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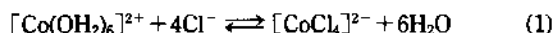
Structure of Unique N,N-Dimethylformamide Solvate of Cobalt(II) Chloride

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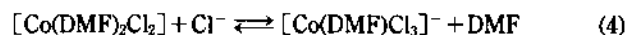
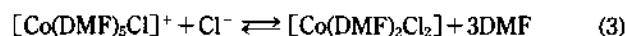
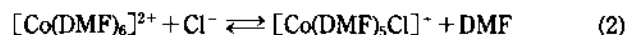
Cobalt(II) complexes adopt two major geometries, distorted octahedral and tetrahedral arrangements. The obvious structures of the two geometries were exemplified by the following well known equilibrium (eq. 1).¹



The local geometry of the d⁷ electronic configuration (Co^{II}) has been found to depend on ligand polarizability as well as ligand size.^{2,3}

N,N-Dimethylformamide (DMF) is an excellent ionizing solvent for various classes of compounds due to its convenient liquid state from -61° to 153 °C. In addition, DMF has good electrochemical stability, which makes it a popular solvent for polarography and electroreduction of organic and inorganic compounds.⁴ DMF adducts as good intermediates

for further reaction have been interesting topic.⁵ DMF has two possible donor sites, N or O, but all the DMF metal compounds were elucidated as metal-oxygen bond by X-ray crystal studies.⁶ In particular, attention has been paid to the ionization equilibria and stability of cobalt(II) chloride in DMF. In the presence of chloride ions, DMF molecules of [Co(DMF)₆]²⁺ were successively replaced by chloride ions to form the following various coordination complexes (eq. 2-5).⁷ [Co(DMF)Cl₃]⁻ and [Co(DMF)₅Cl]⁺ species were found to be the electroactive components on nickel electrode in DMF.⁷ Furthermore, based on the visible absorption spectra and molar conductance, Grzybkowski *et al.* suggested that cobalt(II) chloride predominantly undergoes a disproportionation to yield of [Co(DMF)₆]²⁺ · 2[Co(DMF)Cl₃]⁻ in DMF solution at room temperature.⁸



The formation of the cobalt solvate molecule is very sensitive to the chemical condition, and thus is controversial. In order to elucidate the isolated species in the solid state, X-ray structure of DMF adduct of cobalt(II) chloride is herein established.

Experimental

Materials and Instrumentation. Cobalt(II) chloride (CoCl₂·6H₂O) and N,N-dimethylformamide (DMF) were purchased from Junsei. Elemental analysis (C, H, N) was carried out at the Korea Basic Science Center. Infrared spectra were obtained in 5000-400 cm⁻¹ range on a Perkin Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellets.

Preparation of [Co(DMF)₆]²⁺ · 2[Co(DMF)Cl₃]⁻. CoCl₂·6H₂O (2.38 g, 1.0 mmol) was dissolved in 20 mL of DMF. Excess ethylether was added into the solution, and left at -10 °C to obtain blue crystals suitable for X-ray crystallography in 76% yield. Anal. found (Calcd. for C₂₄H₅₆N₈O₈Cl₆Co₃): C, 29.40 (29.59); H, 5.68 (5.79); N, 11.45 (11.50). IR (KBr, cm⁻¹): 1665 (sh), 1650 (br, s), 1498 (m), 1438 (m), 1382 (s), 1254 (m), 1114 (s), 1062 (w), 686 (s).

X-ray Crystal Analysis. The crystal was wedged in a Lindemann capillary with mother liquor. The X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα (λ=0.71073 Å) at ambient temperature. Unit cell dimension was based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections monitored every hour did not show any significant intensity variation. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical psi-scan method. The structure was solved by Patterson method (SHELXS-86), and was refined by full-matrix least squares techniques (SHELXL-93).⁹ All non-hydrogen atoms were refined anisotropically. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. Final atomic coordinates and isotropic thermal parameters are given in Table 2.

Table 1. Details of Crystallographic Data for $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2[\text{Co}(\text{DMF})\text{Cl}_3]^-$

formula	$\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_4\text{Cl}_3\text{Co}_{1.5}$
fw	475.03
crystal system	triclinic
space group	$\text{P}\bar{1}$ (no. 2)
a, Å	8.854(3)
b, Å	9.282(3)
c, Å	15.120(3)
α , deg	72.20(2)
β , deg	75.21(2)
γ , deg	89.71(2)
V, Å ³	1140.3(5)
Z	2
d_{calc} , g/cm ³	1.383
absorption coefficient, mm ⁻¹	1.474
F(000)	479
crystal size, mm	0.20 × 0.20 × 0.40
θ range, deg	1.47–24.93
absorption correction range	0.902–0.966
index ranges	$0 \leq h \leq 10$, $-11 \leq k \leq 10$, $-17 \leq l \leq 17$
independent reflections	2497 [R(int) = 0.0191]
data to parameter ratio	2338/223
GOF on F ²	0.999
final R indices [I > 2 σ (I)]	$R_1 = 0.0581$, $wR_2 = 0.1488$
largest diff. peak and hole	0.303 and $-0.252 \text{ e}\text{Å}^{-3}$

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4} \right\}^{1/2},$$

where $w = 1/[\sigma^2 F_o^2 + (0.0948P)^2 + 1.24P]$, where $P = \{\text{Max}(F_o^2, 0) + 2F_c^2\}/3$

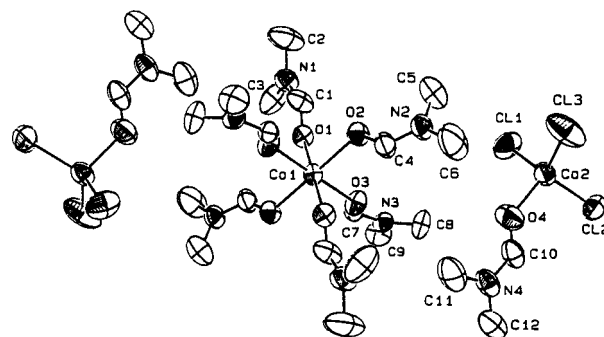
Results and Discussion

Cobalt(II) chloride adduct isolated in a mixture solvent of DMF and ethyl ether was the salt, $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2[\text{Co}(\text{DMF})\text{Cl}_3]^-$, which was already suggested in solution by Gryzbowski and Pilarczyk in 1986.⁸ Among various possible structures such as $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2\text{Cl}^-$, $[\text{Co}(\text{DMF})_5\text{Cl}]^+ \cdot [\text{Co}(\text{DMF})\text{Cl}_3]^-$, or $[\text{Co}(\text{DMF})_4\text{Cl}_2]$, only the present adduct was obtained as crystals in high yield. The structure seems to dissociate in chloroform and water based on UV, NMR, and molar conductivity.

The molecular structure of the present product is depicted in Figure 1, and the relevant bond distances and angles are listed in Table 3. The structure is centrosymmetric molecule positioned two anionic groups at both side a cationic group. A stacking array was visualized by its packing diagram (Figure 2). The cationic cobalt atom, $[\text{Co}(\text{DMF})_6]^{2+}$ is octahedrally surrounded by the oxygen atoms of DMF molecules. Its two counter anionic cobalt atoms, $[\text{Co}(\text{DMF})\text{Cl}_3]^-$ found in the remaining space are tetrahedral arrangement with one DMF and three chloride ions. The ionized structure indicates that the more polarizable and bigger ligand, chlorine anion favors to form the tetrahedral geometry with cobalt(II) atom. The Co-O bond lengths of the cation are in the range of 2.059(5)–2.105(5) Å, which are similar to general Co-O bond lengths.¹⁰ The Co-O bond lengths (2.014(6) Å) of the anion are slightly shorter than that of the cation. The bond lengths

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2[\text{Co}(\text{DMF})\text{Cl}_3]^-$

	x	y	z	U(eq)
Co(1)	0	0	5000	44(1)
Co(2)	7044(1)	-2898(1)	1877(1)	65(1)
Cl(1)	7152(3)	-3068(3)	3361(2)	94(1)
Cl(2)	9410(4)	-2206(3)	818(2)	117(1)
Cl(3)	5777(4)	-4937(3)	1809(3)	123(1)
O(1)	509(6)	-755(6)	6346(4)	54(1)
O(2)	519(6)	-2099(6)	4790(4)	58(1)
O(3)	2297(5)	760(6)	4276(4)	59(1)
O(4)	5754(8)	-1147(8)	1470(5)	87(2)
N(1)	104(9)	-2317(8)	7852(5)	70(2)
N(2)	1589(8)	-3337(7)	3734(5)	63(2)
N(3)	4711(7)	1658(7)	4145(4)	52(2)
N(4)	5538(9)	1316(9)	687(5)	72(2)
C(1)	91(11)	-1974(10)	6948(6)	70(2)
C(2)	-339(17)	-3835(12)	8526(8)	131(5)
C(3)	642(12)	-1208(13)	8208(7)	105(4)
C(4)	795(9)	-2252(9)	3986(6)	64(2)
C(5)	2260(12)	-4445(11)	4378(7)	93(3)
C(6)	1764(17)	-3456(14)	2778(8)	135(5)
C(7)	3201(8)	1449(8)	4541(5)	47(2)
C(8)	5440(10)	1045(11)	3382(6)	80(3)
C(9)	5726(10)	2564(10)	4424(7)	78(3)
C(10)	6331(11)	117(11)	877(7)	72(3)
C(11)	3898(13)	1257(13)	1143(8)	110(4)
C(12)	6264(13)	2760(11)	22(8)	100(3)

**Figure 1.** ORTEP drawing of $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2[\text{Co}(\text{DMF})\text{Cl}_3]^-$ shown at the 50% probability level.

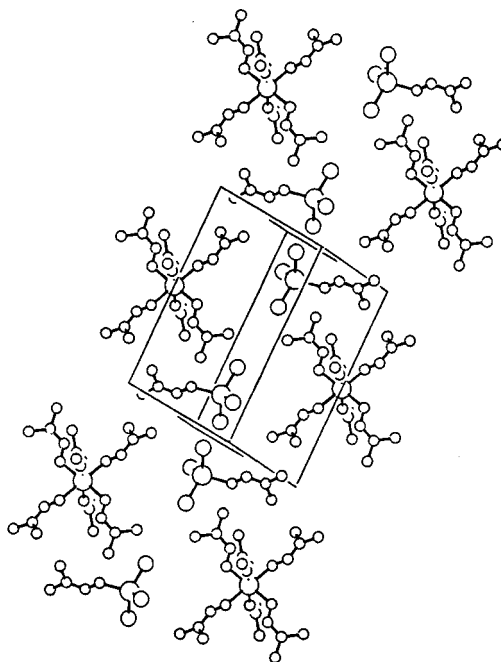
of Co-Cl (2.228(2)–2.247(3) Å) are also similar to the corresponding values.¹¹ In particular, the C=O bond lengths (1.204(9)–1.239(8) Å) of DMF coordinated to the cation are slightly shorter than those (1.25(1) Å) of DMF coordinated to the anions, which seems to be attributable to the two bands (1665 cm^{-1} , 1650 cm^{-1}) of C=O stretching frequencies. Bond angles around a cobalt atom of the anion are in the range of 104.5(2)–118.4(8)°, where the angles of Cl-Co-Cl are splayed out with the concomitant closing of the angles of Cl-Co-O. As expected, the bond angles of the cation unambiguously correspond to typical octahedral arrangement.

Table 3. Bond Lengths (Å) and Angles (deg) for $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2[\text{Co}(\text{DMF})\text{Cl}_3]^-$

Co(1)-O(3)	2.059(5)	Co(1)-O(3) # 1	2.059(5)
Co(1)-O(2)	2.098(5)	Co(1)-O(2) # 1	2.098(5)
Co(1)-O(1)	2.105(5)	Co(1)-O(1) # 1	2.105(5)
Co(2)-O(4)	2.014(6)	Co(2)-Cl(1)	2.228(2)
Co(2)-Cl(2)	2.244(3)	Co(2)-Cl(3)	2.247(3)
O(1)-C(1)	1.204(9)	O(2)-C(4)	1.229(9)
O(3)-C(7)	1.239(8)	O(4)-C(10)	1.253(11)
N(1)-C(1)	1.309(10)	N(1)-C(3)	1.431(11)
N(1)-C(2)	1.449(12)	N(2)-C(4)	1.321(9)
N(2)-C(5)	1.426(10)	N(2)-C(6)	1.452(11)
N(3)-C(7)	1.307(8)	N(3)-C(8)	1.446(10)
N(3)-C(9)	1.452(10)	N(4)-C(10)	1.309(10)
N(4)-C(11)	1.433(12)	N(4)-C(12)	1.441(11)
O(3)-Co(1)-O(3) # 1	180.0	O(3)-Co(1)-O(2)	87.6(2)
O(3) # 1-Co(1)-O(2)	92.4(2)	O(3)-Co(1)-O(2) # 1	92.4(2)
O(3) # 1-Co(1)-O(2) # 1	87.6(2)	O(2)-Co(1)-O(2) # 1	180.0
O(3)-Co(1)-O(1)	92.7(2)	O(3) # 1-Co(1)-O(1)	87.3(2)
O(2)-Co(1)-O(1)	90.3(2)	O(2) # 1-Co(1)-O(1)	89.7(2)
O(3)-Co(1)-O(1) # 1	87.3(2)	O(3) # 1-Co(1)-O(1) # 1	92.7(2)
O(2)-Co(1)-O(1) # 1	89.7(2)	O(2) # 1-Co(1)-O(1) # 1	90.3(2)
O(1)-Co(1)-O(1) # 1	180.0	O(4)-Co(2)-Cl(1)	106.4(2)
O(4)-Co(2)-Cl(2)	104.5(2)	Cl(1)-Co(2)-Cl(2)	111.31(13)
O(4)-Co(2)-Cl(3)	105.6(2)	Cl(1)-Co(2)-Cl(3)	113.25(12)
Cl(2)-Co(2)-Cl(3)	114.81(14)	C(1)-O(1)-Co(1)	126.0(5)
C(4)-O(2)-Co(1)	121.5(5)	C(7)-O(3)-Co(1)	126.2(5)
C(10)-O(4)-Co(2)	123.3(6)	C(1)-N(1)-C(3)	120.8(8)
C(1)-N(1)-C(2)	122.3(8)	C(3)-N(1)-C(2)	116.8(8)
C(4)-N(2)-C(5)	122.5(7)	C(4)-N(2)-C(6)	119.8(8)
C(5)-N(2)-C(6)	117.6(8)	C(7)-N(3)-C(8)	121.3(6)
C(7)-N(3)-C(9)	121.7(7)	C(8)-N(3)-C(9)	116.9(7)
C(10)-N(4)-C(11)	121.3(9)	C(10)-N(4)-C(12)	122.1(9)
C(11)-N(4)-C(12)	116.6(8)	O(1)-C(1)-N(1)	125.4(8)
O(2)-C(4)-N(2)	124.7(8)	O(3)-C(7)-N(3)	123.0(7)
O(4)-C(10)-N(4)	124.0(10)		

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

In conclusion, only a unique solvate of cobalt(II) chloride, $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2[\text{Co}(\text{DMF})\text{Cl}_3]^-$ was isolated in high yield, and its crystal structure is unambiguously characterized. In particular, the structure discloses that $[\text{Co}(\text{DMF})\text{Cl}_3]^-$ species is favorable and stable species even at the solid state. The cation and anions of the present compound are also suitable in crystal packing without any other solvation even though the species is salt. Such a result indicates that caution should be taken when preparing sample solution of cobalt(II) chloride if DMF is used in synthesis of new cobalt complexes.

**Figure 2.** Crystal packing of $[\text{Co}(\text{DMF})_6]^{2+} \cdot 2[\text{Co}(\text{DMF})\text{Cl}_3]^-$.

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