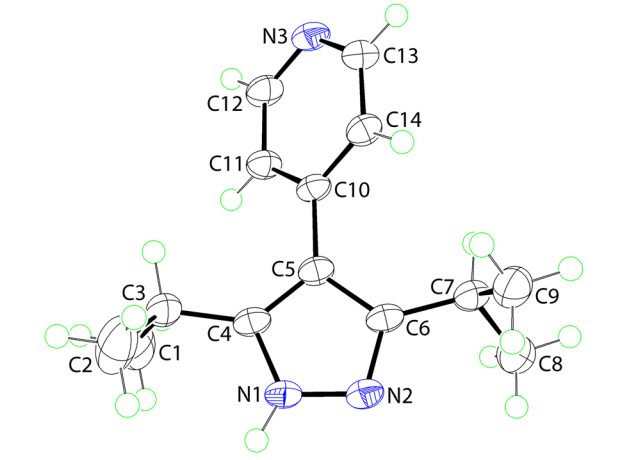
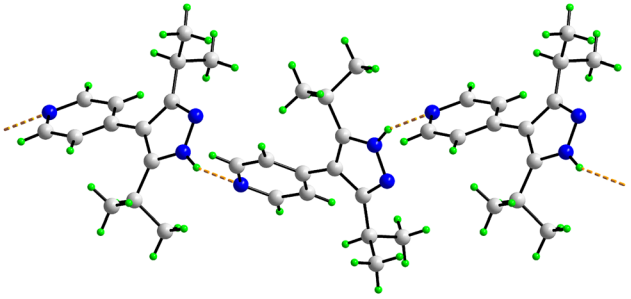
Harukaze Kanazawa, Edward R. T. Tiekink* and Kiyoshi Fujisawa*

Crystal structure of 4-[3,5-bis(propan-2-yl)-1*H*-pyrazol-4-yl]pyridine, $C_{14}H_{19}N_3$





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Abstract

$C_{14}H_{19}N_3$, monoclinic, $P2_1/c$ (no. 14), a = 5.64918(12) Å, b = 17.0755(4) Å, c = 13.4012(3) Å, β = 92.053(2)°, V = 1291.88(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0377, wR_{ref} (F^2) = 0.0983, T = 178 K.

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***Corresponding authors: Edward R. T. Tiekink**, Department of Chemistry, Universitat de les Illes Balears, Crta de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain, E-mail: edward.tiekink@uib.es. https://orcid.org/0000-0003-1401-1520; and **Kiyoshi Fujisawa**, Department of Chemistry, Ibaraki University, Mito, Ibaraki 310–8512, Japan, E-mail: kiyoshi.fujisawa.sci@vc.ibaraki.ac.jp. https://orcid.org/0000-0002-4023-0025

Harukaze Kanazawa, Department of Chemistry, Ibaraki University, Mito, Ibaraki 310-8512, Japan, E-mail: 24nm012h@vc.ibaraki.ac.jp. https://orcid.org/0009-0002-4417-5059

Table 1: Data collection and handling.

Crystal:	Colourless slab
Size:	0.19 × 0.13 × 0.05 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.07 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB P200, φ and ω scan
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19063, 2630, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2355
$N(param)_{refined}$:	161
Programs:	CrysAlis^{PRO}[1], IL MILIONE[2], SHELX [3], WinGx[4]

1 Source of material

The title compound, (I), was prepared in a two-step process. **L1(Py)pzTs** [3,5-bis(propan-2-yl)-1-(*p*-toluenesulfonyl)-pyrazol-4-(4′-pyridine)]: A mixture of 2-pyridyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.00 g, 4.88 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.200 g, 0.173 mmol) was stirred in 1,2-dimethoxyethane (DME) (20 mL) at room temperature under an argon atmosphere. To this mixture was added L1(Br)pzTs[5] (1.58 g, 4.10 mmol) in DME (10 mL) and a saturated aqueous Na_2CO_3 solution (10 mL). The solution was heated to reflux at 393 K overnight under an argon atmosphere and then cooled to ambient temperature. The solution was removed under vacuum, acetone (30 mL) was added followed by filtration to remove undissolved material. The solvent was removed under vacuum. The crude solid was purified via column chromatography on silica gel with acetone and hexane (1/1 v/v) as the eluent to give a cream solid, characterised as L1(Py)pzTs (1.34 g, 3.49 mmol, 85 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.05 (d, J = 7 Hz, 6H, CHMe_2), 1.07 (d, J = 7 Hz, 6H, CHMe_2), 2.44 (s, 3H, C_6H_4 *Me*), 2.62 (m, J = 7 Hz, 1H, C*H*Me$_2$), 3.81 (m, J = 7 Hz, 1H, C*H*Me$_2$), 7.12 (d, J = 6 Hz, 2H, 2,6-py), 7.13 (d, J = 8 Hz, 2H, 3,5–Ts), 7.90 (d, J = 8 Hz, 2H, 2,5–Ts), 8.61 (d, J = 6 Hz, 2H, 3,5-py), NH not observed. The molecular structure is shown in the figure. Table 1 contains crystallographic data.

L1(Py)pzH [3,5-bis(propan-2-yl)-1*H*-pyrazol-4-(4′-pyridine)]: L1(Py)pzTs (1.34 g, 3.49 mmol) in MeOH (20 mL) was deprotected by heating for 5 h in the presence of 5 M NaOH solution (10 mL). The mixture was subsequently extracted with dichloromethane (3 × 15 mL). The organic layers were combined and washed with aqueous saturated NaCl solution and dried over $MgSO_4$. The solvent was removed under vacuum. The crude solid was purified via column

chromatography on silica gel with acetone and hexane (1/1 v/v) as the eluent to give a white solid, L1(Py)pzH (0.59 g, 2.57 mmol, 74 %). Anal. Calcd. for $C_{14}H_{19}N_3$: C 73.33, H 8.35, N 18.32; Found: C 73.21, H 8.52, N 18.41 %. **IR** (KBr, cm^{-1}): 3147s ν(N–H), 3110 s ν(N–H), 3061 s ν(C–$H_{aromatic}$), 3004 s ν(C–$H_{aromatic}$), 2968 s ν(C–$H_{aliphatic}$), 2929 m ν(C–$H_{aliphatic}$), 2870 m ν(C–$H_{aliphatic}$), 1601 s ν(C=N), 1568 m ν(C=N). **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 1.22 (d, J = 7 Hz, 12H, CHMe_2), 3.04 (m, J = 7 Hz, 2H, CHMe$_2$), 7.19 (d, J = 6 Hz, 2H, 2,6-py), 8.62 (d, J = 6 Hz, 2H, 3,5-py), NH not observed. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ 22.5 (CHMe_2), 25.4 (CHMe$_2$), 113.8 (4-pz), 124.9 (2,6-py), 142.8 (1-py), 149.9 (3,5-py), 3,5-pz not observed.

2 Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with U_{iso} (H) = 1.2–1.5U_{eq} (C). The N-bound H atom was refined with N–H = 0.88 + -0.01 Å and with U_{iso} (H) = 1.2U_{eq} (N).

3 Discussion

Coinage metal(I)-based, cyclic trinuclear complexes have been extensively studied as they represent a fascinating class of trinuclear metallocycles with M(I)···M(I) interactions.[6] One of the useful ligands used to generate these complexes is pyrazole, a five-numbered, heterocyclic aromatic ring. The present study was motivated by continuing interest in the exploration of the effects of the pyrazole substituent(s) upon the structures and physicochemical properties of these trinuclear complexes. In this connection, recently, halide and phenyl groups were successfully introduced into the 4-position of the pyrazole ring.[5,7] In this contribution, a pyridyl group has been introduced into the 4-position of the pyrazole ring employing a similar synthetic method used for the introduction of a phenyl group into the 4-position.[5] Thus, the Suzuki–Miyaura cross-coupling reaction from L1(Br)pzTs[5] was performed to yield L1(Py)pzTs in 85 % yield. After deprotection of L1(Py)pzTs with base, L1(Py)pzH, (I), was obtained in 74 % yield. Related synthetic methods to generate 3,5-dimethyl-4-(4′-pyridyl)pyrazole[8] and 3,5-diethyl-4-(4′-pyridyl)pyrazole[9] have been published.

The IR spectrum of L1(Py)pzH, (I), features a complicated pattern of absorption bands between 3147 and 3110 cm^{-1}, assigned to N–H stretching, which is clearly different from the single, strong absorption band at 3219 cm^{-1} of L1(Ph)pzH.[5] This complicated pattern is likely to arise from the hydrogen-bonding in the crystal (see below). Moreover, a strong absorption band at 1601 cm^{-1}, absent in the IR spectrum of L1(Ph)pzH,[5] was observed for (I), assignable to ν(C=N) of the pyridyl substituent. The expected signal in ^{1}H NMR spectrum of L1(Py)pzH due to methyl–H appeared at 1.22 ppm, which is shifted downfield compared to those of the precursor, L1(Py)pzTs, which resonated at 1.05 and 1.07 ppm.[5] Further, solid-state details of (I) were revealed through an X-ray crystallographic study. The molecular structure is shown in the figure. Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

The molecular structure of (I) is illustrated in the upper view of the figure (70 % displacement ellipsoids). The molecule comprises a 1,2-pyrazolyl ring substituted in the 4-position by a pyridyl group, and in the 3- and 5-positions by *i*-propyl groups. The wider angle subtended at the N1 atom cf. the N2 atom, i.e. 113.24(9) and 105.03(9)°, respectively, confirms protonation at the N1 atom. Within the pyrazolyl ring, there are significant disparities in the C–N bond lengths, i.e. C4–N1 = 1.3516(14) Å and C6–N2 = 1.3291(14) Å, and between the C–C bonds, i.e. C4–C5 = 1.3887(16) Å and C5–-C6 = 1.4238(15) Å, consistent with significant localisation of π-electron density in the C6–N2 and C4–C5 bonds. The angle between the least-squares planes through the five- and six-membered rings is 40.83(6)°, indicating a twisted confirmation. The N1–N2 bond length is 1.3557(14) Å.

The title bifunctional ligand, containing both pyridyl and pyrazolyl residues, (I), is the *i*-propyl derivative of the previously explored methyl, (II), and ethyl, (III), species. Of these, only (II) has been characterised crystallographically, as a hydrate.[10] In (II),[10] with two independent molecules in the asymmetric-unit, the dihedral angles between the five- and six-membered rings are 36.48(10) and 47.25(9)°, i.e. a range of angles incorporating the value in (I). Similar trends in C–N bond lengths were noted in (II) and in the C–C bond lengths for one of the independent molecules of (II) but not in the second independent molecule; rather high standard uncertainty values in (II) are noted.

These bifunctional molecules have been noted for their ability to form a mononuclear species with (II), i.e. pyridyl-bound in all-*trans* Ph_2SnCl_2(II)$_2$,[8] and a two-dimensional coordination polymer with bridging, via pyrazolyl- and pyridyl–N atoms derived from two molecules of (III), i.e. in six-coordinate $\{CdCl_2(III)_2\}_n$.[11]

In the molecular packing of (I), pyrazolyl–N–H···N(pyridyl) hydrogen bonds [N1–H1n···N3^i: H1n···N3^i = 2.034(12) Å, N1···N3^i = 2.8794(14) Å with angle at H1n = 157.6(11)° for symmetry operation (i): 1 + x, 1/2 −y, −1/2 + z] within supramolecular chains are apparent as shown in the lower view of the figure. These have a twisted topology and are aligned along [2 0 −1]. The chains assemble into a layer parallel to (1 0 1) featuring several C–H···π(pyrazolyl, pyridyl) interactions between them. The shortest and most directional of these is a

pyridyl–C–H···π(pyrazolyl) contact [C12–H12···Cg(pyrazolyl)^{ii}: H12···Cg(pyrazolyl)^{ii} = 2.55 Å, C12···Cg(pyrazolyl)^{ii} = 3.3744(12) Å with angle at H12 = 145° for (ii): –1 + *x*, y, z]. The shortest contact between layers along the b-axis are of the type H···H [C2–H2a···H2a^{iii}: H2a···H2a^{iii} = 2.31 Å, C2···H2a^{iii} = 3.09 Å with angle at H2a = 135° for (iii): –x, 1 –y, 1 –z]. A comparison between the molecular packing in (I) and that of (II)[10] is not valid owing the presence of water molecules of crystallisation in the latter.

The dominance of hydrogen in forming surface contacts between layers in the molecular packing was confirmed by an analysis of the calculated Hirshfeld surface and two-dimensional fingerprint plots using CrystalExplorer[12] and following standard protocols.[13] The H···H surface contacts amounted to 66.5 %, following by 17.4 % for N···H/H···N and 15.6 % for C···H/H···C contacts; the remaining 0.5 % was accounted for by C···C contacts.

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Conflict of interest: The authors declare no conflicts of interest.

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