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Nickel(II)-dppa-arylazoimidazole Complexes: Synthesis and Detailed Spectroscopic Study[1]

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Abstract—The reaction of $[Ni(dppa)(Cl)_2]$ or $[Ni(dppa)(Br)_2]$ with AgOTf gives $[Ni(dppa)(OTf)_2]$, which then form $[Ni(dppa)(RaaiR)](OSO_2CF_3)_2$ under the action of arylazoimidazole(RaaiR) in a dichloromethane medium [RaaiR' = *p*-R–C_6H_4–N=N–C_3H_2–NN–1-R', (**I–III**), abbreviated as *N,N*'-chelating agent, where N(imidazole) and N(azo) represent N and N', respectively; R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**I**), CH_2CH_3 (**II**), CH_2Ph (**III**), OSO_2CF_3 is the triflate anion]. The ^1H NMR spectral measurements suggest that a bound azoimine is responsible for a number of signals of phenyl protons in the aromatic region. The molecules of the complexes contain a number of different carbon atoms which gives a number of different peaks in the ^{13}C (^1H) NMR spectrum.

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Many authors have investigated modes of nickel(II) coordination to diphosphines **I–III** [16–19], as well as the structures and the spectroscopic properties of the resulting complexes, as these systems are rather attractive for understanding a number of important features of coordination compounds, namely π-bonding, lability and *trans* influence of ligands, and geometry. The molecular self-assembly by non-covalent bonds has emerged as an attractive approach in crystal engineering. There is hardly a compound that has raised more interest than water because of its fundamental importance in chemical processes, biological and other aspects, for example, by stabilizing native conformations of biopolymers, determining the assembly of supramolecular species in solid state or the structure of the medium in gaseous, liquid, and solid states. The key to understanding the behavior of water is precise structural data on various hydrogen-bonded water networks in diverse environments. The syntheses of hetero-*tris*-chelates, $[Ru(bpy)_n(RaaiR')_{3-n}]\cdot(ClO_4)_2$ [bpy = 2,2'-bipyridine; n = 1, n = 2) from the aqua complexes $[Ru(OH_2)_2(bpy)_2]^{2+}$/$[Ru(OH_2)_2(RaaiR')_2]^{2+}$ containing labile reaction centres were reported by Prof. Sinha and co-workers [4–16]. The syntheses of molybdenum bis-chelates containing carbonyl and this ligand reaction centres are reported by Prof. Ankermann and co-workers. Prof. A Chakravorty has developed the chemistry of rhenium compounds with these ligands. In this article I have synthesised a novel series of nickel(II) diphosphinoammine square planar complexes with arylazoimidazole linkage and have charecterised the complexes by CHN analysis, IR and multinuclear NMR spectroscopy and ESI mass spectrometry unfolded.

EXPERIMENTAL

Published methods [1–4] were used to prepare [Ni(dppa)Cl_2/Br_2] and [Ni(dppa)(Cl/$Br)_2$]. All other chemicals and organic solvents used in the work were of the reagent grade (SRL, Sigma Alhrich). The C, H, N elemental analyses were carried out using a Perkin Elmer 2400 CHN instrument. The IR spectra were taken on a JASCO 420 spectrophotometer (using KBr disks, 4000–400 cm^{-1}). The ^1H NMR spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT NMR spectrometer using $SiMe_4$ as the internal reference and $CFCl_3$ as the external ^{19}F standard. Mass spectra were recorded in dry acetonitrile solutions.

Preparation of the complexes, {diphenylphosphinoamine}{1-(ethyl)-2-(phenylazo)imidazole-(nickel(II)} and [Ni(dppa)(HaaiEt)](OTf)$_2$ (IIa). To a dichloromethane colourless solution (15 cm^3) of [Ni(dppa)Cl_2] (0.604 g, 0.1 mmol) a stoichiometric amount of AgOTf (0.520 g, 0.2 mmol) was added and the mixture was filtered off. A dichloromethane solution of 1-(ethyl)-2-(phenylazo)imidazole (0.190 g, 0.1 mmol) and one of the other ligands, HeaaiMe

[1] The text was submitted by the author in English.

(0.0186 g, 0.1 mmol, **Ia**), MeaaiMe (0.020 g, 0.1 mmol, **Ib**), ClaaiMe (0.0220 g, 0.1 mmol, **Ic**), MeaaiEt (0.0214 g, 0.1 mmol, **IIb**), ClaaiEt (0.0235 g, 0.1 mmol, **IIc**), HaaiBz (0.0262 g, 0.1 mmol, **IIIa**), MeaaiBz (0.0276 g, 0.1 mmol, **IIIb**), or ClaaiBz (0.0297 g, 0.1 mmol, **IIIc**) was added drowse to this filtrate, and the mixture was stirred at 343–353 K for 4 h. The resulting solution was concentrated (4 cm^3) and kept in a refrigerator for 1 h. The addition of hexane to the above orange solution gives a precipitate which was separated by filtration, washed thoroughly with hexane to remove an excess ligand, and then dried in vacuo with pumping down overnight. Analytically pure complexes were obtained. Yield 70–80%.

[Ni(dppa)(HaaiEt)](OTf)$_2$ (IIa). IR: ν(C=C) 1610 cm^{-1}, ν(N=N) 1300 cm^{-1}, ν(C=N) 1560 cm^{-1}, ν(dppa) 1102, 755, 695 cm^{-1}, ESI–MS: 942.7 (M^+); ^{1}H NMR ($CDCl_3$): 7.59 d, (7,11-H, J = 5Hz), 7.29 d (8,10-H, J = 5.3 Hz), 7.023–7.020 (20H, Ph of dppa), 7.28 m, (4,5-H), 7.30 d.d (9-H), 4.29 q (Et, J = 5.3 Hz), 2.19 s (Et); ^{13}C NMR ($CDCl_3$) : 132.99 (C^6), 132.69 (C^2), 131.88 (C^7), 131.00 (C^8), 130.84 (C^9), 130.61 (C^4), 130.49 (C^5), 129.14, 128.83, 128.80, 123.3 (24C, Ph of dppa). $[C_{36}H_{34}N_5NiP_2](OSO_2CF_3)_2$. Found, %: C 48.4, H 3.61, N 5.9. Calculated, %: C: 48.4, H: 3.61, N: 5.9.

[Ni(dppa)(MeaaiEt)](OTf)$_2$ (IIb). IR: ν(C=C) 1610 cm^{-1}, ν(N=N) 1330 cm^{-1}, ν(C=N) 1570 cm^{-1}, ν(dppa) 1102, 750 cm^{-1}, ESI–MS: 956.7 (M^+); ^{1}H NMR ($CDCl_3$): 7.5 d (7,11-H, J = 6 Hz), 7.24 d (8,10-H, J = 5.3 Hz), 7.02–7.02 (20H, Ph of dppa), 7.28 m (4,5-H), 1.33 s (9 Me), 4.2 q (Et, J = 5 Hz), 2.09 s (Et); ^{13}C NMR ($CDCl_3$): 132.9 (C^6), 132.6 (C^2), 131.8 (C^7), 131.0 (C^8), 130.8 (C^9), 130.6 (C^4), 130.4 (C^5), 129.14, 128.83, 128.80, 123.3 (24C, Ph of dppa). $(C_{37}H_{36}N_5NiP_2]\cdot(OSO_2CF_3)_2$. Found, %: C 48.94, H 3.76, N 5.9. Calculated, %: C 48.7, H 3.6, N 5.9.

[Ni(dppa)(ClaaiEt)](OTf)$_2$ (IIc). IR: ν(C=C) 1610 cm^{-1}, ν(N=N) 1330 cm^{-1}, ν(C=N) 1580 cm^{-1}, ν(dppa) 1102, 695 cm^{-1}, ESI–MS: 976.7 (M^+); ^{1}H NMR ($CDCl_3$): 7.59 d (7,11-H, J = 5Hz), 7.29 d (8,10-H, J = 5.3 Hz), 7.023-7.02 (20H, Ph of dppa), 7.28 m (4,5-H), 4.29 q (Et, J = 5.3 Hz), 2.19 s (Et); ^{13}C NMR ($CDCl_3$): 132.99 (C^6), 132.69 (C^2), 131.88 (C^7), 131.00 (C^8), 130.84 (C^9), 130.61 (C^4), 130.49 (C^5), 129.14, 128.83, 128.80, 123.3 (24C, Ph of dppa). $[C_{36}H_{33}N_5NiClP_2]\cdot(OSO_2CF_3)_2$. Found, %: C 46.7, H 3.41, N 5.7. Calculated, %: C: 46.4, H: 3.41, N: 5.9.

[Ni(dppa)(HaaiMe)](OTf)$_2$ (Ia). IR: ν(C=C) 1630 cm^{-1}, ν(N=N) 1340 cm^{-1}, ν(C=N) 1550 cm^{-1}, ν(dppa) 1102, 755 cm^{-1} ESI–MS: 928.7 (M^+); ^{1}H NMR ($CDCl_3$) : 7.5 d (7,11-H, J = 5Hz), 7.2 d (8,10-H, J = 5 Hz), 7.02–7.02 (20H, Ph of dppa), 7.2m (4,5-H), 7.30 d.d (9-H), 1.99 s (Me); ^{13}C NMR ($CDCl_3$): 132.99 (C^6), 132.6 (C^2), 131.8 (C^7), 131 (C^8), 130.4 (C^9), 130.1 (C^4), 130.9 (C^5), 129.1, 128.8, 128.8, 123.3 (24C, Ph of dppa). $[C_{35}H_{32}N_5NiP_2](OSO_2CF_3)_2$. Found, %: C 48.4, H 3.6, N 5.9, Calculated, %: C 48.4, H 3.6, N 5.9.

[Ni(dppa)(MeaaiMe)](OTf)$_2$ (Ib). IR: ν(C=C) 1607 cm^{-1}, ν(N=N) 1305 cm^{-1}, ν(C=N) 1566 cm^{-1}, ν(dppa) 1102, 755 cm^{-1}, ESI–MS: 942.7 (M^+); ^{1}H NMR ($CDCl_3$): 7.5 d (7,11-H, J = 5Hz), 7.2 d (8,10-H, J = 5.3 Hz), 7.023–7.020 (20H, Ph of dppa), 7.28 m (4,5-H), 1.30 s (9Me), 1.99 s (Me); ^{13}C NMR ($CDCl_3$): 132.99 (C^6), 132.69 (C^2), 131.88 (C^7), 131.00 (C^8), 130.84 (C^9), 130.61 (C^4), 130.49 (C^5), 129.14, 128.83, 128.80, 123.3 (24C, Ph of dppa). $[C_{36}H_{34}N_5NiP_2]\cdot(OSO_2CF_3)_2$. Found, %: C 48.4, H 3.61, N 5.9, Calculated, %: C: 48.4, H: 3.61, N: 5.9.

[Ni(dppa)(ClaaiMe)](OTf)$_2$ (Ic). IR: ν(C=C) 1610 cm^{-1}, ν(N=N) 1320 cm^{-1}, ν(C=N) 1590 cm^{-1}, ν (dppa), 1102, 755, 695 cm^{-1}, ESI–MS: 963.7(M^+); ^{1}H NMR ($CDCl_3$) : 7.9 d (7,11-H, J = 5Hz), 7.2 d (8,10-H, J = 5 Hz), 7.02–7.02 (20H, Ph of dppa), 7.21 m (4,5-H), 1.89 s (Me); ^{13}C NMR ($CDCl_3$): 132.9 (C^6), 132.9 (C^2), 131.8 (C^7), 131.0 (C^8), 130.8 (C^9), 130.6 (C^4), 130.4 (C^5), 129.1, 128.8, 128.8, 123.3 (24C, Ph of dppa). $[C_{35}H_{31}N_5NiClP_2](OSO_2CF_3)_2$. Found, %: C 43.6, H 3.2, N 5.8, Calculated, %: C 43.4, H 3.21, N 5.9.

[Ni(dppa)(HaaiBz)](OTf)$_2$ (IIIa). IR: ν(C=C) 1620 cm^{-1}, ν(N=N) 1350 cm^{-1}, ν(C=N) 1520 cm^{-1}, ν(dppa) 1102, 755 cm^{-1}, ESI–MS: 1004.7(M^+); ^{1}H NMR ($CDCl_3$): 7.5 d (7,11-H, J = 5Hz), 7.22 d (8,10-H, J = 5Hz), 7.02–7.02 (20H, Ph of dppa), 7.25 m (4,5-H), 7.3 d.d (9-H), 5.09 q (Bz, J = 5 Hz), 7.19–7.2 (Bz); ^{13}C NMR ($CDCl_3$): 132.9 (C^6), 132.6 (C^2), 131.8 (C^7), 131.0 (C^8), 130.8 (C^9), 130.6 (C^4), 130.4 (C^5), 129.14, 128.83, 128.80, 123.3 (24C, Ph of dppa). $[C_{41}H_{36}N_5NiP_2]\cdot(OSO_2CF_3)_2$. Found, %: C 48.9, H 3.6, N 5.6. Calculated, %: C 48.4, H 3.6, N 5.5.

[Ni(dppa)(MeaaiBz)](OTf)$_2$ (IIIb). IR: ν(C=C) 1630 cm^{-1}, ν(N=N) 1330 cm^{-1}, ν(C=N) 1550 cm^{-1}, ν(dppa) 1102, 755 cm^{-1}, ESI–MS: 1018.7 (M^+); ^{1}H NMR ($CDCl_3$): 7.59 d (7,11-H, J = 5Hz), 7.29 d (8,10-H, J = 5 Hz), 7.02–7.02 (20H, Ph of dppa), 7.28 m (4,5-H), 1.8 s (9Me), 5.19 m (Bz, J = 5 Hz), 7.1–7.2 (Bz); ^{13}C NMR ($CDCl_3$) : 132.9 (C^6), 132.6 (C^2), 131.8 (C^7), 131.0 (C^8), 130.8 (C^9), 130.1 (C^4), 130.4 (C^5),

129.1, 128.83, 128.8, 123.3 (24C, Ph of dppa). $[C_{42}H_{38}N_5NiP_2](OSO_2CF_3)_2$. Found, %: C 49.5, H 3.7, N 5.5. Calculated, %: C: 49.4, H: 3.71, N: 5.5.

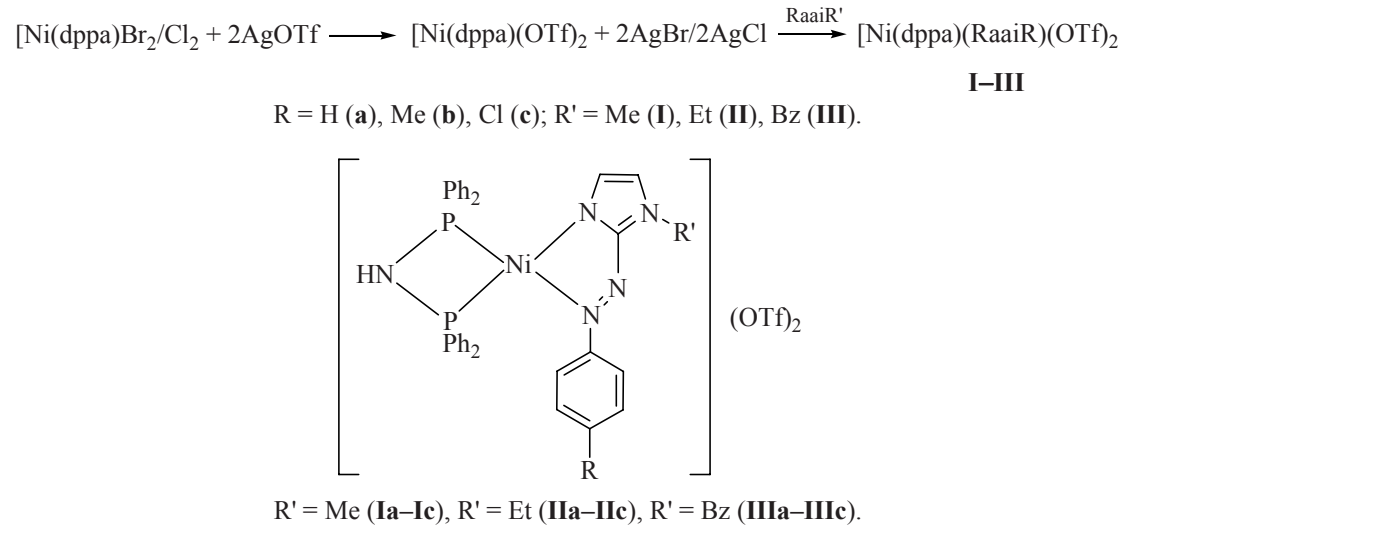
[Ni(dppa)(ClaaiBz)](OTf)$_2$ (IIIc). IR: ν(C=C) 1660 cm^{-1}, ν(N=N) 1300 cm^{-1}, ν(C=N) 1560 cm^{-1}, ν(dppa) 1102, 755, 695 cm^{-1}, ESI–MS: 1039.7 (M^+); ^{1}H NMR ($CDCl_3$): 7.59 d (7,11-H, J = 5Hz), 7.29 d (8,10-H, J = 5 Hz), 7.02–7.02 (20H, Ph of dppa), 7.28 m (4,5-H), 5.29 m (Bz, J = 5 Hz), 7.1–7.2 (Bz); ^{13}C NMR ($CDCl_3$): 132.9 (C^6), 132.69 (C^2), 131.88 (C^7), 131.00 (C^8), 130.84 (C^9), 130.61 (C^4), 130.49 (C^5), 129.1, 128.8, 128.8, 123.3 (24C, Ph of dppa). $[C_{41}H_{36}N_5NiClP_2](OSO_2CF_3)_2$. Found, %: C 47.3, H 3.51, N 5.4, Calculated, %: C 47.4, H 3.5, N 5.4,

The reactions of [Ni(dppa)(Cl)$_2$] or [Ni(dppa)(Br)$_2$] with AgOTf gives [Ni(dppa)(OTf)$_2$], which then gives [Ni(dppa)(RaaiR)] under the action of arylazo-imidazole(RaaiR) in a dichloromethane medium, (**I–III**), [RaaiR' = *p*-R-C_6H_4-N=N-C_3H_2-NN-1-R', abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**I**), CH_2CH_3 (**II**), CH_2Ph (**III**), OSO_2CF_3 is the triflate anion, dppa = diphenylphosphinoammine]. All these complexes were obtained with very high yields (the scheme, nearly 75 %). All these nine diphosphines have an yellow to orange color. The compositions of all the complexes were proved by the CHN elemental analysis and the complexes were characterized by multinuclear NMR [^{1}H, ^{13}C(H), ^{31}P(H), ^{19}F(H)] and IR, ESI–MS spectroscopy data.

The IR spectra of the [Ni(dppa)(RaaiR)](OTf)$_2$ complexes show the 1:1 correspondence to the spectra of the dichloro and dibromo analogues, except for the appearance of intense stretching bands at 1600–1650 and 1300–1350 cm^{-1} with a concomitant loss of ν(Ni–Cl) or ν(Ni–Br) at 380–340 cm^{-1}. They are assigned to ν(C=C) and ν(N=N) appearing near 1600 and 1300 cm^{-1}, respectively. Other important frequencies are ν(dppa) at 1510–1520, 950–960 and 790–810 cm^{-1} along with weak bands at 1070 and 1072 cm^{-1}.

The ESI mass spectrum of a MeCN solution in the positive ion mode is structurally enlightening. The data for each molecular ion **I–III** are given in the experimental section.

The ^{1}H NMR spectra of complexes **I–III** were unambiguously assigned (measured in $CDCl_3$) by comparing with the data of [Ni(dppa)(Cl)$_2$] and the free ligand dppa. The aromatic part shows a broad peak mainly in the 7.22–7.66 ppm range for the phenyl protons of the diphosphine ligands and also a sharp peak near 4 ppm due to the ethyl substitution on RaaiR group. Complexes **Ic, IIc,** and **IIIc**, show a broad peak at 5.6–5.8 ppm from CH_2 of the benzyl ring, whereas complexes **Ib, IIb,** and **IIIb** show peaks near 1.6 from the methyl group of RaaiEt. The methylene signal of [Ni(dppa)(RaaiCH$_2$CH$_3$)](OTf)$_2$, 1-CH_2–(CH_3), exhibit a complex splitting pattern including the chemical signals of –CH_2 protons at ca. 4.8 and 4.9 ppm along with two overlapping triplet signals of –CH_3 group at 1.68, 1.73 ppm for **IIa**; 1.67, 1.70 ppm for **IIb**, and 1.73, 1.70 ppm for **IIc**. Similarly the methylene



protons of 1-CH_2–(Ph) of [Ni(dppa)(RaaiCH$_2$Ph)]·$(OTf)_2$ show two pairs of *AB* type quartets in the range from 5.5 to 5.9 ppm. The signal splitting can result from a combined effect of a restricted rotation on the ligand coordinated to the metal center and the geometrical perturbation due to symmetry violation.

The ^{19}F{^{1}H}NMR spectra of all the complexes, [Ni(dppa)(RaaiR)]$(OTf)_2$ (measured in $CDCl_3$), show a sharp peak of the triflate ion near –78 ppm.

The ^{13}C–{^{1}H} NMR spectra (measured in $CDCl_3$) provide a direct information about the carbon skeleton of the molecules. Various resonant peaks are assigned to certain carbon atoms of the nine complexes, the data are given in the experimental section. The signals of carbon atoms next to the nitrogen atom are upfield shifted due to an increased electron density resulting from the presence of the electronegative nitrogen atom and π-electron delocalisation in the magnetic environment. The signals of the non-protonated carbon atoms at dppa are shifted to the farthest downfield in the spectrum affected by the magnetic interaction of bulky phenyl rings environment. The methylene carbon signal of [Ni(dppa)(RaaiCH$_2$CH$_3$)]$(OTf)_2$, 1-CH_2–(CH_3), exhibits the chemical shift near ca. 40.8 ppm for –CH_2 protons along with –CH_3 group near 20.68, 21.73 ppm for **IIa**; 21.67, 21.70 ppm for **IIb** and 21.73, 21.70 ppm for **IIc**. Similarly the methylene carbons of 1-CH_2–(Ph) resonance near 46 ppm lies in a higher field in all three complexes **IIIa–IIIc** than the previous signal, which is attributable to the presence of π-conjugated phenyl ring.

In conclusion it may be noted that this work describes the isolation of a novel series of nickel(II) arylazoimidazole complexes with a diphenylphosphino link and their spectral and elemental characterization. The ^{1}H NMR study are indicative of the presence of azoimine and dppa linkage and the solution conformation of the azoimine moiety. The methylene signal, 1-CH_2–(CH_3), exhibit a complex splitting pattern. The chemical shifts are ca. 4.8 and 4.9 ppm along with two overlapping triplet signals at 1.68, 1.73. The ^{19}F {^{1}H}NMR points to the presence of the triflate ion. The ^{13}C (^{1}H)NMR gives the carbon skeleton in the solution phase.

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