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Synthesis and characterization of nickel-, palladium- and platinum(II) complexes of three *o,o'*-dihydroxydiarylazo dyes: Determination of the coordination geometry of this comprehensive series of tridentate diaryl dye complexes by combining results from NMR and X-ray experiments with theoretical *ab initio* calculations

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Abstract

The syntheses of the square-planar platinum(II) complexes [Pt(L)(tba)] (L = 5,5'-dichloro-2,2'-dihydroxyazobenzenate (dhab), (5-chloro-2-hydroxyphenylazo)-3-oxo-N-phenylbutanamidate (hpab) or (5-chloro-2-hydroxyphenylazo)-2-naphtholate (hpan) and (tba) = tributylamine) is reported, together with those of the complete set of analogous complexes [M(L)(py)] (M = nickel(II), palla-dium(II), platinum(II) and (py) = pyridine).

The coordinating nitrogen has been assigned to the azo-nitrogen attached to the 5-chloro-2-hydroxyphenyl substituent in both [Ni(h-pab)(py)] and [Pt(hpan)(tba)] by single crystal X-ray diffraction methods. It has been established that complexes with different group 10 metals are *iso*-structural by isomorphology of the crystals as determined by X-ray powder diffraction studies on the complexes containing pyridine in the fourth coordination site.

Furthermore, we present a method to determine the coordination geometry by comparison of calculated ¹³C chemical shifts for possible coordination modes optimized by *ab initio* methods with experimentally measured ¹³C chemical shifts. © 2006 Elsevier B.V. All rights reserved.

Keywords: o,o'-dihydroxydiarylazo dye complexes; Group 10 metals; X-ray crystal structures; ab initio; NMR

1. Introduction

Since it was firmly established by single crystal X-ray crystallography [1-3] that only one of the two azo-nitro-

gens is coordinated to the central metal atom in the commercially important tridentate diarylazo dye complexes, and that a different coordinating nitrogen affects the colouring properties, several attempts have been made to find methods for assignment of the ligating azo-nitrogen in unsymmetrically substituted $o_{,o'}$ -dihydroxydiarylazo-complexes (N_{α}-N_{β}-isomerism), and to describe the factors determining this type of isomerism.

Very few unambiguous coordinating nitrogen assignments have been made, which should be compared to the

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large number of complexes reported [1,4–16]. In order to overcome the solubility problem and facilitate the full assignment [17] of the ¹³C-spectra by heteronuclear NMR correlation techniques, a number of soluble square planar platinum complexes have been designed and synthesized.

Mono anionic octahedral chromium(III)- and cobalt (III) complexes with two $o_{,o'}$ -dihydroxy-diarylazo ligands would be expected to exist in six different isomers, one meridional and five facial [2,18]. It has been found [19-21] that the type of isomer formed is determined by the resulting angular strain of the chelate rings. It is generally stated that tridentate diarylazo ligands, which form one five-membered and one six-membered chelate ring with the central metal atom, coordinate in the meridional mode, while tridentate diaryl-azo ligands forming two annelated six-membered chelate rings form facially coordinated complexes. The evidence for this assumption is largely the number of isomers formed and separated by chromatography. The present study describes square planar complexes of three tridentate $o_{,o'}$ -dihydroxydiarylazo ligands with nickel, palladium and platinum, thus avoiding the ambiguities of coordination geometry and enabling studies of N_{α} -N_β-isomerism.

Analogous nickel(II), palladium(II) and platinum(II) complexes with pyridine in the fourth coordination site should be isostructural, if they exhibit the same N_{α} - N_{β} -isomerism. Isostructural complexes may form isomorphous crystals [22], and accordingly the three series of analogous complexes (each series containing three complexes with different metal ion but identical diazo ligand) were studied using X-ray powder diffraction.

o,o'-Dihydroxydiarylazo compounds may exist as tautomers. Hintermaier *et al.* [15] discuss the possibility that a "keto-hydrazone" coordination plays a role in a Pd complex of an azonaphthalene derivative, a question which has been addressed.

Ab initio DFT calculations [23–26] may be used both to obtain realistic structures [27–30] and NMR chemical shifts [28,29,31–34]. ¹³C chemical shifts have previously been suggested as a way of determining which nitrogen is ligating [17]. In order to support this conclusion, further *ab initio* calculated and experimental ¹³C chemical shifts have been compared for [Ni(hpab)py], the structure of which has been determined by X-ray crystallography and also calculated correctly.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and were used as received unless otherwise stated. Potassium tetrachloroplatinate and palladium(II) chloride were obtained from Johnson Matthey, England. Hexaaquanickel(II) chloride, sodium nitrite, sodium carbonate, sodium hydroxide, hydroxylammonium chloride, copper(II) sulfate pentahydrate, 5-chloro-2-hydroxyaniline, acetoacetic acid anilide, 2-naphthol, hydrochloric acid (37%), ammonia (25%), chloroform, pentane and silica gel 60 F_{254} TLC plates were from Merck, Germany. Pyridine, dimethylsulfoxide and tributylamine were from Fluka AG, Switzerland. Deionized water (cond. <2 μ S/cm) was used without further purification.

2.2. Preparations

2.2.1. 5,5'-Dichloro-2,2'-Dihydroxyazobenzene ($dhabH_2$)

dhabH₂ was made by a coupling reduction in a freshly prepared 5-chloro-2-hydroxyphenyldiazonium-copper(I) complex according to the method of Freeman et al. [35] using 14.5 g (0.10 mol) of 5-chloro-2-hydroxyaniline for the diazonium mixture. Purification was achieved through treating a solution of the product and sodium methanolate in methanol with activated carbon after which precipitation was accomplished by neutralization with aqueous hydrochloric acid. Yield of the pure compound (6.9 g, 49%). (*Anal.* Calc. for C₁₂H₈Cl₂N₂O₂: C, 50.91; H, 2.85; N, 9.89. Found: C, 51.12; H, 2.87; N, 9.79%).

2.2.2. 2-(5-Chloro-2-hydroxyphenylhydrazo)-3-oxo-N-phenylbutanamide (hpabH₂)

hpabH₂ was prepared by diazonium coupling of the in situ prepared 5-chloro-2-hydroxyphenyldiazoniumchloride to 8.85 g (0.05 mol) of acetoacetic anilide in alkaline aqueous solution [36] using 7.23 g (0.05 mol) of 5-chloro-2-hydroxyaniline for the diazonium mixture. Recrystallisation from ethanol (6.7 g, 77%). (*Anal.* Calc. for C₁₆-H₁₄ClN₃O₃: C, 57.93; H, 4.25; N, 12.69. Found: C, 57.88; H, 4.19; N, 12.65%.)

2.2.3. 2-(5-Chloro-2-hydroxyphenylazo)-2-naphthol (hpanH₂)

hpanH₂ was prepared by diazonium coupling of the in situ prepared 5-chloro-2-hydroxyphenylazonium-chloride to 7.16 g (0.05 mol) of 2-naphthol in alkaline aqueous solution [37] using 7.23 g (0.05 mol) of 5-chloro-2-hydroxyaniline for the diazonium mixture. Purification as for dhabH₂ (9.2 g, 62%). (*Anal.* Calc. for C₁₆H₁₁ClN₂O₂: C, 64.33; H, 3.71; N, 9.38. Found: C, 64.14; H, 3.73; N, 9.32%.)

2.2.4. (5,5'-Dichloro-2,2'-dihydroxyazobenzenate)pyridinenickel(II) ([Ni(dhab)(py)])

[Ni(dhab)(py)] was prepared by the dropwise addition of a solution of 0.71 g (3.0 mmol) of hexaaquanickel chloride in 15 ml dimethylsulfoxide and 5 ml pyridine to a boiling solution of 0.85 g (3.0 mmol) of dhabH₂ and sodium methanolate (from 0.2 g (8.7 mmol) of sodium) in 100 ml methanol. After 1 h reflux the suspension was cooled at room temperature, and the reddish precipitate was filtered off, washed with water and ethanol and dried at 100 °C. The product was recrystallized from hot pyridine and precipitation of the red crystals was completed by slow addition of twice the volume of water at room temperature. (.92 g, 75%). (*Anal.* Calc. for C₁₇H₁₁Cl₂N₃O₂Ni: C, 48.74; H, 2.65; N, 10.03. Found: C, 48.84; H, 2.64; N, 9.93%.)

2.2.5. ([5-Chloro-2-hydroxyphenylazo]-3-oxo-Nphenylbutanamidate)pyridinenickel(II) ([Ni(hpab)(py)])

[Ni(hpab)(py)] was prepared as described for [Ni(d-hab)(py)] using 0.99 g (3.0 mmol) of hpabH₂ giving yellow crystals (.88 g, 65%). (*Anal.* Calc. for $C_{21}H_{17}ClN_4O_3Ni: C$, 53.95; H, 3.66; N, 11.98. Found: C, 53.99; H, 3.59; N, 11.96%.)

2.2.6. ([5-Chloro-2-hydroxy-phenylazo]-2-naphtholate)pyridinenickel(II) ([Ni(hpan)(py)])

[Ni(hpan)(py)] was prepared as described for [Ni(d-hab)(py)] using 0.90 g (3.0 mmol) of hpanH₂ giving red crystals. (1.01 g, 75%) (*Anal.* Calc. for $C_{21}H_{14}ClN_3O_2Ni$: C, 58.05; H, 3.25; N, 9.67. Found: C, 58.11; H, 3.15; N, 9.57%.)

2.2.7. (5,5'-Dichloro-2,2'-dihydroxy-azobenzenate)pyridinepalladium(II) ([Pd(dhab)(py)])

[Pd(dhab)(py)] was prepared by dropwise addition of a solution of 0.27 g (1.5 mmol) of palladium chloride in 25 ml of dimethylsulfoxide to a stirred refluxing solution of 0.43 g (1.5 mmol) of dhabH₂ and sodium methanolate (from 0.2 g (8.7 mmol) of sodium) in 100 ml methanol. After 1 h the addition of 5 ml pyridine caused precipitation, and the reaction mixture was allowed to cool down to room temperature. The precipitate was filtered off, washed with water and ethanol and dried at 100 °C. Recrystallisation from pyridine using twice the volume of ethanol for complete precipitation gave orange crystals (.57 g, 80%). (*Anal.* Calc. for C₁₇H₁₁Cl₂N₃O₂Pd: C, 43.76; H, 2.38; N, 9.01. Found: C, 43.68; H, 2.34; N, 8.81%.)

2.2.8. ([5-Chloro-2-hydroxy-phenylazo]-3-oxo-N-phenylbutanamidate)pyridinepalladium(II) ([Pd(hpab)(py)])

[Pd(hpab)(py)] was prepared as described for [Pd(dhab)(py)] using 0.50 g (1.5 mmol) of hpabH₂ giving yellow crystals (0.71 g, 90%) of. (*Anal.* Calc. for $C_{21}H_{17}ClN_4O_3Pd: C, 48.95; H, 3.33; N, 10.87.$ Found: C, 49.02; H, 3.18; N, 10.79%.)

2.2.9. ([5-Chloro-2-hydroxyphenylazo]-2-naphtholate)pyridinepalladium(II) ([Pd(hpan)(py)])

[Pd(hpan)(py)] was prepared as described for [Pd(dhab)(py)] using 0.45 g (1.5 mmol) of (hpan)H₂ giving orange crystals (0.60 g, 80%) of. (*Anal.* Calc. for $C_{21}H_{14}ClN_3O_2Pd: C, 52.31; H, 2.93; N, 8.71.$ Found: C, 52.12; H, 2.92; N, 8.56%.)

2.2.10. (5,5'-Dichloro-2,2'-dihydroxyazobenzenate)pyridineplatinum(II) ([Pt(dhab)(py)])

[Pt(dhab)(py)] was prepared by dropwise addition of a solution of 0.62 g (1.5 mmol) of potassium tetrachloroplatinate in 25 ml dimethylsulfoxide to a stirred refluxing solution of 0.43 g of (1.5 mmol) dhabH₂ and sodium methanolate (from 0.2 g (8.7 mmol) of sodium) in 100 ml methanol. After 1 h of reflux, the reaction mixture was allowed to cool and the yellow precipitate filtered off, washed with water and ethanol and dried at 100 °C. The product was recrystallised by dissolving it in 50 ml of hot pyridine, which was filtered and allowed to cool down to room temperature, followed by the slow addition of 50 ml of ethanol. (0.31 g, 35%). (*Anal.* Calc. for $C_{17}H_{11}Cl_2N_3O_2Pt$: C, 36.77; H, 2.00; N, 7.57. Found: C, 36.86; H, 1.99; N, 7.54%.)

2.2.11. ([5-Chloro-2-hydroxyphenylazo]-3-oxo-N-phenylbutanamidate)pyridineplatinum(II) ([Pt(hpab)(py)])

[Pt(hpab)(py)] was prepared as described for [Pt(dhab)(py)] using 0.50 g (1.5 mmol)of hpabH₂ giving yellow crystals (0.39 g, 45%). (*Anal.* Calc. for $C_{21}H_{17}$ -ClN₄O₃Pt: C, 41.76; H, 2.84; N, 9.28. Found: C, 41.72; H, 2.72; N, 9.01%.)

2.2.12. ([5-Chloro-2-hydroxyphenylazo]-2-naphtholate)pyridineplatinum(II) ([Pt(hpan)(py)])

[Pt(hpan)(py)] was prepared as described for [Pt(dhab)(py)] using 0.45 g (1.5 mmol) of hpanH₂ giving red crystals (0.69 g, 80%). (*Anal.* Calc. for $C_{21}H_{14}ClN_{3}$ -O₂Pt: C, 44.18; H, 2.47; N, 7.36. Found: C, 44.14; H, 2.45; N, 7.27%.)

2.2.13. (5,5'-Dichloro-2,2'-dihydroxyazobenzenate)tributylamineplatinum(II) ([Pt(dhab)(tba)])

[Pt(dhab)(tba)] was prepared by treating 0.83 g (2.0 mmol) of potassium tetrachloroplatinate with 1 ml of dimethylsulfoxide at 100 °C for about 15 min to complete the colour change to yellow. To the suspension was added a solution of 0.56 g (2.0 mmol) of $(dhab)H_2$ and 0.42 g (4.0 mmol) of sodium carbonate in 15 ml methanol, and the mixture was refluxed for 30 min. The reaction mixture was allowed to cool, the yellow precipitate filtered off, washed with water and dried at 100 °C. The precipitate was treated with 10 ml of tributylamine at 150 °C for 6 h after which a deep red solution had formed. The solution was allowed to cool, 40 ml of acetone was added and a red precipitate was obtained by slow addition of 25 ml of 0.5 M hydrochloric-acid to the stirred solution. For purification the precipitate was dissolved in 40 ml of acetone, the solution filtered; slow addition of 10 ml of water resulted in the formation of red crystals which was filtered off, washed with water, and dried at 100 °C (0.44 g, 35%). (Anal. Calc. for C₂₄H₃₃Cl₂N₃O₂Pt: C, 43.57; H, 5.03; N, 6.35. Found: C, 43.61; H, 4.92; N, 6.30%.)

2.2.14. ([5-Chloro-2-hydroxyphenylazo]-3-oxo-Nphenylbutanamidate)tributylamineplatinum(II) ([Pt(hpab)(tba)])

[Pt(hpab)(tba)] was prepared as described for [Pt(dhab)(tba)] using 0.66 g (2.0 mmol) of hpabH₂ giving yellow crystals (0.31 g, 20%). (*Anal.* Calc. for

 $C_{28}H_{39}ClN_4O_3Pt:$ C, 47.36; H, 5.53; N, 7.89. Found: C, 47.29; H, 5.51; N, 7.85%.)

2.2.15. ([5-Chloro-2-hydroxyphenylazo]-2-naphtholate)tributylamineplatinum(II) ([Pt(hpan)(tba)])

[Pt(hpan)(tba)] was prepared by dissolving 1.25 g (3.0 mmol) of potassium tetrachloroplatinate in 10 ml of dimethylsulfoxide at 100 °C resulting in a yellow suspension. This mixture was added drop by drop to a stirred solution of 0.90 g (3.0 mmol) of hpanH₂ and 0.64 g(6.0 mmol) of sodium carbonate in 25 ml of dimethylsulfoxide. After 1 h at 110 °C, the stirred solution was cooled and 70 ml of water was added slowly. The resulting red precipitate was filtered off and washed with water, methanol and dried at 100 °C (1.67 g, 98% based on [Pt(hpan)(DMSO)]). A fraction of this compound was used for the synthesis of [Pt(hpan)(tba)]. Another fraction was recrystallized from toluene from which red crystals were obtained by cooling at -20 °C for 12 h. (Anal. Calc. for C₁₈H₁₅ClN₂O₃SPt: C, 37.93; H, 2.65; N, 4.92. Found: C, 38.29; H, 2.64; N, 4.64%.)

1.14 g (2.0 mmol) of [Pt(hpan)(DMSO)] was treated with 10 ml of tributylamine for 1 h at 150 °C after which most of the solvent had evaporated. 40 ml of hot acetone was added to the suspension and the red complex was precipitated from the cooled and stirred solution by slow addition of 25 ml of 1.0 M hydrochloric acid. For purification the precipitate was dissolved in 125 ml of hot acetone, the solution was filtered and after cooling the slow addition of 20 ml of water resulted in the precipitation of red crystals which were filtered off, washed with water, and dried at 100 °C (.83 g, 61%). (*Anal.* Calc. for $C_{28}H_{36}ClN_{3}O_{2}Pt$: C, 49.66; H, 5.36 N, 6.21. Found: C, 49.61; H, 5.38; N, 6.03%.)

2.3. Single crystal X-ray diffraction analyses

Deep red plate-like crystals suitable for structure determination of [Ni(hpab)(py)] were grown from a filtered solution of 9.4 mg of [Ni(hpab)(py)] in a 3.0 ml of pentane/ chloroform mixture (1:9) in a test tube. The tube was placed in a sealed 1000 ml container together with 20 ml of pentane at room temperature for 2 days. Crystals of [Pt(hpan)(tba)] were grown from a filtered solution of 25 mg [Pt(hpan)(tba)] in 3 ml of chloroform in a test tube, covered with thin film of polyethylene through which the solvent gradually diffused over 7 days.

Data were collected with an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo K α radiation on crystals cooled to 122.4(5) K. The unit cell parameters were determined from 18 reflections (17.92° < θ < 22.34°) for [Ni(hpab)(py)] and 22 reflections (18.73° < θ < 21.22°) for [Pt(hpan)(tba)]. The data were corrected for background, polarisation and Lorentz effects with the DREAR program suite [38]. Corrections for absorption were performed using numerical Gaussian integration [39]. The space groups were determined from an analysis of the Laue symmetry of the diffraction pattern and the systematically absent reflections were $P2_1/n$ for [Ni(hpab)(py)] and C2/c for [Pt(hpan)(tba)]. Weissenberg photographs revealed the same space groups at room temperature.

The structures were solved with the program shelxs97 [40], [Ni(hpab)(py)] by direct methods and [Pt(hpan)(tba)] by the Patterson method. The structures were refined by full-matrix least-squares on F^2 using SHELXL97 [41] with anisotropic temperature parameters for all non-hydrogen atoms, except for C303, C313, C403, and C413 in [Pt(hpan)(tba)], which were refined with isotropic displacement parameters due to structural disorder of tba. The population of the two conformations of one of the butyl groups is refined to be 0.55(2) and 0.45(2), respectively. The ADP's of the ligating oxygens, O1 and O2, in [Pt(hpan)(tba)] were restrained to be close to isotropic. Hydrogen atoms could be located in the difference Fourier map and their positions were refined without constraints in the structure of [Ni(hpab)(py)]. In [Pt(hpan)(tba)], the hydrogen atom positions were constrained to follow the connected atom. The isotropic displacement parameters of the hydrogen atoms were constrained to 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom in both structures. Further details about the data collections and refinements are presented in Table 1.

2.4. X-ray powder-diffraction analyses

Crystals of [MLpy] (M = Ni, Pd, and Pt, L = dhab, hpab, and hpan, cf. Table 2) were obtained from pyridine solutions of the complexes by slow vapour phase diffusion of the precipitating liquid (water or ethanol) at room temperature over several weeks, rather than by dropwise

Table 1

Crystallographic data and structure refinement results for [Ni(hpab)(py)] and [Pt(hpan)(tba)]

Formula	NiC ₂₁ H ₁₇ ClN ₄ O ₃	PtC ₂₈ H ₃₆ ClN ₃ O ₂
$M_{ m r}$	467.54	677.14
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
<i>T</i> (K)	122.4(5)	122.4(5)
a (Å)	6.941(3)	24.113(7)
b (Å)	14.031(3)	11.041(2)
<i>c</i> (Å)	20.148(3)	20.812(6)
β (°)	90.88(2)	102.71(2)
$V(\text{\AA}^3)$	1962.0(10)	5405(2)
Ζ	4	8
λ (Å)	0.71073	0.71073
μ , (Mo K α) (mm ⁻¹)	1.157	5.320
Crystal size (mm ³)	$0.34 \times 0.15 \times 0.07$	$0.30 \times 0.28 \times 0.04$
Θ_{\max} (°)	30	25
T_{\min}, T_{\max}	0.719, 0.942	0.272, 0.752
Measured reflections	6517	8488
Independent reflections	5691	4752
R _{int}	0.0255	0.0591
Data/restraints/parameters	5691/0/322	4752/12/317
$R(F^2) [F^2 \ge \sigma(F^2)]$	0.0432	0.0667
$wR(F^2)$	0.0907	0.1068

Table 2 Isomorphous complex crystals

[Ni(dhab)(py)]		[Ni(hpab)(py)]		[Ni(hpan)(py)]
[Ni(dhab)(py)]/[Pd(dhab)(py)](1:1)		[Ni(hpab)(py)]/[Pd(hpab)(py)] (1:1)		
	[Pd(dhab)(py)]		[Pd(hpab)(py)]	[Pd(hpan)(py)]
	[Pt(dhab)(py)]		[Pt(hpab)(py)]	[Pt(hpan)(py)]

Complexes, in columns, established to be isomorphous by identical powder diffraction patterns, but with some intensity differences between the individual lines in the photographs.

addition, cf. the recrystallisation procedures for the pyridine containing complexes described above.

X-ray powder-diffraction photographs were taken in a 50 mm radius Guinier-camera. The complexes were finely ground in an agate mortar, mixed with xylol and silicon as internal reference (a = 5.41959 Å at 293 K [42]) and fixed on a piece of tape on the rotating sample-holder. The X-ray films were exposed for several hours to Cu K α radiation. Analysis of possible isomorphology of the complex crystals was simply established by visual inspection, as the photographs showed many very weak reflections of which some might be unobservable and this could lead to wrong assignments.

2.5. Co-crystallization of dhab complexes

Co-crystals were obtained by mixing filtered solutions of equimolar amounts of the two complexes (*i.e.* 5.0 mg (12 μ mol) of [Ni(dhab)(py)] and 5.6 mg of (12 μ mol) [Pd(dhab)(py)]) in 30 ml of 1:9 pentane/chloroform mixture in a test tube. The tube was placed in a sealed container with 30 ml pentane for several days. In the resulting clusters of small thread-like crystal only one external shape could be detected by polarization microscopy. The complex mixture migrated as two equal-sized spots, with identical retention as the pure complexes, in pyridine/chloroform (1:9) on silica gel TLC-plates, completely vapor phase equilibrated with the solvent. The co-crystals had ¹H NMR spectra in deutero-chloroform identical with a 1:1 mixture of the two complexes.

2.6. Co-crystallization of hpab complexes

Co-crystals of the nickel and palladium complexes of ligand hpab were obtained and analysed with TLC and NMR in the same way as with the dhap complexes described above using 23.4 mg ($50 \mu mol$) of [Ni (hpab)(py)] and 25.8 mg ($50 \mu mol$) of [Pd(hpab)(py)] in 6 ml of a 1:9 pentane/chloroform mixture and using 12 ml of pentane for diffusion. The resulting needle-formed crystals were 3–5 mm long with the dark colour of the nickel complex.

2.7. Computational methodology

Ab initio DFT calculations were performed with the GAUSSIAN98 and 03 program packages [23,24] using the

hybrid functional B3PW91 [25,26] and the basis set 6-31G(d) for all atoms except Ni for which 6-311G(d) was used. The use of the latter basis set for all atoms was also tested, but this did not give rise to any improvement in the prediction of the molecular geometries (cf. Table S1). Calculations with the functional BPW91 B3PW91 [25,26] were also performed, but these were found to give a slightly poorer prediction of the ¹³C chemical shifts. Chemical shifts were calculated using the GIAO method [43,44]. Calculations of the complexes [Ni(hpab)(py)] and [Ni (hpan)(py) were performed with both N_a and N_b as ligating atom, but due to a symmetric ligand in [Ni(dhab)(py)] only one calculation was necessary. In order to determine the predominant species, the structure and NMR shifts were calculated for all tautomers and relevant rotamers of the protonated ligands.

3. Results and discussion

3.1. Stability and coordination geometry

The nickel complexes, giving sharp and well resolved ¹H NMR spectra, are obviously square planar in CDCl₃ solution in agreement with a low-spin d^8 nickel(II) electron configuration. In DMSO- d_6 solution, this is not true since the signals shift to low field and are broad with no fine structure at all. Unlike the more robust palladium and platinum analogues, the nickel complexes are changed in the presence of 1 M hydrochloric or nitric acid.

3.2. Crystal structures

The crystal structure of both [Ni(hpab)(py)] and [Pt(hpan)(tba)] shown in Figs. 1 and 2 (as ORTEPII drawings [45]) unequivocally establishes these complexes to be N_{α} -isomers, the nitrogen atom being attached to the 5chloro-2-hydroxyphenyl substituent. The coordinating nitrogen (N_{α}) lies exactly in the plane described by the metal atom, the second azo-nitrogen (N_{β}) and the aromatic carbon atom bound to the coordinating nitrogen (C1), and indeed all the atoms composing the two annelated 5- and 6-membered chelate rings are planar, and have very similar dimensions in the two complexes. The distances between the azo nitrogens of 1.286(2) Å and 1.278(8) in [Ni(hpab)(py)] and [Pt(hpan)(tba)], respectively, strongly suggest that the azo-bond in ligand dianions should be described as having a high degree of double bond character (Table 3).



Fig. 1. ORTEPII drawing [44] showing structure and labelling of [Ni(hpab)(py)]. The ellipsoids are drawn at the 50% probability level.



Fig. 2. ORTEPII drawing [44] showing the structure and labelling of [Pt(hpan)(tba)]. The ellipsoids are drawn at the 50% probability level.

These structural features are in good agreement with the previously published structures of the Pd and Cu complexes [15,16] (see Table 3) and the chromium(III)-complexes of 2,2'-dihydroxyazobenzene and (2-hydroxy-4-nitrophenylazo)-2-naphthol [2,3]. The pyridinium salt of the latter chromium complex is the meridional isomer,

and the two planar dianionic ligands coordinate through the nitrogen which is attached to the 2-hydroxy-4-nitrophenyl substituent, *i.e.* in the N_{α} -mode.

In [Ni(hpab)(py)], the distances Ni–N1 and Ni–N4 (Table 3) are typical for low-spin complexes (cf. the Ni–N of 1.87 Å in bisdimethylglyoximatonickel [46]), whereas in *trans*-dichlorotetrakis(pyridine)nickel(II) [47] it is 2.00 Å and in bis[2-{2-(phenylamido)phenyl}azopyridine]nickel(II) [48] they are 1.99–2.10 Å.

The pyridine ring of the Ni complex is twisted 38.9° out of the coordination plane defined by the planar tridentate ligand and the nickel atom. In other d^{10} systems a large twist is also found. For example, in *trans*-[Pdpy₂Cl₂], the two pyridines are twisted about 20° relative to each other, and 48° and 68° relative to the coordination plane [49]. In the similar copper(II)-systems (cf. Table 3), the twist is rather small [16].

The X-ray powder diffraction photographs of the complexes show that they can be divided in five isomorphic groups for which diffraction lines at identical 2θ angles but with significant relative intensity differences are in agreement with varying diffractive power and absorption by the different group 10 metals. The comparisons clearly show that the platinum and palladium complex crystals with the same ligand are isomorphous, and in the case of the (hpan) complexes all three, nickel, palladium and platinum-(L)-pyridine, complexes are isomorphous (Table 2). Hence, we conclude that these complexes are isostructural. The fact that the nickel and palladium complexes of both dhab and hpab co-crystallise maintaining the nickel complex morphology strongly suggests that they are isostructural as well. Such a change in crystal form when co-crystallised with an isostructural, analogous complex has been shown in other series of complexes [22].

3.3. Theoretical calculations

Structures of the [Ni(hpab)(py)], [Ni(hpan)(py)] and [Ni(dhab)(py)] have been calculated using DFT with the B3PW91 functional and 6-31G(d)/6-311G(d) basis sets [24–26]. Calculations both with the α and β nitrogen atoms as ligating atoms were performed. The structure of [Ni(hpab)(py)] with coordination to the N_{α} has been compared with the one determined by X-ray crystallography (Table 1). The calculated structure of [Ni(hpab)(py)] is in good agreement with that determined by X-ray crystallography with most bond distances and angles deviating less than 2 standard uncertainties (Table 3). Structures of the two other complexes, [Ni(hpan)(py)] and [Ni(dhab) (py)], have also been calculated and show very similar structures to that of [Ni(hpab)(py)] (Table 3). [Ni(hpan)(py)] is a naphthalene derivative, but shows very little tendency to "hydroazone" complexation contrary to the suggestion by Hintermaier et al. [15] for [Pd(1-(2-hydroxy-4-nitrophenylazo)-2-naphthol)(PPh₃).

¹³C chemical shifts have been calculated using the optimised structures just mentioned and the calculated nuclear

Table 3 Selected bond distances (Å) and angles(°)

Me = Ni, Pt	[Ni(hpab)- (py)] ^a	[Ni(hpab)- (py)] ^b	[Ni(hpan)- (py)] ^b	[Ni(dhab)- (py)] ^{b,g}	[Pt(hpan)- (tba)] ^a	[Cu(DAB)- (py)] ^{ac}	Cu(py)- (azophenolate) ^{a,d}	[Pd(DAB)PPh ₃] ^{a,e}
Me-N1	1.8319(18)	1.8305	1.8321	1.8381	1.946(6)	1.946(6)	1.923(6)	1.999(5)
Me-N4/3	1.9301(18)	1.9277	1.9351	1.9351	2.121(6)	2.040(4)	2.007(6)	2.298(3) Phosph ^f
Me-O1	1.8518(16)	1.8229	1.8301	1.8320	2.004(6)	1.933(5)	1.905(4)	2.011(4)
Me-O2	1.8423(15)	1.8352	1.8066	1.8079	1.974(5)	1.880(5)	1.867(4)	1.969(4)
N1-Me-O1	87.50(7)	87.7	87.6	87.4	83.5(2)	82.9 (2)	84.5(2)	83.7(2)
N1-Me-O2	92.70(7)	93.1	93.9	94.5	94.6(2)	94.3(2)	93.0(2)	92.3(2)
N4/3-Me-O1	90.50(7)	89.1	89.3	89.1	95.2(2)	93.2(2)		91.58(16) Phosph ^f
N4/3-Me-O2	89.31(7)	90.2	89.3	89.0	86.8(2)	91.0(2)		92.68(13) Phosph ^f
N1-N2	1.286(2)	1.2736	1.2749	1.2716	1.278(8)	1.249(9)	1.263(8)	1.212(8)
N1-C1	1.412(3)	1.4103	1.4047	1.4037	1.406(9)	1.464(8)	1.405(8)	1.474(9)
O1–C2	1.331(3)	1.3211	1.3147	1.3124	1.342(9)	1.300(8)	1.331(9)	1.333(9)
O2–C7/8	1.278(3)	1.2765	1.2960	1.2996	1.309(8)	1.316(8)	1.309(8)	1.321(7)
N2-C8/7	1.345(3)	1.3492	1.3549	1.3656	1.387(9)	1.429(10)	1.390(9)	1.410(8)
C7–C8	1.456(3)	1.4527	1.4259	1.4331	1.413(10)	1.398(10)	1.44(10)	1.407(9)
C1–C2	1.405(3)	1.4093	1.4119	1.4115	1.404(10)	1.408(10)	1.400(9)	1.388(11)

^a X-ray data.

^b B3PW91/6-31G(d)/6-311G(d) DFT data (see text).

^c Taken from Ref. [16].

^d Taken from Ref. [14].

^e Taken from Ref. [15].

^f Distance to phosphorous.

^g Numbering as given in structure:



shielding (σ) and experimental chemical shifts (δ) are correlated.

For the [Ni(hpab)(py)] structure (see Fig. 1), a reasonable correlation with experimental results $\sigma_{\text{calc}} = -0.942 * \delta_{\text{exp}} + 190.88 \text{ ppm}; R^2 = 0.996 \text{ was obtained (for a com$ parison of experimental and calculated values, see Table 4). For the corresponding complex with Ni coordination to the N_{β} atom, a significant poorer $R^2 = 0.951$ was obtained. Including only the aromatic carbons the discrimination is even better, $R^2 = 0.995$ for the α -coordination and only 0.870 for β -coordination. In case of the [Ni(hpan) (py)] complex the, picture is even clearer : $\sigma_{calc} = -0.942 * \delta_{exp} + 190.88 R^2 = 0.971$, whereas for β -coordination, $R^2 = 0.67$. The [Ni(dhab) (py)] complex gives very similar results: $\sigma_{calc} = -0.900 * \delta_{exp} + 184.23 R^2 = 0.973.$ The discrimination between coordination to the α and the β nitrogen atoms is thus very good. The above given correlations are slightly improved if the data for the chlorine substituted carbons are excluded. The shortcomings found here in the prediction of ¹³C chemical shifts for halogenbonded carbon nuclei have recently been pointed out by Bagno et al. [50]. Therefore, for non-halogen bonded carbon nuclei, the calculation of ¹³C chemical shifts can be performed by density functional methods employing the functional B3PW91 together with the 6-31G(d)/6-311G(d)basis set that reflect those determined experimentally. These calculations confirm the assignments made earlier by Abildgaard et al. [17] and hence contradict to the assumptions made by Hintermaier et al. [15] for a series of Pd, Pt, Ni and Rh complexes as they assume that the chemical shifts of C16 (ortho-position of five-membered ring) are at lower frequency than that of C6 of the other phenyl ring. From the experimental data [17], it can be seen that the chemical shifts of the Ni, Pd and Pt complexes are very similar. The values obtained by the calculation of a Ni complex can therefore be extrapolated to other complexes of similar coordination.

To establish the method further, ${}^{13}C$ chemical shifts of the hpanH₂, hpabH₂ and dhabH₂ have been calculated including both tautomers and rotamers (see Fig. 3).

For hpabH₂, for which three different tautomers can be envisaged, the hydrazo-form resulting in the 5-chlorophenyl

Table 4 Calculated and measured [17] ¹³C chemical shifts in ppm

Atom	[Ni(hpab)(py)]			[Ni(hpan)(p	y)]	[Ni(dhab)(py)]		
N	Measured	Calculated N-a	Calculated N-β	Measured	Calculated N-a	Calculated N-β	Measured	Calculated ^a
C1	147.7	149.1	141.3	147.8	149.1	149.5	146.9	148.0
C2	161.4	161.0	145.5	163.0	162.7	163.1	164.5	164.1
C3	116.0	117.0	122.0	117.3	117.5	118.0	117.9	116.2
C4	127.5	128.1	129.9	129.8	130.2	130.7	129.4	131.0
C5	120.4	126.5	127.0	121.0	127.5	128.1	121.5	126.6
C6	114.8	114.9	130.0	116.1	116.1	116.6	116.6	115.0
C7	153.6	153.3	166.7	132.5	134.2	134.5	140.5	140.1
C8	121.7	122.1	127.7	150.7	151.7	152.2	149.2	149.2
C9	197.9	197.5	187.9	124.5	123.5	124.0	121.9	120.8
C10	26.6	26.5	34.3	138.6	134.6	135.1	132.6	131.2
C11	136.7	136.8	138.0	127.8	127.8	128.3	122.2	126.3
C12	122.5	118.7	118.3	124.5	122.8	123.3	131.7	130.3
C13	128.8	127.6	128.1	127.8	127.4	127.9		
C14	124.2	122.2	121.8	122.6	122.6	123.1		
C15				132.5	132.3	132.8		
C16				127.8	125.1	125.6		
C1′(C15/C17/C13)	150.1	152.6	152.7	149.9	152.2	152.6	149.8	151.7
C2′(C16/C18/C14)	125.3	123.2	123.8	124.5	123.1	123.6	124.5	121.5
C3′(C17/C19/C15)	138.7	136.8	137.5	138.6	136.7	137.1	138.8	136.0

^a There is no α - β isomerism with this symmetrical ligand.



Fig. 3. Tautomers/rotamers of $dhabH_2$ (calculated nuclear shieldings and energies are given in Table 6). Numbering for c-h as in a.

ring becoming quinoid was not found to contribute at all. A weighting of the two remaining ones in the ratio (hydrazo/azo) 0.71:0.29 leads to a correlation: $\sigma_{calc} = -0.92 * \delta_{exp} + 186.8 \text{ ppm}; R^2 = 0.98$. For hpanH₂ a similar picture was found. For dhabH₂, it emerged that only the rotamer in Fig. 3d contributes leading to a correlation: $\sigma_{calc} = -1.068 * \delta_{exp} + 208.6 \text{ ppm}; R^2 = 0.92$. This indicates that dhabH₂ is not forming an intramolecular hydrogen bond in DMSO.

In order to see how coordination of the ligand affects the ¹³C chemical shifts, we have compared theoretically pre-

Table 5 Calculated nuclear shieldings σ in ppm

Atom	[Ni(hpab)(py)]	[Ni(hpan)(py)]	[Ni(dhab)(py)]
C1	50.4	50.4	51.0
C2	39.2	37.6	36.5
C3	80.7	80.2	79.7
C4	70.2	68.3	66.3
C5	71.8	70.8	70.3
C6	82.7	81.5	80.7
C7	46.4	64.5	58.1
C8	75.9	48.0	49.9
C9	4.8	74.6	75.5
C10	65.9	64.2	66.1
C11	62.0	70.5	70.6
C12	79.0	75.2	66.9
C13	70.6	70.9	
C14	75.8	75.4	
C15		66.3	
C16		73.1	
C1′(C15/C17/C13)	47.1	47.5	47.6
C2′(C16/C18/C14)	74.9	74.9	74.8
C3′(C17/C19/C15)	62.0	62.2	61.9

Table 6 Calculated nuclear shieldings^a σ in ppm and energies for tautomers and rotamers of dhabH₂ (cf. Fig. 3)

	a	b	c	d	e	f	g	h
C1		74.1	57.7	58.2	60.5	59.6	60.6	57.6
C2	46.1	48.2	55.8	45.2	48.0	41.9	46.2	45.1
C3	78.3	78.3	81.5	82.3	82.6	81.4	80.5	82.1
C4	64.4	68.7	68.2	65.9	66.3	62.7	64.1	66.1
C5	67.3	66.9	66.6	65.1	64.3	66.0	64.8	65.3
C6	66.8	78.0	59.2	81.2	81.2	84.4	81.1	83.5
C7	64.2	66.2	57.7	58.2	60.8	58.8	61.2	58.7
C8	46.1	24.1	55.8	45.2	46.9	54.5	48.1	54.8
C9	78.3	70.5	81.5	82.3	78.6	81.4	79.1	81.5
C10	64.4	59.5	68.2	65.9	64.1	67.8	63.5	67.9
C11	67.3	66.4	66.6	65.1	68.1	65.4	66.8	66.6
C12	66.8	68.7	59.2	81.2	63.8	60.4	63.4	59.5
Calculated energies ^b	0	20	105	81	32	55	25	96

^a B3PW91/6-31G(d).

^b In kJ mol⁻¹ relative to rotamer **a**.

dicted nuclear shieldings for dhabH₂ in the co-ordinationlike mode (*i.e.* with oxygens to the same side as the diazo group and a hydrogen-bond forming a six-membered ring, cf. Figs. 3e, g and Table 6) with those calculated for the [Ni(dhab)(py)] complex (cf. Table 5). The calculated data show that the complex formation leads to a large difference in the nuclear shieldings of carbons 2 and 8. The same is true though to a slightly lesser extent for carbon atoms 1 and 7 (Table 6). For the remaining nuclei, the changes in chemical shifts upon coordination are only moderate. The chemical shifts are therefore very distinct in discriminating the carbon nuclei of the five- and the six-membered coordination rings.

4. Conclusions

Nine new nickel-, palladium- and platinum(II) complexes of three o,o'-dihydroxydiarylazo dyes have been synthesized.

The X-ray structure determinations of both [Ni (hpab)(py)] and [Pt(hpan)(tba)] unambiguously showed that N_{α} is the coordinating atom in both cases. Further, analogous Ni, Pd and Pt complexes are isostructural since the X-ray powder diffraction patterns show the crystals to be isomorphous. The calculated structure and the calculated ¹³C chemical shifts correspond well to the X-ray structure and the measured ¹³C chemical shifts in solution showing that the structure is the same in the solid and in solution. It has also been shown that the structure of the complexes can be determined based on a comparison of experimentally measured ¹³C chemical shifts of the compound with ¹³C chemical shifts calculated for the possible structures.

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Appendix A. Supplementary material

X-ray crystallographic data, in files of the CIF format, for the structures of Figs. 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference Nos. 268776 and 268777. Copies of the data can be obtained free of charge, on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, email: <u>deposit@ccdc.cam.uk</u> or on the web: <u>http://www.ccdc.cam.ac.uk</u>. Calculated structural data are also available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.05.027.

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