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The crystal structure of tris(4-methyl-1*H*-pyrazol-1-yl)methane, C₁₃H₁₆N₆

Table 1: Data collection and handling.

Crystal:	Colourless block
Wavelength:	Size 0.20 × 0.10 × 0.10 mm
μ :	Mo K α radiation (0.71073 Å)
Diffractometer, scan mode:	0.08 mm ⁻¹
$\theta_{\max}$, completeness:	Bruker APEX-II, φ and ω
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	25.5°, >99%
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	19561, 2544, 0.031
$N(\text{param})_{\text{refined}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1960
Programs:	175
	Brucker [1], Olex2 [2], SHELX [3, 4]

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Abstract

C₁₃H₁₆N₆, orthorhombic, *Pbca* (No. 61), $a = 16.097(2)$ Å, $b = 9.8309(13)$ Å, $c = 17.349(2)$ Å, $\beta = 90^\circ$, $V = 2745.4(6)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0434$, $wR_{\text{ref}}(F^2) = 0.1302$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Distilled water (30 mL) was added to a 50 mL round bottom flask containing a mixture of 4-methyl-1*H*-pyrazole (8.2 g, 0.1 mol) and tetra-*n*-butylammonium bromide (0.32 g, 1 mmol). With vigorous stirring, sodium carbonate (10.5 g, 0.1 mol) was added to the reaction mixture at room temperature. After stirring for 1 h chloroform (30 mL) was

added. This mixture was heated at gentle reflux for three days turning to a pale yellow emulsion. The mixture was allowed to cool to room temperature and filtered through a Büchner funnel to remove the excess base. To the filtrate was added diethyl ether (100 mL) and H₂O (30 mL). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (20 mL). The organic layer was dried over sodium sulfate and concentrated by rotary evaporation. The resulting pale yellow solid (5.5 g, 65%) was then dried under vacuum. Crystals were obtained by slow evaporation in CH₃OH within 10 days.

Comment

Tri(pyrazolyl)methanes are a class of ligands that has attracted much attention in recent years due to their ready coordination to metals in a facial arrangement [5–7]. These neutral ligands are formally derived from tris(pyrazolyl) borate ligands by replacing the central boron anion with a carbon atom and their generally higher stability than related pyrazolyl boron based systems. Trofimenko reported the syntheses of several tris(pyrazolyl)methane ligands based on pyrazole-3-yl or pyrazole-5-yl substituents and demonstrated that these neutral ligands bind both early (Cr, Mo, W and Mn) and late transition metals pyridine-4-yl substituents (Co, Ni, and Pd). The aim of these changes is to provide a small degree of steric hindrance and considerable coordinative flexibility [8–10].

Keeping the aforementioned research in mind, we herein describe the synthesis and the crystal structure of a

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
C1	0.21029 (9)	1.08294 (15)	0.55016 (8)	0.0437 (4)
H1	0.187962	1.173265	0.562071	0.052*
C2	0.12640 (10)	0.87939 (17)	0.50670 (9)	0.0504 (4)
H2	0.158921	0.849186	0.465834	0.061*
C3	0.05414 (10)	0.82261 (17)	0.53151 (11)	0.0560 (4)
C4	0.03063 (11)	0.9042 (2)	0.59252 (12)	0.0687 (5)
H4	−0.017326	0.889550	0.621235	0.082*
C5	0.00951 (14)	0.7018 (2)	0.49969 (16)	0.0911 (8)
H5A	0.029605	0.682721	0.448725	0.137*
H5B	−0.048988	0.720451	0.497621	0.137*
H5C	0.019226	0.624478	0.532290	0.137*
C6	0.30414 (11)	1.00906 (18)	0.44127 (11)	0.0564 (4)
H6	0.336176	0.943716	0.466151	0.068*
C7	0.30784 (12)	1.0425 (2)	0.36546 (11)	0.0641 (5)
C8	0.24796 (13)	1.1421 (2)	0.35705 (10)	0.0689 (5)
H8	0.236471	1.184603	0.310350	0.083*
C9	0.36499 (18)	0.9829 (3)	0.30556 (16)	0.1057 (9)
H9A	0.415363	1.035060	0.303518	0.159*
H9B	0.338245	0.985171	0.256122	0.159*
H9C	0.377784	0.890467	0.318886	0.159*
C10	0.30912 (10)	1.14057 (17)	0.65582 (9)	0.0478 (4)
H10	0.297547	1.233046	0.659345	0.057*
C11	0.36572 (10)	1.07116 (19)	0.69867 (10)	0.0533 (4)
C12	0.35990 (11)	0.93813 (19)	0.67086 (10)	0.0584 (5)
H12	0.392037	0.866627	0.689368	0.070*
C13	0.41946 (14)	1.1257 (2)	0.76230 (13)	0.0865 (7)
H13A	0.433794	1.218519	0.751420	0.130*
H13B	0.469199	1.072195	0.765949	0.130*
H13C	0.389754	1.121240	0.810215	0.130*
N1	0.14227 (7)	0.98762 (13)	0.55228 (7)	0.0465 (3)
N2	0.08281 (10)	1.00506 (18)	0.60616 (9)	0.0680 (5)
N3	0.24534 (8)	1.08819 (13)	0.47384 (7)	0.0449 (3)
N4	0.20856 (9)	1.17114 (15)	0.42189 (8)	0.0594 (4)
N5	0.27272 (8)	1.05141 (13)	0.60724 (7)	0.0449 (3)
N6	0.30392 (9)	0.92423 (14)	0.61542 (9)	0.0571 (4)

pyrazole-4-yl substituent tri(pyrazolyl)methane. The pyrazole ring (N1, N2, C2–C4) makes dihedral angles of 86.33(11)° and 79.14(10)° with other two pyridine rings (N3, N4, C6–C8 and N5, N6, C10–C12), respectively. In addition, the crystal structure exhibits weak C–H⋯π interactions [C(2)–H(2)⋯Cg2^a = 2.99(2) Å; Cg2 is the centroid of pyridine ring (N3, N4, C1–C3); $a = 1/2 - x, 1/2 + y, z$]. Furthermore, there are a weak π⋯π stacking interactions between pyrazole rings in the crystal structure. The short stacking distance Cg1⋯Cg1^b is 3.7954(11) Å, and Cg1 is the centroid of pyrazole ring (N1, N2, C2, C3, C4), a symmetry code for

Cg1^b was given as (1−x, −y, −z). The stability of crystal structure can be accounted by those interactions.

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