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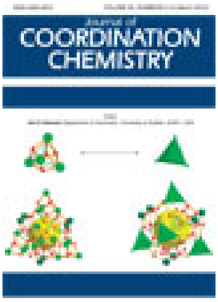

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Syntheses, structures, and properties of Ni(II) complexes with 5,5′-bis(4-halogenphenyl)diazo-dipyrromethane

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Syntheses, structures, and properties of Ni(II) complexes with 5,5′-bis(4-halogenphenyl)diazo-dipyrromethane

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Ni(II) complexes with 5,5′-bis(4-halogenphenyl)diazo-dipyrromethane have been synthesized and characterized by X-ray crystallography. All the complexes have similar crystal structures in which Ni(II) is square-planar by coordinating to two pyrrole and two azo nitrogen atoms. The azo-pyrroles of the ligands can be converted to the hydrazone tautomer after complexing nickel. Moreover, the C–H $\cdots$ Ni interaction played an important role in directing self-assembly of the complexes. The UV-Vis spectra of the complexes showed great difference with the metal complexes of pyrrol-2-imine.

Keywords: Diazo-dipyrromethane; Metal complex; Azo-hydrazone tautomerism; C–H $\cdots$ Ni interaction

1. Introduction

Due to unique redox and optical properties introduced by the azo ($-N=N-$) group [1–4], azoaromatic compounds have received much attention in nonlinear optics, optical storage, and other photoelectric applications. Metal complexes incorporated with azo ligands revealed remarkable electron-transfer properties, photophysical behavior, and biological activities [5–11]. Azobenzene [12–14], azobispyridine [15–18], and phenylazoimidazole [19–23] ligands have been widely studied. Aryl- and hetarylazopyrrole dyes have received much attention because of their significance in advanced materials and devices [24–32]. The 2-azopyrrole is structurally similar with the well-known bidentate pyrrol-2-imine [33–36]; 2-azopyrrole can form complexes with Ni(II) and Cu(II) [37, 38]. Many aryl and hetarylazopyrroles and their metal complexes have been patented as thermal transfer printing dyes and optical recording materials [39–42]. However, compared with pyrrol-2-imine, studies on metal complexes of 2-azopyrrole are limited. Previously, we reported the synthesis and hydrogen-bonded self-assemblies of some 5,5′-bisdiazo-dipyrromethanes (**H_2L^1–H_2L^5**) [43, 44]. Herein, we report the syntheses, structures, and properties of Ni(II) complexes with the 5,5′-bisdiazo-dipyrromethanes (**NiL^1–NiL^5**). The Ni(II) complexes were studied because nickel ions are present in the active sites of large numbers of metalloproteins, as well as having

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catalytic activity. X-ray crystallographic studies reveal that the complexes have similar structures in which Ni(II) is square-planar by coordinating to two pyrrole and two azo nitrogen atoms; C–H ··· Ni interaction plays an important role in directing the self-assemblies of the complexes. UV-Vis spectra of the Ni(II) complexes were also reported.

2. Experimental

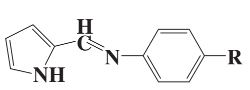
^{1}H NMR spectra were recorded in $CDCl_3$, with TMS as internal standard, on a BRUKER AV400 MHz spectrometer. Analyses of C, H, and N were determined on a Perkin-Elmer 240 elemental analyzer. UV-Vis spectra were obtained with a HITACHI U-3000 spectrophotometer. The 5,5′-bisdiazo-dipyrromethane compounds $\mathbf{H_2L^1}$–$\mathbf{H_2L^5}$ were synthesized as previously reported [43, 44]. All other commercially available reagents were used without purification.

2.1. *Synthesis of NiL^1–NiL^5*

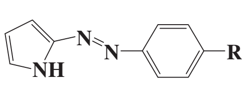
The Ni(II) complexes ($\mathbf{NiL^1}$–$\mathbf{NiL^5}$) were synthesized by the reaction of 5,5′-bisdiazo-dipyrromethane with $NiCl_2$ in methanol in the presence of Et_3N (scheme 1) and purified by column chromatography on silica. The structures of the complexes were characterized by^{1}H NMR spectra and elemental analyses.

$\mathbf{NiL^1}$: yield 83%,^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.53 (t, 6 H, $J = 7.2$ Hz, $-CH_3$), 2.17 (q, 4 H, $J=7.2$ Hz, CH_2), 6.41 (d, 2 H, $J=3.6$ Hz, pyrrole CH), 6.86–6.92 (m, 6H, ArCH), 7.12 (d, 4H, $J=7.2$ Hz, ArCH), 7.30 (d, 2H, $J=3.6$ Hz, pyrrole CH); Elemental analysis: Calcd for $C_{25}H_{24}N_6Ni$ (%): C, 64.27; H, 5.18; N, 17.99. Found: C, 63.95; H, 5.44; N, 17.56.

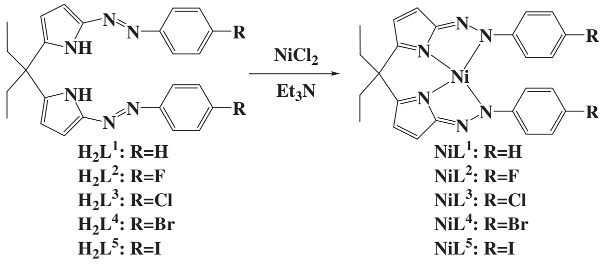
$\mathbf{NiL^2}$: yield 80%,^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.52 (t, 6H, $J=7.2$ Hz, $-CH_3$), 2.17 (q, 4 H, $J=7.2$ Hz, CH_2), 6.42 (d, 2H, $J=4.0$ Hz, pyrrole CH), 6.63 (t, 4H,



pyrrol-2-imine



2-azopyrrole



Scheme 1. Synthesis of $\mathbf{NiL^1}$–$\mathbf{NiL^5}$.

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$J = 8.8$ Hz, ArCH), 7.09 (q, 4H, $J = 4.8$ Hz, ArCH), 7.30 (d, 2H, $J = 4.4$ Hz, pyrrole CH); Elemental analysis: Calcd for $C_{25}H_{22}F_2N_6Ni$ (%): C, 59.67; H, 4.41; N, 16.70. Found: C, 59.77; H, 4.33; N, 17.06.

NiL^3: yield 81%,^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.51 (t, 6H, $J = 7.2$ Hz, $-CH_3$), 2.18 (q, 4H, $J = 7.2$ Hz, CH_2), 6.44 (d, 2H, $J = 4.4$ Hz, pyrrole CH), 6.91 (d, 4H, $J = 8.4$ Hz, ArCH), 7.04 (d, 4H, $J = 8.4$ Hz, ArCH), 7.31 (d, 2H, $J = 4.4$ Hz, pyrrole CH); Elemental analysis: Calcd for $C_{25}H_{22}Cl_2N_6Ni$ (%): C, 56.01; H, 4.14; N, 15.68. Found: C, 55.89; H, 4.20; N, 15.66.

NiL^4: yield 75%,^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.51 (t, 6H, $J = 7.6$ Hz, $-CH_3$), 2.18 (q, 4H, $J = 7.6$ Hz, CH_2), 6.44 (d, 2H, $J = 4.0$ Hz, pyrrole CH), 6.972 (d, 4H, $J = 8.4$ Hz, ArCH), 7.07 (d, 4H, $J = 8.4$ Hz, ArCH), 7.31 (d, 2H, $J = 4.4$ Hz, pyrrole CH); Elemental analysis: Calcd for $C_{25}H_{22}Br_2N_6Ni$ (%): C, 48.04; H, 3.55; N, 13.45. Found: C, 48.41; H, 3.61; N, 13.51.

NiL^5: yield 72%,^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.51 (t, 6H, $J = 7.6$ Hz, $-CH_3$), 2.17 (q, 4H, $J = 7.2$ Hz, CH_2), 6.43 (d, 2H, $J = 4.4$ Hz, pyrrole CH), 6.85 (d, 4H, $J = 8.4$ Hz, ArCH), 7.28 (d, 4H, $J = 8.8$ Hz, ArCH), 7.31 (d, 2H, $J = 4.0$ Hz, pyrrole CH); Elemental analysis: Calcd for $C_{25}H_{22}I_2N_6Ni$ (%): C, 41.76; H, 3.08; N, 11.69. Found: C, 41.47; H, 3.31; N, 11.41.

2.2. *X-ray crystallography studies*

Crystals of **Ni$_2$L^1–NiL^5** were grown by slowly evaporating their solutions in $CHCl_3$/MeOH. X-ray single-crystal diffraction data were collected from a Bruker Apex II CCD diffractometer at room temperature using Mo-Kα radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied (SADABS), and the program SAINT was used for integration of the diffraction profiles [45]. All structures were solved by direct methods with SHELXS and refined by full-matrix least-squares on F^2 with SHELXL of the SHELXTL package [46]. The crystal data are summarized in table 1.

3. Results and discussion

3.1. *Crystal structures*

Crystal structures of **NiL^1–NiL^5** are shown in figure 1. The first common feature of the five complexes is that they all consist of one dianionic ligand and an Ni(II) with square-planar geometry by coordinating to two pyrrole and two azo nitrogen atoms. The structure is similar to a binuclear Ni(II) complex with macrocyclic dipyrromethane Schiff base [47]. Selected bond lengths and dihedral angles are collected in table 2. The Ni(II)–N(azo) bond lengths are longer than those of Ni(II)–N(pyrrole) and also longer than those of the Ni(II)–N(imine) (1.844–1.867 Å) in the literature [48].

Bond distances of N2–N3 and N4–N5 in the complexes are 1.306(7) Å–1.335(5) Å, longer than in the crystals of free ligands (1.264–1.292 Å) [43, 44]. Moreover, distinct changes of the bond distances of the pyrrole rings are also found when compared with the free ligands [43]. The C7–N2, C8–C9, C10–N1, C16–N6, C17–C18, and C19–N5 bonds are shortened (0.03–0.08 Å) showing double bond character, whereas the C7–C8, C9–C10, C16–C17, and C18–C19 bonds are lengthened (0.01–0.03 Å) and show single

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Table 1. Crystal data of $\mathbf{Ni_2L^1}$–$\mathbf{NiL^5}$.

Crystals	$\mathbf{Ni_2L^1}$	$\mathbf{NiL^2}$	$\mathbf{NiL^3}$	$\mathbf{NiL^4}$	$\mathbf{NiL^5}$
CCDC No.	793425	793426	793427	850781	793428
Empirical formula	$C_{25}H_{24}N_6Ni$	$C_{25}H_{22}F_2N_6Ni$	$C_{25}H_{24}Cl_2N_6Ni$	$C_{25}H_{22}Br_2N_6Ni$	$C_{25}H_{22}I_2N_6Ni$
Formula weight	467.21	503.20	536.10	625.02	719.00
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P*2(1)/*c*	*P*21/*c*	*Pbca*	*Pbca*	*Pbca*
Unit cell dimensions (Å,°)					
a	9.3156(17)	12.927(2)	23.615(4)	23.565(4)	23.251(15)
b	13.804(3)	24.785(4)	7.5556(12)	7.6464(14)	7.813(5)
c	17.281(3)	7.3152(13)	26.212(4)	26.582(5)	26.757(17)
α	90	90	90	90	90
β	92.077(4)	101.207(3)	90	90	90
γ	90	90	90	90	90
Volume ($Å^3$), *Z*	2220.7(7), 4	2299.1(7), 4	4676.9(13), 8	4789.7(5), 8	4861(5), 8
Calculated density ($g\,cm^{-3}$)	1.397	1.454	1.523	1.733	1.965
Absorption coefficient (mm^{-1})	0.899	0.886	1.085	4.174	3.366
F(000)	976	1040	2208	2496	2784
Total reflections	10,809	11,609	22,202	22,626	22,466
Unique reflections	3920	4055	4110	4210	4279
Goodness-of-fit on F^2	1.007	1.048	1.041	1.042	1.069
R_1/wR_2 $[I > 2\sigma(I)]$	0.0382/0.0767	0.0254/0.0684	0.0390/0.0807	0.0438/0.1050	0.0436/0.1156
R_1/wR_2 (all data)	0.0914/0.0956	0.0291/0.0707	0.0645/0.0903	0.0611/0.1119	0.0626/0.1416

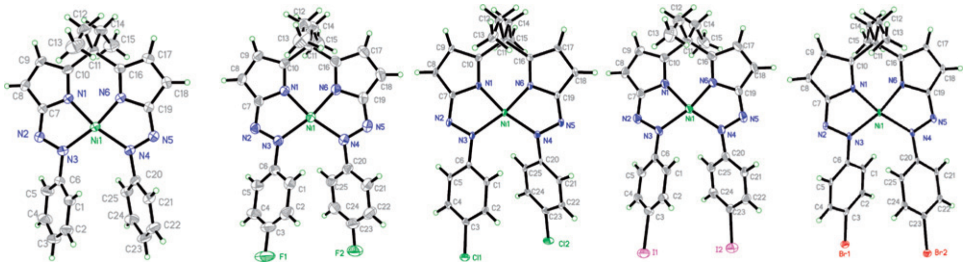

Figure 1. ORTEP diagrams for $\mathbf{NiL^1}$–$\mathbf{NiL^5}$ (from left to right), with the displacement ellipsoids drawn at the 30% probability level.

bond character (table 2). This suggests azo-hydrazone tautomerism of azo-pyrrole after deprotonation as shown in scheme 2. The azo-hydrazone tautomerism has been proposed for the shoulder peak of UV-Vis spectrum of 2-azopyrrole compounds and the lack of vinylation of azopyrrole. Until now, however, no experimental evidence was found. Our result is clear evidence for azo-hydrazone tautomerism of 2-azopyrrole compounds.

The dihedral angles between phenyl rings and adjacent pyrrole rings in the complexes are smaller than in the crystals of free ligands [43] from steric repulsion between the two neighboring phenyl rings. The two ethyl groups are almost vertical to the plane of coordinated Ni(II).

The second feature is that the complexes formed pillar structures through C–H ··· Ni interactions in the crystals of $\mathbf{NiL^2}$–$\mathbf{NiL^5}$ (figure 2) (H ··· Ni distances are 3.10 Å, 3.05 Å, 3.06 Å, and 3.08 Å for $\mathbf{NiL^2}$, $\mathbf{NiL^3}$, $\mathbf{NiL^4}$, and $\mathbf{NiL^5}$, respectively, shorter than the sum of

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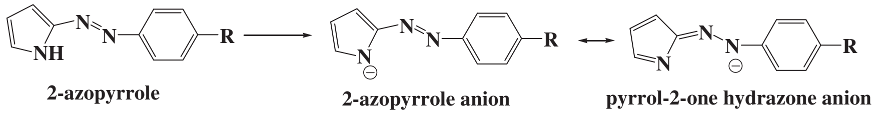
Table 2. Selected bond lengths (Å) and dihedral angles (°) for **NiL^1–NiL^5**.

Selected bond	**NiL^1**	**NiL^2**	**NiL^3**	**NiL^4**	**NiL^5**
Ni–N1(pyrrole)	1.819(3)	1.812(2)	1.814(2)	1.808(3)	1.782(5)
Ni–N3(azo)	1.936(3)	1.930(2)	1.936(2)	1.939(3)	1.897(5)
Ni–N4(azo)	1.940(3)	1.934(2)	1.922(2)	1.939(3)	1.914(5)
Ni–N6(pyrrole)	1.807(3)	1.814(2)	1.812(2)	1.818(3)	1.784(5)
N2–N3	1.321(3)	1.318(2)	1.320(3)	1.335(5)	1.309(7)
N4–N5	1.309(3)	1.308(2)	1.327(3)	1.317(5)	1.306(7)
C6–N3	1.441(4)	1.427(2)	1.426(4)	1.419(5)	1.404(7)
N2–C7	1.348(4)	1.337(2)	1.337(4)	1.331(6)	1.294(8)
C7–C8	1.407(4)	1.406(2)	1.404(4)	1.415(6)	1.398(9)
C8–C9	1.363(5)	1.379(3)	1.376(4)	1.388(6)	1.349(10)
C9–C10	1.414(4)	1.422(2)	1.421(4)	1.429(6)	1.395(9)
C10–N1	1.346(4)	1.336(2)	1.336(4)	1.337(5)	1.314(8)
C7–N1	1.364(4)	1.378(2)	1.385(4)	1.384(5)	1.384(8)
C20–N4	1.432(4)	1.431(2)	1.426(4)	1.414(6)	1.395(8)
N5–C19	1.345(4)	1.343(2)	1.339(4)	1.331(5)	1.305(8)
C19–C18	1.401(5)	1.401(3)	1.408(4)	1.398(6)	1.374(9)
C18–C17	1.364(5)	1.373(3)	1.382(4)	1.383(6)	1.331(10)
C17–C16	1.401(4)	1.421(3)	1.423(4)	1.420(6)	1.394(9)
C16–N6	1.348(4)	1.342(2)	1.338(4)	1.332(6)	1.316(8)
C19–N6	1.371(4)	1.376(2)	1.382(4)	1.391(5)	1.362(8)
Dihedral angle					
Cg1/Cg2	6.8	9.9	9.6	7.9	7.7
Cg1/Cg3	43.6	35.2	28.1	37.7	38.9
Cg2/Cg4	51.1	44.0	38.0	33.2	30.4
Cg3/Cg4	16.2	21.6	23.7	22.8	21.6

Cg1: C7–C10, N1; Cg2: C16–C19, N6; Cg3: C1–C6; Cg4: C20–C25.



Scheme 2. Azo-hydrazone tautomerism of azo-pyrrole after deprotonation.

the van der Waals radii) [49]. Short distances between a hydrogen atom attached to carbon and a metal are mainly observed in square-planar Group VIII complexes [50–53]. These weak X–H···M interactions are important in metal protonation and reactivity, especially when square-planar metal centers are involved [54]. Very recently, C–H···Ni(II) interactions were responsible for the facile formation of homochiral helices of the chiral, neutral, mononuclear (R,R)-, and/or (S,S)-bis(pyrrol-2-ylmethyleneamino)-cyclohexane complexes in crystal lattices [48, 55, 56]. The pillars propagate through C–H···F hydrogen bonds in **NiL^2** (C14–H14B···F1$^{\mathrm{i}}$: 2.52 Å, 3.32 Å, 140°,$^{\mathrm{i}}$:$-1+x$, y,$-1+z$) (figure 2b), C–H···Br hydrogen bonds in **NiL^4** (C13–H13B···Br2$^{\mathrm{ii}}$: 3.05 Å, 3.71 Å, 128°,$^{\mathrm{ii}}$: x, $1/2-y$, $1/2+z$) (figure 2d), and C–H···I hydrogen bonds in **NiL^5** (C15–H15B···I2$^{\mathrm{iii}}$: 3.19 Å, 3.84 Å, 139°,$^{\mathrm{iii}}$: x, $5/2-y$,$-1/2+z$) (figure 2c). However, the C–H···Cl hydrogen bonds were not found in **NiL^3** (figure 2a). The reason may be the slightly different crystal packing of **NiL^3**. None of the halogens was involved in any kind of halogen bonding [57, 58] in the crystal structures of the complexes, whereas the chloride, bromide, and iodide were involved in halogen···π interactions playing an

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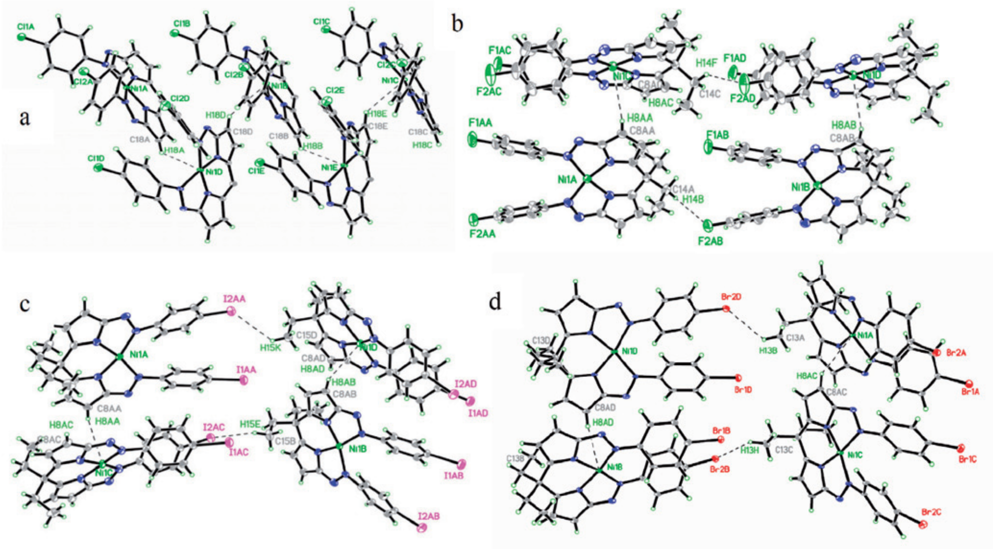

Figure 2. Self-assembly of **NiL^2**–**NiL^5** through C–H $\cdots$ Ni interaction.

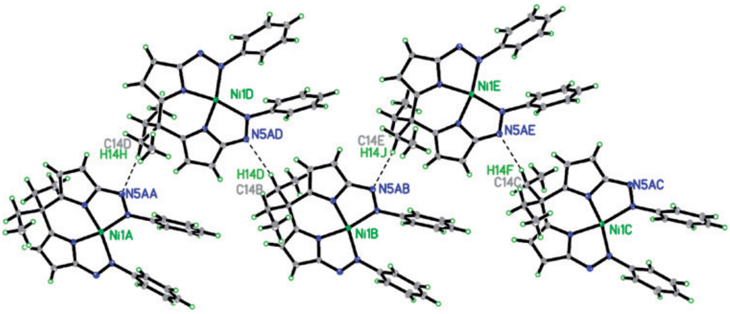

Figure 3. Self-assembly of **NiL^1** through C–H $\cdots$ N interaction.

important role in directing the crystal structures in the crystals of the free ligands [43]. Different from its halide substituted ligands, **NiL^1** forms a 1-D structure through C–H $\cdots$ N hydrogen bonds (C14–H14B $\cdots$ N5^{iv}: 2.55 Å, 3.51 Å, 170°,^{iv}: $3/2-x, -1/2+y, 3/2-z$) (figure 3).

3.2. *^{1}H NMR spectra of Ni$_2$L^1–NiL^5*

^{1}H NMR spectra of **NiL^2** in CDCl$_3$ (figure 4) show disappearance of the NH protons from the free ligand, which means double deprotonation of 5,5′-bisdiazo-dipyrromethane. The downfield shifts of pyrrole CH can be ascribed to coordination caused charge transfer from pyrrole to nickel. The upfield shifts of phenyl CH may result from parallel packing of the two phenyl rings in the complex. The downfield

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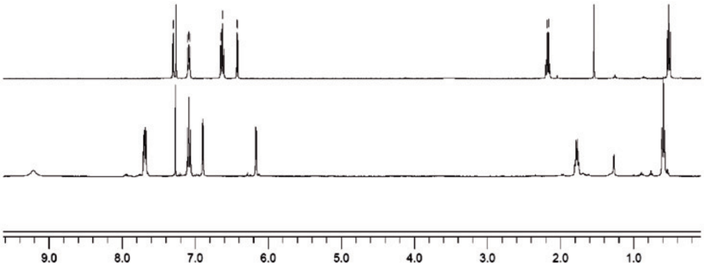

Figure 4. ^{1}H NMR spectra of $\mathbf{H_2L^2}$ (bottom) and $\mathbf{NiL^2}$ (top).

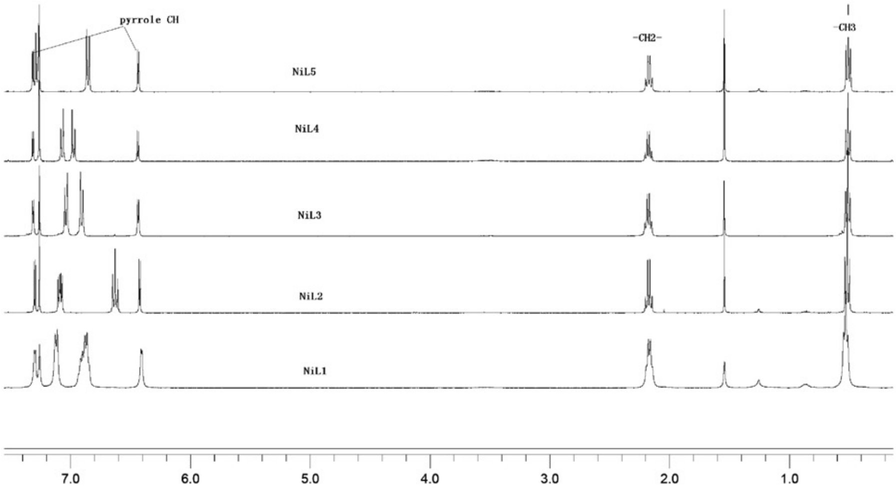

Figure 5. ^{1}H NMR spectra of $\mathbf{NiL^1}$–$\mathbf{NiL^5}$ (from bottom to top).

shifts of –CH_2– and upfield shifts of –CH_3 may be caused by deshielding and shielding from the plane formed by two 2-azopyrroles and Ni(II), respectively. Similar^{1}H NMR spectral changes were found from other four complexes. Comparing the^{1}H NMR spectra of the five complexes, all C–H signals are almost identical except for the phenyl C–H signals which are affected by halogen substituents (figure 5). The^{1}H NMR results are consistent with X-ray crystallographic results and suggests that these metal complexes have same structure in solution and solid states.

3.3. *UV-Vis spectra of H_2L^1–NiL^5*

Absorptions of the ligands and their Ni(II) complexes are listed in table 3. Chloroform solutions of H_2L display an intense broad absorption (380–391 nm) in the UV-Vis spectra, comparable to that of 2-phenylazo-1-vinylpyrrole (383.1 nm) [24] and pyrrole-2-imine [59] but shorter than that of π-resonance enhanced thienylpyrrole azo dyes (473–530 nm) [32] and bisazopyrroles (486–615 nm) [29]. Clearly, it is due to the lack of π-conjugation of dipyrromethane moiety. As for the^{1}H NMR results and crystal

Table 3. Absorption data of L^1–L^5 and **NiL^1–NiL^5** in chloroform and acetonitrile.

Compounds	λ(ε) (nm) in $CHCl_3$	λ(ε) (nm) in CH_3CN
H_2L^1	380.0 (25,700)	–
H_2L^2	384.5 (15,000)	–
H_2L^3	385.0 (22,700)	–
H_2L^4	387.0 (23,100)	–
H_2L^5	391.0 (22,900)	–
NiL^1	394.5 (27,200); 617.5 (6900)	392.0 (26,900); 608.0 (6300)
NiL^2	394.5 (31,700); 618.5 (8000)	392.0 (28,100); 612.0 (6700)
NiL^3	397.5 (39,900); 621.5 (10,500)	392.0 (39,700); 615.0 (10,300)
NiL^4	398.0 (43,200); 621.0 (11,400)	394.0 (37,200); 615.0 (9300)
NiL^5	400.0 (38,800); 622.0 (10,500)	396.0 (37,200); 617.0 (9400)

structures, the UV-Vis spectra of the dark red solutions of **NiL^1–NiL^5** are the same, with the absorption at 394–400 nm and also a relatively weak absorption at 617–622 nm. The weak bond can be assigned to the absorption of the plane formed by N_4 donors and Ni(II), which has enhanced π-resonance and ligand-to-metal charge transfer character. Because of the long-wavelength absorption, **NiL^1–NiL^5** seemed to be candidates for near-infrared materials [29, 60]. The UV-Vis spectra of the complexes showed large bathochromic-shift when compared with metal complexes of pyrrol-2-imine [61], apparently, from the existence of the azo double bond. As shown in table 3, halogen groups and solvent have little effect on UV-Vis spectra of the ligands and Ni(II) complexes.

4. Conclusion

Five Ni(II) complexes with 5,5′-bis(4-halogenphenyl)diazo-dipyrromethane have been synthesized and their structures are characterized by X-ray crystallography. The diazo-dipyrromethane is a new tetradentate N4 ligand which can coordinate by two pyrrole and two azo nitrogen atoms. There are a few crystal structures of metal complexes of azopyrrole in the literature [62, 63]. Our structures also show evidence for azo-hydrazone tautomerism of azo-pyrrole and the role of C–H$\cdots$Ni interaction in directing the crystal structure. UV-Vis spectrum of the complexes reveals that the metal complex of azo-pyrrole has different properties than metal complex of pyrrol-2-imine.

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