



Synthesis, characterization and optical absorption studies of Na[Fe(CN)₄(C₃H₄N₂)NO]2H₂O crystals

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MS received 11 August 2020; accepted 23 November 2020

Abstract. Crystals of Na[Fe(CN)₄(C₃H₄N₂)NO]2H₂O (SNP-d) have been prepared by photochemical route using sodium nitroprusside (SNP) as precursor complex. The crystals were subjected to various characterization techniques such as energy dispersive X-ray analysis, Fourier transform infrared, UV–visible spectroscopy and X-ray diffraction. From X-ray diffraction, it has been observed that SNP-d belongs to orthorhombic crystal system with primitive lattice. Crystallite size has been found to be 79.2 nm. Molecular structure of SNP-d depicts its non-centrosymmetric nature. As observed from UV–visible spectroscopy, SNP-d crystals form a double bandgap material, between which transitions have been found to be direct allowed. High value of refractive index and low value of reflectance, as obtained from Reddy, Anjaneyulu and Fresnel's equations, indicate transparency of material to visible radiation. This is clearly justified from UV–visible spectra as the wavelength cutoff is around 300 nm.

Keywords. SNP; photo-substitution; imidazole; non-linear optics.

1. Introduction

The photo-substitution reactions in transition metal complexes provide a better and easy route for the synthesis of many desirable metal complexes. The desirability of metal complexes lies in the use of opted ligands [1,2]. This provides the prepared metal complexes with novel and improved properties. For instance, the photo-substitution reactions of octacyanometallates of Mo(IV), W(IV) and Fe(III) with many ligands of choice like 2,2' bipyridyl, ethylenediamine, 8-hydroxyquinoline, pyrazine, ethanolamine, imidazole, etc. have been reported to reflect many improved and novel properties [3,4]. In addition to octacyanometallates, photo-substituted products obtained from sodium nitroprusside (SNP) with ligands like 2,2' bipyridyl, hexamine, EDTA have been found to exhibit enhanced catalytic activities, EMI shielding and sensor applications, respectively, in polymer matrices [5–7]. Similarly, photo-products obtained from [Co(NH₃)₅Cl]Cl₂ with ligands such as hexamine and EDTA showed essence in improving electronic properties [8,9]. However, limited literature is available with regard to optical properties of the photo-substituted products.

Keeping the above facts into consideration, this work is based on the synthesis of a derivative of SNP with imidazole (C₃H₄N₂) as an exchanging ligand via a photochemical route. This is then subjected to optical absorption studies to analyse its suitability for some particular application.

2. Synthesis of SNP-d

Imidazole derivative of SNP abbreviated as SNP-d has been prepared by taking an equimolar mixture of SNP and imidazole ligand (C₃H₄N₂) in 1:1 ratio (30 ml each). The mixture was then irradiated for about 25 min using Osram UV-Visible photolamp [8]. During irradiation, a change in the colour of mixture has been observed from red to brownish yellow, which indicated the occurrence of photo-substitution process.



After concentration and cooling, brownish yellow coloured crystals separated out, which were thoroughly washed with water and dried to constant yield. The crystals,

thus, formed has been subjected to different spectroscopic characterization techniques.

3. Results and discussion

3.1 Elemental analysis

The chemical formula for the prepared SNP-d has been obtained with the help of elemental analysis and energy dispersive X-ray absorption spectroscopy (EDAX). Based on the observed percentage of elements from CHN analysis (C: 25.57%, H: 2.02% and N: 29.62%) and EDAX (figure 1), the empirical formula assigned to the photosynthesized SNP-d was found to be $\text{Na}[\text{Fe}(\text{CN})_4(\text{C}_3\text{H}_4\text{N}_2)\text{NO}]2\text{H}_2\text{O}$. The calculated percentage of elements as obtained from the above formula was found to be 26.3% (C), 2.5% (H), 30.7% (N), 17.62% (Fe), 7.26% (Na) and 15.15% (O). This is in close agreement with the observed values and the above formula thus obtained for the synthesized SNP-d is rigorous. This clearly shows the replacement of one CN ligand by an imidazole ligand upon irradiation.

3.2 Fourier transform infrared spectroscopy

SNP exhibits vibrational frequencies at (2178, 2143, 2083), 1945, 666 and 433–417 cm^{-1} , which have been assigned to the characteristic stretching frequencies of –CN (axial and equatorial ligands), –NO, Fe–NO and Fe–CN, respectively [6]. Imidazole on the other hand depicts vibrational modes at around 3656, 1558–1434, 1100–1019 and (816, 730) cm^{-1} . These have been attributed to the N–H stretching vibrations, –C=N and C=C stretching vibrations in the aromatic ring, C–H in-plane bending vibration and C–H out-of-plane bending of aromatic H-atoms, respectively [10]. In SNP-d, there are vibrational modes from 3200 to 3600 cm^{-1} due to –OH stretch of the water of crystallization and the broadness is owing to the hydrogen bonding. The sharper ones in it have been assigned to the –NH stretching vibrations. Peak at 2144 cm^{-1} is due to the –CN stretching mode (figure 2).

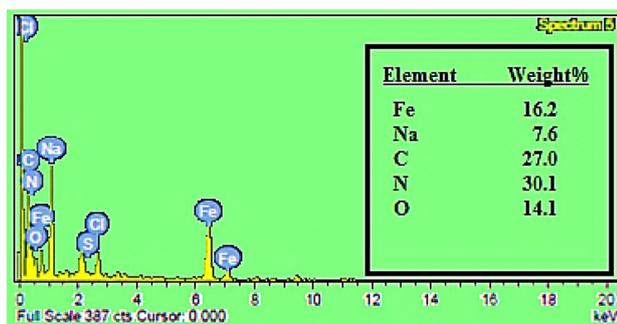


Figure 1. EDAX of the photosynthesized SNP-d.

However, the absence of other –CN vibrational modes at 2178 and 2083 cm^{-1} clearly reflects the loss of a –CN ligand and subsequently causes its replacement with an imidazole ligand, as the vibrational frequencies due to imidazole do exhibit their appearance in SNP-d. Peaks due to –C=N and C=C vibrations of imidazole ring occur in SNP-d at 1429–1639 cm^{-1} , due to C–H in-plane bending at 1065 cm^{-1} and due to C–H out-of-plane bending at (834, 750 cm^{-1}). –CN replacement is justified as the vibrational mode for the –NO ligand and Fe–NO stretch is clear at 1940 and 662 cm^{-1} , respectively. The replacement of –CN ligand by a comparatively more bulky imidazole ligand can be the reason for the observed shifts in the vibrational frequencies of SNP-d. Peak due to Fe–CN is observed at 428 cm^{-1} . This is in direct agreement with the empirical formula assigned to the synthesized SNP-d, and the proposed structure is shown in scheme 1, with Fe lying at the intersection of bonds.

3.3 X-ray diffraction

Figure 3 shows the X-ray diffraction pattern of the prepared SNP-d. Clearly, there are well-defined and sharp peaks with very low full-width at half-maximum indicating its crystalline nature. These sharp peaks were indexed using powder-X software to analyse the crystal structure of SNP-d. While indexing, SNP-d has been found to belong to an orthorhombic crystal system with a primitive (P) lattice. The lattice parameters were found to be as follows: $a = 13.87250$, $b = 10.88460$, $c = 7.28852$ and $\alpha = \beta = \gamma = 90^\circ$. The crystallite size has been obtained as 79.2 nm. As far as the structure of SNP-d (scheme 1) is concerned, complex lacks centre of inversion, hence is non-centrosymmetric in nature which is an essential conduction for the material to be analysed for SHG.

3.4 Optical absorption studies and optical constants

UV–visible spectra of SNP before and after irradiation with imidazole ($\text{C}_3\text{H}_4\text{N}_2$) using Osram UV-Visible photolamp is shown in figure 4a. Before irradiation, spectra exhibits one prominent peak at about 277 nm and an absorption edge which are attributed to the $d \rightarrow d^*$ ($6e \rightarrow 5a_1$) transition and $M \rightarrow L$ ($2b_2 \rightarrow 8e$) charge transfer band, respectively. After irradiating the mixture for half an hour, there occurs the decrease in the intensity of $d \rightarrow d^*$ peak along with a bathochromic shift of around 5 nm, as the peak now stands at 282 nm. Moreover, a change in the absorption edge also takes place as it reflects a shoulder also. Such a bathochromic shift in $d \rightarrow d^*$ peak can be attributed to the replacement of a stronger field ligand ($\text{CN}^- \pi$ acceptor) by a weaker field imidazole ligand in the metal complex owing to photolabilization. It is pertinent to mention here that it is the CN^- ligand that is replaced instead of nitrosyl (NO) as is

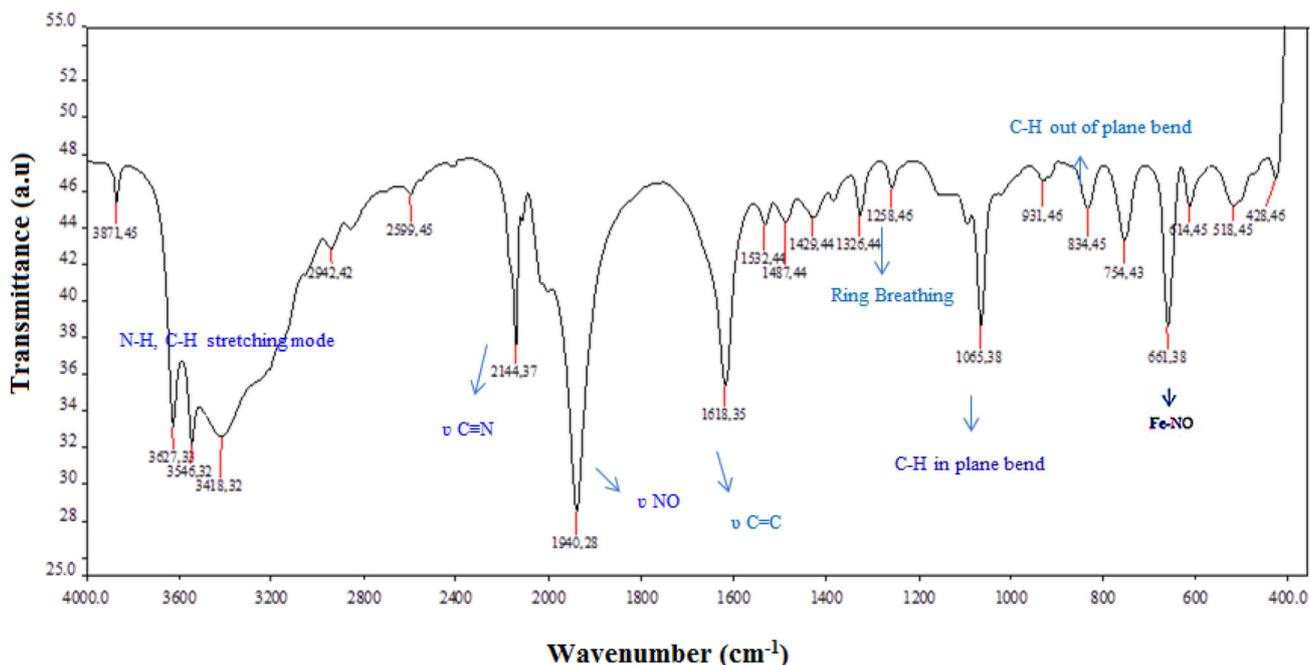
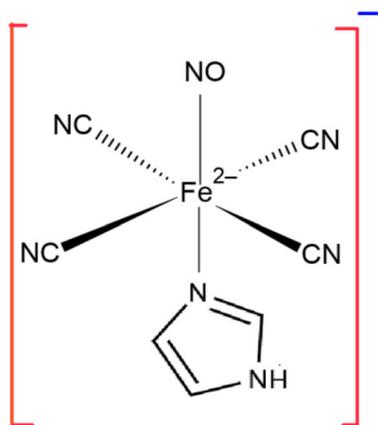


Figure 2. Fourier transform infrared spectra of SNP-d.



Scheme 1. Proposed structure of SNP-d.

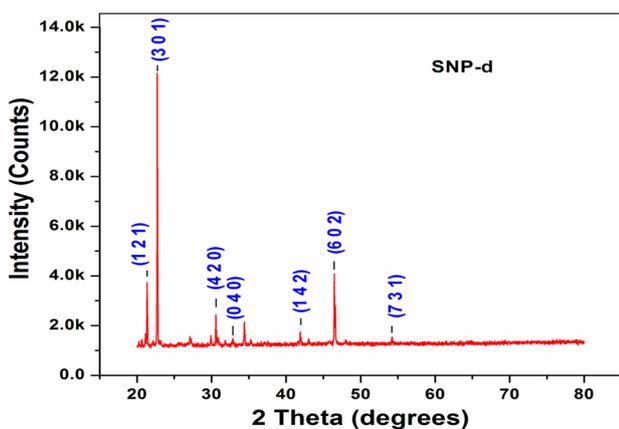


Figure 3. X-ray diffraction pattern of SNP-d.

justified by Fourier transform infrared. This leads to an increased electron density on Fe, as back donation is prevented owing to CN⁻ replacement, which in turn cause changes in the absorption edge of spectrum. This clearly justifies the formation of a photosynthesized SNP-d. Inset of figure 4a shows the absorption in IR region that clearly reflect almost 100% transparency.

Figure 4b shows the optical bandgap determination, which is essential to assess the electrical and optoelectronic properties of materials. This has been carried out using Tauc relationship:

$$\alpha hv = A(hv - E_g)^n,$$

where α is the absorption coefficient, A a constant which depends on the transition probability and n an index that describes an electron transition process and is related to the density of states. It assumes the values 1/2, 2, 3/2 and 3 depending upon the nature of electronic transition responsible for the absorption. For $n = 1/2, 2, 3/2$ and 3, the transitions are said to be direct allowed, indirect allowed, forbidden direct transition and forbidden indirect transition, respectively [7]. From the plot of $(\alpha hv)^n$ against hv , a linear fit has been obtained for $n = 1/2$, indicating the transition to be direct allowed. By extrapolating $(\alpha hv)^n = 0$, bandgaps for the SNP/imidazole mixture before and after irradiation have been found to be 4.05 and 4.7, and 3.93 and 4.5, respectively. Decrease in bandgap after irradiation also reflects the substitution by a weaker field imidazole ligand. High value of bandgap clearly reveals the dielectric nature of SNP-d.

Furthermore, spectra show a wide transparency window in the entire visible region even over 1000 nm (IR region), which is an essential condition for the material to exhibit

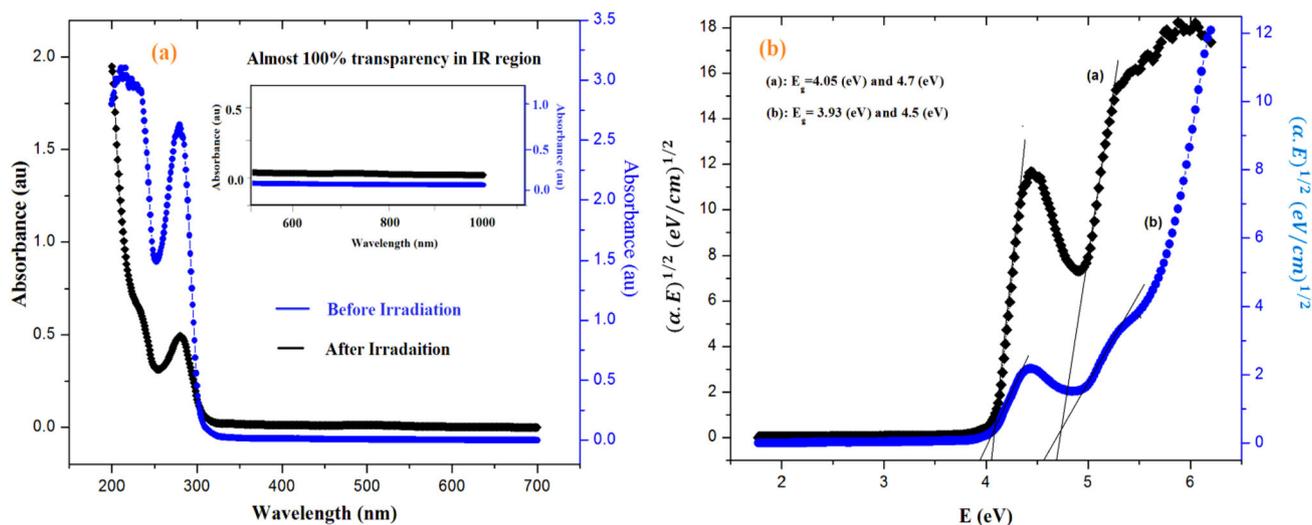


Figure 4. UV-visible spectra of SNP/imidazole mixture (a) before and after irradiation; inset shows transparency in IR region, the bandgap calculation using Tauc relationship (b).

non-linear optical properties. Wavelength cutoff in both the cases is around 300 nm, suggesting its suitability for second harmonic generation (SHG) of the 1064 nm Nd: YAG laser radiation. Refractive index (μ) for SNP-d was calculated, relating bandgap with refractive index [11], while Fresnel equation helps us to determine reflectance (R) from refractive index [12], i.e.,

$$E_g e^\mu = 36.3$$

$$R = \left(\frac{(\mu - 1)}{(\mu + 1)} \right)^2$$

The values obtained were found to be 2.23 (μ) and 0.14 (R), respectively. High value of refractive index and low value of reflectance indicate more transparency of material to visible radiation [6].

4. Conclusion

Photochemical route has been found to be a convenient route for the synthesis of some desirable metal complexes. By such a photochemical route, SNP-d has been prepared which is then confirmed by various characterization techniques. SNP-d belongs to orthorhombic crystal system and has been arranged in a primitive lattice. Owing to its

non-centrosymmetric nature and wide transparency in entire visible region, the material can be expected to show non-linear optical properties.

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