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(18-Crown-6- κ^6O)(pyrazolato- κ^2N,N')-potassium(I)

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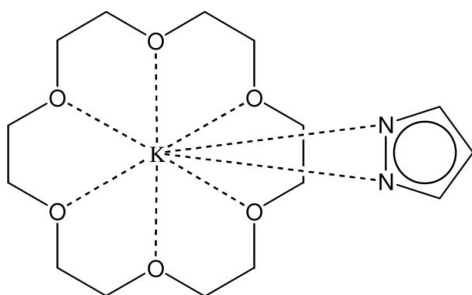
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(C-C) = 0.002$ Å; R factor = 0.026; wR factor = 0.066; data-to-parameter ratio = 16.5.

The asymmetric unit of the title compound, $[K(C_3H_3N_2)(C_{12}H_{24}O_6)]$, is composed of a potassium cation bonded to the six O atoms of a crown ether molecule and the two N atoms of a pyrazolate anion. The $K \cdots O$ distances range from 2.8416 (8) to 3.0025 (8) Å, and the two $K \cdots N$ distances are 2.7441 (11) and 2.7654 (11) Å. The K cation is displaced by 0.8437 (4) Å from the best plane through the six O atoms. The latter plane is almost perpendicular to the plane of the pyrazolate ring [dihedral angle 83.93 (3)°].

Related literature

 For related literature on scorpionate complexes, see: Bieller *et al.* (2006); Morawitz *et al.* (2008); Trofimenko (1993).


Experimental

Crystal data

 $[K(C_3H_3N_2)(C_{12}H_{24}O_6)]$
 $M_r = 370.49$
 Monoclinic, $P2_1/n$
 $a = 11.5330$ (6) Å
 $b = 8.2369$ (5) Å
 $c = 20.7622$ (10) Å
 $\beta = 101.612$ (4)°

 $V = 1931.96$ (18) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.31$ mm⁻¹
 $T = 173$ (2) K
 $0.25 \times 0.12 \times 0.12$ mm

Data collection

 STOE IPDS II two-circle-diffractometer
 Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)
 $T_{\min} = 0.919$, $T_{\max} = 0.966$

 23118 measured reflections
 3602 independent reflections
 3234 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.066$
 $S = 1.03$
 3602 reflections

 218 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Data collection: X-Area (Stoe & Cie, 2001); cell refinement: X-Area; data reduction: X-Area; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL-Plus (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2281).

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supplementary materials

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(18-Crown-6- κ^6O)(pyrazolato- κ^2N,N')-potassium(I)

K. Kunz, H.-W. Lerner and M. Bolte

Comment

We report here the X-ray crystal structure analysis of the potassium pyrazolide as complex with 18-crown-6, [K(18-crown-6)(C₃H₃N₂)] or [K(18-crown-6)(pz)]. Following the first synthesis of a scorpionate complex, considerable progress has been made towards extending this area of chemistry (Trofimenko, 1993). Our studies have shown that an important factor influencing the stability of scorpionates appears to be the degree of steric crowding around the boron centre. The results of investigations in our group show that the scorpionates RB(3-*R'*pz)₃⁻ and RB(4-*R'*pz)₃⁻ decompose in the presence of transition metal salts much more easily when *R* and *R'* are bulky (Bieller *et al.*, 2006; Morawitz *et al.*, 2008). Now we have found that irradiation of Mn(C₅H₃)(Bpz₃)₂(THF)₂ (I) in the presence of 18-crown-6 leads to the formation of potassium pyrazolide (II).

The asymmetric unit of the title compound, [C₁₂H₂₄O₆]K⁺[C₃H₃N₂]⁻, is composed of a potassium cation bonded to the six O atoms of a crown ether molecule and the two N atoms of a pyrazolate anion. The K...O distances range from 2.8416 (8) Å to 3.0025 (8) Å, and the two K...N distances are 2.7441 (11) Å and 2.7654 (11) Å. The K cation is displaced by 0.8437 (4) Å from the best plane through the six O atoms. The latter plane is almost perpendicular to the plane of the pyrazolate ring [dihedral angle 83.93 (3) °].

Experimental

Mn(C₅H₃)(Bpz₃)₂(THF)₂ (64 mg, 75.4 μmol) was dissolved in THF (25 ml). The solution was irradiated using an UV lamp (TQ 150, λ_{max} = 510 nm) for 16 h, whereupon the colourless solution turned orange. After stirring overnight at ambient temperature the reaction mixture was treated with 18-crown-6 (20 mg, 81.2 μmol) and was stirred for 10 minutes. After a small amount of colourless precipitate had been removed by filtration, the clear filtrate was evaporated to dryness *in vacuo*. Single crystals of (II) were grown from a solution of (II) in THF at -35°C.

Refinement

H atoms were geometrically positioned and refined using a riding model with fixed individual displacement parameters [U(H) = 1.2 U_{eq}(C)] and with C_{aromatic}-H = 0.95 Å and C_{methylene}-H = 0.99 Å.

Figures

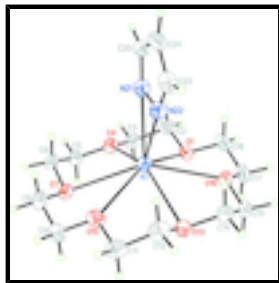


Fig. 1. Perspective view of the title compound with the atom numbering scheme. Displacement ellipsoids are at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii.

(18-Crown-6)(pyrazolato- κ^2N,N')potassium(I)

Crystal data

[K(C₃H₃N₂)(C₁₂H₂₄O₆)]

$M_r = 370.49$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 11.5330$ (6) Å

$b = 8.2369$ (5) Å

$c = 20.7622$ (10) Å

$\beta = 101.612$ (4)°

$V = 1931.96$ (18) Å³

$Z = 4$

$F(000) = 792$

$D_x = 1.274$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 23906 reflections

$\theta = 2.5$ – 25.9 °

$\mu = 0.31$ mm⁻¹

$T = 173$ K

Needle, colourless

$0.25 \times 0.12 \times 0.12$ mm

Data collection

STOE IPDS II two-circle-diffractometer

Radiation source: fine-focus sealed tube graphite

ω scans

Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)

$T_{\min} = 0.919$, $T_{\max} = 0.966$

23118 measured reflections

3602 independent reflections

3234 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 25.6$ °, $\theta_{\min} = 2.7$ °

$h = -12 \rightarrow 14$

$k = -9 \rightarrow 9$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.066$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 0.3751P]$

where $P = (F_o^2 + 2F_c^2)/3$

| | |
|--|---|
| $S = 1.03$ | $(\Delta/\sigma)_{\max} = 0.001$ |
| 3602 reflections | $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$ |
| 218 parameters | $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$ |
| 0 restraints | Extinction correction: <i>SHELXL</i> , $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.0099 (8) |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|---------------|----------------------------------|
| K1 | 0.50031 (2) | 0.36001 (3) | 0.173982 (11) | 0.02711 (9) |
| O1 | 0.70384 (7) | 0.33603 (10) | 0.10488 (4) | 0.03149 (19) |
| C2 | 0.72895 (12) | 0.16959 (15) | 0.09518 (6) | 0.0375 (3) |
| H2A | 0.7929 | 0.1606 | 0.0699 | 0.045* |
| H2B | 0.6576 | 0.1149 | 0.0700 | 0.045* |
| C3 | 0.76649 (11) | 0.09050 (15) | 0.16099 (6) | 0.0341 (3) |
| H3A | 0.7879 | -0.0243 | 0.1554 | 0.041* |
| H3B | 0.8366 | 0.1469 | 0.1866 | 0.041* |
| O4 | 0.67091 (7) | 0.09896 (9) | 0.19483 (4) | 0.02900 (18) |
| C5 | 0.69922 (11) | 0.02037 (14) | 0.25736 (6) | 0.0316 (3) |
| H5A | 0.7675 | 0.0750 | 0.2856 | 0.038* |
| H5B | 0.7209 | -0.0943 | 0.2517 | 0.038* |
| C6 | 0.59374 (11) | 0.02826 (13) | 0.28891 (6) | 0.0312 (3) |
| H6A | 0.5233 | -0.0153 | 0.2585 | 0.037* |
| H6B | 0.6078 | -0.0382 | 0.3295 | 0.037* |
| O7 | 0.57370 (7) | 0.19353 (9) | 0.30449 (4) | 0.02792 (18) |
| C8 | 0.48115 (11) | 0.20382 (16) | 0.34087 (6) | 0.0369 (3) |
| H8A | 0.5059 | 0.1486 | 0.3838 | 0.044* |
| H8B | 0.4093 | 0.1489 | 0.3164 | 0.044* |
| C9 | 0.45417 (11) | 0.37812 (16) | 0.35159 (6) | 0.0358 (3) |
| H9A | 0.3904 | 0.3860 | 0.3770 | 0.043* |
| H9B | 0.5254 | 0.4330 | 0.3768 | 0.043* |
| O10 | 0.41787 (7) | 0.45411 (10) | 0.28931 (4) | 0.0337 (2) |
| C11 | 0.38264 (12) | 0.61956 (15) | 0.29539 (6) | 0.0373 (3) |
| H11A | 0.4487 | 0.6822 | 0.3219 | 0.045* |

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|------|--------------|--------------|-------------|--------------|
| H11B | 0.3143 | 0.6243 | 0.3176 | 0.045* |
| C12 | 0.34937 (11) | 0.68958 (16) | 0.22762 (7) | 0.0390 (3) |
| H12A | 0.2892 | 0.6198 | 0.2000 | 0.047* |
| H12B | 0.3147 | 0.7989 | 0.2298 | 0.047* |
| O13 | 0.45191 (7) | 0.70035 (10) | 0.19903 (4) | 0.03146 (19) |
| C14 | 0.42386 (12) | 0.77471 (15) | 0.13533 (6) | 0.0396 (3) |
| H14A | 0.3977 | 0.8880 | 0.1394 | 0.047* |
| H14B | 0.3586 | 0.7147 | 0.1069 | 0.047* |
| C15 | 0.53103 (13) | 0.77270 (14) | 0.10522 (6) | 0.0397 (3) |
| H15A | 0.5160 | 0.8371 | 0.0641 | 0.048* |
| H15B | 0.5988 | 0.8219 | 0.1359 | 0.048* |
| O16 | 0.55811 (8) | 0.60970 (9) | 0.09139 (4) | 0.03225 (19) |
| C17 | 0.65728 (12) | 0.59892 (16) | 0.05956 (6) | 0.0390 (3) |
| H17A | 0.7291 | 0.6427 | 0.0887 | 0.047* |
| H17B | 0.6418 | 0.6632 | 0.0184 | 0.047* |
| C18 | 0.67551 (12) | 0.42399 (17) | 0.04447 (6) | 0.0396 (3) |
| H18A | 0.6026 | 0.3793 | 0.0167 | 0.047* |
| H18B | 0.7408 | 0.4138 | 0.0202 | 0.047* |
| N21 | 0.32022 (9) | 0.19783 (12) | 0.09279 (5) | 0.0333 (2) |
| N22 | 0.27171 (9) | 0.34696 (12) | 0.10107 (5) | 0.0347 (2) |
| C23 | 0.16225 (12) | 0.34869 (17) | 0.06409 (6) | 0.0405 (3) |
| H23 | 0.1094 | 0.4381 | 0.0609 | 0.049* |
| C24 | 0.13632 (13) | 0.20214 (18) | 0.03103 (6) | 0.0444 (3) |
| H24 | 0.0654 | 0.1709 | 0.0019 | 0.053* |
| C25 | 0.23868 (13) | 0.11318 (16) | 0.05093 (6) | 0.0387 (3) |
| H25 | 0.2499 | 0.0057 | 0.0368 | 0.046* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|-------------|-------------|
| K1 | 0.02916 (14) | 0.02496 (13) | 0.02754 (13) | -0.00022 (9) | 0.00652 (9) | 0.00046 (9) |
| O1 | 0.0406 (5) | 0.0316 (4) | 0.0228 (4) | -0.0045 (4) | 0.0075 (3) | -0.0025 (3) |
| C2 | 0.0438 (7) | 0.0348 (6) | 0.0376 (6) | -0.0046 (5) | 0.0171 (5) | -0.0118 (5) |
| C3 | 0.0315 (6) | 0.0282 (6) | 0.0451 (7) | 0.0019 (5) | 0.0140 (5) | -0.0058 (5) |
| O4 | 0.0277 (4) | 0.0273 (4) | 0.0321 (4) | 0.0044 (3) | 0.0064 (3) | 0.0016 (3) |
| C5 | 0.0347 (6) | 0.0243 (5) | 0.0333 (6) | 0.0070 (5) | 0.0008 (5) | 0.0029 (4) |
| C6 | 0.0368 (6) | 0.0217 (5) | 0.0335 (6) | -0.0004 (5) | 0.0030 (5) | 0.0039 (4) |
| O7 | 0.0281 (4) | 0.0248 (4) | 0.0323 (4) | -0.0005 (3) | 0.0096 (3) | 0.0020 (3) |
| C8 | 0.0344 (6) | 0.0399 (7) | 0.0404 (7) | -0.0027 (5) | 0.0172 (5) | 0.0077 (5) |
| C9 | 0.0364 (7) | 0.0442 (7) | 0.0308 (6) | 0.0010 (5) | 0.0161 (5) | 0.0006 (5) |
| O10 | 0.0379 (5) | 0.0327 (4) | 0.0324 (4) | 0.0066 (3) | 0.0114 (3) | -0.0026 (3) |
| C11 | 0.0365 (7) | 0.0350 (6) | 0.0440 (7) | 0.0067 (5) | 0.0166 (5) | -0.0078 (5) |
| C12 | 0.0308 (6) | 0.0353 (6) | 0.0506 (7) | 0.0106 (5) | 0.0076 (5) | -0.0033 (6) |
| O13 | 0.0326 (4) | 0.0292 (4) | 0.0309 (4) | 0.0047 (3) | 0.0022 (3) | 0.0008 (3) |
| C14 | 0.0527 (8) | 0.0266 (6) | 0.0340 (6) | 0.0080 (5) | -0.0041 (6) | 0.0017 (5) |
| C15 | 0.0595 (8) | 0.0254 (6) | 0.0309 (6) | -0.0083 (6) | 0.0010 (6) | 0.0042 (5) |
| O16 | 0.0400 (5) | 0.0275 (4) | 0.0293 (4) | -0.0071 (3) | 0.0070 (3) | 0.0027 (3) |
| C17 | 0.0415 (7) | 0.0466 (7) | 0.0294 (6) | -0.0077 (6) | 0.0086 (5) | 0.0126 (5) |

| | | | | | | |
|-----|------------|------------|------------|-------------|-------------|-------------|
| C18 | 0.0452 (7) | 0.0526 (8) | 0.0224 (5) | -0.0014 (6) | 0.0104 (5) | 0.0028 (5) |
| N21 | 0.0387 (6) | 0.0322 (5) | 0.0298 (5) | -0.0024 (4) | 0.0092 (4) | 0.0017 (4) |
| N22 | 0.0397 (6) | 0.0325 (5) | 0.0331 (5) | -0.0026 (4) | 0.0099 (4) | 0.0003 (4) |
| C23 | 0.0384 (7) | 0.0470 (7) | 0.0373 (7) | 0.0047 (6) | 0.0107 (5) | 0.0084 (6) |
| C24 | 0.0434 (7) | 0.0596 (9) | 0.0271 (6) | -0.0151 (6) | -0.0002 (5) | 0.0047 (6) |
| C25 | 0.0556 (8) | 0.0352 (6) | 0.0265 (6) | -0.0092 (6) | 0.0107 (5) | -0.0017 (5) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|------------|-------------|
| K1—N21 | 2.7441 (11) | C9—H9B | 0.9900 |
| K1—N22 | 2.7654 (11) | O10—C11 | 1.4349 (14) |
| K1—O16 | 2.8416 (8) | C11—C12 | 1.4976 (19) |
| K1—O10 | 2.8557 (8) | C11—H11A | 0.9900 |
| K1—O4 | 2.8877 (8) | C11—H11B | 0.9900 |
| K1—O13 | 2.9254 (8) | C12—O13 | 1.4286 (15) |
| K1—O1 | 2.9938 (9) | C12—H12A | 0.9900 |
| K1—O7 | 3.0025 (8) | C12—H12B | 0.9900 |
| K1—C12 | 3.5242 (12) | O13—C14 | 1.4341 (14) |
| O1—C2 | 1.4239 (15) | C14—C15 | 1.493 (2) |
| O1—C18 | 1.4282 (14) | C14—H14A | 0.9900 |
| C2—C3 | 1.4969 (18) | C14—H14B | 0.9900 |
| C2—H2A | 0.9900 | C15—O16 | 1.4207 (15) |
| C2—H2B | 0.9900 | C15—H15A | 0.9900 |
| C3—O4 | 1.4231 (14) | C15—H15B | 0.9900 |
| C3—H3A | 0.9900 | O16—C17 | 1.4343 (15) |
| C3—H3B | 0.9900 | C17—C18 | 1.498 (2) |
| O4—C5 | 1.4284 (13) | C17—H17A | 0.9900 |
| C5—C6 | 1.4946 (17) | C17—H17B | 0.9900 |
| C5—H5A | 0.9900 | C18—H18A | 0.9900 |
| C5—H5B | 0.9900 | C18—H18B | 0.9900 |
| C6—O7 | 1.4287 (13) | N21—C25 | 1.3405 (16) |
| C6—H6A | 0.9900 | N21—N22 | 1.3748 (15) |
| C6—H6B | 0.9900 | N22—C23 | 1.3391 (17) |
| O7—C8 | 1.4290 (14) | C23—C24 | 1.391 (2) |
| C8—C9 | 1.4951 (18) | C23—H23 | 0.9500 |
| C8—H8A | 0.9900 | C24—C25 | 1.380 (2) |
| C8—H8B | 0.9900 | C24—H24 | 0.9500 |
| C9—O10 | 1.4216 (14) | C25—H25 | 0.9500 |
| C9—H9A | 0.9900 | | |
| N21—K1—N22 | 28.90 (3) | C9—C8—H8B | 109.7 |
| N21—K1—O16 | 102.83 (3) | H8A—C8—H8B | 108.2 |
| N22—K1—O16 | 90.65 (3) | O10—C9—C8 | 108.63 (10) |
| N21—K1—O10 | 107.98 (3) | O10—C9—H9A | 110.0 |
| N22—K1—O10 | 91.60 (3) | C8—C9—H9A | 110.0 |
| O16—K1—O10 | 117.88 (2) | O10—C9—H9B | 110.0 |
| N21—K1—O4 | 97.94 (3) | C8—C9—H9B | 110.0 |
| N22—K1—O4 | 126.79 (3) | H9A—C9—H9B | 108.3 |
| O16—K1—O4 | 113.20 (2) | C9—O10—C11 | 112.02 (9) |
| O10—K1—O4 | 114.09 (2) | C9—O10—K1 | 123.81 (6) |

supplementary materials

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|------------|-------------|---------------|-------------|
| N21—K1—O13 | 115.33 (3) | C11—O10—K1 | 118.66 (7) |
| N22—K1—O13 | 86.54 (3) | O10—C11—C12 | 107.85 (10) |
| O16—K1—O13 | 59.34 (2) | O10—C11—H11A | 110.1 |
| O10—K1—O13 | 58.88 (2) | C12—C11—H11A | 110.1 |
| O4—K1—O13 | 146.67 (2) | O10—C11—H11B | 110.1 |
| N21—K1—O1 | 104.07 (3) | C12—C11—H11B | 110.1 |
| N22—K1—O1 | 119.22 (3) | H11A—C11—H11B | 108.4 |
| O16—K1—O1 | 57.10 (2) | O13—C12—C11 | 109.71 (10) |
| O10—K1—O1 | 147.69 (2) | O13—C12—K1 | 54.11 (5) |
| O4—K1—O1 | 56.39 (2) | C11—C12—K1 | 87.18 (7) |
| O13—K1—O1 | 110.15 (2) | O13—C12—H12A | 109.7 |
| N21—K1—O7 | 111.90 (3) | C11—C12—H12A | 109.7 |
| N22—K1—O7 | 122.74 (3) | K1—C12—H12A | 72.7 |
| O16—K1—O7 | 144.82 (2) | O13—C12—H12B | 109.7 |
| O10—K1—O7 | 56.51 (2) | C11—C12—H12B | 109.7 |
| O4—K1—O7 | 57.65 (2) | K1—C12—H12B | 160.8 |
| O13—K1—O7 | 107.84 (2) | H12A—C12—H12B | 108.2 |
| O1—K1—O7 | 107.25 (2) | C12—O13—C14 | 110.96 (9) |
| N21—K1—C12 | 102.02 (3) | C12—O13—K1 | 102.58 (7) |
| N22—K1—C12 | 74.09 (3) | C14—O13—K1 | 105.13 (6) |
| O16—K1—C12 | 79.86 (3) | O13—C14—C15 | 109.23 (10) |
| O10—K1—C12 | 42.01 (3) | O13—C14—H14A | 109.8 |
| O4—K1—C12 | 153.02 (3) | C15—C14—H14A | 109.8 |
| O13—K1—C12 | 23.31 (3) | O13—C14—H14B | 109.8 |
| O1—K1—C12 | 133.39 (3) | C15—C14—H14B | 109.8 |
| O7—K1—C12 | 97.71 (3) | H14A—C14—H14B | 108.3 |
| C2—O1—C18 | 112.41 (9) | O16—C15—C14 | 109.22 (10) |
| C2—O1—K1 | 109.43 (6) | O16—C15—H15A | 109.8 |
| C18—O1—K1 | 108.93 (7) | C14—C15—H15A | 109.8 |
| O1—C2—C3 | 108.64 (9) | O16—C15—H15B | 109.8 |
| O1—C2—H2A | 110.0 | C14—C15—H15B | 109.8 |
| C3—C2—H2A | 110.0 | H15A—C15—H15B | 108.3 |
| O1—C2—H2B | 110.0 | C15—O16—C17 | 112.31 (9) |
| C3—C2—H2B | 110.0 | C15—O16—K1 | 118.32 (7) |
| H2A—C2—H2B | 108.3 | C17—O16—K1 | 122.61 (7) |
| O4—C3—C2 | 108.59 (10) | O16—C17—C18 | 108.32 (10) |
| O4—C3—H3A | 110.0 | O16—C17—H17A | 110.0 |
| C2—C3—H3A | 110.0 | C18—C17—H17A | 110.0 |
| O4—C3—H3B | 110.0 | O16—C17—H17B | 110.0 |
| C2—C3—H3B | 110.0 | C18—C17—H17B | 110.0 |
| H3A—C3—H3B | 108.4 | H17A—C17—H17B | 108.4 |
| C3—O4—C5 | 111.62 (9) | O1—C18—C17 | 108.73 (10) |
| C3—O4—K1 | 122.31 (6) | O1—C18—H18A | 109.9 |
| C5—O4—K1 | 119.86 (6) | C17—C18—H18A | 109.9 |
| O4—C5—C6 | 108.74 (9) | O1—C18—H18B | 109.9 |
| O4—C5—H5A | 109.9 | C17—C18—H18B | 109.9 |
| C6—C5—H5A | 109.9 | H18A—C18—H18B | 108.3 |
| O4—C5—H5B | 109.9 | C25—N21—N22 | 107.20 (10) |
| C6—C5—H5B | 109.9 | C25—N21—K1 | 175.53 (9) |

| | | | |
|---------------|-------------|-----------------|--------------|
| H5A—C5—H5B | 108.3 | N22—N21—K1 | 76.41 (6) |
| O7—C6—C5 | 108.89 (9) | C23—N22—N21 | 107.35 (10) |
| O7—C6—H6A | 109.9 | C23—N22—K1 | 176.68 (9) |
| C5—C6—H6A | 109.9 | N21—N22—K1 | 74.69 (6) |
| O7—C6—H6B | 109.9 | N22—C23—C24 | 110.97 (12) |
| C5—C6—H6B | 109.9 | N22—C23—H23 | 124.5 |
| H6A—C6—H6B | 108.3 | C24—C23—H23 | 124.5 |
| C6—O7—C8 | 110.38 (9) | C25—C24—C23 | 103.12 (11) |
| C6—O7—K1 | 105.07 (6) | C25—C24—H24 | 128.4 |
| C8—O7—K1 | 110.19 (7) | C23—C24—H24 | 128.4 |
| O7—C8—C9 | 109.61 (9) | N21—C25—C24 | 111.35 (12) |
| O7—C8—H8A | 109.7 | N21—C25—H25 | 124.3 |
| C9—C8—H8A | 109.7 | C24—C25—H25 | 124.3 |
| O7—C8—H8B | 109.7 | | |
| N21—K1—O1—C2 | -57.90 (8) | O10—C11—C12—O13 | -66.75 (13) |
| N22—K1—O1—C2 | -84.52 (8) | O10—C11—C12—K1 | -16.62 (9) |
| O16—K1—O1—C2 | -154.25 (8) | N21—K1—C12—O13 | -127.69 (7) |
| O10—K1—O1—C2 | 114.66 (8) | N22—K1—C12—O13 | -120.20 (7) |
| O4—K1—O1—C2 | 32.36 (7) | O16—K1—C12—O13 | -26.59 (6) |
| O13—K1—O1—C2 | 177.93 (7) | O10—K1—C12—O13 | 128.70 (8) |
| O7—K1—O1—C2 | 60.82 (7) | O4—K1—C12—O13 | 95.46 (8) |
| C12—K1—O1—C2 | 179.95 (7) | O1—K1—C12—O13 | -4.80 (8) |
| N21—K1—O1—C18 | 65.36 (7) | O7—K1—C12—O13 | 117.87 (7) |
| N22—K1—O1—C18 | 38.75 (8) | N21—K1—C12—C11 | 115.40 (8) |
| O16—K1—O1—C18 | -30.99 (7) | N22—K1—C12—C11 | 122.89 (8) |
| O10—K1—O1—C18 | -122.08 (8) | O16—K1—C12—C11 | -143.49 (8) |
| O4—K1—O1—C18 | 155.62 (8) | O10—K1—C12—C11 | 11.80 (7) |
| O13—K1—O1—C18 | -58.81 (7) | O4—K1—C12—C11 | -21.45 (11) |
| O7—K1—O1—C18 | -175.92 (7) | O13—K1—C12—C11 | -116.90 (11) |
| C12—K1—O1—C18 | -56.79 (8) | O1—K1—C12—C11 | -121.70 (7) |
| C18—O1—C2—C3 | 175.73 (10) | O7—K1—C12—C11 | 0.96 (8) |
| K1—O1—C2—C3 | -63.09 (10) | C11—C12—O13—C14 | -177.06 (10) |
| O1—C2—C3—O4 | 62.21 (12) | K1—C12—O13—C14 | 111.83 (9) |
| C2—C3—O4—C5 | 177.94 (9) | C11—C12—O13—K1 | 71.11 (10) |
| C2—C3—O4—K1 | -29.89 (12) | N21—K1—O13—C12 | 58.90 (7) |
| N21—K1—O4—C3 | 101.35 (8) | N22—K1—O13—C12 | 56.37 (7) |
| N22—K1—O4—C3 | 103.29 (8) | O16—K1—O13—C12 | 149.19 (7) |
| O16—K1—O4—C3 | -6.34 (8) | O10—K1—O13—C12 | -37.60 (7) |
| O10—K1—O4—C3 | -144.84 (8) | O4—K1—O13—C12 | -124.72 (7) |
| O13—K1—O4—C3 | -75.35 (9) | O1—K1—O13—C12 | 176.29 (7) |
| O1—K1—O4—C3 | -0.30 (7) | O7—K1—O13—C12 | -66.97 (7) |
| O7—K1—O4—C3 | -147.70 (8) | N21—K1—O13—C14 | -57.21 (8) |
| C12—K1—O4—C3 | -121.14 (9) | N22—K1—O13—C14 | -59.73 (7) |
| N21—K1—O4—C5 | -108.68 (8) | O16—K1—O13—C14 | 33.09 (7) |
| N22—K1—O4—C5 | -106.74 (8) | O10—K1—O13—C14 | -153.70 (8) |
| O16—K1—O4—C5 | 143.63 (7) | O4—K1—O13—C14 | 119.17 (8) |
| O10—K1—O4—C5 | 5.13 (8) | O1—K1—O13—C14 | 60.18 (8) |
| O13—K1—O4—C5 | 74.62 (9) | O7—K1—O13—C14 | 176.92 (7) |
| O1—K1—O4—C5 | 149.67 (8) | C12—K1—O13—C14 | -116.10 (10) |

supplementary materials

| | | | |
|----------------|--------------|-----------------|--------------|
| O7—K1—O4—C5 | 2.26 (7) | C12—O13—C14—C15 | -175.93 (9) |
| C12—K1—O4—C5 | 28.83 (11) | K1—O13—C14—C15 | -65.73 (10) |
| C3—O4—C5—C6 | -177.84 (9) | O13—C14—C15—O16 | 67.33 (12) |
| K1—O4—C5—C6 | 29.22 (11) | C14—C15—O16—C17 | 177.37 (9) |
| O4—C5—C6—O7 | -67.15 (11) | C14—C15—O16—K1 | -30.65 (12) |
| C5—C6—O7—C8 | -173.98 (9) | N21—K1—O16—C15 | 111.08 (8) |
| C5—C6—O7—K1 | 67.25 (9) | N22—K1—O16—C15 | 84.64 (8) |
| N21—K1—O7—C6 | 51.07 (7) | O10—K1—O16—C15 | -7.51 (9) |
| N22—K1—O7—C6 | 81.39 (7) | O4—K1—O16—C15 | -144.33 (8) |
| O16—K1—O7—C6 | -119.30 (7) | O13—K1—O16—C15 | -0.94 (8) |
| O10—K1—O7—C6 | 148.71 (7) | O1—K1—O16—C15 | -150.32 (9) |
| O4—K1—O7—C6 | -34.43 (6) | O7—K1—O16—C15 | -78.07 (9) |
| O13—K1—O7—C6 | 178.94 (6) | C12—K1—O16—C15 | 10.94 (8) |
| O1—K1—O7—C6 | -62.45 (7) | N21—K1—O16—C17 | -99.97 (8) |
| C12—K1—O7—C6 | 157.38 (6) | N22—K1—O16—C17 | -126.41 (8) |
| N21—K1—O7—C8 | -67.83 (7) | O10—K1—O16—C17 | 141.43 (8) |
| N22—K1—O7—C8 | -37.51 (8) | O4—K1—O16—C17 | 4.61 (9) |
| O16—K1—O7—C8 | 121.80 (7) | O13—K1—O16—C17 | 148.00 (9) |
| O10—K1—O7—C8 | 29.81 (7) | O1—K1—O16—C17 | -1.38 (8) |
| O4—K1—O7—C8 | -153.33 (8) | O7—K1—O16—C17 | 70.88 (9) |
| O13—K1—O7—C8 | 60.04 (7) | C12—K1—O16—C17 | 159.88 (8) |
| O1—K1—O7—C8 | 178.65 (7) | C15—O16—C17—C18 | -177.58 (10) |
| C12—K1—O7—C8 | 38.48 (7) | K1—O16—C17—C18 | 31.82 (12) |
| C6—O7—C8—C9 | -175.05 (10) | C2—O1—C18—C17 | -176.81 (10) |
| K1—O7—C8—C9 | -59.45 (11) | K1—O1—C18—C17 | 61.72 (11) |
| O7—C8—C9—O10 | 59.92 (13) | O16—C17—C18—O1 | -62.76 (13) |
| C8—C9—O10—C11 | 176.08 (10) | O16—K1—N21—N22 | -67.14 (6) |
| C8—C9—O10—K1 | -30.63 (13) | O10—K1—N21—N22 | 58.19 (6) |
| N21—K1—O10—C9 | 106.21 (9) | O4—K1—N21—N22 | 176.78 (6) |
| N22—K1—O10—C9 | 130.46 (9) | O13—K1—N21—N22 | -5.23 (7) |
| O16—K1—O10—C9 | -137.95 (8) | O1—K1—N21—N22 | -125.99 (6) |
| O4—K1—O10—C9 | -1.51 (9) | O7—K1—N21—N22 | 118.53 (6) |
| O13—K1—O10—C9 | -144.56 (9) | C12—K1—N21—N22 | 15.04 (6) |
| O1—K1—O10—C9 | -66.20 (10) | C25—N21—N22—C23 | 0.02 (12) |
| O7—K1—O10—C9 | 1.40 (8) | K1—N21—N22—C23 | 177.28 (9) |
| C12—K1—O10—C9 | -165.70 (10) | C25—N21—N22—K1 | -177.26 (9) |
| N21—K1—O10—C11 | -102.15 (8) | O16—K1—N22—N21 | 116.04 (6) |
| N22—K1—O10—C11 | -77.90 (8) | O10—K1—N22—N21 | -126.04 (6) |
| O16—K1—O10—C11 | 13.69 (9) | O4—K1—N22—N21 | -3.98 (7) |
| O4—K1—O10—C11 | 150.13 (8) | O13—K1—N22—N21 | 175.27 (6) |
| O13—K1—O10—C11 | 7.09 (8) | O1—K1—N22—N21 | 64.07 (6) |
| O1—K1—O10—C11 | 85.44 (9) | O7—K1—N22—N21 | -75.70 (6) |
| O7—K1—O10—C11 | 153.04 (9) | C12—K1—N22—N21 | -164.70 (6) |
| C12—K1—O10—C11 | -14.06 (8) | N21—N22—C23—C24 | 0.11 (14) |
| C9—O10—C11—C12 | 178.50 (10) | N22—C23—C24—C25 | -0.18 (14) |
| K1—O10—C11—C12 | 23.70 (12) | C23—C24—C25—N21 | 0.19 (14) |

Fig. 1

