SHORT-FORMAT PAPERS

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18-Crown-6–Potassium Picrate(1/1)

BY JOHN C. BARNES* AND JANE COLLARD

Chemistry Department, The University, Dundee DD1 4HN, Scotland

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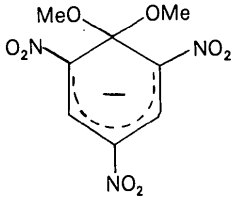
Abstract. 1,4,7,10,13,16-Hexaoxacyclooctadecane–potassium picrate (1/1), $C_{12}H_{24}O_6.K^+.C_6H_2N_3O_7^-$, M_r = 533·53, triclinic, $P\bar{1}$, a = 9·078 (3), b = 11·796 (5), c = 11·843 (5) Å, α = 89·70 (4), β = 77·41 (3), γ = 75·81 (3)°, V = 1198·31 Å^3, Z = 2, D_x = 1·47 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 2·462 mm^{-1}, $F(000)$ = 554, T = 293 K, R = 0·082 for 2459 reflexions. The six O atoms of 18-crown-6 are alternately ±0·195 (9) Å from their mean plane with the O–C–C–O torsion angles |65·8 (8)|°. The K atom lies 0·892 (1) Å below the centre of this group of O atoms with the diametric O–K–O angles 144·5 (3)°. The shortest K–O distances are 2·741 (3) Å, from the picrate O atom, and 2·846 (4) Å, from an *o*-nitro group. The K–$O_{(crown)}$ distance lie between 2·862 (4) and 2·989 (4) Å.

Experimental. Yellow plates as by-product from the recrystallization of the orange 18-crown-6 potassium salt of the Meissenheimer anion (I) from ethyl acetate.



(I)

Stoe–Siemens 4-circle diffractometer (Edinburgh University). Capillary-mounted crystal 0·50 × 0·65 × 0·04 mm. Unit cell refined from 18 precisely set reflexions with $36 < 2\theta < 45°$. 3394 measured reflexions gave 3379 unique data (R_{int} meaningless with only 15 repeated determinations, all weak). Index range $-9 \le h \le 9$, $-13 \le k \le 13$, $0 \le l \le 13$, $2\theta_{max}$ 119°. 2459 reflexions with $F_o > 3\sigma_F$ used in the refinement. Programs used: *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Atomic scattering curves from *SHELX*76.

Structure solution by routine direct methods. Refinement minimizing $\sum w|F_o - |F_c||^2$ to R 0·082, wR 0·119. All non-H atoms anisotropic; H atoms on calculated positions, U(H) refined to 0·106 (5) Å^2 for

Table 1. *18-Crown-6–potassium picrate coordinates* (× 10^4) *for non*-H *atoms and* U_{eq} *values* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i a_j \mathbf{a}_i^*.\mathbf{a}_j^*$.

	x	y	z	U_{eq}
K1	723 (1)	7921 (1)	3148 (1)	63 (1)
C1	−2961 (8)	7045 (6)	3582 (7)	91 (2)
C2	−2779 (8)	6873 (6)	4773 (6)	90 (2)
O3	−1201 (5)	6680 (3)	4800 (3)	80 (1)
C4	−959 (9)	6507 (6)	5947 (5)	95 (2)
C5	724 (9)	6377 (5)	5914 (5)	90 (2)
O6	1090 (5)	7442 (3)	5565 (3)	78 (1)
C7	2622 (8)	7463 (6)	5646 (5)	86 (2)
C8	2856 (8)	8647 (6)	5365 (5)	83 (2)
O9	2839 (5)	8820 (3)	4190 (3)	76 (1)
C10	3045 (9)	9936 (6)	3866 (6)	91 (2)
C11	2894 (8)	10122 (6)	2650 (5)	85 (2)
O12	1332 (5)	10221 (3)	2602 (3)	76 (1)
C13	1127 (8)	10457 (6)	1476 (5)	84 (2)
C14	−564 (9)	10588 (6)	1488 (5)	98 (2)
O15	−917 (5)	9507 (4)	1738 (3)	84 (1)
C16	−2521 (8)	9523 (7)	1784 (5)	92 (2)
C17	−2775 (8)	8346 (6)	2062 (6)	89 (2)
O18	−2549 (4)	8106 (3)	3187 (3)	76 (1)
C21	4582 (6)	6586 (4)	1056 (4)	53 (1)
C22	5674 (6)	6627 (4)	−46 (4)	56 (1)
C23	7023 (6)	5832 (4)	−489 (4)	61 (1)
C24	7530 (6)	4914 (5)	187 (5)	66 (1)
C25	6618 (6)	4792 (4)	1267 (4)	63 (1)
C26	5257 (6)	5585 (4)	1673 (4)	53 (1)
O27	3345 (4)	7308 (3)	1394 (3)	69 (1)
N28	5202 (6)	7612 (4)	−756 (4)	71 (1)
O29	5260 (6)	7415 (4)	−1772 (4)	111 (2)
O30	4846 (6)	8591 (4)	−310 (4)	104 (1)
N31	8973 (6)	4046 (5)	−261 (5)	88 (2)
O32	9672 (5)	4135 (4)	−1258 (5)	121 (2)
O33	9438 (6)	3265 (5)	381 (5)	122 (2)
N34	4362 (6)	5381 (4)	2807 (4)	68 (1)
O35	5078 (5)	4869 (4)	3498 (4)	96 (1)
O36	2939 (5)	5726 (4)	3028 (3)	85 (1)

* To whom correspondence should be addressed.

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Table 2. *18-Crown-6–potassium picrate interatomic distances* (Å) *and angles* (°)

O3–K1	2·959 (4)	C14–C13	1·501 (11)
O6–K1	2·989 (4)	O15–C14	1·405 (9)
O9–K1	2·896 (5)	C16–O15	1·441 (9)
O12–K1	2·941 (4)	C17–C16	1·487 (11)
O15–K1	2·862 (4)	O18–C17	1·409 (8)
O18–K1	2·914 (4)	C22–C21	1·465 (6)
O27–K1	2·741 (3)	C26–C21	1·461 (7)
O36–K1	2·846 (4)	O27–C21	1·219 (5)
C2–C1	1·463 (11)	C23–C22	1·348 (6)
O18–C1	1·440 (8)	N28–C22	1·465 (7)
O3–C2	1·402 (8)	C24–C23	1·390 (7)
C4–O3	1·428 (8)	C25–C24	1·392 (7)
C5–C4	1·490 (12)	N31–C24	1·446 (6)
O6–C5	1·413 (8)	C26–C25	1·345 (6)
C7–O6	1·421 (9)	N34–C26	1·463 (6)
C8–C7	1·488 (10)	O29–N28	1·214 (7)
O9–C8	1·409 (7)	O30–N28	1·211 (7)
C10–O9	1·414 (8)	O32–N31	1·229 (8)
C11–C10	1·486 (9)	O33–N31	1·244 (8)
O12–C11	1·408 (8)	O35–N34	1·221 (7)
C13–O12	1·403 (7)	O36–N34	1·224 (7)
O6–K1–O3	55·6 (1)	C10–O9–C8	111·8 (5)
O9–K1–O3	112·5 (1)	C11–C10–O9	110·2 (6)
O9–K1–O6	57·1 (1)	O12–C11–C10	108·6 (5)
O12–K1–O3	144·1 (1)	C11–O12–K1	106·3 (3)
O12–K1–O6	108·0 (1)	C13–O12–K1	108·0 (4)
O12–K1–O9	58·4 (1)	C13–O12–C11	110·3 (4)
O15–K1–O3	115·5 (1)	C14–C13–O12	107·8 (5)
O15–K1–O6	144·8 (1)	O15–C14–C13	108·4 (5)
O15–K1–O9	115·3 (1)	C14–O15–K1	120·7 (4)
O15–K1–O12	57·1 (1)	C16–O15–K1	118·2 (4)
O18–K1–O3	57·4 (1)	C16–O15–C14	113·7 (5)
O18–K1–O6	106·0 (1)	C17–C16–O15	109·5 (5)
O18–K1–O9	144·4 (1)	O18–C17–C16	108·6 (6)
O18–K1–O12	107·7 (1)	C1–O18–K1	110·2 (3)
O18–K1–O15	58·4 (1)	C17–O18–K1	107·7 (3)
O27–K1–O3	136·6 (1)	C17–O18–C1	112·2 (6)
O27–K1–O6	117·7 (1)	C26–C21–C22	108·8 (4)
O27–K1–O9	80·8 (1)	O27–C21–C22	124·1 (4)
O27–K1–O12	78·8 (1)	O27–C21–C26	127·1 (4)
O27–K1–O15	92·0 (1)	C23–C22–C21	126·9 (4)
O27–K1–O18	131·6 (1)	N28–C22–C21	115·9 (4)
O36–K1–O3	81·3 (1)	N28–C22–C23	117·1 (4)
O36–K1–O6	73·3 (1)	C24–C23–C22	118·3 (4)
O36–K1–O9	85·0 (1)	C25–C24–C23	120·4 (4)
O36–K1–O12	127·8 (1)	N31–C24–C23	119·7 (5)
O36–K1–O15	141·8 (1)	N31–C24–C25	119·8 (5)
O36–K1–O18	122·4 (1)	C26–C25–C24	119·8 (5)
O36–K1–O27	58·0 (1)	C25–C26–C21	125·6 (4)
O18–C1–C2	109·7 (6)	N34–C26–C21	118·1 (4)
O3–C2–C1	109·6 (5)	N34–C26–C25	116·2 (4)
C2–O3–K1	117·7 (4)	C21–O27–K1	144·4 (3)
C4–O3–K1	120·5 (4)	O29–N28–C22	118·8 (5)
C4–O3–C2	111·8 (5)	O30–N28–C22	117·9 (5)
C5–C4 O3	108·6 (5)	O30–N28–O29	123·2 (5)
O6–C5–C4	107·9 (5)	O32–N31–C24	117·5 (5)
C5–O6–K1	111·2 (4)	O33–N31–C24	118·5 (5)
C7–O6–K1	109·3 (3)	O33–N31–O32	124·0 (5)
C7–O6–C5	112·4 (5)	O35–N34–C26	118·0 (5)
C8–C7–O6	108·8 (5)	O36–N34–C26	119·3 (4)
O9–C8–C7	108·8 (6)	O36–N34–O35	122·7 (4)
C8–O9–K1	119·9 (4)	N34–O36–K1	136·3 (4)
C10–O9–K1	116·8 (4)		

18-crown-6, 0·109 (15) Å^2 for picrate. 329 refined parameters, $w=[11\cdot3684/\sigma^2(F)+0\cdot000574F^2]$; max. Δ/σ 0·323; max. features on final difference map 0·45, −0·49 e Å^{-3}. Final coordinates are given in Table 1, with bond lengths and angles in Table 2.* The molecule

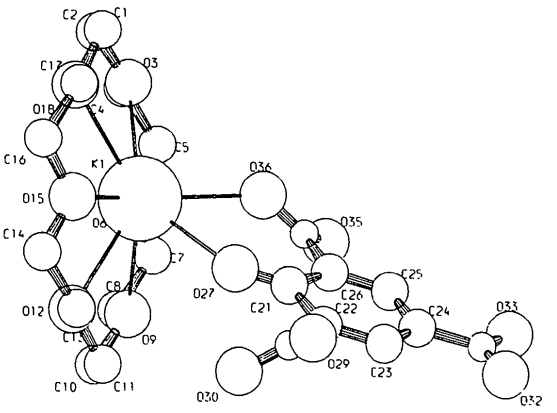

Fig. 1. 18-Crown-6–potassium picrate (1/1).

is shown in Fig. 1. The high final R and Δ/σ values are probably due to incomplete absorption correction for the very thin plate-like specimen used. The final refinement showed some oscillation of parameters. There was no evidence of disorder in the final model.

Related literature. The structures of K^+ 18-crown-6 complexes have been reviewed by (*inter alia*) Dalley (1978). Recent examples include the (tetraphenylporphyrinato)iron(III) bis(benzenedithiolate) salt (Bryn & Strouse, 1981) in which the K^+ 18-crown-6 unit is centrosymmetric and a phthalocyanine complex in which the K^+ atom is 1·6 Å from the O-atom plane (Ziolo, Gunther & Troup, 1981). In potassium benzo-15-crown-5 picrate the K^+ atom is 1·71 Å from the plane of the O atoms but there is no interaction between K^+ and picrate (Bhagwat, Manohar & Poonia, 1981). Both $-O^-$ and $-NO_2$ groups are coordinated to K^+ in potassium picrate (Palenik, 1972).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44522 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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