Mixed Alkali Metal Cages Containing the Cap-shaped $[S(NtBu)_3]^{2-}$ Triazasulfite Dianion

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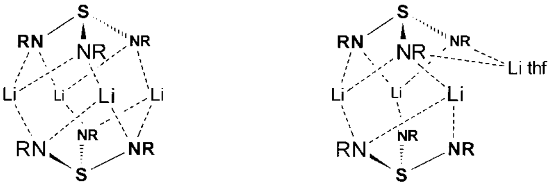
Abstract: Synthesis and crystal structure analysis of the mixed alkali metal complexes $[(thf)_2Li_4M_2(OtBu)_2\{(NtBu)_3S\}_2]$ (**1**, M = Na; **2**, M = K) are discussed. They result from the 1:1 co-complexation process between the triazasulfite $[Li_4\{(NtBu)_3S\}_2]$ and the related heavy alkali metal *tert*-butanolates. The cap-shaped $[S(NtBu)_3]^{2-}$ dianion stays intact and co-complexation is favored over a transmetalation reaction, with two monomeric units inserted into the cage and with no elimination of LiO*t*Bu. Apparently the $[S(NtBu)_3]^{2-}$ triazasulfite anion can easily accommodate more metal atoms than the two lithium atoms from the starting material.

Keywords: lithium · potassium · sodium · structure determination · sulfur

Introduction

Recently, we described the synthesis and structures of some nitrogen analogues of simple sulfur–oxygen anions. In these derivatives the oxygen atoms are substituted by isoelectronic NR groups to yield the dilithium triazasulfite dimer[1] $[(thf)Li_4\{(NtBu)_3S\}_2]$ (the analogue of Li_2SO_3) and the dilithium tetraazasulfate monomer[2] $[(thf)_4Li_2(NtBu)_4S]$ (analogous to Li_2SO_4). Polyimido polyanions containing p-block-element bridgeheads like $[\{RSi(NSiMe_3)_3\}_2]^{3-}$,[3] $[RE(E'R'_2NR'')_3]^{3-}$ (R, R' = H, alkyl; R'' = alkyl, aryl; E, E' = C, Si)[4], $[Sb(NR)_3]^{3-}$,[5a] $[Sb_2(NR)_4]^{2-}$,[5b] and $[E(NtBu)_3]^{2-}$ (E = Se, Te)[6] furnish a new family of ligand systems from which macromolecular architectures of mixed metal cages and clusters may be constructed.[7] While the alkali metal salts of these polyanions have mainly been employed in metal metathesis reactions, little is known of their ability to form complexes with anions. The flexible electronic structure of their alkali metal derivatives, that is, the ability to localize or delocalize the charge in the anion core backbone, provides the opportunity to complex neutral metal salts generated in situ. For example, the reaction of dilithium-*N*,*N'*,*N''*-tri(*tert*-butyl)azasulfite $[(thf)Li_4\{(NtBu)_3S\}_2]$ and trimethylsilyl azide results in the soluble lithium azide adduct $[(thf)_2Li_3(\mu_4N_3)\{(NtBu)_3S\}]_\infty$.[8]

This paper is concerned with the application of the $[S(NtBu)_3]^{2-}$ dianion in the formation of mixed metal cages by an anion solvation process. The coordination chemistry of the triazasulfite anion is unique among the chelating nitrogen ligands, due to the combination of its dianionic nature and cap-shaped geometry. The combination of tripodal coordination and the steric demands of the nitrogen-bonded substituents should give homoleptic metal(II) complexes, as well as facilitate incorporation of this structural residue into cage complex architectures. The cage structures of the solvent free $[Li_4\{(NtBu)_3S\}_2]$, as well as the THF solvate $[(thf)Li_4\{(NtBu)_3S\}_2]$, already verify this (Scheme 1).[1, 9] The four lithium atoms present in the dimers are located in the area between the two cap-shaped dianions leaving all metals tricoordinated. The dilithium triazaselenite and -tellurite adopt the same solid-state structures.[6]



$[Li_4\{(NtBu)_3S\}_2]$ $[(thf)Li_4\{(NtBu)_3S\}_2]$

Scheme 1. Structures of the solvent free and THF solvated dilithium triazasulfites.

Results and Discussion

We aimed to replace the lithium atoms in the triazasulfite by other main group metal cations. While transmetalation with

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metal halides (ECl_2; E = Ge, Sn, Pb) is precluded by complex redox processes, partial substitution of lithium by alkaline earth metal cations can be achieved by employing the alkaline earth metal bis[bis(trimethylsilyl)amides].[10] While the heavier alkali metal diaminosulfinates are accessible either by deprotonation reactions of RS(NHR)NR with MH[11] or addition of the secondary metal amides MNR_2 (M = Na, K, Rb, Cs) to $S(NR)_2$,[12] direct syntheses of the heavier alkali metal triazasulfites is thwarted by the difficult syntheses of the required primary metal amides MN(H)R in preparative yields. However, inspired by the fundamental work by Lochmann and Schlosser in the late 60s on the so-called super-basic mixtures,[13] we embarked on transmetalation by the heavier alkali metal alkoxides MOR. In the reaction of potassium *tert*-butylalkoxide with $[Te(NtBu)_2]_2$ the cage complex $[KTe(NtBu)_2(OtBu)]_2$ is obtained.[14]

Preparation of $[(thf)_2Li_4M_2(OtBu)_2\{(NtBu)_3S\}_2]$ (1, M = Na; 2, M = K): With this background in mind, we treated solvent free $[Li_4\{(NtBu)_3S\}_2]$ with the heavy alkali metal *tert*-butanolates MO*t*Bu (M = Na, K) to see whether this reaction pathway is governed by transmetallation [Eq. (1)] or co-complexation [Eq. (2)].

$$[Li_4\{(NtBu)_3S\}_2] + 4\,MOtBu \not\longrightarrow [M_4\{(NtBu)_3S\}_2] + 4\,LiOtBu \tag{1}$$

$$[Li_4\{(NtBu)_3S\}_2] + 2\,MOtBu \longrightarrow [(thf)_2Li_4M_2(OtBu)_2\{(NtBu)_3S\}_2] \tag{2}$$

The energetically very attractive Li–O interaction in the formed lithium *tert*-butanolate is often regarded to be the driving force in metal-metathesis reactions.[15] However, in the reactions of triazasulfite $[Li_4\{(NtBu)_3S\}_2]$ with sodium and potassium butanolate transmetalation does not occur, and formation of lithium butanolate LiO*t*Bu is not observed. Instead two equivalents of butanolate are incorporated into the complex structure [Eq. (2)].

Abstract in German: *In dieser Arbeit werden die Synthesen und Einkristallstrukturanalysen der gemischtmetallischen Komplexe* $[(thf)_2Li_4M_2(OtBu)_2\{(NtBu)_3S\}_2]$ *(**1**, M = Na; **2**, M = K) vorgestellt. Sie werden durch die 1:1-Cokomplexierung der entsprechenden Alkalimetall-tert-butanolate mit dem dimeren Dilithiumtriazasulfit* $[Li_4\{(NtBu)_3S\}_2]$ *erhalten. Das kappenförmige Triazasulfit* $[S(NtBu)_3]^{2-}$ *bleibt dabei erhalten. Offensichtlich ist die Cokomplexierung gegenüber der Metallmetathese bevorzugt, denn es kommt nicht zur LiOtBu-Eliminierung. Statt dessen werden zwei Einheiten MOtBu (M = Na, K) in das Käfigmolekül eingebaut. Formal kann man sich die Entstehung der Komplexe durch folgenden Prozeß vorstellen: In der Ausgangsverbindung* $[Li_4\{(NtBu)_3S\}_2]$ *werden vier LiN-Bindungen gebrochen. Duch Drehen der einen Dilithiumtriazasulfit-Kappe um 180° relativ zur anderen kommt es zu einer ekliptischen Anordnung der vier Lithiumatome und aller tBuN-Substituenten. Die vier Lithiumatome koordinieren daraufhin ein* $[(thf)M(OtBu)_2]$*-Anion, während vier Stickstoffatome ein [M(thf)]-Kation komplexieren. Das* $[S(NtBu)_3]^{2-}$*-Triazasulfit-Ion kann offensichtlich mehr Metallkationen komplexieren als lediglich die beiden Lithiumatome der Ausgangsverbindung.*

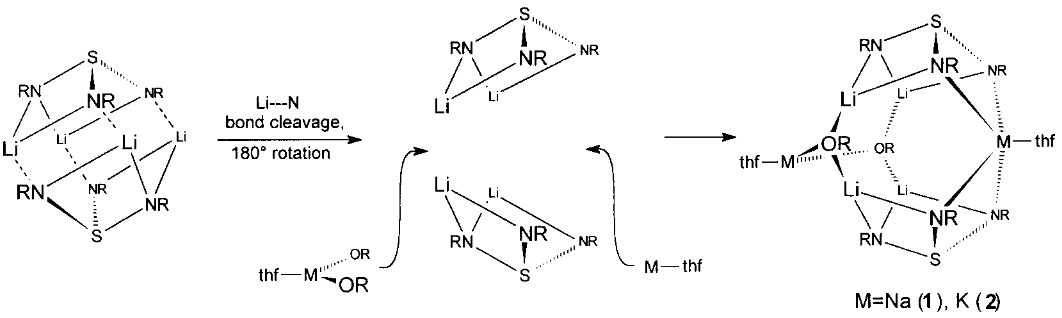
Addition of four equivalents of sodium and potassium butanolate in THF to one equivalent of $[Li_4\{(NtBu)_3S\}_2]$ at room temperature yields clear orange solutions. After several days at ambient temperature colorless crystals are obtained (see Experimental Section).

Structures of $[(thf)_2Li_4M_2(OtBu)_2\{(NtBu)_3S\}_2]$ (1, M = Na; 2, M = K): The low-temperature structure analysis proves both compounds exhibit cage-like structures with the concave sides of the triazasulfite dianions facing each other; a similar structure is observed in $[Li_4\{(NtBu)_3S\}_2]$. The area between the dianions in **1** and **2** is expanded by two molecules of MO*t*Bu (**1**, M = Na; **2**, M = K). The distance between the central sulfur atoms in $[Li_4\{(NtBu)_3S\}_2]$ of 459.5 pm is considerably widened to 584.0 pm in **1** and 610.1 pm in **2** to give the required room for additional salt co-complexation (Scheme 2).

Compound **1** displays C_2 symmetry with both sodium atoms and both THF oxygen atoms on a twofold axis (Figure 1). The structure of **2** is isomorphous, but not isostructural. Compound **2** shows notably higher molecular symmetry (Figure 2). There is a mirror plane through both potassium atoms, the oxygen atoms of the *tert*-butanolate groups and of the THF molecules, and a second orthogonal mirror plane goes through both central sulfur atoms, the two potassium atoms, and both oxygen atoms of the THF molecules. This orientation generates an eclipsed arrangement of the six *t*BuN groups rather than the staggered placement as in $[Li_4\{(NtBu)_3S\}_2]$.

The heavier alkali metals occupy different coordination sites. While Na1 (K1 in **2**) adopts a square planar pyramidal environment with four nitrogen atoms in the basal positions and the oxygen atom of a donating THF molecule at the apical position, Na2 (K2 in **2**) adopts a trigonal planar geometry, complexed by the two oxygen atoms of the $tBuO^-$ groups and one THF donor molecule. The Na2–O1 distance of 233.5(2) pm in **1** is considerably longer than the distances in the solid-state structure of the starting material[16] (224 pm in $[NaOtBu]_6$ and 226 pm in $[NaOtBu]_9$), while the K2–O1 distance of 262.7(2) pm in **2** is of comparable length with the distance in $[KOtBu]_4$ (262.3 pm).[17] The two symmetry independent Na–N distances in **1** of 249.3(2) (Na1–N1) and 266.8(3) pm (Na1–N2) are within the range covered in sodium amides,[18] whereas the Na2–N3 distance of 309.4(5) pm is too long to be regarded an interaction. The potassium nitrogen distances in **2** to the N_4 square plane (K1) of 286.4(2) pm match the lengths observed in potassium amides.[18, 19] The K2–N2 distance of 317.8(2) pm, however, is well above that value and should not regarded as an interaction, even if the additional coordination of a hard heteroatom is taken into account. In the potassium fluorosilyl amide $[(thf)_2KNtBuFSitBu_2]_2$, the potassium atom is hexacoordinated by two nitrogen atoms, two fluorine atoms, and two THF molecules, and the K–N distance is only 296 pm on average.[20] In the complex $[KTe(NtBu)_2(OtBu)]_2$ a $[Te(NR)_2(OR)]^-$ monoanion is generated by formation of a Te–O bond (204.9(5) pm) in the reaction of potassium *tert*-butylalkoxide with $[Te(NtBu)_2]_2$.[14] An analogous S–O bond formation is precluded in the reactions presented here.

The rather asymmetric coordination to two different metals within the cage structures of **1** and **2** induces different S–N



Scheme 2. Rearrangement of $[Li_4\{(NtBu)_3S\}_2]$ and complexation of two molecules of MO*t*Bu (**1**, M = Na; **2**, M = K).

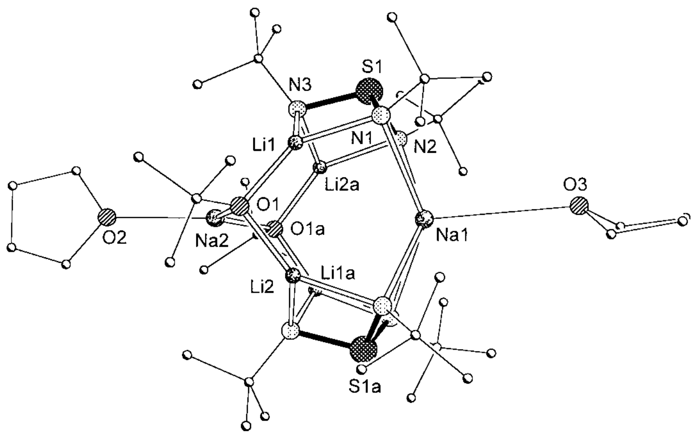


Figure 1. Solid-state structure of $[(thf)_2Li_4Na_2(OtBu)_2\{(NtBu)_3S\}_2]$ (**1**).

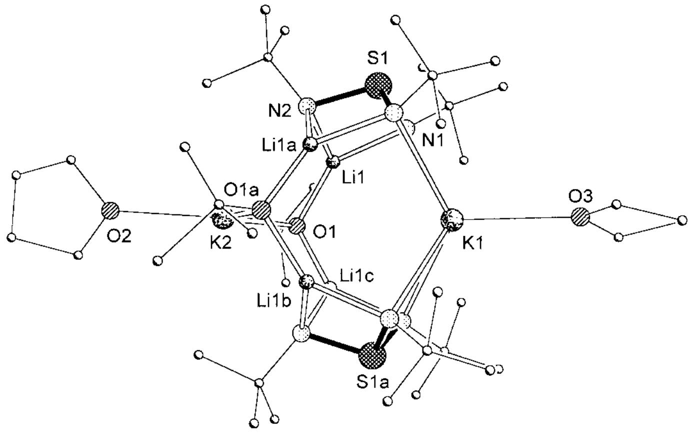


Figure 2. Solid-state structure of $[(thf)_2Li_4K_2(OtBu)_2\{(NtBu)_3S\}_2]$ (**2**).

bond lengths in their triazasulfite dianions. While the two nitrogen atoms coordinated to the heavier alkali metals display similarly long S–N bond lengths of 163.2(2) in **1** and 162.1(2) pm in **2**, the S–N distance in the imide function coordinated to the two lithium atoms is significantly longer (167.5(2) pm both S1–N3 in **1** and S1–N2 in **2**). This effect has been pinpointed earlier in the coordination of this ligand to various s- and p-block metals.[10] It demonstrates the ability of this ligand to localize or delocalize the charge in the S–N dianion core backbone.[8, 21]

This asymmetry in the solid state is even emphasized in solution. Although the crystallographically different lithium sites in **1** were not verified in the ^7Li NMR spectrum from solution, the two sites for the *t*BuN substituents were resolved. The four lithium positions in **2** are equivalent by crystallographic requirements, but the ^7Li NMR spectrum from solution displays three signals. The ^1H NMR spectrum shows five signals in the methyl region. The tentative assignment in **1** seems arbitrary in **2**. The signal pattern in both cases might be complicated by a monomer–dimer (oligomer) equilibrium. The ^7Li solid-state NMR spectra (both quadrupolar nutation and multiple quantum experiments) of **1** and **2** show only one lithium signal.

Both structures are reminiscent of the co-complexation product, the trimetallic cage $[Li_6M_3(OtBu)_3\{(NCy)_3Sb\}_2]$ (Cy = cyclohexyl), formed from $[Li_6\{(NCy)_3Sb\}_2]$ and three equivalents of KO*t*Bu.[22] Like the $[Sb(NCy)_3]^{3-}$ trianion, the $[S(NtBu)_3]^{2-}$ dianion in the reactions discussed here represents the chemically robust entity. Apparently the $[Li_4\{(NtBu)_3S\}_2]$ dimer dissociates into monomeric $[Li_2(NtBu)_3S]$ units that reassemble in **1** and **2** on complexation to the two [MO*t*Bu] residues. Evidently the oligomeric solid-state structures of the [MO*t*Bu] starting materials (tetrameric, hexameric, or nonameric cages[23]) are broken down in the course of reaction, because the elementary structural motif of metal–oxygen four-membered rings in the alkali metal alkanolates is not retained in the structures presented here. It is only under reductive conditions (i.e., in the presence of elemental alkali metals) that we have detected disintegration of the $[S(NtBu)_3]^{2-}$ dianion giving the metal sulfide adducts of triazasulfite, $[(thf)_6M_6(\mu_6S)\{(NtBu)_3S\}_2]$ (M = Li, Na).[24]

Conclusion

The polyimido polyanions in general seem to provide access to soluble mixed metal aggregates. This occurs by the incorporation of in situ generated inorganic solids into complex residues and is detected for the first time in the polymeric structure of a lithium azide adduct $[(thf)_2Li_3(\mu_4N_3)\{(NtBu)_3S\}]_\infty$. In addition, the lithium triazasulfite disaggregates $[MOtBu]_n$ oligomers and incorporates them into metal salt co-coordination complexes, owing to the capability of the $[S(NtBu)_3]^{2-}$ triazasulfite anion to coordinate more than two metal centers. Transmetalation and formation of lithium *tert*-butanolate is not observed.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen gas with Schlenk techniques or in an argon drybox. Solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were

Table 1. Selected bond lengths [pm] and angles [°] of **1** and **2**.

1				**2**			
S(1)–N(1)	163.1(2)	Li(1)–N(1)	193.5(5)	S(1)–N(1)	162.1(2)	Li(1)–N(1)	194.8(4)
S(1)–N(2)	163.2(2)	Li(2a)–N(2)	201.8(5)	S(1)–N(2)	167.5(2)	Li(1)–N(2)	205.7(4)
S(1)–N(3)	167.5(2)	Li(1)–N(3)	205.9(5)	Li(1)–O(1)	184.6(4)	K(1)–N(1)	286.4(2)
Na(2)–O(1)	233.5(2)	Li(2a)–N(3)	201.0(5)	K(2)–O(1)	262.7(2)	K(2)–N(2)	317.8(2)
Na(2)–O(2)	248.6(4)	Na(1)–N(1)	249.3(2)	K(2)–O(2)	270.2(5)	N(1)-S(1)-N(2)	99.3(1)
Na(1)–O(3)	338.9(4)	Na(1)–N(2)	266.8(3)	K(1)–O(3)	281.5(5)	N(1a)-S(1)-N(1)	108.0(1)
Li(1)–O(1)	186.7(5)	N(1)-S(1)-N(2)	106.6(1)				
Li(2)–O(1)	187.1(5)	N(1)-S(1)-N(3)	99.4(1)				
		N(2)-S(1)-N(3)	100.0(1)				

obtained with a Bruker DMX300 instrument. The NMR spectra were recorded with $SiMe_4$ (^1H, ^{13}C) and LiCl (^7Li) as external standards.

Compound 1: $[(\mathrm{thf})_2\mathrm{Li}_4\mathrm{Na}_2(\mathrm{O}t\mathrm{Bu})_2\{(\mathrm{N}t\mathrm{Bu})_3\mathrm{S}\}_2]$ (1.20 g, 2.0 mmol) in THF (20 mL) was treated with NaO*t*Bu (0.39 g, 4.0 mmol). The reaction mixture was stirred for 12 h at room temperature to give an orange solution. The solvent was removed in vacuum until a colorless precipitate started to form. The suspension was redissolved on heating. Storage at room temperature (3 d) gave colorless crystals of **1** (0.7 g, 40 %). M.p. 115 °C (decomp); ^1H NMR (300 MHz, $[D_8]$toluene): $\delta = 1.075$ (s, 18 H, O*t*Bu), 1.158 (s, 9 H, N*t*Bu), 1.230 (s, 18 H, N*t*Bu), 1.279 (m, thf), 3.371 (m, thf); ^{13}C NMR (75 MHz, $[D_8]$toluene): $\delta = 23.48$ ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$, thf), 32.41, 32.80, 34.18 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 51.47, 52.58 ($\mathrm{N}\mathit{C}(\mathrm{CH_3})_3$), 64.81 ($\mathrm{O}\mathit{C}(\mathrm{CH_3})_3$), 65.41 ($\mathrm{O}\mathit{C}\mathrm{H_2}$, thf); ^7Li NMR (117 MHz, $[D_8]$toluene): $\delta = 1.74$.

Compound 2: $[(\mathrm{thf})_2\mathrm{Li}_4\mathrm{K}_2(\mathrm{O}t\mathrm{Bu})_2\{(\mathrm{N}t\mathrm{Bu})_3\mathrm{S}\}_2]$ (1.20 g, 2.0 mmol) in THF (20 mL) was treated with KO*t*Bu (0.45 g, 4.0 mmol). The mixture was stirred for 12 h at room temperature to give an orange solution. The solvent was removed in vacuum until a colorless precipitate started to form. The suspension was redissolved on heating. Storage at room temperature (3 d) gave colorless crystals of **2** (1.1 g, 61 %). M.p. 98 °C (decomp); ^1H NMR (300 MHz, C_6D_6): $\delta = 1.359$, 1.395, 1.461, 1.518, 1.583 (s, 9 H each, *t*Bu), 1.524 (m, thf), 3.691 (m, thf); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 25.72$ ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2}$, thf), 33.70, 34.15, 35.07, 35.57, 35.89 ($\mathrm{C}(\mathit{C}\mathrm{H_3})_3$), 53.40, 53.77, 54.38 ($\mathrm{N}\mathit{C}(\mathrm{CH_3})_3$), 66.89 67.24; ($\mathrm{O}\mathit{C}(\mathrm{CH_3})_3$), 67.85 ($\mathrm{O}\mathit{C}\mathrm{H_2}$, thf); ^7Li NMR (117 MHz, C_6D_6): $\delta = 1.93$, 2.27, 3.34.

X-ray measurements of 1 and 2: All data were collected at low temperatures with oil-coated shock-cooled crystals[25] on a Stoe-Huber-Siemens Eigenbau diffractometer fitted with a Siemens CCD detector and with graphite monochromated $Mo_{K\alpha}$ ($\lambda = 71.073$ pm) radiation. Semiempirical absorption corrections[26] were employed. The structures were solved by direct or Patterson methods with SHELXS-96[27] and refined with all data on F^2 with a weighting scheme with SHELXL-96.[28] All non-hydrogen atoms were refined anisotropically. A riding model was applied in the refinement of the hydrogen atoms. Selected bond lengths and angles of both structures can be found in Table 1, relevant crystallographic data are presented in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101163. 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; e-mail: deposit@ccdc.cam.ac.uk).

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Table 2. Crystal data for **1** and **2** at 193 K.

	1	**2**
formula	$C_{40}H_{88}Li_4N_6Na_2O_4S_2$	$C_{40}H_{88}K_2Li_4N_6O_4S_2$
M_r	855.02	887.24
crystal size [mm]	0.7 × 0.4 × 0.4	0.7 × 0.6 × 0.6
space group	*Pbcn*	*Cmcm*
a [pm]	1697.7(1)	1722.4(1)
b [pm]	1878.5(1)	1884.8(5)
c [pm]	1655.0(1)	1665.0(1)
V [nm³]	5.278(1)	5.405(1)
Z	4	4
ρ_{calcd} [$Mg\,m^{-3}$]	1.076	1.090
μ [mm^{-1}]	0.157	0.291
F(000)	1872	1936
Θ range [°]	2–25	2–25
no. of reflections measured	49681	22162
no. of unique reflections	4502	2579
no. of restraints	130	212
refined parameters	391	278
$R1$[a] [$I > 2\sigma(I)$]	0.068	0.044
$wR2$[b] (all data)	0.161	0.107
$g1$; $g2$[c]	0.049; 4.159	0.039; 5.811
highest diff peak [$10^{-6}\,e\,pm^{-3}$]	0.23	0.20
absorption correction	semiempirical	semiempirical
transmission min; max	0.372; 0.956	0.741; 0.862

[a] $R1 = \Sigma||F_o - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (g1\,P)^2 + g2\,P]$; $P = (F_o^2 + 2\,F_c^2)/3$.

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