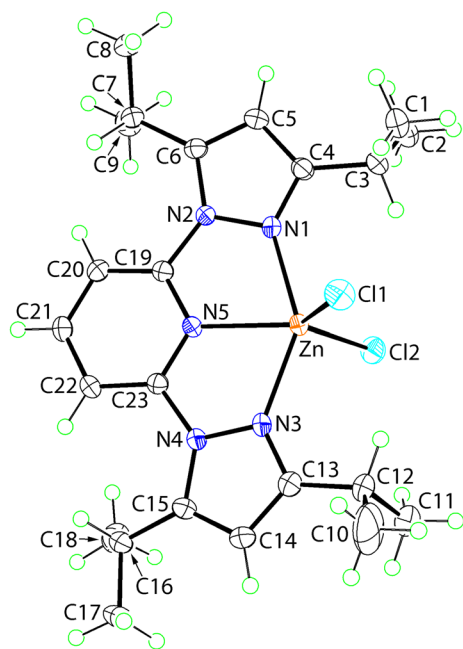


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Crystal structure of dichlorido{2,6-bis(3,5-diisopropyl-*N*-pyrazolyl)pyridine}zinc(II), $C_{23}H_{33}Cl_2N_5Zn$



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Abstract

$C_{23}H_{33}Cl_2N_5Zn$, monoclinic, $Pca2_1$ (no. 29), $a = 15.9299(3)$ Å, $b = 12.8205(2)$ Å, $c = 12.7157(2)$ Å, $V = 2596.92(8)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0169$, $wR_{ref}(F^2) = 0.0459$, $T = 178$ K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.17 × 0.11 × 0.06 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ :	1.17 mm ^{−1}
Diffractometer, scan mode:	RIGAKU XtaLAB P200, ω scan
θ_{max} , completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	18773, 5071, 0.021
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4886
$N(param)_{refined}$:	288
Programs:	RIGAKU, ¹ IL MILIONE, ² SHELX, ³ WINGX ⁴

1 Source of material

A solution of ligand, 2,6-bis(3,5-diisopropyl-*N*-pyrazolyl)pyridine (denoted as L;⁵ 99.9 mg, 0.263 mmol) in CH_2Cl_2 (10 mL) was added slowly to a solution of $ZnCl_2$ (36.7 mg, 0.269 mmol) in MeOH (5 mL). After the stirring for 3 h at room temperature, the solvent was evaporated under reduced pressure to afford a white powder. Colourless crystals suitable for X-ray crystallography were obtained by the slow evaporation of a saturated dichloromethane/methanol (1:1 v/v) solution held at room temperature which were characterised as $[ZnCl_2(L)]$ (84.8 mg, 0.164 mmol, 62%). **Anal. Calcd.** for $C_{23}H_{33}Cl_2N_5Zn$: C, 53.55; H, 6.45; N, 13.58. Found: C, 53.42; H, 6.35; N, 13.59. **IR** (KBr, cm^{-1}): 3119 m ν (Ar–H), 2967s ν (C–H), 2934s ν (C–H), 2871 m ν (C–H), 1608s, 1561s, 1470s, 1388s, 1311s. **Far-IR** (CsI, cm^{-1}): 303s ν (Zn–Cl), 279 m ν (Zn–Cl). **Raman** (neat, solid, cm^{-1}): 3134w ν (Ar–H), 2966 m ν (C–H), 2931 m ν (C–H), 2872 m ν (C–H), 1589s, 1563s, 1490s, 1449s, 1372s, 999s, 279 m ν (Zn–Cl). **¹H NMR** ($CDCl_3$, 500 MHz): δ 8.13 (t, $J = 8.5$ Hz, 1H, 4-pyH), 7.41 (d, $J = 8.5$ Hz, 2H, 3,5-pyH), 6.31 (s, 2H, 4-pzH), 3.84 (m, $J = 7$ Hz, 2H, $(CH(CH_3)_2)$), 3.36 (m, $J = 7$ Hz, 2H, $(CH(CH_3)_2)$), 1.40 (d, $J = 7$ Hz, 12H, $(CH(CH_3)_2)$), 1.34 (d, $J = 7$ Hz, 12H, $(CH(CH_3)_2)$). **¹³C NMR** ($CDCl_3$, 125 MHz): δ 163.2 (2,6-py), 152.6 (3 or 5-pz), 147.6 (3 or 5-pz), 144.6 (4-py), 108.8 (3,5-py), 106.2 (4-pz), 27.5 $(CH(CH_3)_2)$, 27.2 $(CH(CH_3)_2)$, 22.8 $(CH(CH_3)_2)$, 22.7 $(CH(CH_3)_2)$. **UV–vis** (MeOH, λ_{max} , nm (ϵ , $M^{-1}cm^{-1}$)): 246 (20900), 265 (sh, 15000), 296(11900), 324 (sh, 6200). **UV–vis** (nujol, λ , nm): 250, 280, 337. **Diffuse reflectance** (solid neat, λ , nm): 280, 336.

2 Experimental details

The C-bound H atoms were geometrically placed ($C-H = 0.95-1.00 \text{ \AA}$) and refined as riding with $U_{iso}(H) = 1.2-1.5U_{eq}(C)$. Owing to poor agreement, two reflections, i.e. (2 0 0) and (3 6 0), were omitted from the final cycles of refinement. The absolute structure was determined based on differences in Friedel pairs included in the data set.

3 Discussion

Planar, tridentate nitrogen ligands have been employed extensively in coordination chemistry, since these ligands can stabilise transition metal complexes by the chelate effect, with the resulting fascinating complexes exhibiting diverse catalytic performance and photochemical behaviour.⁶⁻¹⁰ These planar tridentate ligands can be classified into three groups, viz. 2,2';6',2''-terpyridine (terpy),^{6,8} 2,6-bis(1*H*-pyrazol-3-yl)pyridine,^{9,10} with two covalent $C_{\text{pyrazole}}-C_{\text{pyridine}}$ bonds, and 2,6-bis(*N*-pyrazol)pyridine with two covalent $N_{\text{pyrazole}}-C_{\text{pyridine}}$ bonds.^{5,9} Recently, we reported a zinc(II) chlorido complex with 2,6-bis(5-isopropyl-1*H*-pyrazol-3-yl)pyridine (denoted as L^1), viz. $[ZnCl_2(L^1)]$ to explore chemistry aimed towards new planar tridentate ligands.¹⁰

The title complex, $[ZnCl_2(L)]$, (I), was obtained by the reaction of L with $ZnCl_2$ in 62 % yield. The IR, NMR and UV-vis spectral data for (I) are slightly shifted from those data of L .⁵ In the far-IR spectrum, the most intense bands appeared at 303 and 279 cm^{-1} for (I), while those for $[ZnCl_2(L^1)]$ appeared at 302 and 276 cm^{-1} .¹⁰ Interestingly, the 1H and ^{13}C NMR spectra for (I) were not broadened compared with those observed in $[ZnCl_2(L^1)]$ due to the absence of N-H bonds in complex (I).¹⁰

The molecular structure of (I) is illustrated in the figure (50 % displacement ellipsoids). The zinc(II) atom is coordinated by the tridentate ligand, L, with the penta-coordinate geometry completed by two chlorido ligands. The coordination geometry is possibly best described as being based on a trigonal-bipyramid. In this description, the trigonal plane and zinc(II) atom are co-planar [r.m.s. deviation = $0.0038 \text{ \AA}$] with the pyrazolyl-N1 and -N3 atoms lying $2.0314(17) \text{ \AA}$ above and $2.0400(17) \text{ \AA}$ below the plane, respectively. The distortion of the N1-Zn-N3 angle from 180° , i.e. $144.50(6)^\circ$, is related to the restricted bite angles subtended by the tridentate ligand [N1-Zn-N5 and N3-Zn-N5 = $72.32(6)$ and $72.20(6)^\circ$, respectively]. An alternate description is indicated by the geometric parameter, τ_5 , which is calculated from the equation, $\tau_5 = \beta - \alpha / 60$, where α and β are the largest angles ($\beta > \alpha$) around a five-

coordinate metal centre.¹¹ In (I), τ_5 computes to 0.36, a value intermediate between 0.0, for a square-pyramidal geometry, and 1.0, for a trigonal-bipyramidal geometry.¹¹ When compared to (I), this value (0.36) is smaller than that of $[ZnCl_2(L^1)]$ (0.43). This difference arises from the angle between the two-pyrazole nitrogen and the zinc(II) centre, possibly due to a difference in the position of the five-membered ring-N atoms, i.e. $144.50(6)^\circ$ for (I) versus $148.76(6)^\circ$ for $[ZnCl_2(L^1)]$. Small twists are noted in the coordinated molecule L, as seen in the dihedral angles formed by the pyridyl residue and the N1- [7.64(13)°] and N3-pyrazoyl [7.41(14)°] rings; the dihedral angle between the two pyrazoyl rings = $9.27(16)^\circ$. As anticipated, the Zn-N1, N3 bond lengths [2.1367(15) and 2.1384(16) Å] are equal within experimental error and significantly shorter than the Zn-N5 bond length [2.1869(15) Å], involving the pyridyl-N atom. The Zn-Cl1, Cl2 bond lengths are close to each other [2.2610(6) and 2.2572(5) Å].

In the molecular packing, molecules assemble into a helical chain along the *c*-axis featuring pyrazolyl-C-H...Cl interactions [$C5-H5 \cdots Cl2^i$: $H5 \cdots Cl2^i = 2.80 \text{ \AA}$, $C5 \cdots Cl2^i = 3.596(2) \text{ \AA}$ with the angle subtended at H5 = 142° for symmetry operation (i) $2 - x, 1 - y, -1/2 + z$]. The chains assemble into undulating layers parallel to the *ac*-plane with methyl-C-H... π (chelate) interactions [$C18-H18a \cdots Cg(Zn, N3, N4, N5, C23)^{ii}$: $H18a \cdots Cg(Zn, N3, N4, N5, C23)^{ii} = 2.59 \text{ \AA}$, $C18 \cdots Cg(Zn, N3, N4, N5, C23)^i = 3.481(3) \text{ \AA}$ with angle at H18a = 152° for (ii) $3/2 - x, y, 1/2 + z$] evident between them. The layers inter-digitate along the *b*-axis with close methyl-H...H(methyl) contacts between them [$C10-H10a \cdots H18b^{iii}$: $H10a \cdots H18b^{iii} = 2.25 \text{ \AA}$ with the angle at H10a = 172° for (iii) $2 - x, 2 - y, -1/2 + z$].

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References

1. Rigaku Oxford Diffraction. *CrysAlis^{PRO}*; Rigaku Corporation: Oxford, UK, 2021.

2. Burla, M. C.; Caliendo, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D.; Spagna, R. IL MILIONE: a Suite of Computer Programs for Crystal Structure Solution of Proteins. *J. Appl. Cryst.* **2007**, *40*, 609–613.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Farrugia, L. J. WinGX and ORTEP for Windows: An Update. *J. Appl. Cryst.* **2012**, *45*, 849–854.
5. Fujisawa, K.; Yamada, A.; Koyama, M.; Young, D. J. The Copper(II) Coordination Chemistry of Alkyl Substituted Bispirazole Pyridine Ligands: Structure and Spectral Properties. *Inorg. Chim. Acta.* **2023**, *555*, 121567.
6. Bessel, C. A.; See, R. F.; Jameson, D. L.; Churchill, M. R.; Takeuchi, K. J. Structural Considerations of Terdentate Ligands: Crystal Structures of 2, 2': 6', 2''-Terpyridine and 2, 6-Bis (pyrazol-1-yl) Pyridine. *J. Chem. Soc. Dalton Trans.* **1992**, 3223–3228. <https://doi.org/10.1039/dt9920003223>.
7. Mukherjee, R. Coordination Chemistry with Pyrazole-based Chelating Ligands: Molecular Structural Aspects. *Coord. Chem. Rev.* **2000**, *203*, 151–218.
8. Baranoff, E.; Collin, J.; Flamigni, L.; Sauvage, J. From Ruthenium(II) to Iridium(III): 15 Years of Triads Based on Bis-Terpyridine Complexes. *Chem. Soc. Rev.* **2004**, *33*, 147–155.
9. Halcrow, M. A. The Synthesis and Coordination Chemistry of 2,6-Bis(Pyrazolyl)Pyridines and Related Ligands — Versatile Terpyridine Analogues. *Coord. Chem. Rev.* **2005**, *249*, 2880–2908.
10. Fujisawa, K.; Minakawa, Y.; Young, D. J. Transition metal(II) Coordination Chemistry Ligated by a New Coplanar Tridentate Ligand, 2,6-Bis(5-isopropyl-1H-pyrazol-3-yl)pyridine. *Inorganics* **2025**, *13*, 189.
11. Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J.; van Verschoor, G. C. Nitrogen-sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane] copper(II) Compounds Containing nitrogen-sulphur Donor Ligands; the Crystal and Molecular Structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]-copper(II) perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356. <https://doi.org/10.1039/dt9840001349>.