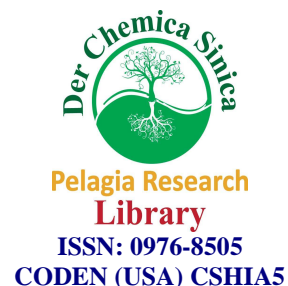




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### Synthesis, Optical and X-ray diffraction study of transition metal complex of Cu (II) containing naphthaquinone dibenzo 18- crown-6

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#### ABSTRACT

The *trans*- (dinitrobenzo)-18-crown-6 to *trans* -*di* (aminobenzo)-18 crown -6 was reduced to *trans*-*di*- (aminobenzo)-18 crown -6 and subsequently condensed with the 1,4-naphthaquinone to give the target molecule (4b) (Scheme I). The synthesized compounds have showed the chromogenic ionophoric properties examined by UV-Visible absorption of the host in DMF. The DMF solvent was found to be an efficient and selective for chromogenic responses for different alkali and transition metals like Ca, Sr, Ba, Ni and Cu. among these Ni (II) and Cu (II) showed excellent results. In addition to this, we have reported the X-ray diffraction study of Cu (II) complexes.

**Key Words:** Reduction *trans*-*di* (nitrobenzo) 18-crown-6, Schiff base naphthaquinone, UV-Visible spectrophotometric study and X-Ray Diffraction study of Cu (II) complexes.

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#### INTRODUCTION

The rapid expansion in supramolecular chemistry over the past 15 years has resulted in an enormous diversity of chemical systems, both designed and accidentally stumbled upon which they may lay some claims either in concept, origin or nature being supramolecular entity. Much of supramolecular chemistry has sprung from development in macrocyclic chemistry in the mid to late 1960's particularly the development of macrocyclic ligands for metal cations. C. J. Pederson in 1967 accidentally discovered crown ether [1]. Macromolecules find their applications due to their unique chemical and biological properties [2].

Macrocyclic compounds are commonly used as the phase transfer catalyst, in biometric studies and as specific and selective complexing agents for metals. Recently, crown ether with ethereal

or anionic groups on the periphery of the macrocycles have been developed, in order to increase metal selectivity and the complex stability in analytical separations as well as in biological membranes [3-8]. Several workers have reported modified crown ethers with chromogenic groups [9-12]. The crown ether ring or the chromophoric side arm can modify the properties of these compounds with different sensitivities and selectivities for metal ions such as the crown ether dyes possessing a potential anionic site attached to the chromophore [13]. B.R. Pandya, Y.K. Agrawal have reported the crown ethers azo- dyes capable of fixing on the cotton fibers [14]. macromolecules are used as PTC and reagents for extraction due to their high complexation ability and as dye intermediates and optical brighteners [15]. There has been much interest for the development of efficient and selective chromogenic and fluorogenic ionophore systems [16]. These compounds possess applications in cation recognition processes redox properties of transition metal complexes bound to the Schiff base [18]. Several workers have reported the optical and spectral properties of the crowned retinals and Bacteriorhodopsin analogs for different metal ions [19]. However, the ionophoric properties of naphthaquinone containing Schiff bases of dibenzo 18- crown- 6 have not been reported (Scheme-II).

## MATERIALS AND METHODS

**General:** Melting points were taken in open capillary and are uncorrected. IR spectra were recorded on a Perkin Elmer FTIR- spectrometer using KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR (400 MHz) spectra were recorded on a Bruker spectrometer in  $\text{CDCl}_3/\text{DMSO}$  as solvent using TMS as an internal standard. The UV-Vis spectra were measured using Elico UV-Visible spectrophotometer and X-ray diffraction measurement. XR has been performed on a Phillips Analytical spectrophotometer.

### Synthesis of di -(nitrobenzo)-18-crown-6 (2a and 2b):

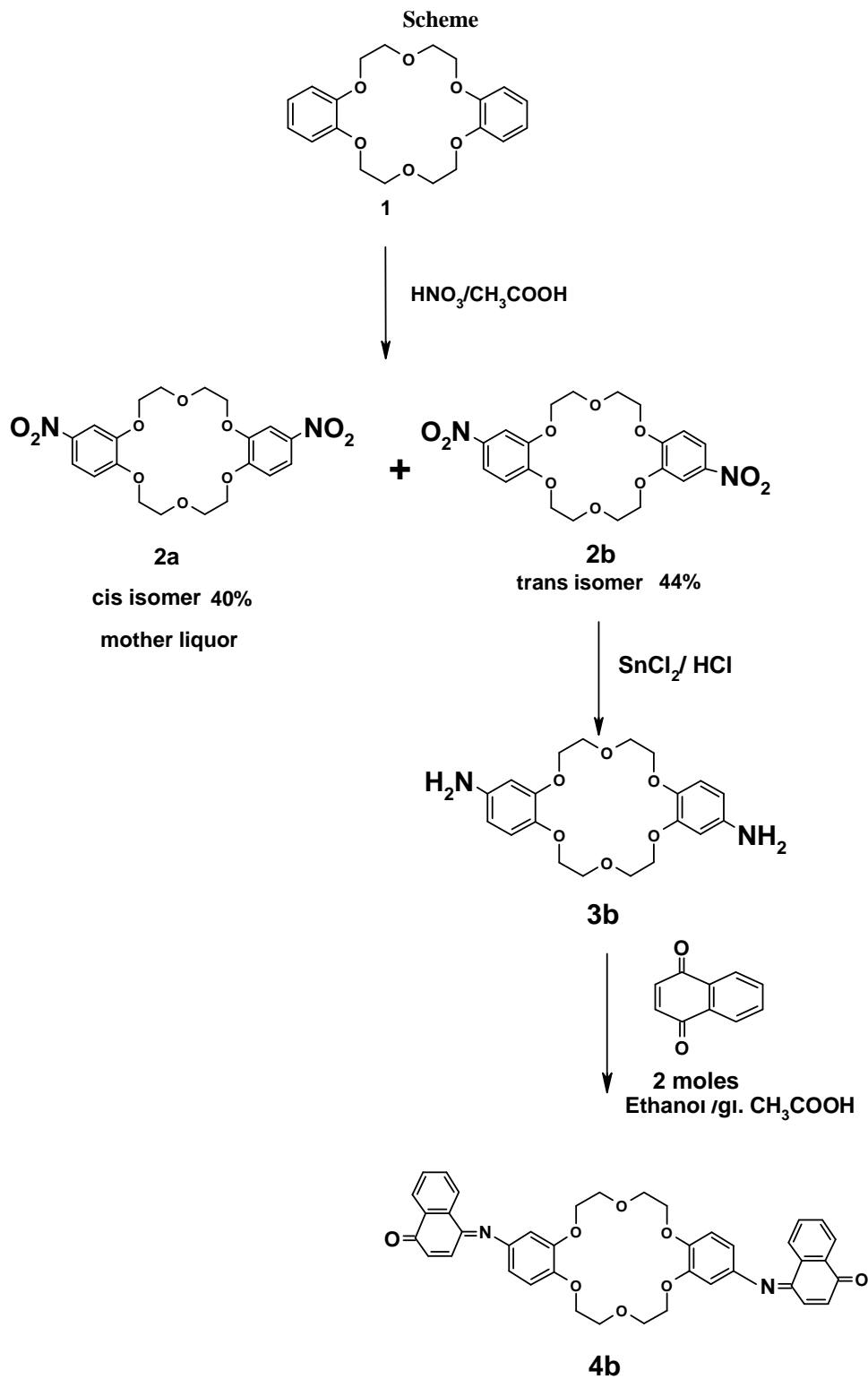
Dibenzo-18-crown-6 (0.519 g 1.44 mmol) dissolved in  $\text{CHCl}_3$  (10.4 mL) to which acetic acid (7.8 mL) was added over the period of 10 min, the reaction mixture stirred at room temperature for 5 min. Then a solution of  $\text{HNO}_3$  (0.360 mL) in acetic acid (10.4 mL) was added through dropping funnel over 15-20 min. The solution was further stirred at room temperature for 1 h and refluxed for 3 h and the precipitate obtained (predominantly the *trans* isomer) was filtered (0.285 g, 0.633 mmol, 44%, mp 237-242 °C, lit.8 247-252 °C) where as *cis* isomer precipitated out after 48 hrs from the mother liquor (0.2566 g, 0.569 mmol, 40%, mp 203-205 °C, lit.8 206-232 °C). Each compound was isolated as a pale yellow solid with total yield of 84%. Here, we used the “*trans*” isomer for the further study.

### Synthesis of trans-Di (aminobenzo)-18-crown-6, (3b):

The mixture of *trans*-di (nitrobenzo)-18-crown-6, 0.450g (0.001mmol) and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  0.112 gm (0.005mmol) in 10 ml of absolute ethanol was heated at 80°C and after the completion the reaction the mixture is allowed to cooled and poured into ice water mixture. The pH of solution was made alkaline by 5% sodium bicarbonate before the extraction with the help of ethyl acetate. The organic phase is thoroughly washed with brine, and dried over sodium sulphate to get brown colored compound 3b 0.300 g. M.p. 178-182 °C, lit. 180-184 °C).

IR (KBr) ( $\text{cm}^{-1}$ ): 3414.30, 3079.71, 2924.28, 2854.10, 1592.2, 1515.49, 1454.49, 1344.87, 1274.49, 1232.99, 1134.17, 994.82.

$^1\text{H}$  NMR (300MHz, DMSO-  $d_6$ ):  $\delta$  2.67-2.75 (m, 8H), 2.83-2.91 (m, 8H), 3.84 (bs, 2H), 4.19(bs, 2H) 6.05 (dd, 2H,  $J$  8.4, 2.4 Hz), 6.23 (d, 2H,  $J$  2.3 Hz), 6.62 (d, (2H) ppm.



**Synthesis of trans- di- (naphthaquinone) benzo)-18-crown-6 (4b):**

*Trans*-Di (aminobenzo)-18-crown 6 (0.392 gm, 1mmol) in (10ml) methanol and 1,4-naphthaquinone (0.300 g, 2 mmol) to which 2,3 drops of glacial acetic acid were added and reaction mixture refluxed further for 2-3 h in water bath. After the completion of reaction pour the reaction mixture on the crushed ice and the pH was adjusted between to 10-11 and extracted with ether. Then ether extract is dried over the sodium sulphate when Compd. 4b isolated as a crystalline solid (0.200 g) M.p. above 300 °C.

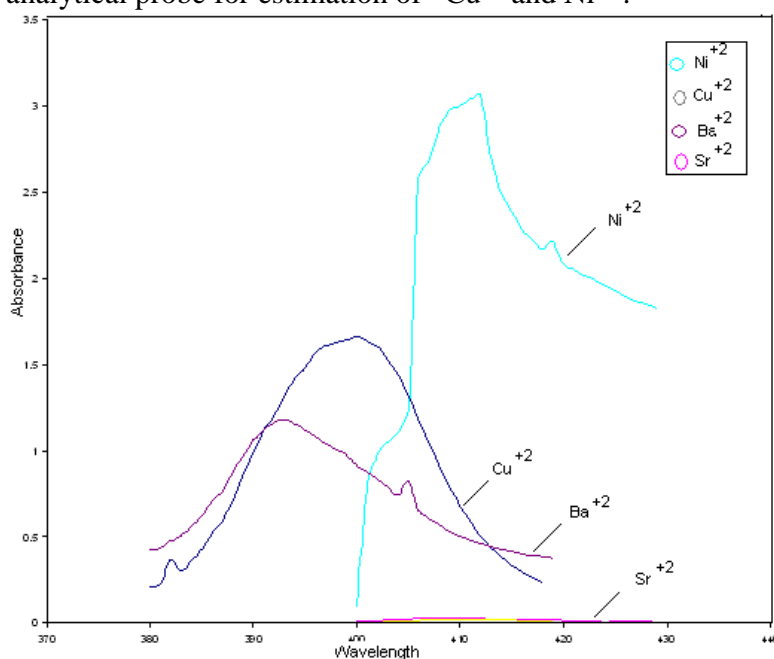
$^1\text{H NMR}$  (300MHz,  $\text{DMSO-}d_6$ ):  $\delta$ , 1.68-2.18 (m, 8H), 2.49-2.95 (m, 8H), 5.44 (dd, 2H, ), 6.39-6.43 (d, 3H, ), 6.57-6.71 (dd, 3H), 6.73-6.98(dd, 2H), 7.006-7.071(dd, 8H) ppm.

IR (KBr) ( $\text{cm}^{-1}$ ): 2924, 2853, 1665, 1591, 1557, 1515, 1336, 1300, 1143, 772.

$^{13}\text{CNMR}$ (300MHz,  $\text{DMSO}$ ):  $\delta$ , 169, 163, 153, 149, 146., 139, 139, 135, 131, 127, 125, 125, 124, 114, 109, 86, 74, 60, 59, 47, 40, 20, 19, 14, 14.

**Optical Spectral Properties:**

**UV measurements:** Stock solutions of 4b ( $1 \times 10^{-4}$  M, in DMF) and metal ions such as Cu (II), Ni (II), Ba (II), Ca (II) ( $1 \times 10^{-2}$  M) in methanol were prepared to get  $1 \times 10^{-3}$  M and  $1 \times 10^{-4}$  M solutions. Aliquot of metal solution was added to the ionophore solution and the final concentrations and compositions of the solution were adjusted to the desired value by adding extra DMF. Out four metal ions only Cu (II), Ni (II) gave the satisfactory results as shown in UV-Visible spectral absorption band at 287 nm characteristics absorption band of DMF solvent. Addition of 100-mmole equivalent of metal ions like Ca (II), Ba (II), Sr (II), Cu (II) and Ni (II) in ionophore resulted in the formation of metal complex. In case of  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$  ions colour change observed from colorless to blue and green respectively (Fig-1). The shift of the absorption band from 287 nm to 400 nm and 413 nm for  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$  respectively which indicate that there is good complexation ability of naphthaquinone derivative of dibenzo 18 crown 6 and  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$  from that we concluded that Naphthaquinone derivative of dibenzo 18 crown 6 used as analytical probe for estimation of  $\text{Cu}^{+2}$  and  $\text{Ni}^{+2}$ .



**X-Ray Diffraction study:****Preparation of Cu (II) complex of naphthaquinone containing dibenzo -18-crown -6:**

A solution of 0.960 g. (2 mmol) of naphthaquinone dibenzo 18 -crown 6 in ethanol (10 ml) was added in 0.344 g. (2 mmol) of Cu (NO<sub>3</sub>)<sub>2</sub> containing catalytic amount of sodium acetate 0.3 g. and stirred when the colour of solution changes from colorless to greenish blue. After completion of reaction the solid formed was filtered paper, yield: 80%, m.p: above 300<sup>0</sup>C.

<sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>): δ, 1.8-2.28 (m, 8H), 2.47-2.87(m, 8H), 5.34 (dd, 2H, *J*), 6.39-6.53 (d, 3H, *J*), 6.57-6.61 (dd, 3H), 6.83-6.95(dd, 2H), 7.16-7.71(dd, 8H)ppm.

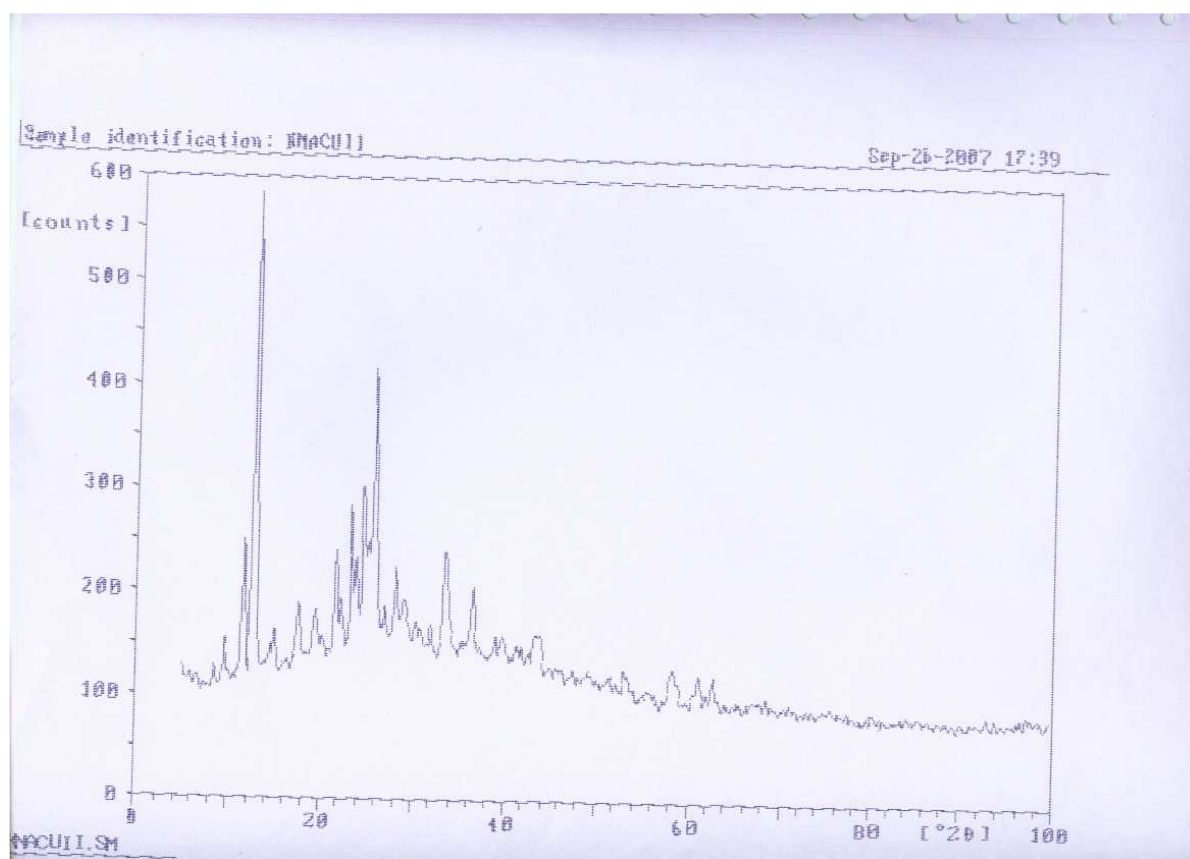
IR (KBr) (cm<sup>-1</sup>): 2914, 2863, 1655, 1581, 1547, 1515.78, 1336, 1200, 1043,772.

<sup>13</sup>CNMR(300MHz,DMSO): δ167,162,154,148,146,137,139,138,137,126

126,126,124,118,110,86,77,65,58,47,45,25,18,14,14

**X-ray diffraction study of Cu (II) complex of naphthaquinone containing dibenzo 18-crown-6:**

X-ray scattering measurement was performed on a Phillips Analytical XRD spectrophotometer. The diffractometer used for the same compound was of the type PW 3710 based. The anode tube used for the same compound was of Copper. X- ray diffraction pattern observed gave very sharp peaks indicating crystalline nature of the complex.

**X-ray diffraction spectrum:**

## RESULTS AND DISCUSSION

Due to the commendable applications of the crown ethers in the field of supramolecular chemistry, we have reported the synthesis of some new macromolecules containing naphthaquinone nucleus. The dinitro-trans -isomer of dibenzo 18-crown-6 was subsequently reduced by stannous chloride method to gives the diamino derivatives of the dibenzo 18-crown-6 [21]. This reduced compound further condensed with the 1,4-naphthaquinone in ethanol using glacial acetic acid as a protocol. The structures of synthesized compound were established on the basis of IR, PMR and  $^{13}\text{C}$  NMR spectral data.

## CONCLUSION

In conclusion, the naphthaquinone derivative of dibenzo-18-crown-6 shows a selective molecular recognition behavior toward copper (II) and Nickel (II) ions. The prepared naphthaquinone derivative of dibenzo 18- crown-6 can be used as a new and selective chromogenic probe for the sensing the Copper (II) and Nickel (II) ion in chemical system.

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