMR spectrum of the compound **3**

The ^{1}H NMR investigation of compound **1** provided the characteristic chemical shifts for the expected structure. The ^{1}H NMR spectrum of the compound **1** showed signals with δ ranging from 7.26 to 7.89, belonging to aromatic protons integrating for a total of 6 protons.

In the ^{13}C NMR spectrum of this compound, all the signals are identical to those of the precursor compound except for the dicyano carbon atoms.

In the IR spectrum of compound **2**, stretching vibrations of CN (2227 cm^{-1}) and aromatic CH (3068 cm-1) appeared at expected frequencies, respectively. In the ^{1}H-NMR spectrum of **2** OH group of 7-Hydroxy-4-methylcoumarin disappeared as expected. The ^{13}C-NMR spectrum of **2** indicated the presence of nitrile carbon atoms in **2** at δ = (115.7, 115.4) ppm. The mass spectra of compounds **1-3** confirmed the proposed structures . The molecular ions were easily identified at m/z= 287.2 for **1** , 301.2 for **2** and 301.2 for **3** .The elemental analysis results of the newly coumarin phtalonitriles **1-3** also confirmed the structure of these compounds**.**

8. Complexation of metal cations in acetonitrile

The logarithms of the stability constants $\log\beta_{xy}$ and the stoichiometries for the different complexes formed by ligand **1**, **2** and **3** with alkali metal, alkaline-earth metal and some transition metal in acetonitrile are given in **TABLES 1**.

TABLE 1: Stability Constants $\log\beta_{xy}$ of the Complexes of **1**, **2**, **3** with Alkali, Alkaline earth and some transition metal cations in acetonitrile at 25 °C, I = 10^{-2} M. (0.01 ≤σ_{n-1}≤ 0.16).

	M :L	**Li^+**	**Na^+**	**K^+**	**Rb^+**	**Mg^{2+}**	**Ca^{2+}**	**Sr^{2+}**	**Ba^{2+}**	**Co^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Ni^{2+}**
1	1:1	3.22	3.71	3.39	3.25	3.14	3.86	3.32	3.32	3.90	3.80	4.23	4.20
2	1:1	3.08	3.11	3.81	3.83	3.37	4.31	3.94	3.34	4.21	4.42	4.05	3.96
3	1:1	3.16	3.33	3.86	4.01	3.28	4.08	3.62	3.40	3.76	4.30	4.11	4.01

a: Absorbance changes too small to enable satisfactory fitting

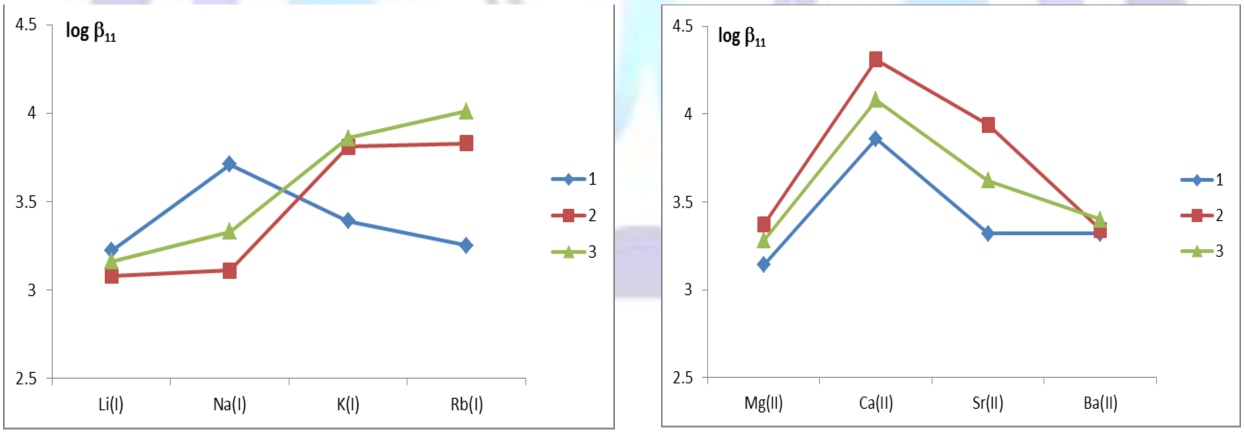


Figure 1. Trends of the stability constants log β11 (determined in acetonitrile) for (left) alkali and (right) alkaline earth cations with ligands **1, 2** and **3.**

The selectivity profile shows a best affinity for Ca(II) with all considered ligands **1-3** . In addition ligands **1-3** have the same profile of complexation. The affinity for Na(I) with ligand **1** changed for Rb(I) with ligands **2** and **3**. We note a particular selectivity for Ca(II) compared to Ba(II) $S_{Ca/Ba}$ ≈10 .

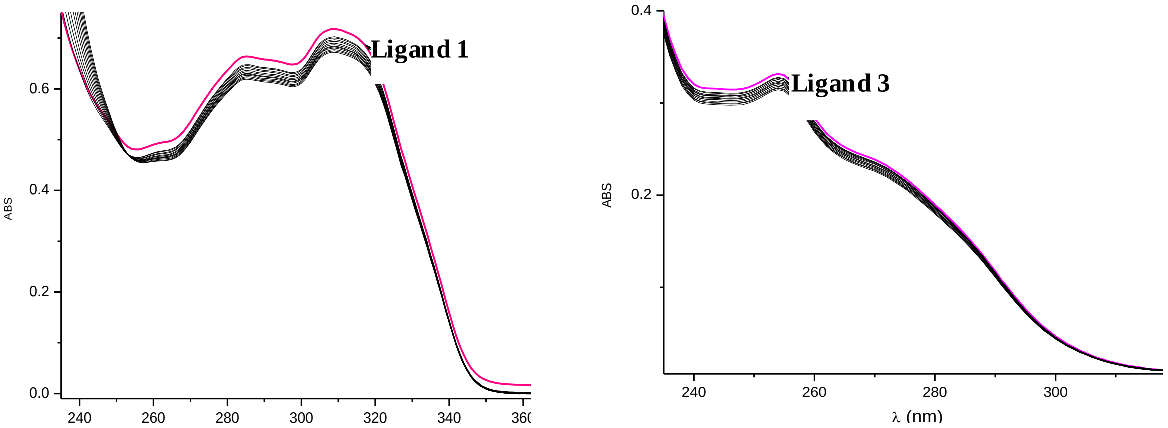


Figure 2. UV absorption spectra on complexation of (left) sodium (I) with **1**, (right) barium (II) with **3** in acetonitrile. (0 ≤ $R_{M/L}$ ≤ 10) at 25°C

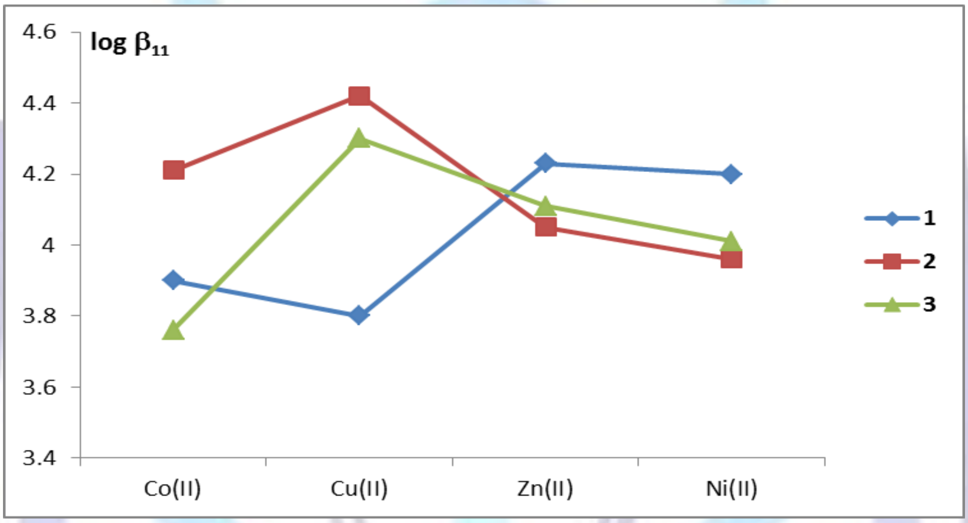


Figure 3. Trends of the Stability constants log β_{11} (determined in acetonitrile) for Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} with ligands **1, 2** and **3**.

The selectivity profile of **3** in the series of transition metal cations, shows an affinity for copper, such us ligand **2**, whereas the affinity is in favor of zinc with ligand **1**. We can suggest that the presence of the methyl group in the ligands **2-3** activates the coumarinic donor site. This activity prevails before the intake of oxygen linking the two aromatic rings in case of Co(II) and Cu(II) complexes. However, the obtained results show reverse effects with the Zn(II) and Ni(II) complexes.

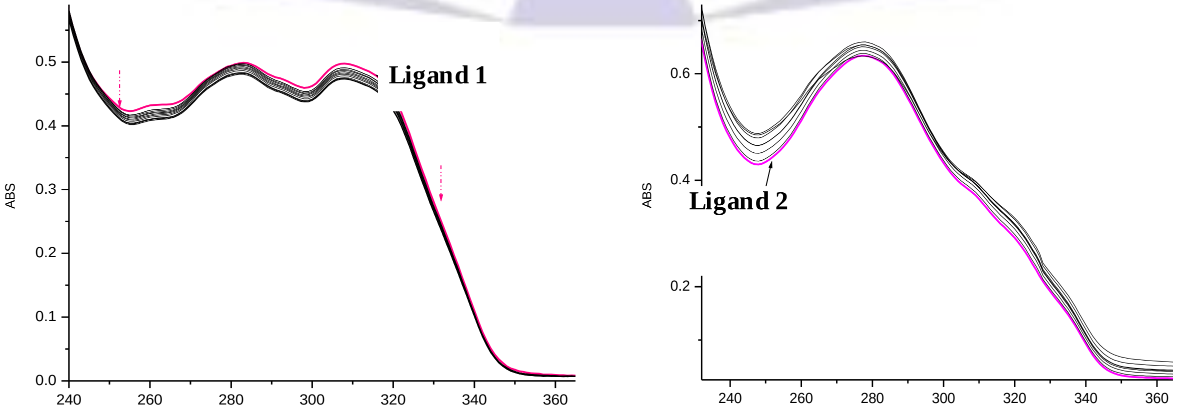


Figure 4. UV absorption spectra on complexation of (left) cupper(II) with **1** (right) zinc(II) with **2** in acetonitrile. at 25°C

Furthermore, the stoichiometries of 1:1 for the complexes with the compounds **1**, **2** and **3** were confirmed by conductometric titration in some cases (**Figure 5**).

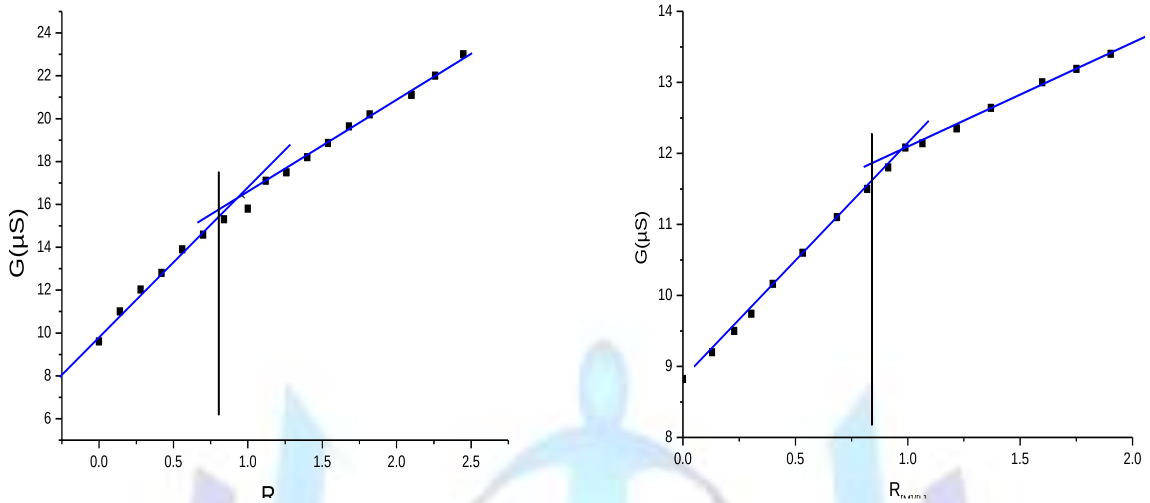


Figure 5: Conductimetry titration of (left) ligand **1** by Rb^+, (right) ligand **2** by Zn^{2+} in acetonitrile solution

Conclusions

In conclusion, New coumarin phtalonitriles derivatives have been synthesized using conventional methodology and characterized in high yields (65%–75%). The complexing properties of these coumarin derivatives toward alkali metal, alkaline earth metal, some transition metals and some heavy metal cations have been investigated in acetonitrile by means of UV spectrophotometry absorption and conductivity methods.

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