



ORIGINAL RESEARCH ARTICLE

Synthesis and Solvatochromic of 3-(4-N-Pyridine -2-yl benzene sulfonamide azo)-1-nitroso naphthol and use it for determination of trace amount of Cobalt (II) as complex

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Received: July 24, 2016; Revised: July 28, 2016; Accepted: August 11, 2016

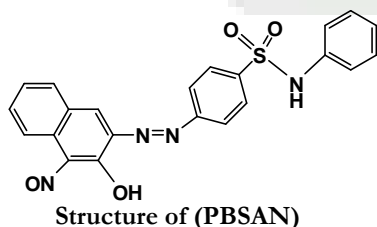
Available online: 1st September 2016

Abstract: The azo reagent 3-(4-N-Pyridine -2-yl benzene sulfonamide azo)-1-nitroso naphthol was synthesized and characterized by FT-IR, ¹H-NMR and ¹³CNMR spectral techniques. The solvatochromism of the azo compound was studied by using different solvents. Spectrophotometric determination of cobalt (II) is based on the formation of a 2:1 complex with above reagent. The complex has λ_{max} at (452) nm and ϵ_{max} of (2.0567*10⁴) L. mol⁻¹. cm⁻¹. A linear correlation (0.1- 3.5 μ g. ml⁻¹) was found between absorbance at λ_{max} and concentration. The effect of diverse ions on the determination of cobalt (II) to investigate the selectivity of the method were also studied. The stability constant of the product was (2.68*10⁸). The proposed method was successfully applied to the analysis of honey sample.

Key words: Solvatochromic; 3-(4-N-Pyridine -2-yl benzene sulfonamide azo)-1-nitroso naphthol; cobalt (II); spectroscopy

Introduction

Azo dyes belong to the one of the largest class of analytical reagents. Their important feature is electro activity, which makes them very important reagents for the voltammetric determination of metal ions [1-3]. Recently many researchers developed a sensitive method for the determination of metal ions with heterocyclic azo compounds as complexometric agents by polarographic and voltammetric techniques. In addition sulphadiazine alone have ability to coordinate with different metal ions [4]. Heterocyclic azo compound reagents have received a great deal of attention as they are sensitive and selective chromogenic reagents. To continue improving the sensitivity, selectivity of this kind of reagents and their metal complexes, the electrochemical characteristics of the reagents and their metal complexes have been studied [5-11]. PBSAN is bidentate via azo group and hydroxyl group it has the following structure:



Structure of (PBSAN)

Materials and Methods

All chemicals used in this work were of analytical grade. In this study the FT-IR spectra of azo compound was recorded on Shimadzu FT-IR spectrophotometer model in KBr wafer and the

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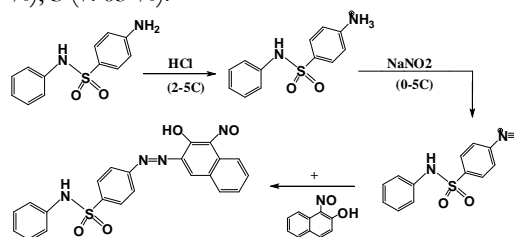
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NMR spectra was obtained on BRUKER AV 400 Advance III 400MHz instrument using DMSO as solvent and reported relative to TMS as internal standard, CE440CHN/O/S Elemental. All measurements were carried out at room temperature.

Synthesis of pyridine derivative

Sulphapyridine (0.0040 mole) 1.0000 gm was diazotized by dissolving it in 30 ml ethanol then 10ml of HCl (4M) was adding keeping the temperature at (2-5°C) and then adding NaNO₂ solution gradually and left the solution about 1hr. The coupling material (1-Nitroso-2-Naphthol) (0.004 mole) (0.7g) was dissolved in ethanol (30ml), 10ml of NaOH (4M) was added and leave to cool well then the last solution was added slowly dropwise to diazonium salt solution. The mixture was allowed precipitate was filtered off and washed several times with (1:1) (alcohol: water) mixture then recrystallized from boiling ethanol and left to dry. Scheme (1). Dark orange powder, m. p 174°C Anal (calc) for C₂₁H₁₅N₅O₄S (%): C (58. %), H (3.46 %), N (16.157%), S (7.39%). Found (%): C (60.65 %), H (3.95 %), N (15.160 %), S (7.63 %).



Scheme (1): Synthesis of reagent (PBSAN)



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Reagents:

Cobalt stock solution ($200 \mu\text{g. ml}^{-1}$) The solution was prepared by dissolving (0. 2018 g) of cobalt chloride hexahydrate in (250 ml) of deionized water.

3- (4-N-Pyridine -2-yl benzene sulfonamide azo)-1-nitroso naphthol ($1 \times 10^{-3}\text{M}$): This solution was prepared by using (0. 0321 g) of reagent in (100 ml) of DMSO.

Other ions (foreign) solution: All of ions were prepared by using a suitable amount of the compound in deionized water in a calibrated flask.

Results and Discussion**Absorption Spectra:**

The reagent (PBSAN) possess a maximum absorption at (425 nm) Figure 1 reacts with ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) at room temperature to give a (PBSAN-Co (II)) colored complex at pH 9. The absorption spectrum shows a maximum at (452 nm), whereas the reagent blank gives no absorption at this wavelength Figure. 2.

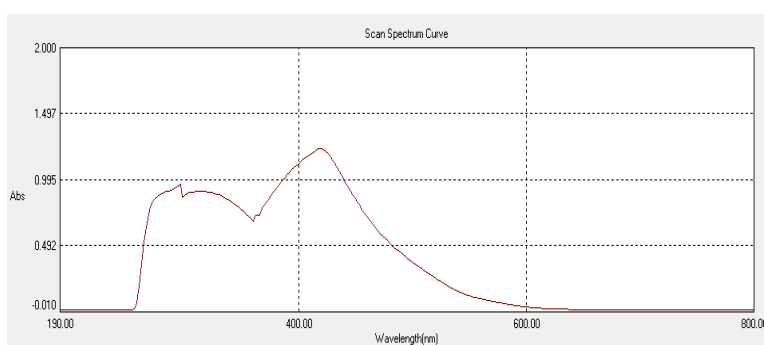


Figure (1): Absorption spectrum of reagent (PBSAN)

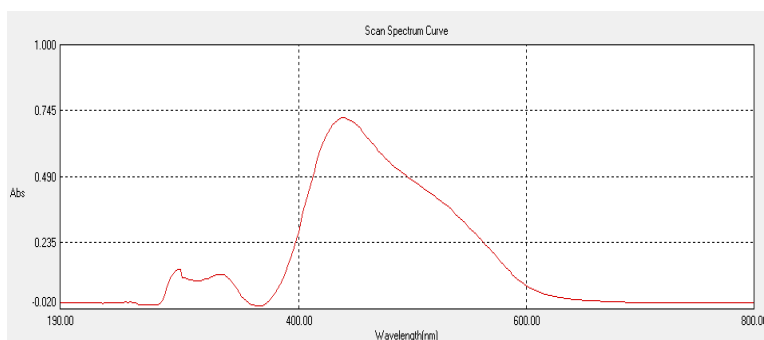


Figure (2): Absorption spectrum of [PBSAN-Co (II)]

A Study Solvatochromism of Sulphapyridine Azo Compound:

To determination of solvate chromic range of azo dyes according to sensitivity to solvent change by using UV-Visible, more than (18) empirical scales of solvent polarity has been used, i. e Et (30) scale has more comprehensive applications for characterization of the chromatographic materials and polarity of polymers in addition of measurements of the polarity of all type of solvents, electrolyte solution and binary solvent mixture [12-15]. The popular comparison methods of solvatochromic, demonstrated by Kamlet and Taft and improved by Abraham, Carr and Abboud has been to explain the solvent effect. A solvatochromic equation with three parameters λ^* , β and, α can be used to determine two type

hydrogen bonding [16]. The absorption spectra of dye carried out over the range between (200-800) nm in various selected solvent and the results are summarized in Table. 1.

Dye of {3- (4-N-Pyridine -2-yl benzene sulfonamide azo)-1-nitroso naphthol} showed a weak peak at region 190-300 nm assigned to hydrazone tautomeric form at 370-600nm [17]. Dye showed the positive solvatochromism due to the absorbance of the first band was decreased via increasing solvent polarity. This mean that the excitation state more stable and have polarity different from ground state. It was also observed that the negative solvatochromism exhibit by the second band absorbance it was increase via increasing solvent polarity and it shifted to lower wavelength [18] Fig.3.

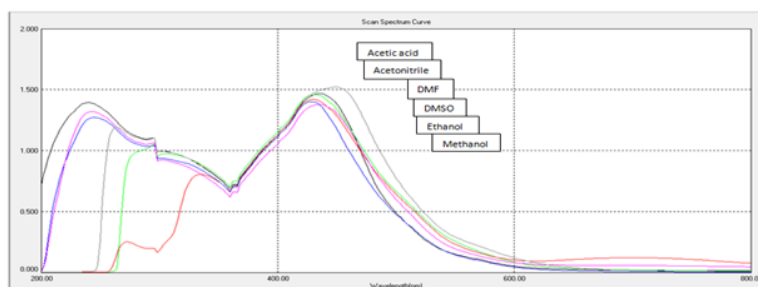


Figure (3): The Absorption Spectra of Azo compound (PBSAN) using different solvents

Table 1: Influence of solvent on maximum band nm.

Solvent	Absorption maximum band nm	
	Peak 1	Peak 2
Methanol	242.00	436.00
Ethanol	244.00	428.00
Acetic acid	264.00	448.00
DMF	332.00	434.00
DMSO	336.00	430.00
Acetonitrile	240.00	436.00

DMF = (N, N dimethylformamide), DMSO = dimethylsulfoxide

The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized.

Effect of pH

The effect of pH on the absorption of the complex formed by the reaction of (PBSAN) with Co (II) was studied at different pH by using HCl or NaOH (0.05N) in the range (2-12). It was found that the chelating complex was formed at pH 9. Figure 4

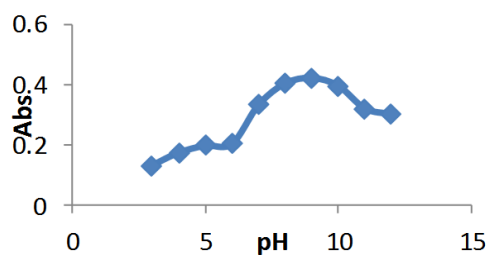


Figure (4): Effect of pH on the absorption intensity of [PBSAN-Co (II)] complex

Effect of (PBSAN) concentration:

The effect of changing reagent concentration on the absorbance of solution keeping affixed amount of Co (II) and pH 9 was studied. It was found that absorbance rises with increasing reagent concentration and got its maximum value on using (2.5)ml of PBSAN in subsequent experiment. Figure 5

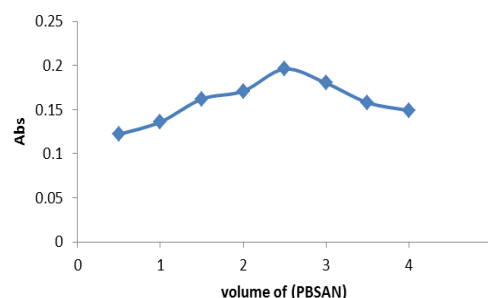


Figure (5): Effect of (PBSAN) (1*10⁻³) M on the absorption intensity of [PBSAN-Co (II)] complex

Quantification

In order to study the range in which the colored complex adhere to Beer's law the absorbance of the complex was measured at λ_{max} for sequence of solutions containing increasing amounts of Co (II) at optimum conditions. The validity of Beer's law, molar absorptivity and Sandell's sensitivity values were estimated and are given in Table. 2, showed that the method is sensitive. The proposed method showed a good linearity for the determination of Co (II) with a good correlation coefficient (0.996) Figure 6. The relative standard deviation % (RSD) for the analysis of six replicates of Co (II) is equal to (0.495) showed that the method is precise and accurate, while detection limit is equal to (0.01485).

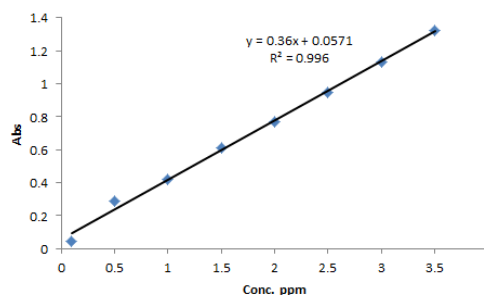


Figure (6): Calibration Curve of [PBSAN-Co(II)]

Table. 2: characteristics data of [PBSAN- Co (II)] complex

Values of Method	Parameter
(0. 1-3. 5)	Beers law limits (µg. ml ⁻¹)
2. 0567*10 ⁴	Molar absorptivity (L. mol ⁻¹ . cm ⁻¹)
0. 014845	LOD (µg. ml ⁻¹)
0. 495%	R. S. D %
0. 996	Correlation coefficient
0. 00286	Sandell's sensitivity µg. cm ⁻²

Composition of complex:

In the present work, it was found that Co (II) reacted with reagent (PBSAN) in 1:2 ratio forming a complex to give intense dark red colored. The stoichiometric ratio of (PBSAN) and Co (II) was studied applying the continuous variation (Job's) and mole ratio methods [19, 20] using equimolar solutions of the new ligand and Co (II) (1×10^{-4}). It was found that (PBSAN) forms a dye coupled product with Co (II) in the ratio 2:1 as in Figure7, 8.

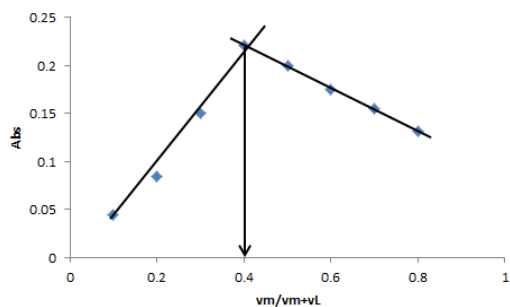


Figure (7): continuous variation plot of the [PBSAN-Co (II)]

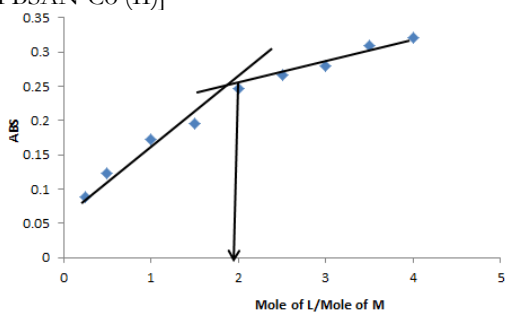
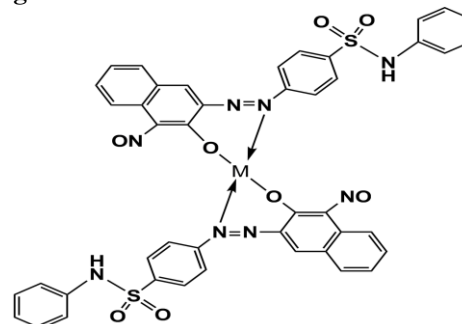


Figure (8): Mole Ratio Plot of The [PBSAN-Co (II)]

According to the results of the FT-IR, ¹H-NMR, ¹³C-NMR, stoichiometric and elemental analysis the structure of complex can be suggested as the following:

Structure of complex of Co II with (PBSAN) reagent



Where M = Co (II)

FT-IR Analysis

The FT-IR of the free ligand and its metal chelate were carried out in the (400-4000) cm^{-1} Range. IR bands of the (PBSAN) and its Co (II) complex with their probable assignment are given in Table. 3. The spectrum of the free ligand have a broad band about (3429) cm^{-1} which could be attributed to (-OH) stretching vibration Figure 9, the shape and intensity of band were changed that led to expect coordination was accurate in complex (PBSAN-Co), likewise the frequency corresponding to (N=N) at (1527.62) cm^{-1} was shifted towards lower frequency in complex which led to predict the chelating behavior [21]. The band of (N-H) unchanged from those in azo dye. Other bands such as (C-H) Δ_r , (C=C), (C-N) were shifted towards lower intensity Figure 10. The FT-IR spectra of cobalt complex also shows additional bands in (667.37) cm^{-1} which is due to the formation of (M-O) [22, 23].

Table 3: The Important IR bands of the (PBSAN)

Compound	OH)-v (NH)-v) cm^{-1}	(CH) Δ_r -v cm^{-1}	N=N)-v(cm^{-1}	C=C)-v(cm^{-1}	(C-N) v cm^{-1}	(C=N) Δ_r v cm^{-1}	(SO ₂ N) v cm^{-1}
PBSAN	3429.43 3064	2933.73	1527.62	1625.99	1388.75	1591.27	1261.45 1139.93
PBSAN-Co (II)	---	2931.8	1516.05	1625.99	1444.68	1589.34	1265.30 1213.23

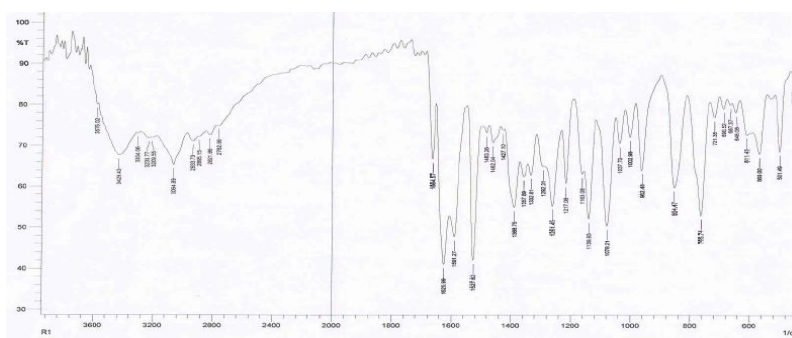


Figure 9: The FT-IR Spectrum of the dye (PBSAN)

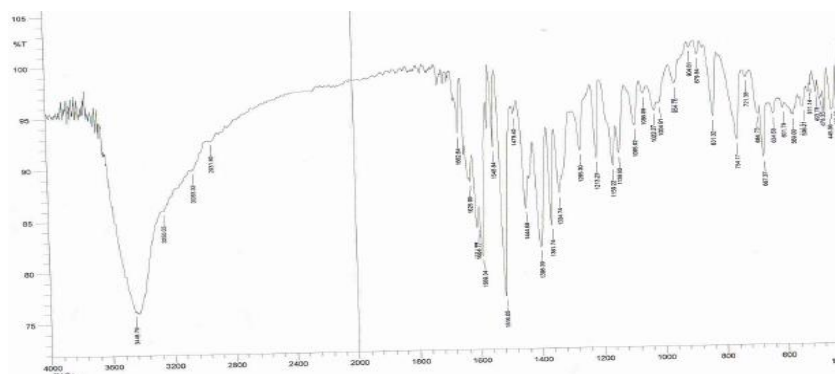


Figure 10: The FT-IR Spectrum of [PBSAN-Co(II)] complex

¹H-NMR data of (PBSAN) and it complex with Cobalt (II):

The ¹H-NMR and ¹³C-NMR spectra of the prepared azo compound was made ligand in

DMSO solution with tetra methylsilane as an internal standard indication the following signals as in Table. 4, Figure 11, 12.

Table 4: ¹H-NMR data of PBSAN and it complex with Cobalt (II)

CH pyridine	C-H naphthalene	NH	Ar-H benzene	CH-N pyridine	-OH npound	
6. 859	8. 205- 7. 592	8. 905 8. 877 8. 837	7. 374 7. 205	7. 036	8. 678 8. 651	PBSAN
6. 441- 6. 409	7. 645- 7. 520	8. 916	7. 274 7. 183	6. 893 6. 854	-----	PBSAN-Co

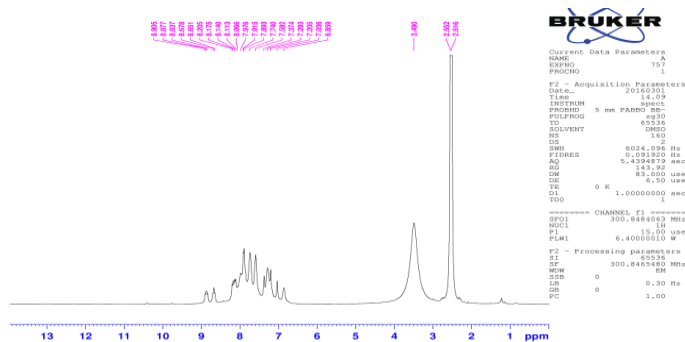


Figure 11: ¹H-NMR Spectrum of (PBSAN)

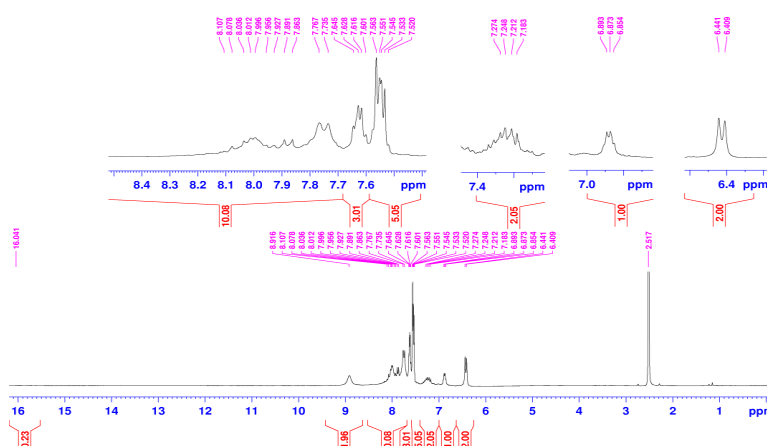


Figure 12: ¹H-NMR Spectrum of [PBSAN-Co (II)]

Table 5: Interference of ions and removed them by masking agents

No	Foreign ions	Conc. ppm	Error %	Masking agent	Error %
1	Pb ²⁺	10	24.88	Formaldehyde (1 ml)	- 0.543
2	Sr ²⁺	10	1.5	---	
3	Cr ³⁺	10	2.711	---	
4	Cd ²⁺	10	14.34	Formaldehyde (0.5 ml)	0.265
5	Sn ²⁺	10	1.42	---	
6	Cs ²⁺	10	0.921	---	
7	Zn ²⁺	10	40.75	Formaldehyde (0.5 ml)	0.752
8	Ni ²⁺	10	0.79	---	
9	Mn ²⁺	10	40.75	Formaldehyde (1 ml)	- 0.311
10	Hg ²⁺	10	1.721	---	
11	Ag ⁺	10	30.80	Formaldehyde (0.5 ml)	0.542
12	Cu ²⁺	10	2.18	---	

Interferences

The effect of different ions in the determination of cobalt (II) was studied. Co (II) can be determined in presence of 10 or more-fold excess of cation and the interference via the various ions were removed by using suitable masking agent Table. 5.

Determination of Cobalt (II) In Honey sample:

1g of honey digested in microwave with 5ml of concentrated HNO₃ and 3ml of 30% H₂O₂. The result of digested solution was diluted to 100ml with deionized water, from this solution transfer 2ml in centrifuge tube for 10 min and analysis with UV-Vis proposed method and atomic absorption [21]. The results are shown in Table. 6, indicate that satisfactory precision and accuracy could be attained with proposed method.

Table 6: Co (II) levels in Honey Sample

*Amount found by Atomic Absorbition (µg. ml ⁻¹)	*Amount found by our spectrophotometric method (µg. ml ⁻¹)	Type of Honey
0.650	0.669	Granja San Francisco

*For five determinations

Conclusion

This work employing 3- (4-N-Pyridine -2-yl benzene sulfonamide azo)-1-nitroso naphthol was successfully applied for the estimation of Cobalt (II) ion. Due to of the sensitivity, rapidly and selectivity of the method, its application can be estimation of this ion in biological sample, as well as a study solvatochromic behavior of azo dye (PBSAN) by using various solvents with different polarities.

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Cite this article as:

Fatma A. Khazaal, Hussein J. Mohammed. Synthesis and Solvatochromic of 3-(4-N-Pyridine-2-yl benzene sulfonamide azo)-1-nitroso naphthol and use it for determination of trace amount of Cobalt (II) as complex. *International Journal of Bioassays* 5.9 (2016): 4878-4884.

DOI: <http://dx.doi.org/10.21746/ijbio.2016.09.0018>

Source of support: Nil.

Conflict of interest: None Declared