

Kiyoshi Fujisawa*, Masaya Shimizu and Edward R. T. Tiekink*

Crystal structure of chlorido{hydridotris [3-phenyl-5-methylpyrazol-1-yl-κN³]borato} copper(II), C₃₀H₂₈BClCuN₆

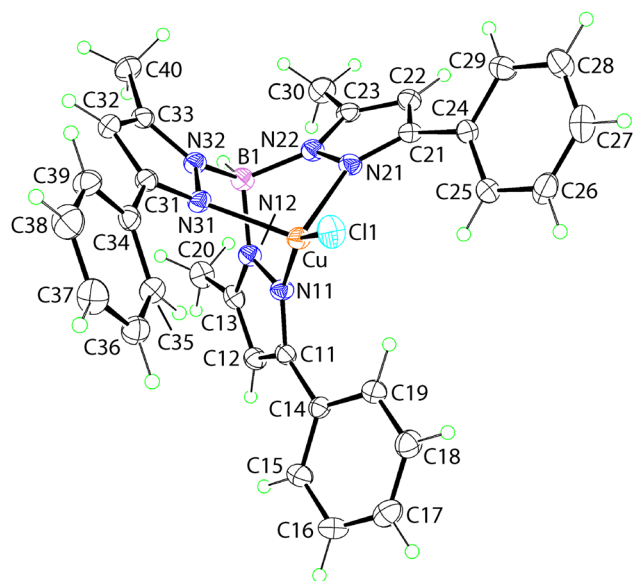


Table 1: Data collection and handling.

Crystal:	Red slab
Size	0.20 × 0.20 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.93 mm ⁻¹
Diffractometer, scan mode	Rigaku Mercury70, ω
θ_{\max} , completeness:	27.5°, 99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11245, 6149, 0.024
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4903
$N(\text{param})_{\text{refined}}$:	355
Programs:	REQAB [1], CrystalClear [2], SIR2014 [3], SHELX [4], WinGX/ORTEP [5]

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.

<https://doi.org/10.1515/ncrs-2020-0410>

Received July 26, 2020; accepted September 8, 2020; published online October 2, 2020

Abstract

C₃₀H₂₈BClCuN₆, triclinic, $P\bar{1}$ (no. 2), $a = 11.549(3)$ Å, $b = 12.321(3)$ Å, $c = 12.348(4)$ Å, $\alpha = 111.785(1)^\circ$, $\beta = 116.664(3)^\circ$, $\gamma = 97.513(1)^\circ$, $V = 1361.3(7)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0440$, $wR_{\text{ref}}(F^2) = 0.1063$, $T = 197$ K.

CCDC no: 2027352

*Corresponding authors: Kiyoshi Fujisawa and Edward R. T. Tiekink, Department of Chemistry, Ibaraki University, Mito, Ibaraki, 310-8512, Japan; and Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, Bandar Sunway, 47500, Selangor Darul Ehsan, Malaysia, E-mail: kiyoshi.fujisawa.sci@vc.ibaraki.ac.jp (K. Fujisawa), edwardt@sunway.edu.my (E. R. T. Tiekink). <https://orcid.org/0000-0002-4023-0025> (K. Fujisawa). <https://orcid.org/0000-0003-1401-1520> (E.R.T. Tiekink)

Masaya Shimizu, Department of Chemistry, Ibaraki University, Mito, Ibaraki, 310-8512, Japan

Source of material

A solution of [Ti{HB(3-Ph-5-Mepz)₃}] (300.5 mg, 0.437 mmol) [6] in dichloromethane (20 mL) was added slowly to a solution of CuCl₂·2H₂O (82.1 mg, 0.482 mmol) in acetone (10 mL). After the mixture was stirred for 1 h, the solvent was evaporated under vacuum, and the resulting solid was extracted with dichloromethane (30 mL). The filtrate was evaporated under vacuum, and a brown powder was obtained. Red crystals were obtained by the slow evaporation of a saturated dichloromethane/*n*-heptane solution held at room temperature. The second crop was contaminated by other adducts involving free pyrazole and/or coordinating solvents. Yield: 28% (72.5 mg, 0.124 mmol).

Anal. Calcd. for C₃₀H₂₈BClCuN₆. C, 61.87; H, 4.85; N, 14.43%. Found: C; 61.80, H; 4.70, N; 14.10.

IR (JASCO FT/IR-6300 spectrophotometer, KBr; cm⁻¹): 3058 (w) ν (C–H), 2927 (w) ν (C–H), 2535 (m) ν (B–H), 1542 (s) ν (C=N).

UV–Vis (JASCO V–570 at 298 K); λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 369 (1660), 408 (sh, 1510), 520 (sh, 390), 906 (180).

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

Atom	x	y	z	U_{iso}^*/U_{eq}
Cu	0.82167 (3)	0.24667 (3)	0.61708 (3)	0.02796 (10)
Cl1	0.68003 (7)	0.19846 (7)	0.67373 (7)	0.04129 (18)
N11	0.8585 (2)	0.25491 (19)	0.4816 (2)	0.0284 (4)
N12	0.9911 (2)	0.32572 (19)	0.5349 (2)	0.0289 (5)
N21	0.9821 (2)	0.1791 (2)	0.6851 (2)	0.0297 (5)
N22	1.0988 (2)	0.24965 (19)	0.7027 (2)	0.0297 (5)
N31	0.92672 (19)	0.43375 (19)	0.7398 (2)	0.0281 (4)
N32	1.0636 (2)	0.45820 (19)	0.7810 (2)	0.0284 (4)
C11	0.7821 (2)	0.2237 (2)	0.3469 (2)	0.0274 (5)
C12	0.8682 (3)	0.2763 (2)	0.3141 (3)	0.0314 (6)
H12	0.841817	0.269743	0.226487	0.038*
C13	0.9983 (3)	0.3391 (2)	0.4332 (3)	0.0299 (5)
C14	0.6342 (2)	0.1456 (2)	0.2596 (2)	0.0278 (5)
C15	0.5436 (3)	0.1558 (3)	0.1458 (3)	0.0384 (6)
H15	0.577374	0.214502	0.124564	0.046*
C16	0.4044 (3)	0.0811 (3)	0.0631 (3)	0.0462 (7)
H16	0.343603	0.088487	-0.014804	0.055*
C17	0.3535 (3)	-0.0034 (3)	0.0928 (3)	0.0434 (7)
H17	0.257771	-0.054016	0.035956	0.052*
C18	0.4415 (3)	-0.0146 (3)	0.2048 (3)	0.0404 (7)
H18	0.406435	-0.072940	0.225727	0.048*
C19	0.5807 (3)	0.0584 (2)	0.2872 (3)	0.0354 (6)
H19	0.640878	0.049079	0.363809	0.043*
C20	1.1312 (3)	0.4105 (3)	0.4588 (3)	0.0389 (6)
H20A	1.165795	0.497345	0.531047	0.058*
H20B	1.114794	0.408978	0.373106	0.058*
H20C	1.199976	0.371937	0.488945	0.058*
C21	1.0096 (3)	0.0827 (2)	0.7032 (3)	0.0313 (5)
C22	1.1426 (3)	0.0901 (3)	0.7303 (3)	0.0347 (6)
H22	1.187269	0.033175	0.746222	0.042*
C23	1.1959 (2)	0.1961 (2)	0.7294 (2)	0.0316 (5)
C24	0.9135 (3)	-0.0114 (2)	0.7008 (3)	0.0319 (5)
C25	0.7719 (3)	-0.0630 (3)	0.6035 (3)	0.0379 (6)
H25	0.733737	-0.038153	0.534657	0.045*
C26	0.6852 (3)	-0.1506 (3)	0.6053 (3)	0.0442 (7)
H26	0.588177	-0.184993	0.538445	0.053*
C27	0.7405 (3)	-0.1875 (3)	0.7047 (3)	0.0481 (8)
H27	0.681462	-0.247629	0.706124	0.058*
C28	0.8809 (3)	-0.1375 (3)	0.8015 (3)	0.0478 (7)
H28	0.918698	-0.163725	0.869125	0.057*
C29	0.9673 (3)	-0.0491 (3)	0.8006 (3)	0.0415 (7)
H29	1.064036	-0.013940	0.868688	0.050*
C30	1.3350 (3)	0.2512 (3)	0.7552 (3)	0.0419 (7)
H30A	1.322954	0.256575	0.673799	0.063*
H30B	1.389240	0.197965	0.772773	0.063*
H30C	1.384053	0.335206	0.836018	0.063*
C31	0.9219 (2)	0.5303 (2)	0.8329 (2)	0.0287 (5)
C32	1.0568 (3)	0.6166 (2)	0.9363 (3)	0.0338 (6)
H32	1.083400	0.693129	1.014902	0.041*
C33	1.1430 (3)	0.5676 (2)	0.9007 (3)	0.0320 (6)
C34	0.7886 (3)	0.5402 (2)	0.8124 (3)	0.0288 (5)
C35	0.6679 (3)	0.4770 (2)	0.6810 (3)	0.0323 (6)
H35	0.671325	0.426002	0.603732	0.039*
C36	0.5429 (3)	0.4871 (3)	0.6611 (3)	0.0383 (6)
H36	0.461034	0.442974	0.570770	0.046*

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C37	0.5375 (3)	0.5615 (3)	0.7727 (3)	0.0451 (7)
H37	0.451690	0.568259	0.759759	0.054*
C38	0.6564 (3)	0.6259 (3)	0.9026 (3)	0.0486 (8)
H38	0.652619	0.678477	0.979036	0.058*
C39	0.7817 (3)	0.6155 (3)	0.9242 (3)	0.0378 (6)
H39	0.862945	0.659722	1.014922	0.045*
C40	1.2977 (3)	0.6183 (3)	0.9764 (3)	0.0422 (7)
H40A	1.335859	0.567438	1.018113	0.063*
H40B	1.333380	0.705032	1.049312	0.063*
H40C	1.325289	0.615647	0.911359	0.063*
B1	1.1019 (3)	0.3679 (3)	0.6867 (3)	0.0312 (6)
H1	1.195644	0.411377	0.709640	0.037*

Experimental details

The C- and B-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å & B–H = 1.00 Å) and refined as riding with $U_{iso}(H) = 1.2-1.5U_{eq}(C)$ and $1.2U_{eq}(B)$. Owing to poor agreement, two reflections, i.e. (4 8 4) and (–11 11 3), were manually omitted from the final cycles of refinement.

Discussion

Comment

The coordination chemistry of hydrotris(pyrazolyl)borate ligands has proven to be a very productive area of research. This is mainly because the coordination environment of a metal can be readily controlled by these ligands which also exert a significant influence upon second sphere coordination effects [7, 8]. This control can be moderated by altering the steric profiles of pyrazoles by substitution at the 3- and/or 5-positions of the pyrazolyl ring. By using the less hindered, parent hydridotris(pyrazolyl)borate, the formation of unreactive and coordinatively saturated complexes, $[M\{HB(3,5-R_2pz)_3\}_2]$ (R = H and Me), were easily obtained [7, 8]. In 1986, bulkier substituents were introduced at the 3-position of the pyrazolyl ring, $[HB(3-Rpz)_3]^-$ (R = tBu or Ph) [9], which then lead to 3,5-disubstitution by isopropyl and phenyl groups to prevent the formation of the unreactive, bischelate formation [10–12]. Therefore, these hindered hydridotris(pyrazolyl)borate ligands were given the term "tetrahedral enforcer" [13]. In copper(II) coordination chemistry, a D_{2d} distorted tetrahedral structure is very important in inorganic and bioinorganic chemistry, since in copper proteins tetrahedral geometries have been reported for copper(II) centres [14]. However, it remains very difficult to obtain tetrahedral copper(II)

complexes as pure compounds, since some additional ligands and/or coordinating solvents can be easily coordinated to the copper(II) centre to form five- or six-coordinate species instead. In this connection, the present work reports the X-ray structural characterization and some properties of a four-coordinate copper(II) complex with a phenyl-substituted hydridotris(pyrazolyl)borate, i.e. $[Cu(Cl)\{HB(3-Ph-5-Mepz)_3\}]$, (I).

As mentioned above, tetrahedral copper(II) geometries are not common in coordination chemistry. Therefore, to synthesise complexes with this difficult to obtain geometry, a judicious choice of ligand needs to be made. Among these, the N3-type hydridotris(pyrazolyl)borate ligands are good candidates. By using sterically hindered hydridotris(pyrazolyl)borate ligands, tetrahedral copper(II) complexes have been obtained previously, such as $[Cu(Cl)\{HB(3,5-iPr_2pz)_3\}]$ [15], $[Cu(SC_6F_5)\{HB(3,5-iPr_2pz)_3\}]$ [16], $[Cu(OOC(CH_3)_2C_6H_5)\{HB(3,5-iPr_2pz)_3\}]$ [17], $[Cu(OH)\{HB(3-tBu-5-iPrpz)_3\}]$ [18], $[Cu(Cl)\{HB(3-tBu-5-iPrpz)_3\}]$ [19], $[Cu(Cl)\{HB(3-Ad-5-iPrpz)_3\}]$ [19] and $[Cu(Cl)\{HB(3-tBu-5-Mepz)_3\}]$ [20]. However, these complexes with a tetrahedral geometry were quite unstable with ligands such as $[HB(3,5-iPr_2pz)_3]$, i.e. with reduced steric hindrance. Indeed, the addition of small amount of a coordinating solvent such as DMF into a CH_2Cl_2 solution of $[Cu(Cl)\{HB(3,5-iPr_2pz)_3\}]$ results in the immediate formation of the solvent adduct, $[Cu(Cl)(dmf)\{HB(3,5-iPr_2pz)_3\}]$, which was characterized by X-ray diffraction [15]. For the preparation of coordinatively unsaturated $[Cu(Cl)\{HB(3-Ph-5-Mepz)_3\}]$, care must be made to avoid contamination by solvent and other species. Therefore, in the present study, the thallium(I) salt $[Tl\{HB(3-Ph-5-Mepz)_3\}]$ [6] was employed. However, the yield was very low (28%), partly because the second crop of crystals was green, consistent with the formation of five-coordinate products.

The molecular structure of (I) is shown in the figure (35% probably displacement ellipsoids). The Cu–Cl bond length in (I) is 2.1446(7) Å, which lies in the range for Cu–Cl bonds in other tetrahedral chlorido copper(II) complexes with pz ligands, viz. $[Cu(Cl)\{HB(3,5-iPr_2pz)_3\}]$ (2.125(6) Å) [15], $[Cu(Cl)\{HB(3-tBu-5-iPrpz)_3\}]$ (2.167(1) Å) [19], $[Cu(Cl)\{HB(3-Ad-5-iPrpz)_3\}]$ (2.1706(9) Å) [19] and $[Cu(Cl)\{HB(3-tBu-5-Mepz)_3\}]$ (2.1738(14) and 2.1760(13) Å, for the two independent molecules) [20]. On the other hand, examples of Cu–Cl bond lengths in five-coordinate chlorido complexes are 2.260(2) Å in $[Cu(Cl)(dmf)\{HB(3,5-iPr_2pz)_3\}]$ [15] and 2.2833(8) Å in $[Cu(Cl)\{HB(3-Ph-5-Mepz)_3\}(3-Ph-5-MepzH)]$ [21], which represent approximately 0.1 Å elongations compared with the Cu–Cl distances in the four coordinate, chlorido copper(II) precursor complexes. These parameters are comparable with those found in tetrachloridocuprates [14]. This dramatic change is due to

differences in the ground state electronic configurations, which change from d_{z^2} to $d_{x^2-y^2}$. This change can also be observed in the d–d transition energies: 906 nm ($180 M^{-1} cm^{-1}$) in $[Cu(Cl)\{HB(3-Ph-5-Mepz)_3\}]$, 996 nm ($150 M^{-1} cm^{-1}$) in $[Cu(Cl)\{HB(3,5-iPr_2pz)_3\}]$ and 758 nm ($100 M^{-1} cm^{-1}$) in $[Cu(Cl)(dmf)\{HB(3,5-iPr_2pz)_3\}]$ [15].

The Cu–N bond lengths in (I) are experimentally distinct with Cu–N11 [1.9348(19) Å] being significantly shorter than Cu–N21 [2.088(2) Å] and Cu–N31 [2.027(2) Å]. The range of tetrahedral angles is broad, i.e. from a narrow $89.02(8)^\circ$ for N11–Cu–N31 to a wide $150.98(6)^\circ$ for N11–Cu–Cl1, indicating the N11 atom is approximately trans to the Cl1 atom, which accounts for the disparity in the Cu–N bonds, and a significant deviation from molecular three-fold symmetry.

In the crystal, a prominent intermolecular contact is a phenyl–C–H...Cl [$C18-H18...Cl1^i$: $H18...Cl1^i = 2.66$ Å, $C18...Cl1^i = 3.596(4)$ Å with angle at H18 = 169° ; symmetry operation (i) $1-x, -y, 1-z$] interaction between centrosymmetrically related molecules which leads to the formation of a two-molecule aggregate. The only other identified contacts are methyl–C–H... π (pyrazolyl) [$C20-H20a...Cg(N11,N12,C11-C13)^{ii}$: $H20a...Cg(N11,N12,C11-C13)^{ii} = 2.82$ Å with angle at H20a = 141° and $C20-H20b...Cg(N31,N32,C31-C33)^{ii}$: $H20b...Cg(N31,N32,C31-C33)^{ii} = 2.89$ Å with angle at H20b = 148° for (ii) $2-x, 1-y, 1-z$] interactions, which connect the dimeric aggregates into a supramolecular layer in the *ab*-plane; layers stack without directional interactions between them.

An analysis of the supramolecular association in the crystal of (I) was also performed by calculating the Hirshfeld surface as well as the full and delineated two-dimensional fingerprint plots employing Crystal Explorer 17 [22] and literature methods [23]. The specified H...Cl contacts leading to the dimeric aggregates appear as sharp spikes in the fingerprint plot delineated into H...Cl/Cl...H contacts; overall, these contribute 8.0% of all contacts to the surface. In the same way, characteristic wings are noted in the delineated fingerprint for H...C/C...H contacts, which contribute 28.7% to the calculated Hirshfeld surface. The major contribution to the surface comes from H...H contacts at 52.7%. Smaller contributions but, at relatively long separations are made by H...N/N...H [6.2%] and C...C [3.8%] contacts.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: KF is grateful for support from the joint usage/research programme “Artificial Photosynthesis”

based at Osaka City University. Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001-2019.

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

References

1. *REQAB*; Rigaku Corporation: Tokyo, Japan, 1998.
2. CrystalClear. *SMEExpert*; Rigaku Corporation: Tokyo, Japan, 2019.
3. 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.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Farrugia L. J. WinGX and ORTEP for windows: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.
6. Rheingold A. L., Ostrander R. L., Haggerty B. S., Trofimenko S. Homoscorpionate (tris(pyrazolyl)borate) ligands containing tethered 3-phenyl groups. *Inorg. Chem.* 1994, *33*, 3666–3676.
7. Trofimenko S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
8. Pettinari C. *Scorpionates II: Chelating Borate Ligands*; Imperial College Press: London, 2008.
9. Trofimenko S., Calabrese J. C., Thompson J. S. Novel polypyrazolylborate ligands: coordination control through 3-substituents of the pyrazole ring. *Inorg. Chem.* 1987, *26*, 1507–1514.
10. Kitajima N., Fujisawa K., Fujimoto C., Moro-oka Y. Preparation of copper(I) complexes ligated with novel hindered pyrazolylborates. *Chem. Lett.* 1989, *18*, 421–424.
11. 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-R₂pz)₃)]₂(O₂) (R = *i*-Pr and Ph). *J. Am. Chem. Soc.* 1992, *114*, 1277–1291.
12. Fujisawa K. A personal perspective on the discovery of dioxygen adducts of copper and iron by Nobumasa Kitajima. *J. Biol. Inorg. Chem.* 2017, *22*, 237–251.
13. Kitajima N., Tolman W. B. Coordination chemistry with sterically hindered hydrotris(pyrazolyl)borate ligands: organometallic and bioinorganic perspectives. *Prog. Inorg. Chem.* 1995, *43*, 419–531.
14. Solomon E. I., Heppner D. E., Johnston E. M., Ginsbach J. W., Cirera J., Qayyum M., Kieber-Emmons M. T., Kjaergaard C. H., Hadt R. G., Tian L. Copper active sites in biology. *Chem. Rev.* 2014, *114*, 3659–3853.
15. Kitajima N., Fujisawa K., Moro-oka Y. Tetrahedral copper(II) complexes supported by a hindered pyrazolylborate. formation of the thiolato complex, which closely mimics the spectroscopic characteristics of blue copper proteins. *J. Am. Chem. Soc.* 1990, *112*, 3210–3212.
16. Kitajima N., Fujisawa K., Tanaka M., Moro-oka Y. X-ray structure of thiolatocopper(II) complexes bearing close spectroscopic similarities to blue copper proteins. *J. Am. Chem. Soc.* 1992, *114*, 9232–9233.
17. Kitajima N., Katayama T., Fujisawa K., Iwata Y., Moro-oka Y. Synthesis, molecular structure, and reactivity of (alkylperoxo) copper(II) complex. *J. Am. Chem. Soc.* 1993, *115*, 7872–7873.
18. Fujisawa K., Kobayashi T., Fujita K., Kitajima N., Moro-oka Y., Miyashita Y., Yamada Y., Okamoto K. Mononuclear copper(II) hydroxo complex: structural effect of a 3-position of tris(pyrazolyl) borates. *Bull. Chem. Soc. Jpn.* 2000, *73*, 1797–1804.
19. Fujisawa K., Tada N., Ishikawa Y., Higashimura H., Miyashita Y., Okamoto K. The most hindered hydrotris(pyrazolyl)borate ligand; X-ray structures of chlorocopper(II) complexes: [Cu(Cl){HB(3-Ad-5-Pr^tpz)₃}] as compared with [Cu(Cl){HB(3-Bu^t-5-Pr^tpz)₃}]. *Inorg. Chem. Commun.* 2004, *7*, 209–212.
20. Fujisawa K., Iwamoto H., Tobita K., Miyashita Y., Okamoto K. Copper(II) nitrate and chloro complexes with sterically hindered tridentate ligands: influence of ligand framework and charge on their structure and physicochemical properties. *Inorg. Chim. Acta.* 2009, *362*, 4500–4509.
21. Lupidi G., Marchetti F., Masciocchi N., Reger D. L., Tabassum S., Astolfi P., Damiani E., Pettinari C. Synthesis, structural and spectroscopic characterization and biomimetic properties of new copper, manganese, zinc complexes: identification of possible superoxide-dismutase mimics bearing hydroxyl radical generating/scavenging abilities. *J. Inorg. Biochem.* 2010, *104*, 820–830.
22. 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.
23. 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.