Supporting Information

Isolation and Properties of the Long Elusive Deep Blue Soluble [K₃{(N'Bu)₃S}₂]• Cage Radical

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S1. Synthesis and characterization

S1.1 Generalities

All reactions were carried out with strict exclusion of air and moisture under inert atmosphere, either with Schlenk techniques or in an Argon glovebox. Highly pure potassium metal was purchased from Sigma-Aldrich and used as received. I, II and 1_Li were synthesized as previously reported\[^{[S1]}\]. All solvents were dried and distilled from Na, K or Na/K prior to use. Elemental analyses were performed on a Vario EL3 at the Mikroanalytische Labor, Institut für Anorganische Chemie, University of Göttingen.

**Synthesis of 1_K:** In an argon glovebox, II (2eq, 300mg, 1.2mmol) and potassium metal (3eq, 72mg, 1.8 mmol) were reacted in 2-3 mL toluene. Upon heavy stirring for one hour while the mixture turned troubled and light blue, the potassium was tritutated in order to dissolve the blue product forming on its surface. The solution then turned deep blue, was filtered and the solvent removed in vacuo. Crystals were grown from a highly concentrated toluene solution at -35°C. Crystalline yield: 35%. Attempts to improve the yield by stirring longer after trituration resulted in solution color loss after a few minutes. Anal. Calc. for C\textsubscript{48}H\textsubscript{108}K\textsubscript{3}N\textsubscript{12}S\textsubscript{4} (the best fit was found for one radical molecule and two II molecules): M = 1097.66 g/mol. C, 52.46; H, 9.91; N, 15.29; S, 11.67. Found: C, 53.05; H, 9.65; N, 14.98; S, 11.97.vis (toluene): \(\lambda_{\text{max}} = 635\) nm (broad).

S1.2 Vis spectroscopy

Vis spectra were recorded on an Agilent Cary 60 or an Agilent Cary 50 spectrometer using quartz cuvettes fitted with Young-type Teflon-valves. IR data were measured on neat samples with a Bruker ALPHA FT-IR spectrometer with Platinum ATR module and visualized with the Opus/Origin programs. \(10^{-4}\)M toluene solutions of 1_K (blue) and I (colorless) were freshly prepared inside of an argon glove box and measured ASAP on the instrument. For I, a first spectrum was recorded prior to O\textsubscript{2} exposure. Upon removal of the sealing cap, the absorption spectra were recorded in 0.1 min steps, while stirring to ensure homogeneity and O\textsubscript{2} diffusion into the solution, until the transient product 1_Li entirely decomposed.
S2. X-ray measurements

The datasets were collected on an Incoatec Mo Microsource\textsuperscript{[S2]} with mirror optics and an APEX II detector with a D8 goniometer. The data were integrated with SAINT.\textsuperscript{[S3]} A multi-scan absorption correction was applied using SADABS\textsuperscript{[S4]} or TWINABS\textsuperscript{[S5]}. The structures were solved by SHELXT\textsuperscript{[S6]} and refined on \(F^2\) using SHELXL\textsuperscript{[S7]} in the graphical user interface ShelXle.\textsuperscript{[S8]} For the refinement of disordered moieties, distance restraints and restraints for the anisotropic displacement parameters were used.\textsuperscript{[S9]}

The crystals of 1_K are extremely sensitive and difficult to handle. Data sets were collected on two crystals. The first dataset was measured at 100 K. The structure crystallizes in space group \(P2_1/c\) with two molecules in the asymmetric unit. A small amount of non-merohedral twinning could be detected, but the twin integration does not improve the model. In both molecule three of the six t-butyl groups are disordered. Both molecules have very similar geometry and both show the described difference in the two caps: The S-N bond lengths are identical within 3 \(\sigma\) for cap B, while in cap A, two S-N bond lengths are shorter while the third one is similar to the S-N lengths of cap B.

In the endeavour to improve the structure quality data of a second crystalline sample were collected at 120 K. Here the cell volume is halved and, in the space group \(P2_1/n\), only one molecule is present in the asymmetric unit. However, the two cells are related. The smaller cell corresponds to the primitive cell which can be derived from the larger one, as a B centred cell. No intermediate reflections violating the B centring could be found. Additionally, also in this data set a small amount of twinning could be detected, but the twin integration does not lead to an improvement of the model. Now all t-butyl groups are disordered. The ADPs of the nitrogen atoms are elongated but the atoms are not included in the disorder, which could have a small influence on the S-N bond lengths. Now the differences between cap A and B are even more pronounced. In cap A the two smaller bond lengths are even smaller and the longer one is significantly longer than the S-N bond lengths of cap B.

Afterwards we performed refinements against the 120K data in the larger cell and against the 100 K data in the smaller cell. For both data sets the new refinements showed the same behaviour of the S-N bond lengths as before but the quality of the models decreases (see Table S2.1).

The difference between the two data sets could be either explained by the different temperature or a different polymorph. In both crystals the t-butyl groups are strongly vibrating and are also statistically disordered, with a lower temperature two positions for some of them could be frozen, which could result in the intermediate reflections. However, no intermediate reflection could be found in a matrix scan at 100 K for the second crystal.
Table S2.1 Comparison of the different refinements (in bold final models)

| Data set | **120K small cell** | **100 K small cell** | **120 K large cell** | **100 K large cell** |
|----------|---------------------|----------------------|----------------------|----------------------|
| a [Å]    | 12.622(2)           | 12.549(2)            | 23.752(3)            | 23.665(3)            |
| b [Å]    | 15.913(3)           | 16.005(3)            | 15.913(2)            | 16.005(2)            |
| c [Å]    | 17.579(3)           | 17.530(3)            | 19.299(3)            | 19.223(3)            |
| β [V]    | 102.48(2)           | 102.50(2)            | 109.05(2)            | 109.23(2)            |
| V [Å³]   | 3447.4(11)          | 3437.4(11)           | 6897.9(18)           | 6874.3(18)           |
| S-N cap A | S1-N1 1.608(3) | S(1)-N(2) 1.608(5)  | S(2)-N(5) 1.594(4)  | S(2)-N(5) 1.617(3)  |
|          | S1-N2 1.610(3)     | S(1)-N(1) 1.624(5)  | S(2)-N(6) 1.615(3)  | S(2)-N(6) 1.623(3)  |
|          | S1-N3 1.676(3)     | S(1)-N(3) 1.630(5)  | S(2)-N(4) 1.674(4)  | S(2)-N(4) 1.647(3)  |
|          | S(2)-N(5) 1.642(3) | S(2)-N(5) 1.640(5)  | S(2)-N(10) 1.639(4) | S(2)-N(10) 1.648(3) |
|          | S(2)-N(4) 1.643(3) | S(2)-N(6) 1.649(5)  | S(1)-N(3) 1.639(4)  | S(1)-N(1) 1.649(3)  |
|          | S(2)-N(6) 1.647(3) | S(2)-N(4) 1.655(6)  | S(1)-N(2) 1.648(3)  | S(1)-N(2) 1.652(3)  |
| S-N cap B | S(2)-N(5) 1.642(3) | S(2)-N(5) 1.640(5)  | S(4)-N(10) 1.639(4) | S(4)-N(10) 1.645(3) |
|          | S(2)-N(4) 1.643(3) | S(2)-N(6) 1.649(5)  | S(4)-N(12) 1.642(4) | S(4)-N(11) 1.648(3) |
|          | S(2)-N(6) 1.647(3) | S(2)-N(4) 1.655(6)  | S(4)-N(11) 1.642(3) | S(4)-N(12) 1.656(3) |
| Compound | 1 K @120K | 1 K @100K |
|----------|-----------|-----------|
| Formula  | C_{24}H_{54}K_{3}N_{6}S_{2} | C_{24}H_{54}K_{3}N_{6}S_{2} |
| Mol. w., g mol\(^{-1}\) | 608.15 | 608.15 |
| CCDC n°. | 2117636 | 2117635 |
| Wavelength, Å | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2\(_1\)/n | P2\(_1\)/c |
| a, Å | 12.622(2) | 23.664(3) |
| b, Å | 15.913(3) | 16.005(2) |
| c, Å | 17.579(3) | 19.223(3) |
| β, ° | 102.48(2) | 109.23(2) |
| V, Å\(^3\) | 3447.4(11) | 6874.3(18) |
| Z | 4 | 8 |
| Density, Mg/m\(^3\) | 1.172 | 1.175 |
| Absorption coefficient, mm\(^{-1}\) | 0.539 | 0.540 |
| Crystal size, mm | 0.201 x 0.123 x 0.094 | 0.500 x 0.367 x 0.184 |
| Crystal shape and color | Deep dark blue blocks | Deep dark blue blocks |
| Theta range, ° | 1.745 to 25.981 | 0.912 to 28.292 |
| Refl. measured | 79811 | 104942 |
| Refl. unique | 6757 | 17069 |
| R\(_{int}\) | 0.0756 | 0.0615 |
| Data/ restr./para. | 6757 / 2591 / 394 | 17069 / 6621 / 853 |
| \(R_1\) [\(I>2\sigma(I)\)] | 0.0545 | 0.0646 |
| \(wR_2\) (all refl.) | 0.1381 | 0.1730 |
| \(Δρ_{fin},\) eÅ\(^{-3}\) | 0.637 / -0.725 | 1.667 / -0.959 |
S2.1 Crystal structure of 1_K @ 120 K

Figure S2.1 Asymmetric unit of 1_K at 120 K. The thermal ellipsoids are represented at 50% probability level. The disordered groups and the hydrogen atoms are omitted for clarity.
Figure S2.2. Asymmetric unit of 1_K at 120 K. The thermal ellipsoids are represented at 50% probability level and the disordered groups are depicted. The hydrogen atoms are omitted for clarity.

All ‘Bu groups are disordered. The occupancies of the minor components refine to 0.318(4) (C1A – C4A), 0.273(5) (C5A – C8A), 0.280(6) (C9a – C12A), 0.214(5) (C13A – C16A) 0.405(6) (C17 – C20), and 0.458(10) (C21 – C24), respectively.

Table S2.3: Bond lengths and angles for 1_K @120K

| Bond (Å)                                                                 | Value      |
|--------------------------------------------------------------------------|------------|
| K(1)-N(6)                                                                | 2.664(3)   |
| K(1)-N(2)                                                                | 2.834(3)   |
| K(1)-N(5)                                                                | 2.836(3)   |
| K(1)-N(1)                                                                | 2.897(3)   |
| K(1)-C(20A)#1                                                           | 3.185(10)  |
| K(1)-C(20)                                                               | 3.278(15)  |
| K(1)-S(2)                                                                | 3.4200(12) |
| K(1)-C(17A)                                                              | 3.470(7)   |
| K(1)-S(1)                                                                | 3.5442(12) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|----------------------|--------------|
| K(2)-K(3)            | 3.8169(14)   | C(17)-C(20)          | 1.522(11)    | K(2)-K(3)            | 3.8169(14)   |
| K(3)-N(4)            | 2.616(3)     | C(17)-C(18)          | 1.524(10)    | K(3)-N(4)            | 2.616(3)     |
| K(3)-N(6)            | 2.836(3)     | N(6)-C(21A)          | 1.474(9)     | K(3)-N(6)            | 2.836(3)     |
| K(3)-N(2)            | 2.863(3)     | N(6)-C(21)           | 1.494(10)    | K(3)-N(2)            | 2.863(3)     |
| K(3)-N(3)            | 3.022(3)     | C(21)-C(22)          | 1.527(11)    | K(3)-N(3)            | 3.022(3)     |
| K(3)-C(15A)#2        | 3.221(16)    | C(21)-C(24)          | 1.529(11)    | K(3)-C(15A)#2        | 3.221(16)    |
| K(3)-S(2)            | 3.3877(12)   | C(21)-C(23)          | 1.535(11)    | K(3)-S(2)            | 3.3877(12)   |
| K(3)-C(8A)           | 3.524(18)    | C(1A)-C(3A)          | 1.522(12)    | K(3)-C(8A)           | 3.524(18)    |
| K(3)-S(1)            | 3.6929(13)   | C(1A)-C(4A)          | 1.539(12)    | K(3)-S(1)            | 3.6929(13)   |
| S(1)-N(1)            | 1.608(3)     | C(1A)-C(2A)          | 1.563(12)    | S(1)-N(1)            | 1.608(3)     |
| S(1)-N(2)            | 1.610(3)     | C(5A)-C(8A)          | 1.516(13)    | S(1)-N(2)            | 1.610(3)     |
| S(1)-N(3)            | 1.676(3)     | C(5A)-C(7A)          | 1.521(13)    | S(1)-N(3)            | 1.676(3)     |
| N(1)-C(1)            | 1.477(7)     | C(5A)-C(6A)          | 1.526(13)    | N(1)-C(1)            | 1.477(7)     |
| N(1)-C(1A)           | 1.521(12)    | C(9A)-C(11A)         | 1.502(12)    | N(1)-C(1A)           | 1.521(12)    |
| C(1)-C(4)            | 1.508(8)     | C(9A)-C(10A)         | 1.516(13)    | C(1)-C(4)            | 1.508(8)     |
| C(1)-C(3)            | 1.513(8)     | C(9A)-C(12A)         | 1.520(12)    | C(1)-C(3)            | 1.513(8)     |
| C(1)-C(2)            | 1.518(8)     | C(13A)-C(14A)        | 1.519(13)    | C(1)-C(2)            | 1.518(8)     |
| N(2)-C(5A)           | 1.486(13)    | C(13A)-C(15A)        | 1.520(13)    | N(2)-C(5A)           | 1.486(13)    |
| N(2)-C(5)            | 1.487(6)     | C(13A)-C(16A)        | 1.535(13)    | N(2)-C(5)            | 1.487(6)     |
| C(5)-C(8)            | 1.519(8)     | C(17A)-C(20A)        | 1.516(9)     | C(5)-C(8)            | 1.519(8)     |
| C(5)-C(7)            | 1.520(8)     | C(17A)-C(18A)        | 1.533(8)     | C(5)-C(7)            | 1.520(8)     |
| C(5)-C(6)            | 1.527(7)     | C(17A)-C(19A)        | 1.542(8)     | C(5)-C(6)            | 1.527(7)     |
| N(3)-C(9A)           | 1.462(13)    | C(21A)-C(22A)        | 1.520(10)    | N(3)-C(9A)           | 1.462(13)    |
| N(3)-C(9)            | 1.498(7)     | C(21A)-C(24A)        | 1.522(10)    | N(3)-C(9)            | 1.498(7)     |
| C(9)-C(11)           | 1.521(8)     | C(21A)-C(23A)        | 1.523(10)    | C(9)-C(11)           | 1.521(8)     |
| C(9)-C(12)           | 1.530(7)     |                       |              | C(9)-C(12)           | 1.530(7)     |
| C(9)-C(10)           | 1.549(7)     | N(6)-K(1)-N(2)       | 99.01(9)     | C(9)-C(10)           | 1.549(7)     |
| S(2)-N(5)            | 1.642(3)     | N(6)-K(1)-N(5)       | 55.87(8)     | S(2)-N(5)            | 1.642(3)     |
| S(2)-N(4)            | 1.643(3)     | N(2)-K(1)-N(5)       | 117.96(8)    | S(2)-N(4)            | 1.643(3)     |
| S(2)-N(6)            | 1.647(3)     | N(6)-K(1)-N(1)       | 122.39(9)    | S(2)-N(6)            | 1.647(3)     |
| N(4)-C(13)           | 1.486(5)     | N(2)-K(1)-N(1)       | 52.84(8)     | N(4)-C(13)           | 1.486(5)     |
| N(4)-C(13A)          | 1.508(13)    | N(5)-K(1)-N(1)       | 91.16(9)     | N(4)-C(13A)          | 1.508(13)    |
| C(13)-C(15)          | 1.521(7)     | N(6)-K(1)-C(20A)#1   | 105.4(4)     | C(13)-C(15)          | 1.521(7)     |
| C(13)-C(16)          | 1.535(7)     | N(2)-K(1)-C(20A)#1   | 113.5(4)     | C(13)-C(16)          | 1.535(7)     |
| C(13)-C(14)          | 1.536(7)     | N(5)-K(1)-C(20A)#1   | 127.1(4)     | C(13)-C(14)          | 1.536(7)     |
| N(5)-C(17A)          | 1.483(7)     | N(1)-K(1)-C(20A)#1   | 131.0(4)     | N(5)-C(17A)          | 1.483(7)     |
| N(5)-C(17)           | 1.510(10)    | N(6)-K(1)-C(20)#1    | 109.3(6)     | N(5)-C(17)           | 1.510(10)    |
| C(17)-C(19)          | 1.521(11)    | N(2)-K(1)-C(20)#1    | 112.3(6)     | C(17)-C(19)          | 1.521(11)    |
N(5)-K(1)-C(20)#1 129.1(5)  C(17A)-K(1)-K(2)  62.75(14)
N(1)-K(1)-C(20)#1 127.2(5)  C(1)-K(1)-K(2)  60.37(2)
N(6)-K(1)-S(2) 28.05(5)  K(3)-K(1)-K(2)  62.40(2)
N(2)-K(1)-S(2) 106.28(6)  N(6)-K(1)-K(1)#1 85.97(7)
N(5)-K(1)-S(2) 28.53(6)  N(2)-K(1)-K(1)#1 155.34(6)
N(1)-K(1)-S(2) 104.65(7)  N(5)-K(1)-K(1)#1 84.88(6)
C(20A)#1-K(1)-S(2) 123.6(4)  N(1)-K(1)-K(1)#1 141.96(7)
C(20)#1-K(1)-S(2) 127.1(5)  C(20)#1-K(1)-K(1)#1 44.2(5)
N(6)-K(1)-C(17A) 69.40(14)  S(2)-K(1)-K(1)#1 89.48(3)
N(2)-K(1)-C(17A) 140.83(15)  S(1)-K(1)-K(1)#1 162.50(3)
N(5)-K(1)-C(17A) 24.69(14)  K(3)-K(1)-K(1)#1 135.52(3)
N(1)-K(1)-C(17A) 100.67(16)  K(2)-K(1)-K(1)#1 125.97(3)
C(20A)#1-K(1)-C(17A) 105.6(4)  N(5)-K(2)-N(4) 56.20(9)
S(2)-K(1)-C(17A) 47.29(12)  N(5)-K(2)-N(1) 97.59(10)
N(6)-K(1)-S(1) 111.53(7)  N(4)-K(2)-N(1) 116.76(9)
N(2)-K(1)-S(1) 26.35(6)  N(5)-K(2)-N(3) 121.00(8)
N(5)-K(1)-S(1) 104.79(6)  N(4)-K(2)-N(3) 91.44(9)
N(1)-K(1)-S(1) 26.55(6)  N(1)-K(2)-N(3) 51.09(9)
C(20A)#1-K(1)-S(1) 127.3(4)  N(5)-K(2)-S(2) 27.85(6)
C(20)#1-K(1)-S(1) 124.5(5)  N(4)-K(2)-S(2) 28.57(6)
S(2)-K(1)-S(1) 106.03(3)  N(1)-K(2)-S(2) 106.70(7)
C(17A)-K(1)-S(1) 121.69(15)  N(3)-K(2)-S(2) 105.82(7)
N(6)-K(1)-K(3) 50.43(6)  N(5)-K(2)-S(1) 106.73(7)
N(2)-K(1)-K(3) 50.47(6)  N(4)-K(2)-S(1) 102.20(6)
N(5)-K(1)-K(3) 77.66(6)  N(1)-K(2)-S(1) 24.72(7)
N(1)-K(1)-K(3) 79.57(7)  N(3)-K(2)-S(1) 27.02(6)
C(20A)#1-K(1)-K(3) 132.1(4)  S(2)-K(2)-S(1) 103.85(3)
C(20)#1-K(1)-K(3) 134.4(6)  N(5)-K(2)-K(1) 49.59(6)
S(2)-K(1)-K(3) 57.13(2)  N(4)-K(2)-K(1) 75.87(6)
C(17A)-K(1)-K(3) 101.78(13)  N(1)-K(2)-K(1) 50.39(7)
S(1)-K(1)-K(3) 61.72(3)  N(3)-K(2)-K(1) 77.37(6)
N(6)-K(1)-K(2) 80.35(6)  S(2)-K(2)-K(1) 57.17(2)
N(2)-K(1)-K(2) 78.68(6)  S(1)-K(2)-K(1) 57.50(2)
N(5)-K(1)-K(2) 44.76(6)  N(5)-K(2)-K(3) 77.04(6)
N(1)-K(1)-K(2) 48.52(6)  N(4)-K(2)-K(3) 43.27(6)
C(20A)#1-K(1)-K(2) 164.8(4)  N(1)-K(2)-K(3) 77.65(6)
C(20)#1-K(1)-K(2) 163.2(6)  N(3)-K(2)-K(3) 50.86(7)
S(2)-K(1)-K(2) 56.96(2)  S(2)-K(2)-K(3) 55.55(3)
| Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|
| S(1)-K(2)-K(3) | 59.21(3)   | N(4)-K(3)-K(2) | 47.32(7)   |
| K(1)-K(2)-K(3) | 58.00(2)   | N(6)-K(3)-K(2) | 76.56(5)   |
| N(4)-K(3)-N(6) | 56.91(9)   | N(2)-K(3)-K(2) | 76.59(6)   |
| N(4)-K(3)-N(2) | 119.43(8)  | N(3)-K(3)-K(2) | 50.72(7)   |
| N(6)-K(3)-N(2) | 94.43(8)   | C(15A)#2-K(3)-K(2) | 133.1(4) |
| N(4)-K(3)-N(3) | 95.14(10)  | S(2)-K(3)-K(2) | 56.15(2)   |
| N(6)-K(3)-N(3) | 119.03(9)  | C(8A)-K(3)-K(2) | 115.7(3)   |
| N(2)-K(3)-N(3) | 50.28(8)   | K(1)-K(3)-K(2) | 59.597(19) |
| N(4)-K(3)-C(15A)#2 | 108.1(3) | S(1)-K(3)-K(2) | 58.18(2)   |
| N(6)-K(3)-C(15A)#2 | 128.4(4) | N(1)-S(1)-N(2) | 104.86(16) |
| N(2)-K(3)-C(15A)#2 | 128.9(4) | N(1)-S(1)-N(3) | 100.28(18) |
| N(3)-K(3)-C(15A)#2 | 110.9(4) | N(2)-S(1)-N(3) | 99.27(16)  |
| N(4)-K(3)-S(2)  | 28.19(7)   | N(1)-S(1)-K(1) | 53.64(12)  |
| N(6)-K(3)-S(2)  | 28.99(5)   | N(2)-S(1)-K(1) | 51.38(10)  |
| N(2)-K(3)-S(2)  | 106.44(6)  | N(3)-S(1)-K(1) | 102.75(12) |
| N(3)-K(3)-S(2)  | 106.27(8)  | N(1)-S(1)-K(2) | 47.12(11)  |
| C(15A)#2-K(3)-S(2) | 124.5(4) | N(2)-S(1)-K(2) | 98.61(10)  |
| N(4)-K(3)-C(8A) | 160.8(2)   | N(3)-S(1)-K(2) | 54.80(13)  |
| N(6)-K(3)-C(8A) | 115.5(3)   | K(1)-S(1)-K(2) | 62.13(3)   |
| N(2)-K(3)-C(8A) | 41.4(2)    | N(1)-S(1)-K(3) | 98.13(11)  |
| N(3)-K(3)-C(8A) | 72.7(3)    | N(2)-S(1)-K(3) | 47.49(10)  |
| C(15A)#2-K(3)-C(8A) | 90.3(4) | N(3)-S(1)-K(3) | 53.78(11)  |
| S(2)-K(3)-C(8A) | 140.3(3)   | K(1)-S(1)-K(3) | 60.58(3)   |
| N(4)-K(3)-K(1)  | 79.14(6)   | K(2)-S(1)-K(3) | 62.61(3)   |
| N(6)-K(3)-K(1)  | 46.40(6)   | C(1)-N(1)-S(1) | 113.3(3)   |
| N(2)-K(3)-K(1)  | 49.77(6)   | C(1A)-N(1)-S(1) | 128.3(6)  |
| N(3)-K(3)-K(1)  | 78.29(7)   | C(1)-N(1)-K(2) | 128.7(3)   |
| C(15A)#2-K(3)-K(1) | 167.2(4) | C(1A)-N(1)-K(2) | 119.5(6)  |
| S(2)-K(3)-K(1)  | 57.98(2)   | S(1)-N(1)-K(2) | 108.16(15) |
| C(8A)-K(3)-K(1) | 83.8(2)    | C(1)-N(1)-K(1) | 118.7(3)   |
| N(4)-K(3)-S(1)  | 105.20(7)  | C(1A)-N(1)-K(1) | 105.8(6)  |
| N(6)-K(3)-S(1)  | 103.56(6)  | S(1)-N(1)-K(1) | 99.80(14)  |
| N(2)-K(3)-S(1)  | 24.49(5)   | K(2)-N(1)-K(1) | 81.10(8)   |
| N(3)-K(3)-S(1)  | 26.58(6)   | N(1)-C(1)-C(4) | 118.4(5)   |
| C(15A)#2-K(3)-S(1) | 127.6(4) | N(1)-C(1)-C(3) | 102.0(5)   |
| S(2)-K(3)-S(1)  | 103.49(3)  | C(4)-C(1)-C(3) | 110.0(6)   |
| C(8A)-K(3)-S(1) | 57.6(3)    | N(1)-C(1)-C(2) | 105.1(5)   |
| K(1)-K(3)-S(1)  | 57.69(2)   | C(4)-C(1)-C(2) | 111.7(6)   |
| Bond Lengths (Å) | Angle (°) |
|-----------------|-----------|
| C(3)-C(1)-C(2)  | 108.9(6)  |
| N(4)-S(2)-K(2)  | 54.78(10)|
| C(5A)-N(2)-S(1) | 113.1(7)  |
| N(6)-S(2)-K(2)  | 106.67(10)|
| C(5)-N(2)-S(1)  | 117.9(3)  |
| K(3)-S(2)-K(2)  | 68.29(3)  |
| C(5A)-N(2)-K(1) | 126.2(6)  |
| N(5)-S(2)-K(1)  | 55.59(10)|
| C(5)-N(2)-K(1)  | 127.5(3)  |
| N(4)-S(2)-K(1)  | 101.24(10)|
| S(1)-N(2)-K(1)  | 102.27(12)|
| N(6)-S(2)-K(1)  | 49.53(10) |
| C(5A)-N(2)-K(3) | 122.1(7)  |
| K(3)-S(2)-K(1)  | 64.89(3)  |
| C(5)-N(2)-K(3)  | 114.6(3)  |
| K(2)-S(2)-K(1)  | 65.87(3)  |
| S(1)-N(2)-K(3)  | 108.01(12)|
| C(13)-N(4)-S(2) | 119.8(3)  |
| K(1)-N(2)-K(3)  | 79.76(7)  |
| C(13A)-N(4)-S(2)| 99.2(7)   |
| N(2)-C(5)-C(8)  | 113.0(5)  |
| C(13)-N(4)-K(3) | 131.4(3)  |
| N(2)-C(5)-C(7)  | 107.1(4)  |
| C(13A)-N(4)-K(3)| 149.1(7)  |
| C(8)-C(5)-C(7)  | 108.7(6)  |
| S(2)-N(4)-K(3)  | 103.00(12)|
| N(2)-C(5)-C(6)  | 110.9(5)  |
| C(13)-N(4)-K(2) | 106.2(3)  |
| C(8)-C(5)-C(6)  | 109.4(6)  |
| C(13A)-N(4)-K(2)| 109.1(7)  |
| C(7)-C(5)-C(6)  | 107.6(6)  |
| S(2)-N(4)-K(2)  | 96.66(12) |
| C(9A)-N(3)-S(1) | 129.8(6)  |
| K(3)-N(4)-K(2)  | 89.41(9)  |
| C(9)-N(3)-S(1)  | 115.2(3)  |
| N(4)-C(13)-C(15)| 110.3(4)  |
| C(9A)-N(3)-K(2) | 111.6(6)  |
| N(4)-C(13)-C(16)| 113.2(4)  |
| C(9)-N(3)-K(2)  | 111.6(3)  |
| C(15)-C(13)-C(16)| 108.7(5) |
| S(1)-N(3)-K(2)  | 98.18(16) |
| N(4)-C(13)-C(14)| 107.8(4)  |
| C(9A)-N(3)-K(3) | 124.7(7)  |
| C(15)-C(13)-C(14)| 107.3(5) |
| C(9)-N(3)-K(3)  | 140.9(3)  |
| C(16)-C(13)-C(14)| 109.4(5) |
| S(1)-N(3)-K(3)  | 99.64(13) |
| C(17A)-N(5)-S(2)| 124.2(4)  |
| K(2)-N(3)-K(3)  | 78.42(8)  |
| C(17)-N(5)-S(2)| 105.4(4)  |
| N(3)-C(9)-C(11) | 109.6(5)  |
| C(17A)-N(5)-K(2)| 129.5(4)  |
| N(3)-C(9)-C(12) | 117.0(5)  |
| C(17)-N(5)-K(2)| 141.1(5)  |
| C(11)-C(9)-C(12)| 108.2(6)  |
| S(2)-N(5)-K(2)  | 103.86(12)|
| N(3)-C(9)-C(10) | 106.8(5)  |
| C(17A)-N(5)-K(1)| 102.3(3)  |
| C(11)-C(9)-C(10)| 105.3(6)  |
| C(17)-N(5)-K(1)| 115.9(5)  |
| C(12)-C(9)-C(10)| 109.4(5)  |
| S(2)-N(5)-K(1)  | 95.88(11) |
| N(5)-S(2)-N(4)  | 102.54(15)|
| K(2)-N(5)-K(1)  | 85.65(8)  |
| N(5)-S(2)-N(6)  | 103.42(15)|
| N(5)-C(17)-C(19)| 101.6(8)  |
| N(4)-S(2)-N(6)  | 104.71(14)|
| N(5)-C(17)-C(20)| 110.2(13)|
| N(5)-S(2)-K(3)  | 104.50(10)|
| C(19)-C(17)-C(20)| 108.1(14)|
| N(4)-S(2)-K(3)  | 48.81(9)  |
| N(5)-C(17)-C(18)| 119.8(8)  |
| N(6)-S(2)-K(3)  | 56.56(10) |
| C(19)-C(17)-C(18)| 107.5(9) |
| N(5)-S(2)-K(2)  | 48.28(10) |
| C(20)-C(17)-C(18)| 108.9(13)|
| Bond                        | Angle  | Bond                        | Angle   |
|-----------------------------|--------|-----------------------------|---------|
| C(21A)-N(6)-S(2)            | 117.5(5) | N(3)-C(9A)-C(11A)          | 108.3(13) |
| C(21)-N(6)-S(2)             | 113.4(5) | N(3)-C(9A)-C(10A)          | 101.6(10) |
| C(21A)-N(6)-K(1)            | 133.6(5) | C(11A)-C(9A)-C(10A)        | 112.9(13) |
| C(21)-N(6)-K(1)             | 142.3(6) | N(3)-C(9A)-C(12A)          | 106.6(11) |
| S(2)-N(6)-K(1)              | 102.41(12) | C(11A)-C(9A)-C(12A)       | 112.2(14) |
| C(21A)-N(6)-K(3)            | 114.2(4)  | C(10A)-C(9A)-C(12A)       | 114.3(13) |
| C(21)-N(6)-K(3)             | 104.6(5)  | N(4)-C(13A)-C(14A)        | 122.6(13) |
| S(2)-N(6)-K(3)              | 94.44(13) | N(4)-C(13A)-C(15A)        | 99.0(11)  |
| K(1)-N(6)-K(3)              | 83.17(8)   | C(14A)-C(13A)-C(15A)      | 109.0(14) |
| N(6)-C(21)-C(22)            | 113.2(9)   | N(4)-C(13A)-C(16A)        | 110.8(14) |
| N(6)-C(21)-C(24)            | 103.8(9)   | C(14A)-C(13A)-C(16A)      | 107.4(14) |
| C(22)-C(21)-C(24)           | 107.9(11)  | C(15A)-C(13A)-C(16A)      | 106.8(16) |
| N(6)-C(21)-C(23)            | 114.7(8)   | N(5)-C(17A)-C(20A)        | 115.2(10) |
| C(22)-C(21)-C(23)           | 109.2(9)   | N(5)-C(17A)-C(18A)        | 108.8(5)  |
| C(24)-C(21)-C(23)           | 107.6(9)   | C(20A)-C(17A)-C(18A)      | 108.1(9)  |
| N(1)-C(1A)-C(3A)            | 111.5(10)  | N(5)-C(17A)-C(19A)        | 109.0(5)  |
| N(1)-C(1A)-C(4A)            | 112.4(10)  | C(20A)-C(17A)-C(19A)      | 107.8(9)  |
| C(3A)-C(1A)-C(4A)           | 106.8(11)  | C(18A)-C(17A)-C(19A)      | 107.8(6)  |
| N(1)-C(1A)-C(2A)            | 114.7(10)  | N(5)-C(17A)-K(1)          | 53.0(3)   |
| C(3A)-C(1A)-C(2A)           | 102.9(11)  | C(20A)-C(17A)-K(1)        | 76.0(8)   |
| C(4A)-C(1A)-C(2A)           | 107.8(11)  | C(18A)-C(17A)-K(1)        | 159.0(5)  |
| N(2)-C(5A)-C(8A)            | 102.6(11)  | C(19A)-C(17A)-K(1)        | 89.8(4)   |
| N(2)-C(5A)-C(7A)            | 105.1(10)  | N(6)-C(21A)-C(22A)        | 113.1(8)  |
| C(8A)-C(5A)-C(7A)           | 113.2(13)  | N(6)-C(21A)-C(24A)        | 115.3(7)  |
| N(2)-C(5A)-C(6A)            | 118.0(12)  | C(22A)-C(21A)-C(24A)      | 107.9(8)  |
| C(8A)-C(5A)-C(6A)           | 109.1(12)  | N(6)-C(21A)-C(23A)        | 105.2(7)  |
| C(7A)-C(5A)-C(6A)           | 109.0(12)  | C(22A)-C(21A)-C(23A)      | 106.8(10) |
| C(5A)-C(8A)-K(3)            | 91.2(8)    | C(24A)-C(21A)-C(23A)      | 108.1(8)  |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1  #2 -x+1,-y+1,-z+1
Figure S2.3 Asymmetric unit of 1_K at 100 K. The thermal ellipsoids are represented at 50% probability level. The disordered groups and the hydrogen atoms are omitted for clarity.
Figure S2.4 Asymmetric unit of 1_K at 100 K. The thermal ellipsoids are represented at 50% probability level and disordered groups are depicted. The hydrogen atoms are omitted for clarity.

The occupancies of the minor components of the disordered tBu groups refine to 0.354(1) (C1 – C4), 0.318(1) (C13A – C16A), 0.206(1) (C22A – C24A), 0.313(1) (C29A – C32A), 0.36(3) (C34 – C36), and 0.218(1) (C41 – C44), respectively.

Table S2.4. Bond lengths [Å] and angles [°] for 1_K@100K.

| Bond          | Length [Å] | Angle [°] |
|---------------|------------|-----------|
| K(1)-N(1)     | 2.642(3)   | 3.7236(10) |
| K(1)-N(6)     | 2.858(3)   |           |
| K(1)-N(2)     | 2.866(3)   | 2.615(3)  |
| K(1)-N(4)     | 2.982(3)   | 2.851(3)  |
| K(1)-S(1)     | 3.4184(1)  | 2.891(3)  |
| K(1)-C(48)#1  | 3.479(4)   | 2.928(3)  |
| K(1)-C(6)     | 3.498(5)   | 3.256(19) |
| K(1)-S(2)     | 3.6829(11) | 3.4402(11)|
K(2)-S(2) 3.6394(13) N(5)-C(17) 1.485(4)
K(2)-K(3) 3.7726(10) C(17)-C(19) 1.522(5)
K(3)-N(2) 2.651(3) C(17)-C(18) 1.528(5)
K(3)-N(3) 2.820(3) C(17)-C(20) 1.532(5)
K(3)-N(5) 2.841(3) N(6)-C(21) 1.488(4)
K(3)-N(6) 2.859(3) C(21)-C(23) 1.511(5)
K(3)-C(40) 3.249(4) C(21)-C(22A) 1.512(11)
K(3)-S(1) 3.4254(11) C(21)-C(24A) 1.521(11)
K(3)-C(20) 3.452(5) C(21)-C(22) 1.525(6)
K(3)-C(12) 3.524(4) C(21)-C(24) 1.526(5)
K(3)-S(2) 3.5685(10) C(21)-C(23A) 1.550(11)
K(3)-K(4) 5.0126(10) K(4)-N(11) 2.671(3)
S(1)-N(3) 1.648(3) K(4)-N(7) 2.841(3)
S(1)-N(1) 1.649(3) K(4)-N(8) 2.871(3)
S(1)-N(2) 1.652(3) K(4)-N(10) 2.874(3)
N(1)-C(1A) 1.489(8) K(4)-C(40) 3.381(4)
N(1)-C(1) 1.493(11) K(4)-S(4) 3.4297(10)
C(1)-C(2) 1.522(11) K(4)-S(3) 3.5745(11)
C(1)-C(3) 1.529(11) K(4)-K(5) 3.6837(10)
C(1)-C(4) 1.533(11) K(4)-K(6) 3.7005(11)
C(2)-K(6)#1 3.423(17) K(5)-N(10) 2.650(3)
N(2)-C(5) 1.480(4) K(5)-N(12) 2.785(3)
C(5)-C(6) 1.528(5) K(5)-N(7) 2.821(3)
C(5)-C(8) 1.531(5) K(5)-N(9) 2.955(3)
C(5)-C(7) 1.535(5) K(5)-C(42)#2 3.39(2)
N(3)-C(9) 1.471(4) K(5)-S(4) 3.4172(12)
C(9)-C(11) 1.534(4) K(5)-C(35) 3.47(3)
C(9)-C(12) 1.534(4) K(5)-C(45) 3.539(4)
C(9)-C(10) 1.541(5) K(5)-S(3) 3.6373(13)
C(12)-K(4) 3.184(3) K(5)-K(6) 3.8057(12)
S(2)-N(5) 1.617(3) K(6)-N(12) 2.620(3)
S(2)-N(6) 1.623(3) K(6)-N(8) 2.885(3)
S(2)-N(4) 1.647(3) K(6)-N(11) 2.908(3)
N(4)-C(13) 1.473(7) K(6)-N(9) 2.945(3)
N(4)-C(13A) 1.515(12) K(6)-C(44A) 3.335(7)
C(13)-C(15) 1.519(8) K(6)-S(4) 3.4356(12)
C(13)-C(16) 1.521(8) K(6)-C(2A)#3 3.483(12)
C(13)-C(14) 1.524(8) K(6)-C(32) 3.509(8)
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| K(6)-S(3)             | 3.6801(12)   | C(1A)-C(3A)           | 1.533(9)     |
| S(3)-N(8)             | 1.626(3)     | C(13A)-C(15A)         | 1.536(13)    |
| S(3)-N(7)             | 1.627(3)     | C(13A)-C(16A)         | 1.541(12)    |
| S(3)-N(9)             | 1.646(3)     | C(13A)-C(14A)         | 1.548(12)    |
| N(7)-C(25)            | 1.486(4)     | C(29A)-C(30A)         | 1.523(12)    |
| C(25)-C(28)           | 1.519(5)     | C(29A)-C(32A)         | 1.526(12)    |
| C(25)-C(27)           | 1.523(5)     | C(29A)-C(31A)         | 1.528(12)    |
| C(25)-C(26)           | 1.546(5)     | C(41A)-C(43A)         | 1.532(7)     |
| N(8)-C(29)            | 1.492(7)     | C(41A)-C(44A)         | 1.537(7)     |
| N(8)-C(29A)           | 1.498(12)    | C(41A)-C(42A)         | 1.547(7)     |
| C(29)-C(30)           | 1.518(8)     |                       |              |
| C(29)-C(32)           | 1.524(8)     |                       |              |
| C(29)-C(31)           | 1.532(7)     |                       |              |
| N(9)-C(33)            | 1.479(4)     |                       |              |
| C(33)-C(36)           | 1.493(11)    |                       |              |
| C(33)-C(34)           | 1.498(11)    |                       |              |
| C(33)-C(34A)          | 1.518(7)     |                       |              |
| C(33)-C(35A)          | 1.540(8)     |                       |              |
| C(33)-C(36A)          | 1.552(8)     |                       |              |
| C(33)-C(35)           | 1.558(11)    |                       |              |
| S(4)-N(10)            | 1.645(3)     |                       |              |
| S(4)-N(11)            | 1.648(3)     |                       |              |
| S(4)-N(12)            | 1.656(3)     |                       |              |
| N(10)-C(37)           | 1.475(4)     |                       |              |
| C(37)-C(39)           | 1.524(5)     |                       |              |
| C(37)-C(40)           | 1.537(4)     |                       |              |
| C(37)-C(38)           | 1.539(5)     |                       |              |
| N(11)-C(41)           | 1.478(12)    |                       |              |
| N(11)-C(41A)          | 1.478(6)     |                       |              |
| C(41)-C(43)           | 1.527(13)    |                       |              |
| C(41)-C(44)           | 1.528(13)    |                       |              |
| C(41)-C(42)           | 1.539(13)    |                       |              |
| N(12)-C(45)           | 1.483(4)     |                       |              |
| C(45)-C(47)           | 1.531(5)     |                       |              |
| C(45)-C(46)           | 1.539(4)     |                       |              |
| C(45)-C(48)           | 1.541(5)     |                       |              |
| C(1A)-C(2A)           | 1.529(9)     |                       |              |
| C(1A)-C(4A)           | 1.532(8)     |                       |              |
C(6)-K(1)-S(2)  144.50(7)  S(1)-K(2)-S(2)  103.72(3)
N(1)-K(1)-K(3)  79.70(6)  N(3)-K(2)-K(1)  77.65(6)
N(6)-K(1)-K(3)  49.37(6)  N(4)-K(2)-K(1)  51.44(6)
N(2)-K(1)-K(3)  45.16(6)  N(1)-K(2)-K(1)  44.48(5)
N(4)-K(1)-K(3)  76.30(6)  N(5)-K(2)-K(1)  77.84(6)
S(1)-K(1)-K(3)  57.13(2)  C(4)-K(2)-K(1)  90.4(2)
C(48)#1-K(1)-K(3)  161.54(6)  S(1)-K(2)-K(1)  56.49(2)
C(6)-K(1)-K(3)  87.89(7)  S(2)-K(2)-K(1)  59.69(2)
S(2)-K(1)-K(3)  57.604(18)  N(3)-K(2)-K(3)  48.32(6)
N(1)-K(1)-K(2)  50.08(6)  N(4)-K(2)-K(3)  76.94(6)
N(6)-K(1)-K(2)  77.36(6)  N(1)-K(2)-K(3)  76.03(5)
N(2)-K(1)-K(2)  77.24(5)  N(5)-K(2)-K(3)  48.16(6)
N(4)-K(1)-K(2)  48.37(7)  C(4)-K(2)-K(3)  116.6(3)
S(1)-K(1)-K(2)  57.05(2)  S(1)-K(2)-K(3)  56.48(2)
C(48)#1-K(1)-K(2)  118.15(7)  S(2)-K(2)-K(3)  57.53(2)
C(6)-K(1)-K(2)  114.14(8)  K(1)-K(2)-K(3)  59.27(2)
S(2)-K(1)-K(2)  58.55(2)  N(2)-K(3)-N(3)  56.21(8)
K(3)-K(1)-K(2)  60.557(18)  N(2)-K(3)-N(5)  123.05(8)
N(3)-K(2)-N(4)  120.23(8)  N(3)-K(3)-N(5)  91.57(8)
N(3)-K(2)-N(1)  55.79(8)  N(2)-K(3)-N(6)  97.23(8)
N(4)-K(2)-N(1)  94.07(8)  N(3)-K(3)-N(6)  115.64(8)
N(3)-K(2)-N(5)  93.93(9)  N(5)-K(3)-N(6)  52.46(7)
N(4)-K(2)-N(5)  51.23(8)  N(2)-K(3)-C(40)  105.86(10)
N(1)-K(2)-N(5)  116.32(8)  N(3)-K(3)-C(40)  125.72(8)
N(3)-K(2)-C(4)  73.0(3)  N(5)-K(3)-C(40)  130.28(10)
N(4)-K(2)-C(4)  127.7(3)  N(6)-K(3)-C(40)  117.39(8)
N(1)-K(2)-C(4)  49.0(2)  N(2)-K(3)-S(1)  28.02(5)
N(5)-K(2)-C(4)  164.2(3)  N(3)-K(3)-S(1)  28.55(6)
N(3)-K(2)-S(1)  27.52(6)  N(5)-K(3)-S(1)  106.39(6)
N(4)-K(2)-S(1)  106.73(6)  N(6)-K(3)-S(1)  105.25(6)
N(1)-K(2)-S(1)  28.54(5)  C(40)-K(3)-S(1)  122.02(8)
N(5)-K(2)-S(1)  104.04(6)  N(2)-K(3)-C(20)  161.35(9)
C(4)-K(2)-S(1)  60.3(3)  N(3)-K(3)-C(20)  106.73(10)
N(3)-K(2)-S(2)  105.55(6)  N(5)-K(3)-C(20)  43.97(9)
N(4)-K(2)-S(2)  25.95(6)  N(6)-K(3)-C(20)  83.22(9)
N(1)-K(2)-S(2)  103.60(6)  C(40)-K(3)-C(20)  90.21(11)
N(5)-K(2)-S(2)  25.70(5)  S(1)-K(3)-C(20)  133.97(8)
C(4)-K(2)-S(2)  148.9(2)  N(2)-K(3)-C(12)  67.83(9)
| Bond               | Length (Å) | Error (Å) |
|--------------------|------------|-----------|
| N(3)-K(3)-C(12)   | 45.33(8)   | 84.91(2)  |
| N(5)-K(3)-C(12)   | 123.78(8)  | 105.82(7) |
| N(6)-K(3)-C(12)   | 160.02(8)  | 39.12(6)  |
| C(40)-K(3)-C(12)  | 80.56(9)   | 168.46(2) |
| S(1)-K(3)-C(12)   | 55.34(7)   | 130.68(2) |
| C(20)-K(3)-C(12)  | 106.63(10) | 125.84(2) |
| N(2)-K(3)-S(2)    | 110.17(6)  | 103.42(13)|
| N(3)-K(3)-S(2)    | 102.92(6)  | 102.97(13)|
| N(5)-K(3)-S(2)    | 26.21(5)   | 104.20(13)|
| N(6)-K(3)-S(2)    | 26.41(5)   | 102.07(9) |
| C(40)-K(3)-S(2)   | 130.17(7)  | 48.80(9)  |
| S(1)-K(3)-S(2)    | 105.55(3)  | 56.68(9)  |
| C(20)-K(3)-S(2)   | 63.47(7)   | 54.86(9)  |
| C(12)-K(3)-S(2)   | 145.05(6)  | 104.75(9) |
| N(2)-K(3)-K(1)    | 50.03(6)   | 48.95(9)  |
| N(3)-K(3)-K(1)    | 76.06(6)   | 65.92(2)  |
| N(5)-K(3)-K(1)    | 79.45(6)   | 47.13(9)  |
| N(6)-K(3)-K(1)    | 49.34(6)   | 56.91(10)|
| C(40)-K(3)-K(1)   | 135.46(8)  | 105.40(9) |
| S(1)-K(3)-K(1)    | 56.95(2)   | 66.46(2)  |
| C(20)-K(3)-K(1)   | 122.94(7)  | 66.66(2)  |
| C(12)-K(3)-K(1)   | 112.11(7)  | 118.14(4) |
| S(2)-K(3)-K(1)    | 60.63(2)   | 109.6(5)  |
| N(2)-K(3)-K(2)    | 79.39(6)   | 133.3(4)  |
| N(3)-K(3)-K(2)    | 43.84(5)   | 144.7(6)  |
| N(5)-K(3)-K(2)    | 50.16(6)   | 103.19(11)|
| N(6)-K(3)-K(2)    | 77.10(6)   | 110.4(4)  |
| C(40)-K(3)-K(2)   | 163.05(7)  | 104.2(6)  |
| S(1)-K(3)-K(2)    | 56.86(2)   | 94.55(11)|
| C(20)-K(3)-K(2)   | 82.57(7)   | 85.44(7)  |
| C(12)-K(3)-K(2)   | 86.83(6)   | 85.44(7)  |
| S(2)-K(3)-K(2)    | 59.36(2)   | 98.9(11)  |
| K(1)-K(3)-K(2)    | 60.18(2)   | 116.7(9)  |
| N(2)-K(3)-K(4)    | 81.34(6)   | 116.3(10)|
| N(3)-K(3)-K(4)    | 83.87(5)   | 107.9(12)|
| N(5)-K(3)-K(4)    | 146.46(6)  | 107.8(10)|
| N(6)-K(3)-K(4)    | 155.70(5)  | 152.9(14)|
| C(40)-K(3)-K(4)   | 41.89(7)   | 88.6(8)  |
C(5)-N(2)-S(1) 116.0(2) N(5)-S(2)-K(1) 99.09(10)
C(5)-N(2)-K(3) 136.4(2) N(6)-S(2)-K(1) 47.78(9)
S(1)-N(2)-K(3) 103.03(12) N(4)-S(2)-K(1) 52.52(10)
C(5)-N(2)-K(1) 109.43(18) K(3)-S(2)-K(1) 61.77(2)
S(1)-N(2)-K(1) 94.52(11) K(2)-S(2)-K(1) 61.76(2)
K(3)-N(2)-K(1) 84.80(7) C(13)-N(4)-S(2) 119.7(4)
N(2)-C(5)-C(6) 114.3(3) C(13A)-N(4)-S(2) 110.8(6)
N(2)-C(5)-C(8) 113.6(3) C(13)-N(4)-K(2) 114.8(4)
C(6)-C(5)-C(8) 108.3(3) C(13A)-N(4)-K(2) 117.5(7)
N(2)-C(5)-C(7) 105.5(3) S(2)-N(4)-K(2) 104.82(14)
C(6)-C(5)-C(7) 108.1(3) C(13)-N(4)-K(1) 127.7(4)
C(8)-C(5)-C(7) 106.6(3) C(13A)-N(4)-K(1) 136.0(7)
C(5)-C(6)-K(1) 82.8(2) S(2)-N(4)-K(1) 101.48(12)
C(9)-N(3)-S(1) 116.7(2) K(2)-N(4)-K(1) 80.19(8)
C(9)-N(3)-K(2) 132.5(2) N(4)-C(13)-C(15) 112.1(6)
S(1)-N(3)-K(2) 105.35(12) N(4)-C(13)-C(16) 105.3(5)
C(9)-N(3)-K(3) 107.34(18) C(15)-C(13)-C(16) 109.9(6)
S(1)-N(3)-K(3) 96.58(11) N(4)-C(13)-C(14) 108.0(6)
K(2)-N(3)-K(3) 87.84(8) C(15)-C(13)-C(14) 110.7(7)
N(3)-C(9)-C(11) 113.3(3) C(16)-C(13)-C(14) 110.6(6)
N(3)-C(9)-C(12) 114.6(3) C(17)-N(5)-S(2) 119.7(2)
C(11)-C(9)-C(12) 107.8(3) C(17)-N(5)-K(3) 118.6(2)
N(3)-C(9)-C(10) 105.7(3) S(2)-N(5)-K(3) 102.91(13)
C(11)-C(9)-C(10) 108.0(3) C(17)-N(5)-K(2) 124.0(2)
C(12)-C(9)-C(10) 107.1(3) S(2)-N(5)-K(2) 102.56(13)
C(9)-C(12)-K(4) 170.0(3) K(3)-N(5)-K(2) 81.67(7)
C(9)-C(12)-K(3) 78.35(17) N(5)-C(17)-C(19) 106.2(3)
K(4)-C(12)-K(3) 96.58(9) N(5)-C(17)-C(18) 116.2(3)
N(5)-S(2)-N(6) 102.08(15) C(19)-C(17)-C(18) 109.4(3)
N(5)-S(2)-N(4) 99.94(16) N(5)-C(17)-C(20) 106.8(3)
N(6)-S(2)-N(4) 99.33(14) C(19)-C(17)-C(20) 108.3(3)
N(5)-S(2)-K(3) 50.89(11) C(18)-C(17)-C(20) 109.6(3)
N(6)-S(2)-K(3) 51.60(9) C(17)-C(20)-K(3) 90.3(2)
N(4)-S(2)-K(3) 100.05(11) C(21)-N(6)-S(2) 116.8(2)
N(5)-S(2)-K(2) 51.74(11) C(21)-N(6)-K(1) 120.45(18)
N(6)-S(2)-K(2) 98.33(9) S(2)-N(6)-K(1) 107.34(12)
N(4)-S(2)-K(2) 49.23(12) C(21)-N(6)-K(3) 122.74(19)
K(3)-S(2)-K(2) 63.11(2) S(2)-N(6)-K(3) 101.99(12)
C(29)-C(32)-K(6)  91.0(4)  C(37)-N(10)-K(4)  107.96(18)
C(33)-N(9)-S(3)  118.4(2)  S(4)-N(10)-K(4)  94.85(10)
C(33)-N(9)-K(6)  127.3(2)  K(5)-N(10)-K(4)  83.56(7)
S(3)-N(9)-K(6)  102.85(13)  N(10)-C(37)-C(39)  105.5(3)
C(33)-N(9)-K(5)  119.0(2)  N(10)-C(37)-C(40)  114.0(3)
S(3)-N(9)-K(5)  100.58(14)  C(39)-C(37)-C(40)  107.6(3)
K(6)-N(9)-K(5)  80.33(8)  N(10)-C(37)-C(38)  114.3(3)
N(9)-C(33)-C(36)  101.9(9)  C(39)-N(37)-C(38)  107.5(3)
N(9)-C(33)-C(34)  118.3(11)  C(40)-C(37)-C(38)  107.6(3)
C(36)-C(33)-C(34)  114.0(11)  C(37)-C(40)-K(3)  167.0(3)
N(9)-C(33)-C(34A)  113.6(4)  C(37)-C(40)-K(4)  85.85(18)
N(9)-C(33)-C(35A)  108.2(6)  K(3)-C(40)-K(4)  98.20(10)
C(34A)-C(33)-C(35A)  107.8(6)  C(41)-N(11)-S(4)  121.8(8)
N(9)-C(33)-C(36A)  111.5(6)  C(41A)-N(11)-S(4)  114.1(3)
C(34A)-C(33)-C(36A)  107.0(5)  C(41)-N(11)-K(4)  130.0(8)
C(35A)-C(33)-C(36A)  108.6(7)  C(41A)-N(11)-K(4)  139.2(3)
N(9)-C(33)-C(35)  101.0(9)  S(4)-N(11)-K(4)  102.52(12)
C(36)-C(33)-C(35)  109.8(10)  C(41)-N(11)-K(6)  113.3(8)
C(34)-C(33)-C(35)  110.8(10)  C(41A)-N(11)-K(6)  110.8(3)
C(33)-C(35)-K(5)  93.7(10)  S(4)-N(11)-K(6)  93.77(12)
N(10)-S(4)-N(11)  104.02(14)  K(4)-N(11)-K(6)  82.98(8)
N(10)-S(4)-N(12)  102.32(14)  N(11)-C(41)-C(43)  110.3(12)
N(11)-S(4)-N(12)  104.67(14)  N(11)-C(41)-C(44)  115.1(13)
N(10)-S(4)-K(5)  49.09(9)  C(43)-C(41)-C(44)  109.1(14)
N(11)-S(4)-K(5)  106.11(10)  N(11)-C(41)-C(42)  106.5(13)
N(12)-S(4)-K(5)  53.94(10)  C(43)-C(41)-C(42)  108.4(15)
N(10)-S(4)-K(4)  56.60(9)  C(44)-C(41)-C(42)  107.2(14)
N(11)-S(4)-K(4)  49.49(10)  C(41)-C(42)-K(5)#4  118.4(13)
N(12)-S(4)-K(4)  99.98(9)  C(45)-N(12)-S(4)  114.6(2)
K(5)-S(4)-K(4)  65.10(2)  C(45)-N(12)-K(6)  133.6(2)
N(10)-S(4)-K(6)  105.76(9)  S(4)-N(12)-K(6)  104.69(12)
N(11)-S(4)-K(6)  57.63(10)  C(45)-N(12)-K(5)  108.11(19)
N(12)-S(4)-K(6)  47.53(9)  S(4)-N(12)-K(5)  97.34(12)
K(5)-S(4)-K(6)  67.47(3)  K(6)-N(12)-K(5)  89.46(8)
K(4)-S(4)-K(6)  65.23(2)  N(12)-C(45)-C(47)  105.8(3)
C(37)-N(10)-S(4)  114.9(2)  N(12)-C(45)-C(46)  114.5(3)
C(37)-N(10)-K(5)  138.74(19)  C(47)-C(45)-C(46)  109.8(3)
S(4)-N(10)-K(5)  102.92(12)  N(12)-C(45)-C(48)  111.7(3)
| Bond | Distance (Å) | Bond | Distance (Å) |
|------|-------------|------|-------------|
| C(47)-C(45)-C(48) | 106.7(3) | N(4)-C(13A)-C(14A) | 120.0(12) |
| C(46)-C(45)-C(48) | 108.0(3) | C(15A)-C(13A)-C(14A) | 105.4(12) |
| N(12)-C(45)-K(5) | 48.41(15) | C(16A)-C(13A)-C(14A) | 106.7(12) |
| C(47)-C(45)-K(5) | 86.6(2) | N(8)-C(29A)-C(30A) | 109.5(10) |
| C(46)-C(45)-K(5) | 80.9(2) | N(8)-C(29A)-C(32A) | 113.8(10) |
| C(48)-C(45)-K(5) | 159.4(2) | C(30A)-C(29A)-C(32A) | 106.5(12) |
| C(45)-C(48)-K(1)#3 | 111.4(2) | N(8)-C(29A)-C(31A) | 108.5(10) |
| N(1)-C(1A)-C(2A) | 107.8(7) | C(30A)-C(29A)-C(31A) | 107.8(13) |
| N(1)-C(1A)-C(4A) | 111.9(6) | C(32A)-C(29A)-C(31A) | 110.5(12) |
| C(2A)-C(1A)-C(4A) | 108.2(8) | N(11)-C(41A)-C(43A) | 117.0(4) |
| N(1)-C(1A)-C(3A) | 111.8(6) | N(11)-C(41A)-C(44A) | 111.2(4) |
| C(2A)-C(1A)-C(3A) | 108.4(8) | C(43A)-C(41A)-C(44A) | 108.8(5) |
| C(4A)-C(1A)-C(3A) | 108.7(7) | N(11)-C(41A)-C(42A) | 104.3(4) |
| N(4)-C(13A)-C(15A) | 106.8(13) | C(43A)-C(41A)-C(42A) | 106.8(5) |
| N(4)-C(13A)-C(16A) | 110.8(12) | C(44A)-C(41A)-C(42A) | 108.3(5) |
| C(15A)-C(13A)-C(16A) | 106.2(13) | C(41A)-C(44A)-K(6) | 91.1(3) |

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z  #2 x,-y+3/2,z+1/2  #3 x,y+1,z  #4 x,-y+3/2,z-1/2
S3. Electron Paramagnetic Resonance

EPR spectra were recorded on a EPR Bruker ELEXSYS E 500 Spectrometer, equipped with the digital temperature control system ER 4131VT using nitrogen as a coolant. The presented spectrum was recorded at room temperature, with about 9.43 GHz microwave frequency, 0.15 G field modulation amplitude, 100 kHz field modulation frequency, and around 10 mW microwave power. The 10⁻³ M toluene diluted solutions were freshly prepared inside of an argon glovebox and immediately inserted in the instrument for measurement.

S4. Theoretical calculations

TD-DFT and spin density calculations were performed in this order:

- 1_K_UNSYMM: coordinates from the X-ray structure, without symmetry restrictions, at the theory level def2-svp in the orca suite[^10].
- 1_K_UNSYMM coordinates from the previous calculation, at the theory level def2-TZVP in the orca suite.
- 1_K_SYMM: modified coordinates to match a Cs symmetry (based on the EPR results), using the orca software suites, at the theory level def2-TZVP.

The results were visualized with the Chemcraft software[^11] and are reported in the following sections.
### Calculations on 1_K (UNSYMM)

Atom coordinates:

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| S    | 14.39129 | 11.79861 | 12.97238 |
| S    | 19.26398 | 9.82614  | 14.87628 |
| K    | 16.04872 | 8.86458  | 14.16818 |
| K    | 16.86865 | 12.15449 | 15.61176 |
| N    | 14.46647 | 11.20021 | 14.47711 |
| K    | 17.91467 | 11.26662 | 12.06121 |
| N    | 18.04984 | 9.82149  | 15.99604 |
| N    | 19.21928 | 11.38715 | 14.32303 |
| C    | 13.17675 | 11.05843 | 15.21113 |
| C    | 13.54263 | 10.41906 | 16.57915 |
| H    | 13.94643 | 9.53855  | 16.43065 |
| H    | 12.73180 | 10.31951 | 17.12049 |
| H    | 14.18043 | 10.99588 | 17.04916 |
| C    | 12.20247 | 10.13530 | 14.50657 |
| H    | 11.94801 | 10.52552 | 13.64438 |
| H    | 11.40299 | 10.01927 | 15.06132 |
| H    | 12.62655 | 9.26431  | 14.35851 |
| C    | 12.50911 | 12.38128 | 15.49750 |
| H    | 12.23875 | 12.80014 | 14.65378 |
| H    | 13.13683 | 12.96900 | 15.96755 |
| H    | 11.71825 | 12.23368 | 16.05709 |
| N    | 15.10879 | 10.62559 | 12.10068 |
| C    | 14.48088 | 10.24065 | 10.81014 |
| C    | 14.26616 | 8.71255  | 10.90654 |
| H    | 13.65840 | 8.51431  | 11.64932 |
| H    | 13.87692 | 8.38391  | 10.06935 |
|   |    |    |    |
|---|----|----|----|
| H | 15.12706 | 8.27088 | 11.06205 |
| C | 13.06159 | 10.85194 | 10.54954 |
| H | 12.46103 | 10.60844 | 11.28470 |
| H | 13.13138 | 11.82789 | 10.49435 |
| H | 12.70483 | 10.50174 | 9.70665 |
| C | 15.39554 | 10.60592 | 9.69990 |
| H | 14.98787 | 10.35489 | 8.84479 |
| H | 15.55645 | 11.57252 | 9.71379 |
| H | 16.24624 | 10.13155 | 9.80798 |
| N | 15.64187 | 12.86853 | 13.01994 |
| C | 15.36198 | 14.29526 | 12.72586 |
| C | 14.73333 | 15.03711 | 13.88854 |
| H | 14.57364 | 15.96964 | 13.63304 |
| H | 13.88213 | 15.1281 | 14.12489 |
| H | 15.33772 | 15.00854 | 14.65943 |
| C | 16.71736 | 14.93216 | 12.40793 |
| H | 16.59199 | 15.88255 | 12.20434 |
| H | 17.31143 | 14.83948 | 13.18181 |
| H | 17.11629 | 14.48218 | 11.63413 |
| C | 14.38782 | 14.43936 | 11.53804 |
| H | 14.22082 | 15.38958 | 11.36593 |
| H | 14.78152 | 14.02724 | 10.74081 |
| H | 13.54235 | 13.99279 | 11.75292 |
| C | 18.20448 | 8.81395 | 17.06014 |
| C | 19.75303 | 8.37223 | 17.79610 |
| H | 20.37986 | 8.03721 | 17.12139 |
| H | 19.74734 | 7.76618 | 18.56622 |
| H | 20.03179 | 9.26596 | 18.08578 |
| C | 17.25941 | 9.25904 | 18.16645 |
| Atom | X  | Y  | Z  |
|------|----|----|----|
| H    | 16.35099 | 9.33890 | 17.80757 |
| H    | 17.55050 | 10.12748 | 18.51499 |
| H    | 17.39830 | 8.23023 | 19.01833 |
| C    | 17.81161 | 7.38928 | 16.64491 |
| H    | 18.07167 | 6.41366 | 17.53108 |
| H    | 16.87017 | 7.37615 | 16.37303 |
| H    | 18.37237 | 7.10138 | 15.89455 |
| N    | 18.65853 | 8.93430 | 13.62726 |
| C    | 19.63690 | 8.10825 | 12.90858 |
| C    | 18.68365 | 7.44213 | 11.82953 |
| H    | 19.20699 | 6.84403 | 11.25614 |
| H    | 17.98373 | 6.92878 | 12.28449 |
| H    | 18.27134 | 8.14210 | 11.28140 |
| C    | 20.05984 | 6.89325 | 13.79634 |
| H    | 20.71248 | 6.34600 | 13.31161 |
| H    | 20.46157 | 7.22059 | 14.62811 |
| H    | 19.27061 | 6.35139 | 14.00588 |
| C    | 20.79993 | 8.75442 | 12.27821 |
| H    | 21.35460 | 8.07456 | 11.84170 |
| H    | 20.49170 | 9.40239 | 11.61074 |
| H    | 21.32772 | 9.21643 | 12.96261 |
| C    | 20.31806 | 12.24676 | 14.82761 |
| C    | 20.41238 | 12.33350 | 16.37180 |
| H    | 20.56970 | 11.43911 | 16.74022 |
| H    | 19.57378 | 12.69176 | 16.73069 |
| H    | 21.15330 | 12.92448 | 16.62115 |
| C    | 20.05678 | 13.63960 | 14.24514 |
| H    | 19.96297 | 13.57433 | 13.27182 |
| H    | 20.80788 | 14.23053 | 14.46203 |
Table S4.1: Calculated wavelengths and their relative intensity for 1_K UNSYMM

| Wavelength (nm) | Relative intensity (fosc) |
|-----------------|---------------------------|
| 748.5           | 0.003025132               |
| 577.7           | 0.098984232               |
| 571.8           | 0.070635463               |
| 508.2           | 0.001263995               |
| 455.6           | 0.002388872               |
| 441.2           | 0.001870807               |
| 388.5           | 0.011874911               |

Figure S4.1.1: Calculated absorption spectrum of 1_K (UNSYMM) in the vis range with Lorentzian band broadening (Bandwidth at ½ height of 150 nm to simulate experiment).
Figure S4.1.2: TD-DFT difference density plots for the states responsible for the absorption bands at 578, 572 and 388 nm for 1_K. Top and side views are shown for better clarity, while carbon and hydrogen atoms are omitted for clarity. Positive and negative densities are depicted in orange and blue, respectively (isosurfaces at 0.005 level (a.u.)).
S4.2 TD-DFT calculations on 1_K SYMM

Atom coordinates:

K  -2.19728349  -0.21532233  0.00000000
K   1.28581958  -1.79611090  0.00000000
K    0.91255558   2.01051602  0.00000000
S   -0.00000635  -0.00030680  -2.66490465
N   -0.41874452  -1.44551909  -2.01730789
C   -1.28353469  -2.31471785  -2.84267931
N   -1.04218108   1.08537241  -2.01791826
C   -1.36220352   2.26847747  -2.84386810
N    1.46141190   0.36001015  -2.01841130
C    2.64589693   0.04631617  -2.84481250
S   -0.00000635  -0.00030680   2.66490465
N    1.46141190   0.36001015   2.01841130
C    2.64589693   0.04631617   2.84481250
N   -0.41874452  -1.44551909   2.01730789
C   -1.28353469  -2.31471785   2.84267931
N   -1.04218108   1.08537241   2.01791826
C   -1.36220352   2.26847747   2.84386810
C   -2.63853717   2.85775667  -2.22929489
H   -3.46243695   2.14634107  -2.31581116
H   -2.48374851   3.07351510  -1.16995740
H   -2.93080308   3.78468195  -2.72821980
C   -1.64521123   1.92456271  -4.31847167
H   -2.40096781   1.14042088  -4.38458106
H   -2.01195717   2.80334254  -4.85375469
H   -0.74671655   1.56923431  -4.82279882
C   -0.25564792   3.34518083  -2.79974477
H   -0.48163746   4.17325439  -3.47570052
H   -0.17148409   3.77240250  -1.79595671
H    0.70704564   2.91895872  -3.08055607
|   |      |      |      |      |
|---|------|------|------|------|
| C | -2.76890671 | -1.89339224 | -2.80081357 |
| H | -3.37288360 | -2.50383542 | -3.47628797 |
| H | -3.18216782 | -2.03194585 | -1.79722128 |
| H | -2.87998480 | -0.84695827 | -3.08351065 |
| C | -0.84281972 | -2.39114707 | -4.31670026 |
| H | 0.21380789 | -2.65528405 | -4.38126256 |
| H | -1.42104850 | -3.14820588 | -4.85131455 |
| H | -0.98243869 | -1.43600014 | -4.82274222 |
| C | -1.15769269 | -3.71355332 | -2.22524834 |
| H | -0.12985800 | -4.07248112 | -2.30981815 |
| H | -1.42315015 | -3.68504489 | -1.16629357 |
| H | -1.81432321 | -4.43054245 | -2.72354672 |
| C | 3.02369151 | -1.45073944 | -2.80395665 |
| H | 3.85401033 | -1.66820115 | -3.47995161 |
| H | 3.35068283 | -1.73995469 | -1.80064754 |
| H | 2.17291106 | -2.07005733 | -3.08658144 |
| C | 3.79492650 | 0.85465252 | -2.22817848 |
| H | 3.59153680 | 1.92423733 | -2.31207256 |
| H | 3.90414891 | 0.61008579 | -1.16942677 |
| H | 4.74368058 | 0.64491257 | -2.72759050 |
| C | 2.49007912 | 0.46691063 | -4.31848566 |
| H | 2.19064851 | 1.51413663 | -4.38215779 |
| H | 3.43412845 | 0.34474712 | -4.85433251 |
| H | 1.73193917 | -0.13116483 | -4.82387979 |
| C | -1.15769269 | -3.71355332 | 2.22524834 |
| H | -1.42315015 | -3.68504489 | 1.16629357 |
| H | -0.12985800 | -4.07248112 | 2.30981815 |
| H | -1.81432321 | -4.43054245 | 2.72354672 |
| C | -0.84281972 | -2.39114707 | 4.31670026 |
| H | -1.42104850 | -3.14820588 | 4.85131455 |
| H | 0.21380789 | -2.65528405 | 4.38126256 |
| H | -0.98243869 | -1.43600014 | 4.82274222 |
Table S4.2. Calculated absorption bands (with relative intensity) for 1_K SYMM

| Wavelength (nm) | Relative intensity (fosc) |
|-----------------|--------------------------|
| 736.0           | 0.190678783              |
| 735.6           | 0.190572297              |
| 655.9           | 0.000000103              |
| 655.6           | 0.000000023              |
| 404.2           | 0.011999462              |
| 404.2           | 0.011930088              |
| 380.2           | 0.000000007              |

Figure S4.2.1: Calculated absorption spectrum of 1_K (SYMM) in the vis range with Lorentzian band broadening (Bandwidth at ½ height of 150 nm to simulate experiment).

Figure S4.2.2 TD-DFT difference density plots for the states responsible for the absorption bands at 736 and 404 nm for 1_K. Top and side views are shown for better clarity, while carbon and hydrogen atoms are omitted for clarity. Positive and negative densities are depicted in orange and blue, respectively (isosurfaces at 0.005 level (a.u.)).
S4.3 Spin density calculations

The EPR simulation was performed with the EPR simulator developed by Viktor Chechik at the University of York (victor.chechik@york.ac.uk) based on EasySpin and as well as with SPINFIT (Bruker software).

The spin density was furthermore calculated on the level of theory PBE0 D3BJ def2-tzvp def2/J RIJCOSX in Orca. The same coordinates reported above were used (UNSYMM) Spin density plots were generated with the Chemcraft software. The following spin density plot was obtained:

**Figure S4.3.1**: Calculated spin density plots for 1_K_UNSYMM. Positive and negative densities are depicted in orange and blue, respectively (isosurfaces at 0.005 level). Both top-down (left) and side views (right) are depicted for better clarity. Hydrogens are omitted for clarity.

The results depicted in Figure S4.3.1 suggest that the spin density is located only on three nitrogen atoms of the same cap. The experimental EPR data, however, clearly suggest hyperfine coupling to six equivalent nitrogen atoms and thus two equivalent sulfurrtriaimide units. When the structure of the radical was computationally freely optimized (gas phase conditions) the ‘asymmetric’ (cap A/cap B) type of structure observed in the crystal structure was retained. Spin density in these structures was almost entirely located on one sulfurtriaimide fragment. In order to computationally probe a species that reflects the EPR-spectroscopically observed features, a symmetry restricted optimization enforcing (C$_3h$, or C$_s$) symmetry was performed. Spin density of these C$_s$ symmetric molecules is then equally distributed between both sulfurtriaimide fragments.
**Figure S4.3.2.** Calculated spin density plots for **1_K_SYMM**. Positive and negative densities are depicted in orange and blue, respectively (isosurfaces at 0.005 level). Both top-down (left) and side views (right) are depicted for better clarity. Hydrogens are omitted for clarity.

These results are now in good agreement with the experimental EPR spectrum regarding the spin density locating on all six nitrogen atoms of the compound.

**Calculated Mulliken spin densities:**

Calculated Mulliken spin population for **1K_UNSYMM**

On average per atom:

| Atom     | Averaged spin population | # of atoms |
|----------|--------------------------|------------|
| K        | ≈ -0.010                 | 3          |
| S(cap A) | ≈ -0.120                 | 1          |
| S(cap B) | ≈ -0.001                 | 1          |
| N(capA)  | ≈ 0.364                  | 3          |
| N(capB)  | ≈ 0.003                  | 3          |
| C/H      | ≈ 0                      | 78         |
| **Av. sum**<sub>calc</sub> | ≈ 0.940                 | 89         |
| **Sum**<sub>theo</sub> | 1                       | 89         |

Detailed per atom (as calculated): (atom, atomic charge, atomic spin population)

0 S :  0.467249  -0.120076
1 S :  0.466805  -0.000816
2 K :  0.606469  -0.010245
3 K :  0.618551  -0.009915
4 N : -0.573039  0.287992
5 K :  0.613340 -0.013521
6 N : -0.630999  0.002772
7 N : -0.667694  0.003053
8 C :  0.178976 -0.000860
9 C : -0.358560 -0.001724
10 H :  0.120135  0.000499
11 H :  0.123925 -0.000826
12 H :  0.119722  0.000509
13 C : -0.373030  0.007803
14 H :  0.125852  0.000322
15 H :  0.125700 -0.000042
16 H :  0.110214  0.001477
17 C : -0.363320  0.010321
18 H :  0.121178 -0.000371
19 H :  0.113523  0.000598
20 H :  0.125995 -0.000068
21 N : -0.495077  0.364577
22 C :  0.179536 -0.025566
23 C : -0.365343  0.016898
24 H :  0.117425 -0.000202
25 H :  0.120535  0.002118
26 H :  0.120276 -0.000653
27 C : -0.386861  0.001863
28 H :  0.120836 -0.000001
29 H :  0.146446 -0.000391
30 H :  0.127692 -0.000369
31 C : -0.401676  0.018705
32 H :  0.128041  0.001538
33 H :  0.136014 -0.000918
|    | X      | Y      | Z      |
|----|--------|--------|--------|
| 34 | 0.121612 | -0.000575 |
| 35 | -0.479946 | 0.438851 |
| 36 | 0.189478 | -0.012431 |
| 37 | -0.371049 | 0.022435 |
| 38 | 0.120873 | 0.001697 |
| 39 | 0.129270 | -0.000298 |
| 40 | 0.112731 | 0.000476 |
| 41 | -0.364534 | 0.000236 |
| 42 | 0.125993 | -0.001023 |
| 43 | 0.128508 | 0.000079 |
| 44 | 0.121101 | 0.001041 |
| 45 | -0.405729 | 0.011687 |
| 46 | 0.132194 | -0.000633 |
| 47 | 0.118684 | 0.000120 |
| 48 | 0.134138 | -0.000194 |
| 49 | 0.176939 | -0.000220 |
| 50 | -0.449248 | 0.000070 |
| 51 | 0.132969 | -0.000004 |
| 52 | 0.131649 | -0.000003 |
| 53 | 0.113260 | 0.000006 |
| 54 | -0.319583 | 0.000009 |
| 55 | 0.106951 | 0.000059 |
| 56 | 0.109387 | -0.000003 |
| 57 | 0.078358 | -0.000020 |
| 58 | -0.368012 | 0.000055 |
| 59 | 0.067958 | -0.000020 |
| 60 | 0.090830 | -0.000018 |
| 61 | 0.161737 | -0.000009 |
| 62 | -0.673598 | 0.000367 |
| 63 | 0.260094 | -0.000188 |
|   |   |   |
|---|---|---|
| 64 C | -0.406159 | 0.000034 |
| 65 H | 0.123033  | 0.000003 |
| 66 H | 0.111871  | 0.000014 |
| 67 H | 0.099805  | 0.000095 |
| 68 C | -0.389845 | 0.000176 |
| 69 H | 0.104563  | 0.000007 |
| 70 H | 0.119019  | 0.000002 |
| 71 H | 0.110777  | 0.000020 |
| 72 C | -0.352205 | 0.000079 |
| 73 H | 0.116404  | 0.000003 |
| 74 H | 0.085840  | 0.000064 |
| 75 H | 0.139810  | 0.000005 |
| 76 C | 0.148028  | -0.000141|
| 77 C | -0.324603 | 0.000132 |
| 78 H | 0.142381  | 0.000005 |
| 79 H | 0.060040  | 0.000040 |
| 80 H | 0.109911  | 0.000005 |
| 81 C | -0.333844 | 0.000146 |
| 82 H | 0.115404  | 0.000021 |
| 83 H | 0.116211  | 0.000005 |
| 84 H | 0.075333  | 0.000014 |
| 85 C | -0.370180 | 0.000066 |
| 86 H | 0.120807  | 0.000000 |
| 87 H | 0.107797  | 0.000007 |
| 88 H | 0.117884  | 0.000001 |

Sum of atomic charges: -0.000000

Sum of atomic spin populations: 1.000000
Calculated Mulliken spin population for **1K_SYMM**

On average per atom:

| Atom | Averaged spin population | # of atoms |
|------|--------------------------|------------|
| K    | ≈ -0.013                 | 3          |
| S    | ≈ 0.036                  | 2          |
| N    | ≈ 0.156                  | 6          |
| C/H  | ≈ 0                      | 78         |
| Approx. | ≈ 0.969               | 89         |
| Sum\text{calc} |                     | 89         |
| Sum\text{theo} |                     | 89         |

Detailed per atom (as calculated): (atom, atomic charge, atomic spin population)

0 K : 0.680784 -0.013333
1 K : 0.678413 -0.013501
2 K : 0.687467 -0.012915
3 S : 0.661629  0.035817
4 N : -0.647621  0.155913
5 C : 0.213135 -0.004159
6 N : -0.647860  0.156297
7 C : 0.209583 -0.004364
8 N : -0.647984  0.155952
9 C : 0.209725 -0.004402
10 S : 0.661511  0.035819
11 N : -0.647940  0.155972
12 C : 0.209581 -0.004412
13 N : -0.647693  0.155918
14 C : 0.213465 -0.004144
15 N : -0.647791  0.156305
16 C : 0.209532 -0.004361
17 C : -0.367482 -0.000453
18 H : 0.113573  0.000048
19 H : 0.106090  0.000216
20 H : 0.116524 -0.000549
21 C : -0.389925  0.008294
22 H :  0.117574  0.000017
23 H :  0.110632  -0.001422
24 H :  0.131726  -0.000192
25 C : -0.407785  0.004138
26 H :  0.120687  -0.000396
27 H :  0.088247  0.000452
28 H :  0.135488  -0.000512
29 C : -0.409026  0.004027
30 H :  0.121133  -0.000400
31 H :  0.087868  0.000455
32 H :  0.135935  -0.000512
33 C : -0.389779  0.008287
34 H :  0.117275  0.000015
35 H :  0.110656  -0.001418
36 H :  0.131463  -0.000190
37 C : -0.368165  -0.000428
38 H :  0.113567  0.000048
39 H :  0.106063  0.000205
40 H :  0.116472  -0.000548
41 C : -0.407274  0.004072
42 H :  0.121070  -0.000398
43 H :  0.088922  0.000444
44 H :  0.135296  -0.000506
45 C : -0.365031  -0.000405
46 H :  0.113108  0.000050
47 H :  0.105393  0.000192
48 H :  0.116143  -0.000547
49 C : -0.389659  0.008317
50 H :  0.117176  0.000012
51 H :  0.110306  -0.001422
52 H :  0.131743  -0.000192
53 C :  -0.368316  -0.000433
54 H :  0.105942   0.000206
55 H :  0.113547   0.000048
56 H :  0.116489  -0.000548
57 C :  -0.389817   0.008288
58 H :  0.110650  -0.001418
59 H :  0.117305   0.000016
60 H :  0.131492  -0.000188
61 C :  -0.408938   0.004016
62 H :  0.087812   0.000461
63 H :  0.121175  -0.000399
64 H :  0.135920  -0.000512
65 C :  -0.407446   0.004080
66 H :  0.089080   0.000438
67 H :  0.121099  -0.000398
68 H :  0.135267  -0.000506
69 C :  -0.364774  -0.000402
70 H :  0.105386   0.000192
71 H :  0.113052   0.000050
72 H :  0.116121  -0.000548
73 C :  -0.389664   0.008318
74 H :  0.110314  -0.001422
75 H :  0.117217   0.000013
76 H :  0.131756  -0.000193
77 C :  -0.389644   0.008293
78 H :  0.110634  -0.001422
79 H :  0.117500   0.000017
80 H :  0.131702  -0.000193
81 C : -0.367402 -0.000451
82 H :  0.106037  0.000215
83 H :  0.113541  0.000048
84 H :  0.116383 -0.000549
85 C : -0.407738  0.004134
86 H :  0.088236  0.000453
87 H :  0.120704 -0.000395
88 H :  0.135437 -0.000512

Sum of atomic charges : -0.000000
Sum of atomic spin populations:  1.000000
S4.4 Discussion regarding the free electron

Let us assume the start is the localisation of the electron in red at the upper sulfur atom (a). This results in four electrons at that sulfur, one each from the S–N single bonds plus the unpaired electron, causing a double positive formal charge. Now the electron moves to the first nitrogen atom at the left (b), formally by one nitrogen lone pair to form a S=N double bond first and further giving the lone pair at sulfur. That reduced the sulfur formal charge to one and the negative charge at the nitrogen atom, hosting the unpaired electron, vanishes. Next the electron moves on to a potassium cation (c), formally generating an uncharged alkali metal atom while the nitrogen atom only holds two covalent bonds plus a single lone pair. Hence that nitrogen is now formally positive charged. The unpaired electron can move on to the lower SN₃-cap in the same fashion (d) and reaches eventually the sulfur atom in the lower cap (e). Obviously all three nitrogen atoms in the upper cap can be engaged in the same way (h, g) and the electron can couple to any of the potassium cations (f). Of course, the same is valid for the lower cap, resulting of a delocalised unpaired electron in the whole S₂N₆K₃ uncharged cage.
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