PRELIMINARY DESIGN OF LEARNING MATERIAL ON KOLBE-SCHMITT REACTION MECHANISM VISUALIZED BY CRYSTAL DATA

Daisuke Noguchi
Graduate School of Integrated Science and Technology, Nagasaki University, Japan
Corresponding author e-mail: a.chemist.noguchi.d@gmail.com

ABSTRACT

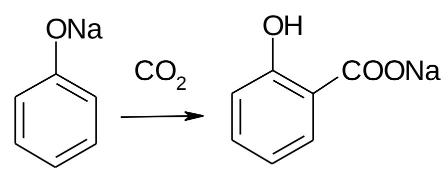
In order to educate introductory chemistry, both imagining and visualizing the structures of molecules and complex ions have been considered to be of significance for learners. Some of sodium phenoxide (NaOPh), common compound in organic chemistry as a reactant of the well-known industrial process, ‘Kolbe-Schmitt reaction’, have unique crystal structures including square units consisting like “cubane” form. Sodium salicylate is a product of the reaction, and its crystal structure was reported recently. However, this fact is seemed to be almost unknown in chemical education. Therefore, I report a study herein about the possibility of crystal structural data available in the Cambridge Crystallographic Data Centre (CCDC) as potential learning material in chemical education. Consequent searched some crystal structures; it was found that pure NaOPh crystal has rigid polymer chain structures involving four-membered square Na_2O_2 unit. On the other hand, others have structures with one or several crown ethers or solvent molecules. The crystals of NaOPh coordinated by several solvent molecules are indicating as if they are in the dynamic reacting process with solvation, in spite of that they indeed are in solid state. Regrettably, there seemed no exact crystal data of NaOPh solvated with CO_2 itself. Instead, combined with the crystal structure of the product, i.e., sodium salicylate, a reaction mechanism could be speculated. When teaching chemistry, these crystallographic data would be effective enough to explain the dynamic reacting process of the Kolbe-Schmitt reaction for students with their impression. *[African Journal of Chemical Education—AJCE 14(3), July 2024]*

INTRODUCTION

Understanding the geometry of basic molecules is crucial for students studying chemistry [1-3]. Typically, a course of introductory chemistry covers the shapes of fundamental molecules, i.e., CO_2 (linear), H_2O (bent), NH_3 (triangular pyramidal), and CH_4 (tetrahedral). Subsequently, forms of some complex ions such as hexacyanidoferrate(II) ion $[Fe(CN)_6]^{2-}$ in regular octahedral and tetraamminecopper(II) ion $[Cu(NH_3)_4]^{2+}$ in square planar configuration are studied [4]. Recent studies have suggested that employing teaching materials to visualize organic molecular structures could significantly enhance the effectiveness of chemistry education [5-7]. Consequently, the combination of both reactants and products in basic chemical reactions, along with those data on crystal structures, could serve as valuable potential learning materials to image chemical reaction mechanisms. For instance, demonstrating the neutralization of an acid-base indicator 'methyl orange' [8], the ammonia-soda process, production of Na_2CO_3 involving NaCl, CO_2, NH_3, and H_2O [9], and halogenation of aromatic compounds (pre-reactive intermediates of Br_2 with C_6H_6 and $C_6H_5CH_3$ in crystals) [10] have been provided.

The Kolbe-Schmitt reaction well-learned in chemistry is an important synthetic route, producing aromatic hydroxycarboxylic acids from phenoxides with CO_2 under high temperature and pressure in the solid phase [11]. In scheme 1, Kolbe-Schmitt reaction from sodium phenoxide

(NaOPh) to sodium salicylate (NaSA) with CO_2 are illustrated. One of my previous studies on pure NaOPh crystal with rigid polymer chain structures having four-membered square Na_2O_2 unit and others with one or more crown ether or solvent molecules as a teaching material for Information and Communication Technology (ICT) was reported [5]. These crystallographic data for both the reactants and products of NaOPh and NaSA (and salicylic acid, SA) for the Kolbe-Schmitt reaction are available via online [5, 12]. Integration of these data into chemical educational materials holds potential to deepen students' comprehension of chemical reactions and expected to increase their interest in studying chemistry. However, no research has yet provided insight into the mechanism of the Kolbe-Schmitt reaction in chemical education. Therefore, this study aims to fill this gap by demonstrating a preliminary visual learning material based on the crystal structures of NaOPh along with solvent molecules including crown ether, and the product of NaSA, to enhance understanding chemical education related to the Kolbe-Schmitt reaction.



Scheme 1. Kolbe-Schmitt Reaction from sodium phenoxide (NaOPh) to sodium salicylate (NaSA) with CO_2.

METHODOLOGY

Crystallographic information and bibliography thereof as to crystal compounds at Cambridge Crystallographic Data Centre (CCDC) have been searched and obtained through the Internet with no fee (https://www.ccdc.cam.ac.uk/structures/). Each 3D chemical structural graphics could be displayed through web browsing.

RESULTS AND DISCUSSION

Tables 1-2 show the results of bibliographic survey at CCDC on the reactants (sodium phenoxides; NaOPh) and the products (sodium salicylate; NaSA, salicylic acid; SA) of the Kolbe-Schmitt reaction. Pure NaOPh crystalline 3D graphic when the CCDC ID (ROQFEI or ROQFEI01) is input at the web site of the CCDC is shown in Fig. 1. The units of cubic Na_2O_2, resembling 'cubane' in structure, are characteristic. There are 12 types of NaOPh crystals that consist of a eutectic. Two compounds containing a different number of crystalline water molecules, $NaOPh{\cdot}3H_2O$ and $NaOPh{\cdot}H_2O$, exist. And other eutectics are containing organic solvent molecules such as methanol (CH_3OH), THF (C_4H_8O), and acetonitrile (CH_3CN). On the other hand, eutectics including some crown ethers; viz., dicyclohexano-18-crown-6 (DC-18-crown-6), cyclohexano-15-crown-5 (C-15-crown-5), and 15- crown-5 are also existing. Here, crown ethers are cyclic compounds that consist of a ring containing several ether groups (R−O−R') potentially multidentating to cations. Interestingly, the reports of these crystal data of (solvated) NaOPh have been concentrated over a limited range of time period compared to SA.

Table 1: Crystal data on the (solvated) reactants of the Kolbe-Schmitt reaction with their CCDC ID, chemical formulae of the compounds, and references

CCDC ID	Compound	Ref.
DUNSUA	4NaOPh·2(DC-18-crown-6)	Fraser, et al. (1986) [13]
GANZOK	NaOPh·PhOH·(DC-18-crown-6)	Fraser, et al. (1987) [14]
VIXDAH	2NaOPh·(C-15-crown-5)	Watson, et al. (1991) [15]
VIXDEL	2NaOPh·(15-crown-5)	
LEGCEF	NaOPh·(*N*-Me-ε-CPL)	Walther, et al. (1994) [16]
PIPGIE	NaOPh·3H_2O	Sieler, et al. (1994) [17]
PIPGEA	NaOPh·H_2O	
YURJAW	NaOPh·2PhOH	Jörchel, Sieler (1995) [18]
ZAVGAE	NaOH·4CH_3OH	Kunert, et al. (1995) [19]
ROQFIM	6NaOPh·8THF	Kunert, et al. (1997) [20]
ROQFOS	4NaOPh·4TMU	
ROQFEI	$\{NaOPh\}_n$	
ROQFEI01	$\{NaOPh\}_n$	Dinnebier et al. (1997) [21]
HIDCOM	NaOPh·CH_3CN	Czado, Müller (1999) [22]

C = cyclohexano, CPL = caprolactam, DC = dicyclohexano, NaOPh = sodium phenoxide, Me = methyl, PhOH = phenol, THF = tetrahydrofuran, TMU = *N*,*N*,*N'*,*N'*-tetramethylurea

Meanwhile, in the crystal of NaSA, there are an ionic Na^+–O layer sandwiched between aromatic rings (Fig. 2). Only one eutectic of NaSA (including 1,10-phenanthroilne) has been registered on the CCDC. Unfortunately, the detail of the crystal structure of this eutectic remains uncertain due to its preliminary analysis.

Table 2: Crystal data on the (solvated) products of the Kolbe-Schmitt reaction with their CCDC ID, chemical formulae of the compounds, and references

CCDC No.	Compound	Ref.
AMPICB	NaSA·(1,10-phen)$_2$	Tiwari, et al. (1981) [23]
WINXOJ WINXOJ01	NaSA	Spielberg, et al. (2018) [24]
SALIAC01	SA	Cochran (1953) [25]
SALIAC		Sundaralingam, Jensen (1965) [26]
SALIAC03 SALIAC12		Bacon, Jude (1973) [27]
SALIAC13 SALIAC14		Wang, et al. (2005) [28]
SALIAC15		Bolte (2006) [29]
SALIAC16		Munshi, Row (2006) [30]
SALIAC17		Montis, Hursthouse (2012) [31]
SALIAC18		Hamdi, et al. (2013) [32]
SALIAC19		Rajnicova, et al. (2014) [33]
SALIAC20		Woinska, et al. (2016) [34]
SALIAC21		Ivanova, Spiteller (2018) [35]
SALIAC22		Phetmung, et al. (2019) [36]
SALIAC23 SALIAC24 SALIAC25 SALIAC26		Jha, et al. (2022) [37]
SALIAC27		Muthusamy, & Karuppannan (2023) [38]

1,10-phen = 1,10-phenanthroline, NaSA = sodium salicylate, SA = salicylic acid

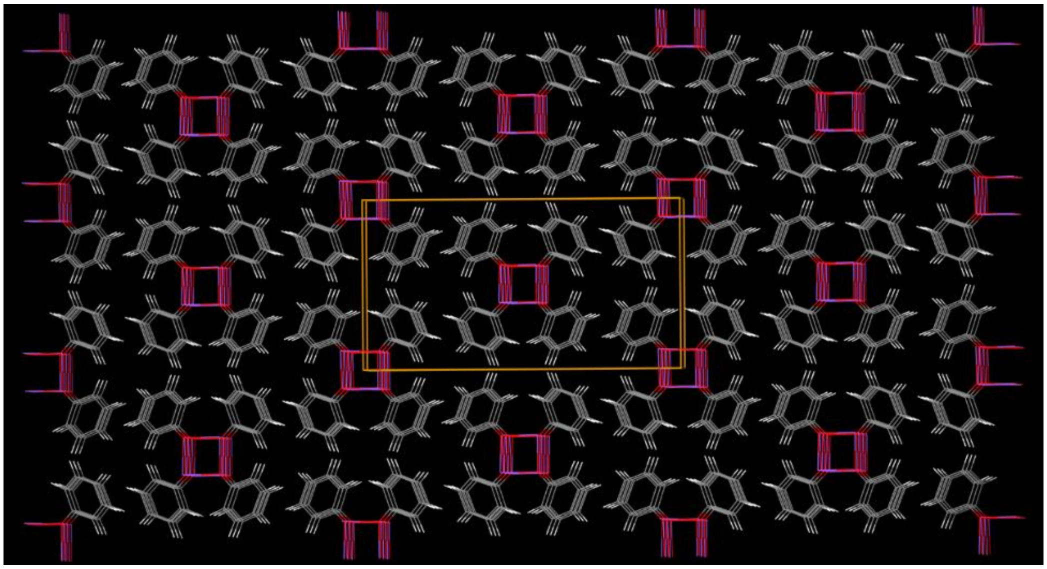


Fig. 1. 3D crystal structural graphic of pure NaOPh (purple = Na, red = O, gray = C, and white = H).

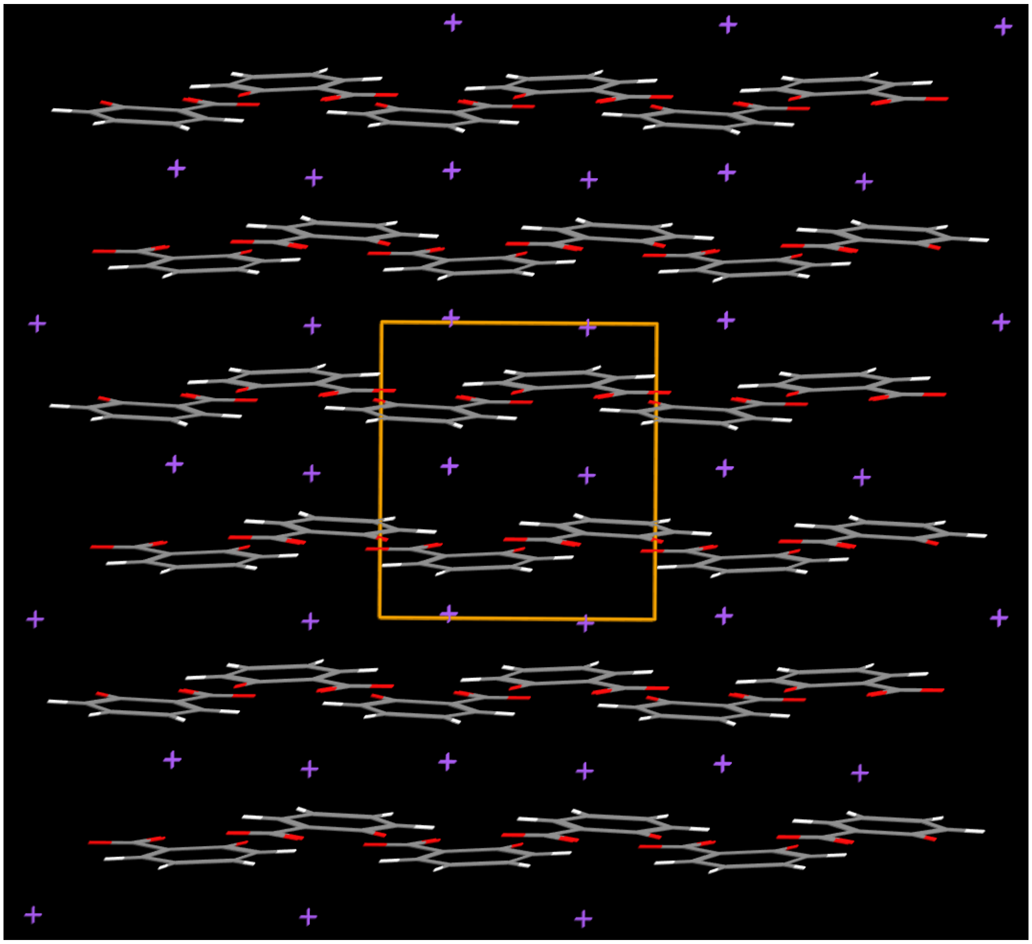


Fig. 2. 3D crystal structural graphic of NaSA (purple = Na, red = O, gray = C, and white = H).

REFERENCES

1. Wu, H.-K., Krajcik, J.S., & Soloway, E. (2001). Promoting understanding of chemical representations: students' use of a visualization tool in the classroom. *J. Res. Sci. Teach.*, 38(7): 821-842. https://doi.org/10.1002/tea.1033
2. Wu, H.-K., & Shah, P. (2004). Exploring visuospatial thinking in chemistry learning. *Sci. Educ.*, 88(3): 465-492. https://doi.org/10.1002/sce.10126
3. Kiernan, N.A., Manches, A., & Seery, M.K. (2024). Resources for reasoning of chemistry concepts: multimodal molecular geometry. *Chem. Educ. Res. Pract.*, 25(2): 524-543. https://doi.org/10.1039/D3RP00186E
4. Noguchi, D. (2022). The CCDC database of crystal structures of tetraamminecopper (II) $[Cu(NH_3)_4]^{2+}$: complicated geometry of a well-known complex ion. *J. Korean Chem. Soc.*, 66(1): 61-66. https://doi.org/10.5012/jkcs.2022.66.1.61
5. Noguchi, D. (2020). Bibliographic survey on crystal structures of sodium phenoxides to develop ICT teaching materials of molecular structures. *JSSE Res. Rep.*, 34(10): 23-28. [In Japanese] https://doi.org/10.14935/jsser.34.10_23
6. Noguchi, D. (2020). A possibility as ICT learning material of the crystal structure of sodium ethoxides. *Proc. Kanto Reg'l Conf. 2020, Soc. Jpn Sci. Teach.*, (59): 69. [In Japanese] http://hdl.handle.net/10069/40448
7. Noguchi, D. (2022). Organic molecules visualizable by crystal data in introductory chemistry. *Int. J. Chem. Math. Phys.*, 6(3): 18-27. https://doi.org/10.22161/ijcmp.6.3.3
8. Noguchi, D. (2022). Methyl orange in acid-base equilibria and ammonium-azonium tautomerism. *Rep. Grad. Sch. Eng., Nagasaki Univ.*, 52(98): 86-93. [In Japanese] http://hdl.handle.net/10069/00041208
9. Shimokawa, M., Egashira, T., & Noguchi, D. (2023). Development of teaching material on 'ammonium carbonate' with crystal structures in high school chemistry: pilot project for applying to classwork of ammonia-soda process. *JSSE Res. Rep.*, 37(5): 127-130. [In Japanese] https://doi.org/10.14935/jsser.37.5_127
10. Vasilyev, A.V., Lindeman, S.V., & Kochi, J.K. (2002). Molecular structures of the metastable charge-transfer complexes of benzene (and toluene) with bromine as the pre-reactive intermediates in electrophilic aromatic bromination. *New J. Chem.*, 26(5): 582-592. https://doi.org/10.1039/B110169M
11. Lindsey, A.S., & Jeskey, H. (1957). The Kolbe-Schmitt reaction. *Chem. Rev.*, 57(4): 583-620. https://doi.org/10.1021/cr50016a001
12. Spielberg, E.T., Campbell, P.S., Szeto, K.C., Mallick, B., Schaumann, J., & Mudring, A.-V. (2018). Sodium salicylate: an in-depth thermal and photophysical study. *Chem. Eur. J.*, 24(58): 15638-15648. https://doi.org/10.1002/chem.201803045

13. Fraser, M.E., Fortier, S., Rodrigue, A., & Bovenkamp, W. (1986). The crystal structures of the 1:2 host:guest complexes of dicyclohexano-18-crown-6 (isomers A and B) with sodium and potassium phenoxide. *Can. J. Chem.*, 64(4): 816-823. https://doi.org/10.1139/v86-134
14. Fraser, M.E., Fortier, S., Markiewicz, M.K., Rodrigue, A., & Bovenkamp, J.W. (1987). The crystal structures of the 1:1:1 complexes of dicyclohexano-18-crown-6 (isomer B) with potassium phenoxide and phenol and dicyclohexano-18-crown-6 (isomer A) with sodium phenoxide and phenol. *Can. J. Chem.*, 65(11): 2558-2563. https://doi.org/10.1139/v87-425
15. Watson, K.A., Fortier, S., Murchie, M.P., & Bovenkamp, J.W. (1991). Crown ether complexes exhibiting unusual 1:2 macrocycle salt ratios: X-ray crystal structures of cyclohexano-15-crown-5·2LiOPh, cyclohexano-15-crown-5·2NaOPh, and 15-crown-5·2NaOPh. *Can. J. Chem.*, 69(4): 687-695. https://doi.org/10.1139/v91-103
16. Walther, D., Ritter, U., Geßler, S., Sieler, J., Kunert, M. (1994). CO_2-transfer by metal phenoxides: *N*-Methyl-ε-caprolactam/sodium phenoxide as a selective reagent for carboxylation reactions. *Z. anorg. allg. Chem.*, 620(1): 101-106. https://doi.org/10.1002/zaac.19946200116
17. Sieler, J., Pink, M., & Zahn, G. (1994). The structures of two hydrates of sodium phenoxide: $C_6H_5ONa \cdot H_2O$ and $C_6H_5ONa \cdot 3H_2O$. *Z. anorg. allg. Chem.*, 620(4): 743-748. [In Germany] https://doi.org/10.1002/zaac.19946200427
18. Jörchel, P., & Sieler, J. (1995). The compound sodium phenoxide·2phenol in the system of its components. *Z. anorg. allg. Chem.*, 621(6): 1058-1062. https://doi.org/10.1002/zaac.19956210628
19. Kunert, M., Zahn, G., & Sieler, J. (1995). Methanol as a ligand in sodium phenoxide: the synthesis and crystal structure of $[Na(CH_3OH)_4][OC_6H_5]$. *Z. anorg. allg. Chem.*, 621(9): 1597-1599. https://doi.org/10.1002/zaac.19956210926
20. Kunert, M., Dinjus, E., Nauck, M., & Sieler, Structure and reactivity of sodium phenoxide - following the course of the Kolbe-Schmitt reaction. *Chem. Ber./Recueil*, 130(10): 1461-1465. https://doi.org/10.1002/cber.19971301017
21. Dinnebier, R.E., Pink, M., Sieler, J., & Stephens, P.W. (1997). Novel alkali-metal coordination in phenoxides: powder diffraction results on C_6H_5OM (M = Li, Na, K, Rb, Cs). *Inorg. Chem.*, 36(16): 3398-3401. https://doi.org/10.1021/ic961385i
22. Czado, W., & Müller, U. (1999). Crystal structure of sodium phenolate-acetonitrile (1/1), $NaOC_6H_5 \cdot CH_3CN$. *Z. Kristallogr. NCS*, 214(1): 63-64. https://doi.org/10.1515/ncrs-1999-0135
23. Tiwari, R.K., Chandrakumar, C., & Singh, T.P. (1981). Crystal data of some model inorganic compounds and their complexes. *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, 156(1-4): 245-246. https://doi.org/10.1524/zkri.1981.156.14.245
24. Spielberg, E.T., Campbell, P.S., Szeto, K.C., Mallick, B., Schaumann, J., & Mudring, A.-V. (2018). Sodium salicylate: an in-depth thermal and photophysical study. *Chem. Eur. J.*, 24(58): 15638-15648. https://doi.org/10.1002/chem.201803045

25. Cochran, W. (1953). The crystal and molecular structure of salicylic acid. *Acta Cryst.*, 6(3): 260-268. https://doi.org/10.1107/S0365110X53000752
26. Sundaralingam, M., & Jensen, L. H. (1965). Refinement of the structure of salicylic acid. *Acta Cryst.*, 18(6): 1053-1058. https://doi.org/10.1107/S0365110X65002517
27. Bacon, G.E., & Jude, R.J. (1973). Neutron-diffraction studies of salicylic acid and α-resorcinol. *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, 138(1-4): 19-40. https://doi.org/10.1524/zkri.1973.138.1-4.19
28. Wang, X., Ponder, C.S., & Kirwan, D.J. (2005). Low molecular weight poly(ethylene glycol) as an environmentally benign solvent for pharmaceutical crystallization and precipitation. *Cryst. Growth Des.*, 5(1): 85-92. https://doi.org/10.1021/cg034208i
29. Bolte, M. (2006). CCDC 297104: experimental crystal structure determination. *CSD Commun*. https://doi.org/10.5517/cc9z50f
30. Munshi, P., & Row, T.N.G. (2006). Intra- and intermolecular interactions in small bioactive molecules: cooperative features from experimental and theoretical charge-density analysis. *Acta Cryst.*, *B*62(4): 612-626. https://doi.org/10.1107/S0108768106017393
31. Montis, R., & Hursthouse, M.B. (2012). Surprisingly complex supramolecular behaviour in the crystal structures of a family of mono-substituted salicylic acids. *CrystEngComm*, 14(16): 5242-5254. https://doi.org/10.1039/C2CE25336D
32. Hamdi, N., Valerga, P., & Puerta, M.C. (2013). CCDC 737930: experimental crystal structure determination. *CSD Commun*. https://doi.org/10.5517/ccsrw6l
33. Rajnicova, B., Valigura, D., Padelkova, Z., & Moncol, J. (2014). CCDC 836668: experimental crystal structure determination. *CSD Commun*. https://doi.org/10.5517/ccx2m9w
34. Woinska, M., Grabowsky, S., Dominiak, P.M., Wozniak, K., & Jayatilaka, D. (2016). Hydrogen atoms can be located accurately and precisely by x-ray crystallography. *Sci. Adv.*, 2(5): e1600192. https://doi.org/10.1126/sciadv.1600192
35. Ivanova, B., Spiteller, M. (2018). CCDC 1557027: experimental crystal structure determination. *CSD Commun*. https://doi.org/10.5517/ccdc.csd.cc1p86pv
36. Phetmung, H., Musikapong, K., & Srichana, T. (2019). Thermal analysis, structure, spectroscopy and DFT calculations of a pharmaceutical cocrystal of salicylic acid and salicylamide. *J. Therm. Anal. Calorim.*, 138(7): 1207-1220. https://doi.org/10.1007/s10973-019-08794-5
37. Jha, K.K., Gruza, B., Kumar, P., Chodkiewicz, M.L., & Dominiak, P.M. (2020). TAAM: a reliable and user friendly tool for hydrogen-atom location using routine X-ray diffraction data. *Acta Cryst. B*76(3): 296-306. https://doi.org/10.1107/S2052520620002917
38. Muthusamy, R., & Karuppannan, S. (2023). CCDC 2161488: experimental crystal structure determination. *CSD Commun.* https://doi.org/10.5517/ccdc.csd.cc2bk6fk