

고감도 수용체에 의한 ClO_4^- 검출 : 수용액에서 주-객 이온간의 평형

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(2001. 11. 5 접수)

Detection of ClO_4^- via A Hypersensitive Receptor : Unusual Electrostatic Equilibria between Host and Guest in Aqueous Media

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(Received Nov. 5, 2001)

요 약 : ClO_4^- 이온만을 선택적으로 감지하는 새로운 수용체가 개발되었다. $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S}) \cdot 2\text{ClO}_4]_4$ (Me_4en = N,N,N',N'-tetramethylethylenediamine; Py_2S = 4,4'-dipyridyl sulfide) 착화합물에서 주-객 화학종 간의 고감도 작용력을 연구하였다. Py_2S 의 피리딜 기는 온도, 농도, 매개체 등에 아주 민감한 두 가지 셋트의 ^1H NMR 공명 시그널을 보여주었다. 이러한 NMR 거동은 수용액에서 고리 사합체의 양이온과 ClO_4^- 음이온 간의 정전기적 인력에 의한 평형 때문인 것으로 해석되었다.

Abstract : A useful receptor for the sensing of ClO_4^- species with remarkable selectivity has been developed. The hypersensitive interaction between a host and a guest has been investigated for the complex $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S}) \cdot 2\text{ClO}_4]_4$ (Me_4en = N,N,N',N'-tetramethylethylenediamine; Py_2S = 4,4'-dipyridyl sulfide). The pyridyl moiety of Py_2S exhibits two sets of ^1H resonances that are delicately dependent upon temperature, concentration, and media. The nonrigidity has been explained in terms of an electrostatic equilibrium between the tetrameric host and the ClO_4^- guest. The equilibrium is a useful method for the detection of ClO_4^- anion with remarkable selectivity via "a restricted guest within a big host" in aqueous solution.

Key words : perchlorate sensing, palladium complex, electrostatic interaction

1. Introduction

Some anions give rise to a considerable pollution problem. Among various anionic species, perchlorate (ClO_4^-) has been widely used in diverse fields such as

ligands, counteranions, oxidants, explosive materials, solid rocket propellants, electrolytes in dry cells, and pyrotechnic devices.¹⁻³ The water-soluble perchlorate can unconsciously reach humans through groundwater or food chain. The perchlorate anion can block iodine uptake in the body, disrupting thyroid function and leading to health problems. Recently, the source and extent of ClO_4^- in several farm and garden fertilizers

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raised a mysterious question.^{4,5} For the purpose of the selective sensing of such harmful anions, low dimensional receptors by the assembly of metal coordination species can be specifically designed according to the selection of basic components such as the coordination geometry of the metal ions, the binding site of the donating atoms, and the length of the spacer. The detection of anions by the specific receptors plays indispensable roles in the multidisciplinary areas such as environmental chemistry, sensing materials, and biomimicry.⁶⁻¹⁰ Our recent development in responsive receptors has advanced towards substantial applications.^{11,12}

This work presents the construction of $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S})_4] \cdot 8\text{X}$ ($\text{Me}_4\text{en} = \text{N},\text{N},\text{N}',\text{N}'\text{-tetramethylethylenediamine}$; $\text{Py}_2\text{S} = 4,4'\text{-dipyridyl sulfide}$ ¹³⁻¹⁵; $\text{X}^- = \text{NO}_3^-$, ClO_4^-) and the selective detection of ClO_4^- in aqueous solution. Our interest is studies on substantial recognition of an explosive chemical, ClO_4^- , via ^1H NMR in aqueous solution.

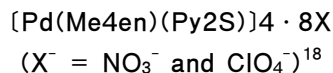
2. Experimental section

2.1 Materials and Physical Measurements.

NaNO_3 and NaClO_4 were purchased from Junsei Chemical Co. and used without further purification. $\text{N},\text{N},\text{N}',\text{N}'\text{-Tetramethylethylenediamine}$ (Me_4en), ethylenediamine (en), 1,2-bis(diphenylphosphino)ethane (dppe), AgNO_3 , and K_2PdCl_4 were purchased from Aldrich. 4,4'-Dipyridyl sulfide (Py_2S) was prepared by the literature procedure.¹³ $\text{PdCl}_2(\text{Me}_4\text{en})$, $\text{PdCl}_2(\text{en})$, and $\text{PdCl}_2(\text{dppe})$ were prepared according to the literature.^{16,17} Elemental microanalyses (C, H, N) were performed on crystalline samples by the Advanced Analytical Center at KIST using a Perkin Elmer 2400 CHNS analyzer. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 or on a Bruker 600 instruments operating at 300.00 (75.48 for ^{13}C) or 600.00 (150.96 for ^{13}C) MHz. The chemical shifts were relative to internal Me_4Si (^1H and ^{13}C). Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellet.

Ion concentrations were measured on a Dionex 300 ion chromatography (flow rate = 1.2 mL/min).

2.2 Construction of



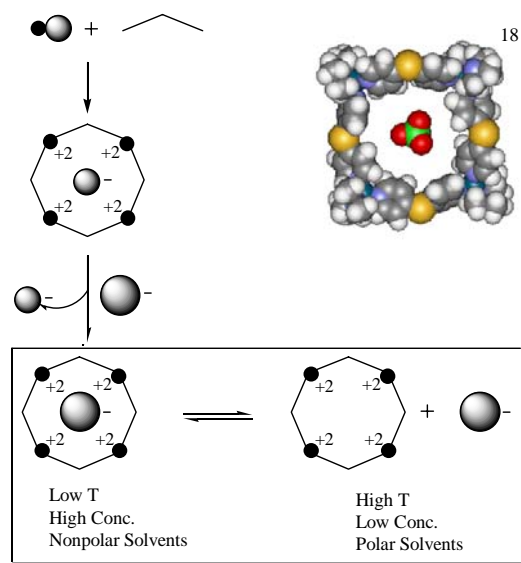
$\text{PdCl}_2(\text{Me}_4\text{en})$ (0.29 g, 1.0 mmol) was suspended in water (50 mL) and stirred for 2 h at room temperature with AgNO_3 (0.34 g, 2.0 mmol). After removal of AgCl by filtration, Py_2S (0.19 g, 1.0 mmol) was added to the filtrate. After the mixture was stirred at 70 °C for 2 h, the solution was evaporated to 5 mL. (This stage compound, $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S})_4] \cdot 8\text{NO}_3$, could be used to recognize ClO_4^-). To obtain crystalline sample for analytical grade, addition of NaClO_4 (0.25 g, 2.0 mmol) to the solution precipitated the ClO_4^- product. Recrystallization of the crude product in water afforded pale yellow crystals in 87% yield (not suitable for X-ray single crystal studies: several attempts to solve the crystal structure failed even at low temperature). Found (Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_8\text{SCl}_2\text{Pd}$): C, 31.60 (31.52); H, 4.02 (3.97); N, 9.09 (9.19). ^{13}C NMR (D_2O , ppm, 75.48 MHz): 151.24, 151.02, 149.69, 149.57, 128.29, 128.03, 63.08, 50.68. Each resonance signal was assigned by the $^1\text{H}/^{13}\text{C}$ heteronuclear COSY spectrum. IR (KBr, cm^{-1}): 3450 (m, br), 1596 (s), 1472 (m), 1428 (m), 1384 (w), 1280 (w), 1224 (w), 1090 (s), 1006 (m), 954 (m), 812 (m), 770 (w), 736 (m), 624 (s), 546 (w), 504 (w).

The analogs, $[\text{Pd}(\text{en})(\text{Py}_2\text{S})_4] \cdot 8\text{ClO}_4$ and $[\text{Pd}(\text{dppe})(\text{Py}_2\text{S})_4] \cdot 8\text{ClO}_4$, were prepared by the similar procedure.

3. Results and discussion

Addition of Py_2S to an aqueous solution of $[\text{Pd}(\text{NO}_3)_2(\text{Me}_4\text{en})]$, followed by the counteranion exchange with ClO_4^- resulted in a pale yellow crystalline product. Elemental analysis and NMR spectra are consistent with the formation of 1 : 1 ($\text{Pd}(\text{Me}_4\text{en})$: Py_2S) stoichiometry. Electrospray ionization mass measurements yielded intense significant peaks. The two

peaks at $m/e = 1117.8$ and 714.3 correspond to the $[\text{M}-2\text{ClO}_4]^{2+}$ and $[\text{M}-2\text{ClO}_4]^{3+}$ species, respectively, establishing the tetranuclear metal content of the compound (Scheme 1).



Scheme 1. Construction and Recognition of Host-Guest Molecules

For the palladium compound, the pyridyl group exhibits two sets of ^1H resonances (8.97 and 7.70; 8.86 and 7.59 ppm) while the Me_4en coligand shows one equivalent signal in aqueous solution. The most striking feature is that the peak ratio of the pyridyl protons is dependent upon temperature, concentration, and solvents, confirming the coexistence of two unique species in the solution. Variable temperature NMR spectra in the range of 0 - 60 $^\circ\text{C}$ were monitored (Fig. 1a). At low temperatures the peaks at 8.97 and 7.70 ppm are more intense while at elevated temperatures the intensities of the peaks at 8.86 and 7.59 ppm are increased. The intensities of the two sets of peaks are nearly equal at 45 $^\circ\text{C}$. The proton signals also show a marked concentration-dependence (Fig. 1b). At high concentrations the signals at 8.97 and 7.70 ppm are predominant whereas the dilution of the solution results in a gradual increase of the signals at 8.86 and 7.59 ppm. Such a process could be observed even at very low concentration level

(<0.05 mM). In aprotic solvents such as acetonitrile and Me_2SO , one set of pyridyl protons appears, indicating that the anion within the skeleton is not dissociated in organic solvents. In particular, the temperature-dependent water-solubility is consistent with the quantity of the dissociated species. Thus, the unusual nonrigid process may be explained in terms of an electrostatic equilibrium around room temperature shown in Scheme 1. A single ClO_4^- encapsulated in the center has significant electrostatic interactions with four palladium cations of the host. Although the intrinsic properties of the host may not be touched, the anisotropic effect of the aromatic wall^{20,21} is sensitive to the host-guest interactions. Appearance of only one equivalent signal for the coligand, Me_4en , is well consistent with such a effect. The coligand peak rules out the equilibrium between quite different species such as the cyclic tetramer and cyclic trimer (or other cyclic oligomer). The volume of ClO_4^- anion is much smaller than the cavity (as visualized in the Scheme), but the host-guest electrostatic interactions retain “a restricted anion within cyclic receptor” even in aqueous solution. Thus, the equilibrium between $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S}) \cdot 1/4\text{ClO}_4]_4 \cdot 7\text{ClO}_4$ (“associated” : 8.97 and 7.70 ppm) and $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S})]_4 \cdot 8\text{ClO}_4$ (“dissociated” : 8.86 and 7.59 ppm) exists in aqueous solution. A van’t Hoff plot for the associated/dissociated species of the ClO_4^- shows that dissociation of the anionic guest into the host is an endothermic process. Since the enthalpy and entropy are positive, the spontaneous dissociation is an entropy-driven process. Because of Gibbs energy difference between associated and dissociated species is always very small and the solvation enthalpies of dipolar solutes are dominant compared to the free energy, the media and concentration can considerably affect the equilibrium between the associated/dissociated species.

In contrast to the ClO_4^- (52.1 cm^3/mol) system, the smaller anion NO_3^- (36.0 cm^3/mol)¹¹ analog shows no such an equilibrium in aqueous solution. This fact indicates that the small anions go in and out freely the host. In contrast, PF_6^- anion (56.2 cm^3/mol) seems to be unsuitable in both bulkiness and water-solubility for

such a unique recognition. An en analog, $[\text{Pd}(\text{en})(\text{Py}_2\text{S}) \cdot 2\text{ClO}_4]_4$ (expectedly exhibits such an equilibrium while a dppe analog, $[\text{Pd}(\text{dppe})(\text{Py}_2\text{S}) \cdot 2\text{ClO}_4]_4$, (dppe = 1,2-bis(diphenylphosphino)ethane) is unfortunately insoluble in water. Thus, a suitable combination of electrostatic interaction, media, and size effects between the host and the guest may ascribe to a driving force for the recognition of ClO_4^- . Further studies on analogs will provide more detailed information on the pervasive influences and applications as specific anion sensors.

responsible for the hypersensitive detection of ClO_4^- with remarkable selectivity in aqueous solution. Delicate modification of the skeletal structure will contribute to the recognition of other anions. In addition to the recognition, the unusual mechanistic process can contribute to the development of desirable molecular materials such as sensor technology, anion transport, and molecular switching.

Supporting information available

A listing of full ^1H NMR spectrum in D_2O (0 °C), full ^1H NMR spectrum in acetonitrile- d_3 , ^1H - ^{13}C HETCOR spectrum, and mass data of $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S}) \cdot 2\text{ClO}_4]_4$. This material is available from OSJ.

Acknowledgment

This research was supported financially by the Ministry of Science and Technology in Korea.

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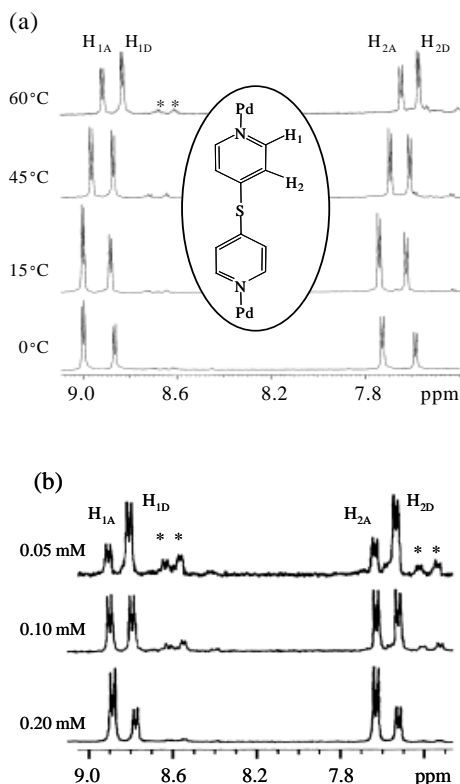


Fig 1. (a) Variable temperature ^1H NMR (600 MHz, D_2O) and (b) variable concentration ^1H NMR (300 MHz, D_2O) of the Py_2S region in $[\text{Pd}(\text{Me}_4\text{en})(\text{Py}_2\text{S}) \cdot 2\text{ClO}_4]_4$. Subscripts A and D denote “associated” and “dissociated”. Asterisk peaks may be due to oligomer(s) under the condition.

In conclusion, the reversible dissociated/associated equilibrium via precise electrostatic interactions is

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