**Supplementary Information for**

# Unusual Reactivity of Lanthanide Borohydride Complexes leading to a Borane Complex.

*Nils Meyer, Jelena Jenter, Peter W. Roesky*, Georg Eickerling, and Wolfgang Scherer**

Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34-36, 14195 Berlin (Germany). Institut für Anorganische Chemie, Universität Karlsruhe (TH), Engesserstr. 15, Geb. 30.45, 76128 Karlsruhe (Germany). Institut für Physik, Universität Augsburg, Universitätsstr. 1, 86159 Augsburg (Germany).

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**S1: Experimental Section**

All manipulations were carried out under anaerobic and anhydrous conditions.

**2**: THF (10 ml) was condensed at -78 °C onto a mixture of $[La(BH_4)_3(THF)_3]$ (0.40 g, 1.0 mmol) and (0.48 g, 1.0 mmol) [($DIP_2$-pyr)K] (**1**) and the resulting yellow reaction mixture was stirred for 16 h at 60 °C. The yellow solution was filtered off and concentrated until a white precipitate appears. The mixture was heated carefully until the solution became clear. The solution was allowed to stand at ambient temperature to obtain the product as yellow crystals after 16 h. - Yield: 0.55 g, 0.7 mmol, 70 %. - $^1$H-NMR (THF-$d_8$, 400 MHz, 25 °C): δ = 0.62-0.84 (br, 8 H, $BH_4$), 1.03 (d, 12 H, $CH(CH_3)_2$, $J_{H,H}$ = 6.7 Hz), 1.20 (d, 12 H, $CH(CH_3)_2$, $J_{H,H}$ = 6.7 Hz), 3.57 (sept, 4 H, $CH(CH_3)_2$, $J_{H,H}$ = 6.7 Hz), 6.62 (s, 2 H, 3,4-pyr), 7.07-7.14 (m, 6 H, Ph), 8.05 (s, 2 H, N=CH). - $^{13}C\{^1H\}$ NMR (THF-$d_8$, 100.4 MHz, 25 °C): δ = 22.1 ($CH(CH_3)_2$), 25.6 ($CH(CH_3)_2$), 27.4 ($CH(CH_3)_2$), 117.1 (3,4-pyr), 123.2 (Ph), 126.4 (Ph), 141.0 (2,5-pyr), 142.9 (Ph), 148.7 (Ph), 163.3 (N=CH). - $^{11}$B NMR (THF-$d_8$, 128.15 MHz, 25°C): δ = -21.3 (br qt, $J_{H,B}$ = 89.1 Hz) - IR (KBr, ν/cm$^{-1}$): 871(m), 1049(m), 1099(m), 1161(s), 1327(s), 1450(m), 1566(vs), 2171(w), 2222(s), 2330(w), 2422(m), 2874(s), 2962(vs) - $C_{38}H_{62}B_2N_3O_2La$ (753.45): calcd. C, 60.58, H, 8.29, N, 5.58; found C, 59.63, H, 8.84, N, 5.40.

**3**: THF (10 ml) was condensed at -78 °C onto a mixture of $[Lu(BH_4)_3(THF)_3]$ (0.63 g, 1.4 mmol) and [($DIP_2$-pyr)K] (**1**) (0.67 g, 1.4 mmol) and the resulting yellow reaction mixture was stirred for 16 h at 60 °C. The yellow solution was filtered off and concentrated until a white precipitate appears. The mixture was heated carefully until the solution became clear. The solution was allowed to stand at ambient temperature to obtain the product as yellow crystals after several hours. - Yield 0.45 g, 0.6 mmol, 43 %. - $^1$H NMR (THF-$d_8$, 400 MHz, 25 °C): δ = 0.82-0.90 (br, 4 H, $BH_4$), 1.12 (d, 6 H, $CH(CH_3)_2$, $J_{H,H}$ = 7.0 Hz), 1.14 (d, 6 H, $CH(CH_3)_2$, $J_{H,H}$ = 7.0 Hz), 1.15 (d, 6 H, $CH(CH_3)_2$, $J_{H,H}$ = 7.0 Hz), 1.21 (d, 6 H, $CH(CH_3)_2$,

$J_{H,H}$ = 7.0 Hz), 2.42 (br, 3 H, $BH_3$), 3.05 (sept, 2 H, C*H*$(CH_3)_2$, $J_{H,H}$ = 7.0 Hz), 3.73 (sept, 2 H, C*H*$(CH_3)_2$, $J_{H,H}$ = 7.0 Hz), 4.51 (s, 2 H, N-$CH_2$), 6.21 (d, 1 H, pyr, $J_{H,H}$ = 3.8 Hz), 6.85 (t, 1 H, Ph, $J_{H,H}$ = 7.3 Hz), 6.95 (d, 2 H, Ph, $J_{H,H}$ = 7.3 Hz), 7.04 (d, 1 H, pyr, $J_{H,H}$ = 3.8 Hz), 7.14-7.22 (m, 3 H, Ph), 7.56 (s, 1 H, N=CH). - $^{13}C\{^1H\}$ NMR (THF-$d_8$, 100.4 MHz, 25 °C): δ = 23.2 (CH(*C*$H_3)_2$), 23.5 (CH(*C*$H_3)_2$), 24.8 (CH(*C*$H_3)_2$), 25.7 (CH(*C*$H_3)_2$), 26.4 (*C*H$(CH_3)_2$), 28.4 (*C*H$(CH_3)_2$), 58.6 (N-$CH_2$), 110.3 (pyr), 122.6, 122.9, 123.6, 127.0, 129.6, 133.2, 142.6, 146.0, 149.6, 153.0, 153.3, 165.7 (N=CH). – $^{11}B$ NMR (THF-$d_8$, 128.15 MHz, 25 °C): δ = -25.2 (br qt, $BH_4$, $J_{H,B}$ = 71.3 Hz), -14.8 (br, $BH_3$). - IR (KBr, ν/$cm^{-1}$): 865(m), 906(w), 1056(s), 1103(m), 1139(m), 1198(s), 1246(s), 1289(s), 1322(s), 1382(m), 1462(s), 1538(w), 1584(s), 1607(vs), 2180(w), 2230(m), 2295(m), 2423(m), 2467(m), 2867(s), 2963(vs). - $C_{38}H_{62}B_2N_3O_2Lu$ (789.51): calcd C, 57.81, H, 7.92, N, 5.32; found C, 57.62, H, 8.09, N, 5.38.

**S2**: Crystal data and structure refinement for **2**.

| | |
|---|---|
| Identification code | 2 |
| Empirical formula | C38 H62 B2 La N3 O2 |
| Formula weight | 753.44 |
| Temperature | 200(2) K |
| Wavelength | 0.71073 A |
| Crystal system, space group | Orthorhombic, P b c a |
| Unit cell dimensions | a = 16.0927(8) A alpha = 90 deg.<br>b = 25.1371(17) A beta = 90 deg.<br>c = 19.9083(10) A gamma = 90 deg. |
| Volume | 8053.4(8) A^3 |
| Z, Calculated density | 8, 1.243 Mg/m^3 |
| Absorption coefficient | 1.094 mm^-1 |
| F(000) | 3152 |
| Crystal size | 0.432 x 0.289 x 0.204 mm |
| Theta range for data collection | 2.54 to 25.02 deg. |
| Limiting indices | -19<=h<=19, -29<=k<=27, -20<=l<=23 |
| Reflections collected / unique | 28300 / 7100 [R(int) = 0.0573] |
| Completeness to theta = 25.02 | 99.9 % |
| Absorption correction | Integration |
| Max. and min. transmission | 0.8509 and 0.7507 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 7100 / 2 / 434 |
| Goodness-of-fit on F^2 | 0.864 |
| Final R indices [I>2sigma(I)] | R1 = 0.0340, wR2 = 0.0652 |
| R indices (all data) | R1 = 0.0709, wR2 = 0.0723 |
| Largest diff. peak and hole | 0.469 and -0.381 e.A^-3 |

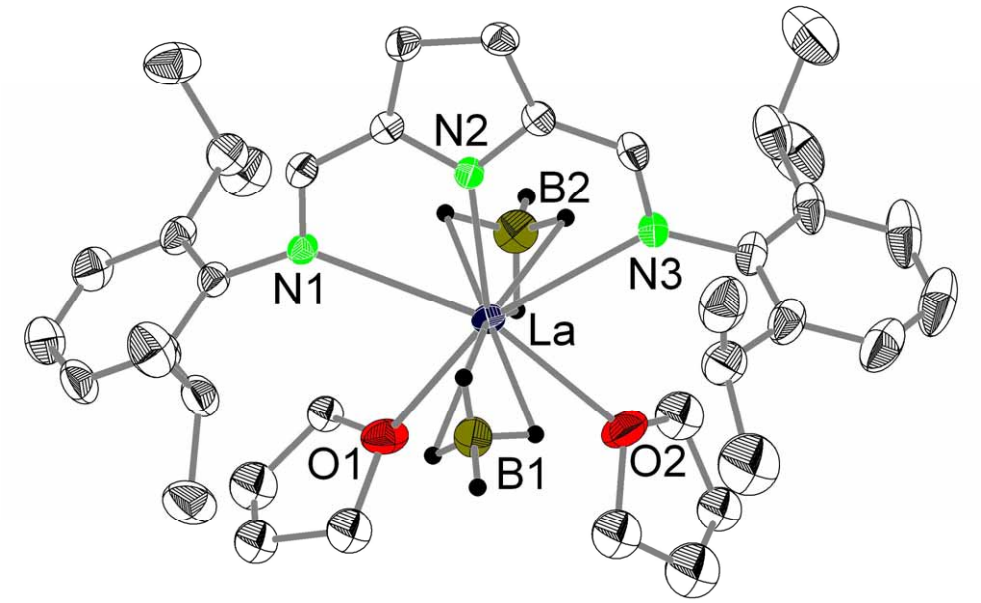


**Figure S2**: ORTEP representations of the solid-state structure of **2** (50% probability). Selected bond lengths [Å] or angles [°]:La-N1 2.852(3), La-N2 2.453(3), La-N3 2.890(3), La-O1 2.616(3), La-O2 2.604(3), La-B1 2.714(5), La-B2 2.711(6); N1-La-N2 61.37(9), N1-La-N3 122.40(8), N2-La-N3 61.15(9), N1-La-O1 77.43(9), N1-La-O2 160.32(10), N2-La-O1 138.51(9), N2-La-O2 138.30(10), N3-La-O1 160.14(9), N3-La-O2 77.20(10), N1-La-B1 91.21(14), N1-La-B2 96.07(15), N2-La-B1 96.2(2), N2-La-B2 94.40(15), N3-La-B1 91.45(15), N3-La-B2 91.4(2), O1-La-O2 83.03(10), O1-La-B1 89.0(2), O1-La-B2 84.8(2), O2-La-B1 86.11(15), O2-La-B2 84.3(2), B1-La-B2 169.1(2).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-689078 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

**S3: Comparison of X-ray structural models of 3 obtained from data measured at 200K and 6K.**

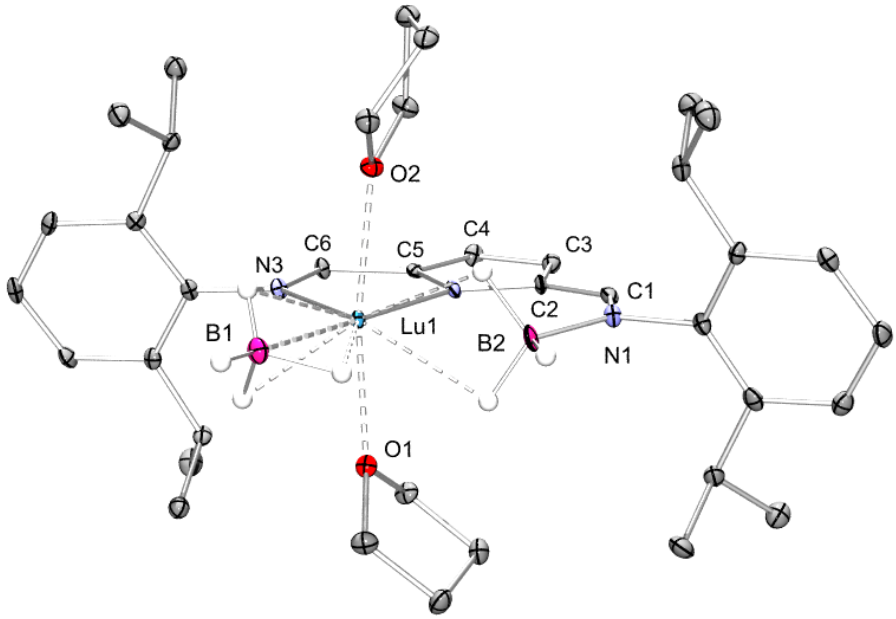


**Figure S3a:** ORTEP representation (ellipsoids at 50% probability level) and labelling scheme of the structural model of **3** at 6K.

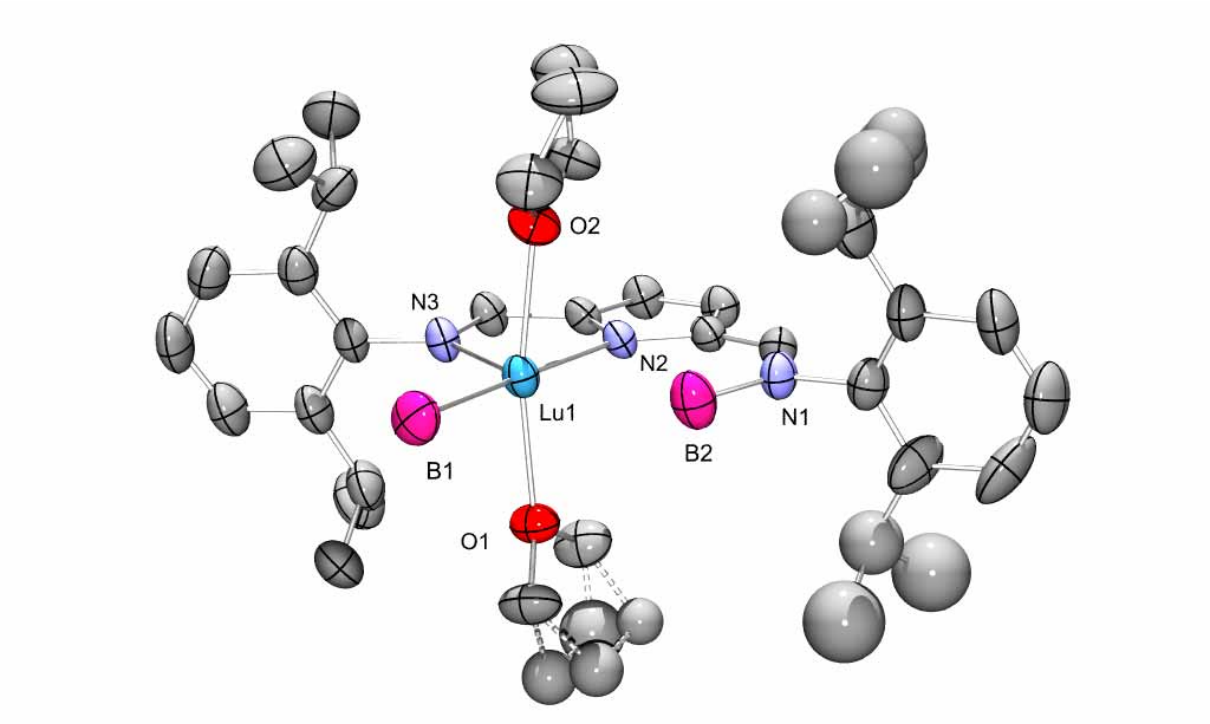


**Figure S3b:** ORTEP representation (ellipsoids at 50% probability level) and labelling scheme of the structural model of **3** at 200K.

The initial X-ray diffraction experiment on **3** was carried out at a temperature of 200K. The structural model obtained from this data set contains one disordered THF ligand at the Lu atom and the isopropyl-groups at one of the diisopropylphenyl ligands could only be refined employing an isotropical description of the atomic displacements. Moreover, all hydrogen atoms had to be placed in calculated positions.

To investigate the coordination geometry of the lutetium atom in greater detail we therefore repeated the diffraction experiment at low temperatures (6K), thus minimizing the effect of thermal smearing on the electron density distribution in the crystal. As can be seen by comparing Figs. S3a and S3b the disorder of the THF ligand could be overcome and is no longer significantly present. Hence, all atoms could be refined employing an anisotropic model describing the thermal motion. In addition, all hydrogen atoms could be located in the difference-Fourier map, including the hydrogen atoms at B1 and B2 in close proximity to the metal centre. This distinct improvement of the structural model of **3** demonstrates the advantages of low-temperature X-ray diffraction experiments compared to measurements performed at the temperatures accessible by standard open-flow nitrogen cooling devices even for “routine” structure determination purposes.

We note, however, that even at 6K the difference-Fourier map was not completely flat in the vicinity of the B2 atoms of the =N-BH3 moiety. Accordingly a fourth peaks was found at possible hydrogen atom positions in the vicinity of B2. Three of these peaks form a distorted tetrahedron around B2 and selecting these positions for the hydrogen atoms H1A, H1B and H1C results in a structural model which is stable in the lease-square refinements (see Fig. S3a). The spurious fourth residual density peak which we located in the Lu-B2-N1 plane is still present in this model. However, a circular search scanning the possible dihedral angles of the $BH_3$ group confirms that there are no further residual density peaks in the vicinity of atom B2 which would indicate an eclipsed position of the $BH_3$ group with respect to the N1-C1 bond of the ligand or a possible disorder of the group. Our final solid state model is therefore consistent with the NMR data of **3** in solution.

## S4: Experimental details

**X-ray data collection.** A yellow fragment of **3** with the dimensions 0.21 x 0.15 x 0.10 mm was glued to a Capton loop using perfluorinated polyether and mounted on a Huber 4-circle diffractometer equipped with a 4K-Displex closed-cycle helium cryostat. The sample was cooled with maximum cooling power to 6(2) K. Due to the usage of beryllium cooling shields the Bragg intensities of the sample were in part contaminated by parasitic X-ray scattering from small crystalline beryllium domains. To correct for these modulated powder diffraction rings in a systematic way one individual background image (with the crystal translated out of the X-ray beam) was recorded for each image. The controlled crystal translation was provided by employing a micro-stepper motor from AttocubeSystems. This setup allowed us to translate the sample within the closed sample chamber at a positioning accuracy of ±0.1 nm. During data reduction each image and its corresponding individual background image were subtracted to eliminate parasitic scattering from the beryllium domains (Fig. S4).

Preliminary examination and final data collection were carried out with graphite-monochromated Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) generated from a Bruker FR 591 rotating anode running at 50 kV and 60 mA. Intensity data were collected employing a MAR345 IP Detector and 1° $\varphi$-scans with a detector-to-sample distance of 200 mm. Two $\varphi$-scan sets (360 frames in total) at a detector off-set angle ($2\theta$) of 0.0 and +20.0° employing a scan time of 600 and 1500 seconds/frame, respectively, were collected.

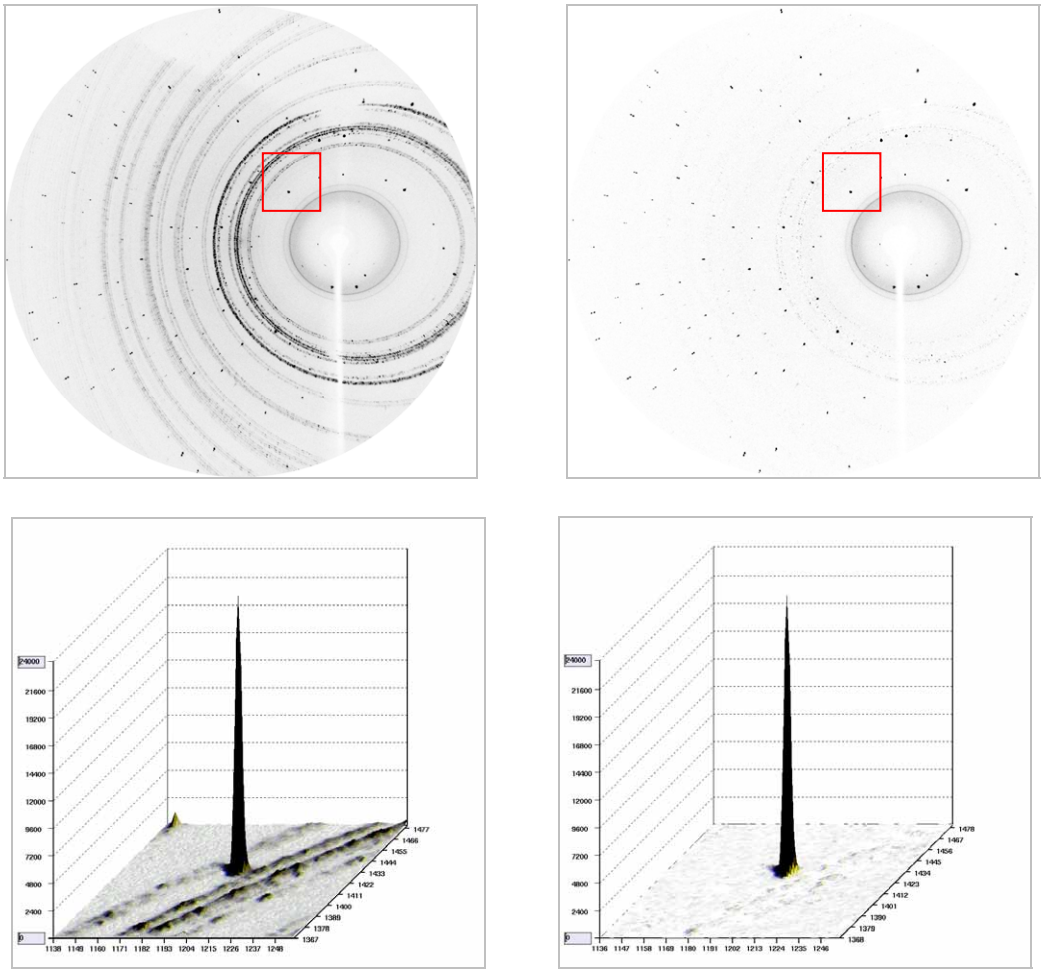

**Figure S4**: (top) Comparison of the background before (left) and after (right) the correction; (below) Relief map of the zoom region (marked by red lines).

**X-ray data reduction.** Crystal data for **3** at 6(2) K: $M_r$ = 933.70, $a$ = 9.5587(9) Å, $b$ = 15.1757(17) Å, $c$ = 16.1030(19) Å, $V$ = 2297.4(4) Å$^3$; monoclinic; space group *Pn*; $Z$ = 2; $F(000)$ = 976; $D_{calc}$ = 1.350 g/cm$^3$; $\mu$ = 2.192 mm$^{-1}$. An initial orientation matrix was determined from 10 frames of the first scan set and refined during the integration of the individual scan sets. Cell refinement and data reduction were performed with the EVAL-14[1] program package.

After integration the symmetry equivalent or multiple measured reflections were merged and a semi-empirical absorption correction was applied ($T_{min}$ = 0.688(4), $T_{max}$ = 0.814(4)) using the program "Sortav"[2]. After rejection of 4370 statistically discrepant reflections the internal

agreement factor was $R_{int}(F^2) = 0.0282$ for a total of 13834 reflections yielding 8265 unique reflections. The full data set provided a completeness of 77.9% in the date range from $3.03° < \theta < 30.23°$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-689232 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

**S5: Fractional atomic coordinates and mean-square atomic displacement parameter for the non-hydrogen atoms of compound 3 at 6K.**

| Atom | *x/a* | *y/b* | *z/c* | $U_{eq}$[1] |
|---|---|---|---|---|
| Lu1 | 0.26964(1) | 0.73646(1) | 0.19960(1) | 0.0068(1) |
| O1 | 0.0551(3) | 0.67712(19) | 0.12567(18) | 0.0110(7) |
| O2 | 0.4605(3) | 0.8118(2) | 0.28327(18) | 0.0115(8) |
| N1 | 0.0917(3) | 0.9669(2) | 0.1858(2) | 0.0101(8) |
| N2 | 0.1442(3) | 0.7948(2) | 0.2944(2) | 0.0083(8) |
| N3 | 0.2844(4) | 0.6368(2) | 0.2973(2) | 0.0084(8) |
| C1 | 0.0492(4) | 0.9470(3) | 0.2569(2) | 0.0104(10) |
| C2 | 0.0685(4) | 0.8710(2) | 0.3066(2) | 0.0097(10) |
| C3 | 0.0141(4) | 0.8619(3) | 0.3829(3) | 0.0109(10) |
| C4 | 0.0577(4) | 0.7803(3) | 0.4167(2) | 0.0109(10) |
| C5 | 0.1377(4) | 0.7412(2) | 0.3609(2) | 0.0082(9) |
| C6 | 0.2119(4) | 0.6540(2) | 0.3684(2) | 0.0092(9) |
| C7 | 0.0488(4) | 1.0530(2) | 0.1513(2) | 0.0091(9) |
| C8 | 0.1494(4) | 1.1217(3) | 0.1612(2) | 0.0098(10) |
| C9 | 0.1056(4) | 1.2046(3) | 0.1306(2) | 0.0120(10) |
| C10 | -0.0350(4) | 1.2213(3) | 0.0931(3) | 0.0139(10) |
| C11 | -0.1320(4) | 1.1521(3) | 0.0824(3) | 0.0133(10) |
| C12 | -0.0923(4) | 1.0670(3) | 0.1108(2) | 0.0120(10) |
| C13 | -0.1987(4) | 0.9922(3) | 0.0922(2) | 0.0122(10) |
| C14 | -0.3495(4) | 1.0192(3) | 0.1020(3) | 0.0162(11) |
| C15 | -0.1984(5) | 0.9573(3) | 0.0035(3) | 0.0165(11) |
| C16 | 0.3013(4) | 1.1066(3) | 0.2073(3) | 0.0118(13) |
| C17 | 0.4104(5) | 1.1676(3) | 0.1783(3) | 0.0174(11) |
| C18 | 0.3079(4) | 1.1174(3) | 0.3031(3) | 0.0151(11) |
| C19 | 0.3470(4) | 0.5509(2) | 0.3051(2) | 0.0089(10) |
| C20 | 0.4951(4) | 0.5392(3) | 0.3334(2) | 0.0097(10) |
| C21 | 0.5512(4) | 0.4540(3) | 0.3434(2) | 0.0113(10) |
| C22 | 0.4674(4) | 0.3803(3) | 0.3256(2) | 0.0123(10) |
| C23 | 0.3214(4) | 0.3914(3) | 0.2967(3) | 0.0118(10) |
| C24 | 0.2600(4) | 0.4747(3) | 0.2856(2) | 0.0095(10) |
| C25 | 0.1049(4) | 0.4825(3) | 0.2456(3) | 0.0108(10) |
| C26 | 0.0879(4) | 0.4619(3) | 0.1512(3) | 0.0124(10) |
| C27 | 0.0070(6) | 0.4231(4) | 0.2879(4) | 0.0171(16) |
| C28 | 0.5933(4) | 0.6171(2) | 0.3564(2) | 0.0100(10) |
| C29 | 0.7235(4) | 0.6143(3) | 0.3137(3) | 0.0146(11) |
| C30 | 0.6383(4) | 0.6235(3) | 0.4529(3) | 0.0146(11) |
| C31 | -0.0765(4) | 0.6745(3) | 0.1581(3) | 0.0121(10) |
| C32 | -0.1788(4) | 0.7299(3) | 0.0962(3) | 0.0143(10) |

| | | | | |
|---|---|---|---|---|
| C33 | -0.1364(4) | 0.7065(3) | 0.0110(3) | 0.0163(11) |
| C34 | 0.0156(4) | 0.6707(3) | 0.0346(3) | 0.0137(11) |
| C35 | 0.4601(4) | 0.8416(3) | 0.3694(3) | 0.0137(11) |
| C36 | 0.6004(4) | 0.8910(3) | 0.3957(3) | 0.0151(11) |
| C37 | 0.6253(4) | 0.9284(3) | 0.3123(3) | 0.0144(10) |
| C38 | 0.5793(4) | 0.8527(3) | 0.2520(3) | 0.0131(10) |
| B1 | 0.4093(5) | 0.6872(3) | 0.0920(3) | 0.0127(11) |
| B2 | 0.1746(5) | 0.9051(3) | 0.1341(3) | 0.0119(11) |
| O3 | 0.7278(3) | 0.4071(2) | 0.0847(2) | 0.0199(9) |
| C39 | 0.6325(4) | 0.3679(3) | 0.1333(3) | 0.0159(11) |
| C40 | 0.4853(6) | 0.4103(4) | 0.1041(4) | 0.0158(14) |
| C41 | 0.5026(4) | 0.4587(3) | 0.0231(3) | 0.0146(11) |
| C42 | 0.6592(4) | 0.4834(3) | 0.0432(3) | 0.0158(11) |
| O4 | 0.9459(3) | 0.0978(2) | 0.3727(2) | 0.0168(8) |
| C43 | 0.8580(5) | 0.1013(3) | 0.4352(3) | 0.0163(11) |
| C44 | 0.7344(4) | 0.1594(3) | 0.3972(3) | 0.0157(11) |
| C45 | 0.8036(5) | 0.2286(3) | 0.3483(3) | 0.0186(11) |
| C46 | 0.9490(5) | 0.1864(3) | 0.3420(3) | 0.0171(11) |

[1] $U_{eq}$ = 1/3 of the trace of the orthogonalized **U** Tensor.

Mean-square atomic displacement parameters [Å$^2$]

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Lu1 | 0.0075(1) | 0.0051(1) | 0.0082(1) | 0.0005(1) | 0.0023(1) | 0.0001(1) |
| O1 | 0.0102(12) | 0.0118(13) | 0.0119(13) | 0.0009(9) | 0.0043(10) | -0.0003(9) |
| O2 | 0.0119(13) | 0.0107(15) | 0.0116(13) | 0.0013(10) | 0.0016(10) | -0.0026(9) |
| N1 | 0.0105(14) | 0.0080(15) | 0.0124(15) | 0.0004(11) | 0.0038(12) | 0.0010(11) |
| N2 | 0.0087(13) | 0.0056(14) | 0.0109(14) | -0.0018(11) | 0.0023(11) | -0.0008(11) |
| N3 | 0.0103(14) | 0.0058(15) | 0.0099(14) | 0.0017(10) | 0.0039(12) | -0.0012(11) |
| C1 | 0.0092(16) | 0.0080(17) | 0.0136(17) | -0.0033(13) | 0.0012(13) | -0.0008(12) |
| C2 | 0.0087(16) | 0.0059(17) | 0.0143(17) | -0.0022(12) | 0.0017(13) | 0.0024(12) |
| C3 | 0.0092(16) | 0.0098(18) | 0.0139(17) | 0.0001(13) | 0.0025(13) | 0.0000(12) |
| C4 | 0.0120(16) | 0.0098(18) | 0.0118(16) | 0.0035(13) | 0.0045(13) | -0.0007(12) |
| C5 | 0.0077(15) | 0.0063(17) | 0.0101(15) | -0.0003(12) | 0.0000(12) | -0.0025(12) |
| C6 | 0.0124(16) | 0.0065(17) | 0.0095(16) | 0.0008(12) | 0.0041(13) | 0.0008(12) |
| C7 | 0.0100(16) | 0.0075(17) | 0.0109(16) | -0.0004(12) | 0.0049(13) | -0.0002(12) |
| C8 | 0.0109(18) | 0.0095(18) | 0.0091(16) | 0.0019(12) | 0.0023(14) | 0.0020(13) |
| C9 | 0.0145(17) | 0.0088(18) | 0.0132(17) | -0.0008(13) | 0.0042(14) | -0.0013(13) |
| C10 | 0.0196(18) | 0.0082(19) | 0.0134(17) | 0.0021(13) | 0.0020(14) | 0.0012(13) |
| C11 | 0.0137(17) | 0.0141(19) | 0.0118(17) | 0.0024(13) | 0.0013(14) | 0.0024(13) |
| C12 | 0.0168(18) | 0.0099(18) | 0.0101(16) | -0.0027(13) | 0.0043(14) | 0.0006(13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C13 | 0.0151(18) | 0.0111(19) | 0.0098(16) | -0.0003(13) | 0.0003(14) | 0.0013(13) |
| C14 | 0.0140(18) | 0.016(2) | 0.019(2) | 0.0034(15) | 0.0040(15) | -0.0008(14) |
| C15 | 0.021(2) | 0.012(2) | 0.0152(19) | -0.0037(14) | -0.0002(15) | -0.0025(14) |
| C16 | 0.013(3) | 0.0083(17) | 0.015(2) | 0.0004(14) | 0.005(2) | 0.0018(11) |
| C17 | 0.0164(19) | 0.014(2) | 0.023(2) | -0.0008(15) | 0.0068(16) | -0.0015(14) |
| C18 | 0.0132(18) | 0.016(2) | 0.0157(19) | -0.0007(14) | 0.0014(15) | 0.0003(14) |
| C19 | 0.0119(16) | 0.0077(18) | 0.0078(16) | 0.0008(12) | 0.0037(13) | 0.0003(12) |
| C20 | 0.0100(16) | 0.0106(18) | 0.0088(16) | 0.0007(12) | 0.0022(13) | 0.0001(12) |
| C21 | 0.0108(16) | 0.0122(19) | 0.0115(17) | 0.0010(13) | 0.0038(13) | 0.0049(13) |
| C22 | 0.0184(19) | 0.0077(18) | 0.0121(17) | 0.0002(12) | 0.0063(14) | 0.0036(13) |
| C23 | 0.0156(18) | 0.0061(18) | 0.0138(17) | -0.0009(13) | 0.0029(14) | -0.0012(13) |
| C24 | 0.0109(16) | 0.0104(18) | 0.0084(16) | 0.0000(12) | 0.0049(13) | 0.0014(12) |
| C25 | 0.0071(15) | 0.0088(18) | 0.0166(18) | 0.0004(13) | 0.0026(13) | -0.0014(12) |
| C26 | 0.0114(17) | 0.0121(19) | 0.0138(17) | 0.0001(13) | 0.0025(14) | 0.0005(13) |
| C27 | 0.015(3) | 0.015(2) | 0.023(3) | 0.0031(17) | 0.008(2) | -0.0008(19) |
| C28 | 0.0086(16) | 0.0093(18) | 0.0113(16) | 0.0018(12) | 0.0001(13) | 0.0012(12) |
| C29 | 0.0118(17) | 0.0129(19) | 0.0197(19) | -0.0019(14) | 0.0047(15) | -0.0005(13) |
| C30 | 0.0161(18) | 0.014(2) | 0.0140(18) | -0.0015(13) | 0.0032(15) | 0.0014(14) |
| C31 | 0.0083(16) | 0.0165(19) | 0.0125(17) | -0.0003(13) | 0.0045(13) | -0.0002(13) |
| C32 | 0.0154(17) | 0.0110(19) | 0.0169(18) | 0.0009(14) | 0.0044(14) | 0.0017(13) |
| C33 | 0.0168(18) | 0.018(2) | 0.0132(17) | 0.0023(14) | 0.0003(14) | 0.0055(15) |
| C34 | 0.0142(18) | 0.018(2) | 0.0095(17) | 0.0005(13) | 0.0037(14) | -0.0014(14) |
| C35 | 0.0146(18) | 0.016(2) | 0.0116(17) | -0.0024(13) | 0.0052(14) | -0.0033(14) |
| C36 | 0.0113(17) | 0.016(2) | 0.0179(19) | -0.0033(14) | 0.0022(15) | -0.0009(13) |
| C37 | 0.0095(16) | 0.0134(19) | 0.0201(19) | 0.0012(14) | 0.0025(14) | -0.0025(13) |
| C38 | 0.0127(17) | 0.0122(19) | 0.0151(18) | 0.0010(13) | 0.0044(14) | -0.0014(13) |
| B1 | 0.0132(19) | 0.012(2) | 0.014(2) | -0.0005(15) | 0.0056(16) | 0.0013(14) |
| B2 | 0.020(2) | 0.0042(19) | 0.0120(19) | 0.0014(14) | 0.0041(16) | 0.0023(14) |
| O3 | 0.0115(13) | 0.0304(18) | 0.0183(15) | 0.0055(12) | 0.0038(11) | 0.0035(11) |
| C39 | 0.0139(18) | 0.020(2) | 0.0139(18) | 0.0020(14) | 0.0030(14) | 0.0025(14) |
| C40 | 0.013(2) | 0.021(3) | 0.014(2) | 0.0032(17) | 0.0037(18) | 0.0020(19) |
| C41 | 0.0159(18) | 0.0129(19) | 0.0139(18) | 0.0004(13) | 0.0000(14) | 0.0019(14) |
| C42 | 0.0129(18) | 0.015(2) | 0.020(2) | -0.0019(14) | 0.0040(15) | -0.0003(14) |
| O4 | 0.0183(14) | 0.0145(15) | 0.0192(15) | -0.0006(11) | 0.0075(12) | 0.0026(11) |
| C43 | 0.0164(18) | 0.015(2) | 0.0186(19) | -0.0011(14) | 0.0060(15) | 0.0000(14) |
| C44 | 0.0129(18) | 0.017(2) | 0.0181(19) | 0.0017(14) | 0.0049(15) | 0.0027(14) |
| C45 | 0.0171(18) | 0.014(2) | 0.025(2) | 0.0048(15) | 0.0045(16) | 0.0030(14) |
| C46 | 0.0177(19) | 0.011(2) | 0.024(2) | 0.0036(15) | 0.0077(16) | 0.0020(14) |

**S6: Bond distances and angles of compound 3 at 6K.**

Bond distances [Å]

| atom1 | atom2 | distance |
|---|---|---|
| Lu1 | O1 | 2.356(3) |
| Lu1 | O2 | 2.358(3) |
| Lu1 | N2 | 2.284(3) |
| Lu1 | N3 | 2.168(3) |
| Lu1 | B1 | 2.486(5) |
| Lu1 | B2 | 2.853(5) |
| Lu1 | H1B | 2.24(6) |
| O1 | C34 | 1.450(6) |
| O1 | C31 | 1.447(5) |
| O2 | C38 | 1.461(5) |
| O2 | C35 | 1.460(6) |
| O3 | C39 | 1.433(5) |
| O3 | C42 | 1.435(5) |
| O4 | C46 | 1.435(6) |
| O4 | C43 | 1.424(6) |
| N1 | C7 | 1.450(4) |
| N1 | C1 | 1.317(5) |
| N1 | B2 | 1.562(6) |
| N2 | C2 | 1.397(4) |
| N2 | C5 | 1.355(4) |
| N3 | C19 | 1.430(5) |
| N3 | C6 | 1.465(5) |
| C1 | C2 | 1.397(5) |
| C2 | C3 | 1.425(6) |
| C3 | C4 | 1.386(6) |
| C4 | C5 | 1.412(5) |
| C5 | C6 | 1.496(5) |
| C7 | C12 | 1.404(5) |
| C7 | C8 | 1.408(5) |
| C8 | C9 | 1.388(6) |
| C8 | C16 | 1.524(6) |
| C9 | C10 | 1.393(6) |
| C10 | C11 | 1.391(6) |
| C11 | C12 | 1.399(6) |
| C12 | C13 | 1.517(6) |
| C13 | C14 | 1.534(6) |
| C13 | C15 | 1.524(6) |
| C16 | C18 | 1.541(7) |
| C16 | C17 | 1.529(6) |

| | | |
|---|---|---|
| C19 | C24 | 1.426(5) |
| C19 | C20 | 1.418(5) |
| C20 | C21 | 1.398(6) |
| C20 | C28 | 1.513(5) |
| C21 | C22 | 1.375(6) |
| C22 | C23 | 1.399(6) |
| C23 | C24 | 1.392(6) |
| C24 | C25 | 1.510(6) |
| C25 | C26 | 1.532(7) |
| C25 | C27 | 1.544(7) |
| C28 | C29 | 1.527(6) |
| C28 | C30 | 1.539(6) |
| C31 | C32 | 1.518(6) |
| C32 | C33 | 1.541(7) |
| C33 | C34 | 1.533(6) |
| C35 | C36 | 1.528(6) |
| C36 | C37 | 1.516(7) |
| C37 | C38 | 1.517(7) |
| C39 | C40 | 1.541(7) |
| C40 | C41 | 1.532(8) |
| C41 | C42 | 1.520(6) |
| C43 | C44 | 1.512(6) |
| C44 | C45 | 1.533(6) |
| C45 | C46 | 1.550(7) |
| B1 | H1D | 0.98(7) |
| B1 | H1C | 1.21(7) |
| B1 | H1A | 1.03(7) |
| B1 | H1B | 1.28(6) |
| B2 | H2B | 1.18(7) |
| B2 | H2C | 1.24(7) |
| B2 | H2A | 1.01(6) |

Selected bond angles [deg]

| atom1 | atom2 | atom3 | angle |
|---|---|---|---|
| O1 | Lu1 | O2 | 170.65(10) |
| O1 | Lu1 | N2 | 88.38(10) |
| O1 | Lu1 | N3 | 92.09(12) |
| O1 | Lu1 | B1 | 93.50(13) |
| O1 | Lu1 | B2 | 88.06(12) |
| O2 | Lu1 | N2 | 82.85(10) |
| O2 | Lu1 | N3 | 88.94(12) |
| O2 | Lu1 | B1 | 94.96(13) |
| O2 | Lu1 | B2 | 86.45(12) |
| N2 | Lu1 | N3 | 76.03(12) |
| N2 | Lu1 | B1 | 174.67(13) |
| N2 | Lu1 | B2 | 74.26(12) |
| N3 | Lu1 | B1 | 108.86(14) |
| N3 | Lu1 | B2 | 150.27(13) |
| B1 | Lu1 | B2 | 100.79(14) |
| O1 | Lu1 | H1B | 85.1(17) |
| O2 | Lu1 | H1B | 100.2(17) |
| N2 | Lu1 | H1B | 144.8(16) |
| N3 | Lu1 | H1B | 138.7(16) |
| B1 | Lu1 | H1B | 30.8(16) |
| B2 | Lu1 | H1B | 71.0(16) |
| C31 | O1 | C34 | 106.2(3) |
| Lu1 | O1 | C31 | 124.2(2) |
| Lu1 | O1 | C34 | 125.5(2) |
| C35 | O2 | C38 | 109.4(3) |
| Lu1 | O2 | C35 | 124.0(2) |
| Lu1 | O2 | C38 | 125.3(2) |
| C39 | O3 | C42 | 107.9(3) |
| C43 | O4 | C46 | 105.1(3) |
| C1 | N1 | C7 | 115.4(3) |
| C1 | N1 | B2 | 126.3(3) |
| C7 | N1 | B2 | 118.2(3) |
| Lu1 | N2 | C2 | 139.7(2) |
| C2 | N2 | C5 | 106.7(3) |
| Lu1 | N2 | C5 | 113.6(2) |
| Lu1 | N3 | C6 | 117.7(2) |
| C6 | N3 | C19 | 110.1(3) |
| Lu1 | N3 | C19 | 132.1(2) |
| N1 | C1 | C2 | 131.1(4) |
| N2 | C2 | C1 | 128.4(3) |
| C1 | C2 | C3 | 122.9(3) |
| N2 | C2 | C3 | 108.7(3) |
| C2 | C3 | C4 | 107.1(3) |

| | | | |
|---|---|---|---|
| C3 | C4 | C5 | 106.5(3) |
| N2 | C5 | C4 | 111.0(3) |
| C4 | C5 | C6 | 128.6(3) |
| N2 | C5 | C6 | 120.4(3) |
| N3 | C6 | C5 | 112.3(3) |
| N1 | C7 | C8 | 119.0(3) |
| N1 | C7 | C12 | 119.7(3) |
| C8 | C7 | C12 | 121.3(3) |
| C9 | C8 | C16 | 120.6(4) |
| C7 | C8 | C16 | 121.0(4) |
| C7 | C8 | C9 | 118.4(3) |
| C8 | C9 | C10 | 121.6(4) |
| C9 | C10 | C11 | 119.0(4) |
| C10 | C11 | C12 | 121.4(4) |
| C7 | C12 | C11 | 118.2(4) |
| C11 | C12 | C13 | 119.6(3) |
| C7 | C12 | C13 | 122.1(4) |
| C12 | C13 | C14 | 112.9(4) |
| C12 | C13 | C15 | 109.3(3) |
| C14 | C13 | C15 | 110.5(3) |
| C8 | C16 | C18 | 109.5(3) |
| C8 | C16 | C17 | 113.7(4) |
| C17 | C16 | C18 | 109.5(4) |
| N3 | C19 | C24 | 120.1(3) |
| N3 | C19 | C20 | 121.3(3) |
| C20 | C19 | C24 | 118.6(3) |
| C19 | C20 | C28 | 121.3(4) |
| C21 | C20 | C28 | 119.1(3) |
| C19 | C20 | C21 | 119.5(4) |
| C20 | C21 | C22 | 122.1(4) |
| C21 | C22 | C23 | 118.7(4) |
| C22 | C23 | C24 | 121.6(4) |
| C19 | C24 | C23 | 119.5(3) |
| C23 | C24 | C25 | 119.0(4) |
| C19 | C24 | C25 | 121.3(4) |
| C26 | C25 | C27 | 110.8(4) |
| C24 | C25 | C27 | 113.1(4) |
| C24 | C25 | C26 | 109.1(3) |
| C20 | C28 | C29 | 112.8(3) |
| C20 | C28 | C30 | 110.1(3) |
| C29 | C28 | C30 | 110.8(3) |
| O1 | C31 | C32 | 104.3(3) |
| C31 | C32 | C33 | 102.4(3) |
| C32 | C33 | C34 | 104.5(4) |
| O1 | C34 | C33 | 106.8(3) |
| O2 | C35 | C36 | 105.2(3) |
| C35 | C36 | C37 | 102.1(4) |

| | | | |
|---|---|---|---|
| C36 | C37 | C38 | 102.1(4) |
| O2 | C38 | C37 | 104.7(3) |
| O3 | C39 | C40 | 107.2(4) |
| C39 | C40 | C41 | 103.1(4) |
| C40 | C41 | C42 | 101.0(4) |
| O3 | C42 | C41 | 104.5(3) |
| O4 | C43 | C44 | 104.7(4) |
| C43 | C44 | C45 | 103.3(3) |
| C44 | C45 | C46 | 103.1(4) |
| O4 | C46 | C45 | 106.9(4) |
| Lu1 | B2 | N1 | 120.0(3) |
| Lu1 | B1 | H1B | 64(3) |
| Lu1 | B1 | H1A | 173(3) |
| H1A | B1 | H1D | 110(5) |
| H1B | B1 | H1C | 98(5) |
| H1B | B1 | H1D | 116(5) |
| H1C | B1 | H1D | 105(5) |
| Lu1 | B1 | H1D | 71(4) |
| H1A | B1 | H1B | 111(5) |
| Lu1 | B1 | H1C | 68(3) |
| H1A | B1 | H1C | 118(5) |
| Lu1 | B2 | H2A | 125(4) |
| Lu1 | B2 | H2B | 59(3) |
| H2A | B2 | H2B | 98(5) |
| H2A | B2 | H2C | 102(5) |
| H2B | B2 | H2C | 111(5) |
| Lu1 | B2 | H2C | 55(3) |
| N1 | B2 | H2A | 115(4) |
| N1 | B2 | H2B | 117(3) |
| N1 | B2 | H2C | 112(3) |

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