



Optical properties and electron transfer in novel bis salicylimine diamino metallo-Schiff-base compounds

by Jeffrey Rockefeller Wilcox

A thesis submitted in partial fulfillment of the requirement for the degree of Masters of science in Chemistry

Montana State University

© Copyright by Jeffrey Rockefeller Wilcox (2002)

Abstract:

A family of bis salicylamine diamino metallo-Schiff-base compounds synthesized by Warren Miller was spectroscopically characterized. Excitation coefficients showed a strong dependence on metal strength of donor substituted on the salicylamine, and presence of strong acceptors on the diamino portion of the ligand. Fluorimetry experiments were performed with an interferometer based instrument.

[N, N', N'', N''']-tetra(4-diethylaminosalicylimine)-1,2,4,5 tetraaminobenzene]Zn(II) 2, a compound containing both acceptor and donor moieties showed a bi-mechanistic electron transfer in solution with C60. Photoinduced absorption through step-scan spectroscopy yields quantum efficiencies for the solvated ions for both pathways of 21.6% and 21.5% respectively. A new kinetic treatment is shown for separating these embedded signals of the two pathways in order to obtain their efficiencies.

OPTICAL PROPERTIES AND ELECTRON TRANSFER IN
NOVEL *BIS* SALICYLIMINE DIAMINO METALLO-SCHIFF-BASE
COMPOUNDS

by

Jeffrey Rockefeller Wilcox

A thesis submitted in partial fulfillment
of the requirement for the degree

of

Masters of science

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

December 2002

N 378
W 443

© COPYRIGHT

by

Jeffrey Rockefeller Wilcox

2002

All Rights Reserved

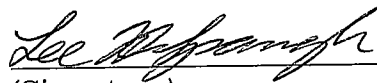
APPROVAL

of a thesis submitted by

Jeffrey Rockefeller Wilcox


This thesis has been read by each of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Dr. Lee Spanger


(Signature)12/20/2002
Date

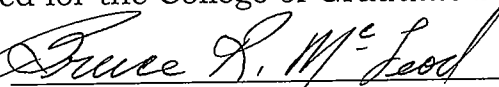
Approved for the Department of Chemistry & Biochemistry

Dr. Paul Grieco


(Signature)12-20-02
Date

Approved for the College of Graduate Studies

Dr. Bruce McLeod

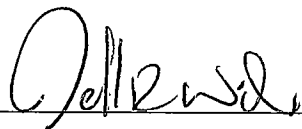

(Signature)1-17-03
Date

STATEMENT OF PERMISSION TO USE

In presenting this thesis in Partial fulfillment of the requirements for a master's degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the library.

If I have indicated my intention to Copyright this thesis by including a copyright notice page, copying is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for permission for extended quotation from or reproduction of this thesis in whole or in parts may be granted only by the copyright holder.

Signature

A handwritten signature in cursive script, appearing to read "Jellison", written over a horizontal line.

Date

02.04.03

Thanks to my family for all their support,
to Jon for seeing me through a time of separation,
and my grandmother for showing me
how life should be lived.

Jeffrey Rockefeller Wilcox was born to parents Wendy Mary Wilcox and Robert Winn Wilcox in Seattle Washington on the 8th of August in the year 1975 along with his twin brother Jon Robert Wilcox. Jeff spent his pre collegiate years living with his family on Bainbridge Island in Washington. After completing a high school education he followed the path of his older siblings, Danny Winn Wilcox and Amy Cathleen Wilcox, to higher education. In 1990, Jeff began his freshman year the University of Oregon in hopes of becoming an historical preservation architect. During his sophomore year he changed his major to chemistry. The following year he transferred to Washington State University to continue his pursuit of Chemistry. Here he participated in physical chemistry groups directed by Dr. St. John Dixon-Warren and Dr. Kevin Bray and quickly became enchanted. Upon entering Montana State University Jeff was given the opportunity to join the Lee Spangler research group wherein he pursued his Master's degree

Jeff's family is one of the close supportive components of his life and they have continually encouraged his endeavors in chemistry. Eventually, Jeff hopes to rejoin his family in sailing the waters of the Northwest.

I would like to acknowledge the efforts of Dr. Lee Spangler and those participants in his group who have guided me through their example. An additional acknowledgement goes to Mr. Warren Miller of the Gallatin Research laboratories whose innovating compounds made our work a reality.

TABLE OF CONTENTS

	Page
1. INTRODUCTION.....	1
2. GROUND STATE SPECTROSCOPY OF SCHIFF-BASES.....	9
Absorption.....	9
Experimental.....	9
Results and Interpretation.....	11
Metal Center Substitution.....	12
Ligand Donor Substitution.....	14
Acceptor-Metal Proximity Effects.....	15
Dimeric Metallo-Schiff-Base.....	17
Fluorimetry.....	18
Michelson interferometer.....	19
Interferometer based fluorimeter.....	22
Excitation Spectroscopy.....	22
Excitation-Emission Spectroscopy.....	25
3. EXCITED STATE SPECTROSCOPY OF A SCHIFF-BASE.....	31
Extinction Coefficient.....	31
Experimental, Bleaching Method.....	31
Results & Interpretation.....	35
4. ELECTRON TRANSFER INVOLVING A SCHIFF-BASE COMPOUND..	38
Schiff-base electron transfer.....	38
Experimental, PIA Methodology.....	38
Data Analysis.....	43
Kinetic Importance of a Bi-mechanistic System.....	49
Analysis for Bi-Mechanistic System.....	51
Results & Interpretation.....	55
5. CONCLUSION.....	67
Absorption.....	67
Electron Transfer.....	68

REFERENCES.....73

APPENDIX A: Warren Miller Compounds.....76

LIST OF TABLES

Table	Page
1. 2-1 Ground State Extinction Coefficients for Miller Compounds.....	12
2. 4-1 Kinetic values for bi-mechanistic sysytem.....	66

LIST OF SCHEMES

Scheme	Page
1. 4-1 Electron transfer mechanism; (a) Acceptor excited case, (b) Donor excited case.....	50

LIST OF FIGURES

Figures	Page
1. 2-1 Metallo-Schiff-bases synthesized by.....	10
2. 2-2 Ground state absorption of Miller.....	13
3. 2-3 Ground state absorption of Miller compounds.....	15
4. 2-4 Ground state absorption of Miller compounds with.....	16
5. 2-5 Ground state absorption of GRB1-19 and C ₆₀	18
6. 2-6 Michelson interferometer chamber.....	20
7. 2-7 Excitation spectrum of Pt ₂ (pop) ₄ ⁴⁺ Probed at.....	23
8. 2-8 3D Fluorimeter data using PMT detector.....	26
9. 2-9a Frequency vs. frequency for Excitation.....	27
10. 2-9b Wavelength vs. frequency for Excitation.....	27
11. 2-10 Total excitation-emission plot for GRB1-11-1.....	29
12. 2-11 Total excitation-emission spectrum of.....	30
13. 3-1 Photo-bleaching experimental layout.....	33
14. 3-2 Photo-excitation from ground state to excited.....	34
15. 3-3 data using Equation 4 for GRB1-19 PIA.....	36
16. 4-1 3D plot of raw Fourier transformed signal.....	40
17. 4-2 PIA layout; a) Pulse laser b) Beam dumps.....	42
18. 4-3 Photoinduced electron transfer free.....	44

19.	4-4) Raw data of ion concentration and ion.....	45
20.	4-5 Energy level transfer scheme.....	48
21.	4-6 3D plot of raw PIA data for G19.....	52
22.	4-7 Subtraction diagram of spectral data.....	54
23.	4-8 Integration ratio contribution diagram.....	54
24.	4-9 Time decays for G19* & ${}^3\text{C}_{60}$ * without.....	56
25.	4-10 Raw data time decay traces of the.....	60
26.	4-11 One over donor ion concentration vs. time.....	61
27.	4-12 Time decay traces of the G19.....	63
28.	4-13 Plot of $d[D^+]/dt$ vs. $[A^*]$. The slope at lower.....	64
29.	4-14 Plot of $d[D^+]/dt$ vs. $[A^*]$	65

Abstract

A family of bis salicylamine diamino metallo-Schiff-base compounds synthesized by Warren Miller was spectroscopically characterized. Excitation coefficients showed a strong dependence on metal strength of donor substituted on the salicylamine, and presence of strong acceptors on the diamino portion of the ligand. Fluorimetry experiments were performed with an interferometer based instrument. [N,N',N'',N'''-tetra(4-diethylaminosalicylimine)-1,2,4,5-tetraaminobenzene]Zn(II)₂, a compound containing both acceptor and donor moieties showed a bi-mechanistic electron transfer in solution with C₆₀. Photoinduced absorption through step-scan spectroscopy yields quantum efficiencies for the solvated ions for both pathways of 21.6% and 21.5% respectively. A new kinetic treatment is shown for separating these embedded signals of the two pathways in order to obtain their efficiencies.

CHAPTER 1

INTRODUCTION

Franken discovered in 1961 that a quartz crystal could double the frequency of a ruby laser.^{1,2} This phenomenon, termed second harmonic generation (SHG), is a result of the nonlinear optic (NLO) properties of the quartz crystal. Any medium that changes an electromagnetic field as it passes through it in terms of phase, frequency, amplitude, or polarization is considered an NLO material.³ The nonlinear response of a compound is depicted in the equation,

$$\rho = \alpha E + \beta E^2 + \gamma E^3 + \dots \quad (1)$$

where E is electronic field strength, α is the linear polarizability, β is the first nonlinear hyperpolarizability and γ is the second molecular hyperpolarizability. Field change occurs due to compounds having an instantaneous electron density displacement (polarization).³ Termed hyperpolarizability, this displacement is the indication of a compound's readiness to "switch on" its second order nonlinear absorption.⁴ Such materials have evolved virtually hand-in-hand with lasers since the introduction of the coherent light source in 1960.¹ The discovery of NLO compounds correlates to the introduction of lasers due to the relatively high electric field needed to cause hyperpolarization within the material.

Exploration of inorganic NLO materials as the only compounds exhibiting nonlinear behavior continued into the 70's. With the interest in NLO compounds expanding for use with laser doubling, mixing and even tripling, new inorganic crystalline compounds were sought. While inorganic NLO crystals have desirable properties such as good thermal stability and being relatively easy to machine, they are expensive and have a relatively low hyperpolarizability per formula unit and thus require strong fields to generate a nonlinear response. This response led to exploration of organic compounds in a quest to generate larger hyperpolarizabilities.

Organic compounds relieve some of the disadvantages and shortcomings found in inorganic crystals but also introduce some inherent new ones. Organic NLO materials, first investigated in 1970 and later reintroduced in a polymer form in 1976, have a surprising increase for the second order hyperpolarizability term over that of the traditional inorganic crystals.¹ Organics show a real sense of optical "tradeoff" in the visible region, with the delocalized π electrons helping by increasing the NLO response, but hindering by introducing strong linear absorption, sometimes in regions of desired transparency.³ The organic compounds tend to have lower manufacturing cost, enhanced NLO properties over a broad frequency range, synthetic flexibility, high optical damage thresholds, and intrinsic tailorability.³ However, with these advantages

come volatility, low thermal stability, mechanical weakness, and a strong aversion to form bulk crystals.^{2,3}

Scientists however continue to make advancements in the organic NLO field, increasing the possibility of suitable compounds. To further improve on organic NLO compounds, Frazier in 1986 produced the first organometallic complex for NLO study.^{2,5} This introduced a marriage between the organic large second order term and that of the inorganic stability. The combined effect is further increased by the open shell nature of the complex and the ability to fine tailor the compounds involving different transition metals or organic moieties.

In 1987 Green introduced the first NLO useful organometallic complex.^{4,5,6} Organometallics, and Schiff-bases in particular, possess several properties that indicate potential utility for NLO applications and optical properties in general. Transition metal complexes are some of the most highly colored compounds known which indicates low energy, high dipole change transitions. These transitions often involve significant charge transfer (CT) from the metal to the ligand or vice versa. (Organic systems with low energy, high CT character have been shown to have strong non-linear optical properties suggesting the potential for the organometallics.) Organometallics also have the advantage of having a larger number of structural variations available. The organic ligand can be functionalized with strong electron donors (D) and acceptors (A) to

construct $D \cdots A$, "push-pull" systems analogous to organic systems which have been successfully engineered for higher β values.⁷ In addition, the metal center can be varied and can play a role as an electron donor (electron "rich" metals) an electron acceptor (electron "poor" metals) or as part of the highly polarizable, conjugated bridge between other donor or acceptor groups.⁶ Variation of the metal also permits synthesis of compounds with an open shell electronic configuration which one study indicated may enhance nonlinearity.⁸ This open shell enhancement of the hyperpolarizability was attributed to a larger number of accessible, low-lying CT states. The Schiff-base also exhibits favorable thermal stability, with decomposition temperatures of 300°C and above in some of the NLO active materials.⁹

The organometallic compounds display properties of general interest for optical applications. The strong and highly tunable absorption bands indicate possible utility as sensitizers for fluorescence and dye laser applications. Highly conjugated organic systems functionalized with multiple electronic donating groups that have been found to be good electron donors in photoinduced electron transfer (PET) were previously investigated in the Lee Spangler research group. The ability to functionalize the Schiff-base ligand and change the possible redox activity of the metal center make this class of compounds intriguing for intermolecular PET studies. In dilute solution, the diffusion

rate and the lifetime of the excited photoinitiator limit intermolecular PET studies. The presence of the heavy atom may increase spin orbit coupling and enhance formation of long-lived triplet states. These states provide two advantages for intermolecular PET in dilute solutions: they do not appreciably decay before diffusion limited collisions occur and an electron transferred from a triplet state results in a state for which geminate recombination is spin-forbidden which should increase ion yield. The fluorescence properties of these compounds are relatively unexplored and not directly mentioned in the bulk of the NLO literature on Schiff-bases, although the experimental section of one paper mentions a red solution yielding dark blue crystals.¹⁰ And finally the existence of low-lying, strongly absorbing CT states in combination with high hyperpolarizabilities suggest the possibility of strong two photon absorption and the possibility of sequential absorption that could produce optical limiting.

Schiff-base compounds introduced new flexibility in geometry due to the metal centers and a high order of tuning with the organic moieties.⁵ These highly conjugated systems possess chirality due to their noncentrosymmetric configuration allowing for the growth of NLO active crystals.^{5,11} Organometallic Schiff-base complexes are speculated to produce a higher nonlinear response in comparison to a solely organic chromophore, and at the present time come close to doing so.² The metal

ligand interaction is thought to increase the conjugation in the excited states between the acceptor and donor moieties. The organometallic bond creates a cage at the center of the organic chromophore which improves the thermal stability of the compound by stabilizing the chelate ring structure. This central metal acts as a π conjugate bridge between the electron donating and electron accepting moieties of the compound (donor-metal-acceptor).⁴ Although the NLO effect is largely enhanced by the Schiff-base conjugation, the ground state absorption is dominated by the organic chromophore.¹⁰ Metal also improves the thermal stability of the compound by stabilizing the chelate ring structure by bonding to the organic ligands through a σ - π interaction.^{4,12} When a low d metal is used it acts as a bridge for the acceptors. High d metals bridge with the donors.⁶ A high degree of configurable geometry is due to the increasing number of bonds between the metal and the ligands, which are flexible through the π delocalization.⁶ These weak bonds between the ligands and metal center are what induce the bridging properties exhibited by the metal.⁵ Any elongation of this delocalized system results in increased hyperpolarizability and so increases NLO response.⁵

Schiff-base complexes absorb intensely in the ultraviolet due to the metal d - d^* and ligand π - π^* transitions around 300-400nm.⁴ Longer wavelength absorption intensities take on the character of the organic ligand and show effects of solvatochromism due to interactions with the

metal.⁴ The metal-ligand bridge also increases the overall intensity of the ligand band shape with more apparent effect toward the red side of the visible range. These lower transitions in nearly all organometallics occur in the visible region reducing the “transparency window”.³ This delicate balance between strong second order absorption and obtaining a large transparency window in the visible region once again reiterates the NLO tradeoff. Scientists now can produce donor and acceptor moieties with varied conjugation that when attached to various transition metals can produce distinct NLO properties. Potentially, with known ligands and compound arrangements, scientists can predict Schiff-base structures that will yield high second order responses. Organometallics offer a multitude of compounds, which have a diversity of oxidation states (e.g. hyperpolarizability), with low energy transition states (from metal-ligand bond), π delocalized systems, and easy crystal packing (due to chiral center).

Because of the potentially strong NLO response of organometallics, the metallo-Schiff-bases have generated interest. But aside from linear absorption and electric field induced second harmonic generation (EFISH) experiments, very little optical characterization has occurred and for a relatively small number of compounds. The Spangler group, interested in a series of novel Bis salicylimine diamino metallo-Schiff-base compounds designed by Warren Miller for NLO properties, has devoted

time to characterize the linear optical properties of the compounds with a nonlinear examination to ensue. Design aspects of such compounds for the use of NLO materials correlate directly to systems rich in applications for electron transfer since both acceptor and/or donor moieties appear in their configuration.^{13,10} With proper characterization of the linear absorption, useful information on the Schiff-base compounds and their possible design aspects may be found other than by simply performing nonlinear experiments.

CHAPTER 2

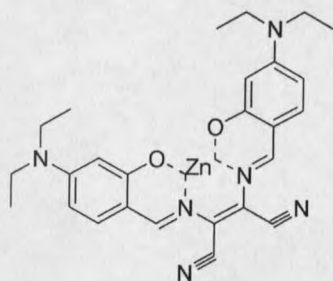
GROUND STATE SPECTROSCOPY OF SCHIFF-BASES

Absorption

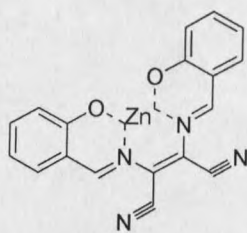
Absorption spectra of the Miller compounds yield the ground state to excited state transitions. These interactions will indicate the best frequencies for pumping when exploring other attributes of the compounds and can also be used to examine the analyte's optical properties through pump-probe methods.

Experimental

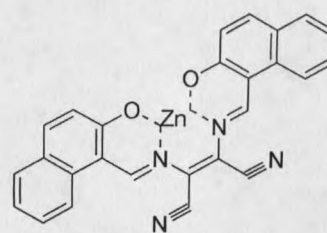
Warren Miller designed and synthesized the Bis salicylimine diamino metallo-Schiff-base compounds investigated in this thesis. The absorption experiments were performed with a Shimadzu (UV-2401pc) spectrophotometer. The compounds investigated are shown in Figure 2-1, and the formal names are provided in appendix A. These metallo-Schiff-base complexes



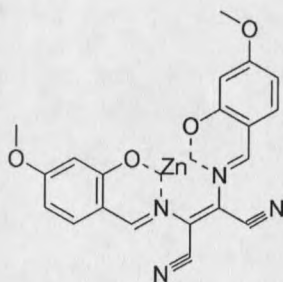
GRB 1-11-1



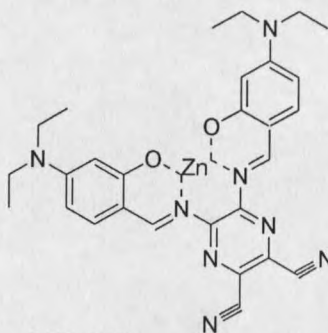
GRB 1-11-2



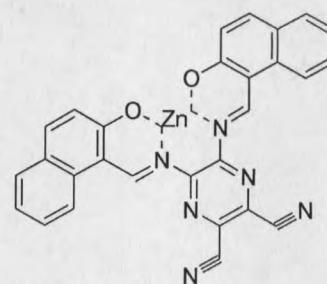
GRB 1-11-3



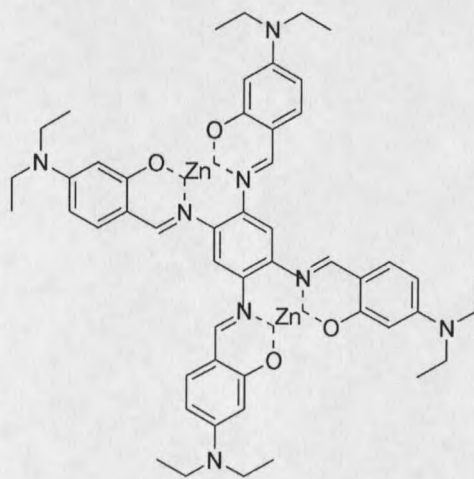
GRB 1-11-4



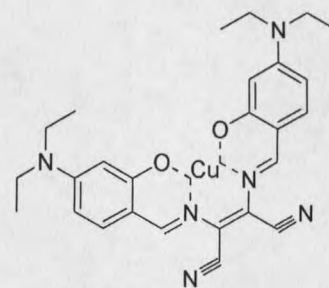
GRB 1-15



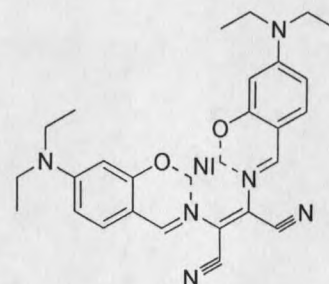
GRB 1-17



GRB 1-19



GRB 1-21



GRB 1-23

(Figure 2-1) Bis salicylimine diamino metallo-Schiff-bases synthesized by Warren Miller and investigated in this thesis. The formal names are provided in Appendix A.

contain multiple diethylamino (strong donor) and cyano (acceptor) groups in an organic ligand which encases a transition metal.

Results and Interpretation

In order to investigate the effects of a number of structural parameters on the ground state absorption behavior, a variety of Bis salicylimine diamino metallo-Schiff-bases were synthesized (by Miller) and measured. The compounds are shown in Figure 2-1 (formal names are provided in appendix A) and are designed to explore effects of varying the metal, conjugation length, and donor/acceptor substitution on the ligand.

The structure labeled GRB1-11-1 serves as the reference compound for the rest of the analogs. This compound was previously reported by Di Bella and co-workers as having a high hyperpolarizability (although the absorption spectrum was not shown) and was identified by Miller as a fluorescent species from a statement within the Di Bella paper noting that in purifying the sample blue crystals were obtained from a red solution.¹⁰ The absorption spectrum obtained in this work strongly resembles the literature spectrum of the nickel Bis salicylimine diamino metallo-Schiff-base (NiL). The spectrum of the ligand itself (H₂L), also reported by Di Bella and co-workers closely resembles that of the metal

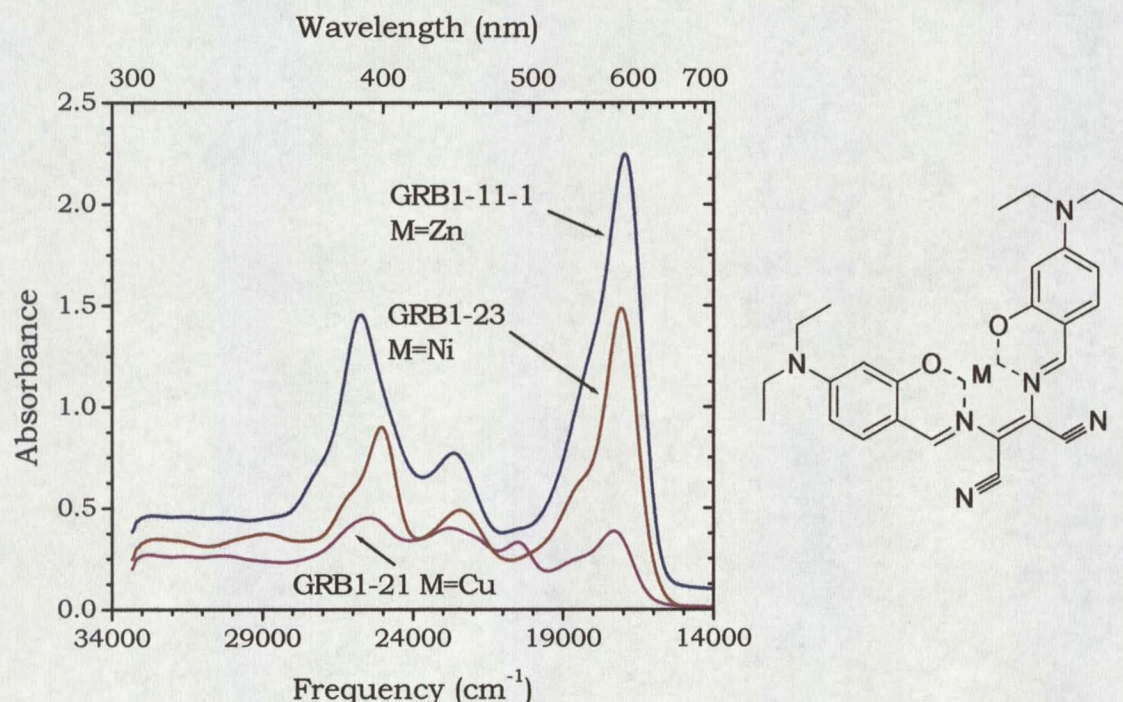
containing species with two exceptions, 1) NiL exhibits an additional peak at ~250nm absent in H₂L that is presumably due to a metal-ligand (M-L) charge transfer band and 2) the ZnL spectrum is red-shifted by ~15nm. These ligands contain strong donor (diethylamino) groups at the ends of the molecules as well as strong cyano group electron acceptors near the center of the molecule (and near the ethylenediamine metal chelating site). Ground state extinction coefficients for these Bis salicylimine diamino metallo-Schiff-bases are listed in Table 2-1.

Compound	Wavelength (nm)	ϵ (L mol ⁻¹ cm ⁻¹)
GRB1-11-1	590	44,900
GRB1-11-2	566	3,200
GRB1-11-3	602.5	15,500
GRB1-11-4	554	29,300
GRB1-15	528	11,700
GRB1-17	512	1,400
GRB1-19	440	47,400
GRB1-21	587	7,700
GRB1-23	586	29,700

(Table 2-1) Ground state extinction coefficients for Miller compounds.

Metal Center Substitution. The effect of metal substitution is shown in Figure 2-2, which shows Zn²⁺, Ni²⁺ and Cu²⁺ all chelated by the same "push-pull" ligand. The spectral bands display very similar wavelength and shapes, but intensities vary dramatically. The ZnL absorbance is 1.5 times as intense as NiL and a factor of 6 larger than CuL. The close resemblance of the band shapes and wavelengths

strongly suggests that the transitions are due to the organic ligand. This is supported by the fact that all the features shown (300nm and above) also appears in the bare ligand spectrum reported by Di Bella and coworkers. Thus we see that for this ligand, which contains strong acceptors, the metal functions to significantly change the oscillator strength of the low-lying electronic transitions without appreciably changing their energies. It is also interesting to note that this effect is not monotonic with d electron population and that the open shell Cu^{2+} (d^9) is lower in intensity than the closed shell d^{10} and d^8 species (Zn^{2+} and Ni^{2+} , respectively).



(Figure 2-2) Ground state absorption of Miller compounds with varying metals; GRB1-11-1 (Zn), GRB1-23 (Ni), GRB1-21 (Cu).

Ligand Donor Substitution. The previous series of compounds indicated that ligands containing strong donors and acceptors dominate the low frequency spectrum of the metallo-Schiff-bases. We now compare a series of molecules containing the same metal (Zn, which exhibits the highest molar absorbtivity) but with varying donor groups on the same ligand structure. GRB1-11-1 (diethylamino) GRB1-11-4 (methoxy), and GRB1-11-2 (H) are a series with decreasing donor strength, and their spectra show a corresponding decrease in intensity with the H substituted compound being dramatically weaker (Figure 2-3). The diethylamino is red-shifted by ~12.5 nm from the methoxy compound indicating slight solvochromism in the oscillator strength. Also shown for comparison is GR1-11-3 which has a naphthal instead of phenol extending the conjugation in the molecule. Its spectrum shows a red shift slightly greater than the diethylamino likely due to the larger conjugated system in the ligand. The molar extinction is intermediate to the H and methoxy substituted compounds consistent with the fused ring being a weak electron donor, but obviously stronger than hydrogen. This series of compounds illustrates that both absorption frequencies and intensities can be engineered in "push-pull" metallo-Schiff-bases in the same way conjugated organic "push-pull" systems are.

