Cobalt(II) Complexes of Ethylenediamine-Based Pyrazole Ligands: The Crystal Structure of [{*N′*,*N′*-Bis(3,5-dimethylpyrazol-1-ylmethyl)}-*N*,*N*-dimethylethylenediamine] Cobalt(II) Tetraphenylborate

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A variety of pyrazole-based ligands have recently been considerable interested in the study for the chelating nature and properties of their compounds and in the design of new pyrazole-based chelating ligands in coordination chemistry.[1] The *N*-substituted pyrazole derivatives such as *N*,*N*-bis(pyrazol-1-ylmethyl)aminoethane,[2] *N*,*N*-bis(3,5-dimethyl-pyrazol-1-ylmethyl)aminoethane,[3] *N*,*N*-bis(3,5-dimethyl-pyrazol-1-ylmethyl)aminobenzene,[4,5] *N*,*N*,*N*-tris(3,5-dimethyl-pyrazol-1-ylmethyl)amine,[6] *N*,*N*-bis(3,5-dimethyl-pyrazol-1-ylmethyl)-1-hydroxy-2-aminoethane[7] have extensively been investigated, but tetradentate pyrazole-based ligands containing *N*,*N*-dimethylethylenediamine have not been studied yet. Accordingly, we have synthesized a new series of ligands, the [*N*′,*N*′-bis(pyrazol-1-ylmethyl)]-*N*,*N*-dimethylethylenediamine **L1** and [*N*′,*N*′-bis(3,5-dimethylpyrazol-1-ylmethyl)]-*N*,*N*-dimethylethylenediamine **L2**, having two pyrazole groups in addition to a fourth, neutral, donor, as well as the preparation and characterization of their cobalt derivatives, considering as they may be expanded to the model of vitamin B_{12}. We describe here the results of our investigation along with structural characterization of representative **L2** complex, [CoCl(**L2**)](BPh_4).1/2CH_3COCH_3.

Experimental Section

All materials and solvents were of reagent grade as received from commercial sources. Pyrazole-1-methanol and 3,5-dimethylpyrazole-1-methanol was similarly synthesized as described in the literature procedure. ^{1}H NMR spectra were recorded on Varian 300-NMR Spectrometer at ambient temperature and chemical shifts were reference to the internal tetramethylsilane. Elemental analyses were performed on the Chemical Analysis Laboratory of Korea Basic Science Institute at Kyungpook National University.

[*N*′,*N*′-Bis(pyrazol-1-ylmethyl)]-*N*,*N*-dimethylethylenediamine (L1). The **L1** ligand was prepared by a similar procedure as described in the literature.[4] To a solution of *N*,*N*-dimethylethylenediamine (0.882 g, 10 mmol) in 80 mL of 1,2-dichloroethane was slowly added pyrazole-1-methanol (1.980 g, 20 mmol) under continuous stirring and the clear solution was stirred for 3 days at 70 °C. The resulting solution was filtered off and the filtrate was removed the solvent *in vacuo* to afford the colorless oil. Yield: 2.036 g (82%). ^{1}H NMR ($CDCl_3$); δ 7.55 (m, 4H, Pz), 6.26 (m, 2H, Pz), 5.05 (s, 4H, CH_2-Pz), 2.74 (t, 2H, CH_2CH_2N-CH_3), 2.39 (t, 2H, CH_2CH_2N-CH_3), 2.13 (t, 6H, N-CH_3).

[*N*′,*N*′-Bis(3,5-dimethylpyrazol-1-ylmethyl)]-*N*,*N*-dimethylethylenediamine (L2). In a similar procedure as that for **L1**, we have synthesized the **L2** ligand. Yield: 2.526 g (83%). ^{1}H NMR ($CDCl_3$); δ 5.79 (s, 2H, Pz), 4.92 (s, 4H, CH_2Pz), 2.75 (t, 2H, CH_2CH_2N-CH_3), 2.23 (t, 2H, CH_2CH_2-N-CH_3), 2.18 (d, 12H, CH_3-Pz), 2.11 (s, 6H, N-CH_3).

[{*N*′,*N*′-Bis(pyrazol-1-ylmethyl)}-*N*,*N*-dimethylethylenediamine] Cobalt(II) Tetraphenylborate (1). To the solution of Co(II)Cl_2 (0.129 g, 1 mmol) in refluxing ethanol was added a solution of **L1** (0.248 g, 1 mmol), prepared similarly as described in the literature procedure,[4] in acetone (15 mL) and then sodium tetraphenylborate (0.342 g, 1 mmol). After several minutes, the resulting violet solids were deposited, filtered off and washed with ethanol. Yield: 0.602 g (91% based on cobalt atom). Anal. Calcd. for $C_{36}H_{40}N_6BClCo$: C, 65.32; H, 6.09; N, 12.70. Found: C, 65.27; H, 6.13; N, 12.89.

[{*N*′,*N*′-Bis(3,5-dimethylpyrazol-1-ylmethyl)}-*N*,*N*-dimethylethylenediamine] Cobalt(II) Tetraphenylborate (2). In the same procedure above, complex **2** was synthesized. To the solution of Co(II)Cl_2 (0.129 g, 1 mmol) in refluxing ethanol was added a solution of **L2** (0.304 g, 1 mmol) in acetone (15 mL) and then sodium tetraphenylborate (0.342 g, 1 mmol). After several minutes, the violet solids were deposited, filtered off and washed with ethanol. An X-ray quality crystal of **2**. 1/2 CH_3COCH_3 was obtained from the recrystallization in acetone-absolute ethanol. Yield: 0.662 g (92% based on cobalt atom). Anal. Calcd. for $C_{40}H_{48}N_6BClCo$: C, 66.91; H, 6.74; N, 11.70. Found: C, 66.53; H, 6.90; N, 11.47. The study of NMR was not carried out due to the paramagnetic properties of complex **1** and **2**.

X-ray Structure Determination. A deep violet crystal ($0.60 \times 0.60 \times 0.35$ mm) of [(**L2**)CoCl](BPh_4).1/2CH_3COCH_3 suitable for X-ray diffraction analysis was grown by the recrystallization of acetone-absolute ethanol. A deep violet crystal sealed in thin walled glass capillary was mounted on an Enraf-Nonius CAD-4 diffractometer Mo-Kα radiation (λ = 0.71073 Å). Unit cell dimensions with estimated standard deviations were determined by least-squares using 25 well-centered reflections in the range of 10-13°. The intensities of the reflections were corrected for Lorentz and polarization effects. Crystal data, data collection, and refinement for complex **2** are listed in Table 1. Data reduction was carried out using a Molen program package; a decay correction based

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Table 1. Details of the X-ray crystal analyses of **2**.1/2$(CH_3)_2CO$

Crystal data	
Empirical formula	$C_{40}H_{48}ClN_6BCo.1/2CH_3COCH_3$
Formula weight	747.07
Temperature	293(2) K
Wavelength, λ(Mo K_α)	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	A = 12.507(1) Å
	B = 25.218(1) Å
	C = 25.802(2) Å
Volume V	8137.9(9) $Å^3$
Formula units per cell Z	8
Calculated density	1.220 Mg/m^3
Absorption coefficient	0.525 mm^{-1}
F(000)	3160
Theta range for data collection	1.58 to 25.96 deg.
Index ranges	0, 15; 0, 30; 0, 31
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3583/0/583
Goodness-of -fit on F^2	1.066
Final R indices [I>2σ(I)]	R_1= 0.0617, wR_2 = 0.1448
Largest diff. Peak and hole	0.461 and -0.253 e/$Å^3$

Table 2. Selected bond lengths [Å] and angles [deg] for **2**.1/2$(CH_3)_2CO$

Bond lenghs (Å)			
Co-N(1)	2.05(1)	Co-N(3)	2.25(1)
Co-N(5)	2.06(1)	Co-N(6)	2.14(1)
Co-Cl	2.288(4)		
Co'-N(1')	2.07(1)	Co'-N(3')	2.24(1)
Co'-N(5')	2.08(1)	Co'-N(6')	2.12(1)
Co'-Cl'	2.277(4)		
Bond Angles (°)			
N(1)-Co-N(3)	77.0(4)	N(1)-Co-N(5)	118.7(4)
N(1)-Co-N(6)	107.7(4)	N(3)-Co-N(5)	76.4(4)
N(3)-Co-N(6)	78.9(4)	N(5)-Co-N(6)	119.6(4)
N(1)-Co-Cl	104.5(3)	N(3)-Co-Cl	176.3(3)
N(5)-Co-Cl	105.6(3)	N(6)-Co-Cl	97.3(3)
N(1')-Co'-N(3')	76.1(5)	N(1')-Co'-N(5')	121.2(4)
N(1')-Co'-N(6')	108.1(5)	N(3')-Co'-N(5')	76.8(4)
N(3')-Co'-N(6')	80.3(5)	N(5')-Co'-N(6')	117.2(5)
N(1')-Co'-Cl'	104.1(4)	N(3')-Co'-Cl'	179.6(4)
N(5')-Co'-Cl'	103.3(3)	N(6')-Co'-Cl'	99.4(4)

on the intensities of two standard reflections and monitoring every hour was performed; empirical absorption corrections were applied based on Ψ scans.[8] The structure in $P2_12_12_1$ for complex **2** were determined by direct methods and refined by full-matrix least-squares using SHELXS-97 and SHELXL-97 program packages.[9] All non-hydrogen atoms were refined anisotropically, except the carbon atoms at phenyl rings of BPh_4 anions, which were refined as rigid groups. Hydrogen atoms were constrained by using riding modes. The final cycle of the refinement yielded to R = 0.0617 with 3583 reflections in the θ range of 1.58-25.96° ($0 \le h \le 15$, $0 \le k \le 30$, $0 \le l \le 31$). Selected bond distances and bond angles are given in Table 2.

Results and Discussion

The reactions of *N,N*-dimethylethylenediamine with pyrazolylmethanol or 3,5-dimethylpyrazolylmethanol in refluxing 1,2-dichloroethane for 72 h give **L1** or **L2**, respectively. The reactions of $CoCl_2$ with **L1** in a 1 : 1 molar ratio in refluxing ethanol-acetone lead to deep violet solids, [CoCl(**L1**)]-BPh_4. In a similar procedure, [CoCl(**L2**)]BPh_4 has been synthesized and the recrytallization of this complex in acetone-absolute ethanol effords a deep violet crystal, [CoCl(**L2**)]-BPh_4.1/2CH_3COCH_3. These complexes are low solubility in common organic solvents such as dichloromethane, chloroform, THF, hexane or ether.

^{1}H NMR spectra of **L1** and **L2** ligands are a similar pattern except dimethyl of pyrazolyl groups. The **L1** ligand appears multiplet assigned to six protons of pyrazole at 7.55 and 6.26 ppm, singlet to methylene of pyrazole-methylene at 5.05 ppm, triplet to ethylenediamine at 2.74 and 2.39 ppm and triplet to dimethyl of ethylenediamine at 2.13 ppm, respectively. The **L2** ligand displays singlet assigned to proton of pyrazole at 5.79 ppm, singlet to methylene of pyrazole-methylene at 4.92 ppm, triplet to ethylenediamine at 2.75 and 2.23 ppm, doublet to dimethyl of pyrazole at 2.18 ppm and singlet to dimethyl of the substituted ethylenediamine at 2.11 ppm. The NMR spectra of **1** and **2** were not measured due to the paramagnetic properties.

To verify the exact molecular structure of complexe we have carried out X-ray structure analysis for a deep violet crystals of complex **2**. The structure shows there are two independent molecules and one solvated acetone per asymmetric unit and the orientations of phenyl rings at the each anion are different. Therefore the structure belongs to the noncentro-symmetric space group. The view for the cation part of atom numbering scheme is shown in Figure 1. Each

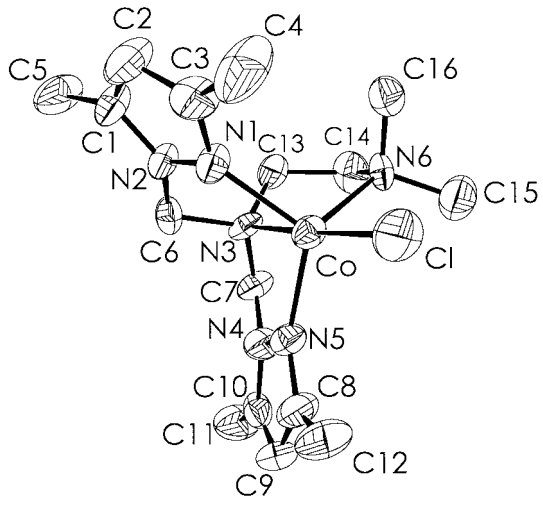

Figure 1. The structure and labeling scheme of cationic complex in **2**.

cobalt atom is the five coordinate environment from two nitrogen atoms of pyrazole groups, two nitrogen atoms of based ethylenediamine and one chloro atom. The geometry around Co(II) ion is in trigonal bipyramidal involving two pyrazole nitrogen atoms and one nitrogen atom dimethyl amine in the equatorial plane and the rest nitrogen atom of ethylenediamine and one chloro atom in the axial positions. The bond distances of Co-N are in the range 2.05(1)-2.25(1) Å and the bond distances of Co-Cl and Co'-Cl' are 2.282(4) Å and the bond distances of Co-N (pyrazole) are shorter about 0.12 Å than those of Co-N (amine) which are compared with that [0.15 Å] of $[Co(ap_3d)(H_2O)](ClO_4)_2.H_2O$ where ap3d is N,N,N'-tris((3,5-dimethylpyrazol-1-yl)methyl)-1.3-diaminopropane.[10] The average Co-N bond distances of an equatorial plane of complex **2** are about 0.16 Å shorter than those of an axial positions. The bond angles of N-Co-N for pyrazole fragments [120.0(4)°] in the complex are appreciably smaller than those [159.31(8)°] of $[CoCl_2(L)]$ where L = 2,2-di-*tert*-butylamino-4,4,6,6-tetrakis(3,5-dimethylpyrazolyl)cyclotriphosphzene.[11] In the complex **2**, it is obvious that **L2** is a flexible ligand. The flexibility of dimethylethylenediamine based dimethylpyrazole ligand leads to the specific co-ordination geometries for its coordination modes of metal ion.

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