

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

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⁵ Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

CoCl₂ was treated with 1, 2, and 6 eq. of 2,6-bis(5-phenylpyrazol-3-yl)pyridine (H₂L) yielding respectively the monosubstituted [(H₂L)CoCl₂], the disubstituted [(H₂L)₂Co][PF₆]₂, and a supramolecular assembly formed by a central disubstituted octahedral complex and four more hydrogen bonded peripheral ligands, [{Co(H₂L)₂}(H₂L)₄][PF₆]₂, as illustrated by X-ray crystal structure analysis.

Pyrazoles and pyrazolides have been the focus of extensive investigation in coordination chemistry and crystal engineering.¹ The versatility of this heterocycle is due, in the case of pyrazole, to the simultaneous presence of a Lewis basic donor and a Lewis acid NH group, capable of forming hydrogen bonds. This feature has been exploited for the preparation of molecular and supramolecular species,² with a variety of applications such as anion sensing³ and hydrometallurgy.⁴ In its deprotonated form, the ring possesses two adjacent pyridinic N atoms, which can bind to multiple metal centres in polymetallic structures. About twenty different coordination modes to metal centres have been identified to date.¹ The introduction of pyrazole rings onto the 2 and 6 positions of a pyridine is a common strategy to synthesise tridentate ligands analogous to 2,2':6',2''-terpyridine (tpy).⁵ Despite the vast number of transition metal and rare earth complexes linked to differently functionalised 2,6-bis(pyrazolyl)pyridine, the coordination chemistry of 2,6-bis(5-phenylpyrazol-3-yl)pyridine (H₂L) has surprisingly received less attention.⁶

We report and discuss here on the isolation of an unexpected supramolecular structure, [{Co(H₂L)₂}(H₂L)₄]²⁺, that was encountered while studying the coordination chemistry of H₂L with Co(II). The structure is composed of the homoleptic pseudo-octahedral disubstituted Co(II) complex, which then incorporates four more H₂L ligands in the second coordination sphere. The high degree of intermolecular hydrogen bonding means that the structure can be considered as an individual supramolecular assembly. This supramolecular arrangement markedly differs from known examples of (and not limited to pyrazole chemistry) i) co-crystallisation of ligands in the lattice or second coordination sphere,⁷ ii) formation of an extensive three-dimensional hydrogen bonded network (coordination polymer or MOF),⁸ or iii) construction of the supramolecular assembly via hydrogen bonding with anions in the lattice.⁹

The H₂L ligand was prepared according to published procedures.⁶ We initially reacted 2.5 eq. of H₂L with hydrated

CoCl₂. After reaction work up, which included exchange of Cl⁻ for PF₆⁻ to improve the solubility of the product in dichloromethane, we attempted to grow single crystals for X-ray diffraction. Two different products were obtained, which corresponded respectively to a 1:6 (crystallised as dark orange prisms) and 1:2 (as orange block-shaped crystals) metal to ligand ratio. We therefore attempted to obtain and characterise both products individually, including the 1:1 monosubstituted complex, [(H₂L)CoCl₂], as summarised in Fig. 1. Reaction of a 1:1 CoCl₂ to H₂L ratio yielded [(H₂L)CoCl₂]. Although we could not obtain a structural determination, the pentacoordinated Co²⁺ environment was confirmed by comparing its solution UV-Vis spectrum (see ESI†) with its analogous [(tpy)CoCl₂]¹⁰ and [(H₂L¹)CoCl₂] (L¹=2,6-bis(pyrazol-3-yl)pyridine).¹¹ The disubstituted complex [(H₂L)₂Co][PF₆]₂, obtained by reacting 1 eq. of metal with 2 eq. of H₂L, was characterised by X-ray diffraction (see ESI†). The structure reveals the expected distorted octahedral complex, with the two H₂L ligands lying perpendicularly with respect to each other. Each of the four NH groups is involved in N-H...O hydrogen bonding with acetone molecules, due to the ditopic nature of the pyrazole rings. However, contrary to previously reported structures, there is no evidence of interaction between the pyrazole NH groups and the PF₆⁻ anions.⁹ Finally, by treating 1 eq. of CoCl₂ with 6 eq. of H₂L we were able to isolate and characterise the 1:6 complex.

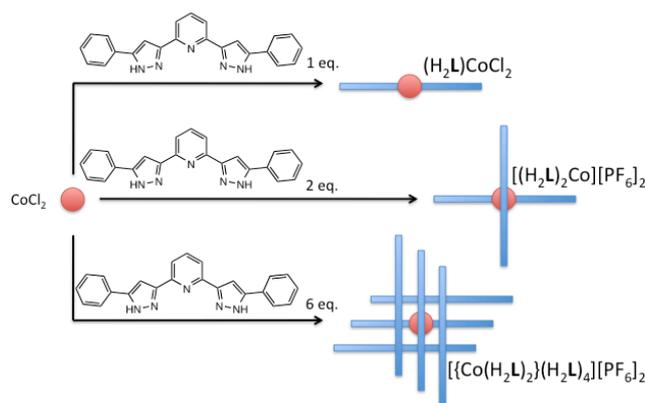


Fig.1 Summary of the attempted reactions and isolated products. The drawing of the H₂L ligand highlights its 1*H*,1*H* tautomeric form.

[{Co(H₂L)₂}(H₂L)₄][PF₆]₂ crystallises in the tetragonal *I* 4₁/*a* space group† (Fig. 2a). The core of the assembly is formed by a homoleptic disubstituted Co complex

(highlighted in Fig. 2b), whose structural features are essentially identical to $[(\text{H}_2\text{L})_2\text{Co}][\text{PF}_6]_2$, apart from a more pronounced rotation of the peripheral phenyl rings for the former. Four more external H_2L ligands lock onto the central complex, forming a structure similar to a twisted grid.¹² In fact, the structure itself could be viewed as a heteronuclear $[3 \times 3]$ grid templated by a central Co^{2+} cation and eight peripheral H^+ . Within each set of parallel ligands on either sides of the structure, the H_2L units lie at an average distance of 3.5 Å, which indicates partial stabilisation of the assembly via π -stacking. Moreover, each external H_2L unit is perfectly anchored via hydrogen bonding, involving the $\text{N-H} \cdots \text{N}'$ groups of the pyrazole rings, to all the three perpendicular H_2L molecules in front. In this respect, the parallel disposition of the three H_2L perfectly match the directional binding of the perpendicular H_2L (Fig. 3). This remarkable arrangement is especially possible due to the coexistence of the various tautomeric forms of the pyrazole rings.¹ In fact, while the formation of the Co complex means the coordinated H_2L ligands assume a $1H,1H$ tautomeric configuration, the external H_2L units assemble with a $1H,2H$ configuration (see Fig. 1). The formation of the three hydrogen bonds seems to be the reason for the shifting of the four peripheral H_2L molecules. The two PF_6^- counterions, along with CH_2Cl_2 molecules trapped within the lattice, lie external to the structure. There is no evidence of hydrogen bonding between the H_2L and PF_6^- units, which makes $[\{\text{Co}(\text{H}_2\text{L})_2\}(\text{H}_2\text{L})_4]^{2+}$ an isolated supramolecular assembly.

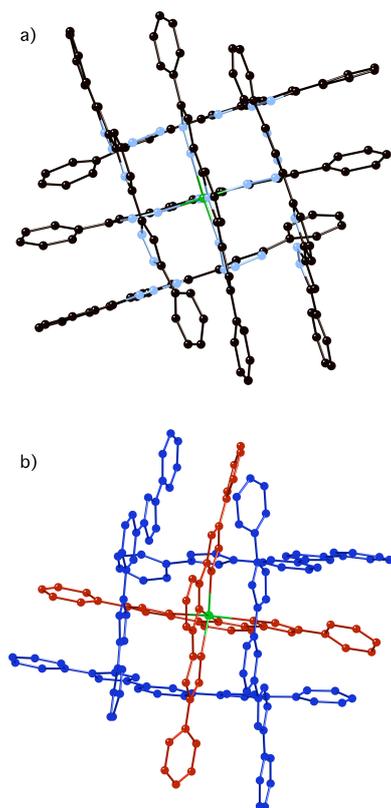


Fig. 2 X-ray crystal structure of $[\{\text{Co}(\text{H}_2\text{L})_2\}(\text{H}_2\text{L})_4][\text{PF}_6]_2$. Fig. 2a highlights the twisted grid shape of the supramolecular complex, whereas Fig 2b shows the central core (red with green central Co atom) and the

peripheral H_2L units (blue). Hydrogen atoms, lattice solvent molecules, and PF_6^- anions are omitted for clarity.

The solid state IR analysis of $[\{\text{Co}(\text{H}_2\text{L})_2\}(\text{H}_2\text{L})_4][\text{PF}_6]_2$ highlights multiple bands corresponding to the pyrazole NH stretchings, with three main peaks appearing at 3646, 3567, and 3366 cm^{-1} . This can be ascribed to presence of both hydrogen bonded and free NH groups. However it cannot be excluded that the local C_{2v} symmetry of the $1H,1H$ H_2L tautomer might activate both the asymmetric and symmetric NH stretchings. All the three peaks disappear if the complex is reacted with an excess of strong base such as NaH, which confirms their assignment to the NH bonds.

The magnetic behaviour for the octahedrally coordinated $[(\text{H}_2\text{L})_2\text{Co}][\text{PF}_6]_2$ and $[\{\text{Co}(\text{H}_2\text{L})_2\}(\text{H}_2\text{L})_4][\text{PF}_6]_2$ were found to be very similar. Plots of the effective magnetic moment per cobalt atom show μ_{eff} values at high temperatures comparable in size to similar cobalt complexes reported elsewhere¹³ (see ESI†).

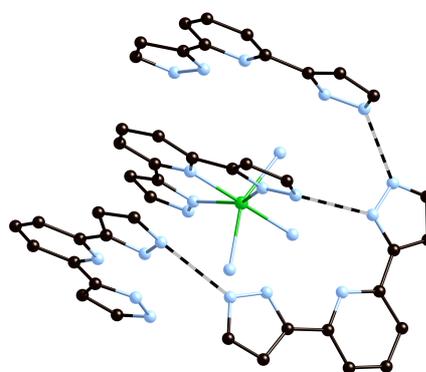


Fig. 3 Anchoring of the peripheral H_2L molecule to the three perpendicular H_2L units. The dashed lines represent the hydrogen bonded structure formed within the supramolecular assembly.

In summary, while investigating the coordination chemistry of H_2L with CoCl_2 , we encountered a supramolecular assembly formed by an inner disubstituted complex and four more peripheral ligands. The novelty of the structure is due to the organising ability of various pyrazole tautomers of the H_2L ligands to template the construction of individual units of $[\{\text{Co}(\text{H}_2\text{L})_2\}(\text{H}_2\text{L})_4]^{2+}$. In this respect, this finding furthers the already developed coordination and supramolecular chemistry of the pyrazole ring. It seems also possible to step-by-step construct this supramolecular assembly, by isolating the mono and disubstituted Co complexes. Since homoleptic complexes of differently substituted 2,6-bis(pyrazol-3-yl)pyridine have been previously reported, but never with a similar behaviour, we are investigating the importance of the peripheral phenyl rings for the construction of the supramolecular assembly.

This work was supported by the Australian Research Council (DP0985481). The authors wish to thank Prof. P. C. Junk and A/Prof. P. C. Andrews (Monash University) for support for X-ray structural determination. Prof. M. I. Ogden (Curtin University) and A/Prof. G. A. Koutsantonis (The University of Western Australia) are kindly acknowledged for useful discussion.

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† Electronic Supplementary Information (ESI) available: experimental procedures and characterisation data for [(H₂L)CoCl₂], [(H₂L)₂Co][PF₆]₂, and [{Co(H₂L)₂}(H₂L)₄][PF₆]₂. CCDC 756326 ([[(H₂L)₂Co][PF₆]₂) and 756327 ([{Co(H₂L)₂}(H₂L)₄][PF₆]₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk or from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033. See DOI: 10.1039/b000000x/

‡ Crystal data and structure refinement for [(H₂L)₂Co][PF₆]₂·(acetone)₆: empirical formula C₆₄H₇₀CoF₁₂N₁₀O₆P₂; M_r=1424.17; radiation wavelength 0.71073 Å; crystal system monoclinic; space group P 2₁/n; unit cell dimensions: a=17.5637(5), b=23.2693(6), c=17.8248(4) Å, b=91.029(2)°; volume 7283.7(3) Å³; Z=4; density (calculated) 1.299 g/cm³; absorption coefficient 0.363 mm⁻¹; F(000)=2948; crystal size 0.40x0.35x0.08 mm³; θ range for data collection 3.50 to 27.50°; reflections collected/unique 68411/16569 [R(int)=0.0763]; completeness to θ 99.0%; data/restraints/parameters 16569/16/868; Goodness-of-fit on F² 0.796; final R indices [I>2σ(I)] R₁=0.0695, wR₂=0.1772; R indices (all data) R₁=0.2357, wR₂=0.2158; largest diff. peak and hole 0.463 and -0.286 eÅ⁻³. Crystals of [(H₂L)₂Co][PF₆]₂ lost solvent rapidly at room temperature and were found to deteriorate below 273K. A dataset was eventually collected after the crystal was coated with fast setting epoxy resin with the diffraction data being collected at 296K. An Oxford Diffraction Gemini diffractometer fitted with graphite-monochromated Mo Kα radiation was used. The structure was refined against F² with full-matrix least-squares using the program SHELXL-97.¹⁴ The geometry of several solvent acetone molecules were restrained to ideal values. All H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms.

§ Crystal data and structure refinement for [{Co(H₂L)₂}(H₂L)₄][PF₆]₂·2CH₂Cl₂: empirical formula C₁₄₀H₁₀₆Cl₄CoF₁₂N₃₀P₂; M_r=2699.22; radiation wavelength 0.71073 Å; crystal system tetragonal; space group I 4₁/a; unit cell dimensions a=26.0796(3), b=26.0796(3), c=17.9843(5) Å; volume 12231.9(4) Å³; Z=4; density (calculated) 1.466 g/m³; absorption coefficient 0.341 mm⁻¹; F(000)=5556; crystal size 0.10x0.08x0.06 mm³; θ range for data collection 2.21 to 25.00°; reflections collected/unique 24769/5384 [R(int)=0.0569]; completeness to θ 99.9%; data/restraints/parameters 5384/71/443; Goodness-of-fit on F² 1.039; final R indices [I>2σ(I)] R₁=0.0869, wR₂=0.2372; R indices (all data) R₁=0.1510, wR₂=0.2916; largest diff. peak and hole 1.267 and -0.721 eÅ⁻³. [{Co(H₂L)₂}(H₂L)₄][PF₆]₂·2CH₂Cl₂ single crystals were mounted upon a glass fibre of highly viscous oil and data was collected on a Bruker X8 Apex KAPPA CCD diffractometer (graphite-monochromated Mo_{Kα} X-ray radiation) at 123(2) K and corrected for absorption using the SADABS package. The structure was refined against F² with full-matrix least-squares using the program SHELXL-97.¹⁴ The PF₆⁻ counterion and a molecule of CH₂Cl₂ are disordered over one position with 50% occupancies. Due to this disorder each of the atoms in the PF₆⁻ and DCM molecules were constrained and their thermal parameters refined together. All H-atoms were added at calculated positions with the exception of those involved in H-bonding which were assigned according to electron density.

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