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Crystal structure of bis {hydridotris(3-trifluoromethyl-5-methylpyrazolyl-1-yl)borato- κN^3 }manganese(II), $C_{30}H_{26}B_2F_{18}MnN_{12}$

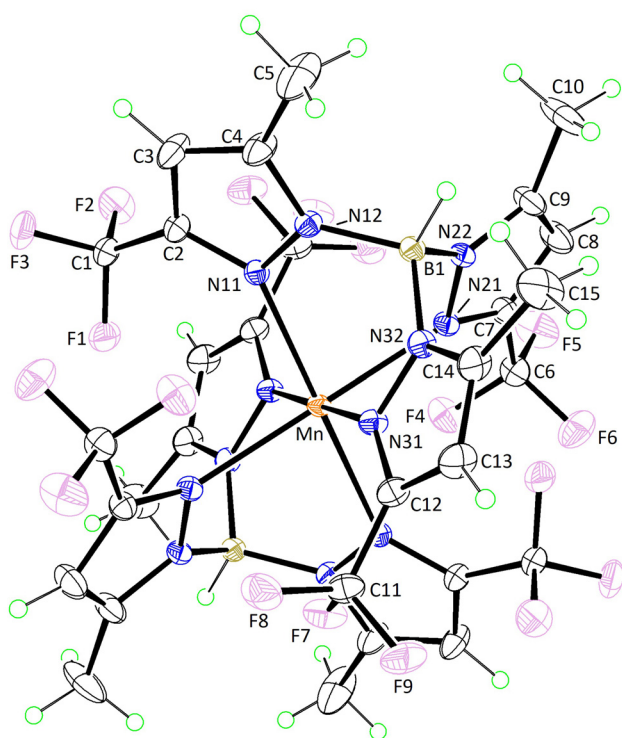


Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.15 × 0.07 × 0.07 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.46 mm ⁻¹
Diffractometer, scan mode:	Rigaku XtaLAB P200, ω
θ_{max} , completeness:	29.8°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	33,278, 5266, 0.055
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 4626
$N(param)_{refined}$:	289
Programs:	CrysAlis ^{PRO} [1], SIR2014 [2], SHELX [3], WinGX/ORTEP [4]

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

A solution of Na{HB(3-CF₃-5-Mepz)₃} (250 mg, 0.519 mmol) [5] in dichloromethane (10 mL) was added slowly to a solution of MnCl₂·4H₂O (103 mg, 0.520 mmol) in methanol (10 mL) over a period of 10 min. After the mixture was stirred for 90 min, degassed dichloromethane (20 mL) was added to the reaction mixture and stirring continued for another 90 min. Then, the solvent was evaporated under vacuum and the resulting solid was extracted with dichloromethane (40 mL). The filtrate was evaporated under vacuum and a white powder obtained. Colourless crystals of [Mn{HB(3-CF₃-5-Mepz)₃}₂] were obtained by crystallisation from its dichloromethane solution (20 mL) held at 243 K. Yield: 28% (139 mg, 0.143 mmol). **Anal. Calcd.** for C₃₀H₂₆B₂F₁₈MnN₁₂: C, 37.03; H, 2.69; N, 17.27%. Found: C; 37.00, H; 2.84, N; 17.09%. **IR** (JASCO FT/IR-550 spectrophotometer, KBr; cm⁻¹): 2941 (s) ν (C–H), 2584 (s) ν (B–H), 1494 (s) ν (C=N), 1465 (s) ν (C=N).

Experimental details

The C- and B-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å & B–H = 1.12 Å) and refined as riding

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Abstract

C₃₀H₂₆B₂F₁₈MnN₁₂, triclinic, $P\bar{1}$ (no. 2), $a = 10.5322(3)$ Å, $b = 10.6475(4)$ Å, $c = 10.9890(4)$ Å, $\alpha = 111.755(3)^\circ$, $\beta = 99.100(2)^\circ$, $\gamma = 112.740(3)^\circ$, $V = 988.07(7)$ Å³, $Z = 1$, $R_{gt}(F) = 0.0338$, $wR_{ref}(F^2) = 0.0907$, $T = 178$ K.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2).

Atom	x	y	z	U_{iso}^*/U_{eq}
Mn	0.5	0.5	0.5	0.01844 (8)
F1	0.60801 (11)	0.71851 (11)	0.85888 (9)	0.0374 (2)
F2	0.67936 (11)	0.95268 (11)	0.90127 (10)	0.0433 (2)
F3	0.51403 (12)	0.84652 (12)	0.97520 (9)	0.0425 (2)
F4	0.78545 (10)	0.59124 (12)	0.37393 (11)	0.0403 (2)
F5	0.84302 (11)	0.72809 (13)	0.26869 (13)	0.0509 (3)
F6	0.69270 (12)	0.48517 (13)	0.15174 (11)	0.0489 (3)
F7	0.30670 (10)	0.10565 (10)	0.38839 (11)	0.0394 (2)
F8	0.10751 (12)	0.06504 (12)	0.43182 (12)	0.0465 (3)
F9	0.09797 (11)	-0.06723 (10)	0.22527 (11)	0.0457 (3)
N11	0.42836 (11)	0.67497 (12)	0.60777 (11)	0.0206 (2)
N12	0.31723 (11)	0.66981 (13)	0.51944 (11)	0.0214 (2)
N21	0.51569 (11)	0.59428 (12)	0.34249 (11)	0.0208 (2)
N22	0.41056 (12)	0.63583 (13)	0.31681 (11)	0.0216 (2)
N31	0.25589 (11)	0.33975 (12)	0.36216 (11)	0.0218 (2)
N32	0.19692 (11)	0.40706 (13)	0.30356 (11)	0.0223 (2)
C1	0.56021 (16)	0.81846 (16)	0.86567 (14)	0.0286 (3)
C2	0.44229 (15)	0.76831 (15)	0.73625 (14)	0.0247 (3)
C3	0.34203 (18)	0.8224 (2)	0.73256 (16)	0.0373 (4)
H3	0.329747	0.889214	0.809885	0.045*
C4	0.26415 (17)	0.75839 (19)	0.59259 (16)	0.0346 (3)
C5	0.1424 (3)	0.7777 (3)	0.5260 (2)	0.0685 (7)
H5A	0.124316	0.848799	0.598896	0.103*
H5B	0.052787	0.677053	0.472567	0.103*
H5C	0.170334	0.819961	0.463073	0.103*
C6	0.73202 (16)	0.61327 (18)	0.26985 (16)	0.0304 (3)
C7	0.60701 (15)	0.64516 (16)	0.27949 (14)	0.0250 (3)
C8	0.56450 (19)	0.7197 (2)	0.21522 (19)	0.0389 (4)
H8	0.611906	0.766133	0.164661	0.047*
C9	0.43846 (18)	0.7118 (2)	0.24071 (18)	0.0351 (3)
C10	0.3439 (3)	0.7737 (3)	0.1975 (3)	0.0628 (7)
H10A	0.385423	0.826195	0.145310	0.094*
H10B	0.339972	0.847296	0.280923	0.094*
H10C	0.244290	0.688148	0.137939	0.094*
C11	0.16908 (16)	0.07481 (16)	0.33558 (17)	0.0313 (3)
C12	0.15652 (14)	0.18939 (15)	0.29447 (15)	0.0263 (3)
C13	0.03585 (16)	0.15804 (17)	0.19204 (16)	0.0347 (3)
H13	-0.048269	0.060414	0.129803	0.042*
C14	0.06480 (16)	0.29914 (17)	0.20045 (15)	0.0316 (3)
C15	-0.0263 (2)	0.3365 (2)	0.1154 (2)	0.0529 (5)
H15A	-0.115493	0.241067	0.045501	0.079*
H15B	0.030551	0.385493	0.067998	0.079*
H15C	-0.053518	0.407377	0.176997	0.079*
B1	0.27407 (15)	0.58382 (17)	0.35890 (15)	0.0208 (3)
H1	0.195363	0.613257	0.310404	0.025*

with $U_{iso}(H) = 1.2-1.5U_{eq}(C)$ and $1.2U_{eq}(B)$. Owing to poor agreement, four reflections, i.e. (1 0 0), (-2 -6 4), (-4 7 0) and (-2 -3 1), were omitted from the final cycles of refinement.

Comment

Hydridotris(alkyl substituted-1-pyrazolyl)borates are well-known in inorganic and coordination chemistry [6, 7]. Among the alkyl groups in these species, the trifluoromethyl group has unique electronegativity, hydrophobicity, metabolic stability and bioavailability. With these attributes, the -CF₃ substituent is widely found in organic molecules for use in medicine, agrochemicals and organic materials [8]; the development of synthetic methods for the inclusion of -CF₃ in molecules is therefore, an active area of research in modern organic chemistry [9–11]. In this connection, investigations have been undertaken on hydridotris(3-trifluoromethyl-5-methylpyrazol-1-yl)borate, hereafter {HB(3-CF₃-5-Mepz)₃}⁻ as a ligand towards various metal centres. For example, the synthesis and characterisation of copper(I) carbonyl and triphenylphosphane complexes such as [Cu(CO){HB(3-CF₃-5-Mepz)₃}] and [(Ph₃P)Cu{HB(3-CF₃-5-Mepz)₃}] have been described [5]. The -CF₃ group is not particularly sterically bulky so that it can form the coordinatively saturated, six-coordinate copper(II) complex, formulated as [Cu{HB(3-CF₃-5-Mepz)₃}₂] [12]. In the present contribution, [Mn{HB(3-CF₃-5-Mepz)₃}₂] was synthesised and characterised by X-ray crystallography.

The molecular structure of [Mn{HB(3-CF₃-5-Mepz)₃}₂] is shown in the figure (35% displacement ellipsoids). The manganese(II) centre is located on a centre of inversion and is coordinated by the six nitrogen atoms derived from two {HB(3-CF₃-5-Mepz)₃}⁻ anions. Globally, the methyl groups are orientated to the either end of the molecule (in the vicinity of the boron termini) and the -CF₃ groups define a perimeter about the manganese centre. When viewed down the HB...Mn...BH axis, the sequence of dihedral angles between the planes of the N11-, N21- and N31-pyrazol-1-yl rings are 60.90(10), 60.61(10) and 65.86(9)°, respectively. The Mn–N11, N21 and N31 bond lengths lie in a narrow range, i.e. from Mn–N11 = 2.2751(11) Å to Mn–N21 = 2.2981(11) Å. This contrasts the experimental observations for [Cu{HB(3-CF₃-5-Mepz)₃}₂] which deviates significantly from three-fold symmetry, as manifested in the range of Cu–N bond lengths, i.e. 2.055(8)–2.437(8) Å. The formation of these bis-chelate complexes with {HB(3-CF₃-5-Mepz)₃}⁻ indicate less steric hindrance exerted by -CF₃ compared with the isopropyl group, as bis-chelates with hydridotris(3,5-diisopropylpyrazol-1-yl)borate are not observed [13, 14]. Further to this point, the title complex was also observed even when the reaction ratio was one metal:one ligand.

Magnetic properties were not conducted in the present study; typical would be high-spin ($S = 5/2$) or low-spin

($S = 1/2$) states. However, based on a comparison of Mn–N bond lengths a safe conclusion may be made. Thus, the independent Mn–N bond lengths of 2.310(3), 2.329(3) and 2.310(3) Å in $[Mn\{HB(3-Phpz)_3\}]$, where $\{HB(3-Phpz)_3\}^-$ = hydridotris(3-phenylpyrazol-1-yl) borate [15], and 2.256(3), 2.268(3) and 2.254(3) Å in $[Mn\{HB(3-Mepz)_3\}]$, where $\{HB(3-Mepz)_3\}^-$ = hydridotris(3-methylpyrazol-1-yl)borate [16] are close to those of $[Mn\{HB(3-CF_3-5-Mepz)_3\}_2]$. Therefore, it can be concluded that the latter complex is in the high-spin state, at least in the crystalline form.

Notable in the molecular packing, are C–H...F interactions, which extend in three-dimensions, with the shortest and most directional of these being a methyl-C–H...F contact $[C10-H10a...F3^i: H10a...F3^i = 2.50$ Å, $C10...F3^i = 3.390(3)$ Å with angle at H10a = 151° for symmetry operation (i): $x, y, -1+z$]. Within this assembly, $F... \pi$ (pyrazol-1-yl) interactions with the shortest of these involving the N31-ring $[C1-F1...Cg(N31-ring)^{ii} = 3.1798(14)$ Å with angle at F1 = $119.26(10)^\circ$ for (ii): $1-x, 1-y, 1-z$]. The predominance of the $F...H$ interactions was verified in an analysis of the calculated Hirshfeld surfaces and of the full and delineated two-dimensional fingerprint plots conducted following established protocols [17] employing Crystal Explorer 17 [18]. This analysis revealed 60.0% of all surface contacts on the Hirshfeld surface were of the type $F...H/H...F$. Next most prominent were $H...H$ contacts, at 23.3%, followed by $C...H/H...C$ [7.6%] and $F...F$ [7.3%] contacts. Minor contributions to the Hirshfeld surface are due to $F...C/C...F$ [1.5%] and $N...H/H...N$ [0.3%] contacts.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rigaku Oxford Diffraction. CrysAlis^{PRO}; Rigaku Corporation: Oxford, UK, 2015.

- Burla M. C., Caliandro R., Carrozzini B., Cascarano G. L., Cuocci C., Giacovazzo C., Mallamo M., Mazzone A., Polidori G. Crystal structure determination and refinement via SIR2014. *J. Appl. Crystallogr.* 2015, 48, 306–309.
- Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
- Farrugia L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, 45, 849–854.
- Fujisawa K., Yoshida M., Miyashita Y., Okamoto K. Copper(II) complexes with fluorinated hydrotris(pyrazolyl)borate: influence of electronic effects on their structure, physicochemical properties, and reactivity. *Polyhedron* 2009, 28, 1447–1454.
- Trofimenko S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
- Pettinari C. *Scorpionates II: Chelating Borate Ligands*; Imperial College Press: London, 2008.
- Müller K., Faeh C., Diederich F. Fluorine in pharmaceuticals: looking beyond intuition. *Science* 2007, 317, 1881–1886.
- Alonso C., de Marigorta E. M., Rubiales G., Palacios F. Carbon trifluoromethylation reactions of hydrocarbon derivatives and heteroarenes. *Chem. Rev.* 2015, 115, 1847–1935.
- Guo S., AbuSalim D. I., Cook S. P. 1,2-(Bis)trifluoromethylation of alkynes: a one-step reaction to install an underutilized functional group. *Angew. Chem. Int. Ed.* 2019, 58, 11704–11708.
- Li C., Xue L., Zhou J., Zhao Y., Han G., Hou J., Song Y., Liu Y. Copper-catalyzed trifluoromethylation of ynones coupled with dearomatizing spirocyclization of indoles: access to CF_3 -containing spiro[cyclopentane-1,3'-indole]. *Org. Lett.* 2020, 22, 3291–3296.
- Hu Z., George G. M., Gorun S. M. Fluorine encapsulation and stabilization of biologically relevant low-valence copper-oxo cores. *Inorg. Chem.* 2001, 40, 4812–4813.
- Nabika M., Kiuchi S., Miyatake T., Fujisawa K. Influences of steric bulkiness in hydrotris(pyrazolyl)borate ligands on ethylene polymerization reaction. *J. Polym. Sci., Part A: Polym. Chem.* 2009, 47, 5720–5727.
- Kitajima N., Fujisawa K., Fujimoto C., Moro-oka Y., Hashimoto S., Kitagawa T., Toriumi K., Tatsumi K., Nakamura A. A new model for dioxygen binding in hemocyanin. synthesis, characterization, and molecular structure of the μ - η^2 : η^2 peroxo dinuclear copper(II) complexes, $[Cu\{HB(3,5-R_2pz)_3\}_2(O_2)]$ (R = *i*-Pr and Ph). *J. Am. Chem. Soc.* 1992, 114, 1277–1291.
- Eichhorn D. M., Armstrong W. H. M{hydrotris(3-phenylpyrazol-1-yl) borate}: sterically encumbered iron(II) and manganese(II) complexes. *Inorg. Chem.* 1990, 29, 3607–3612.
- Kitano T., Sohrin Y., Hata Y., Wada H., Hori T., Ueda K. Improved selectivity for Cu(II) of methyl-substituted poly(pyrazolyl)borates, $[HB(3-Mepz)_3]^-$ and $[B(3-Mepz)_4]^-$, through steric contact. *Bull. Chem. Soc. Jpn.* 2003, 76, 1365–1373.
- Tan S. L., Jotani M. M., Tiekink E. R. T. Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. *Acta Crystallogr.* 2019, E75, 308–318.
- Turner M. J., McKinnon J. J., Wolff S. K., Grimwood D. J., Spackman P. R., Jayatilaka D., Spackman M. A. Crystal Explorer (v17); The University of Western Australia: Australia, 2017.