with the chemical shift of the residual protons of the solvent used as internal standard. ^{13}C NMR chemical shifts are reported in ppm by using the natural abundance of ^{12}C of the solvent as an internal standard. Mass spectra were provided by the University of Illinois mass spectrometry facility. YMC RP and Silica gel (230-400 mesh) were used for flash column chromatography. YMC ODS 30×10 mm column was used for hplc separation.

Collection and Isolation. The sponge was collected Oct., 1992 from Manado bay north along the coast of Sulawesi up to Bunaken Island in Indonesia. The sponge was idetified by Dr. Peter Karuso, University of Macquarie. The freeze-dried sponge (50.5 g) was extracted for 2 days with 400 mL of CH_2Cl_2-*i*PrOH (1 : 1), and the residue (3.02 g) was partitioned between MeOH/H_2O (9 : 1) and *n*-hexane. The MeOH/H_2O layer yielded 2.03 g of red solid. The MeOH/H_2O layer was subjected to RP-C_{18} flash column chromatography and Si gel flash column chromatography sequentially using MeOH-H_2O (75 : 25) and MeOH-CH_2Cl_2 (8 : 92), yielding 40 mg of mixture of bastadins. The mixture was separated by C_{18} reversed-phase hplc [ODS column, MeOH/H_2O/MeCN (1 : 1 : 1), 2 mL/min] to give 5 mg of **1** as a pure white solid and 19 mg of **2** as shown in scheme 1.

HMBC condition for **1**: concentration of sample, 5 mg/DMSO-d_6, 0.6 mL, 256 of blocks x 2048 data matrix with 64 of scan per t_1 increment, 3.0 delay period for long-range couplings, 100° shifted since bell squared filtering for t_1 and 5100 MHz line broadening for it.

Bastadin (1). Hrfabms m/z $[M+H]^+$ 956.8606 (calcd for $C_{34}H_{29}N_4O_{979}Br_2{}^{81}Br_2$, 956.8627); hreims m/z 417.8925 (calcd for $C_{16}H_8N_2O_2{}^{79}Br_2$, 417.8953); ir ν_{max} (Nujol) 3600-3100, 1660, 1640, 1490, 1470, 1285, 1220 cm^{-1}; UV ν_{max} (MeOH) (logε) 278 (4.1) nm; ^1H and ^{13}C nmr see Table 1.

Bastadin 3(2)/[4]. ^1H NMR (in MeOH-d_4); δ 7.36 (2H, d, J=2.2 Hz), 7.28 (2H, d, J=2.2 Hz), 7.12 (2H, d, J=2.2 Hz), 6.89 (2H, dd, J=8.3, 2.2 Hz), 6.72 (2H, d, J=8.3 Hz), 3.80 (4H, s), 3.37 (4H, t, J=6.9 Hz), 2.66 (4H, t, J=7.3 Hz); ^{13}C NMR, δ 165.91, 153.92, 153.74, 153.61, 134.16, 133.29, 133.01, 132.27, 130.31, 130.07, 128.80, 117.21, 114.09, 110.67, 42.09, 35.19, 28.83; Irradiation at δ 3.80 (H-1) induced nuclear Overhauser enhancement (nOe) at δ 7.28 and 7.12. Irradiation at δ 2.62 (H-6) induced nOe at δ 3.37, 7.36 and 6.89. Irradiation at δ 3.37 (H-5) induced nOe at δ 2.62, 7.36 and 6.89.

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Structure of Bis(N,N-dimethyl-2-thiophenemethylammonium)Tetrachlorocobaltate(II)

Mi-A Kwon, Young Jin Kim, Nak Suk Cho, and Sung-Nak Choi*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

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2-(dimethylaminomethyl)thiophene (DMAT) ligand usually provides an [NS] donor set to form a delocalized five membered chelate ring with metal(II) ions and the structural characteristics of (DMAT)CuX_2 and (DMAT)NiX_2 where X^- = Cl^- or Br^- have been characterized and reported (1). However, when cobalt(II)chloride reacts with DMAT in similar condition in ethanol, it does not produce a 1 : 1 complex of type (DMAT)$CoCl_2$. Instead, bis(N,N-dimethyl-2-thiophenemethylammonium)tetra-chlorocobaltate(II), $(DMTMAH)_2CoCl_4$ is formed. We isolated the single crystals of this cobalt (II) complex and conducted X-ray crystallographic studies on it.

Experimental

The $(DMTMAH)_2CoCl_4$ was prepared by the direct reaction of DMAT (0.3 g, 2.0 mmol) with dried $CoCl_2 \cdot 6H_2O$ (0.4 g, 1.7 mmol) in ethanol (50 mL) and triethylorthoformate (10 mL). The mixture was stirred for two hours at warm (yield, 54%). Dark blue single crystals were obtained by slow recrystallization in acetonitrile. A flat crystal of size 0.80×0.60×0.20 mm was used for intensity measurements on an Enraf-Nonius CAD-4 diffractometer using the ω-θ scan technique; lattice parameters from setting angles of 23 reflections in the range $8<\theta<10°$; scan width (0.8+0.350 tanθ) and with variable scan rate 1 to 7°min^{-1}; $2\theta max=45.0°$; $0<h<10$, $0<k<18$, $-14<l<14$. Intensity data for 3175 reflections were collected; 2858 unique observed reflections; 2621 included reflections with $Fo^2>1.5$ (Fo^2). Lorentz and polarization corrections were applied. The linear absorption coefficient is 14.6 cm^{-1} for Mo Kα radiation. An empirical absorption correction based on a series of psi-scans was applied to the data. Relative transmission coefficients ranged from 0.937 to 0.999. A secondary extinction correction was applied (2).

Table 1. Crystal Data, Data Collection, and Refinement of the Structure for $(DTMAH)_2CoCl_4$

chem formula	$C_{14}H_{22}N_2S_2Cl_4Co$
fw	483.22
F (000)	988
crystal dimensions (mm)	0.80×0.60×0.20
peak width at half-height (°)	0.80
Mo Kα radiation	λ=0.71073
temperature (℃)	23± 1
monoclinic space group	$P2_1/c$ (# 14)
a=9.340(3) Å, b=17.667(2) Å, c=13.523(4) Å	
β, deg	101.00(1)
V (Å^3)	2190.4
Z	4
ρ_{calc} (g/cm^3)	1.47
μ (cm^{-1})	14.6
scan type	θ-ω
scan width, deg	0.8+0.350 tanθ
no. of refl. measured	3175 total, 2858 unique
reflections included	2621 with $F_o^2>1.5\sigma$ (F_o^2)
$R=(\Sigma\|F_o-F_c\|)/\Sigma\|F_o$	0.037
$Rw=(\Sigma\|F_o-F_c\|w^{1/2})/\Sigma\|F_o\|w^{1/2}$	0.038

The final coefficient, refined in least-squares, was 0.0000007. The structure was solved by direct methods using 258 reflections (E>1.20). A total of one atom were located from an E-map prepared from the phase set with probability statistics: absolute figure of merit=1.19, residual=1.10, and psi zero=10.750. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares calculations where the function minimized was $\Sigma w(|Fo|-|Fc|)^2$ and the weight w is defined as $4Fo^2/\sigma^2(Fo^2)$. Scattring factors were taken from Cromer and Waber (3). Anomalous dispersion effects were included in Fc (4); the values for $\Delta f'$ and $\Delta f''$ were those of Cromer (5). The final cycle of refinement included 213 variable parameters; max.shift/e.s.d.=0.02. Convergence R=0.037, wR=0.038. The standard deviation of an observation of unit weight was 15.22. $(\Delta\rho)max=0.65$ e/Å^3 with an estimated error based on ΔF (6) of 0.08. All calculations were performed on a VAX computer using MolEN (7).

Discussion

The single crystal structure of $(DMTMAH)_2CoCl_4$ was solved and the crystallographic data are summarized in Table 1. The atomic coordinates are listed in Table 2. The bond distances and angles are given in Table 3. The structure consists of two discrete $DMTMAH^+$ cations and $CoCl_4^{2-}$ anion. Two $DMTMAH^+$ cations are surrounding the $CoCl_4^{2-}$ anion from the opposite directions. Figure 1 illustrates the structure of the $(DMTMAH)_2CoCl_4$.

The cobalt(II) ions are 4-coordinated with chloride ions in normal tetrahedral geometry. The average Cl-Co-Cl angle is 108.5°. Commonly Co-Cl bond length of $CoCl_4^{2-}$ in DMF

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) with e.s.d.'s in parentheses

$U_{eq}=(U_{11}+U_{22}+U_{33})/3$.

	x	y	z	U_{eq}
Co	1.00049(4)	0.14455(2)	0.25620(2)	0.0405(1)
Cl(1)	0.89937(7)	0.11595(4)	0.39484(5)	0.0512(3)
Cl(2)	0.86608(7)	0.23704(4)	0.16020(4)	0.0487(3)
Cl(3)	1.22428(8)	0.19497(5)	0.31206(5)	0.0598(4)
Cl(4)	1.00432(8)	0.03930(4)	0.16226(5)	0.0572(3)
S(1)	1.5547(1)	0.12334(8)	0.5676(1)	0.0754(6)
S(1′)	0.5176(1)	0.13325(7)	0.10565(8)	0.0749(6)
N(7)	1.1708(2)	0.1248(1)	0.5742(2)	0.0441(9)
N(7′)	0.7478(2)	0.1775(1)	−0.0607(2)	0.0462(8)
C(2)	1.6785(4)	0.0759(3)	0.6435(3)	0.0793(2)
C(2′)	0.3400(5)	0.1145(2)	0.0761(4)	0.1127(2)
C(3)	1.6328(4)	0.0173(2)	0.6883(3)	0.0713(2)
C(3′)	0.2961(4)	0.0880(2)	−0.0131(5)	0.0893(4)
C(4)	1.4716(2)	−0.0018(1)	0.6673(2)	0.0661(9)
C(4′)	0.3987(3)	0.0805(1)	−0.0737(2)	0.0710(1)
C(5)	1.4174(3)	0.0638(1)	0.5857(2)	0.0457(1)
C(5′)	0.5449(3)	0.1047(2)	−0.0077(2)	0.0507(1)
C(6)	1.2653(3)	0.0699(2)	0.5293(2)	0.0463(1)
C(6′)	0.6898(3)	0.1016(2)	−0.0378(2)	0.0503(1)
C(8)	1.2262(4)	0.2035(2)	0.5819(2)	0.0597(1)
C(8′)	0.6452(4)	0.2206(2)	−0.1387(3)	0.0637(2)
C(9)	1.1384(4)	0.0984(2)	0.6720(3)	0.0740(2)
C(9′)	0.8936(3)	0.1680(2)	−0.0891(2)	0.0627(2)

Table 3. Bond lengths (Å) and bond angles(°)

Co-Cl(1)	2.3106(8)	N(7′)-C(6′)	1.500(4)
Co-Cl(2)	2.3041(7)	N(7′)-C(8′)	1.492(4)
Co-Cl(3)	2.2650(8)	N(7′)-C(9′)	1.494(4)
Co-Cl(4)	2.2560(8)	C(2)-C(3)	1.312(6)
S(1)-C(2)	1.625(4)	C(2′)-C(3′)	1.286(8)
S(1)-C(5)	1.712(3)	C(3)-C(4)	1.516(4)
S(1′)-C(2′)	1.664(4)	C(3′)-C(4′)	1.381(7)
S(1′)-C(5′)	1.678(3)	C(4)-C(5)	1.613(3)
N(7)-C(6)	1.514(4)	C(4′)-C(5′)	1.543(4)
N(7)-C(8)	1.481(4)	C(5)-C(6)	1.482(4)
N(7)-C(9)	1.486(4)	C(5′)-C(6′)	1.486(4)
Cl(1)-Co-Cl(2)	110.43(3)	S(1)-C(2)-C(3)	116.3(3)
Cl(1)-Co-Cl(3)	108.03(3)	S(1′)-C(2′)-C(3′)	115.0(4)
Cl(1)-Co-Cl(4)	109.24(3)	C(2)-C(3)-C(4)	119.2(3)
Cl(2)-Co-Cl(3)	106.14(3)	C(2′)-C(3′)-C(4′)	117.3(4)
Cl(2)-Co-Cl(4)	109.43(3)	C(3)-C(4)-C(5)	98.0(2)
Cl(3)-Co-Cl(4)	113.52(3)	C(3′)-C(4′)-C(5′)	105.5(3)
C(2)-S(1)-C(5)	93.1(2)	S(1)-C(5)-C(4)	113.2(2)
C(2′)-S(1′)-C(5′)	92.3(2)	S(1)-C(5)-C(6)	123.5(2)
C(6)-N(7)-C(8)	113.9(2)	C(4)-C(5)-C(6)	123.3(2)
C(6)-N(7)-C(9)	112.9(2)	S(1′)-C(5′)-C(4′)	109.8(2)
C(8)-N(7)-C(9)	111.1(2)	S(1′)-C(5′)-C(6′)	124.5(2)
C(6′)-N(7′)-C(8′)	113.2(2)	C(4′)-C(5′)-C(6′)	125.7(2)
C(6′)-N(7′)-C(9′)	109.6(2)	N(7)-C(6)-C(5)	114.6(2)
C(8′)-N(7′)-C(9′)	111.7(2)	N(7′)-C(6′)-C(5′)	114.0(2)

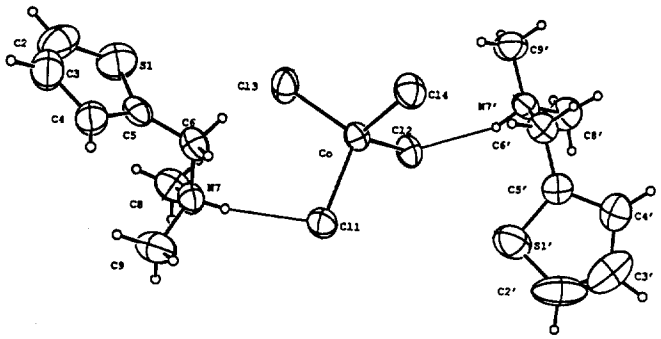

Figure 1. The molecular structure of bis(N,N-dimethyl-2-thiophenemethylammonium)tetrachlorocobaltate(II). Drawing of single molecule showing 50% probability ellipsoids. (Cl---H-N hydrogen bonds are shown in thin lines with bond distances Cl_1---H and Cl_2---H being 2.40 and 2.38 Å, respectively)

and water are reported to be 2.29Å.(8) But in $(DMTMAH)_2CoCl_4$, we found two different type of bond lengths. The four Co-Cl observed bond lengths are 2.3106(8), 2.3041(7), 2.2650(8), and 2.2560(8) Å, respectively. Two chlorine atoms involved in longer bond lengths have been noted to participate in the hydrogen bonding with $DTMAH^+$ unit, *i.e* Co-Cl---H-N. The effect of the intramolecular hydrogen bonding results in the increase in the Co-Cl bond lengths. In most amine compounds such as $(CH_3)_3NHCl$, $(CH_3)_2NH_2Cl$, and $(NH_3OH)Cl$, the N-H---Cl bond lengths are reported to be 3.10± 0.1 Å (9). The N-H---Cl bond lengths estimated for this compounds are 3.16 Å and the N-H---Cl bond angles are 160° for $(DMTMAH)_2CoCl_4$, which are typical structural characteristics found in amine hydrogen-halide system.

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Supplementary Material Available. Detailed descriptions of X-ray works, listings of anisotropic thermal parameters, hydrogen positional parameters, and observed and calculated structure factors are available from one of the authors (S.N. Choi) upon request.

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Jung Ho Park → Jeong Ho Park