

HIGHLY POLARIZABLE METALLIC COMPLEXES WITH SOLVATOCHROMIC BEHAVIOR

Luminița CRĂCIUN¹, Ioana JITARU²

*This paper deals with the synthesis of new mixed ligand transition metal complexes of $[M^{II}(\text{diimine})(\text{dithiolate})]$ type (where $M^{II} = \text{Ni, Pd, Pt, Zn}$; diimine = 4,4'-dimethyl-2,2'-bipyridine (**dmbpy**), 4,4'-dicarboxy-2,2'-bipyridine (**dc bpy**) or 4,4'-dinitro-2,2'-bipyridine (**dn bpy**) and dithiol = 1,2 benzene dithiol (**H₂bdt**)). Complexes have been characterized by chemical analysis, electronic reflectance spectra, molecular electrical conductivities, FTIR spectra, magnetic measurements, stabilities in different solvents (CHCl_3 , CH_3CN , C_6H_6 and $\text{C}_6\text{H}_5\text{-CH}_3$). **Ni(dn bpy)(bdt)** complex has the longest absorption wavelength and the strongest solvatochromic shift of LLCT band among the studied complexes, concluding that an electronic acceptor on the diimine ligand can greatly enhance nonlinear optical properties (the molecular first hyperpolarizability) of the complexes.*

Keywords: nonlinear optical properties, complex compounds, 2,2'-bipyridine.

1. Introduction

Materials that exhibit nonlinear optical (NLO) properties allow manipulation of the laser light beams fundamental properties and are hence of great technological importance in areas such as optical data processing and storage.

Within the research field of molecular NLO materials, increasing attention is being paid to metal complexes of *d*-transition elements which offer possibilities for combination of NLO effects with other molecular electronic properties.

Coordinated metal centers often engage in π -bonding, both with organic ligands and with each other, meaning that they can be involved in various strongly allowed ICT processes like metal-to-ligand CT (MLCT), ligand-to-metal CT (LMCT), or metal-metal/ intervalence CT (MM/IVCT) [1-10]. They can also participate in ligand to ligand charge transfer (LLCT) with less or more directional $\pi \rightarrow \pi^*$ electronic excitation processes [5,7,9-15]. The existence of such last transitions is often associated with strong solvatochromic behavior and large molecular NLO responses (the molecules with solvatochromic shifts often have

¹ Assistant, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania; luminita.craciun71@yahoo.com

² Prof., Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania

nonlinear optical properties - a sizable value of molecular first hyperpolarizability, β) [16-18].

To day the research in the field of nonlinear optics has concentrated on the design of new inorganic chromophores and their incorporation in suitable materials.

A well known example of complexes with pronounced solvatochromism are [Ni(diimine)(dithiolate)] complexes type for which the large solvatochromic shifts are usually associated with considerable directional changes of electron densities within a molecule (the charge shifting from the dithiolate to diimine ligand) [19-22].

Variation in molecular design of the complexes, through changes in the metal ion nature, diimine or dithiol ligands can be used to affect changes in the CT to diimine absorption band frequency and hence β value [23-27].

This paper deals with the synthesis of new mixed ligand transition metal complexes of [M(diimine)(dithiolate)] type (where M = Ni, Pd, Pt, Zn); diimine = 4,4'-dimethyl-2,2' bipyridine (**dmbpy**), 4,4'-dicarboxy-2,2' bipyridine (**dcbpy**) or 4,4'-dinitro-2,2' bipyridine (**dnbpy**) and dithiol = 1,2 benzene dithiol (**H₂bdtd**)).

Complexes have been characterized by chemical analysis, electronic reflectance spectra, molecular electrical conductivities, FTIR spectra, magnetic measurements, stabilities in different solvents (CHCl₃, CH₃CN, C₆H₆ and C₆H₅-CH₃).

2. Experimental part

2.1. Materials and Equipment

All the chemical substances were of analytical grade and were provided by Merck and Sigma-Aldrich.

FTIR spectra were recorded on Bruker Tensor 27 apparatus, using KBr pellets technique.

UV-Vis reflectance spectra were recorded on an Able Jasco V560 spectrophotometer.

Electrical conductivities were measured with a Radelkis 101/2 Conductometer.

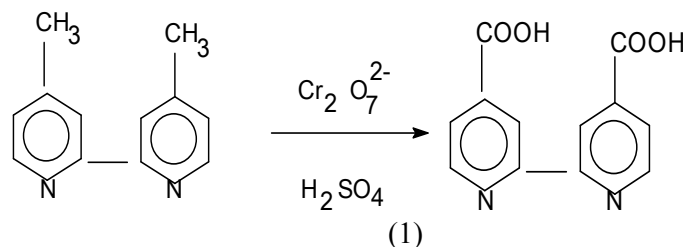
Magnetic measurements were performed on a Gouy balance.

2.2 Synthesis of diimine ligands

Synthesis of 4,4'-dicarboxy-2,2'-bipyridine (dcbpy)

To a solution of 3.14 g (9.7 mmol) of Na₂Cr₂O₇ in 10.6 ml of concentrated sulphuric acid was slowly added, under magnetic stirring, 0.8 g (4.3 mmol) of 4,4'-dimethyl 2,2'-bypiridine. The resultant orange slurry became dark green (the

Cr(VI) reduction to Cr(III)) after a while and reaction was complete after 30 min). The reaction mixture was then poured into 100 ml of cold water forming a light yellow precipitate. After filtration and drying, the solid was dissolved in an alkaline 10% NaOH aqueous solution followed by slow acidification (pH=2) with 10% aqueous HCl solution. This recrystallization afforded the desired compound free of Cr(III) ions. After a second filtration compound was dried under vacuum (P_2O_5 as drying agent) to provide a white solid (0.9 g, 85%) with m.p. $>300^\circ\text{C}$. Anal. Calcd. for $C_{12}H_8N_2O_4$: C, 59.01; N, 11.47; H, 3.28. Found: C, 58.87; N, 10.95; H, 3.12.

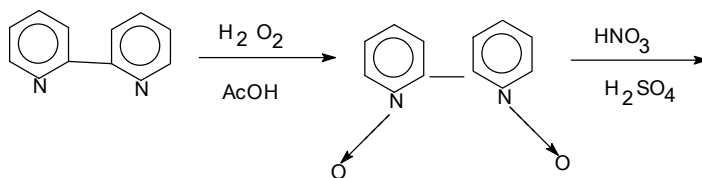


Synthesis of N,N'-dinitro-2,2'-bipyridine

Synthesis of N,N'-dinitro-2,2'-bipyridine was achieved in 3 stages:

(a) *Synthesis of N,N'-dioxide-2,2'-bipyridine*

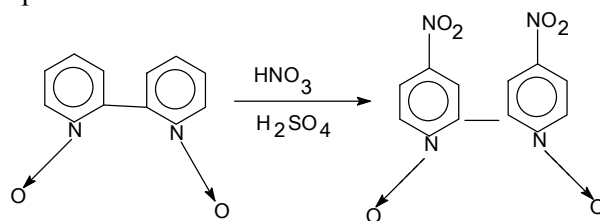
A solution formed from 10g (64mmol) 2,2'-bipyridine, 13 mL H_2O_2 30% and 75 mL glacial ethanoic acid was heated on a water bath at 80°C for 3 hours. Hydrogen peroxide (9 mL H_2O_2 30%) was added and heating continued for 4 hours. The resulted colourless solution was cooled at room temperature and was added slowly at 1L acetone when a white precipitate of N,N'-dioxide-2,2'-bipyridine was obtained. This precipitate was collected by filtration and dried in air (yield 85%). This product is commonly used as obtained from the above preparation, but recrystallisation from a large volume of ethanol gave transparent white plates, m.p. $312\text{--}315^\circ\text{C}$ (decomp.)



(b) *Synthesis of 4,4'-dinitro-2,2'-bipyridine N,N'-dioxide*

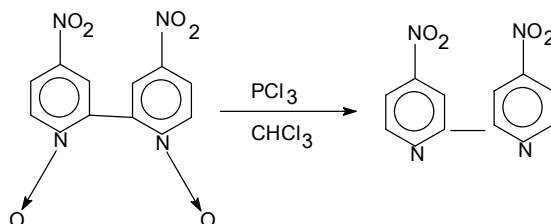
To a mixture of 2,2'-bipyridine N,N'-dioxide (5 g, 27 mmol) and oleum sulphuric acid (1:2 v/v, 25 mL) in an ice-water bath, nitric acid (fuming, 20 cm³) was slowly added. The mixture was heated up to 100°C for 6 hours with the reflux condenser fitted with a calcium chloride drying tube. After this time it was cooled to room temperature and cautiously poured onto 100 g ice-water (crushed ice, 50g) and water (50 mL) to give a yellow solid. This was collected by filtration,

washed with water and air dried to give 4,4'-dinitro 2,2'-bipyridine N,N'-dioxid (3.75 g, 49%) m. p. 272-275°C.



(c) *Synthesis of N,N'-dinitro-2,2'-bipyridine*

A suspension of 1.5 g (5.4 mmol) of 4,4'-dinitro 2,2'-bipyridine N,N'-dioxid in 23 ml of anhydrous chloroform was cooled to 0°C and 3 ml (34 mmol) of phosphorus trichloride was added. The mixture was heated at reflux over a water-bath for one hour, cooled to room temperature and poured into a mixture of ice and water. The resulting suspension was made alkaline with aqueous sodium hydroxide and 1.3 g of unchanged starting material recovered by filtration. The aqueous layer of the filtrate was extracted with several portions of fresh chloroform and discarded. The combined chloroform portions were evaporated to a crystalline residue (0.2 g, m.p. 182-185°C) which was recrystallized from 95% ethanol to yield 0.12 g of orange needles, m.p. 191.5-194.5°C. Repeated recrystallizations from the same solvent raised the melting point to 195-197°C. Anal. Calcd. for $C_{10}H_8N_4O_4$: C, 48.35; N, 22.11; H, 3.22. Found: C, 47.87; N, 21.95; H, 3.10.



Synthesis of [M(diimine)(bdt)] complexes

(where $M = Ni, Pd, Pt$; diimine = dmbpy, dcbpy, dnbpy $H_2bdt = 1,2$ benzenedihtiol)

A solution of diimine in dichloroethane was mixed with a methanolic solution of $NiCl_2 \cdot 6H_2O$, ($PdCl_2$ or $PtCl_2$) and H_2bdt (in $M(II) : diimine : H_2bdt = 1 : 1 : 1$ molar ratio) and was refluxed at 60°C for 3 hours. From the red-brown solution (for Ni(II)), yellow-orange (for Pd(II) or Pt(II)) that was initially obtained, it was separated at slowly evaporation of the solvents (room temperature) a dark blue compound (for Ni(II)), bright orange (for Pd(II)) or brown (for Pt(II)) that was filtered, washed with methanol and chloroform and then dried in vacuum on P_2O_5 .

White $[\text{Zn}(\text{dnbpy})(\text{tdt})]$ complex was obtained in the same conditions using $\text{Zn}(\text{CH}_3\text{COO})_2$.

3. Results and discussions

Molar electrical conductivity for all complexes in DMF solution established their non-electrolyte nature.

Electronic Reflectance Spectra and magnetic measurements

To better understand the electronic structures of the studied complex compounds, we have examined their absorption properties in solid state. The electronic spectra of the solid complexes and the assignments of each maximum are done in table 1.

At first glance the reflectance UV Vis spectra appear very similar to those of other $[\text{Ni}(\text{II})(\text{diimine})(\text{dithiol})]$ complexes. An intense, structured band maximizing near 250-300 nm has been assigned to the lowest diimine-centered spin-allowed $\pi\text{-}\pi^*$ transition. On the analogy of the electronic spectra (in 200-360 nm range) of the studied compounds, we conclude that all $\text{Ni}(\text{II})$ complexes have the same structure.

The absence of some absorption bands under $10\,000\text{ cm}^{-1}$ (over 1000 nm) indicates that the most probable structure of the all tetracoordinate complexes is square planar.

Table 1.

UV-Vis absorption bands of the studied complexes and their assignments

Complex	λ (nm)	Assignment
$[\text{Ni}(\text{dmbpy})(\text{bdt})]$ (1)	250 ; 370 470	Intraligand dmbpy, tdt; $d\text{-}d$ band ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Ni}(\text{dcbpy})(\text{bdt})]$ (2)	250 ; 370 485	Intraligand dcbpy, tdt; $d\text{-}d$ band ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Ni}(\text{dnbpy})(\text{bdt})]$ (3)	240 ; 380 520	Intraligand dnbpy, tdt; $d\text{-}d$ band ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Pd}(\text{dmbpy})(\text{bdt})]$ (4)	400	CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Pd}(\text{dcbpy})(\text{bdt})]$ (5)	410	CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Pd}(\text{dnbpy})(\text{bdt})]$ (6)	427	CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Pt}(\text{dmbpy})(\text{bdt})]$ (7)	465	CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Pt}(\text{dcbpy})(\text{bdt})]$ (8)	479	CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Pt}(\text{dnbpy})(\text{bdt})]$ (9)	500	CT $\text{L} \rightarrow \text{L}$ or $\text{M} \rightarrow \text{L}$
$[\text{Zn}(\text{dnbpy})(\text{bdt})]$ (10)	495	CT $\text{L} \rightarrow \text{L}$

dmbpy = 4,4' dimethyl-2,2' bipyridil; dcbpy = 4,4' dicarboxy-2,2' bipyridil; dnbpy = 4,4' dinitro-2,2' bipyridil; H_2 tdt = 1,2 -benzenedithiol

The low values of magnetic susceptibilities under that for the paramagnetic, octahedral species of Ni(II) (under 3.2 BM) sustain a possible spin equilibrium square planar (diamagnetic) \leftrightarrow octahedral (paramagnetic) that is probably present in crystalline lattices of the studied complexes.

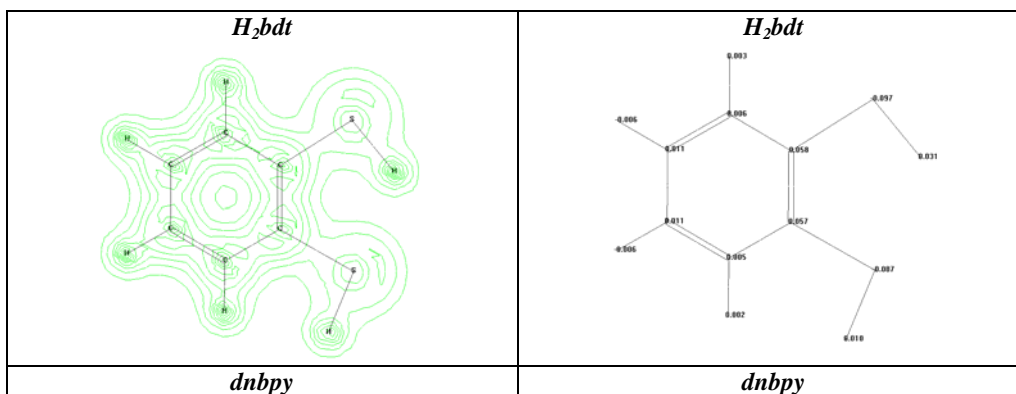
Considering that the obtained complexes are of the type [Ni(diimine)(dithiolate)] which contain two different ligands in which one is more easily reduced and the other one more easily oxidized, it is very probable that the band from the spectra of the complexes in visible range is not only a $d-d$ band but also a CT band (probably the CT band is overlapped over a $d-d$ one).

To support this idea and to assign the nature of CT band ($L \rightarrow M$; $M \rightarrow L$; $L \rightarrow L'$) we have also studied the spectrum of [Zn(dnbpy)(tdt)] complex.

Replacing Ni(II) ion with Zn(II) give a complex which absorbs in visible range (495 nm). This band is very probable of $\pi - \pi^*$ type (ligand-ligand band) because Zn(II) (d^{10}) does not absorb in visible range and MLCT or LMCT bands are also very little possible for Zn(II) (due to the Zn high redox potential).

The influence of the *nature of the metallic ion* and the nature of diimine (with electron-attractive or repulsive substituent group) on the position of the CT band can be also examined on the basis of the aspect of the electronic spectra of complexes.

An increasing of both the wavelength and the intensity of the charge transfer – to diimine absorption band in order Ni(II), Pt(II), Pd(II) complexes is observed. This trend in wavelength (table 1) follows the trend in the second ionization potentials of the metals ($E_i=1753$ for Ni, 1791 for Pt and 1870 for Pd). This observation strongly supports metal orbital involvement in the CT to diimine excited state



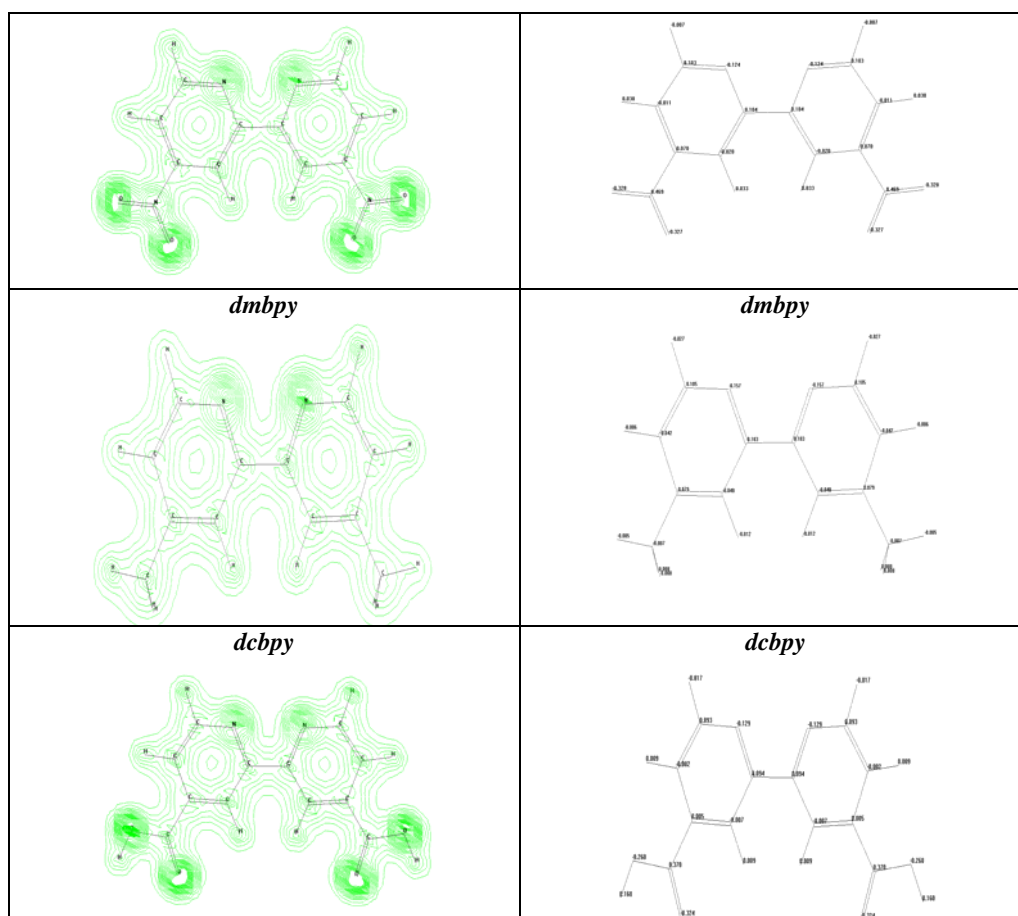


Fig.1. Electronic densities maps of the studied ligands

The influence of the nature of *diimine* on the position of CT band has been also studied by using dipyridine ligands which contain substituents of electron-donating (methyl) type or electron-withdrawing groups (carboxyl or nitro).

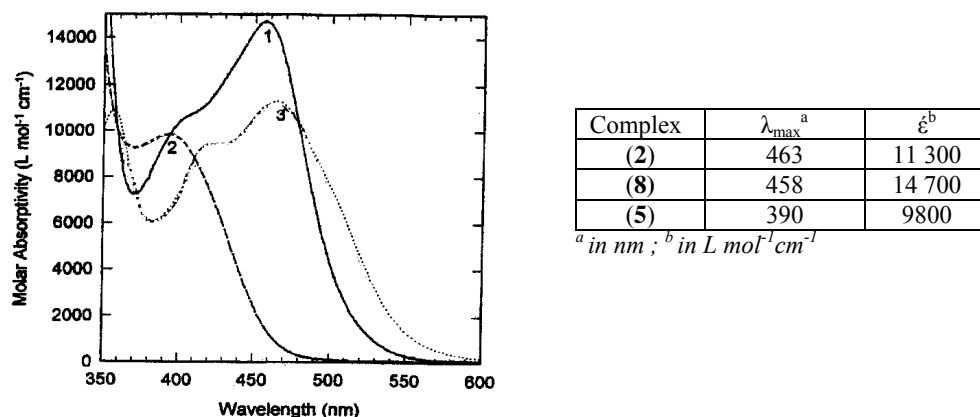


Fig.2. UV-Vis absorption spectra of complexes in dichloromethane solution

It is observed that the longer wavelength charge transfer to diimine absorption band for $[Ni(dnbpy)(tdt)]$ compound relative to that for $[Ni(dmbpy)(bdt)]$ compound is consistent with the fact that the nitro group is a stronger electron acceptor than methyl group.

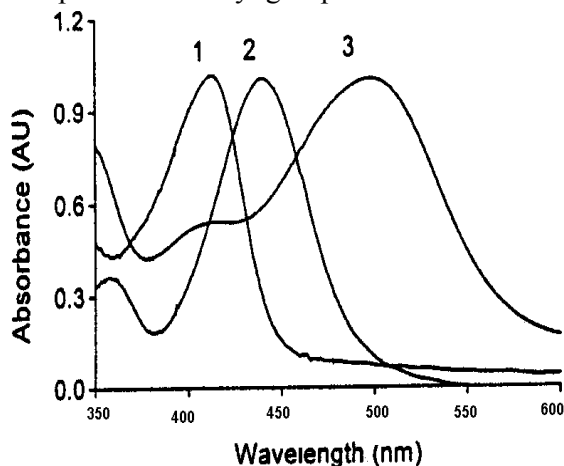


Fig.3. UV-Vis absorption spectra of $[Ni(dmbpy)(bdt)]$ (1); $[Ni(dcbpy)(bdt)]$ (2); $[Ni(dnbpy)(bdt)]$ (3) in toluene solution.

The spectra in dichloromethane solution (Fig.2) of the studied complexes present a bathochromic shift of LLCT bands in function of the central metal nature Pd, Pt, Ni.

The nitro groups with reducing power decreases the redox potential of 2,2'-dipyridine ligand and determine the diminishing of the energetic difference

between the HOMO (especially existent on dithiolat ligand) and LUMO (especially on diimine ligand).

FTIR Spectra measurements

In the IR spectra (table 2) of the studied complex compounds in comparison with those of free ligands are some changes due to the coordination of the ligands at the metallic center:

- the absence of ν_{S-H} dithiol characteristic frequency and the shift to lower values of ν_{C-S} sustain the tdt ligand coordination in the dithiolate form through the two sulfur atoms ;
- the shift to lower values of $\nu_{C=N}$ from dipyrindine cycle in the spectra of complexes with dimethyldipyrindine ligand sustains the coordination of the ligand (dmbpy) to the metal through the heterocyclic nitrogen atoms (this is also sustain by the electronic density map in which heterocyclic nitrogen has $\delta = -0.153$ – Fig .1)
- the same values of dicarboxylic acid characteristic frequency as in the spectrum of the free ligand and the shift to lower values of $\nu_{C=N}$ from dipyrindine cycle sustain the coordination of the ligand (dcbpy) to the metal through the heterocyclic nitrogen atoms (this is also sustain by the electronic density map in which heterocyclic nitrogen has $\delta = -0.129$ – Fig.1)
- the same values of nitro group characteristic frequency as in the spectrum of the free ligand (dnbpy) and the shift lower values of $\nu_{C=N}$ from dipyrindine cycle sustain the coordination of the ligand (dnbpy) to the metal through the heterocyclic nitrogen atoms in $[M(dnbpy)(tdt)]$ complexes ($M = Ni, Pd, Pt, Zn$) (this fact is also sustain by the value of heterocyclic nitrogen in the ligand, $\delta = -0.124$ - Fig.1).

Table 2

FTIR frequencies of $[M(dmbpy)(tdt)]$ complexes

Compound	$\nu_{C-H}/$ ν_{O-H} py cycl	ν_{C-C} py cycle	$\nu_{C=N}$ py cycle	ν_{C-S}	ν_{S-H}	$\nu_{C=O}$	ν_{NO_2}	$\nu_{s,asCH_3}$
dmbpy	3150	1460	1580	-	-	-	-	2910
dcbpy	3150	1460	1580	-	-	1780 1720	-	2910
dnbpy	3150	1460	1580	655	-	-	1560 1370	2926 2860
tdt	-	-	-	680	2580	-	-	2920 2860
(1), (4), (7)	3150		1580	655	-	-	-	2926, 2860
(2), (5), (8)	3150	1770	1560	650	-	-	-	2926

		1720					2860
(3), (6), (9)	3150	1460	1560	655		1560 1370	2926 2860

Stability of complex compounds

The stability of complex compounds in solutions of different organic solvents has been also spectrophotometrically studied. The stability of [Ni(dnbpy)(bdt)] complex in acetonitrile solution after the preparation, at different times is presented in figure 3.

The studies achieved with solutions of other complexes in different organic solvent (like benzene, toluene, dichlormethane, acetonitril) conduct to the observation that these are stable in air and light.

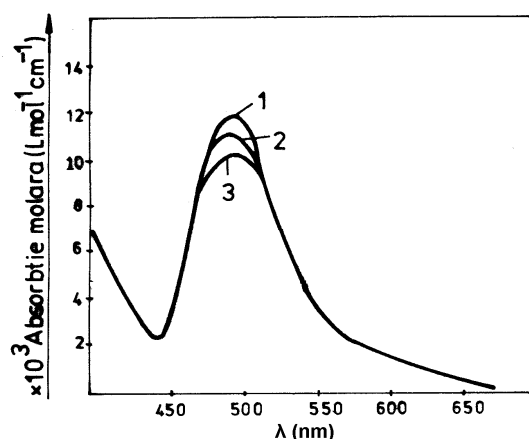


Fig.4. Stability of [Ni(dnbpy)(bdt)] complex in acetonitrile solution after the preparation, at different times : (1) 5 min ; (2) 10 min ; (3) 30 min

Solvatochromism studies of [Ni(diimine)(dithiol)] complexes

The solvatochromism behavior of all [Ni(diimine)(dithiol)] complexes was investigated for solutions at concentration of 2.5×10^{-4} M in different solvents: benzene, toluene, dichlormethane, chlorophorm, acetonitril.

The solvatochromic shift of the LLCT band is characteristic of a large dipole moment change ($\Delta\mu$) between the ground and the excited state and frequently suggestive of a large hyperpolarizability. Importantly, a negative solvatochromism, i.e., a hypsochromic (blue) shift with increasing solvent polarity indicates a reduction of the dipole moment upon electronic excitation.

The analysis of all Ni(II) complexes spectra in different solvents give to the conclusion that the solvatochromic shifts of LLCT absorption follow a general trend, i.e. the higher polarity of the solvent generates a lower λ value of LLCT bands.

Table 3.

Solvatochromic shifts of LLCT absorption bands

Complex/ Solvent	C ₆ H ₆	C ₆ H ₅ CH ₃	CHCl ₃	CH ₃ Cl	CH ₂ Cl ₂	CH ₃ CN
[Ni(dnbpy)(tdt)]	600	610	560	540	535	510
[Ni(dcbpy)(tdt)]	580	590	525	520	510	495

A hypsochromic effect of LLCT bands from nonpolar solvents (like benzene) to polar solvents (like acetonitril) for all Ni(II) complexes is observed in table 3.

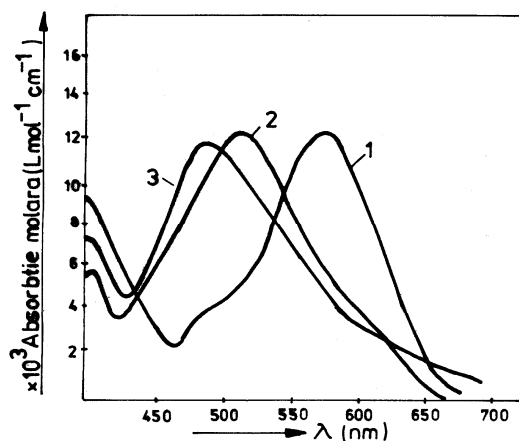


Fig.5. UV-Vis absorption spectra of [Ni(dcbpy)(tdt)] complex in solutions of: C₆H₆ (1); CH₂Cl₂ (2); CH₃CN (3).

4. Conclusions

This study analyzed the influence of the metallic ion nature and diimine ligands nature from highly polarizable [M(diimine)(dithiolate)] complexes (where M^{II} = Ni, Pd, Pt, Zn; diimine = 4,4'-dimethyl-2,2' bipyridine (**dmbpy**), 4,4'-dicarboxy-2,2' bipyridine (**dcbpy**) or 4,4'-dinitro-2,2'bipyridine (**dnbpy**) and dithiol = 1,2 benzene dithiol (**H₂bdt**)) on the LLCT band present in their UV-Vis spectra.

Substituents like potential electron withdrawing nitro groups on 2,2'-dipyridine ligand greatly lengthen the wavelength of absorption maximum of [Ni(diimine)(tdt)] complex. This is due to the fact that the reducing nitro group lowers the redox potential of the 2,2'-dipyridine ligand, which in turn diminishes the energy gap between HOMO (mainly composed of the dithiolate ligand) and LUMO (mainly composed of diimine ligand). The longer absorption wavelength in common organic solvents found for [Ni(dnbpy)(tdt)] complex than found for [Ni(dcbpy)(bdt)] and [Ni(dmbpy)(bdt)] is consistent with the fact that the nitro group is a stronger electronic acceptor than methyl group.

Solvatochromic shifts of LLCT absorption follow a general trend: the higher polarity of the solvent (like acetonitril) generates a lower λ value of LLCT bands for all Ni(II) complexes.

REFERENCES

- [1] T. Rosu, G. Patranoiu, O. Oprea - *Revista de Chimie*, 48(8), 702-706, 1997
- [2] I. Jitaru, M. Bicher, O. Oprea, A. Meghea – *Revue Roumaine de Chimie*, 44, 510-517, 1999
- [3] M. D. Stanescu, I. Jitaru, O. Oprea - *Phosphorus, Sulfur and Silicon and the Related Elements*, 169, 1, 137-140, 2001
- [4] M.D. Stanescu, I. Jitaru, O. Oprea, O.A. Jinga – *Revista de Chimie*, 55(9), 697-700, 2004
- [5] M.G. Alexandru, I. Jitaru, O. Oprea, L. Alexandrescu - *Revista de Chimie* – 60(6), 592-595, 2009
- [6] M.D. Stanescu, L. Alexandrescu, O. Oprea, S. Peres, I. Jitaru - *Revista de Chimie* – 60(9), 863-866, 2009
- [7] A. Kriza, I. Ignat, O. Oprea, N. Stanica - *Revista de Chimie* – 61(8), 733-739, 2010
- [8] O. Oprea, I. Jitaru, M.D. Stanescu, L. Alexandrescu, C. Covaliu, N. Stanica - *Revista de Chimie* – 62(2), 158-162, 2011
- [9] O. Oprea, H. Chivu, D. Ficai, C. Guran - *Revista de Chimie* – 63(3), 285-288, 2012
- [10] I. Ignat, O. Oprea, N. Stanica, A. Kriza - *Revista de Chimie* – 63(10), 1001-1007, 2012
- [11] S. Antonescu, E. Bacu, N. Stănică, O. Oprea, C. Guran - *U.P.B. Sci.Bull., Series B*, 72(4), 145-154, 2010
- [12] L. Bancu, O. Carp, N. Stanica, I. Jitaru, *Revue Roumaine de Chimie*, 2006, 6, 17
- [13] L. Bancu, I. Jitaru, P. Bourosh, Yu. Simonov, J. Lipkowski, *Revue Roumaine de Chimie*, 2006, 5, 14
- [14] L. Bancu, N. Badea, R. M. Nita, A. Meghea, *Molecular Crystals and Liquid Crystals*, 486, 230-238, 2008
- [15] L. Bancu, S. Stefan, I. Jitaru, *Rev. Chim.*, 57(6), 2006, 582-585
- [16] R.D.A. Hudson, K. Clays, L.P. Cuffe, *J. Org Chem.*, 637-639, 435-444, 2001
- [17] Santo Di Bella, I. Fragale, T.J. Marks, *J. Am. Chem. Soc.*, 1995, 117, 9481-9485
- [18] Santo Di Bella, I. Fragale, T.J. Marks, *J. Am. Chem. Soc.*, 1997, 119, 9550-9557
- [19] Santo Di Bella, I. Fragale, T.J. Marks, M.A. Rotner, *J. Am. Chem. Soc.*, 1996, 118, 12747-12751
- [20] Juan A.Zuleta, J.M.Bevilacqua, Davide M.Proserpio, Pierre D.Harvey, *Inorg. Chem.*, 1992, 31, 2396-2404
- [21] S.N.Fedosov, A.E.Sergeeva, *Moldavian Journal of the Physical Sciences*, 2002, 2, 28-31
- [22] Chin-Ti Chen, Tzu-Yao Jeremy, *J.Chinese Chem.Soc.* 2000, 47, 197-201
- [23] Yoo Hong Min, Kwang-Sup Lee, Lee Mi Do, *J. Mater. Chem.* 8(5) 1225-1232
- [24] Santo Di Bella, I. Fragale, *New J.Chem.*, 2002, 26, 285-290
- [25] P.J.Coelho, L.M. Carvalho, A.Mauricio, C.Fonseca, M.Raposo, *Tetrahedron Letters*, 2006, 12, 47, 3711
- [26] Usama El-Ayaan, Alaa A.-M. Abdel-Aziz, Shar Al-Shihry, *Eur.J. Med.Chem.* 2, 2007, 1-9
- [27] L.V.Stepakova, M.Yu.Skripkin, V.V.Korneeva, Ya.M.Grigoriev, K.A.Burkov, *Russian J. Gen.Chem.*, 2009, 79(6) 1053-1058