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A spatially separated $[KBr_6]^{5-}$ anion in the cyanido-bridged uranium(IV) compound $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$

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Abstract: The reaction of uranium tetrabromide with potassium cyanide in anhydrous liquid ammonia at room temperature leads to the formation of brown crystals of $[U_2(CN)_3(NH_3)_{14}]^{5+}$ $[KBr_6]^{5-} \cdot NH_3$. We determined the crystal structure of the compound by single crystal X-ray diffraction. To the best of our knowledge it contains the unprecedented spatially separated $[KBr_6]^{5-}$ anion and presents the first uranium(IV) cyanide compound which forms a layer structure. The compound crystallizes in the trigonal space group $P\bar{3}m1$ (No. 164) with $a = 10.3246(13)$, $c = 8.4255(17)$ Å, $V = 777.8(3)$ Å^3, $Z = 1$ at $T = 100$ K and is well described with the Niggli formula $^{2}_{\infty}\left[U(CN)_{\frac{3}{2}}(NH_3)_{\frac{7}{1}}\right]_2\left[KBr_{\frac{6}{1}}\right]$.

Keywords: ammonia; bromide; crystal structure; cyanide; uranium.

Dedicated to: Professor Dr. rer. nat. Dr. h.c. mult. Arndt Simon on the occasion of his 80th birthday.

1 Introduction

While a multitude of cyanide complexes of the transition metals are known [1, 2], only a few cyanido complexes of uranium(IV) have been reported [3–10]. The first actinoid compound containing cyanide anions was $K_2[UO_2(CN)_4]$ described by *Aloy*, followed by $K_2[UO_2(CN)_2(NO_3)_2]$ [11, 12]. However, the existence of both compounds was doubted and literature suggests to regard them as non-existent [13, 14]. Besides uranium compounds containing hexacyanido complexes of group eight elements, such as $\{[U(H_2O)_{10}][M(CN)_6]\}$ (M^{II} = Fe, Ru, Os), and some tetracyanidoplatinate(II) complexes like $\{U_2(H_2O)_{10}(O)[Pt(CN)_4]_3\} \cdot 4H_2O$, also some CN⁻-containing compounds with organic ligands are described [15, 16]. These are, for example $[UN^*_3CN]$ ($N^* = N(SiMe_3)_2$) or $[M][(UN^*_3)_2(\mu\text{-CN})]$ (M = K(18-crown-6), $N^* = N(SiMe_3)_2$), of which the crystal structures have been determined [8, 9]. Also, some CN⁻-bridged uranium complexes with sterically demanding ligands are known [6, 7, 9, 17–19]. To the best of our knowledge a pseudo-binary uranium cyanide, such as $U(CN)_4$, is still unknown. Our attempts and investigations on the synthesis of uranium cyanides in liquid ammonia led to the discovery of the light-green compound $[UCl_3(CN) \cdot 4NH_3]$, obtained from UCl_4 and NaCN in liquid NH_3 [3, 20]. The reaction of UCl_4 with one equivalent of KCN in liquid ammonia at room temperature gave green crystals of $[U(CN)(NH_3)_8]Cl_3 \cdot NH_3$ [20]. Uranium tetraiodide, UI_4, reacts with one equivalent of KCN leading to a compound with infinite chains of cyanido- and amido-bridged uranium atoms in the crystal structure [20]. Hexaamminetricyanidouranium(IV) iodide $[U(CN)_3(NH_3)_6]I$ can be obtained by increasing the concentration of KCN and heating the reaction mixture [20]. Here we present the synthesis and crystal structure of the cyanido bridged uranium(IV) compound $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$ that contains, to the best of our knowledge, an unprecedented spatially separated $[KBr_6]^{5-}$ anion.

2 Results and discussion

The reaction of UBr_4 with KCN dissolved in liquid ammonia was carried out in a sealed "bomb tube" at room temperature. Over 6 months of storage and crystallization time some dark brown crystals grew of which the composition was evidenced by X-ray diffraction as tetradecaamminetricyanido-κC,κN-diuranium(IV) hexabromidopotassiate(I) ammonia(1/1) $[U_2(CN)_3(NH_3)_{14}]^{5+}$ $[KBr_6]^{5-} \cdot NH_3$. The formation of this compound can be described by eq. (1).

$$2\,UBr_4 + 15\,NH_3 + 3\,KCN \xrightarrow{NH_{3(l)}} [U_2(CN)_3(NH)_{14}]^{5+} [KBr_6]^{5-} \cdot NH_3 + 2\,KBr \qquad (1)$$

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The compound crystallizes in the trigonal space group $P\bar{3}m1$ (No. 164) with $a = 10.3246(13)$, $c = 8.4255(17)$ Å, $V = 777.8(3)$ Å^3 and $Z = 1$ at $T = 100$ K. Selected crystallographic data and details of the structure determination are available from Table 1. Table 2 contains Wyckoff positions and atom coordinates. The crystal structure of this compound contains the $[KBr_6]^{5-}$ anion and the $[U_2(CN)_3(NH_3)_{14}]^{5+}$ cation, as well as an ammonia molecule of crystallization. The $[KBr_6]^{5-}$ anion and the coordination sphere of the U(IV) cation are shown in Fig. 1.

Table 1: Selected crystallographic data and details of the structure determination of $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$.

Formula	$[U_2(CN)_3(NH_3)_{14}][KBr_6] \cdot NH_3$
Molar mass/g · mol^{-1}	1328.09
Space group (No.)	$P\bar{3}m1$ (164)
a/Å	10.3246(13)
c/Å	8.4255(17)
V/Å^3	777.8(3)
Z	1
Pearson symbol	$hP108$
$\rho_{calcd.}$/g · cm^{-3}	2.84
μ/mm^{-1}	18.3
Color	Brown
Crystal habitus	Block
Crystal size/mm^3	0.1 · 0.1 · 0.05
T/K	100(2)
Radiation; λ/Å	Mo$K\alpha$; 0.71073
No. of reflections	14745
θ range/°	3.322–29.357
Range of Miller indices hkl	±14, ±14, ±11
Absorption correction	multi-scan
T_{max}; T_{min}	0.430; 0.204
Completeness of the data set	0.995
No. of unique reflections	816
R_{int}; R_σ	0.0556; 0.0572
No. of parameters	39
No. of restrains	0
No. of constrains	0
S (all data)	1.247
$R(F)$ ($I > 2\,\sigma(I)$; all data)	0.0555; 0.0571
$wR(F^2)$ ($I > 2\sigma(I)$; all data)	0.1360; 0.1413
Extinction coefficient	0.0102(18)
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e · Å^{-3}	2.57; −2.53

The spatially separated $[KBr_6]^{5-}$ anion is, to the best of our knowledge, not described in the literature to date. However, a inversely comparable species has been observed in the compound $[K_{17}(Sb_8)_2(NH_2)] \cdot 17.5NH_3$, where $[(H_2N)K_6]$ octahedra are present that however form straight, infinite chains through *trans*-corner connections. Thus, a similarity to the crystal structure of KNH_2 was noted [21]. In our case, the $[KBr_6]^{5-}$ anion is spatially separated and contains a potassium atom (1*a*, $\bar{3}m.$) as the central atom, which is surrounded by six symmetry-equivalent bromide anions (6*i*, *.m.*) in the shape of a distorted octahedron. The K–Br distances of such a moiety are therefore all equal with 3.2684(19) Å. This distance is in good agreement with K–Br distances observed for pure KBr (3.289(6) Å, $T = 293$ K) [22]. Interatomic distances are available from Table 3. In the compound K_2ZnBr_4, where the coordination polyhedron around K^+ is a trigonal prism, the K–Br distances agree with 3.240–3.420 Å ($T = 125$ K) [23, 24]. An octahedral coordination polyhedron for potassium cations and bromide anions is also present in the compound $KInBr_3$ [25]. There, the K–Br distances of 3.182(9) and 3.284(9) Å are also comparable with those in the spatially separated anion presented here. The Br–K–Br angles in the distorted coordination octahedron of the $[KBr_6]^{5-}$ anion are 102.52(4) and 77.48(4)°; in good agreement with reported data ($KInBr_3$: 105.09 and 74.01°) [25]. Overall, the shape of the spatially separated $[KBr_6]^{5-}$ anion corresponds well to the literature.

The uranium atom occupies the Wyckoff position 2*d* (3*m*.) and is surrounded by seven ammine ligands and three cyanido ligands. The coordination polyhedron can be described as a slightly distorted sphenocorona (Johnson solid J_{86}). This sphenocorona, with a

Table 2: Atomic coordinates and equivalent isotropic displacement parameters U_{iso} for $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$.

Atom	**Wyckoff position**	***x***	***y***	***z***	**U_{iso}/Å^2**	**S.O.F.**
U(1)	2*d*	1/3	2/3	0.35808(10)	0.0188(4)	1
N(1)	6*i*	0.4707(7)	−*x*	0.4790(14)	0.021(2)	0.5
C(1)	6*i*	0.4707(7)	−*x*	0.4790(14)	0.021(2)	0.5
N(2)	2*d*	1/3	2/3	0.651(2)	0.020(4)	1
N(3)	6*i*	0.4320(7)	−*x*	0.1310(14)	0.025(2)	1
N(4)	6*i*	0.1870(7)	2*x*	0.3585(16)	0.028(3)	1
N(5)	1*b*	0	0	1/2	0.061(13)	1
K(1)	1*a*	0	0	0	0.0341(18)	1
Br(1)	6*i*	0.16461(11)	−*x*	0.8313(2)	0.0417(5)	1

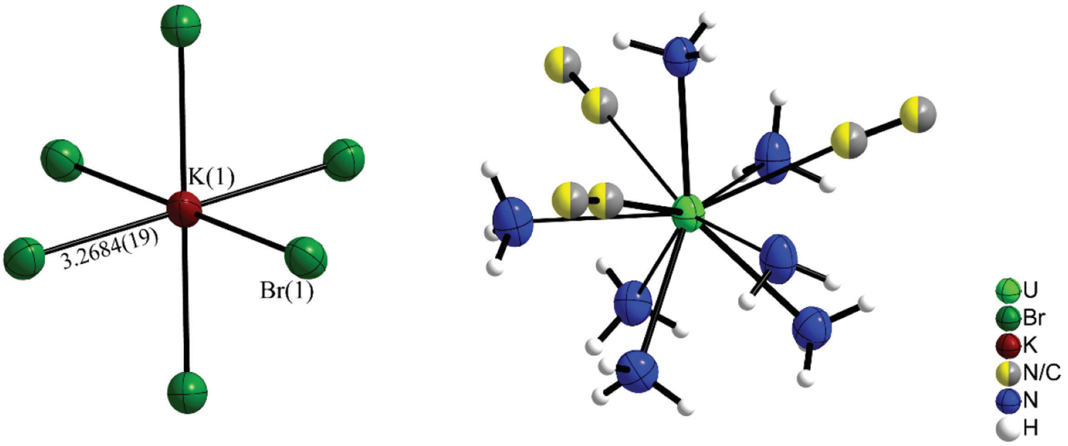

Fig. 1: Section of the crystal structure of $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$, showing the octahedron-like $[KBr_6]^{5-}$ anion (left) and the coordination of the U(IV) cation (right). The displacement ellipsoids are shown at the 70% probability level at $T = 100$ K. As some of the H atoms show site disorder, only one set of positions is shown.

Table 3: Selected interatomic distances *d* and their multiplicities *m* for $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$.

Atom1	Atom2	*m*	*d*/Å
U(1)	N/C(1)	3	2.659(13)
	N(2)	1	2.47(2)
	N(3)	3	2.603(12)
	N(4)	3	2.616(13)
N/C(1)	N/C(1)	1	1.11(3)
K(1)	Br(1)	6	3.2684(19)

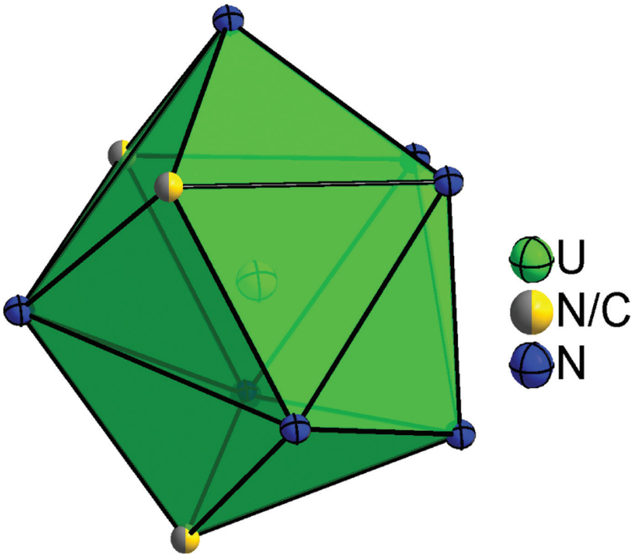

Fig. 2: Section of the crystal structure of $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$, showing the coordination sphere of the uranium atom, which is surrounded by ten ligands in the shape of a slightly distorted sphenocorona (Johnson solid J_{86}). A view along the trigonal prism of the sphenocorona is selected. The displacement ellipsoids are shown at the 70% probability level at $T = 100$ K.

mild distortion of its top quadrangle is shown in Fig. 2. The three disordered cyanido ligands are *κC*,*κN*-bridging two symmetry-equivalent uranium atoms. The C≡N bond length of the disordered cyanido ligand is 1.11(3) Å and despite the disorder it agrees well with C≡N bond lengths of cyanido ligands described in the literature [26–29]. Because of space group symmetry, the C and N atoms of the cyanide anion are indistinguishable and a statistical distribution with a 50:50 mixed site occupancy of the atom position 6*i* (.*m*.) was applied in the refinement. The cyanide anion resides symmetrically in between the bridged U atoms. The U–N distances for the seven ammine ligands range from 2.47(2) to 2.659(13) Å and are also in good agreement with distances observed for ammine ligands in the uranium-ammonia system [20]. Because of the different distances between the uranium atom and the ten ligands, the sphenocorona is slightly distorted. As the U atoms are bridged by the cyanido ligands, the complex cation forms corrugated infinite layers parallel to the *ab* plane. This connection can be described by the Niggli formula $^{2}_{\infty}\left\{\left[U(CN)_{\frac{3}{2}}(NH_3)_{\frac{7}{1}}\right]\right\}$. A section of one layer is shown in Fig. 3 left. As every sphenocorona is connected to three others, a motif of packed sphenocoronas is obtained that reminds of the arrangement of As atoms in the crystal structure of grey arsenic (Fig. 3 right), which is best seen when viewed parallel to the *c* axis. Overall, the sphenocoronas show AB stacking, that is, the AB layers are stacked directly above each other and channels parallel to the *c* axis result (Fig. 3 right).

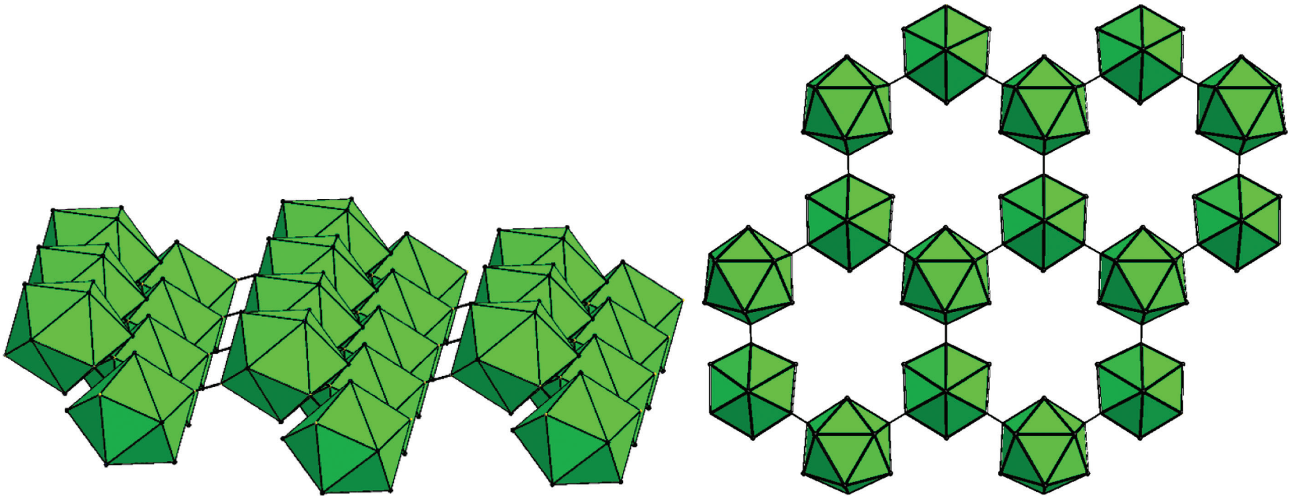

Fig. 3: Section of the crystal structure showing a corrugated $^{2}_{\infty}\{[\mathrm{U(CN)}_{\frac{3}{2}}(\mathrm{NH_3})_{\frac{7}{1}}]\}$ layer (left) and a view along the *c* axis (right).

The $[\mathrm{KBr_6}]^{5-}$ anions fill the octahedral voids, with the potassium atom K(1) occupying the Wyckoff position 1*a* ($\bar{3}m.$). The complex anion can be described by the Niggli formula $^{0}_{\infty}\{[\mathrm{KBr}_{\frac{6}{1}}]\}$. The motif of the arrangement of sphenocoronas and $[\mathrm{KBr_6}]^{5-}$ anions corresponds overall to an ABC-type stacking. Leaving the Br, C, and N atoms aside and looking only on the arrangement of the K and U atoms, one recognizes that the K atoms are surrounded octahedron-like by U atoms. These octahedra reside in the *ab* planes and share common edges corresponding to the Niggli formula $^{2}_{\infty}\{[\mathrm{KU}_{\frac{6}{3}}]\}$. The arrangement of the potassium and uranium atoms reminds of the $\mathrm{Ag_2F}$ structure type [30]. The ammonia molecules of crystallization, with the N(5) atom on the 1*b* ($\bar{3}m.$) position, are thus also surrounded octahedron-like by six uranium atoms, however these octahedra are strongly compressed along the threefold symmetry axis parallel to the crystallographic *c* axis. These polyhedra form $^{2}_{\infty}\{[\mathrm{NU}_{\frac{6}{3}}]\}$ layers which reside at $z=1/2$ parallel to the *ab* plane. Thus, the layers of $^{2}_{\infty}\{[\mathrm{NU}_{\frac{6}{3}}]\}$ octahedra are sharing common faces with the $^{2}_{\infty}\{[\mathrm{KU}_{\frac{6}{3}}]\}$ octahedra. The crystal structure of the compound is shown in Fig. 4.

Between the layers of the interconnected uranium atoms and the spatially separated $[\mathrm{KBr_6}]^{5-}$ anions the only attractive interactions are N–H···Br hydrogen bonds. The hydrogen atoms of the ammine ligands (N(2), N(3) and N(4)) form hydrogen bonds to the bromine atoms Br(1). The donor···acceptor distances of these hydrogen bonds range from 3.377(10) to 3.642(8) Å. This is in good agreement with known N–H···Br hydrogen bonds for example in $[\mathrm{Co(NH_3)_6}]\mathrm{Br(S_2O_3)}\cdot\mathrm{H_2O}$ (3.509(4) to 3.539(3) Å, $T=295$ K) or in $[\mathrm{CoCO_3(NH_3)_5}]\mathrm{Br}\cdot\mathrm{H_2O}$ (3.41–3.63 Å) [31, 32].

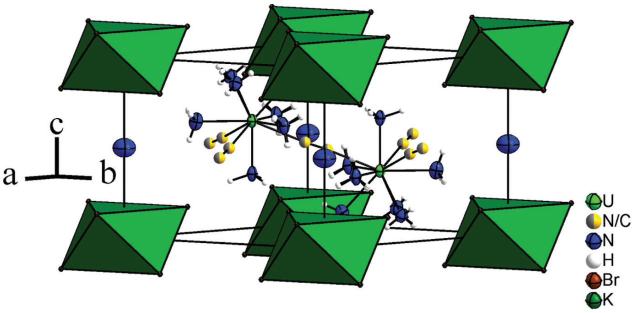

Fig. 4: Section of the crystal structure of $[\mathrm{U_2(CN)_3(NH_3)_{14}}]^{5+}[\mathrm{KBr_6}]^{5-}\cdot\mathrm{NH_3}$. The $[\mathrm{KBr_6}]^{5-}$ anions are shown as dark green polyhedra. Displacement ellipsoids are shown at the 70% probability level at $T=100$ K, H atoms isotropic with arbitrary radii. H atoms of the ammonia molecules of crystallization could not be located.

3 Conclusions

Single crystals of $[\mathrm{U_2(CN)_3(NH_3)_{14}}]^{5+}[\mathrm{KBr_6}]^{5-}\cdot\mathrm{NH_3}$ ($P\bar{3}m1$, No. 164) were obtained by the reaction of $\mathrm{UBr_4}$ and KCN dissolved in liquid ammonia at room temperature over several months of crystallization time. The crystal structure of this compound has been determined and found to contain two peculiar building units: (i) The uranium atoms are coordinated by ten ligands in total of which seven are ammine and three are cyanido ligands. The coordination sphere of the U atom is described best as a sphenocorona. The connection of the κ*C*,κ*N*-cyanido bridged uranium atoms leads to the formation of infinite corrugated layers of sphenocoronas. (ii) The unprecedented spatially separated, octahedron-like $[KBr_6]^{5-}$ anion could be observed for the first time.

4 Experimental section

All work was carried out excluding moisture and air in an atmosphere of dried and purified argon (5.0, Praxair) using high vacuum glass lines and a glovebox (MBraun). The glass vessels were flame dried several times under vacuum before being used. Aluminum bromide (Alfa Aesar, 98%) was purified by sublimation *in vacuo*. Aluminum (Fluka, purum >99%), as well as uranyl nitrate (Riedel de Haën, zur Analyse), was used as supplied.

4.1 Synthesis of UO_2

12.8 g of $UO_2(NO_3)_2 \cdot 6H_2O$ (25.4 mmol) was decomposed to 7.13 g U_3O_8 (8.47 mmol) by heating to 700°C in air for 12 h inside an open silica test tube. The black product was powdered in air and reduced in a stream of hydrogen at 800°C for 8 h to obtain 6.86 g (24.9 mmol, 98%) of phase pure UO_2.

4.2 Synthesis of UBr_4

UBr_4 was synthesized according to the literature [33]. An ampoule was charged with 1088 mg UO_2 (4 mmol) and 2150 + 65 mg $AlBr_3$ (8 mmol + transport agent) and flame sealed under vacuum (1×10^{-3} mbar). The starting materials were reacted at 250°C for 12 h before the transport reaction was conducted with a source temperature of 350°C and a sink temperature of 230°C. One thousand nine hundred and seventy-eight milligram (4.3 mmol, 86%) of large brown plate-shaped crystals of UBr_4 were obtained after 6 days.

4.3 Synthesis of $[U_2(CN)_3(NH_3)_{14}]^{5+}[KBr_6]^{5-} \cdot NH_3$

Thirty milligram of UBr_4 (0.05 mmol) and 13 mg of KCN (0.2 mmol, 4 eq.) were reacted with liquid ammonia in a flame sealed glass ampoule (bomb tube made of borosilicate glass, 6 mm diameter with 1.5 mm wall thickness) at room temperature for 6 months.

4.4 Single-crystal X-ray diffraction

A crystal of the title compound was selected under nitrogen-cooled, pre-dried perfluorinated oil and mounted using a MiTeGen loop. Intensity data of a suitable crystal was recorded with an IPDS 2T diffractometer (STOE & Cie). The diffractometer was operated with Mo*Kα* radiation ($\lambda = 0.71073$ Å, graphite monochromator) and equipped with an image plate detector. Evaluation, integration and reduction of the diffraction data was carried out using the X-AREA software suite [34]. A numerical absorption correction was applied with the modules X-SHAPE and X-RED32 of the X-AREA software suite. The structure was solved with dual-space methods (SHELXT-2014/5) and refined against F^2 (SHELXL-2014/7) [35, 36]. All atoms were refined with anisotropic displacement parameters. The highest residual electron density after the final refinement was 1.142 Å distant from atom K(1).

CCDC 1959129 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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Graphical synopsis

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