

A novel pentaazadentate bismacrocylic cadmium complex

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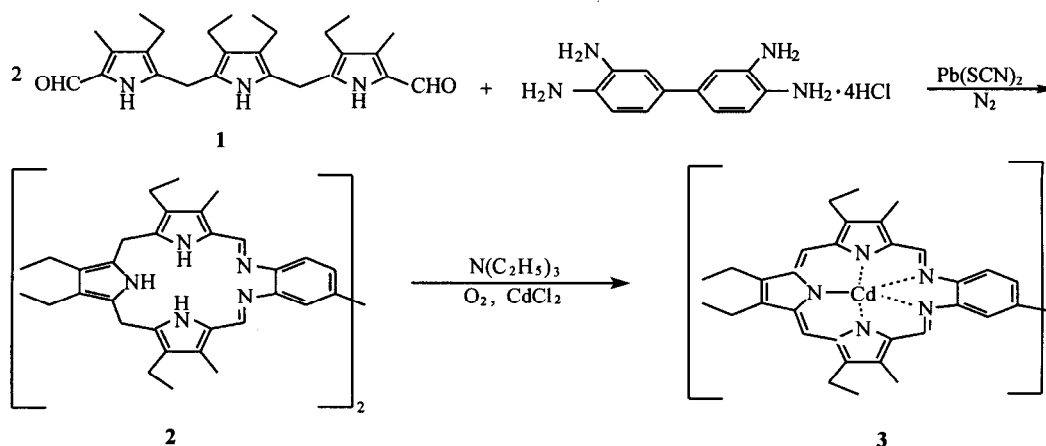
A novel pentaazadentate bismacrocycle was synthesized through an improved procedure of 1:1 Schiff base condensation of diformyltripyrane with 3, 4, 3', 4'-tetraamino-biphenyl hydrochloride using Pb^{2+} as template ion, in which the condensed byproduct water was removed efficiently to make the yield over 90%. Then the bismacrocylic ligand reacted with cadmium chloride to yield the title metal complex with molecular weight being 1200.4 by TOF MS and the λ_{max} being 766 nm.

Keywords Pentaazadentate bismacrocylic cadmium complex, isotopes, absorbance

Introduction

Recently, the pentaazadentate macrocyclic ligands and their metal complexes containing 22 π -electrons have been studied extensively.¹ These expanded porphyrin-like complexes appear an important potential applications in nonlinear optical materials, photodynamic therapy,^{2,3} however all interests of the synthesis and the potential applications were concentrated on the monomacrocylic complexes. Recently, some reports have shown that the diporphyrins and oligoporphyrins possessed more outstanding performances than the monoporphyrins,⁴ therefore, we designed and prepared the first member of tripyrrane-containing pentaazadentate bismacrocylic ligand and its metal complex, which is expected to be a versatile photoresponsive material.

Scheme 1



Experimental

The bismacrocylic ligand: 16, 16'-bis[4, 5, 9,

24-tetraethyl-10, 23-dimethyl-13, 20, 25, 26, 27-pentaazapenta-cyclo [20, 2, 1¹³, 6^{18,11}, 0^{14,19}] heptacos-2, 4, 6, 8, 10, 12(21), 14(19), 16, 18, 20, 22,

* Received September 15, 1999; accepted January 14, 2000.

Project (No.29832030, 29682001) supported by the National Natural Science Foundation of China.

24-undecene] was prepared from the 1 : 1 Schiff base condensation of 3, 4, 3', 4'-tetraamino-biphenyl hydrochloride with 2, 5-bis [(3-ethyl-5-formyl-4-methylpyrrol-2-yl) methyl]-3, 4-diethylpyrrole¹ using Pb^{2+} as template ion. In this procedure, we efficiently removed the byproduct water produced in the condensation reaction by an azeotropic distillate collector. In this way we obtained the tripyrrane-containing pentaazadentate bismacrocylic ligand with 92% yield.

Into an one litre three-necked flask containing a degassed mixture of 440 mL of dry benzene and absolute methanol (3:1, V/V), the diformyltripyrane (1) (110 mg, 0.26 mmol), 3,4,3', 4'-tetraamino-biphenyl hydrochloride (51 mg, 0.13 mmol) and $\text{Pb}(\text{SCN})_2$ (77 mg, 0.24 mmol) were added. The resulted golden solution was heated at reflux for 4.5 h under nitrogen, during which 115 mL of azotropic distillate was removed, and then heated at reflux for another 4.5 h under nitrogen. The reaction solution was filtered to remove lead salts and taken to dryness on a rotavapor. The resulted product was dissolved in 40 mL of dichloromethane and layered with 30 mL of hexane. It was placed in the refrigerator for several days for recrystallizing, the dark red powdered crystallite was afforded (132 mg, 92%). Mp 1800°C. $\lambda_{\text{max}}(\text{MeOH})$: 390 (ϵ 79600) nm. $\nu_{\text{max}}(\text{KBr})$: 2925 (CH), 1636, 1612 (C = N, C = C) cm^{-1} . $\delta_{\text{H}}(\text{XL-400}, d_7\text{-DMF}, \text{TMS})$: 1.05—1.09 (t, $J = 7.4$ Hz, 12H, 4 \times CH_3CH_2), 1.16—1.20 (t, $J = 7.6$ Hz, 12H, 4 \times CH_3CH_2), 2.39 (s, 6H, 2 \times $\text{CH}_3\text{-pyrrole}$), 2.41 (s, 6H, 2 \times $\text{CH}_3\text{-pyrrole}$), 2.42—2.47 (q, $J = 7.4$ Hz, 8H, 4 \times CH_2CH_3), 2.59—2.64 (q, $J = 7.1$ Hz, 8H, 4 \times CH_2CH_3), 4.11 (s, 4H, 2 \times pyrrole- $\text{CH}_2\text{-pyrrole}$), 4.13 (s, 4H, 2 \times pyrrole- $\text{CH}_2\text{-pyrrole}$), 5.30 (br, 3H, 3 \times HSCN), 7.81—7.84 (s, $J = 8.4$ Hz, 2H, 2 \times H-Ph), 7.95—7.97 (d, $J = 9.2$ Hz, 2H, 2 \times H-Ph), 8.29 (s, 2H, 2 \times H-Ph), 8.84 (s, 2H, 2 \times HC = N), 8.95 (s, 2H, 2 \times CH = N), 10.69 (s, 2H, 2 \times HN), 11.90 (s, 2H, 2 \times HN), 12.10 (s, 2H, 2 \times HN). $\delta_{\text{C}}(\text{XL-200}, d_7\text{-DMF})$: 9.42 (8C, 8 \times CH_3CH_2), 15.33 (4C, 4 \times CH_3), 17.11 (2C, 2 \times CH_2CH_3), 17.42 (2C, 2 \times CH_2CH_3), 17.75 (2C, 2 \times CH_2CH_3), 17.97 (2C, 2 \times CH_2CH_3), 23.51 (4C, 4 \times pyrrole- $\text{CH}_2\text{-pyrrole}$), 116.32 (2C, 2 \times C-Ph), 118.43 (2C, 2 \times C-Ph), 121.67—138.61 (32C, Ph and Pyrrole), 143.64 (2C, 2 \times CH = N), 144.70 (2C, 2 \times CH = N), 146.20 (HSCN). $\delta_{\text{C}}(\text{DEPT}, \text{Varian Unity } 200,$

$d_7\text{-DMF})$: 8.90 (8C, 8 \times CH_3CH_2), 14.63 (4C, 4 \times $\text{CH}_3\text{-Pyrrole}$), 115.32 (2C, 2 \times C-Ph), 117.45 (2C, 2 \times C-Ph), 124.28 (2C, 2 \times C-Ph), 142.17 (1C, CH = N), 142.20 (1C, CH = N), 142.37 (1C, CH = N), 142.54 (1C, CH = N). FAB-MS, m/z (%): 1044.5 [(M + H + HSCN)⁺, 0.4], 986.5 (M⁺, 100). Anal. $\text{C}_{64}\text{H}_{76}\text{N}_{10}\cdot 3\text{HSCN}\cdot 2\text{H}_2\text{O}$. Calcd: C, 67.14; H, 6.98; N, 15.19; S, 8.02; O, 2.67. Found: C, 67.82; H, 6.85; N, 15.10; S, 7.84; O, 2.68.

The ligand reacts with cadmium chloride in the dilute solution to yield the title complex with 33.5% yield. Into a 500 mL three-necked flask containing the mixture solvent of 200 mL chloroform and 100 mL methanol, the ligand (2) 49 mg (0.05 mmol), cadmium chloride 22 mg (0.1 mmol) and three ethyl amine (1 mL) were added. The solution was heated at reflux temperature for 10 h under oxygen, then the resulted solution was gradually cooled to room temperature and the solvents were removed under reduced pressure. The new product was purified by column chromatography through a silica gel using mixture solvent of chloroform containing amount of methanol (0%—5% V/V) as the eluting agent. The yellow green elutes were combined and the solvent was removed. The refined product was obtained through recrystallization from the chloroform and *n*-hexane (33.5%). $\lambda_{\text{max}}(\text{MeOH})$: 423 (ϵ 21880), 466 (ϵ 22450), 704 (ϵ 3720), 766 (ϵ 10000) nm. $\nu_{\text{max}}(\text{KBr})$: 2967 (CH), 1636 (C = N), 1214 (C—C) cm^{-1} . $\delta_{\text{H}}(\text{XL-400}, \text{D}_1\text{-chloroform}, \text{TMS})$: 0.81 (12H, 4 \times CH_3CH_2), 1.19 (12H, 4 \times CH_3CH_2), 1.32 (16H, 8 \times CH_2CH_3), 1.66 (12H, 4 \times CH_3), 7.99—8.41 (6H, H-Ph), 9.19—9.49 (4H, 2 \times 2HC = N), 11.28—12.00 (4H, 2 \times 2HC = C). The time of flying (TOF) MS, m/z (%): 1200.4 for the $\text{C}_{64}\text{H}_{66}\text{N}_{10}\text{Cd}_2$ with different abundance cadmium of Cd 112.9 and Cd 113.9; Anal. $\text{C}_{64}\text{H}_{66}\text{N}_{10}\text{Cd}_2\text{Cl}_2\cdot 2\text{CHCl}_3$. Calcd: C, 52.30; H, 4.50; N, 9.27. Found: C, 52.80; H, 4.88; N, 9.70.

Discussion

Emphatically here is that the bismacrocylic pentaazadentate cadmium complexes consist of series of cadmium isotopes with atomic weight from 105.9 to 115.9 which result in the complex molecular weight varying from 1195.4 to 1205.3 while the atomic weight of car-

bon, nitrogen and hydrogen take 12.0, 14.0 and 1.0 respectively.

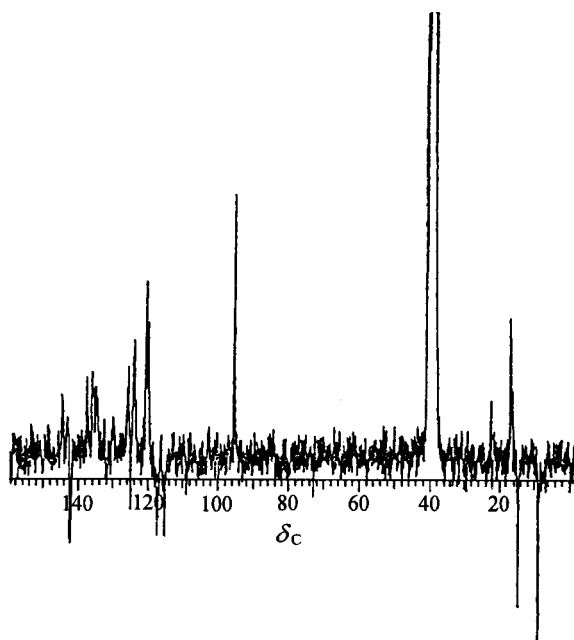


Fig. 1 ^{13}C NMR DEPT spectrum (318 K) of bismacrocylic ligand for negative CH and CH_3 signal in d_7 -DMF. The signals at 38—42 and 95 represent solvent and CCl_4 peaks, respectively.

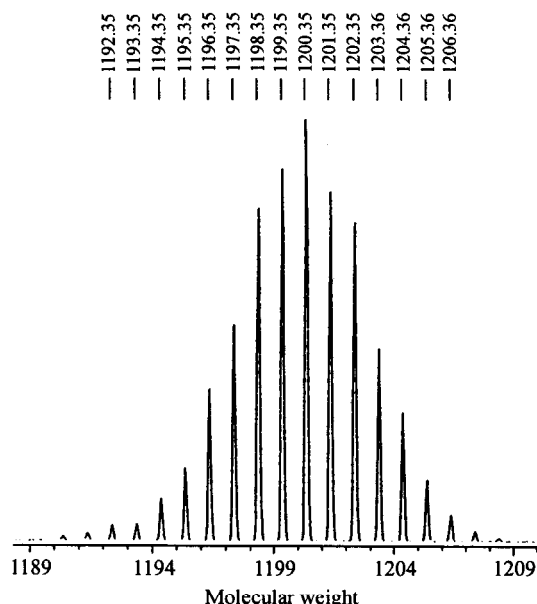


Fig. 2 Theoretical simulated molecular weight distribution for $\text{C}_{64}\text{H}_{66}\text{N}_{10}\text{Cd}_2$ with cadmium isotopes.

The bispentaazamacrocyclic ligand appears maximum absorption peak at 390 nm and its molar extinction

coefficient is $79600 \text{ mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{L}$, the absorption peak has 25 nm red shift and double the absorbance of mono-pentaazamacrocyclic ligand.¹ The observation of only half-line peak patterns for protons and carbons in ^1H NMR and ^{13}C NMR spectra like mono-macrocycle indicates the presence of symmetric characteristic with C_2 axis of biphenyl. In addition, the ^{13}C NMR spectrum was also monitored by DEPT (Distortionless Enhancement by Polarization Transfer) for negative CH and CH_3 but the positive CH_2 signals with and without proton decoupling (Fig. 1). The results are similar to tetraazadentate bisporphyrin compounds.⁵ The symmetry plays an important role in deciding the spectroscopic properties of the pentaazadentate bismacrocycle.

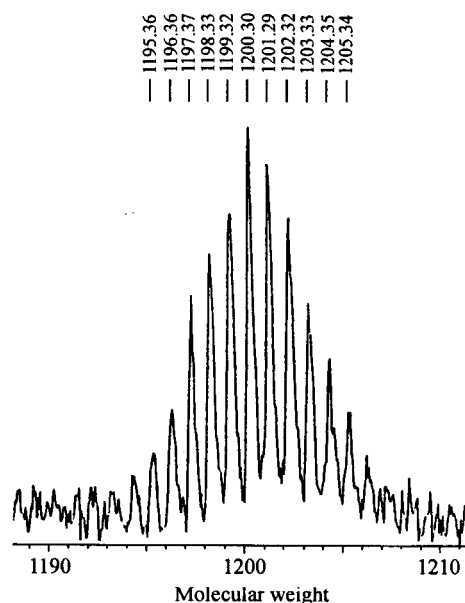


Fig. 3 Found molecular weight distribution for the bismacrocylic cadmium complex.

Besides, according to the elementary analysis, and also the ^1H and ^{13}C NMR spectra, ligand 2 contains three thiocyanic acid molecules like hydrobromine pyrrole, and the ligand has formed a hydro-pyrrole in the macrocycle in the acid-catalyzed 1:1 Schiff base condensation procedure, which can be observed in the ^1H NMR spectrum.

The electronic absorption spectrum of the bismacrocylic cadmium complex contains the Soret B and Q bands. The maximum of the Q band appears at 766 nm, which has a 6 nm red shift compared with the monocyclic pentaazadentate cadmium complex. The B band splits

into two peaks appearing at 423 nm and 466 nm respectively duo to the coordination of the cadmium ions.

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(E9909121 PAN, B.F.; LING, J.)