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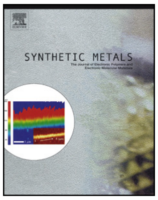

Synthesis, electronic spectroscopy, electrochemistry and catalytic activity of a new Co (II) complex of 1,4,8,11-tetraaza[14]annulene derivative

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ABSTRACT

A new Co (II) complex of 6,13-disubstituted 1,4,8,11-tetraaza[14]annulene derivative has been synthesized by template condensation reaction of 2-(1-quinolinium-1-yl) trimethinium salt (B) with 1,2-diaminopyridine in the presence of Co (II) acetate in DMF. The electrochemical behavior of the metal complex showed a Co^{II}/Co^{I} redox couple at about −0.99 V vs. Ag/Ag^+ in DMF solvent. Axial ligation of N-donor ligands such as pyridine and imidazole was found to shift the reduction potential of Co^{II}/Co^{I} to more negative potential. The binding of N-donor axial ligands to the metal complex was monitored by measuring changes at about 458 nm (maximun absorption of the metal complex) and shifts in the Co^{II}/Co^{I} redox couple potential upon addition of various concentrations of the N-donor axial ligand. Results showed that the number of axial ligand molecules bound to the metal complex is ≈1 and the oxidized state of cobalt (Co^{II}) is more stabilized than the reduced state (Co^{I}) in the presence of the axial ligand. The metal complex also showed catalytic activity toward hydrogen peroxide decomposition in the presence of the N-donor axial ligand.

1. Introduction

Tetraaza[14]annulene-derivatives and their metal complexes find increasing interest in recent years as macrocyclic chelate and simpler model molecules for Metalloporphyrines as well as an active part of metalloenzymes and as biomimetic model compounds [1–9]. They are antiaromatic and their central cavity is smaller than in porphyrins and, as a consequence, the metal-nitrogen distance is shorter and the complexes are more stable. Tetraaza[14]aannulenes accept a large variety of substituents on the carbon atoms of the tetraaza macrocycle [10–19]. The presence of peripheral substituents on the derivatives is more important than for larger macrocycles such as phthalocyanines and porphyrins. The steric hindrance of the substituents can cause planarity distortion of the compounds [3] and therefore, can affect on their chemical properties and catalytic activities. These facts prompted us to report the synthesis of a new cobalt complex of 6,13-disubstituted 1,4,8,11-tetraaza[14]annulene derivative by cyclizing condensation of 1,2-diaminopyridine with a 2-(1-quinolinium-1-yl) trimethinium salt in the presence of Co^{2+} ion in an organic solvent (**Co^{II}DTA**), where the metal cation plays a coordinating role between the two reaction partners, which is so called template reaction (Scheme 1). Furthermore, spectroscopic characterization and electrochemical behavior of the complex were investigated using visible spectroscopy and cyclic voltammetry. The catalytic activity of the complex toward hydrogen peroxide decomposition was also examined in the presence of N-donor axial ligands. To the best of our knowledge, up to date there is no report on the synthesis of this dicationic metal complex using a 2-heteroaryl-substituted trimethinium salt. Generally, these studies can help to better understand and summarize the chemical properties and catalytic activities of 6,13-disubstituted tetraaza[14]annulene metal complexes in the future.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from Fluka and Merck companies or prepared according to literature procedures. Solvents were of analytical grade and used as received from commercial suppliers.

UV/vis absorption spectra were recorded using an *Analytik Jena SPECORD 250* spectrophotometer. Elemental analyses were made with a CHN Analyzer (Flash, 1112 Series (EA). All electrochemical measurements were performed using a Metrohm electroanalyzer Model 797 VA at ambient temperature (25 °C) in a conventional

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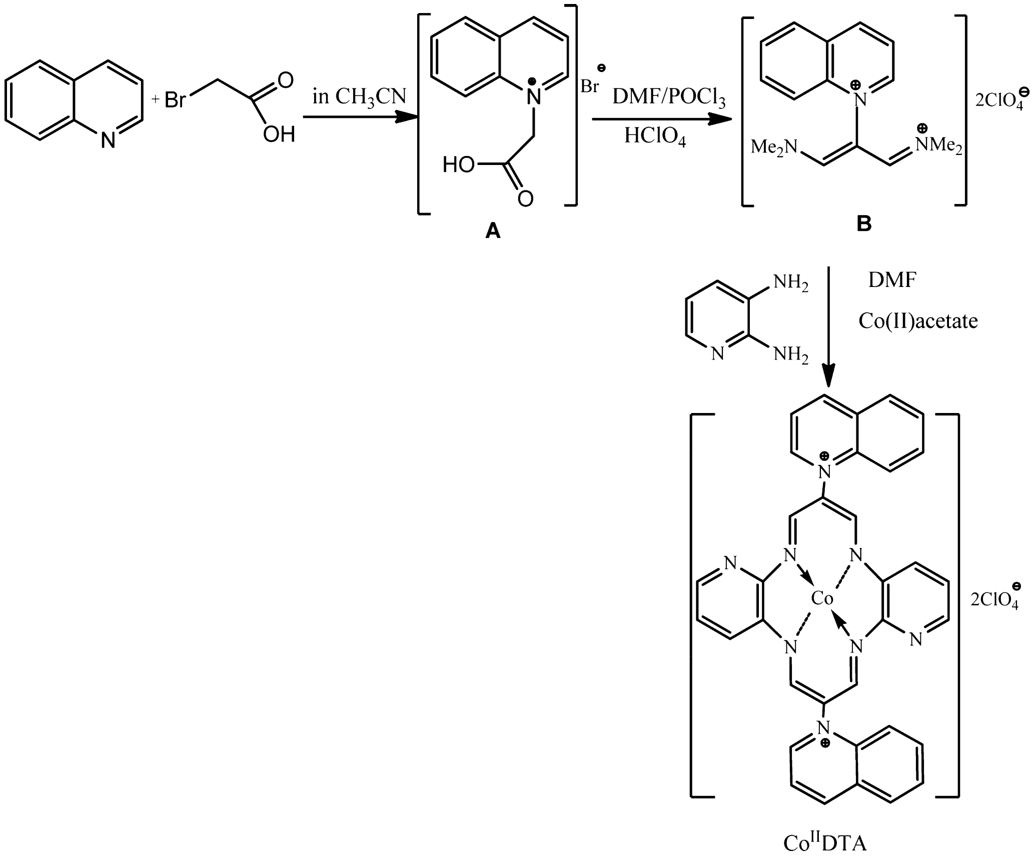

Scheme 1. Reaction pathways for the synthesis of Co^{II}-6,13-Bis[1-quinolinio]-1,8-dihydro-dipyrido[b,i]-[1,4,8,11]-tetraaza cyclotetradecahexaene-bis(perchlorate) (**Co^{II}DTA**).

three-compartment electrochemical cell consisting of a Pt-button working electrode, a platinum rod auxiliary electrode and a Ag/Ag$^+$ (with 0.1 M TBAP in CH$_3$CN solution) electrode as the reference. Cyclic voltammetry measurements were carried out in dimethylformamide (DMF) using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte at a scan rate of 0.1 V s^{-1}. The solvent of choice for the study of the electrochemical properties of the metallic complex is DMF, due to the compound dissolve readily in this solvent and the anodic potential limit of DMF is lower than that of other electrochemical solvents.

2.2. Synthesis

The new metal complex of 6,13-disubstituted 1,4,8,11-tetraaza[14]annulene was synthesized using a two-step procedure as shown in Scheme 1. (i) synthesis of 2-(1-quinolinium-1-yl) trimethinium **B** by Vilsmeier-Arnold formylation of corresponding N-heteroaryl acetic acid salt (**A**) as described in our previous works [20–22]; and (ii) synthesis of **Co^{II}DTA** by the template condensation reaction of salt **B** with the 1,2-diaminopyridine and Co (II) acetate.

Clearly the advantage of this synthetic procedure is readily preparation of the 2-substituted trimethinium salt in a one step reaction from the corresponding substituted acetic acid under Vilsmeier-Haack conditions. In addition, examples of heterocyclic appended trimethinium salts and corresponding metal complexes of 6,13-disubstituted 1,4,8,11-tetraaza[14]annulenes through a nitrogen atom is rare. For these reasons, it appeared to us that the cobalt complex of 6,13-Bis (1-quinolinium-1-yl) 1,4,8,11-tetraaza[14]annulene would be a worthy synthetic target. Application of this methodology resulted in the metal complex being obtained in 50% yield. This metal complex is a well defined, stable solid and has a long shelf life if it is stored in anhydrous environment.

2.2.1. Co^{II}-6,13-Bis[1-quinolinio]-1,8-dihydro-dipyrido[b,i]-[1,4,8,11]-tetraaza cyclotetradecahexaene-bis(perchlorate) (*Co^{II}DTA*)

0.455 g (1.0 mmol) of **B** was dissolved in 4.0 mL of DMF. 1.0 mmol of 1,2-diaminopyridine and 4.0 mmol of Co (II) acetate were added to the solution. The mixture was refluxed at 120 °C for 1 h. The progress of reaction was monitored by thin layer chromatography (TLC). The results showed that after 1 h reflux the total amount of 1,2-diaminopyridine was consumed. Then, the reflux was continued for 24 h at the same temperature. Afterward 30.0 mL of ethylacetate was added to the refluxed solution. The resultant precipitate was filtered, washed with diethyl ether and dried. The solid product was washed with warm methanol (20.0 mL) and dried under vacuum at 80 °C. Molecular mass, elemental analysis, yield, and visible spectral data (measured in DMF) of the new metal complexe of 6,13-disubstituted 1,4,8,11-tetraaza[14]annulene are shown in Table 1. The melting point of the complex is above 350 °C.

Furthermore, In order to confirm the synthesis, we synthesized the corresponding free-metal ligand using salt **B** and 1,2-diaminopyridine as described in our previous work [22] and we characterized its structural properties on the basis of IR, ^{1}H NMR, ^{13}C NMR, and mass spectra as follows: IR: $\bar{\upsilon}/\mathrm{cm}^{-1} = 3453$ (broad, —NH), 1720 (s, C=N), 1089 (s, ClO$_4^-$); ^{1}H NMR (d$_6$-DMSO): δ/ppm = 8.04–8.77 (m, 2OH, quinolino-H, pyridine-H), 9.70–9.72 (m, 4H, CH=N and CH—N), 14.63 (t, J = 7.0 Hz, 2H, NH); ^{13}C NMR (d$_6$-DMSO): δ/ppm = 113.97 (C$_2$ and C$_{13}$), 120.45, 121.25, 122.62, 123.60, 130.56, 136.57, 136.77, 141.18, 141.23, 141.49 149.07,