



Determination of cobalt ions at nano-level based on newly synthesized pendant armed macrocycle by polymeric membrane and coated graphite electrode

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ABSTRACT

Poly(vinylchloride) (PVC) based membranes of macrocycles 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene (L_1) and 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaazacyclotetradeca-2,9-diene (L_2) with NaTPB and KTpCIPB as anion excluders and dibutylphthalate (DBP), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctyl ether (*o*-NPOE) and tri-*n*-butylphosphate (TBP) as plasticizing solvent mediators were prepared and investigated as Co^{2+} selective electrodes. The best performance was observed with the membranes having the composition L_2 :PVC:TBP:NaTPB in the ratio of 6:39:53:2 (w/w; mg). The performance of the membrane based on L_2 was compared with polymeric membrane electrode (PME) and coated graphite electrode (CGE). The PME exhibits detection limit of 4.7×10^{-8} M with a Nernstian slope of 29.7 mV decade⁻¹ of activity between pH 2.5 and 8.5 whereas CGE exhibits the detection limit of 6.8×10^{-9} M with a Nernstian slope of 29.5 mV decade⁻¹ of activity between pH 2.0 and 9.0. The response time for PME and CGE was found to be 11 and 8 s, respectively. The CGE has been found to work satisfactorily in partially non-aqueous media up to 35% (v/v) content of methanol, ethanol and 25% (v/v) content of acetonitrile and could be used for a period of 4 months. The CGE was successfully applied for the determination of Co^{2+} in real and pharmaceutical samples and as an indicator electrode in potentiometric titration of cobalt ion.

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1. Introduction

The increasing use of ion sensors in the fields of environmental, agricultural and medicinal analysis is putting more and more pressure on analytical chemists to develop new sensors for the fast, accurate, reproducible and selective determination of various species. During the past few decades, many intensive studies on the design and synthesis of highly selective ionophores as sensory molecules for ion-selective electrodes have been reported and much interest has been focused on macrocyclic compounds. The design and function of synthesized macrocyclic carriers for cation selective membrane sensors are usually based on such diverse parameters as the structure and cavity size of ion carrier, the stability and its ability to extract the target ion into the membrane phase. Currently, a great deal of attention is being focused on macrocyclic ligands because they play an important role in many aspects of chemistry, medicine and the chemical industry.

The need of selective determination of heavy metal ions has increased immensely during the last few decades due to the growing environmental problems. Among heavy metals, the pollution caused by cobalt is of considerable concern. Determination of cobalt

assumes importance because of its widespread occurrence in sea as well as in fresh water, earth crust, meteorites, animals and plants. It is a vital trace element in animal nutrition and widely distributed in the body with high concentration in liver, bone and kidney. Cobalt is used in high-temperature alloys, in permanent magnets and its salts are useful in paint dryers as catalysts, abrasion resistant glasses, ceramics, batteries and in production of numerous pigments like cobalt blue and cobalt green, in ground coats for porcelain enamels and in electroplating industry. Cobalt, in the form of cobalamin, is an essential component of Vit. B₁₂ required for the production of red blood cells and prevention of pernicious anaemia [1]. Deficiency of cobalt may cause anaemia, retarded growth and loss of appetite. On the other hand, if consumed in large doses, cobalt may be toxic and cause diarrhea, irritation of gastrointestinal tract and vomiting. Exposure to cobalt may cause lung effects, which include respiratory irritation, coughing, asthma, pulmonary edema and pneumonia. The maximum dietary tolerable level of cobalt for common livestock species is 10 ppm [2].

A number of sophisticated methods such as flame atomic absorption [3], electrochemiluminescence [4], thin film sequential injection [5], graphite furnace-atomic absorption spectrometry (GF-AAS) [6], electrothermal-atomic absorption spectrometry [7], differential pulse anodic stripping voltammetry [8] have been reported for the determination of cobalt. However, these methods are disadvantageous as they are time consuming, involves sample

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manipulation, relatively expensive and require large infrastructure back up. Selective analytical methodologies, which are easily operated and involve harmless reagents, cost effective equipment, have therefore been proposed as alternative to standard methods. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantages such as selectivity, sensitivity, good precision, simplicity and low cost [9,10].

A literature survey revealed that the sensors developed for cobalt make use of chelates [11], macrocycles [12–17], extractants [18], organic resins [19,20], mercapto compounds [21], OXCDD (diamide) [22], Schiff base [23,24], isothiazole [25], calixarenes [26,27] and variety of other ligands [28,29]. However, most of these sensors suffer from disadvantages such as narrow working concentration range. With a near or non-Nernstian response, exhibit high response time, poor reproducibility.

The purpose of the present work is to explore the polymeric membrane electrode (PME) and coated graphite electrode (CGE) as Co^{2+} selective sensors based on two newly synthesized macrocyclic ligands (L_1 and L_2).

2. Experimental

2.1. Reagents

Reagent grade sodium tetraphenylborate (NaTPB), potassium tetrakis *p*-(chloro phenyl)borate (KTPCIPB), dibutylphthalate (DBP), tri-*n*-butylphosphate (TBP), benzyl acetate (BA), dioctylphthalate (DOP), *o*-nitrophenyloctyl ether (*o*-NPOE), tetrahydrofuran (THF) and high molecular weight poly(vinylchloride) were purchased from E. Merck (Germany) and used as received. Ethylenediamine and 2,6-dichloropyridine were procured from Aldrich (USA). The nitrate salts of all the cations used were of analytical grade and used without any further purification. The solutions of metal salts were prepared in doubly distilled water and standardized whenever necessary.

2.2. Synthesis of macrocyclic ligand 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaaza-cyclotetradeca-2,9-diene (L_1)

The macrocyclic ionophore L_1 (Fig. 1) was synthesized by dissolving equimolar amounts of ethylenediamine (0.01 M) and 2,6-dichloropyridine (0.01 M). Ethylenediamine was dissolved in minimum quantity of methanol and to this solution 2,6-dichloropyridine dissolved in methanol was added dropwise with stirring. The resulting mixture was refluxed for 10 h and then was concentrated to half of its original volume on a water bath, followed by cooling and keeping aside for 1 day. A white crystalline product was obtained. Yield: 72%. M.pt.: 138 °C. Anal. calcd. for $[\text{C}_{14}\text{H}_{18}\text{N}_6]$

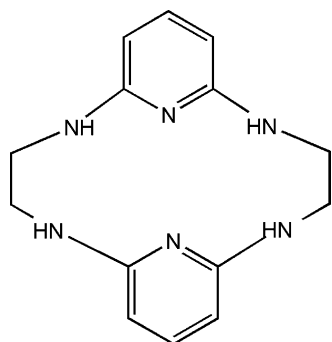


Fig. 1. Structure of macrocyclic ligand 2,3,4:9,10,11-dipyridine-1,3,5,8,10,12-hexaaza-cyclotetradeca-2,10-diene (L_1).

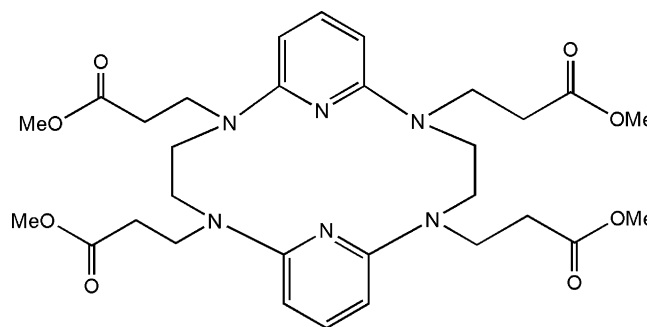


Fig. 2. Structure of macrocyclic pendant ligand 2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaaza-cyclotetradeca-2,10-diene (L_2).

(%): C, 62.19; H, 6.69; N, 31.12; Observed (%): C, 62.20; H, 6.71; N, 31.09, ^1H NMR (MeOH, 500 MHz) δ_{ppm} : 7.02–7.64 (m, H–Ar, 6H), 2.64–2.67 (m, –C–NH–C–, 4H), 2.32 (s, –N–CH₂–C, 8H). FT-IR (KBr, cm^{-1}): 3268 (–NH str.).

2.2.1. Synthesis of macrocyclic ligand

2,3,4:9,10,11-dipyridine-1,5,8,12-tetramethylacrylate-1,3,5,8,10,12-hexaaza-cyclotetradeca-2,9-diene (L_2)

The macrocyclic pendant ligand L_2 (Fig. 2) was synthesized from macrocycle L_1 . To a stirred solution of the macrocycle L_1 (1 mmol) in 10 mL saturated solution of anhydrous K_2CO_3 in anhydrous MeOH, 5 mL methylacrylate (excess amount) was added drop by drop and then it was stirred overnight and refluxed for 24 h. Then the volume was reduced half of its initial amount and was kept in a refrigerator overnight. A creamish coloured oily product was obtained. Yield: 43%. Anal. calcd. for $[\text{C}_{30}\text{H}_{42}\text{N}_6\text{O}_8]$ (%): C, 58.60; H, 6.88; N, 13.67; O, 20.85; Observed (%): C, 58.62; H, 6.89; N, 13.67; O, 20.82. ^1H NMR (MeOH, 500 MHz) δ_{ppm} : 6.90–7.22 (m, H–Ar, 8H), 2.97–3.25 (m, –N–CH₂–C–, 8H), 2.52 (s, N–CH₂–CH₂–N, 8H), 2.38–2.42 (m, –C–CH₂–COOMe, 8H), 1.36 (s, –OCH₃, 12H), FT-IR (KBr, cm^{-1}): 2930 (asymmetric –CH₂– str.), 2848 (symmetric –CH₂– str.), 1747 (ester C=O str.), 1570–1382 (aromatic C=C and C=N str.), 1163 (OC–OCH₃ str.), 1109 (–OCH₃ str.).

2.3. Electrode preparation

The nature and amount of ionophore, nature of plasticizers, plasticizer/PVC ratio and especially the nature of lipophilic additives used, are known to significantly influence the sensitivity and selectivity. Varying amount of the ion-active phase and anion excluder KTPCIPB and NaTPB were dissolved with an appropriate amount of PVC in 3 mL THF. To these, solvent mediators, viz. DBP, TBP, BA, DBS and *o*-NPOE were added to get membranes of different compositions. The mixture was shaken vigorously with a glass rod. When the solution became viscous it was poured in acrylic ring placed on smooth glass plate. The solution was then allowed to evaporate for 24 h at room temperature. Transparent membranes of about 0.1 mm thickness were obtained, which were then cut to size and glued to one end of a pyrex glass tube with araldite. The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the potential recorded were reproducible and stable within the standard deviation. Membrane to membrane reproducibility was assured by carefully following the optimum condition of fabrication. The membrane that gave reproducible results and showed best performance was selected for further studies.

To prepare the coated graphite electrodes, spectroscopic grade graphite rods 10 mm long and 3 mm in diameter were used. A

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