Preparation and Characterization of Nicotinium Tetrahalocuprate(II) and Tetrahalocobaltate(II) Complexes : Structure of Nicotinium Tetrachlorocobaltate(II)

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Nicotine ($C_{10}H_{14}N_2$, nic) is one of the alkaloids well recognized for it's toxin activity, and it's chemistry is an important topic because of its health implications.[1,2] Nicotine possesses the methylated pyrrolidine nitrogen (pK_{b1} = 6.16) and the less basic pyridine nitrogen (pK_{b2} = 10.96), thus it forms a chelate complex resulting in a CuN_2X_2 chromophore when it reacts with the copper(II) halides.[3] The complex shows a distorted tetrahedral geometry around the copper(II) site (C_{2v}) due to the steric hindrance of the nicotine ligand in the resulting chelate complex.[3] Double protonation of nicotine gives a nicotinium cation, $nicH_2^{2+}$, which is expected to form easily into crystalline salts with tetrahalometallate(II) anions of the general formula $[C_{10}H_{16}N_2]^{2+}[MX_4]^{2-}$. Recently we reported on the single crystal structure of $(nicH_2)CuCl_4$.[4] The crystal exhibited two crystallographically non-equivalent pseudo-tetrahedral $[CuCl_4]^{2-}$ anions, each of which was linked to two doubly protonated nicotinium cations *via* hydrogen bonds.[4] The pseudotetrahedral (D_{2d}) geometry around the Cu(II) site in $(nicH_2)CuCl_4$ arose from the packing effect caused from the large $nicH^{2+}$ cation size as well as the strong hydrogen bonding networks between the protonated nicotinium cation and the chloride atoms in $[CuCl_4]^{2-}$. The pseudotetrahedral copper(II) complexes were interesting in that they were proposed as a mimic compound of active sites in copper proteins.[5,6]

Herein, we investigate the optical and magnetic properties of $(nicH_2)CuX_4$ (X=Cl, Br) complexes, and elucidate the observed properties in accordance with the corresponding pseudotetrahedral geometry of the Cu(II) site in the prepared complexes. Furthermore, we synthesize a nicotinium tetrahalocobaltate(II), $(nicH_2)CoX_4$ complex. We report on the single crystal structure of the nicotinium tetrachlorocobaltate(II) complex and compare it to that of $(nicH_2)CuCl_4$ complex. The optical and magnetic properties of $(nicH_2)CoCl_4$ were examined and explained as a symmetric $[CoCl_4]^{2-}$ unit.

Experimental Section

Nicotinium tetrahalocuprate(II), $(nicH_2)CuX_4$ (X=Cl, Br), complexes were prepared by the literature method.[4] Nicotinium tetrahalocobaltate(II) complexes were prepared by a similar method. A direct reaction between $(nicH_2)Cl_2$ and $CoCl_2$ in an ethanol-triethylorthoformate (5 : 1 v/v) mixture solution gives a $(nicH_2)CoCl_4$ complex. The $(nicH_2)Cl_2$ salt was prepared from a reaction of (s)-(−)-nicotine with an excess of concentrated HCl in a solution. The blue single crystals were obtained by a slow evaporation method. Elemental analyses were performed at the Korean Basic Science Center, and the results are listed below:

Anal.(%) Calcd. for $(nicH_2)CuCl_4$, yellow, m.p. 163 °C: C, 32.70; H, 4.39; N, 7.63. Found: C, 33.29; H, 4.21; N, 7.81. Calcd. for $(nicH_2)CuBr_4$, purple, m.p. 158 °C: C, 22.11; H, 2.97; N, 5.16. Found: C, 21.80; H, 2.93; N, 5.26. Calcd. for $(nicH_2)CoCl_4$, blue, m.p. 194 °C: C, 33.06; H, 4.44; N, 7.72. Found: C, 33.83; H, 4.54; N, 7.93. Calcd. for $(nicH_2)CoBr_4$, blue, m.p. 198 °C: C, 22.27; H, 2.99; N, 5.20. Found: C, 22.30; H, 3.01; N, 5.27.

The electronic absorption spectra (200-1600 nm) were recorded on a Shimadzu UV-3101PC spectrophotometer in acetonitrile. Cyclic voltammograms were recorded on a BAS CV-50W Voltammetric Analyzer in a three-electrode system at 0.1 M tetraethylammonium perchlorate (TEAP) in DMF. EPR spectra measurements were carried out for the solution samples (DMF/CH_2Cl = 50/50) at 77 K using a ESP-300S EPR spectrometer at the X-band frequency. Magnetic susceptibility data was collected from 4 K to 300 K by the SQUID method using the MPMS7 (Magnetic Property Measurement System) of U.S.A. Quantum Design. The data was corrected for the diamagnetism of the constituent atoms using Pascal's constants and for the temperature-independent paramagnetism (60×10^{-6} cgsu/Cu(II) and 675×10^{-6} cgsu/Co(II) atom).

The data for X-ray structure determination was collected on a CAD-4 diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 295 K. The unit cell dimensions were determined on the basis of 25 reflections in the range of $11.40° < \theta < 12.52°$. The data was collected by the $\omega/2\theta$ scan mode. The standard direct method was used to position the heavy atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Positional parameters of the H atoms were calculated geometrically and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2\ U_{eq}(CH$ and $CH_2)$ or

1.5 $U_{eq}(CH_3)$. The H atoms on N1 and N9 were located from difference density maps and refined freely. The structure was refined in a full matrix least-squares calculation on F^2. The programs used to solve the structure and to refine the structure are as follows: SHELXS97 and SHELXL97;[7] Molecular graphics; Ortep-3 for windows.[8]

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-279833). The data can be obtained free of charge *via* www.ccdc.cam.ac.kr/perl/catreq/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223 336033; E-mail: deposit@ccdc.cam.ac.uk)

Results and Discussion

Properties of nicotinium tetrahalocuprate(II) complexes. The observed properties of nicotinium tetrahalocuprate(II) are discussed on the basis of the reported pseudotetrahedral (D_{2d}) geometry of $[CuCl_4]^{2-}$ in $(nicH_2)CuCl_4$.[4]

The optical spectra showed the broad and unsymmetric absorption bands centered at 950 nm with a shoulder at 1200 nm for $(nicH_2)CuCl_4$, and at 904 nm with 1400 nm for the corresponding bromo compound in acetonitrile solution. The observed unsymmetric absorption bands were analyzed into three peaks by Gaussian resolution and tentatively assigned to the transitions from the ground state $^2B_2(d_{x2-y2})$ to $^2A_1(d_{z2})$; ν_1, to $^2B_1(d_{xy})$; ν_2 and to $^2E(d_{xz}, d_{yz})$; ν_3 respectively according to the pseudotetrahedral symmetry around the copper(II) ion. The results are summarized in Table 1. The low energy absorption higher than 800 nm are commonly found in pseudotetrahedral copper(II) complexes.[9,10] The maximum d-d transition should increase in energy as distorting from a regular tetrahedron toward a square plane.[10] Harlow R. L. *et al.*[11] proposed this relation experimently as follows: ν (cm^{-1}) = 1.445β–9784, where ν is d-d band maximum. Using this relation, we calculated the Cl-Cu-Cl angle in $(nicH_2)CuCl_4$ (ν = 950 nm) as 140^0, which agrees well with the reported value.[4]

The pseudotetrahedral nicotinium tetrahalocuprate(II) complexes result in relatively higher reduction potentials as shown in Table 2. This result can be explained by the fact that the distortion toward tetrahedral symmetry makes the copper(II) ion easier to reduce.[12] It was found that $(nicH_2)CuBr_4$ showed the higher reduction potential than the analogous chloride complex due to the better reducing bromide ion compared to the chloride ion.[12]

Table 2. Electrochemical data of nicotinium tetrahalocuprate(II) complexes in DMF versus an Ag/Ag + electrode

Compound	E_{pc} (V)	$E_{1/2}$ (V)	E_{pa} (V)	Process
$CuCl_2{\cdot}2H_2O$	−0.290	−0.065	0.160	Cu^{II}/Cu^I
$(nicH_2)CuCl_4$	−0.112	−0.003	0.109	Cu^{II}/Cu^I
$CuBr_2$	0.540	0.627	0.714	–
	0.245	0.341	0.435	Cu^{II}/Cu^I
	−0.250	−0.111	0.029	Cu^I/Cu^0
$(nicH_2)CuBr_4$	0.560	0.704	0.847	–
	0.368	0.435	0.509	Cu^{II}/Cu^I
	−0.204	−0.019	0.166	Cu^I/Cu^0

The ESR spectra showed well defined four hyperfine lines in frozen glass (DMF : CH_2Cl_2 = 50 : 50) at 77 K. The

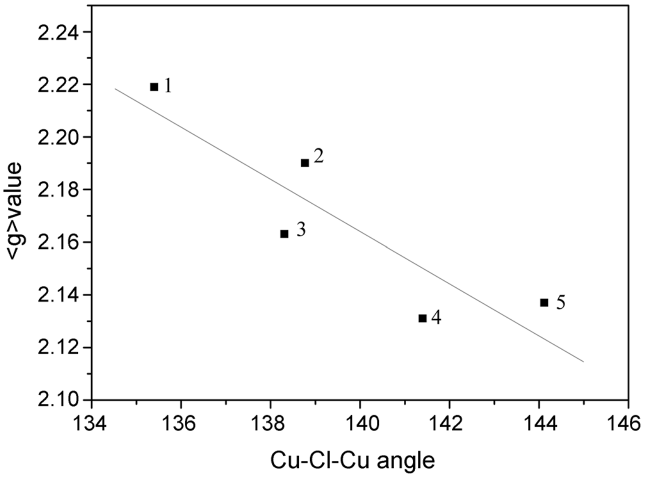

Figure 1. The plot of <g> values against the trans <Cl-Cu-Cl> angles in $[CuCl_4^{2-}]$ anions (tetrahedron; 109.5°, square-plane; 180°): 1; $[nicH_2][CuCl_4]$, 2; $[triamH_2][CuCl_4]$[13], 3; $[H2,6Acgu_2][CuCl_4]$-$Cl{\cdot}H_2O$[14], 4; $[(CinH_2)CuCl_4]_2{\cdot}3H_2O$[15], 5; $[HPrz]_2[CuCl_4]$[16].

Table 1. Optical and magnetic properties of nicotinium tetrahalocuprate(II) and tetrahalocobaltate(II) complexes

compound	electronic spectra	magnetic moment (BM)	Curie-Weiss constant		EPR parameter		
	λ_{max} (ε)		c	Θ	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (gauss)
$(nicH_2)CuCl_4$	968(38); ν_1 1180(32); ν_2 1387(18); ν_3	1.83	0.41	2.32	2.428	2.114	119
$(nicH_2)CuBr_4$	894(91); ν_1 1124(80); ν_2 1401(20); ν_3	1.77	0.39	2.05	2.428	2.114	116
$(nicH_2)CoCl_4$	667(698) 609(391)	4.63	2.71	−4.73	–	–	–
$(nicH_2)CoBr_4$	695(72) 642(50) 534(20)	4.78	2.86	−2.74	–	–	–

Table 3. Crystal data and structure refinement for (nicH$_2$)CoCl$_4$

Empirical formula	$C_{10}H_{16}Cl_4CoN_2$
Formula weight	364.98
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 10.307(7) Å, $\alpha = 90^0$ b = 11.895(2) Å, $\beta = 90^0$ c = 12.317(9) Å, $\gamma = 90^0$
Volume	1510.2(15) Å^3
Z, Calculated density	4, 1.605 mg/m^3
Absorption coefficient	1.824 mm^{-1}
F(000)	740
Crystal size	0.26 × 0.26 × 0.23 mm
Reflections collected / unique	2388 / 2327 [R(int) = 0.0448]
Absorption correction	Psi-scan
Max. and min. transmission	0.6562 and 0.5892
Data / restraints / parameters	2327 / 0 / 154
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	R1 = 0.0444, wR2 = 0.0786
Largest diff. peak and hole	0.459 and −0.316 e.Å^3
R indices (all data)	R1 = 0.0767, wR2 = 0.0886

resulting ESR parameters are listed in Table 1. Figure 1 shows the plot of the average g values against the average trans Cl-Cu-Cl angles in $[CuCl_4]^{2-}$ anions. The g values generally decrease as the geometry distorts from a tetrahedral to a square planar symmetry. (NicH$_2$)CuCl$_4$ agrees well with this relationship. In low symmetry complexes, the easier mixing of 4s and 4p orbitals in the ground state causes an increase in g values as well as a decrease in the parallel hyperfine ($A_{||}$) coupling constants. The values less than 150 × 10^{-4} cm^{-1} are usually examined in the distorted copper(II) complexes.

The magnetic susceptibility data was followed with the temperature in the range 4-300 K and Curie-Weiss law was valid with Θ = +2.32 and +2.05 K for the chloro and bromo complexes respectively. This Curie-Weiss behavior and the small Weiss constants indicate that the magnetic exchange between copper(II) ions is almost negligible.

Structure and properties of nicotinium tetrahalocobaltate(II) complexes. The crystallographic data and structure refinements for (NicH$_2$)CoCl$_4$ are summarized in Table 3. (NicH$_2$)CoCl$_4$ consists of discrete $[CoCl_4]^{2-}$ anions and doubly hydrogenated nicotinium $[nicH_2]^{2+}$ cations. They are held together by N$^+$-H···Cl hydrogen bonds in the unit cell. The selected bond distances and bond angles are summarized in Table 4. An ORTEP view of including the atomic numbering scheme is shown in Figure 2.

Table 4. The selected band distances (Å) and bond angles (°) of (nicH$_2$)CoCl$_4$

Co-Cl(4)	2.245(2)	N(1)-C(6)	1.488(8)
Co-Cl(3)	2.263(2)	N(1)-C(2)	1.512(7)
Co-Cl(1)	2.274(2)	N(1)-C(5)	1.514(7)
Co-Cl(2)	2.312(2)		
Cl(4)-Co-Cl(3)	110.97(8)	C(6)-N(1)-C(2)	113.6(5)
Cl(4)-Co-Cl(1)	110.36(8)	C(6)-N(1)-C(5)	115.0(6)
Cl(3)-Co-Cl(1)	104.99(7)	C(2)-N(1)-C(5)	105.3(5)
Cl(4)-Co-Cl(2)	112.22(7)		
Cl(3)-Co-Cl(2)	109.35(7)	C(10)-N(9)-C(8)	123.9(5)
Cl(1)-Co-Cl(2)	108.69(6)	C(10)-N(9)-H(9)	119.0(4)

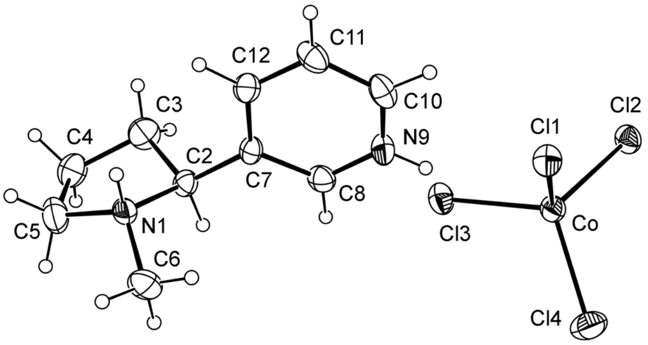

Figure 2. ORTEP diagram of (nicH$_2$)CoCl$_4$, showing the atom numbering scheme.

The $[CoCl_4]^{2-}$ anions possess a tetrahedral geometry with the Cl-Co-Cl angles of 105-112^0. The nicotinium cations are doubly protonated at N1 and N9 atoms, and the pyridinium N9 atom exclusively forms a three-center hydrogen bond (bifurcated H-bond) with *cis*-Cl (Cl1, Cl3) atoms whereas the pyrrolidinium N1 atom forms a common two-center hydrogen bond with a Cl atom in $[CoCl_4]^{2-}$ units. As a result, three Cl atoms in each $[CoCl_4]^{2-}$ anion participate in the formation of hydrogen bonds with nicotinium cations. Figure 3 shows the hydrogen bonding modes between nicotinium cations and $[CoCl_4]^{2-}$ anions. The hydrogen bond

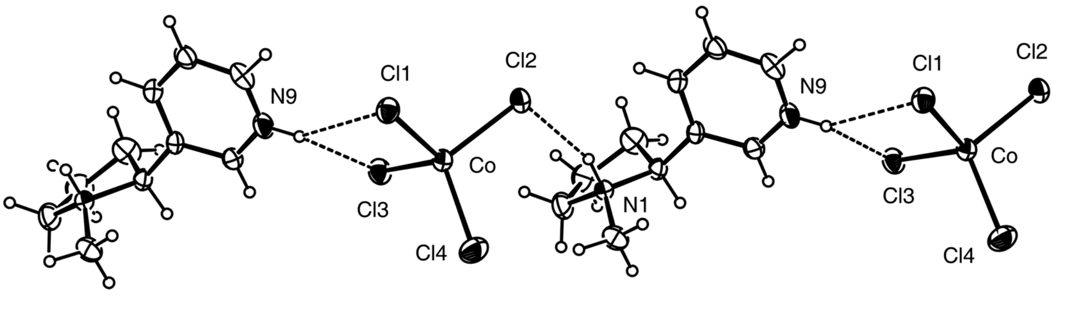

Figure 3. A view of hydrogen-bonding mode between nicotinium cation and $CuCl_4^{2-}$ anion showing selected atom labels.

Table 5. The Hydrogen bonding geometries (Å, °) of $(nicH_2)CoCl_4$

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(1)-H(1)···Cl(2)#1	0.93(4)	2.28(4)	3.170(5)	160(4)
N(9)-H(9)···Cl(1)	0.84(5)	2.58(5)	3.259(5)	140(5)
N(9)-H(9)···Cl(3)	0.84(5)	2.68(5)	3.262(6)	128(5)

Symmetry transformations used to generate equivalent atoms: #1 x, y+1, z

distances (Å) and bond angles (^{0}) are summarized in Table 5. This hydrogen bond altered the Co-Cl bond lengths in $[CoCl_4]^{2-}$ units. We found three kinds of bond lengths as decreasing in the order of Co-Cl2 (2.3116 Å) > Co-Cl3, Cl1 (2.2626 Å, 2.2740 Å) > Co-Cl4 (2.245 Å). The formation of the intramolecular hydrogen bonds results in the increase of the Co-Cl bond lengths due to a reduction of electron density on the chloride ions.[17] Therefore, the Co-Cl lengths of the two-center hydrogen bond is shorter than that of the bifurcated hydrogen bond.

The multiple electronic absorption in the visible region (600-700 nm) with a high molar absorptivity was examined, which is a typical feature of tetrahedral Co(II) complexes assigned to the transition, $^4A_2 \rightarrow {}^4T_1(P)$.[10,18] The results are list in Table 1. The absorption band is complicated due to the transitions between the quartet ground state and the levels originated from the doublet terms of higher energy.

The room temperature magnetic moments of $(nicH_2)CoX_4$ (4.6-4.8 BM) are consistent with the expectation value of noninteracting high spin d^7 Co(II) ions with the negative spin-orbital coupling constants.[19] The effective magnetic moments were calculated from $\mu_{eff} = 2.828(\chi_m \times T)^{1/2}$. The magnetic susceptibility data of $(nicH_2)CoX_4$ is described by the Curie-Weiss law, $\chi_m = C/(T-\Theta)$ with a negative Weiss constants as shown in Table 1. Regardless of the negative Weiss constants, the magnetic interaction between $(nicH_2)CoCl_4$ units is not possible since the nearest distances between Cl-Cl or Co-Co (Cl-Cl; 3.831 Å and Co-Co; 7.324 Å) are longer than the sum of the corresponding van der Waals radii, and this distance is considered to be too long to allow any significant orbital overlap between the units.

In summary, a direct reaction between $(nicH_2)X_2$ and CuX_2 (X = Cl, Br) yields nicotinium tetrahalocuprate(II) complexes. The corresponding tetrahalocobaltate(II) complexes were prepared from CoX_2 (X = Cl, Br). The optical, magnetic and electrochemical properties of $(nicH_2)CuCl_4$ were elucidated on the basis of a pseudotetrahedral symmetry around the copper(II) site in $[CuCl_4]^{2-}$ units. The $[CoCl_4]^{2-}$ anions show an almost tetrahedral symmetry in $(nicH_2)CoCl_4$ and are crystallographically equivalent. There are two kinds of hydrogen bonding between $[nicH_2]^{2+}$ cations and $[CoCl_4]^{2-}$ anions: one is a bifurcated hydrogen bond and the other is a two-center hydrogen bond. The effect of these hydrogen bondings explains the differences of Co-Cl bond lengths in $[CoCl_4]^{2-}$ anions.

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