

The Unexpected Formation of a Tetradentate Tripyrrolic Complex of Nickel(II)

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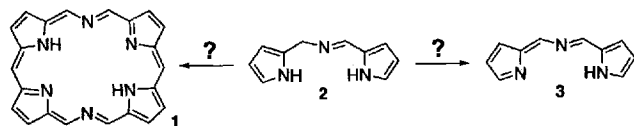
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(2-Pyrrolylmethane)(2-pyrrolylmethyl)imine (**2**) and an equimolar amount of 2-formylpyrrole give, in the presence of nickel(II) in hot methanol, the novel tripyrrolic nickel(II) complex [SP-4]-[(2-dipyrinato- κ^2N,N' -methyl)(2-pyrrolylmeth-

enato- $\kappa N''$)imine- $\kappa N'''$]nickel(II) (**4**). This planar complex has been characterized by X-ray crystallography, a mechanism for its formation is proposed and its mass spectral behavior is discussed.

In 1993, we introduced a novel class of “expanded porphyrins”, the porphocyanines (**1**) and since then we have been interested in the synthesis of various substituted members of this group of compounds^[1]. So far our synthetic strategies have been based on the establishment of the imine linkage as the ring-forming step and, as an alternative, we started to investigate whether an imine linked bipyrrolic compound such as (2-pyrrolylmethene)(2-pyrrolylmethyl)imine (**2**), a known compound^[2a], could be cyclized to **1**. Our additional interest in pyrrolic metal complexing agents such as dipyrins^[3] and bile pigments^[4] prompted us to investigate the oxidation of **2** with the aim to form the fully conjugated and potentially tridentate ligand **3**. Unfortunately, all experiments towards these goals have led, as of now, to no avail. However, in experiments in which **2** was mixed with nickel(II) acetate, the formation of a non-polar, bright orange pigment was observed. We report here the structure, its intriguing mechanism of formation, a convenient synthesis and the molecular structure, as determined by X-ray crystallography, of this unexpected pigment.

Scheme 1. Desired transformations of **4**



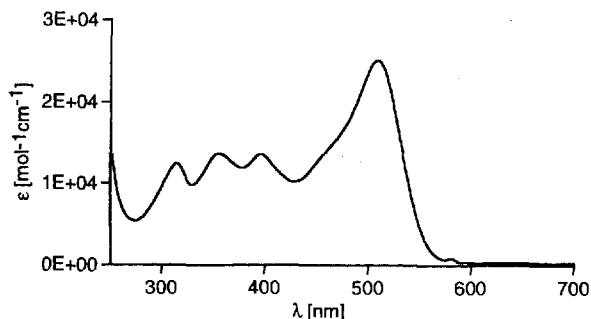
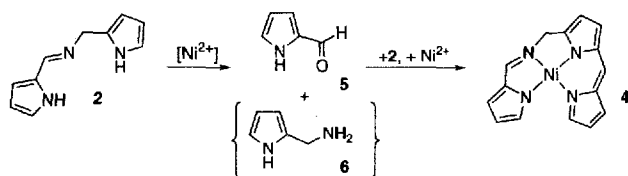
Upon addition of nickel(II) acetate to a warm methanolic solution of **2**, the formation of small amounts of a brilliantly orange pigment, of very low polarity ($R_f = 0.9$ $\text{CHCl}_3/\text{silica}$) was noticed. It was later found that under certain conditions this orange pigment could be made the

major product (vide infra). The UV-visible spectrum of the compound, shown in Figure 1, exhibits some characteristics of the (dipyrinato)nickel chromophore, however, the spectrum features additional bands in the short wavelength region^[5]. The ¹H-NMR spectrum showed ten non-equivalent protons in the aromatic region and the signal for the methylene group of the starting material was still present. No signals indicative of NH protons were observed, suggesting the formation of a nickel complex. Elemental analysis and the HR-MS of the compound corroborated the presence of a nickel atom. Additionally, the compound, by virtue of its sharp NMR signals, proved to be diamagnetic. Therefore a square planar metal complex of nickel(II) was assumed^[6]. Based on the potential lability of the imine linkage towards hydrolysis and the reactivity pattern of any pyrrolealdehyde equivalent formed in such a cleavage, the reaction sequence shown in Scheme 2, and the structure depicted for the pigment **4** was proposed: Lewis acid catalyzed hydrolysis of **2** gives 2-formylpyrrole **5** and, formally, the unstable amino-methyl pyrrole **6**. The aldehyde **5** can react then with a second equivalent of **2** at its most nucleophilic position (the α -position of the pyrrolic unit which is not deactivated by the imine nitrogen) to form a dipyrin unit. This molecule would be poised to “wrap around” the nickel atom and to coordinate it in a square planar fashion to finally give **4**. This structure accounts for all spectroscopic and analytical data.

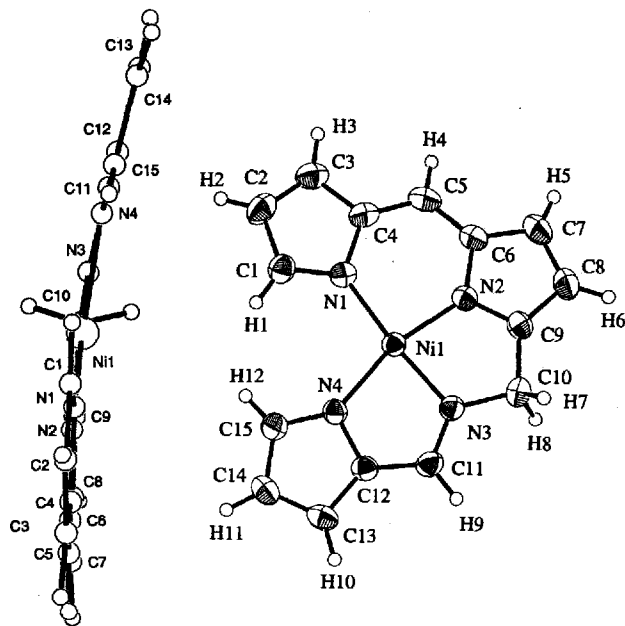
A single crystal X-ray crystal structure of **4** confirms this structural assignment. An ORTEP representation and side view of the structure are shown in Figure 2. The most obvious aspect of this structure is the pronounced flatness of the open-chain ligand-metal complex. As a result, nickel is coordinated in an almost perfectly planar fashion by the four nitrogens with bond distances varying from 1.845(2) to 1.931(2) Å. These distances are in the range expected^[3,7]. Three types of nitrogens are present in the molecule, two of which are part of a dipyrin moiety, one is an imine nitro-

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Figure 1. Optical spectrum (CHCl_3) of **4**Scheme 2. Mechanism of formation and structure of **4**

gen and one is a pyrrole nitrogen. The imine and pyrrole nitrogens as well as both dipyrin nitrogens are in conjugation but the two pairs are isolated from each other by a methylene group. The complete absence of any alkyl substituents in the β - or *meso*-positions is unusual.

Figure 2. Molecular structure of **4** (ORTEP representation at 33% probability level and side view)^[a]

^[a] Selected bond distances [Å]: Ni(1)–N(1) 1.893(2), Ni(1)–N(2) 1.845(2), Ni(1)–N(3) 1.867(2), Ni(1)–N(4) 1.931(2), N(1)–C(1) 1.332(3), N(1)–C(4) 1.409(3), N(2)–C(6) 1.384(3), N(2)–C(9) 1.334(3), N(3)–C(10) 1.470(3), N(3)–C(11) 1.291(3), N(4)–C(12) 1.384(3), N(4)–C(15) 1.352(3), C(1)–C(2) 1.402(4), C(2)–C(3) 1.343(4), C(3)–C(4) 1.412(4), C(4)–C(5) 1.381(4), C(5)–C(6) 1.373(4), C(6)–C(7) 1.419(4), C(7)–C(8) 1.352(4), C(8)–C(9) 1.411(3), C(9)–C(10) 1.480(4), C(11)–C(12) 1.405(4), C(12)–C(13) 1.390(3), C(13)–C(14) 1.371(4), C(14)–C(15) 1.387(4) (numbering scheme differs from that according to IUPAC rules in the experimental section)

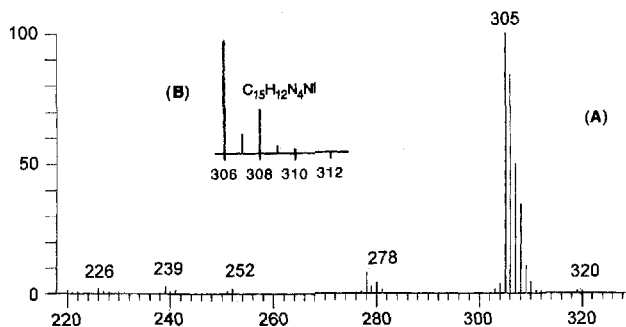
Pigment **4** forms in low yields ($\approx 10\%$) at slightly elevated temperatures ($\approx 50\%$) upon reacting **2** with nickel(II) in methanolic or ethanolic solution. 2-Formylpyrrole **5** can be detected by TLC from the onset of the reaction. This suggests that the first step of the reaction is, indeed, the cleavage of the imine moiety in **2**. The hydrolysis is catalyzed by the Lewis acidity of nickel(II) as the compound is stable under these conditions in the absence of the metal salt. Other Lewis acids such as zinc(II) acetate and Brønsted acids (HCl, HBr, TFA) were shown to catalyze the hydrolysis of the imine linkage under the above conditions. The highly unstable **6** was not seen, nor were the possible self-condensation products of **6**. The occurrence of highly polar and colourful materials in the course of the reaction may indicate its polymerization and/or reaction with any other pyrrolic compounds in the reaction mixture. The acid-catalyzed hydrolysis of imines as well as the instability of aminomethyl pyrroles is well documented in the literature^[8,9].

The second step of the reaction requires the formation of the final ligand and most probably the concomitant formation of complex **4**. It was found that an equimolar alcoholic solution of 2-formylpyrrole (**5**) (independently prepared) and **2** react in the presence of nickel(II) to give complex **4** in a yield three times greater than that observed in the absence of 2-formylpyrrole. This supports the assumption that 2-formylpyrrole is the reactive species in the ligand formation derived from cleavage of the imine moiety. The formation of **4** is of particular interest as it is susceptible to a profound metal template effect. Only nickel(II) is capable of forming a complex of type **4**. Some metals (e.g. zinc) catalyze only the hydrolysis of the imine step while others (e.g. cobalt, iron, copper) form highly coloured precipitates with **2**. These are, however, known complexes of the type $(2)_2\text{M}^{2+}$. A metal-free mixture of 2-formylpyrrole (**5**) and imine **2** does not show any reaction. This mixture when treated with Brønsted acids such as HBr exhibits at first the typical optical spectrum of a dipyrin hydrobromide ($\lambda_{\text{max}} \approx 500 \text{ nm}$), but rapid decomposition sets in and no defined product can be isolated. Neutralization and reaction with nickel(II) yields no isolable products, indicating no formation of, for instance, the free base of **4**. On the other hand, an alcoholic solution of pyrrole and 2-formylpyrrole (**5**) does not form the corresponding dipyrin in the presence of nickel(II), indicating that the presence of the potentially bidentate chelate **2** is required for the reaction to proceed.

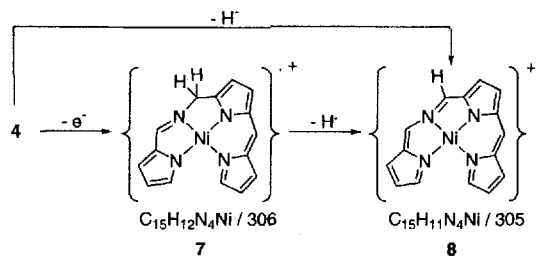
The electron impact mass spectrum (180°C) of **4** (**A**) together with the calculated isotope pattern for $\text{C}_{15}\text{H}_{12}\text{N}_4\text{Ni}$ (**B**) is shown in Figure 3. There are clear discrepancies between the measured and the expected spectrum, both in the value of the molecular peak as well as in the isotope pattern. Instead of the expected molecular ion peak of $m/z = 306$ (or 307 for MH^+) one molecular peak with $m/z = 305$ is observed. The high resolution mass of 305.03370 mu revealed its composition to be $\text{C}_{15}\text{H}_{11}\text{N}_4\text{Ni}$ (expected: 305.03372 mu). This fragmentation pattern, corresponding to a hydride abstraction of complex **4**, finds its explanation in the highly stabilized structure of the resulting cation **8**

(Scheme 3). The computed overlay of a $\approx 1:2$ ratio of **8** (resonance stabilized radical cation, $m/z = 306$) and **7** yields the observed spectral pattern. Attempts to form **8** under solution phase conditions have so far failed. No evidence for the formation of a cyclized product were found in the mass spectrum, nor could a cyclization be performed in solution conditions typically applied in cyclizations of dideoxybiladienes-*a,c* to corroles^[10]. We believe this is due to the strained nature of the resulting macrocycle.

Figure 3. Measured (EI, 180 °C) (A) and expected (B) mass spectrum of **4**



Scheme 3. Fragmentation pattern of **4** under the conditions of EI-mass spectroscopy (180 °C)



In conclusion, we described here a remarkably simple synthesis of a planar tripyrrolic tetradentate N4-donor set ligand complex of nickel(II). It remains to be seen whether this complex may mimic the biochemistry of nickel^[11] or, for instance, function as catalyst for the reductive dehalogenation of aromatic halides^[12].

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Experimental

Melting points were determined on a Thomas Model 40 Micro Hot Stage and are uncorrected. – MS: Kratos MS50 (direct insertion, ion source at 150 °C, EI, 70 eV). – UV/Vis: Hewlett Packard HP 8452A photodiode array spectrophotometer. – ¹H NMR: Bruker WH-400 (400 MHz); ¹³C NMR: Bruker AC-200 (50 MHz). The chemical shifts are reported on the δ scale and are referenced to residual protons in the deuterated solvent [D₆]acetone. The carbon types as obtained in an APT experiment are indicated in parenthesis. – IR: ATI Mattson Genesis Series FTIR. – Elemental Analysis: Microanalytical Laboratory of the Department of Chemistry, University of British Columbia, performed on a Fisons CHN/O Analyzer, Model 1108. – Materials: Imine **2**^[2a] (2-cyanopyrrole)^[13] and 2-formylpyrrole (**5**)^[14] were prepared according to lit-

erature procedures. The silica gel used was Merck Silica Gel 60, 230–400 mesh. R_f values were measured on Merck silica TLC aluminium sheets (silica gel 60 F₂₅₄). All other solvents and materials were commercially available and of analytical grade.

[*SP-4*]-[(2-Dipyrinato- κ^2 N,N'-methyl)(2-pyrrolylmethenato- κ Nⁱⁱⁱ)imine- κ Nⁱⁱⁱ]*nickel(II)* (**4**): Imine **2** (200 mg, 1.16 mmol), 2-formylpyrrole (**5**) (110 mg, 1.16 mmol), and nickel(II) acetate tetrahydrate (500 mg, 2.0 mmol), dissolved in a 2:1 mixture of EtOH and CHCl₃ (15 ml), were heated at reflux temperature for 1 h. The initially pale green color of the solution turned dark orange. Evaporation in vacuo of the reaction mixture gave a solid which was triturated with CHCl₃ (4 × 5 ml). The volume of the dark orange solution was reduced and chromatographed (silica gel, 2 × 12 cm, CHCl₃). The first major orange band was collected and evaporated to dryness. The resulting solid was dissolved in CH₂Cl₂, and slow solvent exchange with cyclohexane resulted in the formation of analytically pure **4** as shiny metallic green dichroic short needles (125 mg, 35%). – M.p. 184 °C (drying conditions 50 °C/0.1 Torr). – R_f (silica gel; CHCl₃) = 0.90. – IR (film): $\tilde{\nu} = 1606 \text{ cm}^{-1}$ s (C=N), 1390 m, 1324 m, 1308 m, 1262 m, 1249, 1201 s (C–H), 997 m, 977 m, 750 m, 716 m. – ¹H NMR (400 MHz, [D₆]acetone) $\delta = 4.60$ (s, 2H), 6.01 (dd, $J = 2.0$ Hz, 3.8H, 1H), 6.29 (d, $J = 4.2$ Hz, 1H), 6.41 (dd, $J = 4.2, 1.7$ Hz, 1H), 6.57 (dd, $J = 3.7, 0.8$ Hz, 1H), 7.02 (d, $J = 4.2$ Hz, 1H), 7.09 (dd, $J = 4.1, 1.1$ Hz, 1H), 7.25 (s, 1H), 7.53 (s, 1H), 7.69 (s, 1H). – ¹³C NMR (50 MHz, CDCl₃/10% [D₆]acetone) δ 54.0 (–C–), 111.3 (=C–), 112.8 (=C–), 117.0 (=C–), 177.8 (=C–), 129.7 (=C–), 129.9 (=C–), 131.6 (=C–), 133.5 (=C=), 136.9 (=C–), 139.7 (=C=), 146.2 (=C=), 151.1 (=C–), 158.9 (=C–), 162.9 (=C=). – UV Vis (CH₂Cl₂): λ_{max} (log ϵ) = 314 nm (4.08), 354 (4.11), 394 (4.12), 508 (4.40). – MS; m/z (%): 311 (1.1), 310 (4.5), 309 (10.5), 308 (34.2), 307 (50.0), 306 (83.9), 305 (100.0). HR MS; m/z : calcd. for C₁₅H₁₂N₄Ni⁵⁸Ni: 306.04153, found 306.04013. – C₁₅H₁₂N₄Ni (306.98): calcd. C 58.69, H 3.94, N 18.25; found C 58.51, H 3.74, N 18.00.

Crystal-Structure Analysis of 4^[15]: Clear, orange-red crystals were obtained by allowing a THF solution to evaporate slowly to dryness; The crystals of **4** were mounted on a glass fibre and measurements were made at 21 ± 1 °C on a Rigaku AFC6S diffractometer. Experimental details of the structure determination are listed in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections in the range $34.1 < 2\theta < 38.8$. Of the 5135 reflections which were collected, 5014 were unique ($R_{\text{int}} = 0.032$). The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decreased by 1.2%. A linear correction factor was applied to the data to account for this phenomenon. The data were processed and corrected for Lorentz and polarization effects, linear decay, and absorption (ψ -scans). The structure was solved by the heavy atom Patterson method and expanded using Fourier techniques. Hydrogens were refined isotropically. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-Ray Crystallography^[16].

Table 1. Crystallographic data for **4**

Crystal color: red prism; dimension: 0.35 × 0.35 × 0.50 mm; empirical formula: C₁₅H₁₂N₄Ni; molecular mass: 306.99; crystal system: monoclinic; space group: C2/c (#15), $a = 21.461(1)$, $b = 5.362(1)$, $c = 22.0841(9)$ Å; $\beta = 92.748(4)^\circ$; $V = 2538.4(4)$ Å³; $Z = 8$; $D_{\text{calcd.}}$ 1.606 g/cm³; radiation: Mo-K α ; $\lambda = 0.71069$ Å; $\mu = 15.22 \text{ cm}^{-1}$; transmission factors: 0.921–1.00; R , R_w : 0.030, 0.024; gof : 1.68.

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