Synthesis and X-ray diffraction study of some nickel(II) complexes of urea and thiourea

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Abstract: XRD of four biologically important nickel(II) complexes having urea and thiourea as primary ligands and sulphate and nitrate as secondary ligands have been studied using Bruker D8 Advance diffractometer at IUC, Indore. The synthesized metal complexes were characterized by XRD measurements in order to elucidate their geometry. The data obtained has been preceded using XRD data analysis program Origin 6.0 Professional. From the experimental measurements, various parameters, e.g., particle size, lattice parameter have been estimated. Particle size for Ni-urea complexes is found in the range of 4.23-9.01 nm while for Ni-thiourea complexes its range is 0.26-9.76 nm. Lattice parameter for all these complexes is found in the range of 7.47-8.06 Å. The XRD analysis revealed the crystalline nature of all the complexes.

1. Introduction:
Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Urea is used for preparing formaldehyde-Urea resin (plastics)[1], barbiturates [2], and fertilizers [3-6]. Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of medicine [7-9]. Recently, urea is used for the manufacture of hydrazine in which urea is treated with alkaline sodium hypochlorite.[2] Urea is used in active dying [10] which has an effect on the formation and cleavage of covalent bond between the reactive dye and cellulose. Complexes of urea with some metal ions are used as fertilizers [11-14].
Recently, urea represents not only an important molecule in biology but also an important raw material in chemical industry [15]. The synthesis and characterization of urea based complexes have been studied and reported [2].

Thioureas have a long history of being used as a ligand in coordination chemistry and to coordinate with a metal via sulfur and oxygen atoms [16]. These hard and soft donor atoms provide a multitude of bonding possibilities [17]. The complexing capacity of thiourea has been reported in several articles [18,19]. The biological activity of complexes with thiourea has been successfully screened for various biological processes. On the other hand some thiourea and their transition metal complexes are also known to exhibit a wide range of biological activities including antiviral, antibacterial, antifungal, anticancer [20-22] antitubercular, antithyroidal, herbicidal and insecticidal activities [23] and as agrochemicals [24]. Recent advances in organic Nonlinear Optical (NLO) materials have involved a large revival of interest on account of their widespread potential importance such as their high nonlinearity, high flexibility in terms of molecular structure, high optical damage threshold [25,26]. The origin of nonlinearity in NLO material like thiourea arises due to the presence of delocalized π electrons system, connecting donor and acceptor groups and responsible for enhancing their asymmetric polarizability [27].

We reported here XRD analysis of some selected complexes of nickel(II) carboxylates with urea and thiourea.

2. Experimental

All chemicals used in this study were obtained from Qualikem Company. Urea and thiourea were received from Rankem Company. All chemicals were of analytical grade and they were used without purification. The complexes were prepared using the following general method as reported earlier [2]. Benzoic acid (5g, 0.0206 moles) was dissolved in 50ml of 2M NaOH and stirred with a magnetic stirrer. Ni(II) salt (1.6g, 0.0100 moles) dissolved in 10ml of water was added dropwise to the solution and stirred for 30 minutes. The resulting solution was filtered through a Buchner funnel using a suction pump and washed with ethanol. The precipitate was light green in colour (0.32g). 30ml of water was added to the precipitate formed (0.32g) and it was stirred using a magnetic stirrer. Urea or thiourea (0.0628g, 0.0010 moles) was diluted with 10ml of water and added to the solution being stirred dropwisely. The resulting solution was stirred for 30 minutes and filtered to dryness through suction. The precipitate (complex) was weighed and dried over KOH. The colour of the complex is light green.

The sample is irradiated with a beam of monochromatic x-rays over a variable incident angle range. The X-ray were produced using a sealed tube and the wavelength of X-ray as 0.154nm (Cu Kα-lamda). The X-ray were detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector). Interaction with atoms in the sample results in diffracted x-rays when the Bragg equation is satisfied. The X-ray were detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector). X-ray diffraction pattern have been recorded by Bruker D8 advance diffractometer at IUC, Indore. All chemicals are prepared by chemical root method.

3. Results and discussion:

XRD patterns are shown in ‘figures 3(a) and 3(b)’ for Ni-urea complexes and in ‘figures 4(a) and 4(b)’ for Ni-thiourea complexes. All the samples are characterized at room temperature by X-ray diffraction using Cu Kα radiation. The diffraction pattern of complexes are recorded between 20 ranging from 10° to 80°. The particle size of the samples is estimated using the Scherrer’s formula. According to Scherrer’s equation, the particle size is given by $t = 0.9 \lambda / B \cos \theta$, where $t$ is the crystal thickness (in nm), $B$ is half width (in radians), $\theta$ is the Bragg angle and $\lambda$ is the wavelength. The particle size corresponding to each diffraction maxima are determined from the measurement of the half width of the diffraction peak. Lattice parameter for simple cubic crystal structure is determined by $a^2 = \lambda^2(h^2+k^2+l^2) / 4\sin^2 \theta$. The value of Lattice
The particle size was found to be within the range 4.23-9.01 nm for nickel-urea complexes and 0.26–9.76 nm for nickel-thiourea complexes.

| Complexes                          | Lattice parameter (Å) | Particle size (nm) |
|------------------------------------|-----------------------|--------------------|
| [Ni(CON\(_2\)H\(_4\))\(_6\)]SO\(_4\).H\(_2\)O | 7.58                  | 4.23               |
| [Ni(CON\(_2\)H\(_4\))\(_6\)]NO\(_3\).H\(_2\)O  | 7.47                  | 9.01               |
| [Ni(CSN\(_2\)H\(_4\))\(_6\)]SO\(_4\).H\(_2\)O  | 8.06                  | 9.76               |
| [Ni(CSN\(_2\)H\(_4\))\(_6\)]NO\(_3\).H\(_2\)O  | 7.83                  | 0.26               |

Figures 3(a) and 3(b): XRD spectra of Ni-urea complexes

Figures 4(c) and 4(d): XRD spectra of Ni–thiourea complexes
4. Conclusion
The XRD pattern is indicative of their crystalline in nature which is confirmed by 5 main peaks positioned. The X-ray analysis reveals that the sample is cubic in phase as seen from the presence of extra peaks in XRD pattern. All the peaks match with the soft wear JCPDF.

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