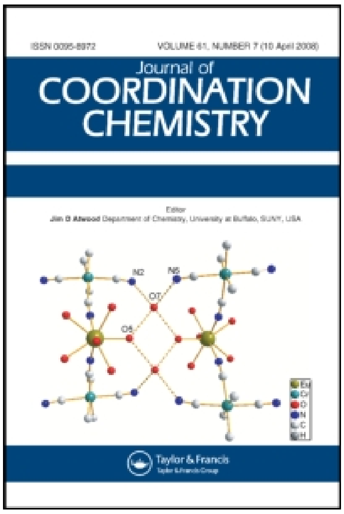

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HIGH-SPIN FOUR AND SIX-COORDINATE COBALT(II) COMPLEXES WITH 3,5-DIMETHYL PYRAZOLE

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The reaction of cobalt dichloride hexahydrate with two equivalents of 3,5-dimethyl pyrazole under reflux in THF gave a deep blue solution of Co(3,5-dimethylpyrazole) dichloride. Suitable crystals for X-ray structural determination were grown in THF. The structural assignment of (**1**) was made by elemental analysis and electronic spectroscopy and confirmed by single crystal X-ray diffraction studies. The crystal structure reveals that compound (**1**) crystallizes in the monoclinic space group $C2/c$ with eight molecules in the unit cell of dimensions $a = 15.012(2)$, $b = 8.275(1)$, and $c = 24.047(2)$Å, and $\beta = 96.05\ (1)°$. The structure has been refined to an R(F) factor of 0.045 based on 1670 observed reflections. The geometry around the Co(II) center is best described as tetrahedral. The four ligating atoms consist of two chlorine atoms and two nitrogen atoms from the 3,5-dimethyl pyrazole. The solution electronic spectra of (**1**) in acetone and THF are consistent with the solid state crystal structure. However, the electronic spectra in water is consistent with a six-coordinate Co(II) in an octahedral environment. These electronic spectral assignments are also consistent with the magnetic moment values in the two solvents.

KEYWORDS: cobalt(II), 3,5-dimethylpyrazole, tetrahedral, electronic spectra, four and six coordination

INTRODUCTION

The synthesis, spectral and structural properties of *pseudo*-tetrahedral Co(II) complexes are of interest for the possible implications they may have in clarifying the structure of the active sites of metalloproteins and metalloenzymes.[1–3] Several four-coordinate tetrahedral cobalt(II) complexes have recently been reported, including the structure of a four-coordinate cobalt(II) complex formed with the ligand tris(3,5-dimethyl-1-pyrazolyl)(ethyl)amine (MeTPYEA),[4–7] reported by Mani and co-workers. The crystal structure of this cobalt(II) complex reveals a tetrahedral geometry around the cobalt, however the electronic spectra show high frequency bands that are not usually seen in tetrahedral cobalt(II) complexes and resemble more closely those of trigonal bipyramidal Co(II) complexes.[7] We decided to

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investigate the coordination compound of cobalt(II) with a simple monodentate ligand, 3,5-dimethylpyrazole. We believe the complex formed between the cobalt(II) salt and this ligand might be sensitive to changes in solvent type and polarity, leading to changes in coordination preferences and stereochemistry. We report the synthesis, spectral and structural characterization of a four-coordinate tetrahedral cobalt(II) complex, and the spectra characterization of four- and six-coordinate complexes in solution.

EXPERIMENTAL

3,5-dimethyl-pyrazole

This ligand was synthesized following a reported procedure.[9]

[dichloro cobalt(II)(3,5-dimethylpyrazole)]

To a solution of 0.20 g (2.0 mmol) of *3,5-dimethyl-pyrazole* in 30 ml of THF was added 0.24 g (1.00 mmol) cobalt(II) chloride hexahydrate. The resultant solution was refluxed for 3 h, and cooled to room temperature. The solution was filtered and the filtrate was allowed to evaporate slowly to give deep blue crystals of (**1**), 0.26 g (0.8 mmol) 68% yield. *Anal* Calc. for $CoC_{10}H_{16}N_4Cl_2$(%): C, 35.9; H, 4.60; N, 15.2; Found*: C, 36.15; H, 4.63; N, 15.1.

Physical Measurements: C, H, and N analyses were performed by Schwarzkopf Microanalytical Laboratory, NY, U.S.A. UV-Visible spectra were measured with a Perkin Elmer Lamda II spectrophotometer in the range of 240 nm–800 nm. The solution paramagnetic susceptibility of **1** in water and in THF were measured by the shift in the proton resonance of the *t*-butyl group of *t*-butanol in the solvent following the Evans method[10] using a Varian EM360A NMR spectrometer.

X-ray Structure Determination

A large blue platelet (0.64×0.16×0.04 mm) of (**1**) was glued to the end of a glass fiber with epoxy and placed on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα (0.71073 Å) radiation. The pertinent crystallographic data are summarized in Table 1. The final unit cell parameters were obtained by a least square fit of 25 accurately centered reflections measured in the range 13.0° $< 2\theta <$15.2° and the intensity data were collected at 293 (2) K in the range of 2° $< 2\theta <$ 25°. Three standard reflections monitored every 3600*s* did not show any significant change in intensity during the data collection. An absorption correction (SHELX-76[10a]) was applied with the minimum and maximum transmission factors of 0.781 and 0.939 respectively. The 2441 total reflections were merged to 2231 independent data (Rint = 0.03), and 1670 with $I < 2\sigma(I)$ were used in the structure refinement. The structure solution and refinement were carried out by the direct method (SHELXS-86[10b]) and the least-squares procedure (SHELXL-93[10c]) was used to refine all coordinates and displacement parameters. The final cycles of refinement converged at $R(F) = 0.045$, $wR(F^2) = 0.080$ based on 1670 observed reflections with $[I>2.0\sigma(I)]$. Anisotropic displacement parameters were applied for all non-hydrogen atoms. For the non-H atoms, the coordinates and equivalent isotropic displacement parameters are given in Table 2.

Table 1 Crystallographic and data collection parameters

Formula	$C_{10}H_{16}N_4Cl_2Co$
fw	322.10
crystal system	Monoclinic
space group	*C2/c*
a, Å	15.012(2)
b, Å	8.275(1)
c, Å	24.047(2)
β,°	96.05(1)
V, Å^3	2970.6(6)
Z	8
θ range for data collection	2 to 25°
Index ranges	0≤h≤17, 4≤k≤9, - 281≤28
Abs. coeff, mm^{-1}	1.500
No. reflections	2441
Independent reflections	2231 [R(int) = 0.03]
Obsd. reflctns, *I>2.0σ(I)*	1670
Refinement Method	Full-matrix least-squares on F^2
R(F)[a]	0.045
wR(F^2)[b]	0.080
Goodness of Fit on F^2	1.046
Largest diff. peak and hole	0.34 and -0.28 e.Å^{-3}

[a] $R(F) = \Sigma\|F_o|-|F_c\|/\Sigma|F_o = 0.045$, [b] $wR(F^2) = \{\Sigma[w(F_o{}^2\text{-}Fc^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2} = 0.080$, where $w = 1/[\sigma^2(F_o{}^2)+ 0.0464 \times P^2+6.1065 \times P]$, and $P = [0.33333 \times MAX(O,F_o{}^2)+ 0.66667 \times F_c{}^2]$

RESULTS AND DISCUSSION

Spectroscopy

Figure 1 shows the electronic absorption spectra of (**1**) in water, methanol, ethanol and in actone or THF. The complex displayed a blue colored solution in acetone and THF, which is consistent with the color observed for most tetrahedral cobalt(II)

Table 2 Atomic coordinates (x10^5 for Co and Cl atoms, x10^4 for all other atoms) and equivalent isotropic displacement parameters (Å^{2}x10^4 for Co and Cl atoms, x 10^3 for all other atoms) for 1 U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	*x*	*y*	*z*	U(eq)
Co	36650(4)	2806(7)	37830(2)	494(2)
Cl(1)	42490(10)	15921(16)	45482(5)	782(4)
Cl(2)	24956(8)	13945(19)	32694(5)	773(4)
N(1)	4508(2)	-99(14)	3205(1)	49(1)
N(2)	4277(3)	7(5)	2644(2)	53(1)
N(3)	3436(2)	-1906(5)	4101(1)	52(1)
N(4)	3686(3)	-2263(6)	4642(2)	60(1)
C(1)	5346(3)	-660(5)	3258(2)	53(1)
C(2)	5625(3)	-900(6)	2738(2)	61(1)
C(3)	4938(3)	-474(6)	2354(2)	57(1)
C(4)	5839(5)	-927(13)	3824(3)	89(2)
C(5)	4834(6)	-529(13)	1729(3)	90(2)
C(6)	3104(3)	-3276(6)	3874(2)	58(1)
C(7)	3151(4)	-4479(7)	4274(2)	69(1)
C(8)	3527(3)	-3807(7)	4762(2)	62(1)
C(9)	3761(7)	-4504(12)	5331(3)	91(2)
C(10)	2760(7)	-3347(12)	3269(3)	93(2)

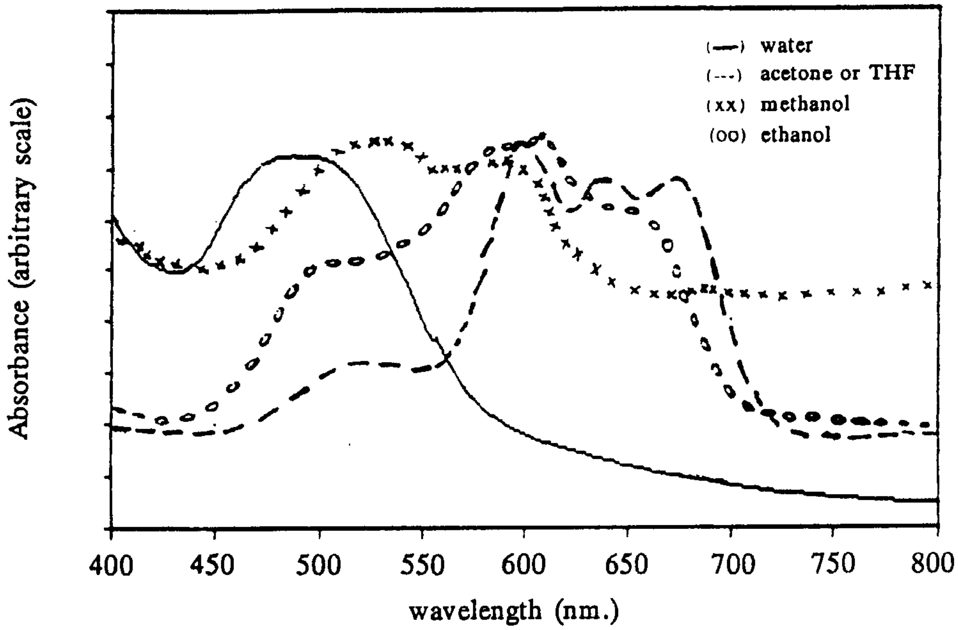

Figure 1 Visible absorption spectra of the [Co(3,5-dimethylpyrazole)$_2$Cl$_2$].

derivatives which are generally intense blue or green.[11–14] The color of the solution, and the spectral band positions and intensities of (**1**) in these solvents *i.e.*, 670 nm, 635 nm and 600 nm are features that indicate tetrahedral coordination around the Co(II) ion and are comparable to other *pseudo*tetrahedral cobalt(II) complexes of related ligands.[11–13] A weaker shoulder also appears around 520 nm. Compound (**1**) in ethanol is a violet colored solution and displayed very interesting visible spectra bands. The bands at 650 nm, 605 nm and 585 nm are characteristic of the tetrahedral cobalt(II) ion. A fourth band appearing at 500 nm which is of lower extinction coefficient is due to another cobalt(II) ion of different stereochemistry in solution. This latter band increases in intensity as the solvent is changed from ethanol to methanol, and the color of the solution changes from violet to pink-violet. When the solvent is changed from methanol to water, the color is completely changed to pink. The pink color in this high spin cobalt(II) complex is consistent with the color observed for most octahedral cobalt(II) complexes. While this color cannot be taken as an infallible guide to the stereochemistry, the visible absorption spectra of (**1**) in water shows only one peak (Figure 1) with marked reduction in the extinction coefficient for the ligand field band. The spectra features displayed in water resemble six-coordinate Co(II) complexes.[14d] It appears that the compound exists as an equilibrium mixture of tetrahedral and octahedral geometries in methanol and ethanol. The tetrahedral geometry appears to be more favored in acetone and THF (consistent with the solid state structure of crystals isolated from THF), while the octahedral geometry is favored in water and methanol for which the tendency for hydrogen bonding is greater. The magnetic moment values of the compound in acetone is 4.24 μB, which corresponds to the lower limit of values observed for pseudotetrahedral cobalt(II) complexes.[14e] The value in water is 4.45 μB which is in line with values expected for octahedral cobalt(II) complexes.[5]

Description of the structures

The molecular structure of [Co-(3,5dimethylpyrazole)Cl_2] is monomeric and the atomic numbering scheme is shown in Figure 2. The cobalt(II) coordination is tetrahedral, with two ligating nitrogen atoms from the 3,5-dimethylpyrazole ligand and two chlorine atoms providing the four coordination sites. Bond distances and angles are presented in Table 3. The Co-N distances of 2.000(3) Å and 2.008 (4) Å. are in the range observed for other cobalt(II) polypyrazole complexes and Co-N distances in general.[15–16] The Co-Cl distances are 2.234(1) Å and 2.236(1) Å. There is some distortion from the idealized tetrahedral geometry, this is displayed in the following angles: N(1)-Co-N(3) = 105.6(1), N(1)-Co-Cl(2) = 101.4°(1), N(1)-Co-Cl(1) = 115.2(1) and Cl(1)-Co-Cl(2) = 118.1°(1). These diverge from the ideal tetrahedral value of 109.5 and may be due to the 3-methyl substituent at the pyrazole ring. The dihedral angle between the two 3,5-dimethyl pyrazole mean planes is 33°(3). The closest Co—Co distance is 6.75Å. Although no significantly short interatomic contact distances (*e.g.,* hydrogen bonding) are observed in this structure, there are several intra- and inter-molecular distances slightly less than, or

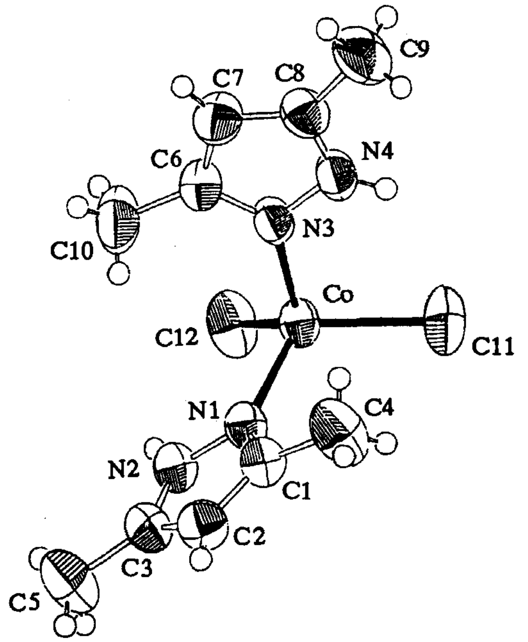

Figure 2 The molecular structure and labelling scheme of [Co(3,5-dimethypyrazole^2 Cl_2]*1*, with thermal ellipsoids drawn at the 50% probability level.

Table 3 Bond lengths [Å] and angles [°] for **1**

Co-N(1)	2.000(3)	Co-N(3)	2.008(4)
Co-Cl(1)	2.234(1)	Co-Cl(2)	2.236(1)
N(1)-C(1)	1.335(5)	N(3)-C(6)	1.331(5)
N(1)-N(2)	1.359(4)	N(3)-N(4)	1.348(5)
N(2)-C(3)	1.334(5)	N(4)-C(8)	1.337(6)
C(1)-C(2)	1.374(6)	C(6)-C(7)	1.381(7)
C(1)-C(4)	1.497(7)	C(6)-C(10)	1.494(8)
C(2)-C(3)	1.355(6)	C(7)-C(8)	1.365(7)
C(3)-C(5)	1.494(7)	C(8)-C(9)	1.492(7)
Cl(1)-Co-Cl(2)	118.15(6)	N(1)-Co-N(3)	105.6(1)
N(1)-Co-Cl(1)	115.2(1)	N(3)-Co-Cl(2)	115.2(1)
N(3)-Co-Cl(1)	101.1(1)	N(1)-Co-Cl(2)	101.4(1)
C(1)-N(1)-N(2)	104.8(3)	C(6)-N(3)-N(4)	105.2(4)
C(1)-N(1)-Co	130.4(3)	C(6)-N(3)-Co	133.1(3)
N(2)-N(1)-Co	124.4(3)	N(4)-N(3)-Co	121.5(3)
C(3)-N(2)-N(1)	112.0(4)	C(8)-N(4)-N(3)	112.4(4)
N(1)-C(1)-C(2)	109.8(4)	N(3)-C(6)-C(7)	109.9(4)
N(1)-C(1)-C(4)	120.5(5)	N(3)-C(6)-C(10)	120.5(5)
C(2)-C(1)-C(4)	129.7(5)	C(7)-C(6)-C(10)	129.6(6)
C(3)-C(2)-C(1)	107.4(4)	C(8)-C(7)-C(6)	106.9(5)
N(2)-C(3)-C(2)	106.0(4)	N(4)-C(8)-C(7)	105.7(5)
N(2)-C(3)C-(5)	122.1(5)	N(4)-C(8)-C(9)	122.6(6)
C(2)-C(3)-C(5)	131.9(5)	C(7)-C(8)-C(9)	131.8(6)

equal to, the sum of the van der Waals radii. Some of these are Cl(1)—H(4N) = 2.76, Cl(2)—H(2N) = 2.85 and Cl(2)—N(2) 3.402Å. While the geometry of (**1**) is consistent with the spectroscopic data in THF and acetone, the same is not true of (**1**) in solvents capable of hydrogen bonding to the metal, such as water and methanol. Solvents capable of H-bonding cause octahedral coordination around the cobalt(II), in which the fifth and sixth coordination sites are occupied by solvent molecules.

SUPPLEMENTARY MATERIAL

Tables of anisotropic thermal motion parameters (Table S-1), H atom coordinates (Table S-2), Torsional angles (Table S-3) and observed and calculated structure amplitudes (Table S-4) are available from the authors.

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