Structural Aspects of Diaquotetrakis(imidazole)cobalt(II) Chloride

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A pink coloured cobalt(II) complex *viz*., $[Co(Imi)_4(H_2O)_2]Cl_2$ was prepared by mixing cobalt(II) chloride with imidazole in 1:4 molar ratio in acetone. The complex was characterized by UV, IR, TG-DTA and single crystal XRD studies. The EPR spectrum of the complex proved its paramagnetic nature which was further analyzed by magnetic susceptibility studies. Susceptibility measurements showed the presence of three unpaired electrons accounting for the high spin nature of the complex.

Key Words: Imidazole, EPR, Magnetic susceptibility, Cobalt(II) complexes.

INTRODUCTION

Cobalt complexes have been widely studied. Cobalt atom, depending on its coordinating environment, exhibits +2 or +3 oxidation states. Magnetic studies are generally helpful in exploring the spin nature of the complexes and consequently their oxidation states. Cobalt(II) forms complexes of both octahedral and tetrahedral geometries[1,2]. Octahedral complexes are common with halides, pseudo halides and O-donors[3]. The interaction of cobalt(II) and cobalt(III) with ligands containing oxygen and nitrogen donor atoms have been studied thoroughly[4]. Cobalt(II) adducts are found be excellent catalysts[5,6]. Imidazole and its derivatives play a key role in pharmacology[7,8]. Hence, an attempt was made to bind cobalt(II) with imidazole and study its structural and magnetic behaviour.

EXPERIMENTAL

The complex was prepared by mixing cobalt(II) chloride hexahydrate with imidazole in 1:4 molar ratio in acetone. The mixture was refluxed, with stirring, for *ca.* 6 h. The resulting purple coloured complex was filtered and dried in vacuum desiccator. The complex was grown into moderately bigger size crystals by slow evaporation method in methanol. The complex was characterized by FABMS (CDRI, Lucknow), thermal analysis, UV-visible, IR, EPR and magnetic studies. The UV-visible spectrum was recorded on LAMBDA-25 spectrophotometer in ethanol using matched quartz cells of path length 1 cm, IR spectrum in KBr pellet on Perkin-Elmer IR Spectrum-1 spectrophotometer. The thermograms (TG/ DTA) were recorded on Perkin Elmer Model Pyris Diamond at a heating rate of 10 °C min^{-1} with argon gas purged at the rate of

12 L h^{-1}. EPR measurements of the complex was done at CLRI with EMX-80 EPR spectrometer operating at X band with 100 KHz field modulation. Recordings at 77 K were done using a cold finger Dewar got from Wilmad Company. The magnetic susceptibility study of the complex was done using 300 Series Lewis Coil Force Magnetometer, George Associate, Berkeley, IISC Bangalore. The X -ray diffraction studies were carried out using Bruker Axs kappa Apex II single crystal X-ray diffractometer equipped with graphite mono chromated MoK_α ($\lambda = 0.7107$ Å) radiation and CCD detector, at SAIF, IIT, Madras, Chennai-36.

RESULTS AND DISCUSSION

Electronic spectrum: The electronic spectrum of the complex showed an high intense absorption band at 220 nm ($\varepsilon_{max} = 15,000$-30,00 M^{-1} cm^{-1}) and moderately intense band around 240 nm, ($\varepsilon_{max} = 35,000$-50,000 M^{-1} cm^{-1}), which may be attributed to π-π* transition of imidazole. A shoulder at 350 nm ($\varepsilon_{max} = 1500$-3600 M^{-1} cm^{-1}) may be due to the ligand to metal charge transfer (LMCT) transition[9].

IR spectrum: In the IR spectrum of the complex, the C-N stretching was observed around 1300 cm^{-1} and the Co-N stretching at 540 cm^{-1}. The C=N stretching was shifted to higher frequency compared to the other cobalt complexes in the same environment. There was only a minimum shift in frequency for the N-H (3250 cm^{-1}) stretching vibration of the complex. The O-H stretching, due to the axial water molecule, was shifted to higher frequency (3125 cm^{-1})[10].

Mass spectrum: The mass spectrum of the complex showed molecular ion peak at z = 438.The fragmentation pattern was further confirmed by thermal analysis.

Thermal analysis: The thermal study of the complex (Fig. 1) reveals that the axial water molecules dissociate first at 180 ºC followed by the dissociation of the imidazole units. The imidazole ligand in the complex undergo a continuous decomposition from 220 ºC onwards. The residual entity was found to be stable upto 450 ºC, thereafter it decompose to leave Co_2O_3 as the final residue[11].
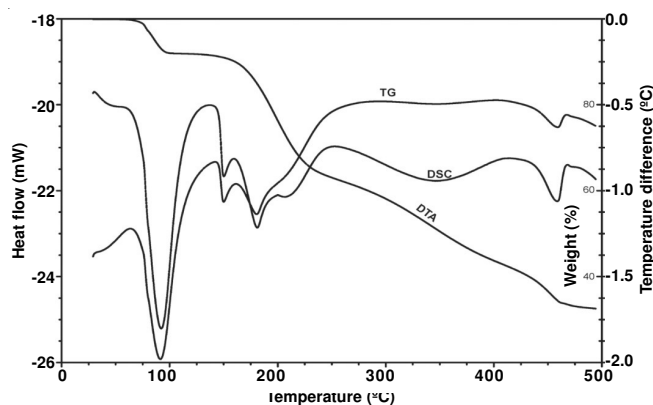

Fig. 1. Thermogram of $[Co(Imi)_4(H_2O)_2]Cl_2$

EPR spectrum: The cobalt complex with four imidazole ligands forms a tetragonally distorted square planar system while the two water molecules form an axially elongated set of ligands. The EPR spectrum of the complex (Fig. 2) gave two signals, one strong signal with a g = 4.177 and a weak signal at g = 2.039. Normally, S = 3/2 systems with strong tetragonal distortion give an EPR signal at $g_\perp$ 4 (strong line) and a weak line at $g_\perp$ 2[12,13].
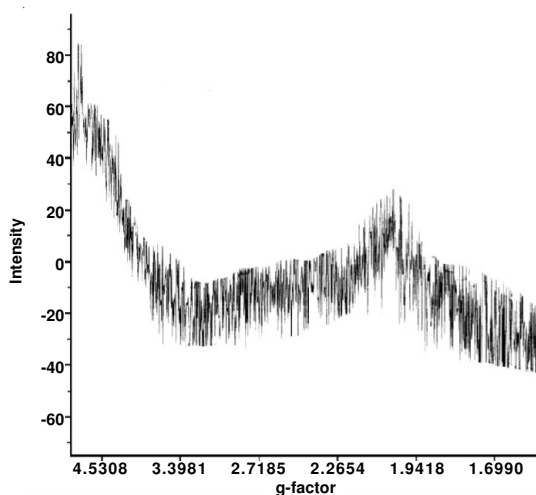

Fig. 2. EPR spectrum of $[Co(Imi)_4(H_2O)_2]Cl_2$

Magnetic susceptibility studies: Magnetic susceptibility measurement of a paramagnetic substance is the measure of number of unpaired electrons in it. The diamagnetic corrections were made by using Pascal's constants. Applying this value molar susceptibility ($\aleph^1$ M) for the complex using the appropriate equations (for solid state and solution) was calculated[14,15]. Finally using the curies equation magnetic moment (µ) of the compound was calculated. Cobalt(II) complexes possessing d^7 configuration exhibit three unpaired electron paramagnetism that corresponds to high spin complexes. Temperature

dependence of the molar magnetic susceptibilities in the temperature range of 2-300 K revealed that the magnetic interactions between the cobalt(II) ions are weak.

The magnetic moment calculated at room temperature for the complex under study is 3.8 BM. This value vary from the previously reported[16] experimental values in the range 4.70-5.20 BM for high spin octahedral cobalt complexes which may be attributed to the interactive response of the complex in the magnetic field. The magnetic moment studies revealed the presence of three unpaired electrons and consequently the high spin nature of the complex[17,18]. The same complex ion with a different counter ion was reported to be octahedral with low spin nature possessing one unpaired electron.

Crystal structure of $[Co(Imi)_4(H_2O)_2]Cl_2$: The complex crystallizes in monoclinic system with a space group $C_{2/c}$. The asymmetric unit contains half molecule and there are 4 complex molecules present per unit cell. The ORTEP representation of the complex with the atom numbering scheme is presented in Fig. 3. Atoms are represented as 50 % probability ellipsoids. Similarly, Fig. 4 gives packing of the molecules in the unit cell.
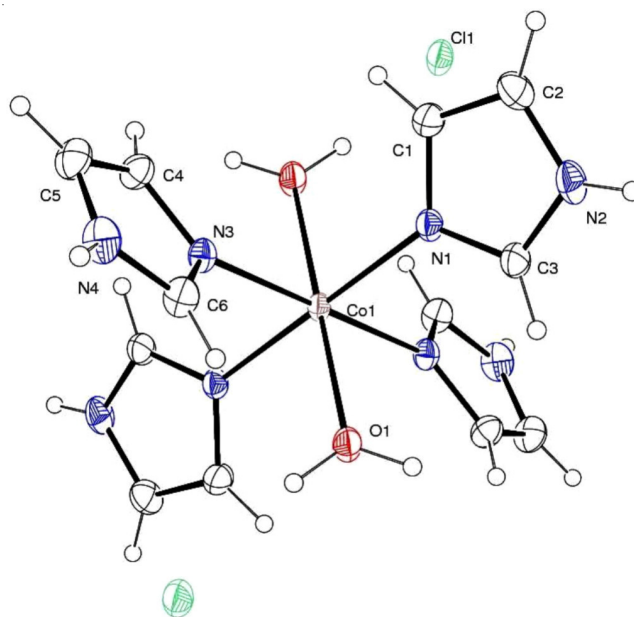

Fig. 3. ORTEP of $[Co(Imi)_4(H_2O)_2]Cl_2$ asymmetric half only labeled
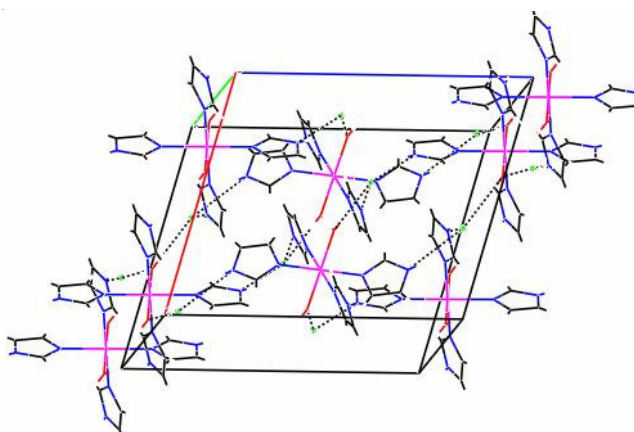

Fig. 4. Packing of $[Co(Imi)_4(H_2O)_2]Cl_2$ dotted lines indicate hydrogen bonds

The complex possesses a slightly distorted octahedral geometry with four nitrogen atoms of the imidazole ligand forming the equatorial network. The bite angles of the imidazole ligands, N(1)#1Co(1)N(3)#, N(1)-Co(1)-N(3)#1 are 88.55(3)° and 91.45(3)°. The water molecules in the axial positions are perpendicular to the plane containing the imidazole ligand.

The crystal parameters are presented in Table-1. The axial plane containing aqua ligand has an angle of O(1)-Co(1)-O(1)#1 is 180.00. The chloride ion exhibits N-H---Cl and O-H---Cl hydrogen bonded interaction with imidazole and aqua ligands, respectively[19] (Table-2). The crystal structure of the complex with a slightly different orientation was reported by Furenlid *et al.*[20].

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT OF [Co(Imi)$_4$(H$_2$O)$_2$]Cl$_2$

Empirical formula	C$_{12}$H$_{20}$Cl$_2$CoN$_8$O$_2$
Formula weight	438.19
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C$_{2/c}$
Unit cell dimensions	a = 12.3756(3) Å; α = 900
	b = 10.9792(3) Å; β = 107.6450(10)°
	c = 14.2856(4) Å; γ = 90°.
Volume	1849.72(9) A^3
Z, Calculated density	4, 1.573 mg/m^3
Absorption coefficient	1.241 mm^{-1}
F(000)	900
Crystal size	0.25 × 0.20 × 0.15 mm
Theta range for data collection	2.53-36.14°
Limiting indices	-20⇐h⇐20, -16⇐k⇐17, -16⇐l⇐23
Reflections collected/ unique	14150/4234 [R$_{(int)}$ = 0.0260]
Completeness to theta =	25.00, 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8357 and 0.7467
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	4234/3/131
Goodness-of-fit on F^2	1.028
Final R indices [I>2σ(I)]	R1 = 0.0313, wR2 = 0.0777
R indices (all data)	R1 = 0.0418, wR2 = 0.0829
Largest diff. peak and hole	0.292 and -0.538 e A^{-3}

TABLE-2
HYDROGEN BONDS [A AND DEG.] [Co(Imi)$_4$(H$_2$O)$_2$]Cl$_2$

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)H(1B)...Cl(1)#1	0.897(9)	2.239(10)	3.1244(8)	169.0(14)
O(1)H(1A)...Cl(1)#2	0.904(9)	2.236(10)	3.1284(8)	169.0(16)
N(4)H(4A)...Cl(1)#3	0.84(2)	2.48(2)	3.2943(11)	163(2)
N(2)H(2A)...Cl(1)#4	0.851(18)	2.433(18)	3.2307(11)	156.5(16)

Conclusion

The single crystal XRD data shows the +2 oxidation state of the complex. The EPR and the magnetic susceptibility study further confirm the high spin nature of the complex.

REFERENCES

1. A.D. Kulkarni, S.A. Patil and P.S. Badami, *J. Sulfur Chem.*, **30**, 145 (2009).
2. X. Lin, J. Tao, R.-B. Huang and L.-S. Zheng, *Inorg. Chem. Commnun.*, **12**, 154 (2009).
3. A. Ciccarese, D.A. Clemente, A. Marzotto and G. Valle, *J. Crystallogr. Spectrosc. Res.*, **23**, 223 (1993).
4. A.T. Ansari and K. Subramani, *Asian J. Chem.*, **20**, 4425 (2008).
5. B.L. Vallee and R.J.P. Williams, *Chem. Br.*, **4**, 397 (1968).
6. D. Dolphin and A.W. Johnson, *J. Chem. Soc.*, **16**, 2174 (1965).
7. S.W. Fox, *Chem. Rev.*, **32**, 47 (1943).
8. A.R. Katritzky and C.W. Rees, Comprehensive Heterocyclic Chemistry, Pergamon Press: England, Vol. 5, p. 469 (1984).
9. C. Carol, C.F. Peter and J.M. Thomas, *Inorg. Chem.*, **45**, 7059 (2006).
10. W.A. Baker Jr. and M.B. Patrick, *J. Am. Chem. Soc.*, **88**, 1314 (1966).
11. N. Adhikari, *Asian J. Chem.*, **20**, 6606 (2008).
12. V.I. Muravev, *Russ. J. Coord. Chem.*, **31**, 609 (2005).
13. S. Chandra and K. Gupta, *Transition Met. Chem.*, **27**, 196 (2002).
14. L.N. Mulay, in eds.: A. Weissberger and B.W. Rossiter, Techniques of Chemistry, Wiley-Interscience, New York, Vol. 4, p. 431 (1972).
15. R.E. Hoffman, *J. Magn. Reson.*, **163**, 325 (2003).
16. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elservier Publishing Co. London (1968).
17. R.C. Stoufer, D.H. Busch and W.B. Hadley, *J. Am. Chem. Soc.*, **83**, 3732 (1961).
18. J. Zhang, Y. Lin, W. Liu and S. Huang, *Polyhedron*, **11**, 419 (1992).
19. D. Piotr, P. Barbara and G. Tadeusz, *J. Mol. Struc.*, **654**, 111 (2003).
20. L.R. Furenlid, D.G. Van Derveer and R.H. Felton, *Acta Cryst.*, **C42**, 806 (1986).