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Di[2,6-bis(5-phenylpyrazol-3-yl)pyridine]Co(II): an old coordination mode for a novel supramolecular assembly

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Electronic Supplementary Information

Synthetic details

All the solvents and starting materials were used as received without any further purification. All the reactions were performed under aerobic conditions. Variable temperature magnetic susceptibility measurements were carried out in the temperature range 5-275 K with an applied magnetic field of 7.96 kA/m using a SQUID based magnetometry system (Quantum Design MPMS-7). The data exhibited Curie-Weiss Law behaviour over the temperature range 100 to 275K. Data in this temperature range were fitted with a Curie-Weiss Law to enable the temperature independent diamagnetic susceptibility contributions from sample holder and sample to be quantified.

Synthesis of $[\text{Co}(\text{H}_2\text{L})\text{Cl}_2]\cdot 2\text{H}_2\text{O}$.

H_2L (100 mg, 0.27 mmol) was added to ethanol (10 ml) and heated until completely dissolved. The solution was then added dropwise to a warm (60 °C) solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (64 mg, 0.27 mmol) in ethanol (5 ml). The resulting mixture was stirred at 60 °C for 2 hours. The precipitate was then filtered, washed with warm ethanol, and dried under reduced pressure for 4 hours, yielding the *title compound* as a green solid. Yield: 104 mg (73%). Anal. Calcd. for $[(\text{H}_2\text{L})\text{CoCl}_2]\cdot 2\text{H}_2\text{O}$ ($\text{C}_{23}\text{H}_{21}\text{Cl}_2\text{CoN}_5\text{O}_2$): C, 52.19; H, 4.00; N, 13.23. Found: C, 52.08; H, 4.01; N, 13.36. IR (ATR): $\nu = 3300(\text{bs}), 3122(\text{s}), 2980(\text{s}), 2854(\text{m}), 2819(\text{m}), 1615(\text{s}), 1537(\text{s}), 1489(\text{m}), 1449(\text{s}), 1292(\text{s}), 1216(\text{w}), 1143(\text{w}), 1182(\text{w}), 1013(\text{s}), 981(\text{w}), 962(\text{w}), 919(\text{w}), 810(\text{m}), 761(\text{s}), 684(\text{m}) \text{ cm}^{-1}$. UV/Vis (DMSO, $1.889\cdot 10^{-3}$ M): λ_{max} (due to the presence of equilibria in solution, it was not possible to obtain a precise value of ϵ which can only be estimated of the order of $10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 679, 654, 631, 616, 599 nm.

Synthesis of $[\text{Co}(\text{H}_2\text{L})_2][\text{PF}_6]_2$.

H_2L (200 mg, 0.54 mmol) was added to ethanol (15 ml) and heated until completely dissolved. The solution was then added dropwise to a warm (60 °C) solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (64 mg, 0.27 mmol) in ethanol (5 ml). The resulting orange solution was refluxed for 8 hours and then filtered over celite. The volume of the filtrate was reduced to 2 ml using a rotary evaporator and a saturated aqueous KPF_6 solution (10 ml) was added. The mixture was stirred at room temperature for 30 minutes, after

which the orange solid was filtered and washed with a 3:1 water/ethanol solution. The solid was then recrystallised from an acetone/hexane mixture. Orange block-shaped single crystals suitable for X-ray diffraction were grown overnight by vapour diffusion of hexane into an acetone solution of the *title compound*. Yield: 197 mg (68%).

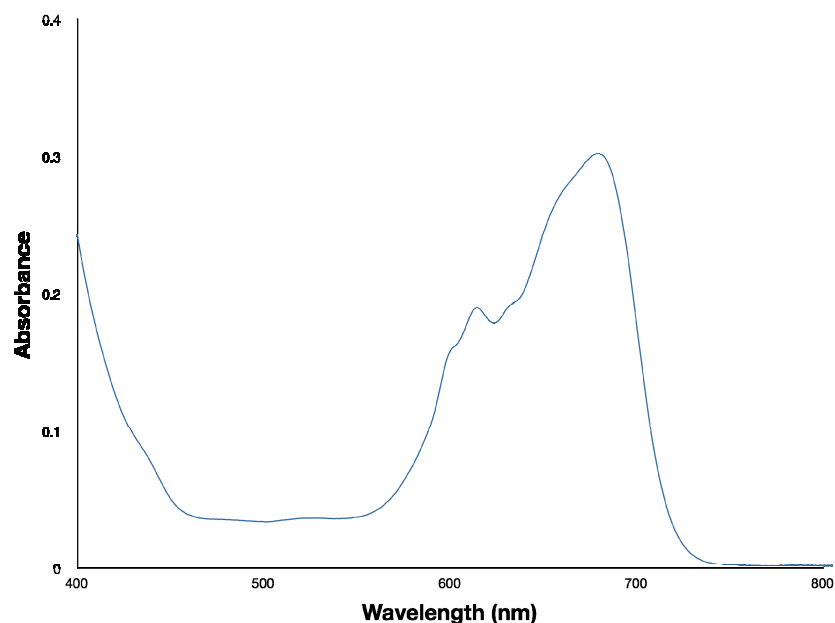
Determination of the molecular formula via elemental analysis was difficult due to the rapid desorption of solvent molecules and possible hydration over time. Anal. Calcd. for $[\text{Co}(\text{H}_2\text{L})_2][\text{PF}_6]_2 \cdot 6(\text{acetone}) \cdot m(\text{H}_2\text{O})$ assuming $n=2$ and $m=3$, ($\text{C}_{52}\text{H}_{50}\text{CoF}_{12}\text{N}_{10}\text{O}_4\text{P}_2$): C, 50.13; H, 4.21; N, 11.24. Found: C, 50.20; H, 4.18; N, 11.16. IR (ATR): $\nu = 3640(\text{m}), 3571(\text{w}), 3364(\text{m}), 3145(\text{m}), 3065(\text{m}), 2937(\text{w}), 1696(\text{s}), 1618(\text{s}), 1577(\text{s}), 1524(\text{w}), 1491(\text{m}), 1466(\text{m}), 1448(\text{s}), 1365(\text{m}), 1291(\text{w}), 1274(\text{m}), 1232(\text{m}), 1206(\text{w}), 1162(\text{w}), 1140(\text{w}), 1114(\text{w}), 1086(\text{m}), 1014(\text{s}), 980(\text{w}), 936(\text{w}), 917(\text{w}), 832(\text{s}), 805(\text{s}), 783(\text{s}), 761(\text{s}), 740(\text{m}), 690(\text{m}) \text{ cm}^{-1}$.

Synthesis of $\{[\text{Co}(\text{H}_2\text{L})_2](\text{H}_2\text{L})_4\}[\text{PF}_6]_2 \cdot 2\text{CH}_2\text{Cl}_2$.

H_2L (600 mg, 1.65 mmol) was added to ethanol (50 ml) and heated until completely dissolved. The solution was then added dropwise to a warm (60 °C) solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (64 mg, 0.27 mmol) in ethanol (5 ml). The resulting orange solution was refluxed for 8 hours and then filtered over celite. The volume of the filtrate was reduced to 10 ml using a rotary evaporator and a saturated aqueous KPF_6 solution (20 ml) was added. The mixture was stirred at room temperature for 30 minutes, after which the aqueous layer was extracted with CH_2Cl_2 (3 x 15 ml). The combined organic phase was dried over MgSO_4 , filtered and evaporated to dryness under reduced pressure. The resulting solid was recrystallised from a CH_2Cl_2 /hexane mixture, yielding the *title compound* as an orange solid. Single crystals suitable for X-ray diffraction, as dark orange prisms, were grown over a couple of days by layering hexane into a CH_2Cl_2 solution of the *title compound*. Yield 213 mg (29%).

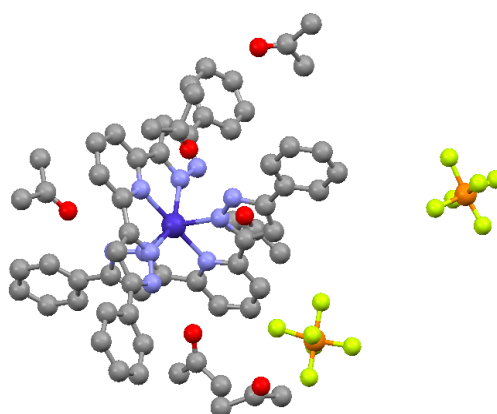
Anal. Calcd. for $\{[\text{Co}(\text{H}_2\text{L})_2](\text{H}_2\text{L})_4\}[\text{PF}_6]_2 \cdot 2\text{CH}_2\text{Cl}_2$: ($\text{C}_{140}\text{H}_{106}\text{Cl}_4\text{CoF}_{12}\text{N}_{30}\text{P}_2$): C, 62.30; H, 3.96; N, 15.57. Found: C, 62.37; H, 4.57; N, 15.53. IR (ATR): $\nu = 3646(\text{m}), 3567(\text{m}), 3366(\text{s}), 3138(\text{m}), 3076(\text{m}), 1617(\text{s}), 1571(\text{s}), 1488(\text{m}), 1464(\text{m}), 1447(\text{s}), 1291(\text{s}), 1274(\text{m}), 1198(\text{w}), 1140(\text{w}), 1075(\text{w}), 1013(\text{s}), 832(\text{s}), 806(\text{s}), 784(\text{s}), 759(\text{s}), 712(\text{m}), 689(\text{m}) \text{ cm}^{-1}$.

UV/Vis spectrum of $[\text{Co}(\text{H}_2\text{L})\text{Cl}_2]\cdot 2\text{H}_2\text{O}$



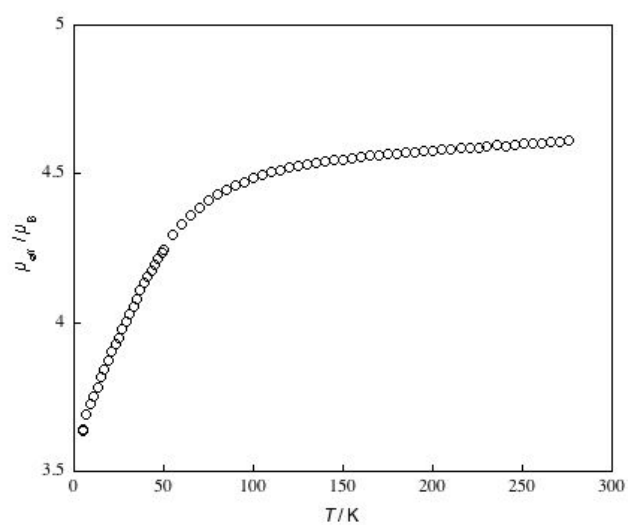
UV/Vis absorption spectrum of a $1.889\cdot 10^{-3}$ M $[\text{Co}(\text{H}_2\text{L})\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ solution in DMSO. It is noteworthy that by reducing the volume of DMSO, the green solution turns orange, whereas by re-adding DMSO the green colour reappears. On concentrating the solution, shoulder bands around 480 nm appear across the intense metal to ligand charge transfer below 400 nm. Absorption in the 450-500 nm region were attributed to hexacoordinated Co complexes of the $[\text{Co}(\text{H}_2\text{L})_2]^{2+}$ type, which was confirmed by the spectrum of the isolated $[\text{Co}(\text{H}_2\text{L})_2][\text{PF}_6]_2$, showing two absorption maxima at 480 and 518 nm tailing off the intense charge transfer band.

X-ray crystal structure of $[\text{Co}(\text{H}_2\text{L})_2][\text{PF}_6]_2$



The structure of the octahedral $[\text{Co}(\text{H}_2\text{L})_2][\text{PF}_6]_2$ was confirmed by X-ray diffraction, IR, and elemental analysis. Decomposition of the crystals occurred as soon as they were taken out from the acetone solution and dried in air, so the IR spectra were recorded immediately after some crystals were harvested. Substitution of Cl^- for PF_6^- was evidenced by the appearance of a strong band at 832 cm^{-1} , whilst the peaks at 1617 cm^{-1} and around $3100\text{--}2900\text{ cm}^{-1}$ were attributed to the CN and aromatic CH stretches of H_2L . The strong carbonyl band at 1696 cm^{-1} confirms the presence of acetone molecules as evidenced in the crystal structure. The lower frequency with respect to free acetone (1731 cm^{-1}) also confirms hydrogen bonding between the carbonyl CO and the pyrazole NH. Three sharp bands at 3640 , 3571 , and 3364 cm^{-1} were all attributed to the pyrazole NH bonds. The splitting of the stretching frequencies might be ascribed on one side to the pseudo- C_{2v} symmetry of the H_2L ligand in the $NI,NI\text{-H}_2\text{L}$ tautomeric form, which renders the asymmetric and symmetric NH stretches IR active. On the other side, due to the rapid loss of solvent molecules when the crystals are exposed to air, different degrees of hydrogen bonding might also be responsible for the appearance of different bands.

Magnetic investigation



Effective magnetic moment, μ_{eff} , per Co atom for $[\text{Co}(\text{H}_2\text{L})_2][\text{PF}_6]_2$. The decrease in μ_{eff} values with decreasing temperature below approximately 100K is indicative of ligand-field and/or spin-orbit effects.