Trigonal-Bipyramidal Geometry in a Cobalt(II) Complex with an Unsymmetrical Tripodal Ligand

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A cobalt(II) complex with bis[2-(3,5-dimethylpyrazol-1-yl)ethyl][(pyrazol-1-yl)methyl]amine (bppa), [CoCl(bppa)][B(C_6H_5)$_4$]·C_2H_5OH, was synthesized and characterized by measurements of the magnetic moment and the electronic spectra. The X-ray crystal structure shows that the compound has a distorted trigonal bipyramid with a N_4Cl coordination environment.

Metal complexes of tripodal ligands have drawn much attention over the last three decades due to a recognition of their utility as model compounds for understanding biological metal systems.[1] The most common tripodal ligands have three identical pendant donor groups, such as amines, pyridyl, imidazolyl, and pyrazolyl groups, and have been utilized to make a trigonal-bipyramidal coordination geometry. On the other hand, tripodal ligands having different pendant groups are not well developed. Such unsymmetrical tripodal ligands may afford a new aspect in coordination geometries and molecular structures. Thus, while pursuing our interest in coordination chemistry with unsymmetrical tripodal ligands, we synthesized a new tripodal ligand, bis[2-(3,5-dimethylpyrazol-1-yl)ethyl][(pyrazol-1-yl)methyl]amine (bppa), and obtained a cobalt(II) complex with bppa, [CoCl(bppa)][B(C_6H_5)$_4$]·C_2H_5OH (**1**). Here, we report on the synthesis and structural characterization of **1**.

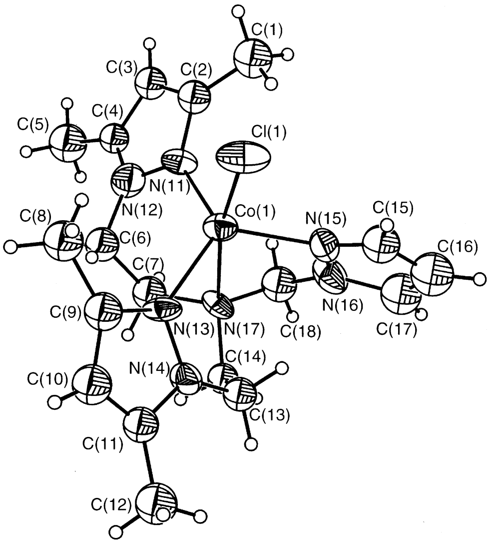

Fig. 1. Perspective view of the structure of **1** showing the atom labeling scheme. Selected bond distances (Å) and angles (°): Co(1)–N(11) 2.036(11), Co(1)–N(13) 2.032(9), Co(1)–N(15) 2.096(11), Co(1)–Cl(1) 2.302(4), Co(1)–N(17) 2.524(10), Co(2)–N(21) 2.005(11), Co(2)–N(23) 2.003(12), Co(2)–N(25) 1.914(11), Co(2)–Cl(2) 2.285(5), Co(2)–N(27) 2.482(12); N(11)–Co(1)–N(13) 121.6(5), N(11)–Co(1)–N(15) 108.2(5), N(13)–Co(1)–N(15) 119.8(4), N(11)–Co(1)–Cl(1) 106.6(4), N(13)–Co(1)–Cl(1) 99.3(3), N(15)–Co(1)–Cl(1) 96.6(4), N(11)–Co(1)–N(17) 81.1(4), N(13)–Co(1)–N(17) 81.5(4), N(15)–Co(1)–N(17) 74.6(4), Cl(1)–Co(1)–N(17) 169.9(3), N(21)–Co(2)–N(23) 119.6(5), N(21)–Co(2)–N(25) 110.3(5), N(23)–Co(2)–N(25) 118.2(4), N(21)–Co(2)–Cl(2) 105.7(3), N(23)–Co(2)–Cl(2) 99.4(4), N(25)–Co(2)–Cl(2) 99.7(4), N(21)–Co(2)–N(27) 83.2(4), N(23)–Co(2)–N(27) 78.4(5), N(25)–Co(2)–N(27) 73.37(4), Cl(2)–Co(2)–N(27) 170.6(3).

The treatment of a reaction mixture of bppa and $CoCl_2 \cdot 6H_2O$ with Na[B(C_6H_5)$_4$] in ethanol afforded a purple precipitate. Recrystallization from acetone–ethanol gave crystals of **1**. An X-ray crystallographic study revealed that the bppa ligand is coordinated to the metal center with a N_4 donor set, giving a distorted trigonal-bipyramidal coordination environment with chloride ion (Fig. 1). The crystal structure contains two crystallographically independent complex cations, [CoCl(bppa)]$^+$, of which the molecular structures are essentially similar. The nitrogen atoms of the three pyrazolyl arms of bppa are in the equatorial positions with the amino nitrogen in one of the axial sites. An unsymmetrical feature can be found in the small bond angle of N(15)–Co(1)–N(17) compared with the N(11)–Co(1)–N(17) and N(13)–Co(1)–N(17) angles. The equatorial Co–N(pyrazolyl) distances are 1.914(11)–2.096(11) Å. The axail Co–N and Co–Cl distances are 2.524(10) or 2.482(12) Å and 2.302(4) or 2.285(5) Å, respectively. Most tripodal ligands have been used to make a trigonal bipyramidal coordination geometry. Mani et al. reported that the tripodal ligand tris[2-(3,5-dimethylpyrazol-1-yl)ethyl]amine (metpea) forms an unusual four-coordinate complex, [Co(metpea)][B(C_6H_5)$_4$]$_2$, contrary to the case for the unmethylated ligand tris[2-(pyrazolyl-1-yl)ethyl]amine (tpea), which affords a trigonal bipyramidal environment in [CoI(tpea)][B(C_6H_5)$_4$].[2,3] They attributed this to a screening effect of bulky 3-methyl substituents at the pyrazole rings. In the present case, the bppa ligand forms a distorted trigonal bipyramidal coordination for Co(II), picking up a fifth donor atom. This result suggests that the effective steric hindrances hold for only the tris methylated ligand.

The magnetic moment of **1** is 4.50 BM at 300 K, and decreases slightly upon lowering the temperature (3.68 BM at 2 K). We introduced the Curie–Weiss law, $\chi_A = 5Ng^2\beta^2/[4k(T -$

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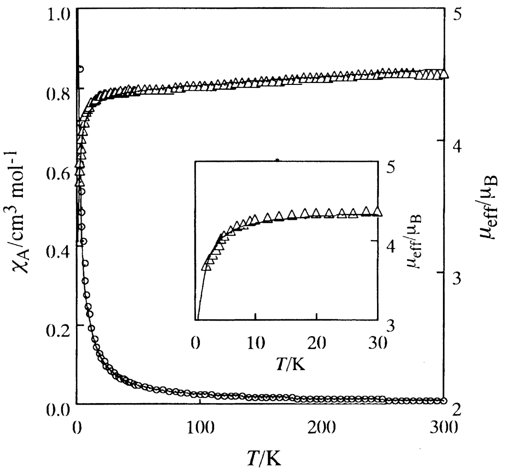

Fig. 2. Temperature dependence of magnetic susceptibility (○) and magnetic moment (△) of **1**.

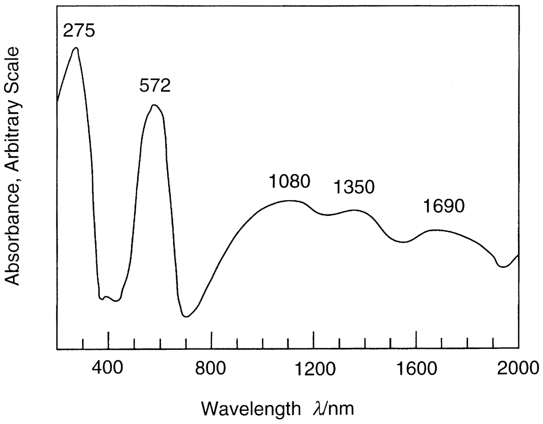

Fig. 3. Diffuse reflectance spectrum of **1**.

$\theta)] + N\alpha$ for an analysis of the magnetic data. The best fitting parameters are $\theta = -0.82$ K, $g = 2.26$, and $N\alpha = 600 \times 10^{-6}$ cm^3 mol^{-1}, as shown by the solid line in Fig. 2. The observed and calculated moments agree well with reasonable g and $N\alpha$ values, in agreement with the $^4A_2'$ state being the lowest as a first approximation.[4] This result indicates that the magnetic interaction between the cobalt ions is very weak. This is understandable, since the closest metal-metal separation is a Co1···Co2 (x, $y-1$, z) distance of 7.699(3) Å in the crystal. The diffuse reflectance spectrum of **1** shows several absorptions in the visible and near-infrared region, as shown in Fig. 3. These absorptions (572, 1080, 1350, and 1690 nm) can be assigned to d–d transitions ($^4A_2' \rightarrow {}^4E''(P) + {}^4A_2'(P)$, $^4A_2' \rightarrow {}^4E'$, $^4A_2' \rightarrow {}^4E''$, and $^4A_2' \rightarrow {}^4A_1'' + {}^4A_2''$ respectively) due to the trigonal-bipyramidal high-spin Co^{II} irrespective of the distorted structure.

Experimental

The ligand, bppa, was synthesized by a condensation reaction of bis[2-(3,5-dimethylpyrazol-1-yl)ethyl]amine[5] with *N*-hydroxymethylpyrazole[6] using 1,2-dichloroethane as a solvent.

Synthesis of 1. To a solution of bppa (29 mg, 0.085 mmol) in 10 cm^3 of ethanol was added 20 mg (0.084 mmol) of cobalt(II) chloride hexahydrate. The reaction mixture was heated at 70 °C for 10 min and then sodium tetraphenylborate (29 mg, 0.085 mmol) was added. A purple precipitate was collected, washed with ethanol, and air-dried. Recrystallization was performed from acetone–ethanol: Yield, 42 mg (65%). Found: C, 65.99; H, 6.63; N,12.46%. Calcd for $C_{42}H_{47}BClCoN_7 \cdot C_2H_5OH$: C, 65.97; H, 6.67; N, 12.24%.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out using a Perkin-Elmer 2400 Series II CHNS/O Analyzer. The magnetic susceptibilities were measured on a Quantum Design MPMS-5S SQUID susceptometer operating at a magnetic field of 0.5 T. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. The effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-ray Crystal Structure Analysis. A purple crystal of **1** was mounted on a glass fiber with epoxy cement at room temperature. A preliminary examination was made and data were collected on a Bruker CCD X-ray diffractometer using graphite-monochromated Mo-$K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters, except for the carbon atoms and the ethanol molecule. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Pentium III Windows NT computer utilizing the SHELXTL software package.

Crystallographic data: for **1**; $C_{44}H_{53}BClCoN_7O$, FW = 801.12, monoclinic, space group Pc, $a = 13.9808(7)$, $b = 14.1777(7)$, $c = 22.2725(11)$ Å, $\beta = 106.456(1)°$, $V = 4233.9(4)$ Å^3, $Z = 4$, $D_c = 1.257$ g cm^{-3}, μ(Mo $K\alpha$) = 0.510 mm^{-1}, crystal dimensions 0.11 × 0.16 × 0.35 mm, 19132 reflections collected, 9683 independent reflections, $R1$ [$I > 2\sigma(I)$] = 0.0645, $wR2$ [$I > 2\sigma(I)$] = 0.1623. The X-ray analysis data have been deposited as Document No. 74051 at the Office of the Editor of Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 167874.

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