Turk J Chem
29 (2005) , 589 – 595.

Spectroscopic and Luminescence Properties of an Isonicotinic Acid

Nurdoğan CAN[1]*, Ahmet ATAÇ[1], Fehmi BARDAK[1],
Şebnem Esen SÖZERLİ CAN[2]
[1] *Physics Department, Faculty of Arts and Sciences, Celal Bayar University,*
Muradiye-Manisa-TURKEY
e-mail: nurdogan.can@bayar.edu.tr
[2] *Chemistry Department, Faculty of Arts and Sciences, Celal Bayar University,*
Muradiye-Manisa-TURKEY

Received 20.11.2004

An isonicotinic acid N-oxide Zn(II) compound was characterized on the basis of elemental analysis. FTIR spectra of the compound and free isonicotinic acid N-oxide (INO) were recorded in the range 4000–400 cm^{-1}. Cathodoluminescence (CL) spectra from the Zn(INO)$_2$ complex were recorded. The luminescence data were interpreted in terms of the emission band at 470 nm. The green luminescence ($\sim$ 470 nm) arises from Zn^{2+} transition $^4T_1(^4G) \rightarrow {}^6A_1$ (^6S). It shows a weak vibronic structure, and short lifetimes less than 150 μs. The lifetime and intensity of the signal are temperature dependent, and the parameters are reported for the 470 nm emission line.

Key Words: Isonicotinic acid N-oxide, Zn(II) complex, IR, Luminescence.

Introduction

Lanthanide complexes of 3 isomers of pyridine carboxylic acid, namely nicotinic acid, isonicotinic acid and picolinic acid, have been extensively investigated[1−3]. Pyridine carboxylic acid N-oxides have an oxygen atom in place of the nitrogen donor site, but studies on ligand behavior toward lanthanides are limited, as so far only one dimeric lanthanium complex of 6-methylpicolinic acid N-oxide (6-mepicno) has been structurally examined[4−5]. N-oxide functionalization of nicotinic acid and isonicotinic acid should increase the flexibility of the resulting ligands in addition to enhancing their capacities for coordination and/or hydrogen bonding. Therefore, their lanthanide complexes are expected to exhibit different characteristics compared with corresponding lanthanide nicotinates and isonicotinates. Zinc plays a key role in liver enzyme function and synthesis. In fact, zinc is so important in the body that enzymes like 17 beta-hydroxy-steroid (17BHSD) become completely nonfunctional in its absence. In addition to requiring zinc, 17BHSD also requires sufficient niacine-based coenzymes for it to become biologically active. The specific niacine (3-pyridine carboxylic

---

[*] Corresponding author

acid amide, commonly known as vitamin B_3) based coenzymes require adenine dinucleotide (NAD)[6-8] or nicotinamide adenine dinucleotide phosphate (NADP).

Luminescence is light emission when energy is deposited into a material. The means of delivering energy can be divided into 2 broad types: stimulation, where the magnitude of the incident energy is less than that of the emitted light, and excitation, when the incident energy is greater. Forms of stimulation include heat (thermoluminescence, TL) and laser light (optically stimulated luminescence, OSL); excitation includes electron beam irradiation (cathodoluminescence, CL) or X-irradiation (radioluminescence, RL). Whatever the nature of the incident energy, the energy cascades associated with the subsequent luminescence are often similar, and hence different forms of excitation/stimulation explore subtly different aspects of luminescence center within materials.

The spectral measurement of the complex indicates luminescence emission. Here we report the spectroscopic and the luminescence property of the title complex. To our knowledge, this is the first such work using luminescence in this complex.

Experimental

Synthesis

All chemicals were reagent grade (Aldrich) and were used without further purification. One millimole (0.136 g) of $ZnBr_2$ was dissolved in absolute hot ethanol (~10 mL). Two millimoles (0.278 g) of isonicotinic acid N-oxide was dissolved in hot ethanol and added to the solution. After the workup described above single crystals were formed at the interface and at the bottom of the solution at 20 °C.

Elemental analysis

The prepared complex was analyzed for C, H and N by a CHN (LECO, CHN-600) with the following results (found (%))/(calculated (%)):$Zn(INO)_2$ C: 42.02/41.91, H: 2.88/2.90, N: 8.06/8.10.

Instrumental measurements

The infrared spectra (KBr discs) of the free ligand and compound $Zn(INO)_2$ were recorded in the range 4000-400 cm^{-1} on a Mattson 1000 FTIR spectrometer calibrated using polystrene film.

Cathodoluminescence time resolved spectroscopy was performed on a apparatus designed and built at the University of Sussex, UK[9]. The acceleration potential was 10 kV and the current was 20 nA, corresponding to an incident power density of 0.8 $mWcm^{-2}$. The primary electron beam was pulsed using a Thandor TG501 5 MHz function generator as a sine function with a frequency of 90 Hz, except for the lifetime measurement. The CL response was gated using an EgandG Ortholoc-SC 9505 2-phase lock-in amplifier. Spectra were measured in the temperature range 40 to 300 K using an $f/4$ scanning monochromator and a cooled red-sensitive photomultiplier tube.

Results and Discussion

Isonicotinic acid N-oxide gives 2 donor sites: a carboxyl group and pyridine N-oxide (N=O). This kind of ligand the bonding take place through the carboxyl oxygen or N=O. If we assume that the carboxyl group

(-COOH) has a single mass point all the molecules under consideration would belong to the C_{2v} point group. This simplified model leads to 30 normal vibrations, of which 21 are planar and 9 non-planar. In addition to these 30-ring vibrations there would be 6 vibrations due to the substutient carboxyl group. The vibrations cannot be classified as to their symmetry with respect to the molecular plane as the carboxyl group makes the molecular non-planar.

The vibrational assignments for the isonicotinamide and nicotinamide were performed and structural characterization and spectroscopic features of their metal halogen and tetracyanonickelate complexes were investigated in previous works[10−14]. For isonicotinic acid a few bands were assigned experimentally[15] and theoretically[16]. The proposed assignments of INO for a few bands were carried out by comparing these results. These are consistent with previous results[17−18].

The present work is a continuation of our previously report[17] on the luminescence properties, structural characterization and spectral properties of $[Mn(H_2O)_6][O\text{-}C_6H_4NO_2]_2$ compound.

The vibrational wavenumbers and proposed assignments and those taken from the literature[18] for a few bands of INO and $Zn(INO)_2$ complex are listed in the Table and the infrared spectra are given in Figures 1 and 2. In the 1800-800 cm^{-1} region INO exhibits characteristic $\nu_{(C=O)}$ (1720-1708 cm^{-1}), $\nu_{(C-O)}$(1439 cm^{-1}), $\nu_{(N-O)}$ (1290 cm^{-1}) and $\delta_{(N-O)}$(867-852 cm^{-1}) absorbtions[19]. In this study significant absorbtion bands in the infrared spectrum of INO are observed at 3450 cm^{-1}, 1705 – 1437 cm^{-1}, 1287 cm^{-1} and 868-851 cm^{-1} and assigned $\nu_{(OH)}$, $\nu_{(C=O)} - \nu_{(C-O)}$, $\nu_{(N-O)}$ and $\delta_{(N-O)}$, respectively.

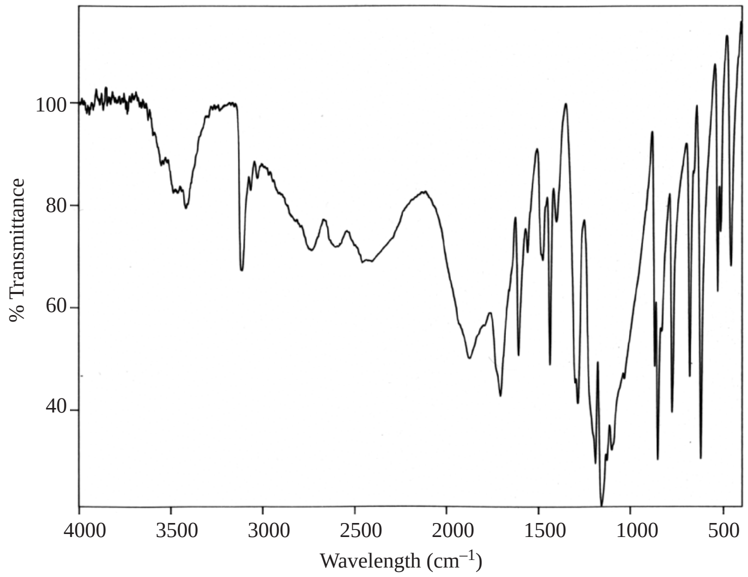

Figure 1. The IR spectra of free isonicotinic acid N-oxide (in KBr).

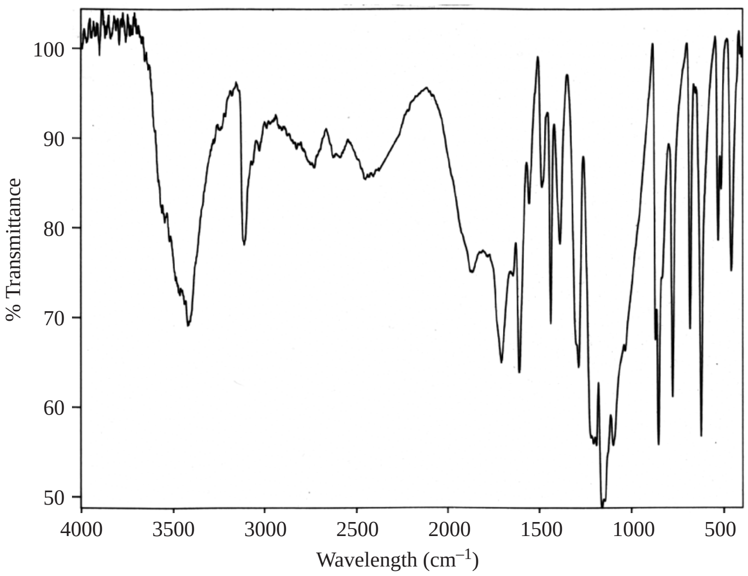

Figure 2. The IR spectra of Zn(INO)$_2$ complex (in KBr).

Table 1. Vibrational wavenumbers (cm^{-1}) for a few bands of free INO and Zn(INO)$_2$ complex with those taken from Ref [18].

Free INO In this study	Ref [18]	Zn(INO)$_2$ In this study	Assignments
3450	3490	3476	$\nu_{(\mathrm{OH})}$
1705	1708	1698	$\nu_{(\mathrm{C=O})}$
1437	1439	1435	$\nu_{(\mathrm{C-O})}$
1287	1290	1288	$\nu_{(\mathrm{N-O})}$
868-851	867-852	872-854	$\delta_{(\mathrm{N-O})}$

In some bivalent metal complexes of isonicotinic acid N-oxide a significant negative shift of the carboxyl frequency takes place because of the coordination through the carboxyl oxygen[20]. In the present work the carboxyl frequency observed at 1705 cm$^{-1}\nu_{(C=O)}$ and 1437 cm$^{-1}\nu_{(C-O)}$ of uncoordinated INO undergo a slight negative shift in the Zn(INO)$_2$ complex.

Coordination through N-O oxygen is demonstrated by shifts of $\nu_{(N-O)}$ mode to lower frequency and small δ_{N-O} shifts[21−22]. However, in this study the $\nu_{(N-O)}$ 1287 cm^{-1} and $\delta_{(N-O)}$ (868-851 cm^{-1}) bands of uncoordinated INO undergo a slight positive shift in the complex formation. This indicates that the N-O donor site of the INO is not involved in the coordination of the Zn(INO)$_2$ complex.

These frequency analyses conclusively indicate that the coordination of INO takes place via the carboxyl oxygen to the metal ion Zn as in Can et al.[17].

The computer system used in the CL analysis records only the magnitude of the emission and not the sign and, therefore, the data are always a positive number. For cosine dependence, the data are always a positive number. For cosine dependence, data extend from positive to negative values, and hence we converted sections of the data to negative values where they pass through zero.ϕ_c is related to the decay lifetime (τ) of the emission and frequency of the pulsed primary beam (f) for isolated luminescence bands by the expression $\tan\phi_c = 2\pi f\tau$. Unfortunately, in the present CL system the maximum chopping frequency is only 100 kHz and this is slow compared with the luminescence lifetimes being considered. Nevertheless, attempts to estimate the lifetime of about 470 nm emission gives a value near 150 μs at room temperature, and near 173 μs at 40 K.

The immediate initial effects of the Zn(INO)$_2$ complex are seen in Figure 3 for CL measurements. At a modulation frequency of just 90 Hz (i.e. effectively continuous ~ dc excitation) the main signal peaks near 470 nm in all cases, but there are poorly resolved additional features in the tails of the central region. Although at first sight the data obtained at higher modulation frequency are similar, Figure 3 reveals that quite different component bands are dominant. There apparent peak movements and changes in the relative intensities of the component bands. Rather than view just the original wavelength signals, the data should be transformed into energy plots.

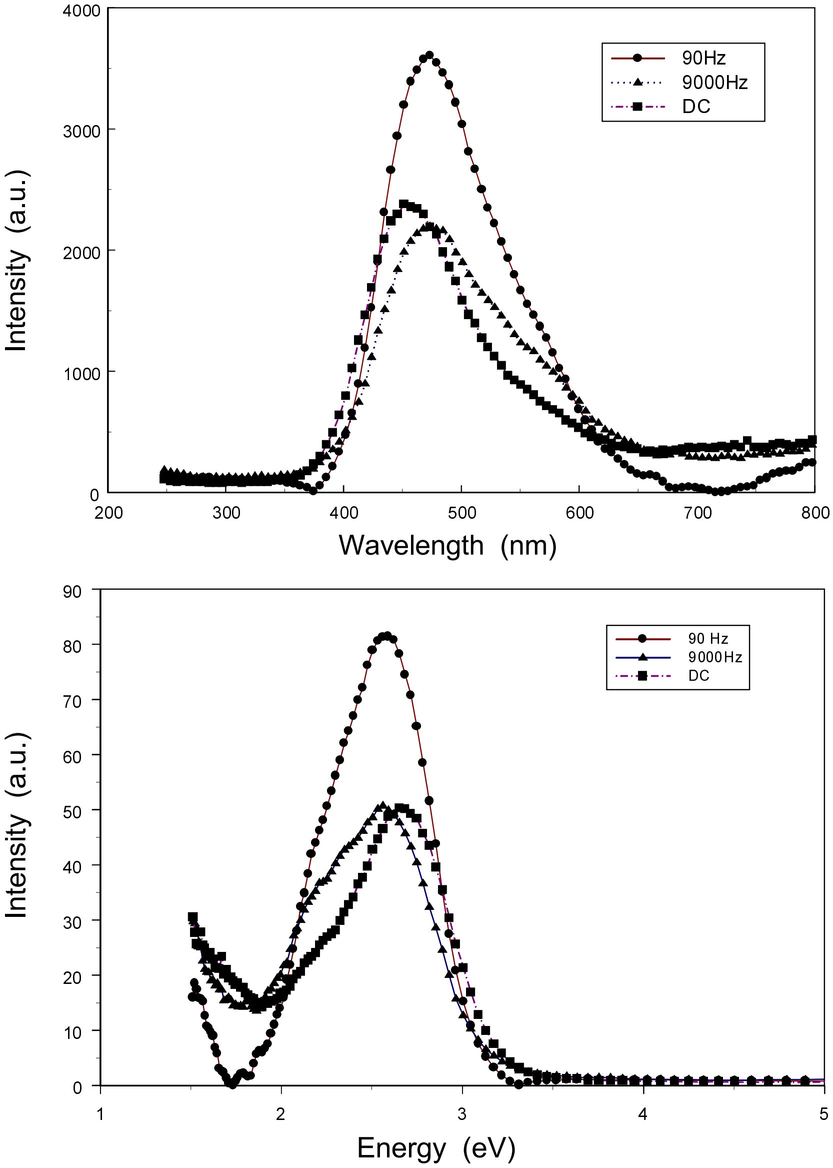

Figure 3. Cathodoluminescence of Zn(INO)$_2$ complex recorded at room temperature, at 90 and 9000 Hz. The top diagram is redorded in wavelength dispersed data, and the bottom diagram shows how the diagram transforms into energy plots.

Note that there have been room temperature structural characterizations of related rare earth complexes with nicotinic and isonicotinic acid N-oxides[23] that included data of erbium and europium site distortions from the changes of the photoluminescence and absorption of the rare earth line spectra. In our recent work, CL spectra from Mn complex were examined and it was shown that the green luminescence resulted from Mn^{2+} transition[17]. The luminescence data were quite limited, but their inherent sensitivity to their site symmetry implies they could be additional probes in temperature dependent explorations.

In this study, time resolved luminescence spectra of a $Zn(INO)_2$ complex were measured. The following features can be deducted from the cathodoluminescence emission spectra. One type of emission spectrum is observed and the decay of the green luminescence is nonexponentional. Analysis of the luminescence spectra shows that Zn^{2+} occupies a similar and well defined octahedral site. The Zn^{2+}-water interactions are weak and affect the lifetime of the green band.

Acknowledgments

We would like to thank Prof. P.D. Townsend (University of Sussex, UK) for kindly allowing us to use his equipment in Sussex.

References

1 P. Starynowicz, **Acta Crystallograpy C 47**, 294 (1991).

2 J.-F. Ma, Z.-S. Jin and J.-Z. Ni, **Polyhedron 14,** 563 (1995).

3 J.-F. Ma, Z.-S. Jin and J.-Z. Ni, **Polyhedron 15,** 1797 (1996).

4 G.F. de Sa, F.R.G. e Silva and O.L.Malta, **J. Alloys Compounds 207**, 457 (1994).

5 L.Yan, J.-M Liu, X. Wang, R.-D Yang and F.-L. Song, **Polyhedron 14,** 3545 (1995).

6 J.W. Park and Y.H. Paik, **Bull. Korean Chem. Soc. 6**, 23 (1985).

7 Y. Miwa, T. Mizuno, K. Tsuchida and T. Taga, **Acta Crystallogr. B55**, 78 (1999).

8 P.A. Thibodeau and B. Paquette, **Free Radic. Biol. Med. 27,** 1367 (1999).

9 P.D. Townsend and A.P. Rowlands, **Cathodoluminescence in Geosciences,** pp 41-57, Springer, Berlin, Heidelberg New York, 2000.

10 Ş. Yurdakul and A. Ataç, **Spectroscopy Letters 37**, 33 (2004).

11 Ş. Yurdakul, A. Ataç, E. Şahin and S. İde, **Vibrational Spectroscopy 31,** 41 (2003).

12 S. Bayarı, A. Ataç and Ş. Yurdakul, **Journal of Molecular Structure 655**, 163 (2003).

13 E. Şahin and S. İde, A. Ataç and Ş.Yurdakul, **Journal of Molecular Structure 616**, 253 (2002).

14 S. İde and A. Ataç, Ş.Yurdakul, **Journal of Molecular Structure 605,** 103 (2002).

15 M.S. Afifi and A.A. Shabana, **Analysis 10**, 239 (1982).

16 P.Koczon, J.Cz. Dobrowolski , W.Lewandowski and A.P.Mazurek, **Journal of Molecular Structure 655,** 89 (2003).

17 N. Can, S.E. Sözerli Can, A. Ataç and F. Bardak, **Polyhedron 23,** 1109 (2004).

18 L.S. Gelfand,L.L. Pytlewski, A.N. Speca, C.M. Mikuski and N.M. Karayannis, **Journal of Inorganic Nuclear Chem. 42,** 209 (1980).

19 G. Costa and A. Pauluzzi, Univ. Studi Trieste, **Fac. Sci. Ist. Chim. Pubbl.** 12 (1956), **Chem.Abst. 4823b** (1957).

20 R.Palepu and M.M. Morrison, **Inorganica Chimica Acta** 36, l437 (1979).

21 L.C.Nathan and R.O. Ragsdale, **Inorganica Chimica Acta** 10, 177 (1974).

22 A.N.Speca , L.S.Gelfand L.L.Pytlewski, C.Owens and N.M.Karayannis, **Journal of Inorganic Nuclear. Chem. 39,** 537 (1977).

23 J-G. Mao, H-J. Zhang, J-Z. Ni, S-B. Wang and T.C.W. Mak, **Polyhedron 17,** 3999 (1998).