Structural Effects on Molecular Dipoles and Solvatochromism of Nickel(diimine)(dithiolate) Complexes

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Received September 18, 1998

A series of acceptor-substituted nickel(diimine)(dithiolate) complexes were synthesized and characterized. Both ground-state and excited-state dipole moments were determined. These complexes have ground-state dipole moments (μ_gs) in the wide range from 4 to 17 D, in contrast to the near constant μ_gs reported earlier for a series of platinum(diimine)(dithiolate) complexes.[3] The excited-state dipole moments of the complexes, ranging between 10 and −9 D, are either smaller than or opposite to the ground-state dipoles. The relative strengths and directions of the ground-state and excited-state dipoles were found to be strongly influenced by the electronic acceptors of the complexes. Ground and excited states dipoles of opposite sign were found for complex nickel(*N*,*N′*-ditolyl-3,4-hexanediimine)(tfd), **5** (tfd = 1,2-trifluoromethylethene-1,2-dithiolate). The opposite dipoles are related to the pronounced solvatochromic shift observed for the ligand to ligand charge-transfer (LLCT) band (544 nm in acetonitrile and 641 nm in toluene) of **5**. On the basis of single-crystal X-ray structures, substantial π-delocalization character is implicated for the central (N=C−C=N)Ni(S−C=C−S) unit of Ni(disn)(tfd), **3** (disn = diimnosuccinonitrile), and nickel(4-benzoyl-*o*-benzoquinonediimine)(tfd), **7**. The π-delocalization character has not been noted for other known M(diimine)(dithiolate) (M = Ni, Pd, Pt) complexes. A number of other unusual optical properties, such as large molar extinction coefficient (12 000−19 000 M^{-1} cm^{-1}), weak solvatochromic shift, and small ground-state dipole moment (4−9 D), found for **3** and **7**, are consistent with the π-delocalization proposed.

Introduction

Recently, a series of platinum(diimine)(dithiolate) complexes were studied for electrical conductivity in the solid state,[1] photoluminescence in solution,[2] and nonlinear optical properties[3] for possible applications in materials chemistry. The complexes belong to a unique family of unsymmetrical mixed-ligand metal complexes.[4] A variety of complexes of these types have been synthesized and characterized by their UV−visible absorption and electrochemical properties.[5] For most M(diimine)(dithiolate) complexes with M = Ni, Pd, and Pt, the molar absorption coefficients (ϵ) are in a range from ~6000 to 13 000 M^{-1} cm^{-1}, and distinct solvatochromic shifts of ligand to ligand charge-transfer (LLCT) bands greater than ~2000 cm^{-1} in solution from acetonitrile to toluene are often observed.[2b,3,5a] During the early seventies, however, a number of square planar nickel(diimine)(dithiolate) complexes were shown to exhibit pronounced negative solvatochromism,[5] i.e., a hypsochromic (blue) shift, with increasing solvent polarity. Theoretically and experimentally, the origin of the solvatochromism was attributed to the LLCT between the dithiolate donor ligand and diimine acceptor ligand.[5] Since the LLCT axis is collinear but antiparallel to the ground-state dipole of the molecule, the complex has a smaller dipole moment in the charge-transferred state than in the ground state and hence showed a negative solvatochromic behavior of the LLCT band. Resonance forms **A** and **C** (Scheme 1) depict qualitatively the composition of the HOMO and LUMO in these nickel(diimine)(dithiolate) complexes. All nickel(diimine)(dithiolate) complexes have resonance form **A** dominating the ground state. The HOMO is an approximately pure dithiolate and the LUMO is essential a diimine. A third resonance form **B** is then appropriate for describing the LLCT excited state.

We describe herein the synthesis and characterization of a series of novel nickel(diimine)(dithiolate) complexes **1**−**7** (Scheme 2) with trifluoromethyl or cyano groups serving as potent dipole substituents. A couple of complexes (**3** and **7**) have been found to be exceptional, with relatively large ϵ values in the range 12 000−19 000 M^{-1} cm^{-1} but unusually small solvatochromic shifts of 820−1150 cm^{-1} in solution from acetonitrile to toluene. In addition, complex **5** has an excited-state (charge-transferred state) dipole not only smaller than but also opposite in direction to the dipole in the ground-state. Through studies of the ground-state dipole moment (μ_g) and the excited-state dipole moment (μ_e), which were determined by the solvatochromic method, we have obtained insightful information relating to the effects of electronic structures on the unusual optical behavior and dipole moment of the

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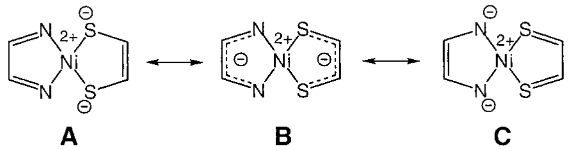
10.1021/ic981125w CCC: $18.00

Scheme 1. Three Limiting Resonance Forms of the Parent Nickel(diimine)(dithiolate) Complex



complexes **3**, **5**, and **7**. To our knowledge, there exist few reports on the μ_g of M(diimine)(dithiolate) complexes, and none on μ_e.[3] Finally, we also use single-crystal X-ray structures to elucidate the relationship between the solvatochromism and the bonding structure. We will show that the π-bonding structure of the nickel complexes and the degree of solvatochromism observed for the LLCT bands are also strongly influenced by the dipole substituents.

Experimental Section

μ_g Measurements. Our method for determining the ground-state dipole moment of the solute in polar solvents has been described in detail elsewhere.[6] Equation 1 was used for determining μ_g:

$$(P_2 - P_1)C_2 + \frac{P_1}{V} = \left[\frac{(\epsilon_{12} - 1)(\epsilon_{12} + 2)}{8\epsilon_{12}} - \frac{(n_{12}^{\ 2} - 1)(n_{12}^{\ 2} + 2)}{8n_{12}^{\ 2}}\right]$$

$$P_1 = \frac{M_1(\epsilon_1 - 1)}{d_1(\epsilon_1 + 2)} \qquad P_2 = \frac{4\pi N}{9kT}\mu_g^{\ 2} \quad (1)$$

Here the subscripts "1" and "2" denote the solvent and solute, respectively. Other symbols are C_2, concentration of solute "2" in units of mol cm^{-3}; k, Boltzmann's constant, 1.381×10^{-16} erg K^{-1}; μ_g, ground-state dipole moment in units of esu cm; ϵ_{12}, dielectric constant of solvent "2" containing solute "1"; n_{12}, refractive index of solvent "2" containing solute "1"; T, temperature (K); and N, 6.02×10^{23}. The μ_g values (with precision within ±10% D) of **1**−**5** and **7**−**9** were determined through measurements on solutes in solutions over the concentration range of 10^{-3}−10^{-5} M. Molecular-sieve-dried spectrograde solvents were used in these experiments. In most cases, chloroform was the solvent used. However, 1,2-dimethoxyethane was used for **3** and **7** due to solubility reasons. On the other hand, for complexes **2** and **5**, μ_g values were also determined in 1,2-dimethoxyethane in addition to chloroform as a control. Dichloromethane was also used for **8** and **9** in order to compare with literature data. The dielectric constants of the samples were calculated from the capacitance. The capacitance of each solution was measured at a frequency of 100 kHz using HP 4284A Precision LCR Meters connected to a HP16452A Liquid Test Fixture as the cell compartment. The refractive indices of the samples were measured with an Abbe's refractometer type 3T with accuracy of ±0.0001.

μ_e Measurements. Most theoretical treatments of solvatochromism are based on a solvent dielectric field model in which the dipole of a polar solute polarizes the surrounding solvent molecules, which in turn create an electric field that perturbs the energy levels of the solute. The perturbing electric field was first described by Onsager and then elaborated by others.[7] A useful expression for the solvatochromic shift in a solvent of bulk dielectric ϵ_i and index of refraction n_i is that of McRae given by eq 2.[8]

$$\tilde{\nu}^{i}_{eg} = \tilde{\nu}^{g}_{eg} + A\left[\frac{(n_i^{\ 2} - 1)}{(2n_i^{\ 2} + 1)}\right] + B\left[\frac{(\epsilon_i - 1)}{(\epsilon_i + 2)} - \frac{(n_i^{\ 2} - 1)}{(n_i^{\ 2} + 2)}\right]$$

$$B = \frac{\mu_g(\mu_g - \mu_e)}{2\pi\epsilon_0 cha^3} \quad (2)$$

The coefficient B was obtained from a least-squares fit of the λ_{max} of the LLCT band in 10−15 different solvents (Table 1), and from B, the dipole moment change, $\mu_e - \mu_g$, was deduced.

Here, $\tilde{\nu}^{i}_{eg}$ is the absorption wavenumber (m^{-1}) in solvent i; $\tilde{\nu}^{g}_{eg}$, the absorption wavenumber (m^{-1}) in the gas phase; μ_g, the ground-state dipole moment (Cm); μ_e, the excited-state dipole moment (Cm); ϵ_0, 8.854×10^{-12} J^{-1} C^2 m^{-1}; h, 6.63×10^{-34} J s; c, 3.0×10^8 ms^{-1}. A few solvents, most often 2-propanol and 4-dioxane, generated results that deviated from least-squares fitting and hence were not included in the μ_e determination. UV−visible absorption spectra of the complexes in various solvents were recorded on an HP 8453 spectrophotometer. Finally, with experimentally predetermined μ_g, μ_e can be calculated. The most uncertain quantity in the solvatochromic method is the poorly defined Onsager radius a (m).[7] We took the sum of spherical radius of solute and solvent for a.[7c] The spherical radii of solutes were calculated from the measured density values of compounds **1**−**9**.

X-ray Crystallography. Single crystals suitable for X-ray diffraction studies were grown by slowly diffusing a nonsolvent (usually hexane) through vapor into solvents dissolving with the complex. Appropriate solvents are chloroform for **1**, **2**, **6**, toluene for **3**, and ethyl acetate for **7**. Each crystal was mounted on a glass fiber. Details of the structure determination of complexes **1**, **2**, **3**, **6**, and **7** are given in Table 2. Diffraction data were collected on an Enraf-nonius CAD4 diffractometer with κ-geometry using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at room temperature (25 °C). The unit cell parameters and orientation matrix were established from a least-squares fit of 25 reflections. All data sets were collected in the ω−2θ scanning mode with three standard reflections monitored for intensity variation throughout the experiment. No significant variation in standards was observed. All data sets were corrected for Lorentz and polarization effects and for absorption by employing φ-scans on several reflections with χ near 90°. The positions of Ni atom were determined by direct methods, and the remaining non-hydrogen atoms were located from the difference Fourier maps using NRCVAX.[9] Typically, all non-hydrogen atoms were refined anisotropically by full-matrix least-squares (based on F^2) using SHELXL-93.[10] All hydrogen atoms, excluding those of water molecules, were placed in idealized positions. Reliable factors are defined as $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $wR_2(F^2) = [(\Sigma(w(F_o^{\ 2} - F_c^{\ 2})^2/(\Sigma(w(F_o^{\ 2})^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^{\ 2}) + (fP)^2]$, where $P = (\max(F_o^{\ 2}, 0) + 2F_c^{\ 2})/3$. $S = [(\Sigma(w(F_o^{\ 2} - F_c^{\ 2})^2/(\Sigma(n - p)]^{1/2}$

Materials. The bis-Schiff base N,N'-ditolyl-3,4-hexanediimine (dthdi) used for preparing **1** and **2** was synthesized from 3,4-hexanedione and 4-toluidine. Stoichiometric amounts of ketone and amine were heated in toluene at the refluxing temperature with a Dean−Stark apparatus for the removal of water. The product, a viscous yellow oil, was purified by vacuum distillation. The diimines 4,4′-bis(butoxycarbonyl)-2,2′-bipyridine (BC-bipy) and 4,4′-bis(2-ethylhexyloxycarbonyl)-2,2′-bipyridine (EHC-bipy) were prepared by pertinent literature methods.[11] Diiminosuccinonitrile (disn), bis(1,2-trifluoromethylethene-1,2-dithiolate)nickel (Ni(tfd)$_2$), bis(*semi*-4-benzoylbenzoquinonediimine)nickel (Ni(bbqdi)$_2$), platinum(4,4′-dimethyl-2,2′-bipyridine)(3,4-toluenedithiolate), **8**, and platinum(1,10-phenanthroline)(3,4-toluenedithiolate), **9**, were known compounds and were synthesized by literature

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Scheme 2. Chemical Structures of M(diimine)(dithiolate) **1**−**9**

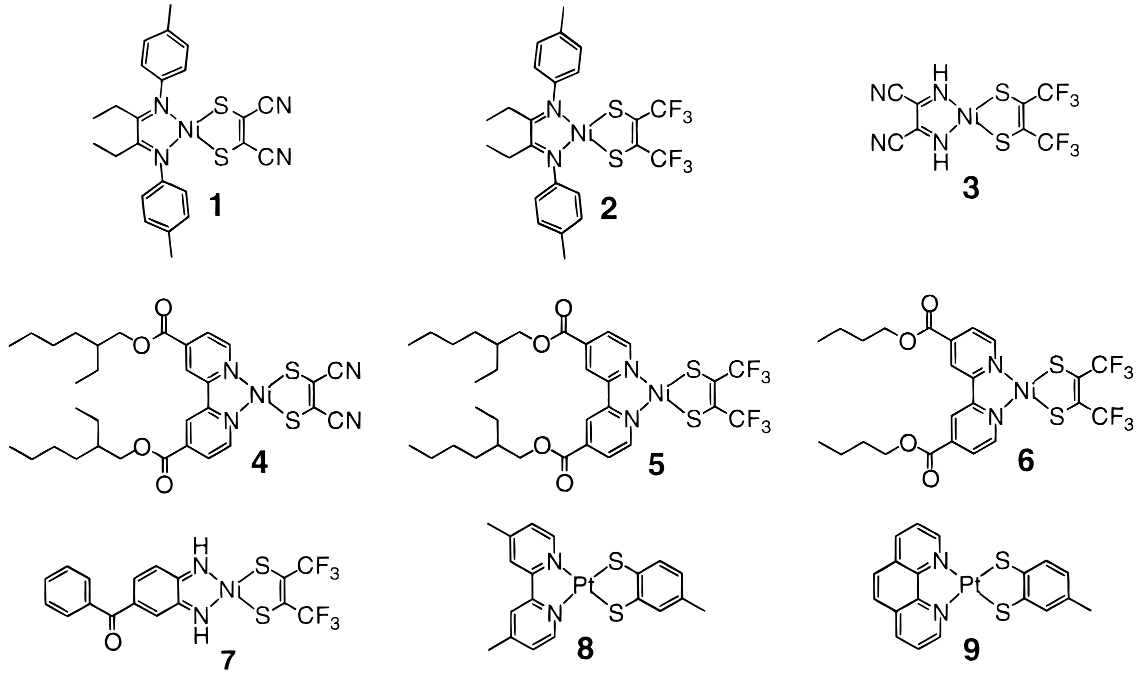

Table 1. UV−Visible Absorption (λ_{max}) of LLCT and Molecular Density of **1**−**5** and **7**−**9**[a]

	ϵ	n	**1**	**2**	**3**	**4**	**5**	**7**	**8**	**9**
DMSO	46.6	1.48	546	615	652	523	541	701	541	556
acetonitrile	37.5	1.34	555	618	688	520	544	701	534	553
DMF	36.7	1.43	555	624	635	520	548	705	550	569
methanol	32.7	1.33	573	644	679	534	564	710	529	×
acetone	20.7	1.36	567	638	669	529	558	709	561	580
2-propanol	18.3	1.38	592	673	692	562	579	724	559	×
DCE	10.4	1.44	627	646	725	555	577	734	556	585
DCM	9.1	1.43	633	650	723	559	581	736	565	583
THF	7.6	1.41	639	660	701	556	583	720	600	619
DME	7.2	1.38	625	655	697	549	576	719	588	610
ethylacetate	6.0	1.37	633	659	701	553	580	717	×	629
chlorobenzene	5.6	1.53	659	675	741	584	607	748	617	634
chloroform	4.8	1.45	651	671	725	583	602	745	589	609
toluene	2.6	1.50	682	696	747	600	641	748	×	653
1,4-dioxane	2.2	1.42	609	696	713	572	591	729	613	628
density (g/mL)			1.34	1.48	1.91	1.32	1.43	1.75	2.12	2.08

[a] ×, insoluble; DCM, dichloromethane; DME, 1,2-dimethoxyethane; DCE, 1,2-dichloroethane; ϵ, dielectric constant;[20] n, refractive index.[20]

methods.[2b,12] Reagent nickel(diammonia)(maleonitrildithiolate) (Ni(NH_3)$_2$(mnt)) was synthesized from disodium maleonitrildithiolate[12c] and nickel(II) chloride in concentrated ammonium hydroxide. Complex Ni(NH_3)$_2$(mnt) was isolated by filtration as an orange solid.

Preparations. Complex 1. dthdi (0.585 g, 0.20 mmol) and Ni(NH_3)$_2$(mnt) (0.466 g, 0.20 mmol) were mixed in acetonitrile (250 mL). The mixture was first stirred at the refluxing temperature for 4 h and continued at room temperature for a further 20 h. The solvent was removed under reduced pressure. The resulting residue was purified by flash column chromatography (4 × 35 cm silica gel, 230−400 mesh) with a mixed solvent starting with 20% up to 60% dichloromethane in hexanes as eluent. The wide purple-blue band on the column containing the product was collected and evaporated. The product was obtained as a dark burgundy solid. Isolated yield = 33% (0.32 g). (Found: C, 58.28; H, 4.84; N, 11.27. $C_{24}H_{24}N_4NiS_2$ requires C, 58.67; H, 4.92; N, 11.40.)

Complex 2. Both dthdi (0.312 g, 1.07 mmol) and Ni(tfd)$_2$ (0.50 g, 0.98 mmol) were mixed in dry dichloromethane (40 mL). The mixture was stirred under nitrogen atmosphere at room temperature for 4 h. The solvent was evaporated and the residue was purified by flash column chromatography (4 × 35 cm silica gel, 230−400 mesh) with a mixed solvent starting with 20% up to 40% dichloromethane in hexanes as eluent. The wide dark blue band was collected and evaporated. The product was obtained as a dark brown solid. Isolated yield = 23% (0.26 g). (Found: C, 49.68; H, 4.11; N, 4.67. $C_{22}H_{24}F_6N_2NiS_2$ requires C, 49.93; H, 4.19; N, 4.85.)

Complex 3. A mixture of disn (0.19 g, 1.79 mmol) and Ni(tfd)$_2$ (0.916 g, 1.79 mmol) was stirred in dry dichloromethane (50 mL). The dark reddish purple solution turned dark blue-green, and a crystalline solid appeared within 30 min. The product was obtained by filtration as a dark green solid. The product isolated in this method was already pure and no further purification was necessary. Isolated yield = 57% (0.40 g). (Found: C, 24.20; H, 0.46; N, 14.05. $C_8H_2F_6N_4NiS_2$ requires C, 24.58; H, 0.52; N, 14.34.)

Complex 4. A mixture of EHC−bipy (0.402 g, 0.86 mmol) and Ni(NH_3)$_2$(mnt) (0.200 g, 0.86 mmol) was first stirred in refluxing acetonitrile (150 mL) for 4 h and continued at room temperature for another 20 h. The solvent was evaporated and a dark brown solid resulted. The product was purified by flash column chromatography (4 × 35 cm silica gel, 230−400 mesh) with a mixed solvent starting

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Table 2. Crystallographic Data and Refinement Details for Complexes **1**, **2**, **3**, **6**, and **7**[a]

	1·2 H_2O	**2**·3H_2O	**3**	**6**	**7**
empirical formula	$C_{24}H_{28}N_4NiO_2S_2$	$C_{24}H_{30}F_6N_2NiO_3S_2$	$C_8H_2F_6N_4NiS_2$	$C_{24}H_{24}F_6N_2NiO_4S_2$	$C_{17}H_{10}F_6N_2NiOS_2$
fw	527.33	631.33	390.93	641.28	495.10
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.734(3)	10.224(2)	7.935(9)	7.814(1)	8.197(2)
b (Å)	13.221(3)	12.529(3)	11.528(2)	10.345(2)	9.462(3)
c (Å)	16.330(3)	13.017(3)	14.450(3)	18.481(8)	12.866(4)
α (deg)		102.49(3)		75.07(2)	77.24(2)
β (deg)	90.18(3)	109.39(3)	91.51(5)	83.97(3)	76.99(2)
γ (degree)		94.08(3)		78.98(2)	74.16(2)
V (Å^3)	2749(1)	1517(1)	1321(2)	1415(1)	921.6(5)
Z	4	2	4	2	2
D_m (g cm^{-3})[a]	1.34	1.48	1.91	1.43	1.75
D_c (g cm^{-3})	1.274	1.382	1.965	1.506	1.784
μ (mm^{-1})	0.883	0.840	1.851	0.905	1.349
2θ limit (deg)	45	45	50	45	45
reflections collected	3781	4222	2493	4008	2608
independent reflections	3591 [R(int) = 0.023]	3949 [R(int) = 0.030]	2317 [R(int) = 0.015]	3683 [R(int) = 0.048]	2405 [R(int) = 0.028]
data [$I > 2\sigma(I)$], parameters	2203, 315	2098, 352	1383, 198	2408, 353	1900, 270
R_1	0.062	0.089	0.037	0.054	0.036
$wR_2(F^2)$	0.219	0.265	0.099	0.166	0.099
goodness-of-fit	1.003	0.944	0.911	0.908	0.996

[a] Determined by flotation method in hexanes/tetrachloromethane/tetrabromomethane.

with 50% dichloromethane in hexanes to pure dichloromethane as the eluent. The wide purple-red band was collected and evaporated. The product was obtained as a dark burgundy solid. Isolated yield = 20% (0.11 g). (Found: C, 58.42; H, 5.88; N, 8.35. $C_{32}H_{40}N_2NiO_4S_2$ requires C, 57.58; H, 6.04; N, 8.39.)

Complex 5. A mixture of EHC-bipy (0.504 g, 1.07 mmol) and Ni(tfd)$_2$ (0.500 g, 0.98 mmol) was stirred in dry dichloromethane (100 mL) at room temperature for 4 h. The solvent was evaporated. The remaining reddish brown solid was purified by flash column chromatography (4 × 35 cm silica gel, 230−400 mesh). The column was eluted with a mixed solvent starting with 20% dichloromethane in hexanes and gradually changing to 80% dichloromethane in hexanes. The wide purple-blue band was collected and evaporated. The product was obtained as a dark burgundy solid. Isolated yield = 25% (0.20 g). (Found: C, 50.85; H, 5.24; N, 3.65. $C_{32}H_{40}F_6N_2NiO_4S_2$ requires C, 51.01; H, 5.35; N, 3.72.)

Complex 6. The complex was synthesized by the method same as for complex **5**, using BC−bpy (0.385 g, 1.07 mmol), Ni(tfd)$_2$ (0.500 g, 0.98 mmol), and dry dichloromethane (100 mL). Isolated yield = 21% (0.13 g). (Found: C, 44.74; H, 3.65; N, 4.26. $C_{24}H_{24}F_6N_2NiO_4S_2$ requires C, 44.95; H, 3.77; N, 4.37.)

Complex 7. A mixture of Ni(bbqdi)$_2$ (0.479 g, 1.00 mmol) and Ni(tfd)$_2$ (0.511 g, 1.00 mmol) was stirred in dry dichloromethane (100 mL) at room temperature. The solution gradually turned to greenish brown. Examined by TLC, the progress of the reaction was relatively slow compared with the reactions of the diimine and Ni(tfd)$_2$. The stirring was continued for another 24 h. The solvent was evaporated and the resulting solid was purified by flash column chromatography (4 × 35 cm silica gel, 230−400 mesh) with a mixed solvent of 40% dichloromethane in hexanes as the eluent. The brown band was collected and evaporated. The product was obtained as a dark brown solid. Isolated yield = 10% (0.10 g). (Found: C, 40.88; H, 1.90; N, 5.32. $C_{24}H_{24}F_6N_2NiO_4S_2$ requires C, 41.24; H, 2.04; N, 5.66.)

Results and Discussion

Synthesis. Due to the flat and rigid structure of the complexes, solubility problems often hampered physical characterizations of M(diimine)(dithiolate) (M = Ni, Pd, Pt) complexes.[2b,3,5a] To enhance the solubility to facilitate the measurement of μ_g and μ_e, an aliphatic substituent such as a 2-ethylhexyl or ethyl group was adopted in designing and synthesizing diimine ligands of complexes **1**, **2**, **4**, and **5**. With the specific diimine synthesized, the preparation procedures of complexes **1**−**6** were rather similar. Complexes possessing CF_3 groups were synthesized from Ni(tfd)$_2$ according to the Miller and Dance method[5a] with an appropriate free diimine in dichloromethane. Complexes with CN substituents were synthesized from the desired diimine and the readily available nickel(diammonia)(maleonitriledithiolato) in acetonitrile.[8e] Complex **7** was prepared via the ligand exchange reaction between two symmetrical nickel complexes Ni(bbqdi)$_2$ and Ni(tfd)$_2$. Except for **3**, most of the complexes obtained from the reaction needed further purification by flash column chromatography, which proved convenient for the complexes due to the enhanced solubility and the intense color of the complexes. However, the complexes seemed to decompose partly during column chromatography (on silica gel, dichloromethane/hexanes). In addition, although stable in nonpolar solvents, complexes **1**−**7** became discolored in polar organic solvents such as dimethyl sulfoxide and *N*,*N*-dimethylforamide within a couple of days. The low isolated yields (<33%) obtained for most of the complexes is attributed in part to the propensity toward decomposition of the product during flash column chromatography. On the other hand, reasonable isolated yields were obtained for the complex **3** (~60%) and Ni(dpphen)(tfd) (~80%).[13] Here, both complexes precipitated out of the solution during the reaction, so the product was isolated by simple filtration and the purification by flash column chromatography was not necessary. Satisfactory analyses were obtained for all complexes **1**−**9**.

Ground-State Dipole Moment (μ_g). Except for **3**, the μ_g values found for complexes **1**−**5** are in a range of 10−17 D. These values are considerably larger than the 8−9 D reported for Pt(diimine)(dithiolate) complexes.[3] Molecules with large μ_g values are uncommon, and there exist only few donor−acceptor substituted chromophores with $\mu_g \geq 15$ D.[14] In addition, the

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[13] Ni(dpphen)(tfd) (dpphen: 4,7-diphenyl-1,10-phenanthroline) was synthesized by a similar procedure to that of **3**. Unpublished results.

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Table 3. λ_{max} (nm), $\Delta\lambda_{max}$ (cm^{-1}), ϵ (10^3 M^{-1} cm^{-1}), μ_g (D, ±10%), and μ_e (D, ±20%) of **1**−**5**, and **7**−**9** in Chloroform; $\Delta\lambda_{max}$ (cm^{-1}) in Toluene and Acetonitrile

	1	**2**	**3**	**4**	**5**	**7**	**8**	**9**
$\lambda_{max}{}^a$	682	696	747	600	641	748	*d*	653
$\lambda_{max}{}^b$	651	671	703	583	602	745	565^e $563^{e,h}$	583^e $583^{e,h}$
$\lambda_{max}{}^c$	585	610	688	520	544	705	534	553
ϵ	6.8	6.9	11.8	6.9	6.2	19.0	6.8^e	7.2^e
$\Delta\lambda_{max}$	2431	2026	1148	2564	2782	816	*d*	2770
μ_g	17	16, 13^f	9^f	14	10, 9^f	4^f	9^e 9^g	9^e 9^g
μ_e	8	10, 5^f	3^f	3	−7, -9^f	0^f	0	−3
$\mu_e - \mu_g$	−9	−6, -8^f	-6^f	−11	−17, -19^f	-4^f	−9	−12

[a] In toluene. [b] In chloroform. [c] In acetonitrile. [d] Insoluble. [e] In dichloromethane. [f] In 1,2-dimethoxyethane. [g] From ref 3.

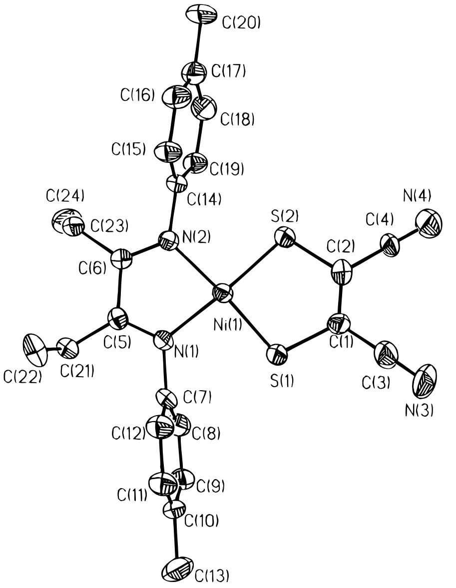

Figure 1. X-ray crystal structure of complex **1** with thermal ellipsoid.

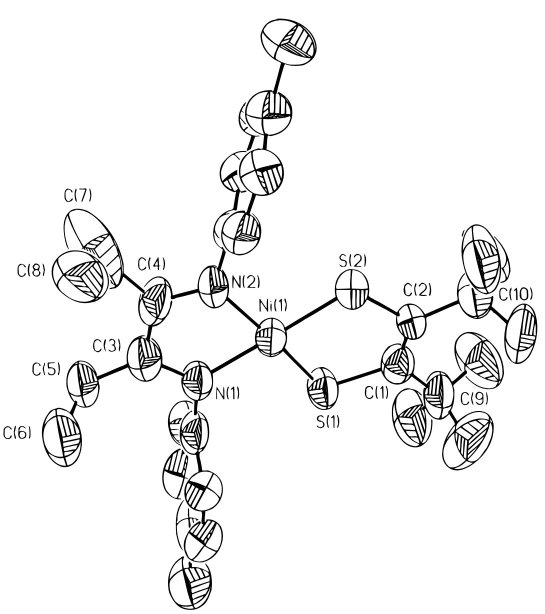

Figure 2. X-ray crystal structure of complex **2** with thermal ellipsoid.

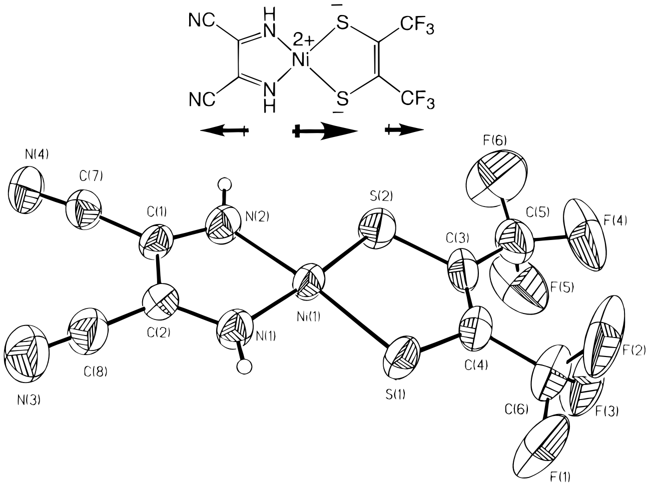

Figure 3. X-ray crystal structure of complex **3** with thermal ellipsoid and analysis of dipole components.

broad μ_g range of **1**−**5** and **7** is in contrast with the essentially constant μ_g for the corresponding platinum complexes.[3] The μ_g values of platinum complexes **8** and **9** were also determined in this study for comparison (Table 3). The μ_g values of the platinum complexes **8** and **9** measured in this work were virtually identical to those of the literature data, validating the procedure of our measurements.

The large and dispersed μ_g values of **1**−**5** and **7** can possibly be rationalized in terms of their molecular and electronic structures. The X-ray single-crystal structure data (see below) suggest a significant charge separation between the cationic metal Ni(II) and the dianionic dithiolate ligand. One would then expect a strong dipole between the charge-separated metal ion and dithiolate ligand. The strength of the acceptor also affects the μ_g of the complexes. For instance, the μ_g values of **1** and **4** are larger than those of **2** and **5**, respectively, due to the stronger electron-accepting power of CN than CF_3. Furthermore, depending on which ligand substituted with the potent acceptor, CF_3 or CN, one may control the magnitude of μ_g either by subtraction or addition to the dipole of the parent complex. Thus, when the dipole of the substituent aligns in parallel to that of the parent molecule, as in **1**, the largest μ_g (17 D) is found among the complexes **1-5** and **7**. When the substituent dipole is antiparallel to the dipole of the parent complex (Figure 3), a small ground-state dipole moment is obtained, as observed for complex **3**. On the other hand, the small μ_g of **7** is difficult to understand just by above simple vectorial dipole addition. In any case, the vectorial approach provides a qualitative picture for the dipole moment, so long as there is not a dramatic change of electronic structure upon the complex formation, as in complex **7**. With an understanding of the bonding structure of **7** (see the section on X-ray crystal structure), the small μ_g of **7** may be rationalized. Nevertheless, the near constant and comparatively small μ_g values found for previous (diimine)(dithiolate)latinum(II) complexes may be qualitatively attributed to the lack of strong dipole substituents.

UV−Visible and Solvatochromism Studies. Like other known M(diimine)(dithiolate) (M = Ni, Pd, Pt) complexes, complexes **1**−**9** all show negative solvatochromic shifts in more than a dozen organic solvents of various polarities (Table 1). However, these complexes can be divided into two groups based on the degree of solvatochromic shift (Table 3), the magnitude of $\mu_e - \mu_g$ (Table 3), λ_{max}, as well as ϵ of LLCT (Figure 6).[15] Complexes **1**, **2**, **4**, **5**, **8**, and **9** tend to exhibit large solvatochromic shifts and sizable dipole moment changes between the

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(15) The apparent two overlapping bands on spectra of **1** and **2** in Figure 6 are due to the vibronic transitions. These vibronic structures with spacing around 1400 cm^{-1} were also observed on low-temperature spectra of Ni(biacetylbisaniline)(mnt).[5f]

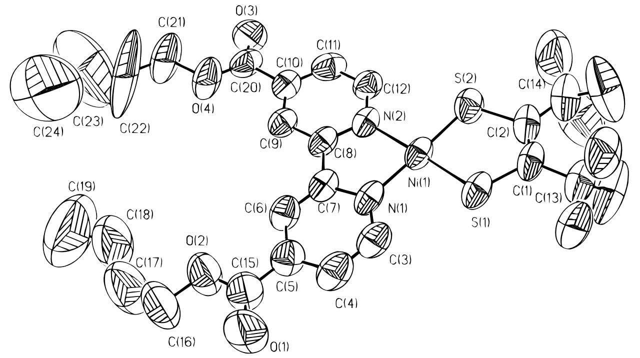

Figure 4. X-ray crystal structure of complex **6** with thermal ellipsoid.

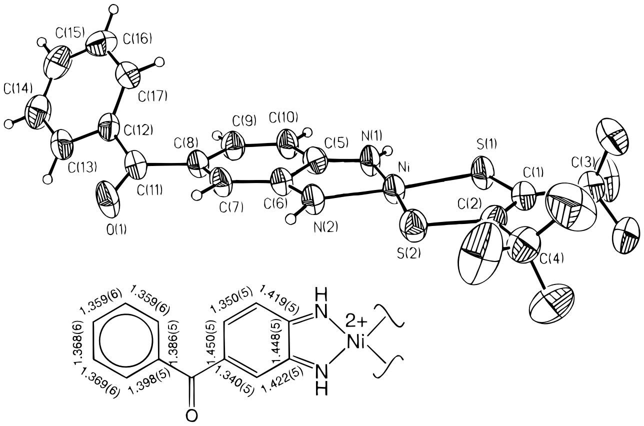

Figure 5. X-ray crystal structure of complex **7** with thermal ellipsoid and selected bond lengths (Å).

excited state (LLCT state) and the ground state. Conversely, complexes **3** and **7** have long absorption wavelength, small |$\mu_e - \mu_g$|, unusually small solvatochromic shift of the LLCT band, and relatively large ϵ. The long absorption wavelength of **3** can be attributed to the strong electron-accepting CN of the diimine (low reduction potential) that diminishes the energy gap between diimine and dithiolate ligands of **3**. For **7**, the extended π^* orbital of benzoquinonediimine in **7** to the longest absorbing wavelength of LLCT among the series. The exceptional optical behavior of **3** and **7** can be further related to their π-delocalization character, to be discussed in the next section.

From the solvatochromism data of **1**−**5** and **7**, **8**, there is a general trend that an aromatic diimine is a more efficient ligand than a nonaromatic diimine for the enhancement of |$\mu_e - \mu_g$|. For instance, **9** containing aromatic 1,10-phenanthrolinediimine has one of the largest |$\mu_e - \mu_g$| among the series and the |$\mu_e - \mu_g$| values of **1** and **2** are smaller than those of **4** and **5**, respectively (Table 3). The extent of solvatochromic shifts is closely related to μ_e and μ_g. Similar observations have been reported for W(CO)$_4$(2,2-bipyridine) and W(CO)$_4$(1,4-diazabutadiene) before.[16] The larger solvatochromic shift found for bipyridine than diazabutadiene complex was attributed to a larger dipolar or polarization interaction of the solvent with the π-system of the former than the later.[16] Herein we provide an alternative and consistent explanation for the observation based on the negative μ_e values found for **5** and **9**. The μ_e values of **5** and **9** are −7 and −3 D, respectively, indicating that the LLCT excited-state dipole is antiparallel to the dipole of the ground state. These opposite dipoles actually reinforce each other in the quantity of $\mu_e - \mu_g$ and hence the largest dipole moment changes −17 and −12 D were found for **5** and **9**, respectively, among the series. The large |$\mu_e - \mu_g$| of **5** and **9** is consistent with the observed large solvatochromic shifts of the LLCT band. The LLCT bands of **5** and **9** exhibit a ∼2800 cm^{-1} shift from acetonitrile to toluene solutions, which is the largest among the series (Table 3 and Figure 7).

Single-Crystal X-ray Structure and π-Delocalization. Structures of complexes **1**−**3**, **6** (an analogue of **5**), and **7** have been determined, providing the ground-state bonding structure of these complexes (Table 4, Figure 1−5). First, the S−C bond lengths are in a range (1.71−1.76 Å), as observed for other metal dithiolate complexes.[17] The data support the above dipole analysis that there is a large dipole originating from the nickel metal and dithiolate ligand of the complex. The crystal structures of **3** and **7** provide insight into the π-bonding structure that was in turn related to the unusual optical and solvatochromic behavior mentioned earlier. The coordination sphere around the nickel ion of **3** or **7** is the most compact among the series: complexes **3** and **7** have shorter Ni−N and Ni−S bond distances compared to other complexes of the series (Table 4). In addition, complexes **3** and **7** have an average C═N distance of 1.30−1.31 Å, longer than the average, 1.29 Å, of both **1** and **2**; the average S−C distance of 1.72−1.73 Å is shorter than 1.74−1.76 Å of **1**, **2**, and **6**. For C═N and C−S bonds, the small differences in bond distances of **3** and **7** compared to the rest of complexes are substantial but not negligible within the experimental error. The bond length differences 0.01−0.02 Å mentioned above are within the range of 0.01−0.03 Å, which is calculated for the bond distortions of Ni(biacetylbisanil)(maleonitriledithiolato) before and after the LLCT.[5f] Therefore, crystal data suggest that **3** and **7** may have greater π-delocalization character (shorter single S−C bonds accompanying longer C═N double bonds) around the metal center than that of other nickel(diimine)(dithiolate) complexes.

The purpose of such bond distance comparison, however, does not imply that both **3** and **7** have a ground-state bonding structure like those of fully π-delocalized bis(*semi*-*o*-benzoquinonediimine)nickel (Ni(*semi*-*o*-bqdi)$_2$) and Ni(tfd)$_2$.[18] The corresponding bond distances C−N of Ni(*semi*-*o*-bqdi)$_2$ and C−S of Ni(tfd)$_2$ are 1.38(2) and 1.71(1) Å, respectively, which are different from those 1.30−1.31 and 1.72−1.73 Å observed for **3** and **7**. The ground-state bonding structure of the present complexes still should be considered as dipositive nickel ion coordinated by one neutral diimine and one dianionic dithiolate ligands, but a certain degree of π-delocalization character of the (N═C−C═N)Ni(S−C═C−S) central unit exists in the case of **3** and **7**. Despite having common π-delocalization character, the origin of π-delocalization is different for **3** and **7**. For **3**, the CN substituent, a potent electron acceptor, lowers the π^*-energies of the corresponding diimine, which in turn favors stronger overlap between diimine and dithiolate and thus stronger delocalization. For **7**, it is the extended π-conjugated diimine with low π^*-energies that results in better coupling between two ligands and hence the delocalization. It is rather evident from the X-ray structure data that the diimine of **7** may

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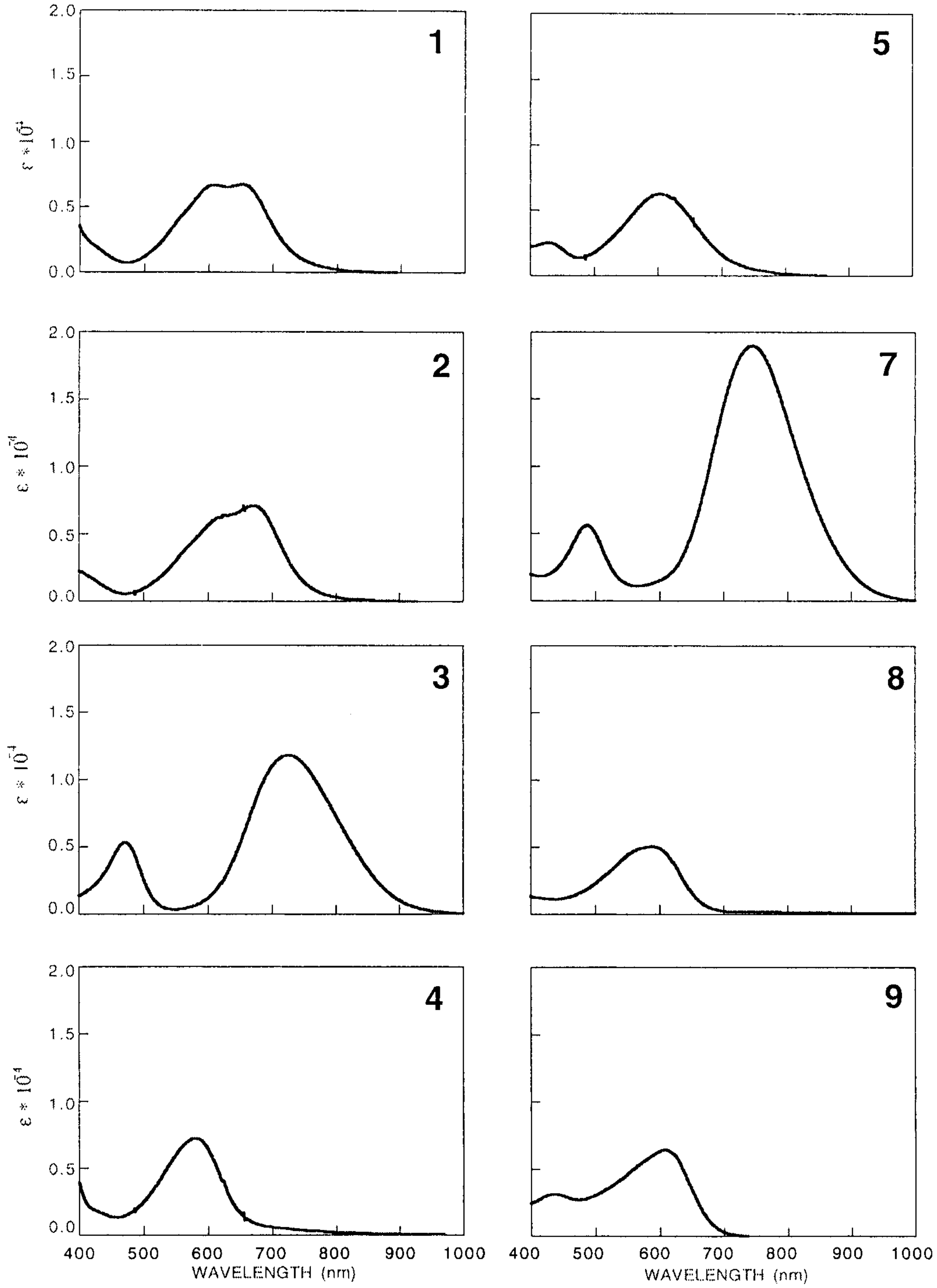

Figure 6. UV−visible absorption spectra of **1**−**5** and **7**−**9** in chloroform.

be better described as a nonaromatic benzoquinonediimine based on the alternative long and short C−C bond distances (Figure 5). The diimine ligand may lower the π^*-energies further through extending the π-conjugation to its benzoyl substituent.

Correlation between π-Delocalization and Optical Properties. It has been known for organic chromophores that conjugated molecules with more π-delocalization exhibit more cyanine-like character.[19] The relatively large extinction coefficient and the small solvatochromic shift of **3** and **7** are common features found for cyanine-like molecules.[20] The cyanine-like character of **3** and **7** may be attributed to the tight bonding of (N=C−C=N)Ni(S−C=C−S) that enhances the π-orbital overlapping among the dithiolate ligand, the nickel cation, and the diimine ligand, and hence the intensity of LLCT. In light of the tight bonding of the (N=C−C=N)Ni(S−C=C−S) central moiety and the small energy difference between the diimine and dithiolate ligands, it is reasonable that **3** and **7** have relatively long wavelength and strong LLCT absorption. The π-delocalization character found for **3** and **7** implies that there is a

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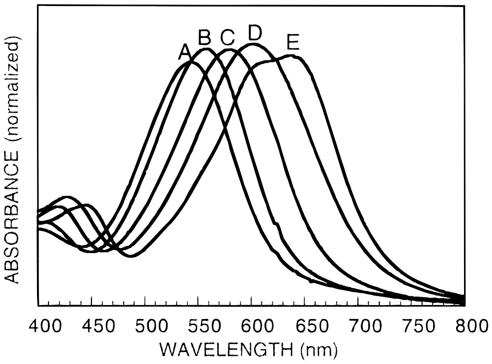
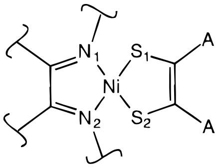


Figure 7. Pronounced solvatochromic shifts observed for the LLCT absorption band for **5** in (A) acetonitrile, (B) acetone, (C) ethyl acetate, (D) chloroform, and (E) toluene.

Table 4. Selected Bond Distances (Å) of **1**−**3**, **6**, and **7**



	N_1−C N_2−C	Ni−N_1 Ni−N_2	Ni−S_1 Ni−S_2	S_1−C S_2−C
1	1.294(10)	1.898(6)	2.131(2)	1.742(8)
	1.295(10)	1.921(6)	2.132(2)	1.729(8)
2	1.269(13)	1.912(8)	2.116(3)	1.773(11)
	1.317(13)	1.899(7)	2.116(3)	1.755(10)
3	1.303(6)	1.861(4)	2.085(1)	1.714(5)
	1.299(5)	1.858(4)	2.089(1)	1.721(5)
6	1.348(7)	1.939(5)	2.122(2)	1.744(6)
	1.359(6)	1.942(4)	2.132(2)	1.733(7)
7	1.310(5)	1.867(4)	2.101(1)	1.734(4)
	1.311(5)	1.846(3)	2.098(1)	1.728(4)

substantial contribution from the resonance form (N−C=C−N)Ni(S=C−C=S) (**C** in Scheme 1) to ground-state structure. The outcome of such contribution greatly reduces the dipole difference between the ground state and the excited state (charge-transferred state) and hence the degree of solvatochromic shift of the LLCT bands. This is consistent with both the small $\mu_e - \mu_g$ and weak solvatochromism observed for **3** and **7**. The π-delocalization character is an unprecedented observation because the resonance form (N=C−C=N)Ni(S−C=C−S) (**A** in Scheme 1) exclusively dominates the ground-state structure of known M(diimine)(dithiolate) (M = Ni, Pd, Pt) complexes.

Conclusions

We have demonstrated that the μ_g and $\mu_e - \mu_g$ of nickel(diimine)(dithiolate) complexes can be both altered significantly by acceptor substituents on either diimine or dithiolate ligand. Two complexes, **3** and **7**, were found to show relatively large absorption intensity and unusually small solvatochromic shift of LLCT bands. On the basis of the single-crystal X-ray structures, the unusual optical and solvatochromic behavior of **3** and **7** is attributed to the π-delocalization of the central (N=C−C=N)Ni(S−C=C−S) unit, which in turn arises from the strong acceptor substituent on the diimine ligand of **3** and the extended π-conjugation of diimine ligand of **7**. According to the measured dipole moment of **5** and **9**, there are antiparallel dipoles in the LLCT excited-state relative to the dipoles in the ground-state. The antiparallel dipoles result in a comparatively large solvatochromic shift of LLCT bands of **5** and **9**. The influence of structures on the molecular dipole and the extent of solvatochromism of nickel(diimine)(dithiolate) complexes is deciphered through this study.

Acknowledgment. This research was supported by the National Science Council of R.O.C. (Grant No. NSC 86-2113-M-001-016 and 88-2113-M-001-052).

Supporting Information Available: Crystallographic data for **1**−**3**, **6**, and **7** and μ_g, ϵ, and n for **1**−**5** and **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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