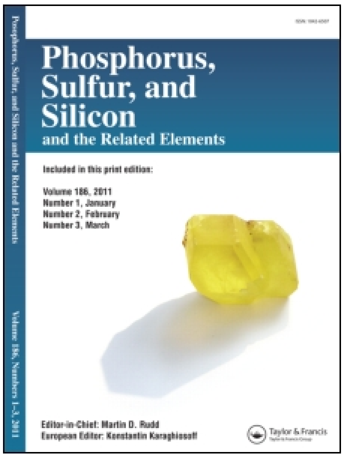

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New 2,2′-thio-bis [4-methyl (2-amino phenoxy) phenyl ether] (***IV***) *was synthesized. The structure of this compound was confirmed on IR, ^1H, and ^{13}C NMR data. A simple, efficient, and sensitive procedure is described for the spectrophotometric determination of a trace amount of Cd(II) or Co(II) in the presence of Zn(II) with this diamine.*

Keywords Cadmium; cobalt; diamine; dibenzosulfide; sulfide

INTRODUCTION

The determination of a trace amount of cadmium has received considerable attention in the battle against environmental pollution. In the determination of cadmium, various methods, including ICP-MS,[1] ion choromatography,[2] anodic stripping,[3] and electrothermal atomic absorption spectrometry,[4] have been used. Many of these methods either are time-consuming or require complicated and expensive instruments. Therefore, methods that could determine a low concentration of heavy metal ions rapidly and conveniently were researched.[5–7] The determination of a cadmium ion has been performed using different ligands such as dithizone (diphenylthiocarbazone),[8–10] 2-aminobenzoic acid (anthranic acid),[11] 2,2′-bipyridine,[12] 8-hydroxy quinoline,[13] sodium diethyldithiocarbamate,[14] 2-acetyl-2-thiazoline hydrazone,[15] and *N*-(5,6-dihydro-4H-1,3-thiazin-2-yl)-2-aminobenzimidazole.[16]

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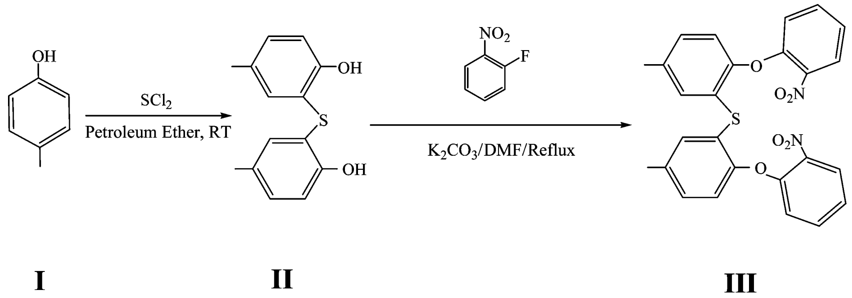
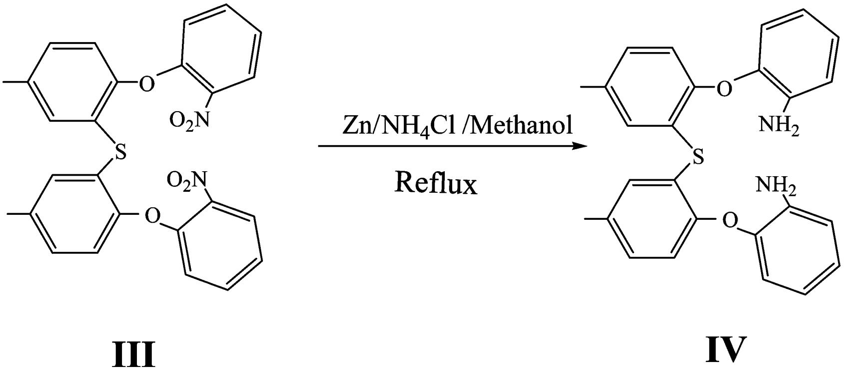


SCHEME 1

In continuation of our previous research for the synthesis of new dibenzosulfoxide and dibenzosulfide monomers and macrocyclic compounds,[17–20] we now wish to report a new interesting dibenzosulfide diamine (**IV**) and its application for the efficient and simple determination of cadmium.

The dibenzosulfide (**II**) was synthesized based on the reported procedure[21] in a 65% yield. The treatment of **II** with the 1-fluoro-2-nitro benzene in the presence of K_2CO_3 at refluxed DMF gave **III** in 90% yields (Scheme 1). A basic reduction of **III** with ammonium chloride in the presence of Zn at refluxed dry methanol afforded **IV** in a 90% yield (Scheme 2).



SCHEME 2

RESULTS AND DISCUSSION

In this article, we describe the syntheses of new 2,2′-thio-bis [4-methyl (2-amino phenoxy) phenyl ether] (**IV**) by the reaction of 1-fluro-2-nitro benzene with **II**, followed by a reduction. Our motive behind the synthesis of this type of ligands was to examine their possible applications in the cation recognition processes. Although this work

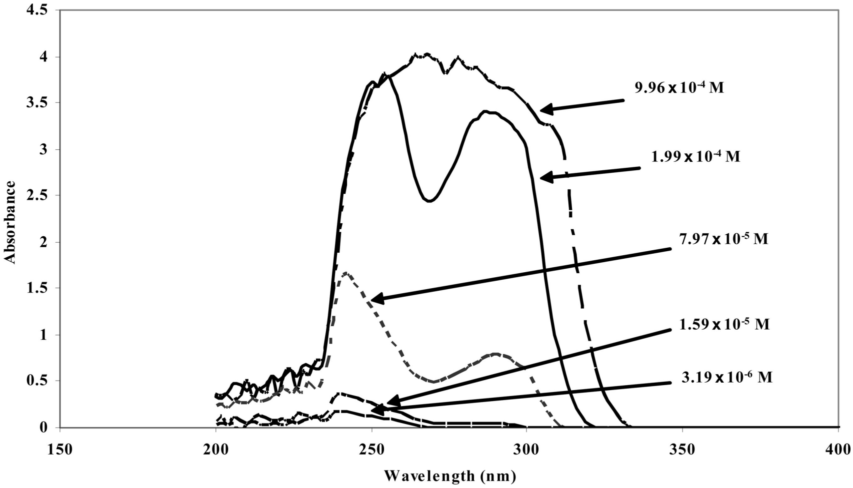


FIGURE 1 Electronic spectra of the diamine (**IV**) ligand in chloroform at different concentrations.

is focused on the determination of cadmium, the evidence obtained in this research indicate that this ligand could also be used for the determination of cobalt with the same procedure.

The electronic absorption spectra of a ligand with various concentrations are represented in Figure 1. An examination of Figure 1 indicates that the electronic spectra of this ligand are largely depending on the concentration. Increasing the compound concentration results in increasing the absorbance of both bands at 254 and 286 nm, where beyond a certain concentration of the compound (9.96×104^{-4} M) a very broad bond is observed. This behavior can be ascribed to the association of molecules through intermolecular hydrogen bonding.

The electronic absorption spectra of ligand and complexes of Cd^{+2}, Zn^{+2}, and Co^{+2} in the same concentration are shown in Figure 2. As can be noticed, the absorption spectra of ligand-Cd and ligand-Co reflects the presence of maximum absorptions at 208 and 244 nm, respectively, which the ligand does not absorb appreciably. The electronic spectrm of ligand-Zn does not show absorption. Therefore, there is no interference from Zn^{+2} in the determination of Cd^{+2} and Co^{+2} with this ligand.

EXPERIMENTAL

Reagent and Material

All experiments were performed with analytical-reagent grade chemicals and pure solvents. Doubly distilled water was used for preparation aqueous solutions.

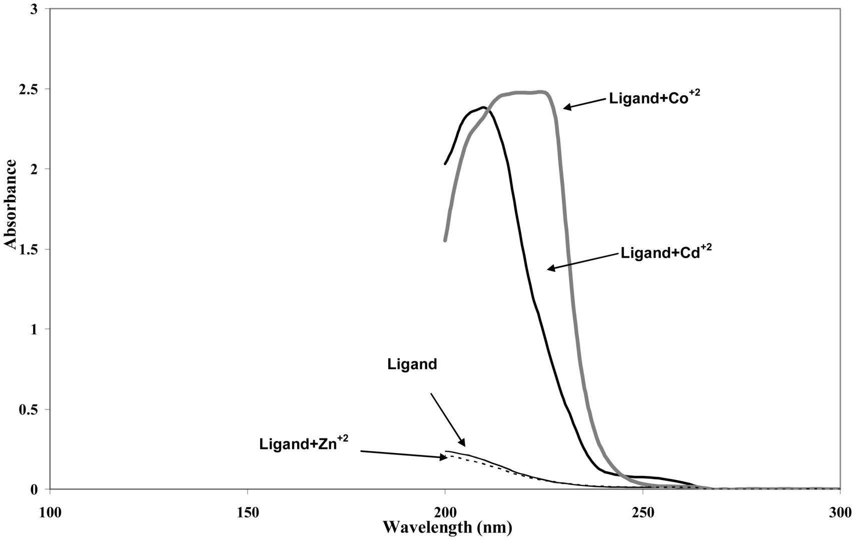


FIGURE 2 Electronic spectra of complexes of diamine (**IV**) ligand with Cd^{+2}, Co^{+2}, and Zn^{+2}.

The ligand was synthesized and purified as described herein. Ligand stock solution (1.07×10^{-3} mol/L) was prepared in chloroform. Stock solutions of 100 ppm of Cd(II), Zn(II), and Co(II) were made by dissolving an appropriate amount of high purity cadmium nitrate, zinc oxide, and cobalt nitrate (Merck, Germany) in distilled water, respectively. Working solutions were prepared by an appropriate dilution of stock solution.

Apparatus

The melting points (uncorrected) were measured by an Electrothermal engineering LTD9100 apparatus. *Elemental analysis was performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA).* IR spectra were measured on a Perkin-Elmer model 543, ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker Avance DRX 500 apparatus. A Milton Roy Model 1201 photomultiplier tube spectrophotometer was interfaced with an IBM PCS-486 microcomputer by the spectro program that was developed to convert the absorption data acquired with the spectrometer used.

Ligand Synthesis and Procedures

2,2′-Thio-bis [4-methyl (2-nitro phenoxy) phenyl ether] (III)

A mixture of **II**, (1 mmol, 0.246 gr) and potassium carbonate (2 mmol, 0.331 gr) was added into a solution of DMF (100 mL) in a 500-mL round-bottom flask. Then *o*-fluoro nitro benzene (2 mmol) was added, and the suspension mixture was heated to a reflux temperature and held for 24 h; then the mixture was allowed to cool to r.t. and subsequently poured into 700 mL of water to precipitate into a yellow solid. The crude product was recrystallized from acetonitrile to afford a crystalline dinitro compound (75% yield) (see Scheme 1); m.p. 103–105°C; IR (KBr) 3109, 3079, 2920, 1610, 1583, 1511, 1487, 1475, 1338, 1249, 1240, 1107, 1053, 864, 850, 843, 754 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$); δ 2.32 (s, 6H, J = 8.4 Hz), 6.75–6.77 (d, 2H J = 8.4Hz), 6.89–6.90 (d, 2H, J = 8.2 Hz), 7.08–7.12 (m, 4H), 7.18 (s, 2H), 7.34–7.37 (t, 2H, J = 7.5 Hz), 7.90–7.92 (d, 2H, J = 8 Hz) ppm; ^{13}C NMR (500 MHz, $CDCl_3$); δ 151.96, 151.31, 140.73, 136.25, 134.49, 134.23, 130.40, 126.61, 125.81, 122.61, 121.09, 118.97, 21.01 ppm; Elemental analysis: (found values) C (63.91), H (4.12), N (5.76); (calculated values) C (63.93), H (4.13), N (5.73).

2,2′-Thio-bis [4-methyl (2-amino phenoxy) phenyl ether] (IV)

A suspension of the intermediate **III** (1 mmol, 0.488 g) in 100 mL of methanol containing Zn (20 mmol, 1.3 g) and ammonium chloride (excess) was heated to a reflux temperature for 18–20 h. The reaction mixture was cooled to r.t. and filtered through celite to remove the catalyst, and the filtrate was concentrated under reduced pressure. The product was recrystallized from ethanol and water to afford a white crystalline diamine compound (85% yield) (see Scheme 2); m.p. 116–118°C; IR (KBr) 3462, 3370, 3034, 2924, 1620, 1597, 1584, 1510, 1500, 1476, 1459, 1302, 1266, 1226, 1137, 1058, 897, 819, 745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$); δ2.27 (s, 6H), 3.14 (b, 4H), 6.63–6.69 (m, 2H), 6.75–6.80 (m, 6H), 6.91–7.0 (m, 4H), 7.15–7.16 (d, 2H, J = 3Hz) ppm; ^{13}C NMR (500 MHz, $CDCl_3$); δ 153.5, 143.4, 137.9, 133.2, 133.0, 129.3, 124.7, 124.4, 119.6, 118.8, 117.0, 116.6, 20.6 ppm; Elemental analysis: (found values) C (72.84), H (5.63), N (6.57); (calculated values) C (72.87), H (5.64), N (6.54).

The Spectrophotometric Determination of Cations

Absorption spectra of **IV** in different concentrations were recorded between 200 and 500 nm (Figure 1). The absorption spectra of complexes are shown in Figure 2. The concentration of the ligand was 1.59×10^{-5} M, and the concentrations of metals were the same (10 ppm).

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