# Supporting Information

## Second-Generation Hexavalent Molybdenum Oxo-Amidinate Precursors for Atomic Layer Deposition

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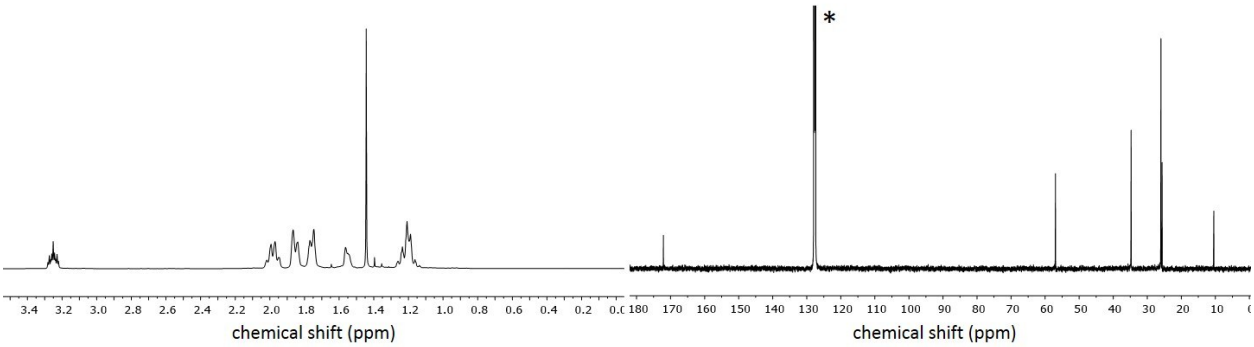



**Figure S1:** (*left*) $^{1}H$ (500 MHz, $C_6D_6$), (*right*) $^{13}C$ (125 MHz, $C_6D_6$) NMR spectra of **2**. * = $C_6D_6$

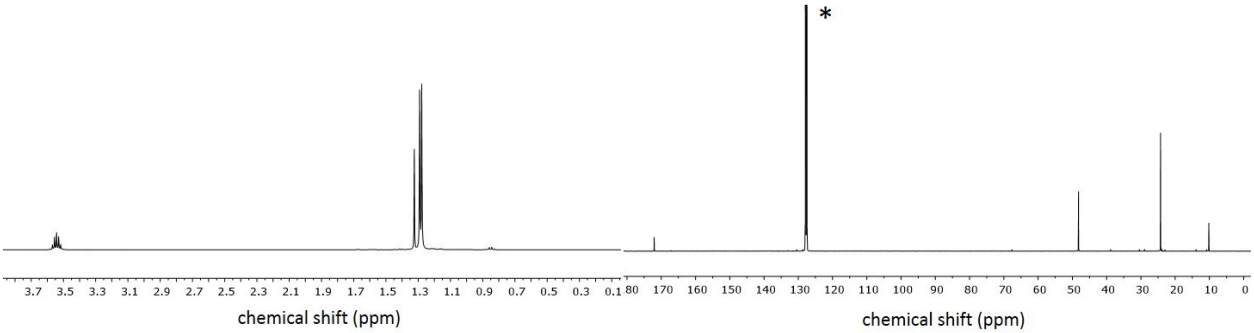



**Figure S2:** (*left*) $^{1}H$ (500 MHz, $C_6D_6$), (*right*) $^{13}C$ (125 MHz, $C_6D_6$) NMR spectra of **3**. * = $C_6D_6$

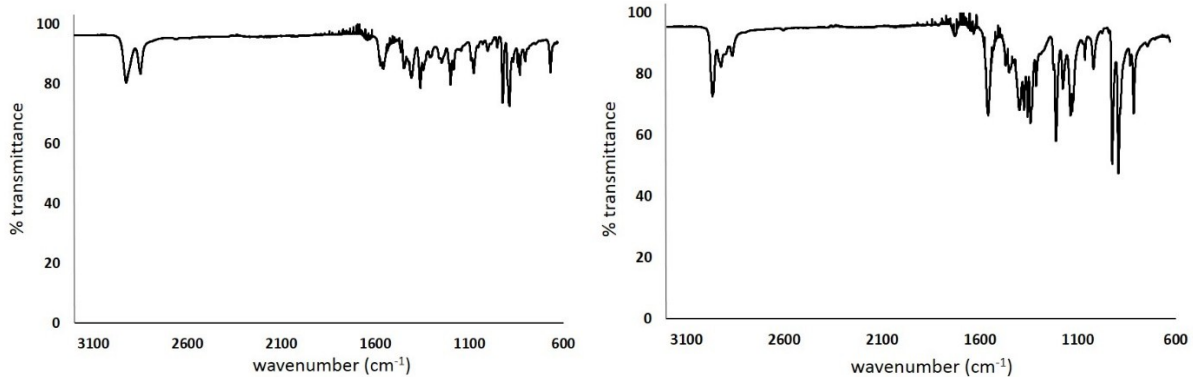



**Figure S3:** Fourier transform infrared spectrum (FTIR) of (*left*) **2**, and (*right*) **3**.

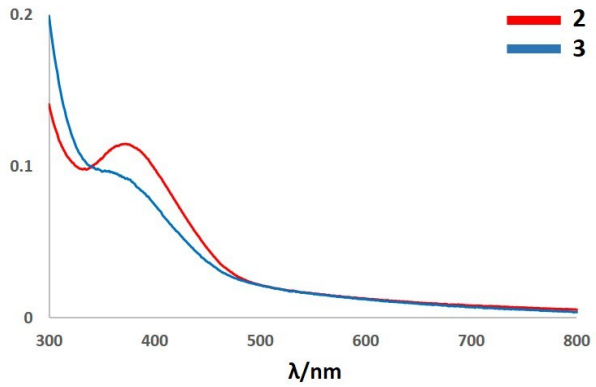
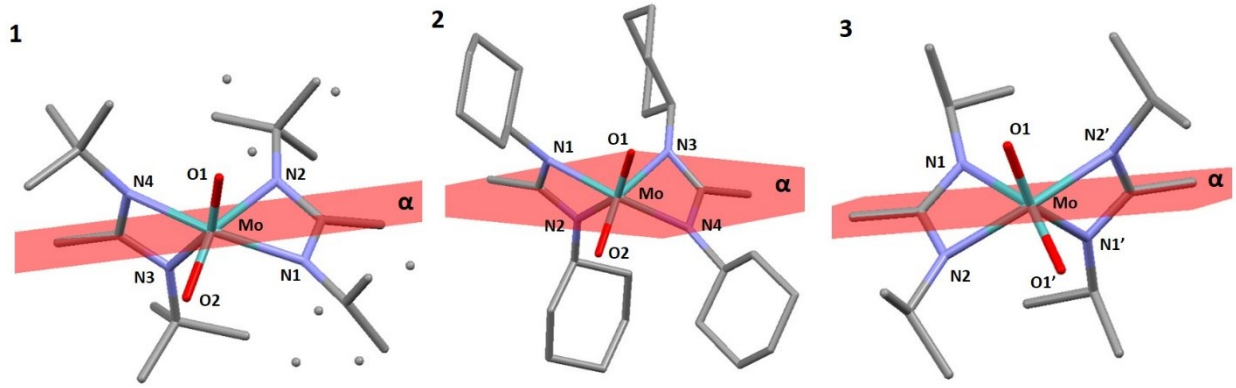



**Figure S4:** UV-Vis spectrum of (*red*) **2**, and (*blue*) **3** (0.2 mmol in toluene).




| 1 | 2 | 3 |
|---|---|---|
| α = O1, N1, N2, Mo, O2, N3, N4 | α = O1, N1, N2, Mo, O2, N3, N4 | α = O1, N1, N2, Mo, O1', N1', N2' |
| **Measured distances (Å)** | | |
| **Mo → α = 0.011** | **Mo → α = 0.007** | **Mo → α = 0.000** |

**Figure S5:** Measurements of Mo distance to the calculated plane α (α = N, N, N, N, Mo, O, O) for **1**, **2**, and **3**.

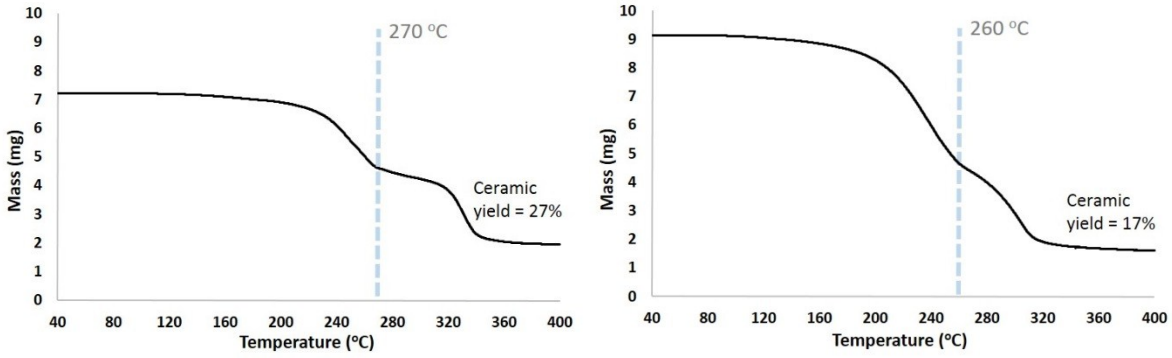



**Figure S6:** Air-free TGA analysis of **2** (*left*) and **3** (*right*). Ramp rate 5°C/min. under flow of $N_2$ (20 mL/min.).

| | Mw (g/mol) | T (°C) at 25% mass loss | % mass loss at 250 °C |
|---|---|---|---|
| 1 | 466.54 | 224 | 50 |
| 2 | 570.69 | 252 | 24 |
| 3 | 410.43 | 227 | 44 |

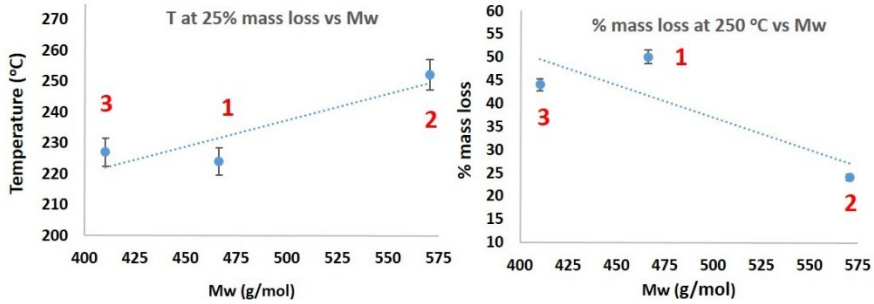



**Figure S7:** Comparison of thermogravimetric properties for **1**,[1] **2** and **3** *vs* molecular weight.

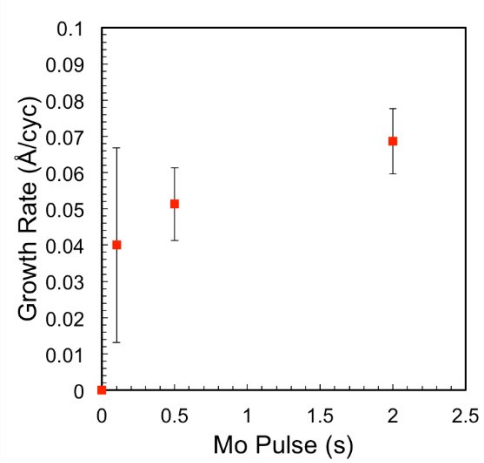



**Figure S8:** Growth rate as a function of the pulse time of precursor **3**. *Large fluctuations of measured thicknesses were observed at lower pulse times due to lack of precursor vapor to fully saturate and react with the surface of the silicon wafers.*

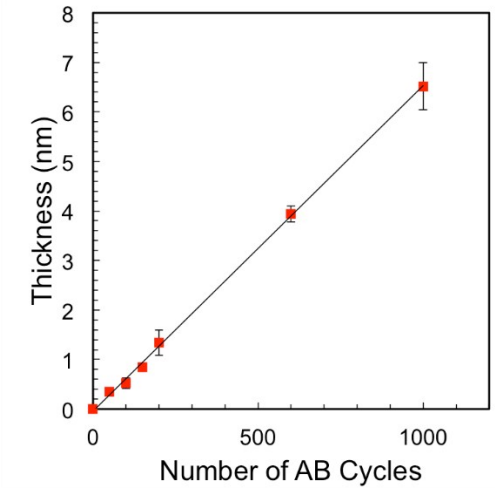



**Figure S9:** Correlation of film thickness vs. number of ALD "A-B" cycles of precursor **3** and $O_3$ as grown on Si wafers measured ex-situ using spectroscopic ellipsometery. A timing sequence ($t_1$–$t_2$–$t_3$–$t_4$) of 2–30–10–45 was used at a reactor temperature of 150 °C.

[1] 1. Mouat, A. R.; Mane, A. U.; Elam, J. W.; Delferro, M.; Marks, T. J.; Stair, P. C., *Chem. Mater.* **2016**, *28*, 1907-1919.

**Table S1: Crystal data and structure refinement for 2 and 3.**

| **Complex** | **2** | **3** |
|---|---|---|
| Empirical formula | $C_{28}H_{50}MoN_4O_2$ | $C_{16}H_{34}MoN_4O_2$ |
| Formula weight | 570.66 | 410.41 |
| Temperature/K | 100.06 | 99.99 |
| Crystal system | orthorhombic | tetragonal |
| Space group | $Pna2_1$ | $P4_12_12$ |
| a/Å | 11.4715(2) | 10.3994(4) |
| b/Å | 11.6621(2) | 10.3994(4) |
| c/Å | 21.5619(5) | 18.7146(9) |
| α/° | 90 | 90 |
| β/° | 90 | 90 |
| γ/° | 90 | 90 |
| Volume/Å$^3$ | 2884.59(10) | 2023.94(15) |
| Z | 4 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.314 | 1.347 |
| μ/mm$^{-1}$ | 0.485 | 0.662 |
| F(000) | 1216.0 | 864.0 |
| Crystal size/mm$^3$ | 0.222 × 0.164 × 0.085 | 0.422 × 0.348 × 0.33 |
| Radiation | MoKα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.328 to 76.422 | 5.952 to 109.634 |
| Index ranges | -19 ≤ h ≤ 19, -16 ≤ k ≤ 20, -37 ≤ l ≤ 37 | -18 ≤ h ≤ 23, -21 ≤ k ≤ 21, -41 ≤ l ≤ 42 |
| Reflections collected | 44589 | 71443 |
| Independent reflections | 15363 [$R_{int}$ = 0.0702, $R_{sigma}$ = 0.0827] | 12623 [$R_{int}$ = 0.0453, $R_{sigma}$ = 0.0337] |
| Data/restraints/parameters | 15363/1/318 | 12623/0/116 |
| Goodness-of-fit on F$^2$ | 0.790 | 1.026 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0491, $wR_2$ = 0.1172 | $R_1$ = 0.0257, $wR_2$ = 0.0537 |
| Final R indexes [all data] | $R_1$ = 0.0745, $wR_2$ = 0.1336 | $R_1$ = 0.0358, $wR_2$ = 0.0564 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.10/-0.53 | 0.90/-0.44 |
| Flack parameter | -0.03(2) | -0.012(9) |

**Table S2: Bond Lengths for 2.**

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| Mo1 | O1 | 1.707(3) | N1 | C15 | 1.353(4) |
| Mo1 | N4 | 2.282(3) | N1 | C23 | 1.464(4) |
| Mo1 | O2 | 1.708(3) | N3 | C3 | 1.470(4) |
| Mo1 | N2 | 2.309(3) | C8 | C3 | 1.523(5) |
| Mo1 | N1 | 2.085(3) | C8 | C7 | 1.532(5) |
| Mo1 | N3 | 2.082(3) | C3 | C4 | 1.530(5) |
| C2 | C1 | 1.501(5) | C21 | C22 | 1.530(5) |
| C1 | N4 | 1.307(4) | C21 | C20 | 1.521(5) |
| C1 | N3 | 1.349(4) | C15 | C16 | 1.506(4) |

| | | | | | |
|---|---|---|---|---|---|
| C10 | C9 | 1.525(5) | C18 | C19 | 1.524(5) |
| C10 | C11 | 1.529(5) | C23 | C28 | 1.520(5) |
| C9 | N4 | 1.452(4) | C23 | C24 | 1.514(5) |
| C9 | C14 | 1.530(4) | C4 | C5 | 1.531(5) |
| C13 | C14 | 1.527(5) | C27 | C28 | 1.532(5) |
| C13 | C12 | 1.525(6) | C27 | C26 | 1.524(6) |
| C11 | C12 | 1.528(6) | C5 | C6 | 1.516(5) |
| N2 | C17 | 1.458(4) | C25 | C24 | 1.528(5) |
| N2 | C15 | 1.300(4) | C25 | C26 | 1.524(6) |
| C17 | C18 | 1.525(4) | C6 | C7 | 1.524(5) |
| C17 | C22 | 1.519(5) | C20 | C19 | 1.532(6) |

**Table S3: Bond angles for 2.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O1 | Mo1 | N4 | 93.87(11) | N2 | C17 | C22 | 111.7(3) |
| O1 | Mo1 | O2 | 105.96(14) | C22 | C17 | C18 | 110.8(3) |
| O1 | Mo1 | N2 | 152.23(11) | C15 | N1 | Mo1 | 99.14(19) |
| O1 | Mo1 | N1 | 94.39(11) | C15 | N1 | C23 | 122.7(3) |
| O1 | Mo1 | N3 | 105.54(13) | C23 | N1 | Mo1 | 136.8(2) |
| N4 | Mo1 | N2 | 78.68(10) | C1 | N3 | Mo1 | 98.45(19) |
| O2 | Mo1 | N4 | 151.41(12) | C1 | N3 | C3 | 123.2(3) |
| O2 | Mo1 | N2 | 91.83(12) | C3 | N3 | Mo1 | 135.7(2) |
| O2 | Mo1 | N1 | 107.79(12) | C3 | C8 | C7 | 111.0(3) |
| O2 | Mo1 | N3 | 94.41(11) | N3 | C3 | C8 | 112.7(3) |
| N1 | Mo1 | N4 | 90.60(10) | N3 | C3 | C4 | 110.1(3) |
| N1 | Mo1 | N2 | 59.37(10) | C8 | C3 | C4 | 110.0(3) |
| N3 | Mo1 | N4 | 59.92(10) | C20 | C21 | C22 | 111.3(3) |
| N3 | Mo1 | N2 | 93.87(11) | N2 | C15 | N1 | 110.8(3) |
| N3 | Mo1 | N1 | 144.82(11) | N2 | C15 | C16 | 126.2(3) |
| N4 | C1 | C2 | 126.1(3) | N1 | C15 | C16 | 122.8(3) |
| N4 | C1 | N3 | 110.8(3) | C19 | C18 | C17 | 110.8(3) |
| N3 | C1 | C2 | 123.1(3) | N1 | C23 | C28 | 113.6(3) |
| C9 | C10 | C11 | 110.7(3) | N1 | C23 | C24 | 111.0(3) |
| C10 | C9 | C14 | 110.3(3) | C24 | C23 | C28 | 109.9(3) |
| N4 | C9 | C10 | 110.8(3) | C17 | C22 | C21 | 110.7(3) |
| N4 | C9 | C14 | 109.4(3) | C3 | C4 | C5 | 111.1(3) |
| C1 | N4 | Mo1 | 90.57(19) | C26 | C27 | C28 | 111.5(3) |
| C1 | N4 | C9 | 123.5(3) | C6 | C5 | C4 | 111.4(3) |
| C9 | N4 | Mo1 | 141.9(2) | C23 | C28 | C27 | 110.7(3) |
| C12 | C13 | C14 | 111.2(3) | C26 | C25 | C24 | 110.8(3) |
| C12 | C11 | C10 | 110.8(3) | C5 | C6 | C7 | 111.5(3) |
| C13 | C14 | C9 | 112.6(3) | C6 | C7 | C8 | 111.2(3) |
| C13 | C12 | C11 | 111.0(3) | C21 | C20 | C19 | 111.0(3) |
| C17 | N2 | Mo1 | 146.0(2) | C18 | C19 | C20 | 111.7(3) |
| C15 | N2 | Mo1 | 90.5(2) | C23 | C24 | C25 | 111.7(3) |
| C15 | N2 | C17 | 123.2(3) | C25 | C26 | C27 | 111.5(3) |
| N2 | C17 | C18 | 109.9(3) | | | | |

**Table S4: Bond Lengths for 3.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Mo1 | O1 | 1.7155(9) | N2 | C3 | 1.4652(8) |
| Mo1 | O11 | 1.7155(9) | N2 | Mo1A | 2.1036(14) |
| Mo1 | N11 | 2.2785(10) | C1 | C2 | 1.5014(10) |
| Mo1 | N1 | 2.2784(10) | C3 | C4 | 1.5231(11) |
| Mo1 | N2 | 2.0832(6) | C3 | C5 | 1.5197(12) |
| Mo1 | N21 | 2.0832(6) | C6 | C7 | 1.5249(13) |
| O1 | Mo1A | 1.674(3) | C6 | C8 | 1.5206(12) |
| N1 | C1 | 1.3056(8) | Mo1A | O11 | 1.674(3) |
| N1 | C6 | 1.4559(9) | Mo1A | N11 | 2.332(3) |
| N1 | Mo1A | 2.332(3) | Mo1A | N21 | 2.1036(14) |
| N2 | C1 | 1.3530(8) | | | |

[1]1-Y,1-X,3/2-Z

**Table S5: Bond angles for 3.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O1 | Mo1 | O11 | 105.63(9) | N1 | C1 | N2 | 110.51(6) |
| O11 | Mo1 | N11 | 92.54(4) | N1 | C1 | C2 | 125.17(6) |
| O1 | Mo1 | N1 | 92.54(4) | N2 | C1 | C2 | 124.31(6) |
| O1 | Mo1 | N11 | 151.46(4) | N2 | C3 | C4 | 110.23(6) |
| O11 | Mo1 | N1 | 151.46(4) | N2 | C3 | C5 | 111.48(6) |
| O1 | Mo1 | N2 | 106.08(3) | C5 | C3 | C4 | 111.35(7) |
| O11 | Mo1 | N21 | 106.08(3) | N1 | C6 | C7 | 109.45(7) |
| O11 | Mo1 | N2 | 93.44(3) | N1 | C6 | C8 | 109.91(6) |
| O1 | Mo1 | N21 | 93.44(3) | C8 | C6 | C7 | 111.18(8) |
| N1 | Mo1 | N11 | 80.48(4) | O1 | Mo1A | O11 | 109.4(2) |
| N21 | Mo1 | N11 | 59.92(3) | O11 | Mo1A | N1 | 149.96(10) |
| N2 | Mo1 | N11 | 94.34(4) | O1 | Mo1A | N1 | 91.75(6) |
| N21 | Mo1 | N1 | 94.34(4) | O11 | Mo1A | N11 | 91.75(6) |
| N2 | Mo1 | N1 | 59.92(3) | O1 | Mo1A | N11 | 149.96(10) |
| N2 | Mo1 | N21 | 147.63(6) | O11 | Mo1A | N2 | 93.93(4) |
| C1 | N1 | Mo1 | 90.83(4) | O1 | Mo1A | N2 | 106.78(5) |
| C1 | N1 | C6 | 124.16(6) | O11 | Mo1A | N21 | 106.77(5) |
| C1 | N1 | Mo1A | 90.54(4) | O1 | Mo1A | N21 | 93.93(4) |
| C6 | N1 | Mo1 | 143.80(5) | N1 | Mo1A | N11 | 78.27(13) |
| C6 | N1 | Mo1A | 143.81(5) | N2 | Mo1A | N11 | 92.26(13) |
| C1 | N2 | Mo1 | 98.28(4) | N2 | Mo1A | N1 | 58.75(7) |
| C1 | N2 | C3 | 125.12(6) | N21 | Mo1A | N1 | 92.26(13) |
| C1 | N2 | Mo1A | 99.55(9) | N21 | Mo1A | N11 | 58.75(7) |
| C3 | N2 | Mo1 | 134.63(5) | N2 | Mo1A | N21 | 144.0(2) |
| C3 | N2 | Mo1A | 133.04(11) | | | | |

[1]1-Y,1-X,3/2-Z