

Metallochromic Properties of Melamine-Derived Organic Reagent N-(2'-Thienylmethylene)-2,4,6-triamino-1,3,5-triazine

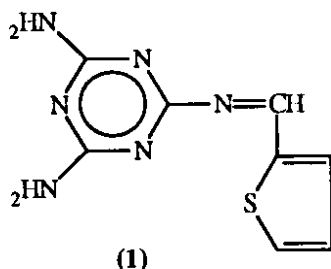
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Summary: A new organic reagent N-(2'-thienylmethylene)-2,4,6-triamino-1,3,5-triazine has been synthesised and studied spectrophotometrically for its metallochromic properties towards Fe(III), Fe(II), Cu(II), Co(II), Ni(II) and Zn(II) metal ions. The reagent forms coloured complexes between pH 5.0 and 6.0. Concentration versus absorbance relationship is linear upto a level as low as 2 ppm.

Introduction

Sulphur-containing chromogenic agents such as dithiazone [1], thiooxamide [2], thioamide [3] and dithiocarbamates [4] are well known. Other sulphur-containing ligands such as mercaptoquinoline [5] and mercaptopurine [6] are well known but have little use as organic reagents. There are some other sulphur-containing compounds such as azo dyes [7,8] in which sulphur is bonded directly to one or both aromatic rings and have been well explored as metallochromic reagents. But, some other class of sulphur-containing reagents in which sulphur is present as a part of heterocyclic ring have not been explored to a great extent for their metallochromic properties. The purpose of this work is to report and evaluate the metallochromic behaviour of such a class of new reagent (1) which has a sulphur-containing heterocyclic ring system and shows its probable colour reactions and stability towards Fe(III), Fe(II), Cu(II), Co(II), Ni(II) and Zn(II) metal ions.



Results and Discussion

The organic reagent (1) is stable and could be indefinitely stored both as solid and in solution form. The reagent contains suitably placed donor

atoms for complex formation with metal atoms. The results of qualitative and spectrophotometric studies summarised in Table-1 show that the reagent generally forms coloured complexes between pH 5.0-6.0. The complexes either precipitated or became turbid in aqueous ethanolic solution.

Table-1: Qualitative and absorption data

Metal Ion	pH	λ_{max}	Colour	Colour/change after 2 h
Fe(III)	5.5	420	Yellow	Yellow-yellow turbid
Fe(II)	5.5	455	Brown	Brown-brown ppt
Co(II)	5.0	412	Orange	Orange-orange ppt
Ni(II)	6.0	390	Yellow	Yellow-yellow turbid
Cu(II)	5.0	620	Blue	Blue-blue turbid
Zn(II)	5.5	380	Yellow	Yellow-pale yellow ppt

The results of qualitative studies showed that when the excess of reagent was added to the solution of metal ions Fe(III), Co(II) and Ni(II), yellow to orange colour was immediately developed which became turbid and precipitated later on. The Fe(II) complex developed a brown colour which also precipitated within 2 h. The Cu(II) complex developed a blue colour which became turbid and then precipitated after 2 h. The Zn(II) complex developed a yellow colour which became turbid and precipitated within 1 h. The absorbance of the colour was, however, measured before they became turbid or precipitated against a corresponding blank reagent.

In order to know if the complexation reaction give the increased intensity of colour with gradually increasing amount of the metal ion, a calibration curve was obtained with the iron. The result as shown in Fig. 1 indicated that it gave a linear relationship with a level as low as 2 ppm.

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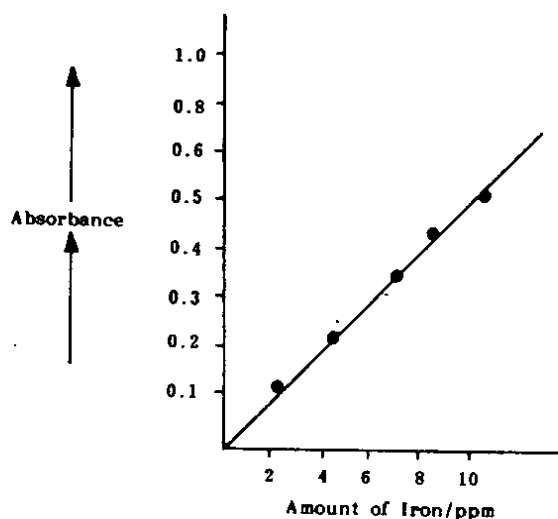


Fig. 1: Calibration curve

Effect of foreign ions

In order to assess the possible application of the reaction, the effect of foreign ions on the spectrophotometric determination was studied by adding known amount of the ions in question to a solution and following the recommended procedure. The Ca^{+2} , Mg^{+2} , Mo^{+2} , Ba^{+2} and Sr^{+2} did not interfere whereas Pb^{2+} , Hg^{2+} and Mn^{2+} ions interfered in the determination.

From the above observations it is thus concluded that the ligand is a reasonably sensitive reagent and suffers few interferences due to foreign ions.

Experimental

Preparation of *N*-(2-Thienylmethylene)2,4,6-triamino-1,3,5-triazine (1)

Thiophene-2-carboxaldehyde (0.92 ml, 1.12 g, 0.01M) in ethanol (15 ml) was added to a stirred ethanolic solution (20 ml) of melamine (1.26 g, 0.01M) at 50°C. Then 2-3 drops of concentrated H_2SO_4 were added in it and mixture refluxed for 0.5 h. After that, it was cooled during which a solid product was formed. It was filtered, washed with ethanol (2x5 ml) and ether (1x5ml) and dried. The compound was then crystallised in aqueous ethanol to yield a light yellow product (53%) m.p. 205°C. IR (nujol) 3225, 3165, 2920, 2870, 2020, 1944, 1692, 1625, 1605, 1544, 1350, 1054, 955, 875, 780 and 725 cm^{-1} . Found: C, 43.62; H, 3.67; N, 38.12% $\text{C}_8\text{H}_4\text{N}_6\text{S}$ requires C, 43.64; H, 3.63; N, 38.15%.

Solution

The solutions of Fe(III), Fe(II), Cu(II), Co(II), Ni(II) and Zn(II) in water were prepared containing 1 mg/ml of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$.

The solution of organic reagent (0.2%) was prepared by dissolving the required amount in aqueous ethanol (50%).

Buffer solutions of various pH values were prepared using HCl (1M)-sodium acetate (1M) having pH 1-3, acetic acid (0.2M)-sodium acetate (0.2M) having pH 4-7 and ammonium chloride (0.2M)-ammonia solution having pH 8-12.

Qualitative studies

Previously prepared each metal solution (1 ml) was added to organic reagent solution (1 ml) and buffer solution (3 ml) of desired pH (1-12) value. The formation of colour and its variation with pH was noted. Then the solutions were allowed to stand at room temperature for 2-4 h. Any change in colour or precipitate formation with different time intervals was noted. In order to assess the extractibility of the complexes, different solvents such as chloroform, ether, alcohol, dimethylformamide and carbon tetrachloride were attempted.

Spectrophotometric determination

The metal solution (1 ml) was transferred to 50 ml volumetric flask and organic reagent solution (5 ml) was added in it, followed by particular buffer solution (5 ml) in each flask. The contents were diluted to volume with distilled water and solution was allowed to remain at room temperature for 0.5-1 h for colour development. When the colour was developed the absorbance was measured at suitable wavelength against a blank reagent solution. Following the same procedure a calibration curve was constructed for iron (Fig. 1).

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