Main-Group Clusters

Ligand and Metal Effects on the Formation of Main-Group Polyhedral Clusters**

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Anion-containing metal clusters in general and interstitial hydrides in particular have a range of uses. The ability of main-group hydrides to store and deliver reactive hydride ions means that they have long been utilised synthetically as reducing agents.[1] They do, however, also have the ability to act as convenient sources of hydrogen and, as such, have potential applications in the hydrogen economy.[2] In the context of such species, we previously reported that the sequential treatment of *N*-2-pridylaniline with one equivalent $AlMe_3$ yields dimethylaluminium(*N*-2-pyridylanilide) (**1**), which then reacts with excess *t*BuLi to give species that X-ray crystallographic analysis suggests to be the cluster complexes $[Li_8(H)\{N(2\text{-}C_5H_4N)Ph\}_6]^+[Li(Me_2Al\mathit{t}Bu_2)_2]^-$ (**2**), and $Li_7(H)\{N(2\text{-}C_5H_4N)Ph\}_6$ (**3**).[3] Such compounds, postulated to incorporate interstitial hydride, are extremely rare with the convoluted hydride/*t*-butoxide superaggregate $[Li_{33}H_{17}(O\mathit{t}Bu)_{16}]$[4] and heterobimetallic $[Li\{(\mathit{t}BuCH_2O)_5Al_3H_5\}]\cdot OEt_2$[5] and $[\{NaMg[N(\mathit{i}Pr)_2](\mu\text{-}H)\cdot PhMe\}_2]$[6] being the only clusters of main-group metals suggested to incorporate hydride in what is otherwise a field dominated by transition-metal species.[7] Recently, a succession of complexes related to **2** and **3** have been characterized in the solid state. However, $[Li_8(H)\{N(2\text{-}C_5H_4N)(C_6H_4\text{-}4\text{-}Me)\}_6]^+[Li(Me_2Al\mathit{t}Bu_2)_2]^-$ (**4**), $[Li_8(H)\{N(2\text{-}C_5H_4N)(C_6H_4\text{-}2\text{-}Me)\}_6]^+[Me(Al\mathit{t}Bu_3)_2]^-$ (**5**), $[Li_8(H)\{N(2\text{-}C_5H_4N)Ph\}_6]^+[Li(Et_2Al\mathit{t}Bu_2)_2]^-$ (**6**, obtained by using $AlEt_3$), and $[Li_8(H)\{N(2\text{-}C_5H_4N)(\mathit{c}\text{-}C_6H_{11})\}_6]^+[Li(Me_2Al\mathit{t}Bu_2)_2]^-$ (**7**) have also yielded only circumstantial evidence for the existence and identity of the interstitial hydride ion.[8] It is only very recently that categorical evidence has been obtained in this respect, with the solution of a single crystal neutron diffraction structure of **2**.[8] To date, attempts to significantly alter the composition of such hydride-yielding systems have met with little success; the employment of, for example, *N,N'*-diphenylbenzamidine gives the hydride-free superlithiate $[Li_4\{PhNC(Ph)NPh\}_3]^+[Li(Me_2AlMe\mathit{t}Bu)_2]^-$

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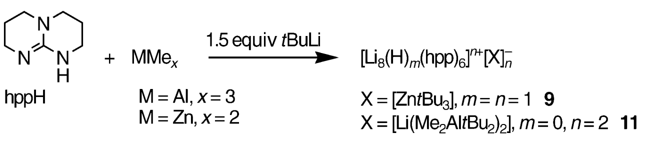
(**8**).[9] In seeking to probe the generality of cage–cluster formation and hydride entrapment, two variations on the methodology that yields **2** and **3** (and also **4**–**7**) have been deployed; 1) *N*-2-pridylaniline has been replaced by a non-aromatic guanidine ligand, and 2) while the use of MeLi and HMDSLi (HMDS = hexamethyldisilazide) has circumstantially established the importance of β-hydrogen-containing *t*BuLi in hydride encapsulation chemistry[10] the Group 13 organometallic substrate is now replaced by a Group 12 analogue. We report herein that a hydride-entrapment cluster can be generated by using bicyclic 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) in tandem with $ZnMe_2$ and *t*BuLi. Remarkably, the use of $AlMe_3$ in such a system leads to the formation of a hydride-free polyhedral cluster of the type known to encapsulate an anion in **2** (see Scheme 1).



Scheme 1. Synthesis of complexes **9** and **11**.

Sequential reaction of $ZnMe_2$ with hppH and 1.5 equivalents of *t*BuLi in toluene gives an oil from which crystals deposit (see Experimental Section). Consistent with ^1H NMR spectroscopy (which indicates the presence of hpp and *t*Bu in a 2:1 ratio), X-ray crystallography reveals this product to be ion-separated $[Li_8(H)(hpp)_6]^+[Zn\mathit{t}Bu_3]^-$ (**9**, see Figure 1). For this formula there also exists half a lattice toluene molecule and, of the two crystallographically independent separated ion pairs that exist in the unit cell, one representative example will be discussed in detail.[11] The tris(*t*-butyl)zincate anion in **9** contains a metal center that deviates only nominally from trigonal planar coordination (sum of angles at the Zn atom = 359.4°, mean Zn–C = 2.065 Å). The cationic component of **9** incorporates an almost exactly cubic array of closely packed alkali-metal centers (Li···Li range 2.473(14)–2.527(14) Å); each metal face is symmetrically straddled by a $\{hpp\}^-$ ion (mean $\angle C(NLi_2)_2$ 118.3°). The Fourier difference map reveals observable interstitial electron density that can only be satisfactorily refined as hydride. Such an assignment is consistent not only with the $[Li_8(hpp)_6]^{2+}$:$[Zn\mathit{t}Bu_3]^-$ stoichiometry observed both crystallographically and by NMR spectroscopy but also with the recent fundamental demonstration of the existence of molecular interstitial hydrides of this type.[8] However, in contrast to previously reported structures the regularity of the alkali-metal cluster in **9** suggests a μ^8-coordination sphere for the trapped anion (see also **2**, which has an octahedrally coordinated hydride by virtue of the displacement of two Li^+ centers away from the cluster core). The observation of a distorted alkali-metal array in **2** correlates with the ligand asymmetry therein. Charge delocalization over all three N centers is suggested in each $\{hpp\}^-$ ligand (mean sum of angles at N3/N6/N9 = 359.5°; Figure 1b). It is reasonable that the ligand symmetry demonstrated by the $\{hpp\}^-$ ligand is responsible for the more regular and thus higher coordination state of the interstitial anion. Consistent with this enhanced coordination, the mean Li–H bond length in **9** (2.16 Å; Li1–H1 2.21(1), Li2–H1 2.17(1), Li3–H1 2.16(1), Li4–H1 2.10(1) Å) is longer than those in both **2** (2.015 Å) and **3** (2.06 Å) and of that in octahedral $(LiH)_\infty$ (2.04 Å).[12] All Li–H bond lengths in **9** are significantly shorter than the nonbonding Li···H distance in **2** (2.828(9) Å) or the extended metal-hydride distance of 2.49(3) Å in **3**. Nevertheless, in the structure of **9**, Li1 (and its symmetry equivalent) are nominally extruded (see **2**) such that they are incorporated both in the most extended Li–H bonds (2.21(1) Å) and in the longest cube–edge distances (mean Li1···Li2A/3A/4 2.509 Å). All metal–hpp bond lengths in **9** are normal for Li–N interactions (range 1.984(11)–2.030(10) Å, mean 2.010 Å).[13]

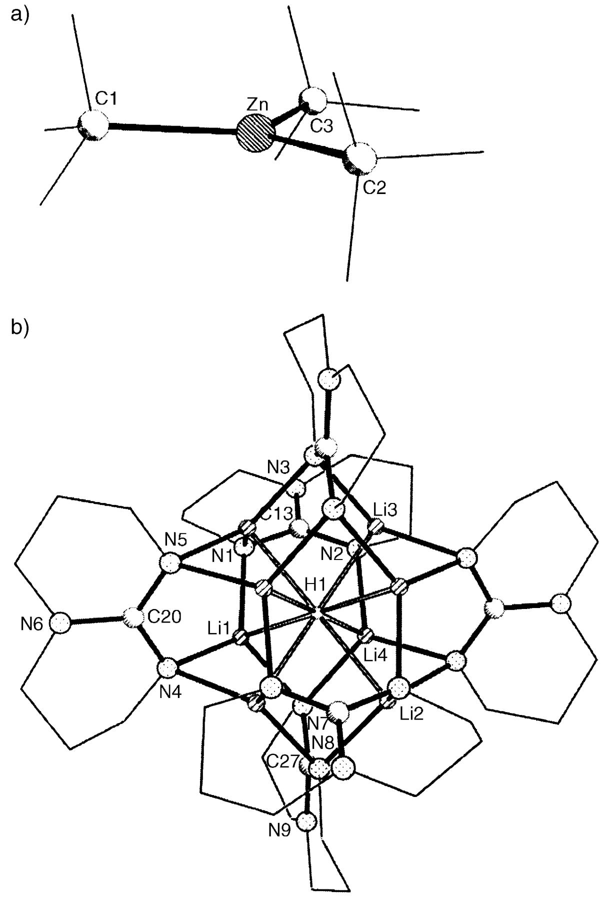


Figure 1. a) Anionic part of **9**. Selected bond lengths [Å] and angles [°]: Zn-C1 2.080(7), Zn-C2 2.059(7), Zn-C3 2.057(8), C1-Zn-C2 118.1(2), C1-Zn-C3 120.7(3), C2-Zn-C3 120.6(3). b) Cationic part of **9**: Li1-H1 2.21(1), Li2-H1 2.17(1), Li3-H1 2.16(1), Li4-H1 2.10(1), Li1-N1 2.019(11), Li1-N4 2.014(11), Li1-N7 2.029(10), Li2-N1A 2.026(11), Li2-N5A 1.984(11), Li2-N8 1.999(11), Li3-N2 2.007(11), Li3-N4A 2.000(11), Li3-N8A 2.030(10), Li4-N2 1.974(11), Li4-N5A 2.031(11), Li4-N7 2.001(11), C13-N1 1.349(8), C13-N2 1.316(8), C13-N3 1.396(8), C20-N4 1.353(7), C20-N5 1.329(7), C20-N6 1.386(7), C27-N7 1.340(7), C27-N8 1.332(7), C27-N9 1.377(7), N1-C13-N2 119.1(5), N4-C20-N5 118.9(5), N7-C27-N8 117.6(5), Li1-N1-Li2A 76.8(4), Li3-N2-Li4 77.4(4), Li1-N4-Li3A 78.0(4), Li2A-N5-Li4A 76.0(4), Li1-N7-Li4 76.2(4), Li2-N8-Li3A 76.5(4).

The reaction of hppH with $AlMe_3$ is known to afford the dimethylaluminium(guanidinate) $Al(hpp)Me_2$ (**10**)[14] the treatment of which with 1.5 equivalents of *t*BuLi gives a single isolable product (**11**). However, ^{1}H NMR spectroscopy reveals that this species does not contain hpp, *t*Bu, and AlMe units in the ratio 3:1:1 (expected for a hydride-encapsulating analogue of **2**) but in the ratio 3:2:2 (see Experimental Section). Rather than pointing to the formation of a **2**-type interstitial hydride, these data suggest the existence of two aluminium-containing anions for each $[Li_8(hpp)_6]^{2+}$ cluster ion and obviates the need for interstitial hydride to achieve electrical neutrality. Accordingly, and in contrast to the data for **2, 3**, and **9** (in all of which the Fourier difference map revealed residual electron density attributable to the trapped anion)[3,8] an X-ray crystallographic study of **11** reveals the existence of an interstitial void and thus the formulation of ion-separated $[Li_8(hpp)_6]^{2+}[\{[Li(Me_2Al\mathit{t}Bu_2)_2]^-\}_2]$ (see Figure 2).[15] The two observed lithium bis(aluminate) anionic components are precisely analogous to that reported for **2**[3] and closely related to that noted recently in **8**.[9] The single countercation incorporates an array of alkali metal centers that is almost perfectly cubic and each face of which is straddled by an $\{hpp\}^-$ ion. This polyhedral regularity contrasts with that seen in the structure of **2**[3] and suggests a relationship with the cationic component of **9**. However, any similarity proves to be superficial, with the intermetal cube edges in **11** being significantly longer those in **9** (namely Li···Li in **9**: 2.473(14)–2.527(14) Å; in **11** 2.751(7)–2.795(7) Å) and are comparable only to those in **2** that involve the extruded alkali-metal centers. Hence, in spite of the similar bite angles of *N*-2-pyridylanilide and $\{hpp\}^-$ (mean $C(NLi_2)_2$ in **2**: 115.5°; in **11**: 117.3°) it is clear that the cluster cation of **11** incorporates a somewhat enlarged alkali-metal cage. To compensate, the Li–N distances in **11** (mean Li–N 1.987 Å, range 1.964(5)–2.013(5) Å) are shorter than those reported for either **2** (mean 2.048 Å, range 1.966(8)–2.130(8) Å) or **9** (mean 2.010 Å, range 1.984(11)–2.030(10) Å). Such geometry is consistent with the absence of bonding interactions involving an interstitial anion. Rather, the positions of the Li^+ ions in **11** are borne of intermetal electrostatic repulsion and the action of $\{hpp\}^-$ ligands only.

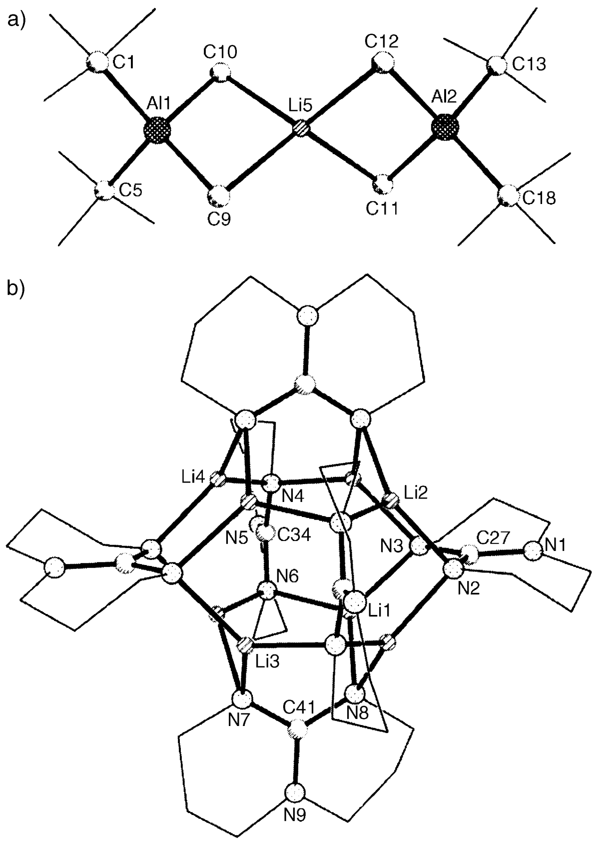


Figure 2. a) Anionic part of **9**. Selected bond lengths [Å] and angles [°]: Li5-C9 2.260(7), Li5-C10 2.271(7), Li5-C11 2.270(8), Li5-C12 2.279(7), Al1-C9 2.035(3), Al1-C10 2.050(3), Al2-C11 2.046(4), Al2-C12 2.047(4), C9-Li5-C10 95.7(3), C11-Li5-C12 95.6(3), Li5-C9-Al1 76.97(19), Li5-C10-Al1 76.43(19), Li5-C11-Al2 76.9(2), Li5-C12-Al2 76.7(2), C9-Al1-C10 110.67(16), C11-Al2-C12 110.82(17). b) Cationic part of **9**: Li1-N3 1.987(5), Li1-N6 2.004(5), Li1-N8 1.973(5), Li2-N2 1.989(5), Li2-N6A 1.969(5), Li2-N7A 2.013(5), Li3-N3A 1.981(5), Li3-N4A 1.998(5), Li3-N7 1.964(5), Li4-N2A 1.981(5), Li4-N4 1.993(5), Li4-N8A 1.993(5), C27-N1 1.365(3), C27-N2 1.346(4), C27-N3 1.349(4), C34-N4 1.353(3), C34-N5 1.359(4), C34-N6 1.340(4), C41-N7 1.348(3), C41-N8 1.348(3), C41-N9 1.360(3), N2-C27-N3 117.6(2), N4-C34-N6 117.4(2), N7-C41-N8 117.0(2), Li1-N3-Li3A 89.4(2), Li2-N2-Li4A 89.5(2), Li1-N6-Li2A 88.0(2), Li3A-N4-Li4 88.2(2), Li1-N8-Li4A 89.4(2), Li2A-N7-Li3 87.5(2).

The observation that $ZnMe_2$ is capable of yielding a hydride-encapsulation complex of the type $[Li_8(H)R_6]^+[X]^-$ is noteworthy and suggests some generality to the organometallic components that evolve such a cluster cation. Moreover, employment of the guanidine substrate hppH yields results that contrast with recent attempts to generate analogues of **2** by using *N,N'*-diphenylbenzamidine,[9] and they suggest that the employment of less sterically demanding amidines should further extend this area of hydride-capture chemistry. The view that the presence of a pyridyl moiety (see **2** and **3**) is not necessary for hydride encapsulation to proceed (see **9**) is borne of the non-aromatic nature of hppH. Evidently, the (known) reductive addition of LiH to pyridines[16] does not represent a required intermediate step in hydride capture of the type noted here. Moreover, previously published data that strongly suggest *t*BuLi to be the lithium hydride source in the preparation of complexes such as **2** point to the role of *t*BuLi differing in the two syntheses reported here.[10,17] That this dichotomy gives a structural congener of **9** that incorporates not a hydride but a core void introduces the possibility of a truly polyhedral structural chemistry for alkali metals.

Experimental Section

Synthesis of **9**: A solution of $ZnMe_2$[18] (2.0 M in toluene; 0.5 mL, 1.0 mmol) was added to hppH (0.139 g, 1.0 mmol) in toluene (8 mL) at room temperature under N_2 and this solution was stirred until the effervescence subsided. A solution of *t*BuLi (0.88 mL, 1.7 M in pentane, 1.5 mmol) was added at −78 °C and this mixture was allowed to reach ambient temperature. The addition of toluene (6 mL) gave a suspension that was heated to reflux and filtered. The resulting oil was stored at room temperature whereupon a solution formed over a period of hours and crystals of **9** deposited over two days. Yield 35 % (based on *t*BuLi), m.p. 314–316 °C. Elemental analysis calcd (%) for $C_{54}H_{100}Li_8N_{18}Zn{\cdot}0.5\,C_7H_8$: C 59.10, H 8.97, N 21.58 %; found, C 58.94, H 8.68, N 21.55 %. ^{1}H NMR spectroscopy (400 MHz, $[^2H_6]$DMSO): $\delta = 7.24$–7.11 (m, 2.5H; Ph), 3.04 (t,

$^{3}J(H,H) = 5.4$ Hz, 24H; NCH_2), 2.92 (t, $^{3}J(H,H) = 6.2$ Hz, 24H; NCH_2), 2.29 (s, 1.5H; Me), 1.62 (quint, $^{3}J(H,H) = 5.8$ Hz, 24H; CH_2), 0.85–0.84 ppm (m, 27H, *t*Bu). ^{13}C NMR spectroscopy (100 MHz, [$^{2}H_6$]DMSO): $\delta = 159.8$ (CN_3), 137.2 (*i*Ph), 129.3, 128.6 (*o-*, *m*-Ph), 125.8 (*p*-Ph), 49.1, 44.5 (NCH_2), 25.5 (CH_2), 24.9 ppm (ZnC*Me*).

Synthesis of **11**: A solution of $AlMe_3$ (2.0 M in hexane; 0.5 mL, 1.0 mmol) was added to hppH (0.139 g, 1.0 mmol) in toluene (5 mL) at room temperature under N_2. The resultant yellow solution was stirred until the reaction ceased. A solution of *t*BuLi (1.7 M in pentane; 0.88 mL, 1.5 mmol) was added at −78 °C and the mixture allowed to reach room temperature giving a suspension. Toluene (2.5 mL) was added to the mixture, which was then filtered and stored at room temperature for one day to give crystals of **11**. Yield 57 % (based on *t*BuLi), m.p. 218–220 °C. Elemental analysis calcd (%) for $C_{41}H_{84}Al_2Li_5N_9$: C 62.19, H 10.69, N 15.92 %; found, C 62.18, H 10.54, N 15.43 %. ^{1}H NMR spectroscopy (400 MHz, [$^{2}H_6$]DMSO): $\delta = 7.24$–7.11 (m, 0.5H; Ph), 2.99 (t, $^{3}J(H,H) = 5.8$ Hz, 24H; NCH_2), 2.96 (t, $^{3}J(H,H) = 5.8$ Hz, 24H; NCH_2), 2.27 (s, 0.3H; Me), 1.70 (quint, $^{3}J(H,H) = 5.8$ Hz, 24H; CH_2), 0.75–0.69 (m, 36H; *t*Bu), −1.40 ppm (sext, $^{2}J(H,Al) = 6.0$ Hz, 12H; Me). ^{13}C NMR spectroscopy (125 MHz, [$^{2}H_6$]DMSO): $\delta = 150.2$ (CN_3), 137.4 (*i*-Ph), 129.0, 128.3 (*o-*, *m*-Ph), 125.4 (*p*-Ph), 47.5, 41.1 (NCH_2), 32.9–32.0 (AlC*Me*), 23.0 (CH_2), 21.1 (Ph*Me*), −7.9 ppm (AlMe, $^{1}J(C,Al) = 71.0$ Hz).

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[11] Crystal data for **9**: $C_{54}H_{100}Li_8N_{18}Zn\cdot 0.5\,C_7H_8$, $M_r = 1168.48$, monoclinic, space group $P2(1)/n$, $a = 16.4567(7)$, $b = 18.6532(8)$, $c = 22.6602(9)$ Å, $\beta = 105.527(2)°$, $V = 6702.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.158$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.415$ mm^{-1}, $T = 173(2)$ K. 27354 data (8151 unique, $R_{int} = 0.1003$, $\theta < 21.99°$) were collected on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELX-97, Program for Crystal Structure Refinement, University of Göttingen, **1997**) to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2025$, conventional $R = 0.0770$ on F values of 5139 reflections with $F^2 > 2\sigma(F^2)$, $S = 1.025$, 763 parameters. Residual electron density extrema ± 0.509 e Å^{-3}. Crystallographic data (excluding structure factors) for **9** and **11** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-209673 and CCDC-209674 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] Crystal data for **11**: $C_{41}H_{84}Al_2Li_5N_9$, $M_r = 791.83$, monoclinic, space group $P2(1)/n$, $a = 14.349(3)$, $b = 20.752(4)$, $c = 18.272(4)$ Å, $\beta = 107.79(3)°$, $V = 5180.7(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.015$ g cm^{-3}, $Mo_{K\alpha}$, $\lambda = 0.71069$ Å, $\mu = 0.090$ mm^{-1}, $T = 180(2)$ K. 25541 data (9051 unique, $R_{int} = 0.0405$, $\theta < 25.03°$) were collected on a Nonius Kappa CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G. M. Sheldrick, SHELX-97, Program for Crystal Structure Refinement, University of Göttingen, **1997**) to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2209$, conventional $R = 0.0649$ on F values of 6397 reflections with $F^2 > 2\sigma(F^2)$, $S = 1.090$, 526 parameters. Residual electron density extrema ± 0.518 e Å^{-3}.

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