

Synthesis, characterization and crystal structure of octahedral Cobalt(III) complex with 5,5'-dimethyl-2,2'-bipyridine ligand

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Abstract: Preparation of two Schiff bases via efficient condensation of α -bromocinnamaldehyde and thiosemicarbazide or bis(4-aminophenyl) ether is described in high yield at 100 °C, methanol solvent and neutral PH. The elemental analyses, FT-IR, ¹H NMR and ¹³C NMR spectroscopy are agreed with two new Schiff bases structure. The complex [Co(5,5'-dmbpy)₃]Cl₃.CH₃CN.2H₂O(**1**) where 5,5'-dmbpy = 5,5'-dimethyl-2,2'-bipyridine was synthesized and characterized by the elemental analysis, IR, UV-Vis, CV, ¹H-NMR and ¹³C-NMR spectroscopies and the single crystal X-ray diffraction method. The X-ray diffraction study of compound **1** indicated the Co(III) ion is six-coordinated in distorted octahedral configuration. The crystal data for [Co(5,5'-dmbpy)₃]Cl₃.CH₃CN.2H₂O at 25°C are as follows: monoclinic, space group *P2₁/n* with *a* = 13.5684(9) Å, *b* = 14.4082(9) Å, *c* = 19.4228(13) Å, β = 92.210(5)° and *Z* = 4.

Keywords: Spectroscopies, Crystal, Monoclinic, Space group.

Introduction

Metal complexes with variety of bidentate nitrogen donor ligands such as pyridine, di- and polypyridine, and their derivatives are also of great interest due to their ability to modify chemical, catalytic, and photochemical properties as well as facile electrochemical processes [1-13]. These complexes have different coordination numbers and configurations such as tetrahedral and octahedral for coordination number four and six respectively [14,15].

Here we describe the structural chemistry of the hindered polypyridyl ligands such as 5,5'-dimethylbipyridine (5,5'-dmbpy) highvalent cobalt precursors.

In this study, we report the synthesis of new cobalt (III) complex with 5,5'-dimethylbipyridine under the formula [Co(5,5'-dmbpy)₃]Cl₃.CH₃CN.2H₂O. The distorted octahedral compound was characterized by spectroscopic studies such as IR, UV-vis, ¹H-NMR and ¹³C-NMR. The cyclic voltammetry (CV) study was

employed to investigate its electrochemical behavior. The structure of the complex was also recognized by X-ray diffraction analysis. These results are presented and discussed next.

Results and discussion

Synthesis and characterization:

Compound (**1**) was obtained from the reaction of 1 equivalent of CoCl₂.6H₂O with 1 equivalent of the appropriate bipyridine ligand in a methanol solution around 50°C over 2 hours. This compound was grown crystallization of their respective microcrystals over a week to obtain suitable crystals for X-ray studies. The compound is soluble in methanol and common organic solvents. [Co(5,5'-dmbpy)₃]Cl₃.CH₃CN.2H₂O is stable in air at room temperature. The coordination mode of the ligands in this compound was studied using spectroscopic methods. The X-ray diffraction study provided evidence regarding the geometry of ligands around cobalt(III) ion.

X-ray crystal structures:

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An ORTEP view with atom numbering scheme of the complex (**1**), is shown in Figure 1.

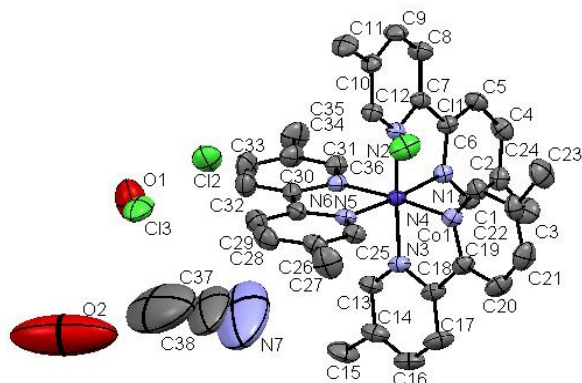


Figure 1. ORTEP view of compound $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ with atom numbering scheme

The coordinated atom present again a compressed distorted octahedral arrangement around Co(III) by six N atoms from three 5,5'-dimethyl-2,2'-bipyridine. The asymmetric unit of the title compound Figure 1, contains one molecule $[\text{CoC}_{36}\text{H}_{36}\text{N}_6]$, three Cl^- , one acetonitrile solvent and two water. The packing diagram for **1** is shown in Figure 2.

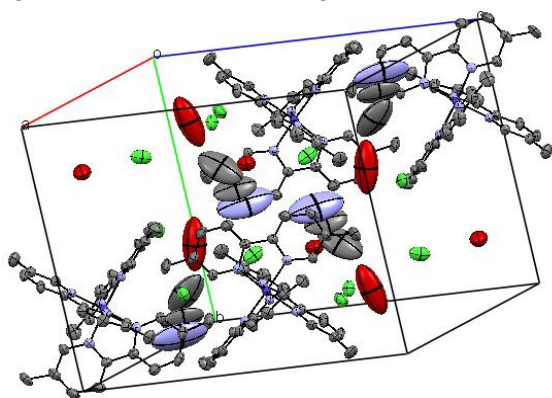


Figure 2. The packing diagram of $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$

In this compound rings A(Co1/N1/C6/C7/N2), B(Co1/N3/C18/C19/N4), C(Co1/N5/C30/C31/N6), D(N1/C1-C6), E(N2/C7-C10/C12), F(N3/C13/C14/C16-C18), G(N4/C19-C22/C24), H(N5/C25/C26/C28-C30) and I(N6/C31-C34/C36) are, of course, planer and the dihedral angles between them are $D/E = 6.19^\circ$. So one of the 5,5'-dimethyl-2,2'-bipyridine systems is not planer. The π - π contacts between the 2,2'-bipyridine rings, $\text{Cg1}-\text{Cg7}$, $\text{Cg1}-\text{Cg9}$, $\text{Cg2}-\text{Cg4}$, $\text{Cg2}-\text{Cg8}$, $\text{Cg3}-\text{Cg5}$, $\text{Cg3}-\text{Cg6}$, [symmetry codes: x, y, z , where $\text{Cg1}, \text{Cg2}, \text{Cg3}, \text{Cg4}, \text{Cg5}, \text{Cg6}, \text{Cg7}, \text{Cg8}$ and Cg9 are centroids of the rings

A-I, respectively] may stabilize the structure, with centroid-centroid distances of $3.928(2), 3.704(2), 3.896(2), 3.752(2), 3.730(2)$ and $3.766(2)\text{\AA}$. Table 1 shows details of the data collection and refinement of the X-ray crystal structure determinations for **1**.

Table 1. Crystal data and structure refinement for compound **1**.

Formula	$\text{C}_{36}\text{H}_{36}\text{CoN}_6, \text{C}_2\text{H}_3\text{N}, 2(\text{H}_2\text{O}), 3(\text{Cl})$
Formula weight	795.07
Temperature /K	298 (2)
Wavelength $\lambda/\text{\AA}$	0.71073
Crystal system	Monoclinic
Space Group	$P2_1/c$
Crystal size / mm^3	$0.4 \times 0.13 \times 0.04$
a / \AA	13.5684(9)
b / \AA	14.4082(9)
c / \AA	19.4228(13)
β°	92.210(5)
Volume / \AA^3	3794.3(4)
Z	4
Density (calc.) / g cm^{-3}	1.392
θ ranges for data collection (deg)	1.76 to 29.33
F(000)	1656
Absorption coefficient mm^{-1}	0.707
Index ranges	$-14 \leq h \leq 18, -19 \leq k \leq 19, -26 \leq l \leq 26$
Data collected	10231
Unique data (Rint)	0.0769
Parameters, restraints	473, 0
Final R1, wR2a (Obs. data)	0.0731, 0.1445
Final R1, wR2a (All data)	0.1223, 0.1647
Absolute structure parameter	1.032
Goodness of fit on F2 (S)	
CCDC	906923

Selected bond lengths and angles relevant to the coordination sphere are listed in Table 2. In this compound the Co(III)-N bond lengths are 1.928–1.942 \AA and bite angles around 83° for bidentate ligands. These are in good agreement with the corresponding in similar Co(III) compounds [16,17].

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) for $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$

Bond lengths (\AA)	bond angles ($^\circ$)		
Co(1)-N(1)	1.933(3)	N(4)-Co(1)-N(1)	90.55(12)
Co(1)-N(2)	1.942(3)	N(4)-Co(1)-N(3)	83.47(13)
Co(1)-N(3)	1.934(3)	N(1)-Co(1)-N(3)	94.67(12)

Co(1)-N(4)	1.928(3)	N(4)-Co(1)-N(5)	93.06(12)
Co(1)-N(5)	1.939(3)	N(1)-Co(1)-N(5)	175.08(13)
Co(1)-N(6)	1.942(3)	N(3)-Co(1)-N(5)	89.06(12)
		N(4)-Co(1)-N(6)	174.99(13)
		N(1)-Co(1)-N(6)	93.54(12)
		N(3)-Co(1)-N(6)	93.32(13)
		N(5)-Co(1)-N(6)	83.02(12)
		N(4)-Co(1)-N(2)	95.65(12)
		N(1)-Co(1)-N(2)	83.01(12)
		N(3)-Co(1)-N(2)	177.51(13)
		N(5)-Co(1)-N(2)	93.31(12)
		N(6)-Co(1)-N(2)	87.72(12)

In compound **1**, there are some strong intermolecular O-H...Cl hydrogen contacts (Table 3.) that seem to be effective in the stabilization of the crystal structure.

Table 3. Hydrogen bond geometries of complex **1** in the crystal packing (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
O1-H1B...Cl3i	0.85(8)	2.38(8)	3.205(8)	165(6)
O1-H1C...Cl2ii	0.85(9)	2.49(8)	3.319(7)	165(7)
O2-H2B...Cl3ii	0.92(4)	2.57(4)	3.095(17)	117(3)
C1-H1...N3i	0.9300	2.5300	3.024(5)	114.00
C8-H8...Cl2iii	0.9300	2.5900	3.514(4)	170.00
C9-H9...Cl3iii	0.9300	2.7000	3.558(4)	153.00
C11-H11A...Cl1i	0.9600	2.7700	3.551(4)	139.00
C11-H11C...Cl3ii	0.9600	2.8100	3.705(4)	156.00
C12-H12...Cl1i	0.9300	2.8000	3.297(4)	115.00
C12-H12...N5i	0.9300	2.5000	3.001(5)	114.00
C13-H13...N6i	0.9300	2.4800	2.989(5)	115.00
C16-H16...Cl3iv	0.9300	2.7000	3.599(4)	163.00
C17-H17...Cl2v	0.9300	2.7900	3.682(4)	162.00
C24-H24...N2i	0.9300	2.5200	3.031(4)	115.00
C25-H25...N4i	0.9300	2.4700	2.975(5)	114.00
C28-H28...Cl3i	0.9300	2.8200	3.523(5)	133.00
C36-H36...N1i	0.9300	2.5500	3.479(8)	175.00
C32-H32...O1i	0.9300	2.4800	2.989(5)	115.00
C37-H37C...O2i	0.9600	2.5000	2.93(4)	107.00

Symmetry codes: (i) x,y,z; (ii) x,3/2-y,1/2+z; (iii) -x,-1/2+y,1/2-z; (iv) 1-x,1-y,1-z; (v) 1-x,-1/2+y,1/2-z

Spectral studies:

The vibrational bands present around 3000 cm^{-1} in complexes **1** was assigned as $\nu(\text{C-H})$. The bands observed in the range 1600-1400 cm^{-1} are assigned to $\nu(\text{C=N})$ and $\nu(\text{C=C})$ vibrations [18]. The medium to strong vibrations in the region 960-550 cm^{-1} are assigned to the deformation vibrations of $\delta(\text{C=C=N})$ and $\delta(\text{C=C=C})$ in the pyridine rings [19,20]. Far infrared spectra of this compound was recorded between 500 - 250 cm^{-1} . Co-N stretching vibration for complex **1** is seen at 292 cm^{-1} [21,22]. The electronic spectra of $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ presented four dominant bands in the region 200–900 nm in DMF solution. One of them at the higher energy with high ϵ value at 300 nm ($\log\epsilon=4.58$), Figure 3, was attributed to intraligand $\pi^* \leftarrow \pi$ excitations [23,24]. The three remaining bands at 507 ($\log\epsilon=1.98$), 607 ($\log\epsilon=2.00$) and 674 nm ($\log\epsilon=2.16$) may be assigned to ${}^3\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$, ${}^1\text{T}_{1g} \leftarrow {}^1\text{A}_{1g}$ and ${}^1\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$ transitions, respectively; these data are in good agreement with other octahedral coordination compounds of Co(III) [25] (Figure 4).

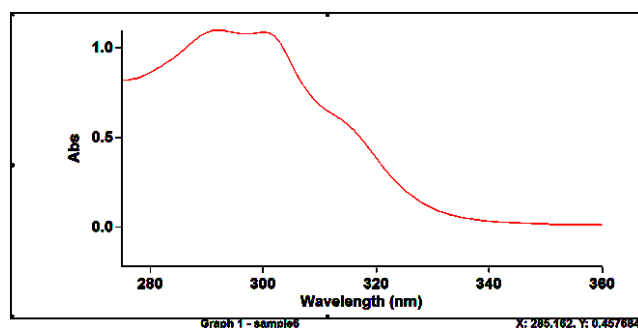


Figure 3. UV absorption spectra of $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$

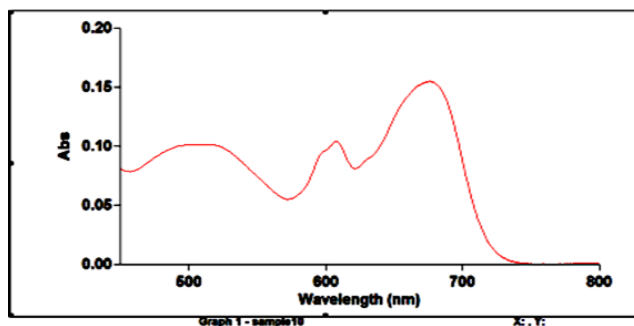
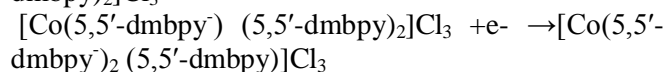
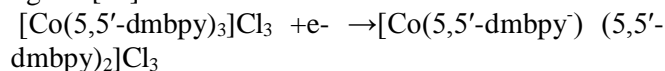


Figure 4. Vis absorption spectra of $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$

NMR spectroscopy reveals that the structure of compound **1**, are held in MeOD solution. In this compound, the ${}^1\text{H}$ NMR spectrum shows three signals

at around 7-9 ppm for aromatic protons and a signal at 2.46 ppm for the methyl protons [26]. Two hydrogen atoms on carbon atoms numbering 20 and 21 (for example) are split and show a doublet pattern as expected. Hydrogen atom on carbon atom numbering 24 (for example), shows a singlet pattern. In the ^{13}C NMR spectrum, five distinct signals are seen for the aromatic carbon at 126 -153 ppm [27]. Both ^1H and ^{13}C spectra confirm the symmetry of the compounds seen in the solid state by X-ray diffraction.

The cyclic voltammogram of the complex shown in Figure 5 was similar with those of other typical compounds containing bipyridine, phenanthroline and terpyridine ligands [28-29]. The ligand 5,5'-dmbpy exhibits two reduction waves at -0.15 V and 1.24V, which is assigned to a one-electron addition to the lowest unoccupied molecular orbital (LUMO), for generation of electronic configuration $(\pi^*)^1$ for each ligand [30].



For the neutral complex, another two reduction waves at approximately 0.69 V and 0.13V versus the Fc/Fc^+ couple attributed to reduction of $\text{Co}(\text{III}) \rightarrow \text{Co}(\text{II})$ and $\text{Co}(\text{II}) \rightarrow \text{Co}(\text{I})$ respectively [31].

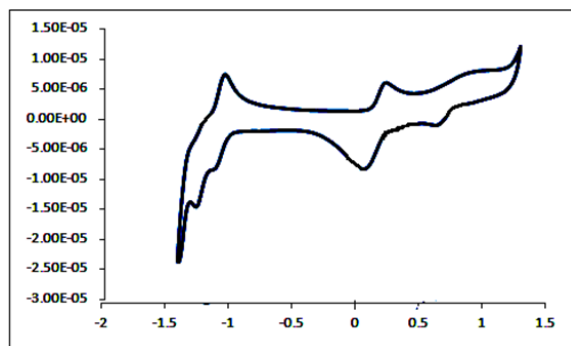
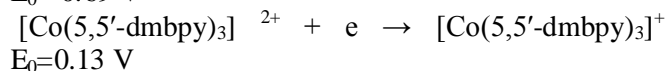
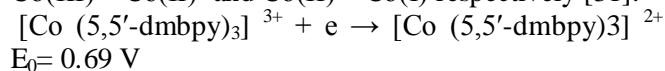


Figure 5. Cyclic voltammogram of (1) in CH_3CN solution, 0.1 M TBAH as a supporting electrolyte

Experimental

Chemicals and instrumentation:

All chemicals and solvents were reagent grade or better, obtained from either Merck or Aldrich and used without further purification. Infrared spectra (4000-250 cm^{-1}) of solid samples were taken as a 1% dispersion

in KBr pellets using a Shimadzu-470 spectrometer. NMR spectra were recorded on a Bruker AC-300 for ^1H at 300.13 MHz and for ^{13}C at 75.45 MHz in CD_3OH solution. Electronic absorption spectra in methanol solution was obtained on a Cary Bio 300 spectrometer. Cyclic voltammograms were recorded using a SAMA500. Melting points are uncorrected and was obtained on an Electrothermal type 9100 melting point apparatus. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer.

X-ray crystallographic analysis:

The X-ray diffraction measurements were made on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation graphite monochromator, $\lambda = 0.71073$. For $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ (1), an orange crystal with dimensions of $0.4 \times 0.13 \times 0.04$ mm was mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection was obtained by least-squares refinement of the diffraction data from 10231 unique reflections. Data was collected at a temperature 298(2) K to a maximum 2θ value of 58.66° in a series of ω scans in 1° oscillations and integrated using the CCD area detector software package. The structure of 1 was solved by SHELXTL ver. 5.1 [32]. A summary of the crystal data, experimental details and refinement results is given in Table 1.

Preparation of $[\text{Co}(5,5'\text{-dmbpy})_3]\text{Cl}_3 \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ (1):

To methanolic solution (20 ml) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48 g, 2 mmol) was added 5,5'-dimethylbipyridine (0.37 g, 2 mmol) dissolved in 20 mL methanol and the resulting solution was stirred at $55\text{-}60^\circ\text{C}$ for 2h. The orange solid product was collected by suction filtration, washed with acetone then air dried. The product dissolved mixture of $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}$ and was left to evaporate slowly at room temperature. After 7 days, yellow plate crystals was isolated. (yield: 69.7%; m.p. $> 300^\circ$; IR (KBr, cm^{-1}): 3031w ($\nu(\text{CH})$), 1608m, 1575w, 1476s, 1386m, 1294w, 1313w, 1231m, 1162m, 1042s, 993w, 840s, 731m, 650m, 569w, 420s, 292s ($\nu(\text{Co}-\text{N})$). Anal. Calc.: C, 57.35; H, 5.41; N, 12.33. Found: C, 57.31; H, 5.38; N, 12.15%.

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