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Synthesis and characterization of rare examples of stable potassium and arylcalcium triethylboranate complexes

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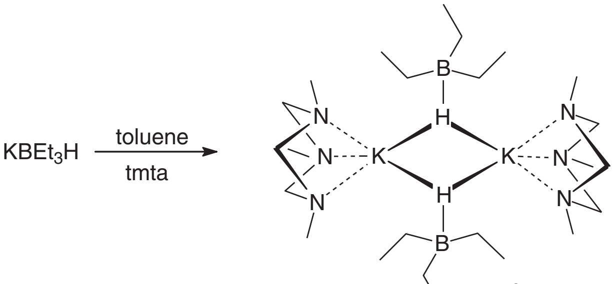
ABSTRACT

Stabilization of potassium triethylboranate can be achieved in solution as well as in the solid state with tridentate 1,3,5-trimethyl-1,3,5-triazinane (tmta) as dimeric $[(\text{tmta})\text{K}(\mu\text{-H})\text{BEt}_3]_2$ (**1**). The metathesis reaction of the post-Grignard reagent $[2,6\text{-(tol)}_2\text{C}_6\text{H}_3\text{-Ca(thf)}_3\text{I}]$ (**2**) with potassium triethylboranate yields an unusual hydrogen bridged organocalcium contact ion pair as hydrocarbon soluble $[(\text{thf})(\text{dme})\text{Ca}(\text{C}_6\text{H}_3\text{-2,6-tol}_2)\text{HBEt}_3]$ (**3**) which shows no tendency to dismutate to the homoleptic derivatives.

Hydrides of main group metals as well as transition metals provide a wide range of applications in synthetic chemistry as versatile catalysts [1] and reducing reagents [2] as well as targets for hydrogen storage [3]. The binary hydride of calcium CaH_2 is an insoluble colorless solid which can be prepared from the elements at 400 °C and crystallizes under standard conditions with a PbCl_2 type structure [4]. This calcium(II) hydride is rather inert and reacts only with acidic compounds such as water or ammonia (yielding corresponding calcium(II) hydroxide or amide). Due to the fact that solid CaH_2 exhibits a very low reactivity numerous attempts were undertaken to prepare soluble calcium derivatives containing a reactive Ca–H bond. Harder and co-workers demonstrated that R–Ca–H is a valuable synthon [5] for the hydrogenation of alkenes [6], an intermediate during hydrosilylation of ketones [7], and reacts also as a strong reducing reagent [8]. Phenylcalcium hydride (R = Ph) was prepared via a cocondensation reaction of calcium with benzene yielding extremely reactive PhCaH [9,10]. Stability of an organylcalcium hydride can be enhanced if R represents an extremely bulky β-diketiminate ligand which is able to prevent the precipitation of insoluble CaH_2 *via* a dismutation reaction [11]. These heteroleptic calcium hydride complexes crystallize as dimers containing the H atoms in bridging positions [12]. Monomerization can be achieved *via* the formation of borane adducts with Ca–H–B bridges [8,12,13]. Generation of organoboranate adducts strongly enhances solubility in common organic solvents [14]. As a consequence of a large lattice energy CaH_2 is nearly insoluble in organic solvents whereas the solubility of $\text{Ca(BH}_4)_2$ in ethereal solvents *via* formation of donor adducts $[\text{L}_2\text{Ca(BH}_4)_2]$ [L = tetrahydrofuran (thf), 1,2-dimethoxyethane (dme), and diglyme] is much larger [15–18]. Furthermore, there exist some structure–property relationships between the heavier organoalkaline earth metal chemistry and the organolanthanide(II) chemistry [19]. Baudry and co-workers studied the steric and electronic control of the stability of organolanthanide alkylborohydrides [20,21] and furthermore, some complexes were structurally characterized such as *e.g.* [(*dipp-nacnac*)$\text{Sm}\{(\mu\text{-H})\text{BEt}_3\}\text{NH-C}_6\text{H}_2\text{-2,4,6-}^t\text{Bu}_3$] [22], $[(\text{C}_5\text{Me}_5)_2\text{La}\{(\mu\text{-H})(\mu\text{-Et}_2)\text{BEt}\}]$ and $[(\text{C}_5\text{Me}_5)_2\text{La(thf)}\{(\mu\text{-H})(\mu\text{-Et})\text{BEt}_2\}]$ [23].

A broad portfolio of alkali metal organoborohydrides is commercially available as ethereal solutions which are used as hydride sources [24] and synthons in preparative chemistry but due to their high reactivity only very few of these compounds are structurally characterized. In the case of potassium triethylboranate a ligand exchange of the monodendate THF by sterically demanding tridendate 1,3,5-trimethyl-1,3,5-triazinane (tmta) led to the formation of $[(\text{tmta})\text{K}(\mu\text{-H})\text{BEt}_3]_2$ (**1**) (Eq. (1)) and isolation succeeded without decomposition [25].



1

(1)

The molecular structure of the dimeric contact ion pair $[(\text{tmta})\text{K}(\mu\text{-H})\text{BEt}_3]_2$ (**1**) is represented in Fig. 1a [26]. The boron-bound hydrogen

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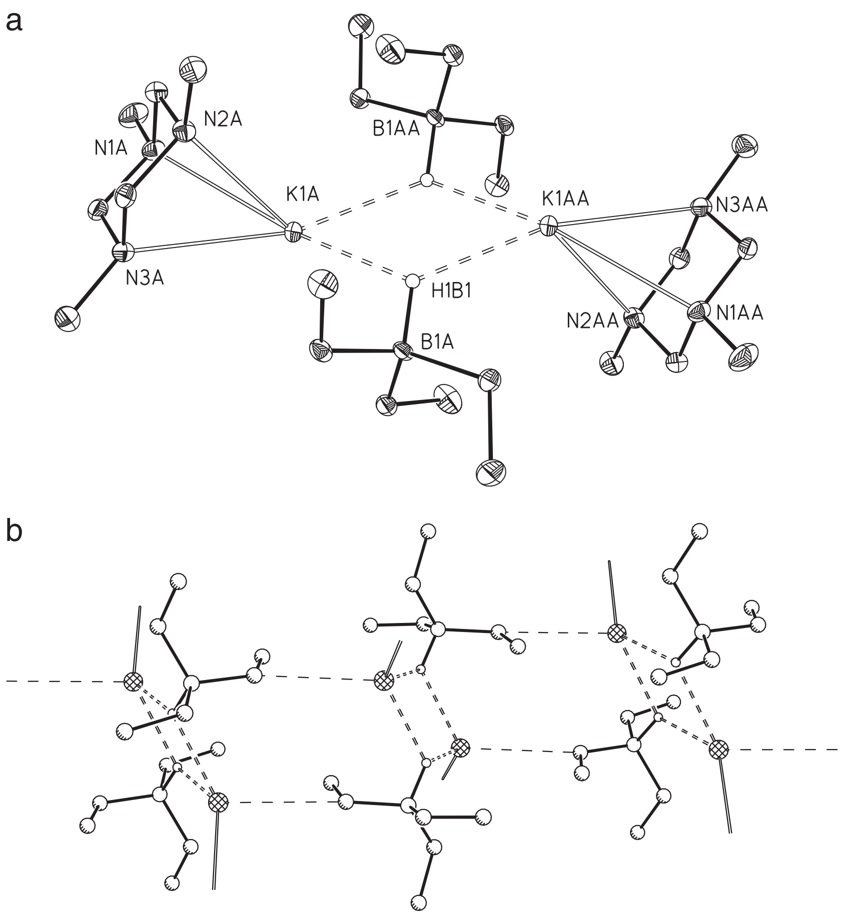
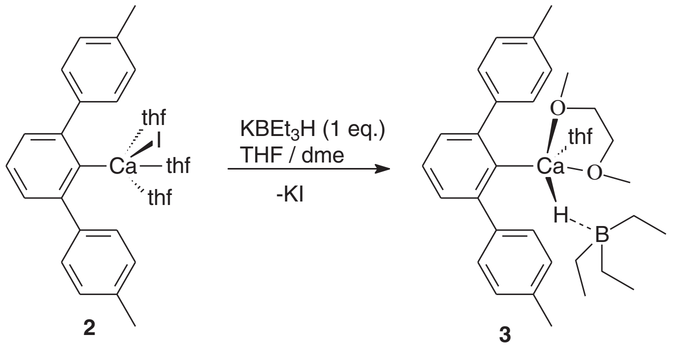


Fig. 1. a: Molecular structure and numbering scheme of $[(tmta)K\text{-}\mu(H)BEt_3]_2$ (**1**). The ellipsoids represent a probability of 40%, H atoms (with the exception of the bridging B–*H*) and intercalated toluene molecules are neglected for clarity reasons. Selected bond lengths (pm): K1A–H1BA 256(3), K1A–H1B1 261(3), K1AA–H1BA 255(4), K1AA–H1B1 259(4), B1A–H1B1 124(4); angles (°): K1A–H1B1–K1AA 117.4(8), H1B1–K1A–H1B2 62.6(8). b: Schematic representation of the chain-like structure of the dimeric units of $[(tmta)K\text{-}\mu(H)BEt_3]_2$ (**1**) (η^3-K-tmta interactions are represented as hollow sticks to the centroids of the nitrogen atoms of the tmta ligands for clarity reasons.).

atoms (av. B–H 125 pm) adopt bridging positions between two potassium centers (av. K–H 258.6 pm) resulting in a rhombus-like geometry with average K1–H–K1A and H1–K–H1B angles of 115.7° and 64.4°, respectively, and a non-bonding potassium contact K···K′ of 431.15 (14) pm. A similar structural fragment with angles of 106.5° and 73.5°, respectively, was found in $[\{\eta^6\text{-}C_6H_3\text{-}1,3,5\text{-}Me_3)Na(\mu\text{-}H)BEt_3\}_2\{Na(\mu\text{-}H)BEt_3\}_2]$ [31] whereas tetrameric $[(Et_2O)\{Na(\mu\text{-}H)BMe_3\}_4]$ contains a distorted heterocubane-type arrangement of the metal atoms and the four-coordinate hydrides [32]. The coordination sphere of the potassium atoms in (**1**) is completed by the tridentate tmta ligand (av. K–N 294.4 pm) resulting in a penta-coordination environment.

In the crystalline state intermolecular long-range agostic interactions between the potassium centers and the ethyl groups of the boranate functionalities (K···H–C) [K–C 330.3(4)–341.9(4) pm] additionally stabilize the complex *via* formation of an oligomeric chain-like structure of the dimers (**1**), represented in Fig. 1b. This aggregation leads to a tetrahedral arrangement of the ligands, due to the tridentate tmta a 5 + 1 coordination number at K results.

Thus far bulky groups are employed in order to kinetically protect Ca–H bonds. Based on our earlier findings that *para*-phenyl substituents destabilize arylcalcium halides [33] we investigated steric protection by *m*-terphenyl groups. Furthermore, substitution of the halides by bulkier anions such as amides and phosphanides additionally stabilize the organocalcium derivatives [34]. The metathetical reaction of the heavier Grignard reagent $[2,6\text{-}(tol)_2C_6H_3\text{-}Ca(thf)_3I]$ (**2**) [35] with an equimolar amount of potassium triethylborohydride yielded $[(thf)(dme)Ca(C_6H_3\text{-}2,6\text{-}tol_2)HBEt_3]$ (**3**) which was recrystallized from a solvent mixture of thf and dme (Eq. (2)) [36].



(2)

The arylcalcium triethylboronate (**3**) is stable as solid and in solution and shows no tendency to dismutate to the homoleptic derivatives. In accordance to the findings of Hanusa and co-workers [14e] regarding $[(thf)_2Ca(HBEt_3)\{1,2,4\text{-}C_5(SiMe_3)_3H_2\}]$ an abstraction of the triethylborane moiety failed both by refluxing in hydrocarbons (toluene, *n*-heptane) and drying *in vacuo*, respectively. Refluxing of a THF solution led to fast decomposition of (**3**) by well-known ether cleavage reactions [34b,37].

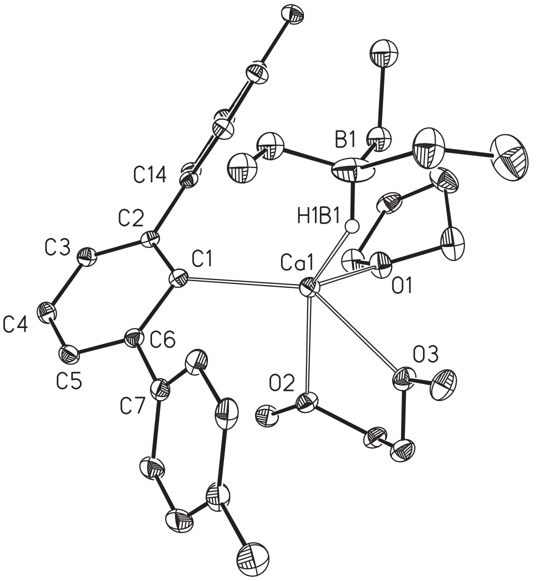


Fig. 2. Molecular structure and numbering scheme of [(thf)(dme)Ca(C_6H_3-2,6-tol$_2$)$HBEt_3$] (**3**). The ellipsoids represent a probability of 40%, H atoms (with the exception of the bridging B–*H*) are neglected for clarity reasons. Selected bond lengths (pm): Ca1–C1 254.8(3), Ca1–O1 235.7(2), Ca1–O2 244.7(2), Ca1–O3 247.1(2), Ca1···B1 293.0(5); angles (deg.): Ca1–C1–C2 131.7(2), Ca1–C1–C6 111.9(2), C2–C1–C6 114.0(3).

The molecular structure of (**3**) is displayed in Fig. 2 [38]. The bridging hydride was not found by X-ray diffraction but its position is obvious from the arrangement of the B and Ca atoms as well as from spectroscopic data. The calcium center is penta-coordinated and in agreement with the VSEPR model the sterically demanding *m*-terphenyl moiety coordinates in the trigonal plane of the resulting distorted trigonal pyramid, whereas the borohydride binds in axial position. The Ca–C_i bond length of 254.8(3) pm lies in a characteristic region for arylcalcium halides, amides, and phosphanides [30a]. Due to the bulkiness of the attached groups strongly different distal Ca–C1–C2 [131.7(2)°] and proximal Ca–C1–C6 angles [111.9(2)°] are observed. The Ca1–B1 bond [293.0(5) pm] is elongated in comparison to the β-diketiminate stabilized complex [(thf)(*dipp-nacnac*)Ca(μ-H)B^{sec}Bu$_3$] (Ca–B 286.1(4) pm) [12]. The boron atom is located in a distorted tetrahedral coordination sphere.

As crystallographically shown for the crystalline state also spectroscopic investigations of (**1**) and (**3**) confirm the presence of the boranate moiety and of metal–hydrogen–boron interactions in solution. In IR spectra strong B–H stretching modes for (μ-H)-B fragments were observed for (**1**) and (**3**) (1918 and 1926 cm^{-1}) in comparison to 1935 cm^{-1} for [(thf)$_2$Ca(HBEt$_3$){1,2,4-C_5(SiMe$_3$)$_3$H$_2$}] [14e], 1924 and 1906 cm^{-1} for [(thf)(*dipp-nacnac*)Ca(μ-H)B^{sec}Bu$_3$)] [12], as well as 1870–1950 cm^{-1} for M[HBEt$_3$] (M = Li, Na, K) [39]. The ^{11}B NMR resonances are detected in a characteristic region for bridging H–B units at −15.9 (**1**) and −15.5 ppm (**3**) and are similar to −13.3 ppm for [(thf)(*dipp-nacnac*)Ca(μ-H)B^{sec}Bu$_3$] [12], and to values of Na[HBEt$_3$] [39].

Stabilization of the hydrido complexes has been achieved by coordination of Lewis acidic BEt$_3$ to the hydride base whereas the Lewis bases tmta or dme bind to the metal cation thus saturating the coordination sphere and preventing oligomerization, dismutation and precipitation of the otherwise insoluble corresponding metal hydrides.

Acknowledgements

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Appendix A. Supplementary material

CCDC 780762 and 773949 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Angew. Chem. Int. Ed. 48 (2009) 1106–1109.

[25] Synthesis of [(tmta)K-μ(H)BEt$_3$]$_2$ (**1**): tmta (1.5 mL) was added dropwise to a solution of commercially available KBEt$_3$H in THF (5 mL, 5.0 mmol) at −25 °C. After stirring for 4 h at −15 °C all volatiles were removed *in vacuo* and the residue was extracted with toluene (6 mL). Storage at −20 °C led to crystallization of colourless prisms of **1·(PhMe)** (1.05 g, 1.67 mmol, 67%). Physical data of **1·(PhMe)**: Dec. above 33 °C. Anal. Calc. for $C_{31}H_{72}B_2K_2N_6$ (628.76 g mol^{-1}): C, 59.22; H, 11.54; N, 13.37. Found: C, 59.30; H, 11.72; N, 13.16. ^{1}H NMR (400.25 MHz, 25 °C, [D6]benzene): δ −0.77 (2H, s(br), B–*H*), 0.54 (18H, s(br), C*H*$_3$, Et), 1.28 (12H, m(br), C*H*$_2$, Et), 2.10 (18H, s, C*H*$_3$, tmta), 3.09 (12H, s(br), C*H*$_2$N). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D$_6$]benzene): δ 11.2 (6C, CH$_2$, Et), 12.0 (6C, *C*H$_3$, Et), 39.7 (6C, *C*H$_2$N, tmta), 77.8 (6C, *C*H$_3$, triaz). ^{11}B NMR (128.42 MHz, 25 °C, [D$_6$]benzene): δ −15.9 (2H, m(br), B–*H*). MS (DEI, m/z [%]): 129 [100] (tmta), 98 [62] (BEt$_3$). IR (Nujol, KBr, cm^{-1}) ν: 2025, m; 1918, m; 1682, s; 1607, s; 1455, vs; 1376, vs; 1262, s; 1234, m; 1157, m; 1116, vs; 1003, m; 914, s; 860, m; 728, s; 695, s; 622, m; 588, m.

[26] Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [27,28]. The structures were solved by direct methods

(SHELXS [29]) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97 [29]). The hydrogen atoms bound to the B atoms were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically[29]. The crystal of **1** was a non-merohedral twin. The twin law was determined by PLATON [30] to (−1, 0, 0/0, −1, 0/1.003, 0.919, 1). The contribution of the main component was refined to 0.584(5). XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. *Crystal Data for* **1**: $C_{24}H_{62}B_2K_2N_6$, C_7H_8, $Mr = 626.75$ g mol^{-1}, colourless prism, size $0.04 \times 0.04 \times 0.04$ mm^3, triclinic, space group P $\bar{1}$, $a = 13.1010(5)$, $b = 13.6471(6)$, $c = 14.0552(7)$ Å, $\alpha = 113.540(2)$, $\beta = 115.009(3)$, $\gamma = 95.764(3)°$ $V = 1975.11(15)$ Å$_3$, $T = -140$ °C, $Z = 2$, $\rho_{calcd.} = 1.054$ g cm^{-3}, μ (Mo-K$_\alpha$) = 2.66 cm^{-1}, $F(000) = 692$, 5865 reflections in $h(-15/13)$, $k(-16/14)$, l(0/16), measured in the range $2.27° \leq \Theta \leq 25.52°$ completeness $\Theta_{max} = 84.1\%$, 5865 independent reflections, 4808 reflections with $F_o > 4\sigma(Fo)$, 392 parameters, 0 restraints, $R1_{obs} = 0.0468$, $wR^2obs = 0.1486$, $R1_{all} = 0.0651$, $wR^2{}_{all} = 0.1794$, GOOF = 0.747, largest difference peak and hole: 0.318/−0.350 e Å^{-3}.

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[36] Synthesis of [(thf)(dme)Ca(C_6H_3-2,6-tol$_2$)HBEt$_3$] (**3**): A solution of [2,6-(tol)$_2$$C_6H_3$-Ca(thf)$_3$I] (**2**) (35 mL, 1.05 mmol) was prepared in THF [35] and KBEt$_3$H (1.1 mmol, in THF) was added dropwise at −40 °C. After stirring for 12 h at −25 °C the mixture was filtered and all volatiles were removed from the mother liquor. The residue was extracted with a mixture of toluene and DME (5 mL, 0.1 mL) and storage at −20 °C led to crystallization of colourless needles of **3** (0.41 g, 0.73 mmol, 70%). Physical data of **3**: Melting point: 72 °C. Anal. Calc. for $C_{34}H_{51}BCaO_3$ (558.66 g mol^{-1}): Ca, 7.17. Found: Ca, 7.30. ^{1}H NMR (400.25 MHz, 25 °C, [D$_6$]benzene): δ −0.54 (1H, s(br), B–*H*), 0.62 (9H, m(br), C*H*$_2$, Et), 1.34 (6H, m(br), C*H*$_3$, Et), 1.54 (4H, m, C*H*$_2$, thf), 2.25 (6H, s, C*H*$_3$), 2.88 (6H, C*H*$_3$, dme), 2.99 (4H, C*H*$_2$O, dme) 3.53 (4H, m, C*H*$_2$O, thf), 7.07 (4H, d, $^3J_{H-H} = 8.00$ Hz, *m′*-C*H*), 7.29 (1H, t, $^3J_{H-H} = 7.8$ Hz, *p*-C*H*), 7.46 (4H, dd, $^3J_{H-H} = 8.1$ Hz, *o′*-C*H*), 7.60 (2H, d, *m*-C*H*). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D$_6$]benzene): δ 12.8 (3C, *C*H$_2$, Et), 15.4 (3C, *C*H$_3$, Et), 20.9 (2C, *C*H$_3$), 25.5 (2C, *C*H$_2$, thf), 59.8 (2C, *C*H$_2$, dme), 68.1 (2C, *C*H$_2$O, thf), 70.9 (2C, *C*H$_2$O, dme), 126.0 (2C, *m*-CH), 127.5 (4C, *o′*-CH), 129.5 (1C, *p*-CH), 129.8 (4C, *m′*-CH), 137.1 (2C, *o*-*C*), 138.9 (2C, *p′*-*C*), 142.2 (2C, *i′*-*C*), 151.3 (1C, *i*-*C*). ^{11}B NMR (128.42 MHz, 25 °C, [D$_6$]benzene): δ −15.7 (1H, m(br), *B*–H). MS (DEI, m/z [%]): 341 [64] (C_6H_4-1,3-tol$_2$), 169 [100] ($C_{13}H_{13}$), 98 [54] (BEt$_3$). IR (Nujol, KBr, cm^{-1}) ν: 2923, vs; 2031, m; 1926, m; 1913, m; 1588, w; 1566, w; 1515, m; 1455, s; 1377, s; 1308, m; 1250, m; 1192, m; 1113, m; 1077, m; 1008, m; 981, m; 889, m; 856, m; 822, m; 785, m; 728, w; 695, s. For the NMR assignments, atoms in the central ring are unprimed and atoms in the ortho phenyl groups are primed.

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[38] *Crystal Data for* (**3**): $C_{34}H_{51}BCaO_3$, $Mr = 558.64$ g mol^{-1}, colourless prism, size $0.04 \times 0.04 \times 0.04$ mm^3, triclinic, space group P $\bar{1}$, $a = 7.9825(4)$, $b = 10.7208(4)$, $c = 19.9796(9)$ Å, $\alpha = 79.128(3)$, $\beta = 84.611(2)$, $\gamma = 74.230(3)°$ $V = 1614.29(12)$ Å^3, $T = -140$ °C, Z = 2, $\rho_{calcd.} = 1.149$ g cm^{-3}, μ(Mo-K$_\alpha$) = 2.25 cm^{-1}, $F(000) = 608$, 10175 reflections in $h(-9/10)$, $k(-11/13)$, l(−25/25), measured in the range $2.89° \leq \Theta \leq 27.41°$ completeness $\Theta_{max} = 97.8\%$, 6861 independent reflections, $R_{int} = 0.0333$, 4643 reflections with $F_o > 4\sigma(F_o)$, 354 parameters, 0 restraints, $R1_{obs} = 0.0750$, $wR^2{}_{obs} = 0.1831$, $R1_{all} = 0.1168$, $wR^2{}_{all} = 0.2107$, GOOF = 0.997, largest difference peak and hole: 1.414/−0.454 e Å^{-3}.

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