Surface, morphology and X-ray diffraction studies of Co (II) complexes of pyrazole ligands

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Abstract. Pyrazole based complexes of the cobalt (II) Bis-(diethyl 4-amino-1-(P-nitrophenyl) 1H-pyrazole-3,5dicarboxylate) [Co (D4A1(P-N)1HP35D)] and cobalt (II) Bis-(diethyl 4-amino-1-(3-chlorophenyl) 1H-pyrazole-3,5dicarboxylate) [Co (D4A1(3-Cl)1HP35D)] were synthesized by chemical root method and characterized by different method viz. X-ray diffraction, Fourier transform infrared spectroscopy and Transmission electron microscopy studies. All these studies were in good agreement with the synthesized complexes.
Keywords: Cobalt (II), XRD, FTIR, TEM.

Introduction

Pyrazole-based complexes are important because of their attractive physicochemical, chemical, structural and biological properties [1-3]. The pyrazole derivatives have been widely used in many fields for their excellent biological properties like pharmaceutical evaluation, antitumor agents and chemical communication. Pyrazole derivatives exhibit important biological properties such as antitumour, anticoagulant, antihyperglycemic, analgesic, anti-inflammatory, anti-pyretic,antibacterial, hypoglycemic and sedative–hypnotic activity [4-6]. These derivatives have attracted significant attention because of the application in drug development.

2. Experimental details

Pertinent aniline derivatives were dissolving in distilled water and kept at freezing temperature in the refrigerator .To this, an aqueous solution of sodium nitrite in of distilled water was added with continuous stirring keeping the temperature in the vicinity of 0- 5°C. Meanwhile, in another beaker ethyl cyanoacetate, sodium acetate and distilled water were taken and cooled in an ice bath. The reaction mixture was kept for overnight period, filtered through suction, washed with water and dried in vacuum. Fine crystals of the compound were obtained, which were recrystallized from ethyl alcohol. To a solution of couple product, Triethylamine and Ethyl Bromo Acetate were added. The reaction mixture was the refluxed, and then poured onto ice-cold water and HCl, the solid product so formed was filtered off and crystallized from ethanol. The complex preparation is now mentioned here. The mixture of ethanolic solution of Ligand and $CoCl_2$ was refluxed for 1 hour. After reflux Solvent was evaporated to afford fine crystal of Bis-(diethyl 4-amino-1-(R-phenyl) 1H-pyrazole-3,5dicarboxylate) Co (II) chloride complexes. This was recrystallized from ethanol [7].
The XRD measurements were carried out with Cu Kα (λ=1.5406A˚) radiation using a Rigaku powder diffractometer equipped with a rotating anode scanning (0.01 step in 2θ) over the angular range 0° to 60° using Ni-filtered at room temperature having voltage 40 KV and current 100 mA.

At Room temperature Fourier transform infrared (FTIR) spectra were recorded in the frequency range of 4000–400 cm−1 employing KBr disc technique using Bruker Germany make Jasco FTIR-300 spectrometer model vertex-70.

TEM images has been obtained on Tecnai (300 kV), FEI, Holland. It has a LaB6 electron gun, which can be operated between 50 to 300 kV.

3. Results and discussion

3.1 X-ray Diffraction (XRD):

The diffraction patterns have been successfully indexed and the values of different parameters are shown in table. X-ray powder diffraction patterns of the complexes are indicative of their crystalline nature and had a monoclinic crystal lattice. In some cases deviation between the calculated and observed d values was nearly equal to one, which indicates that the synthesized complexes are multiphase complexes [8]. Inter-planar d spacing and unit cell volume of the synthesized complexes were calculated by the formulae:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left[\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right]$$

And volume is given by V = abc sinβ [8].

As our synthesized samples are complexes, and due to the lone pair of electrons,distortion occurs due to which it undergoes lower symmetry, yet the characteristic and prominent peaks of complexes and the crystal system have been identified, which are equal and in some cases nearly match the standard diffraction card JCPDS also.

The X-ray diffraction patterns of the complexes are shown in figure 1 and the different results are reported in table 1 and 2.

Table 1. The experimental data and the calculated results for powder X-ray diffraction pattern of Co (D4A1(P-N)1HP35D). JCPDS CARD NO. (100754 - 441628)

2 theta (in degree)	d-spacing (in Å) observed	d-spacing (in Å) calculated	Relative Intensity (%)	h	k	l
6.33	13.97	14.04	43.77	1	0	0
8.58	10.29	10.00	57.34	0	0	1
12.54	7.05	7.02	62.22	2	0	0
16.16	4.48	5.01	50.45	1	1	1
18.29	4.84	5.01	47.87	1	1	1
20.85	4.25	4.01	27.31	0	1	2
27.44	3.24	3.24	57.08	0	2	0
31.85	2.80	2.86	100	-2	1	3
33.09	2.70	2.54	41.53	3	2	1

Lattice parameters and angle calculated are: a = 14.1 nm, b = 6.48 nm, c = 10.29 nm, β = 94.32∘ Unit cell volume of the complex: 936.12 × 10−8 cm3.

Table 2: The experimental and the calculated results for powder X ray diffraction pattern
of the Co (D4A1(3-Cl)1HP35D), JCPDS CARD NO. (100754 - 441628)

2 theta (in degree)	d-spacing (in Å) observed	d-spacing (in Å) calculated	Relative intensity (%)	h	k	l
6.22	14.20	14.14	44.35	1	0	0
11.18	7.90	7.73	38.59	-1	0	1
16.08	4.50	4.87	100	1	1	1
18.42	4.81	4.71	79.19	3	0	0
20.8	4.26	3.60	49.64	-1	1	2
26.68	3.33	3.33	92.33	0	2	0
30.5	2.92	2.90	47.88	0	0	3
32.98	2.71	2.55	51.57	3	2	1
37.3	2.40	2.07	37.46	-1	1	4

Lattice parameters and angle calculated are: a = 14.20 nm, b = 6.66 nm, c = 8.76 nm, β = 95.07◦.Unit cell volume of the complex: 824.20 × 10−8 cm3.
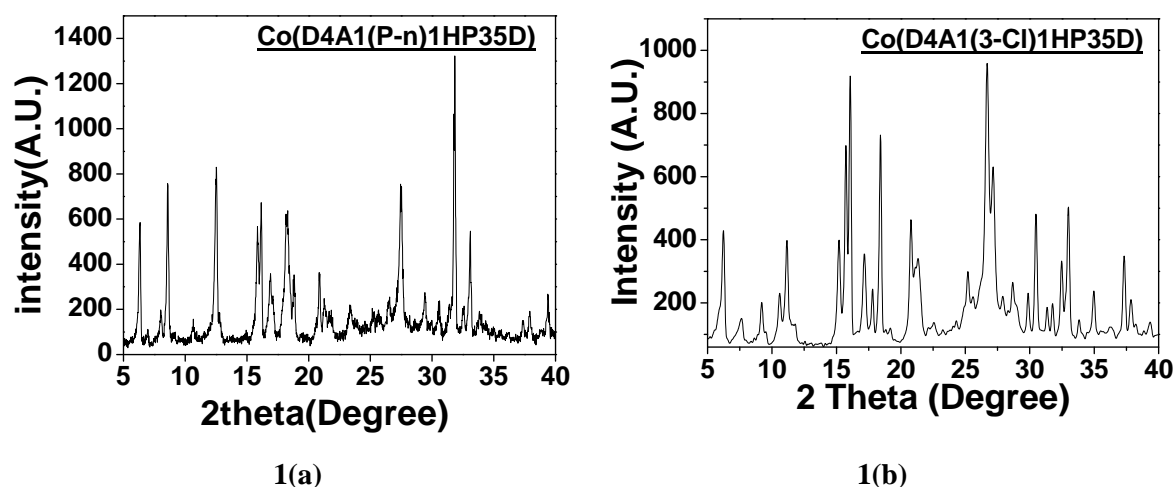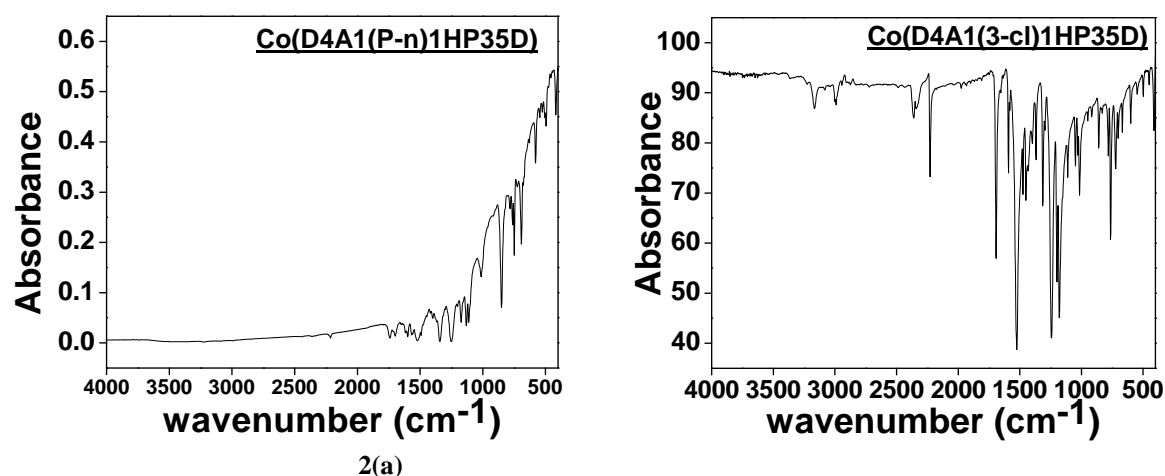

Figure 1: X-ray Diffraction pattern of Co(D4A1(P-N)1HP35D) **1(a)** and Co (D4A1(3-Cl)1HP35D) 1**(b)**

3.2 *Fourier Transform Infrafred Spectroscopy (FTIR)*
The IR spectra of samples were taken in the range between 4000–400 cm^{-1} in KBr pellets. IR spectrums of some of the synthesized samples are depicted in Figure. The IR spectrum of the samples shows that a band in the region from 3217-3230 cm^{-1} is due to –NH stretching. Similarly a strong band in the region between 1740 -1685 cm^{-1} is attributed to the carbonyl –C=O stretching. The other bands in the region between 1240- 1260 cm^{-1} (C-O), 1532-1516 cm^{-1} (-NO$_2$), 785-775 cm^{-1}(-Cl) further confirm the samples structure.[9]
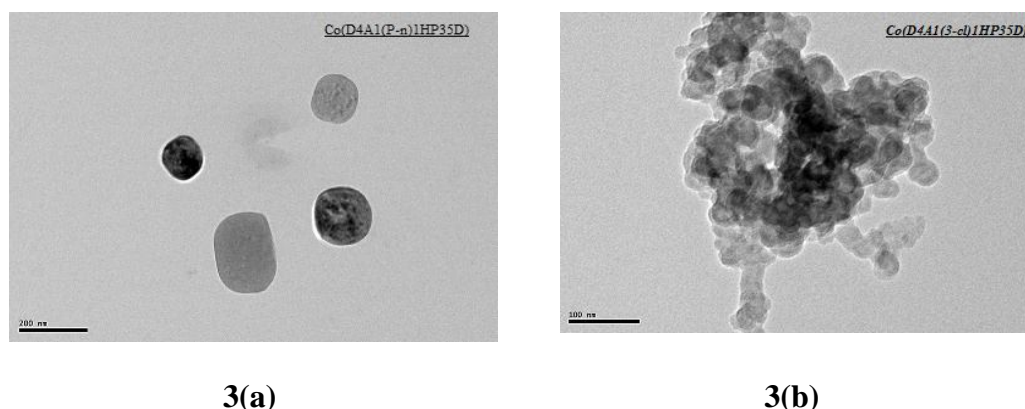
2(a)

2(b)

Figure 2: FTIR spectra of Co(D4A1(P-N)1HP35D) **2(a)** and Co (D4A1(3-Cl)1HP35D) **2(b)**

3.3 Transmission Electron Microscopy (TEM)

The values of particle size of the samples calculated from TEM images for Co (D4A1(3-Cl)1HP35D) is 43.59 nm and Co(D4A1(P-N)1HP35D) 149.55 nm respectively. TEM images are shown in figures 3.

3(a)   3(b)

Figure 3: TEM images Co(D4A1(P-N)1HP35D) **3(a)** and Co (D4A1(3-Cl)1HP35D) **3(b)**

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