2-Picolinoylpyrrole: A New Entry to Metal-complexing Agent

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The Pd(II) and Pt(II) complexes of 2-picolinoylpyrrole were synthesized and the 2:1 square-planar coordination, wherein each pyrrole and pyridine moieties are in trans positions, respectively, were characterized by means of X-ray single-crystal analyses.

Pyridines and pyrroles are representative nitrogenous heterocycles that can coordinate metal cations and the stable metal complexes can be obtained by simply linking two units such as 2,2′-bipyridine and 2,2′-methylenedipyrrole.[1,2] In the case of keto-linker, di-2-pyridyl ketone (**1**) affords neutral chelating complexes with two nitrogen atoms and, more frequently, with an oxygen atom.[3,4] On the other hand, however, there is few report about the metal complexes with di-2-pyrrolyl ketone (**2**) in spite of the existence of metal oxophlorins that contain a similar structure in the porphyrin framework.[5,6] Probably, the slightly longer distance between two nitrogen atoms and the plausible cis,cis- and cis,trans geometry of two pyrrole rings to a carbonyl group would make the ketone **2** difficult to complex metals.[7] Here, we have interested in a hybrid molecule, 2-picolinoylpyrrole (**3**) that possesses both pyridine and pyrrole moieties, because it might serve as a mono-anionic, bidentate ligand when coordinates metals with two nitrogen atoms (Chart 1). In this letter, we report the first crystal structures of metal complexes of **3** as well as the free ligand.[8]

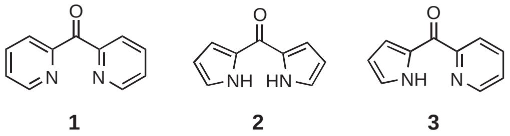
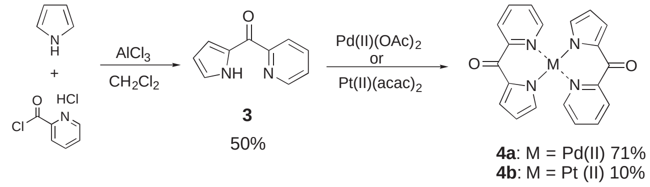


Chart 1.

The title compound **3** was synthesized by Friedel–Crafts acylation of pyrrole ring using HCl salt of picolinoyl chloride (Scheme 1).[9] The single crystals suitable for the X-ray structural analysis were obtained from a CH_2Cl_2/hexane solution (Figure 1).[10] In the crystal, the molecule is almost planar with a mean deviation of 0.09 Å and the pyrrole and pyridine rings are oriented in cis and trans fashion, respectively.[7] The two neighboring molecules are forming a head-to-tail type dimer via hydrogen bonds between the oxygen and pyrrole NH, judging from a short distance 2.8533(8) Å between O and N atoms. This is a marked contrast with the hydrogen-bonded helix structures observed for **2**.[11] Interestingly, in $CDCl_3$ solution, trans,trans-conformation having intramolecular hydrogen bonding between pyrrole NH and pyridine N atoms was suggested from the NH chemical shift at 11.69 ppm, which is ca. 1.9–2.2 ppm downfield-shifted compared to that of 2-benzoylpyrrole.[12]



Scheme 1.

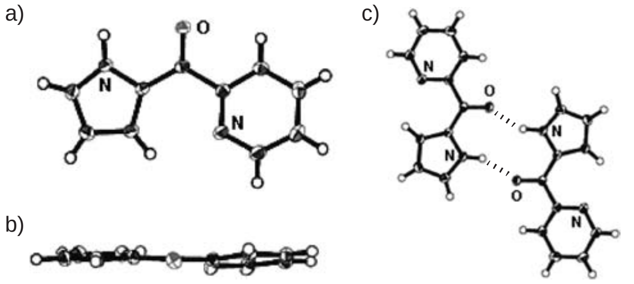


Figure 1. X-ray structure of **3**, a) top, b) side, and c) hydrogen-bonding dimer.

Although the possibility of intermolecular hydrogen bonding observed in the crystal is not completely ruled out, such interactions seem to be less possible because the NH signal in the ^{1}H NMR spectra of **3** remains at the same position in a wide range of concentrations.

Complexation of **3** was performed with Pd(II) and Pt(II) salts (Scheme 1). Pd complex **4a** was obtained by stirring a mixture of **3** and $Pd(OAc)_2$ in CH_2Cl_2 for 2 days at room temperature. After a silica-gel column with 2% $CH_3OH–CH_2Cl_2$, **4a** was obtained in 71% yield. On the other hand, Pt(II) complex **4b** was synthesized in 10% yield as a major product, by refluxing a xylene solution with $Pt(acac)_2$ for 6 days.

The formation of 2:1 (ligand to metal) complexes was suggested for both **4a** and **4b** from MALDI-TOF-MS spectra and the explicit structures were revealed by X-ray single-crystal analyses.[13,14] In both complexes, the metal atoms are trans-coordinated by two pyrrolic and two pyridyl nitrogen atoms in a square-planar fashion (Figure 2). The bond distances between the metal and pyrrolic N and pyridine N are 2.00 and 2.01 Å for Pd atom and 2.01 and 2.02 Å for Pt atom, respectively, and the bond angles N(pyrrole)-M-N(pyridine) are 86.8° (Pd) and 87.3° (Pt), respectively. Reflecting the repulsion between pyridine *ortho*-H and pyrrolic α-H countered, the ligand **3** in the complexes exhibits the butterfly-shaped structure and the dihedral angles between pyrrole and pyridine rings are 136.8° (Pd) and 136.1° (Pt), respectively.

The absorption spectra of **3**, **4a**, and **4b** in toluene are shown in Figure 3. Upon forming metal complexes, the absorption max-

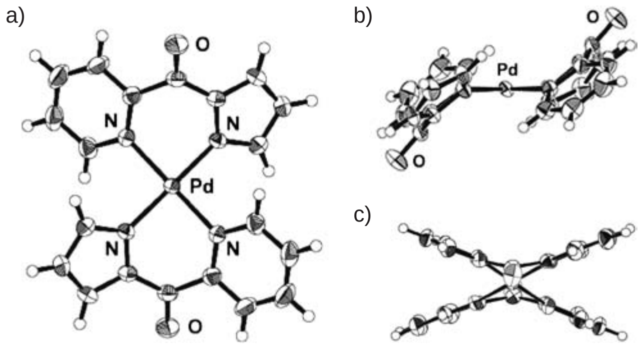


Figure 2. X-ray structure of **4a**, a) top, b) and c) side views.

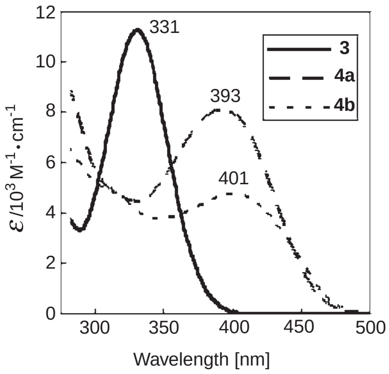
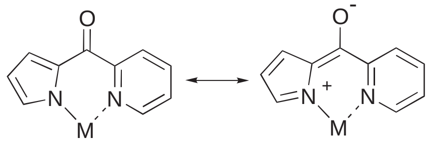


Figure 3. UV–vis spectra of **3**, **4a**, and **4b** in toluene.



Scheme 2.

ima shifted to a longer wavelength; 62 nm for **4a** and 70 nm for **4b**. While the HOMO levels are almost the same ($\Delta E_{\mathrm{HOMO}} =$ 0.076 and 0.052 eV), the large stabilization of LUMO ($\Delta E_{\mathrm{LUMO}} = 0.79$ and 0.88 eV) by the metal complexation was suggested from the DFT (B3LYP/LANL2DZ) calculations.

Pyrrole carbonyl compounds can possess the mesomeric structures and the low carbonyl frequency in the IR spectra is attributed to the contribution of zwitterionic structures.[15,16] The corresponding wave numbers of **3**, **4a**, and **4b** are 1606, 1621, and 1631 cm^{-1}, respectively, which suggests the zwitterionic structures are less significant in the metal complexes probably due to the unfavorable repulsion between the localized positive charge on the pyrrolic moieties and the coordinated metal cation. The C=O bond lengths of above compounds are around 1.23 Å, which also indicates the preferred formation of keto-structures in the solid state (Scheme 2).

Apart from the Pd(II) and Pt(II) complexes, other metals such as Ni(II) and Cu(II) are also coordinated with **3**, but at this moment, their structures are not thoroughly characterized due to the instability of the complexes.

In summary, we have demonstrated the coordination ability of 2-picolinoylpyrrole (**3**) for the first time by synthesizing the 2:1 Pd(II) and Pt(II) complexes. The present pyrrole–pyridine hybrid is, thus, a new entry for the metal coordination ligands.[17] As a variety of metal complexes of **3** could be anticipated and the carbonyl group of **3** may serve as a hydrogen-bond acceptor, the new ligand **3** would be used as building blocks in supramolecular chemistry.

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10 X-ray data of **3**: Yellow prism, $C_{10}H_8N_2O$, MW 172.18, monoclinic, space group $P2_1/c$ (No. 14), $a = 5.9609(4)$, $b = 13.1442(8)$, $c = 10.6141(7)$ Å, $\beta = 95.8120(10)°$, $V = 827.35(9)$ Å^3, $D_{\mathrm{calcd}} = 1.382$ g/cm^3, $Z = 4$, $T = 100$ K, $R = 0.0327$ ($I > 2\sigma(I)$), $R_{\mathrm{w}} = 0.0882$ (all data), GOF on $F^2 = 1.060$, CCDC reference number 601594.

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12 The NH signal of benzoylpyrrole shifted to upfield region upon dilution.

13 X-ray data of **4a**: Yellow prism, $C_{20}H_{14}N_4O_2Pd$, MW 448.76, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.7254(6)$, $b = 13.6383(10)$, $c = 8.3111(6)$ Å, $\beta = 99.296(2)°$, $V = 864.17(11)$ Å^3, $D_{\mathrm{calcd}} = 1.724$ g/cm^3, $Z = 2$, $T = 293$ K, $R = 0.035$ ($I > 2\sigma(I)$), $R_{\mathrm{w}} = 0.035$ (all data), GOF on $F^2 = 0.966$, CCDC reference number 601595.

14 X-ray data of **4b**: Yellow prism, $C_{20}H_{14}N_4O_2Pt$, MW 537.44, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.7125(9)$, $b = 13.6338(15)$, $c = 8.2954(9)$ Å, $\beta = 99.353(2)°$, $V = 860.67(17)$ Å^3, $D_{\mathrm{calcd}} = 2.074$ g/cm^3, $Z = 2$, $T = 299$ K, $R = 0.0264$ ($I > 2\sigma(I)$), $R_{\mathrm{w}} = 0.0689$ (all data), GOF on $F^2 = 1.036$, CCDC reference number 601596.

15 IR of carbonyl compound (cm^{-1}): benzophenone (1651), 2-benzoylpyrrole (1625), di-2-pyrrolyl ketone (**2**) (1572).

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