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Crystal Structure of a Polyether Dicarboxylic Acid Complex with Potassium Picrate, 2,2′-di-*o*-carboxymethoxyphenoxydiethyletherpotassium Picrate

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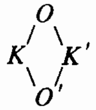
X-ray crystal structure analysis has been carried out on the title compound. In a triclinic unit cell having a = *9.292(9),* b = *11.224(3),* c = *15.000(4)*Å, α = *95.45(2),* β = *99.22(4),* γ = *108.15(4)*° *and space group* P$\bar{1}$, *there are two units of formula* $\{K[HOOC\,CH_2O\,C_6H_4O{-}CH_2CH_2]_2O\}^+\{C_6H_2(NO_2)_3O\}^-$. *Least squares refinement reduced R to 0.0655 for 2210 photographic observations. The hydrogen atoms of the dicarboxylic acid were located unequivocally; one is involved in hydrogen bonding to a centrosymmetrically related carboxylic acid, the other hydrogen bonds the phenolic oxygen of a picrate anion. A centrosymmetrical*



bridge formed by a carbonyl oxygen atom holds the complex cation in a dimeric form. The eight coordinating oxygen atoms form a shallow helix round each potassium ion with K–O distances 2.729–2.903 Å; there are no intramolecular hydrogen bonds within the helix.

Introduction

Some fungal metabolites with antibiotic properties form complexes with alkali and alkaline earth metal cations. There are two types of such antibiotic, (i) neutral and cyclic, (ii) monobasic acids, such as monensin and nigericin. The acids have complicated chemical constitutions including several heterocyclic rings containing oxygen atoms and the common feature that, in all the compounds so far studied by X-ray crystal structure analysis, whether metal salts [1], acids [2], or the sodium bromide complex of monensic acid [3], one or more intramolecular hydrogen bonds hold the molecules in cyclic form.

In a systematic study of analogous compounds in this laboratory, compounds of the general formula $RC_6H_4{-}O({-}CH_2{-}CH_2{-}O)_n{-}C_6H_4R'$ have been synthesised and their reactions with salts of Groups IA and IIA metals investigated. Reaction of one of these, the dicarboxylic acid having R = R′ = OCH_2-COOH and n = 2, with potassium picrate in methanol yielded a 1:1 complex. Crystal structure analysis, as described in a preliminary communication [4], confirmed the spectroscopic evidence that picrate ions were present and showed that there is no intramolecular hydrogen bonding. We now present the full results.

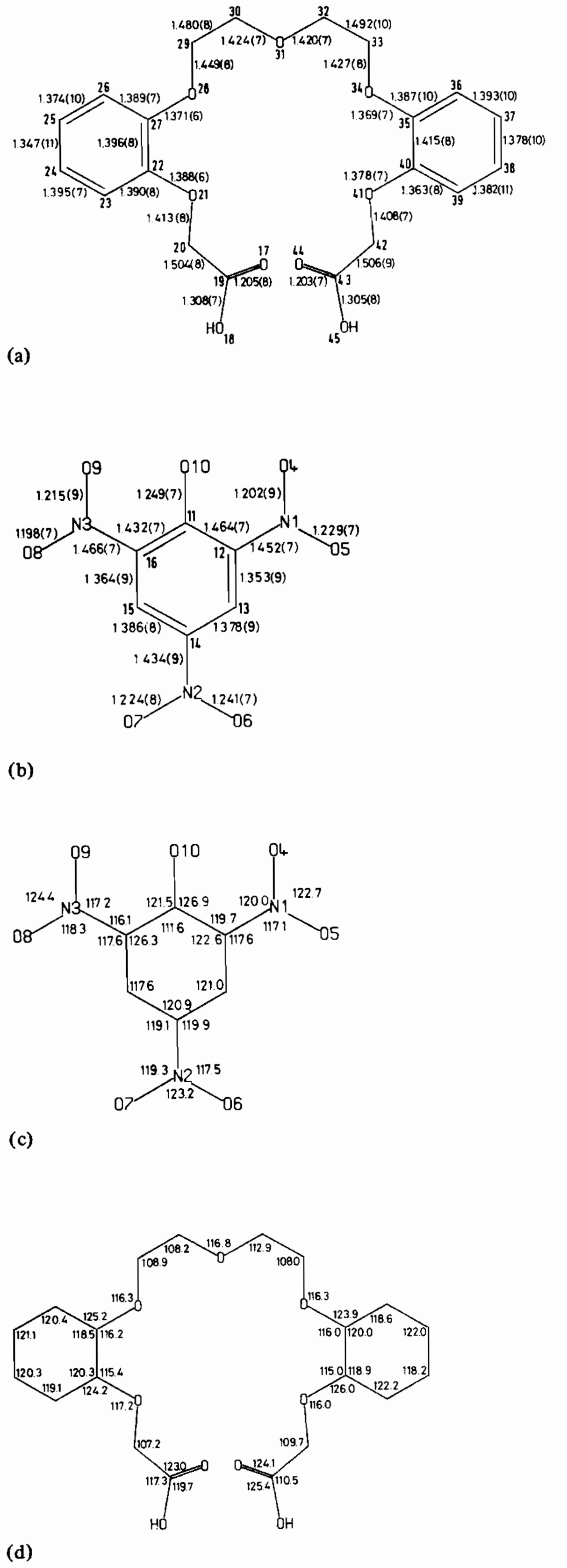
Experimental

Orange subhedral acicular crystals were obtained from methanol. They were pleochroic, colours varying from colourless, through pale green to golden brown where the needle axis was 45° to the plane of polarisation of the light. Preliminary X-ray photographs showed them to be triclinic with two formula units per unit cell. Accurate unit cell dimensions were obtained from the settings of 25 reflections on a CAD-4 diffractometer.

Crystal Data

$C_{26}H_{24}KN_3O_{16}$. *M* 673.6. Triclinic, *a* = 9.292(9), *b* = 11.224(3), *c* = 15.000(4) Å, α = 95.45(2), β = 99.22(4), γ = 108.15(4)°, *U* = 1449.8 Å^3. λ (for cell dimensions) $MoK_{\bar{\alpha}}$ = 0.71069 Å (Å ≡ 10^{-10} m). Space group, *P*$\bar{1}$ (by structure determination), D_m = 1.54 g cm^{-3}, *Z* = 2, D_c = 1.543 g cm^{-3}, F_{000} = 696. Filtered CuK_α radiation for photographic intensity measurement $\mu(CuK_\alpha)$ = 22.9 cm^{-1}.

A crystal 0.25 × 0.25 × 0.3 mm was mounted about the a-axis and equi-inclination Weissenberg photographs taken with multiple film packs for 0*kl* to 7*kl*. A second crystal set about [0$\bar{1}$1] provided one layer for preliminary scaling. Intensities were measured by the Science Research Council Microdensitometer Service. The reflections 001 and 10$\bar{1}$, inaccessible on the Weissenberg camera, were estimated from Guinier powder photographs. Geometrical correction factors were applied by the program SHELX [5] which assigned unit standard deviations to the structure amplitudes then put the observations



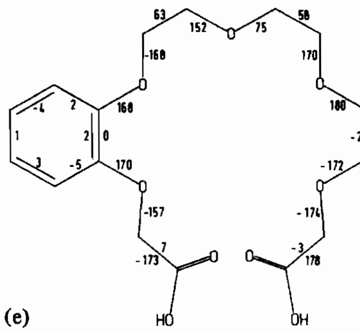


Figure 1. The designations of the atoms (without parentheses) in (a) the dicarboxylic acid, (b) the picrate ion. Also shown in (a) and (b) are the bond lengths, Å, with standard deviations in parentheses. Bond angles in (c) the picrate ion, and (d) the dicarboxylic acid have standard deviations in the range 0.4–0.7°. (e) Torsion angles in the dicarboxylic acid, standard deviations are in the range 0.4–1.1°.

on a common, approximately absolute, scale to give a set of structure amplitudes.

The structure was solved by the direct methods routine EEES of SHELX, the three origin-defining reflections being (4$\bar{1}$5, 3$\bar{7}$6, $\bar{3}$77); signs of 12 other reflections with high E values were permuted and one set gave the best value for internal consistency and an E map which was readily interpreted to show a picrate entity, a potassium ion and 23 other atoms. These gave R = 0.40, and provided phases for a difference map which revealed the remaining non-hydrogen atoms (see Fig. 1 for their designations). From this stage, only the observed structure amplitudes from the first crystal were used and the inter-layer scaling factors were included as parameters. After four cycles of full matrix least squares refinement, R fell to 0.167. Anisotropic vibration parameters were refined for all atoms except the oxygens of the two carboxyl groups and the acidic oxygen of the picrate. When R = 0.076, a difference synthesis revealed two hydrogen atoms on the carboxylate oxygen atoms O(18) and O(45) not coordinated to potassium. Other hydrogen atom coordinates were calculated at 1.08 Å from, and completing trigonal or tetrahedral coordination about the carbon atoms. In further refinement all vibration parameters for hydrogen atoms were refined isotropically and for the other atoms semi-anisotropically. Layer scale factors were included as parameters and U_{11} which is not independent of them, was fixed as the arithmetic mean of U_{22} and U_{33}. Even so, there were several correlations greater than 0.5 between layer scaling factors and U_{ij}. Some of the hydrogen atom coordinates were kept in the calculated positions while those of the remaining atoms were refined. Scattering factors were obtained from ref. 6 for hydrogen and ref. 7 for other atoms. Refinement was concluded when the most significant change in a parameter was 0.19 times

TABLE I. Fractional Coordinates, ($\times 10^4$). Numbers in parentheses are standard deviations in the least significant digits; coordinates fixed by geometrical considerations have (–) as a Standard Deviation. For hydrogen atoms isotropic vibration parameters ($U_{iso} \times 10^3$, Å^2) are also given.

	x	*y*	*z*
K	4268(2)	1240(1)	–1047(1)
N(1)	–223(6)	–396(4)	3183(4)
N(2)	–1080(7)	2494(6)	5474(4)
N(3)	2474(7)	4255(5)	3519(4)
O(4)	503(6)	–637(4)	2638(4)
O(5)	–1219(6)	–1220(4)	3440(4)
O(6)	–2051(6)	1545(5)	5645(4)
O(7)	–809(7)	3570(5)	5870(4)
O(8)	3529(6)	4974(5)	4082(4)
O(9)	2165(7)	4403(5)	2729(4)
O(10)	1895(5)	1847(3)	2644(3)
C(11)	1223(6)	1939(5)	3292(3)
C(12)	158(6)	901(5)	3627(4)
C(13)	–552(7)	1099(6)	4320(4)
C(14)	–268(7)	2306(6)	4766(4)
C(15)	750(6)	3353(5)	4515(4)
C(16)	1440(6)	3144(5)	3806(4)
O(17)	4110(5)	380(4)	632(3)
O(18)	2589(5)	305(3)	1600(3)
C(19)	3576(7)	940(5)	1142(4)
C(20)	3973(8)	2358(5)	1275(4)
O(21)	4884(4)	2817(3)	633(3)
C(22)	5836(6)	4077(5)	826(4)
C(23)	5759(7)	4959(5)	1517(4)
C(24)	6840(8)	6180(5)	1685(5)
C(25)	7897(9)	6515(6)	1155(5)
C(26)	7918(7)	5678(5)	430(4)
C(27)	6905(6)	4438(4)	263(3)
O(28)	6879(4)	3511(3)	–410(3)
C(29)	7752(7)	3931(5)	–1106(4)
C(30)	7332(7)	2871(5)	–1871(4)
O(31)	5737(5)	2564(4)	–2263(3)
C(32)	5259(11)	2028(6)	–3203(5)
C(33)	5171(9)	673(6)	–3371(4)
O(34)	4123(5)	–24(4)	–2856(3)
C(35)	3710(7)	–1319(5)	–3032(4)
C(36)	4247(8)	–1961(6)	–3667(4)
C(37)	3688(9)	–3283(7)	–3814(5)
C(38)	2664(8)	–3963(6)	–3327(4)
C(39)	2170(8)	–3298(6)	–2686(4)
C(40)	2667(6)	–2004(5)	–2522(3)
O(41)	2236(4)	–1268(3)	–1897(3)
C(42)	1360(7)	–1920(5)	–1301(4)
C(43)	845(7)	–1013(5)	–729(4)
O(44)	1204(4)	107(3)	–758(3)
O(45)	–6(5)	–1610(4)	–191(3)

	x	*y*	*z*	U_{iso}
H(13)	–1362(57)	316(45)	4545(33)	37(13)
H(15)	1080(45)	4201(36)	4907(27)	15(10)
H(18)	2096(94)	790(77)	1967(58)	112(30)
H(20A)	4615(50)	2709(37)	1951(31)	23(11)
H(20B)	3075(75)	2535(50)	1237(39)	53(18)
H(23)	4880(–)	4701(–)	1915(–)	120(30)
H(24)	6877(64)	6775(51)	2297(40)	56(16)
H(25)	8884(100)	7429(84)	1341(60)	126(31)
H(26)	8721(–)	5987(–)	–7(–)	70(20)
H(29A)	7483(–)	4719(–)	–1352(–)	75(20)
H(29B)	8966(–)	4212(–)	–825(–)	68(18)
H(30A)	7536(–)	2062(–)	–1621(–)	84(22)
H(30B)	8016(–)	3154(–)	–2374(–)	100(25)
H(32A)	4314(82)	2120(55)	–3296(40)	56(19)
H(32B)	6077(63)	2482(47)	–3520(36)	39(14)
H(33A)	6252(105)	623(74)	–3082(57)	107(27)
H(33B)	4687(62)	308(47)	–4014(39)	45(15)
H(36)	5074(–)	–1451(–)	–4037(–)	110(28)
H(37)	3995(65)	–3709(53)	–4288(40)	53(16)
H(38)	2259(–)	–4978(–)	–3441(–)	89(23)
H(39)	1507(67)	–3736(55)	–2419(40)	52(20)
H(42A)	561(63)	–2605(49)	–1628(35)	39(15)
H(42B)	2162(72)	–2264(54)	–745(42)	61(17)
H(45)	–407(70)	–1176(58)	186(44)	62(20)

the corresponding standard deviation. The function minimised was $R' = \Sigma\, w(|F_o| - |F_c|)^2$ where the weighting factor, refined by the program, was $1/(\sigma_F^2 + 0.008711F^2)$; the final value of R′ was 0.0711 and of R 0.0655 for 2210 observed reflections. In a final difference map the highest peak was 0.28e Å^{-3}. A table of observed and calculated structure factors has been deposited with the Editor.

Results

The final coordinates are given in Table I with the isotropic vibration parameters for the hydrogen atoms. Anisotropic vibration parameters for the other atoms have been deposited with the Table of Structure Factors.

There are picrate anions and dimeric complex cations each consisting of two potassium ions and two molecules of the dicarboxylic acid, as shown in a stereo view in Figure 2. Bond lengths and angles are displayed in Figure 1 with the torsion angles in the dicarboxylic acid. Distances and angles involving potassium are in Table II. Figure 3 shows the structure as a whole with hydrogen bonding indicated, while numerical values for interionic contacts are in Table III. Table IV gives the mean planes through various groups of atoms.

Discussion

Unequivocal location of the hydrogen atoms H(18) and H(45) and the dimensions of the picrate anion, which are diagnostically different from those of picric acid [6, 8] establish the constitution of the

TABLE II. Dimensions round the Potassium Ion.

(a) Bond Lengths, Å, Standard Deviations in Parentheses and 'Bond Valence' [9] in Brackets

K–O(17^I)	2.755(4)	[0.144]	K–O(44)	2.856(4)	[0.120]
K–O(17)	2.791(4)	[0.135]	K–O(41)	2.890(3)	[0.113]
K–O(21)	2.806(4)	[0.131]	K–O(34)	2.903(4)	[0.111]
K–O(28)	2.870(3)	[0.117]	K–O(31)	2.729(4)	[0.151]

(b) Angles in the Form O(a)–K–O(b), Standard Deviations are 0.2°

b	O(17)	O(21)	O(28)	O(31)	O(34)	O(41)	O(44)
a							
O(21)	55.4	–					
O(28)	97.5	54.5	–				
O(31)	154.4	110.1	59.7	–			
O(34)	132.5	169.2	114.8	59.6	–		
O(41)	87.3	137.4	164.7	111.9	53.3	–	
O(44)	65.3	87.5	139.5	139.4	102.5	55.5	–
O(17^I)	64.0	102.2	94.8	103.9	78.7	74.2	107.7

(c) K–O–X Angles, Standard Deviations are 0.4°

K–O(17)–K^I	116.0	K–O(31)–C(30)	103.6
K–O(17)–C(19)	114.8	K–O(31)–C(32)	117.8
K^I–O(17)–C(19)	127.7	K–O(34)–C(33)	116.1
K–O(21)–C(20)	117.1	K–O(34)–C(35)	120.5
K–O(21)–C(22)	124.9	K–O(41)–C(40)	121.4
K–O(28)–C(27)	122.8	K–O(41)–C(42)	112.6
K–O(28)–C(29)	113.6	K–O(44)–C(43)	114.4

Roman numeral superscript I denotes the centrosymmetrically related atom (at 1 – x, –y, –z).
The K—K^I distance is 4.703 Å.

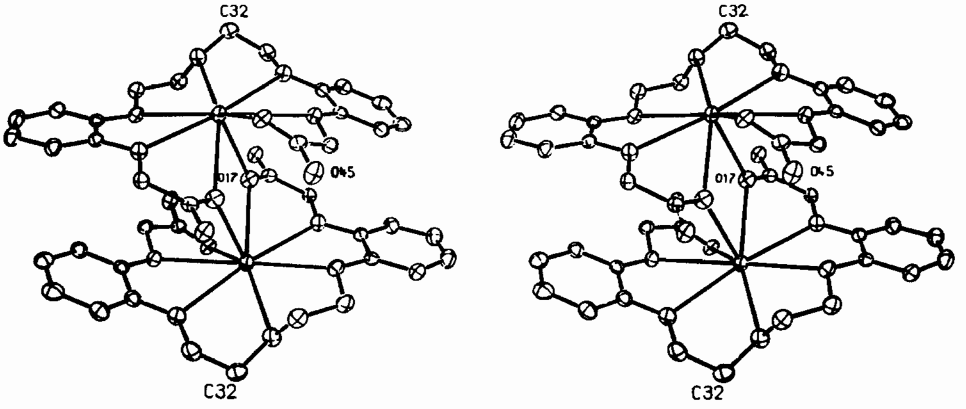


Figure 2. A stereo-pair showing the complex dimeric cation.

compound, the dicarboxylic acid acting as a neutral ligand.

The potassium ion is surrounded by a shallow helix of pitch 3.05 Å; as shown in Table IV, five oxygen atoms are roughly coplanar and the carboxyl oxygen atoms are above and below this plane.

Eight-fold coordination is achieved by sharing of O(17) oxygen atoms between potassium ions related by centres of symmetry at ½, 0, 0 (relation I) so that the complex cation is dimeric. Because the ligand molecule has more flexibility than a macrocycle it is possible that differences in K–O distances might vary with the kind of oxygen atom, but the four from oxygen atoms attached to benzene rings, Table II, range from 2.806 to 2.903 Å without any chemical significance, suggesting that this approach is not valid.

Brown and Shannon [9] have provided a useful summary of K–O distances in the form of an empiri-

TABLE III. Interionic Distances, A, less than 2.4 A between Hydrogen Atoms, and less than 3.5 A between Other Atoms.

(a) Hydrogen Bonding, with Angles Involving Hydrogen Atoms			
O(18)–––O(10)	2.523	C(19)–O(18)–H(18)	117.3
H(18)–––O(10)	1.563	O(18)–H(18)–––O(10)	161
O(18)–––O(4)	2.702	O(18)–H(18)–––O(4)	106
H(18)–––O(4)	2.254	C(43)–O(45)–H(45)	119.6
O(44)–––O(45^{III})	2.708	O(45)–H(45)–––O(44^{III})	168
H(45)–––O(44^{III})	1.813	C(11)–O(10)–––H(18)	139
		N(1)–O(4)–––H(18)	126
		C(43)–O(44)–––H(45^{III})	125
(b) Picrate···picrate			
N(1)···O(6^{II})	3.187	O(5)···C(13^{II})	3.467
N(2)···O(5^{II})	3.240	O(5)···C(14^{II})	3.334
O(5)···O(6^{II})	3.271	N(3)···O(7^{IV})	3.403
O(4)···O(6^{II})	3.157	O(7)···O(8^{IV})	3.417
(c) Picrate···cation			
O(4) ···O(44^{III})	3.209	O(6) ···C(32^{V})	3.403
O(5) ···O(34^{III})	3.438	O(6) ···C(33^{V})	3.119
O(6) ···C(36^{III})	3.478	C(32)···O(6^{X})	3.403
O(10)···C(42^{III})	3.383	C(33)···O(6^{X})	3.119
O(10)···C(43^{III})	3.357	O(7) ···C(38^{VI})	3.477
C(11)···O(41^{III})	3.363	C(38)···O(7^{XI})	3.477
C(12)···O(41^{III})	3.283	O(9) ···C(29^{VII})	3.203
C(12)···C(40^{III})	3.493	O(9) ···C(30^{VII})	3.359
C(13)···O(34^{III})	3.458		
C(13)···C(35^{III})	3.336		
C(13)···C(40^{III})	3.498		
(d) Cation···cation			
C(22)···C(39^{I})	3.435	C(25)···O(45^{VIII})	3.438
C(23)···C(38^{I})	3.330	C(26)···O(45^{VIII})	3.363
C(23)···C(39^{I})	3.468	O(45)···C(25^{XII})	3.438
C(43)···O(44^{III})	3.432	O(45)···C(26^{XII})	3.363
C(43)···O(45^{III})	3.491	H(26)···H(29B^{IX})	2.39

Roman numeral superscripts define the following relations to the coordinates *x, y, z* in Table I.

I	1 − x, −y, −z	VII	1 − x, 1 − y, −z
II	−x, −y, 1 − z	VIII	x + 1, y + 1, z
III	−x, −y, −z	IX	2 − x, 1 − y, −z
IV	−x, 1 − y, 1 − z	X	x + 1, y, z − 1
V	x − 1, y, z + 1	XI	x, y − 1, z − 1
VI	x, y, + 1, z + 1	XII	x − 1, y − 1, z

Note: the centrosymmetrical relations I, II, III, IV, VII and IX are the same for a···b and b···a.

cal relation $S = S_o(R/R_o)^{-N}$. They adjusted parameters S_o, R_o and N by least squares so that the sum of the bond valences, S, round a cation, M^{n+}, reaching it from oxygen neighbours at M–O distances of R was n; for $M^{n+} = K^+$ the values of S_o, R_o and N are 0.125, 2.833 and 5. Bond valences round K^+ are shown in Table II and their sum is 1.022. (We have preferred this to the more recent treatment by Brown and Wu [10] which gives a sum of the bond valences of 1.142).

In the dicarboxylic acid ligand, as Figure 1 shows, there is good agreement between the chemically equivalent pairs of bond lengths, O(31) being the central atom; for the bond angles the largest difference is between C(29)–C(30)–O(31) and O(31)–C(32)–C(33), while the torsion angles involving O(31), the only ones for a CH_2–O–CH_2 entity, are far from the ideal ±60° or 180° and give an H(30B)—H(32B) contact of 2.16 Å. The CH_2–CH_2 bond lengths, at 1.480 and 1.492 Å, shorter than the expected values

TABLE IV. Planes Through Various Groups of Atoms. The equations are in the form $lX + mY + nZ + D = 0$ where X, Y and Z are coordinates in Å with respect to an orthogonal system of axes where X is measured parallel to the crystallographic a axis, Z parallel to c^*, and Y perpendicular to a and c^*. The relationship to the fractional coordinates of Table I is:

$$X = ax + by\cos\gamma + cz\cos\beta$$
$$Y = by\sin\gamma - cz\cos\alpha^*\sin\beta$$
$$Z = cz\sin\alpha^*\sin\beta$$

Deviations of atoms from the planes, 10^3 Å; those excluded from calculation of the planes are shown in italics.

(i) $0.739\,X - 0.190\,Y + 0.646\,Z - 2.625 = 0$

C(11)	9(6)	*N(1)*	*13(5)*	*N(3)*	*34(6)*
C(12)	−11(16)	*O(4)*	*−155(6)*	*O(8)*	*−815(6)*
C(13)	6(7)	*O(5)*	*108(6)*	*O(9)*	*957(6)*
C(14)	6(6)	*N(2)*	*76(6)*	*O(10)*	*31(4)*
C(15)	−7(6)	*O(6)*	*166(6)*	*H(18)*	*−45(88)*
C(16)	−1(6)	*O(7)*	*65(6)*		

(ii) $0.652X - 0.235Y + 0.721Z - 3.111 = 0$
(iii) $0.694X - 0.236Y + 0.680Z - 2.892 = 0$
(iv) $-0.835X + 0.496Y + 0.238Z - 3.121 = 0$

(ii)		(iii)		(iv)	
C(12)	−8(6)	C(14)	2(6)	C(16)	−3(6)
N(1)	26(5)	N(2)	−5(6)	N(3)	13(6)
O(4)	−10(6)	O(6)	2(6)	O(8)	−5(6)
O(5)	−10(6)	O(7)	2(6)	O(9)	−5(6)

(v) $0.661X - 0.032Y + 0.750Z - 3.023 = 0$
(vi) $0.703X + 0.063Y + 0.708Z - 0.120 = 0$

(v)		(vi)	
O(17)	1(4)	O(45)	−2(5)
O(18)	1(4)	O(44)	−2(4)
C(19)	−4(6)	C(43)	8(6)
C(20)	2(6)	C(42)	−3(6)
H(18)	*86(88)*	*H(45)*	*16(67)*
O(10)	*−151(4)*	*O(44^{III})*	*241(4)*
O(4)	*−51(6)*		

(vii) $0.704X - 0.107Y + 0.702Z - 0.238 = 0$
(viii) $0.685X - 0.383Y + 0.619Z - 1.737 = 0$

(vii)		(viii)	
C(35)	11(6)	C(22)	−20(6)
C(36)	−12(7)	C(23)	28(6)
C(37)	6(8)	C(24)	−8(7)
C(38)	2(7)	C(25)	−25(8)
C(39)	− (7)	C(26)	21(6)
C(40)	−4(5)	C(27)	0(5)
O(34)	*52(4)*	*O(21)*	*−71(4)*
O(41)	*−8(4)*	*O(28)*	*−28(4)*

(ix) $0.827X - 0.465Y + 0.315Z - 1.986 = 0$

O(21)	212(4)	*K 66(1)*	
O(28)	−392(4)	*O(17)*	*−1107(4)*
O(31)	426(4)	*O(44)*	*1424(4)*
O(34)	−149(4)		
O(41)	−29(4)	*O(17^{I})*	*−2417(4)*

Angles, °, between normals to planes

(i)–(ii)	7.1	(i) –(vii)	6.1	(v)–(vi)	6.4
(i)–(iii)	4.1	(i) –(viii)	11.6		
(i)–(iv)	123.9	(vii)–(viii)	16.6		

Roman numeral superscripts are defined in Table III.

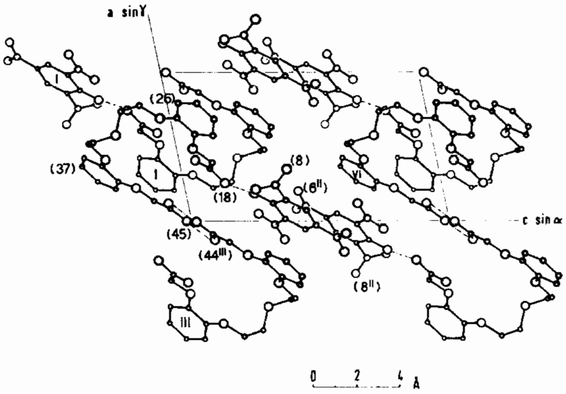


Figure 3. A view of the structure down the b axis. For clarity the potassium ions are omitted. Broken lines indicate hydrogen bonds. Roman numeral designations are defined in Table III. Picrate ions in relation IV lie over those of II and cations in relation VII over those of I. Ions in relations V, VIII and IX are not shown.

for Csp^3–Csp^3, are as usually found in macrocyclic polyethers. Other bond lengths are in good agreement with standard values. The mean C–C bond length in the benzene rings is 1.384 Å with individual standard deviations of ±0.017 Å close to the values obtained in the refinement procedure.

There is no intramolecular hydrogen bonding holding the ligand in the helical conformation round potassium. Both the acid protons take part in hydrogen bonding, Table III. The centrosymmetrical pair of bonds involving C(43), O(44), O(45) and H(45) and those of molecule III is of the kind usually found for carboxylic acids; the differences between C(43)–O(45) and C(43)–O(44), 0.102 Å, and in the corresponding C(42)–C(43)–O(n) angles, 13.6°, are relatively large and indicate [11] no tendency to disorder with the form O(45)···H–O(44^{III}).

Brown's treatment of hydrogen bonding [12] gives an acceptor value of 0.18 for O(44) leaving bond valence of 0.82 for O(45)–H(45), the length being 0.91(10) Å. O(44) also has a bond valence of 0.12 from K^+ to give a total of 0.30; this is comparable with the other carbonyl oxygen O(17) which, being shared by two potassium ions, has a bond valence of 0.279.

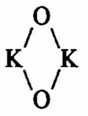
The hydrogen bonding of H(18) is more complicated; there is a short bond to O(10) with the angle 161° at the hydrogen atom, and a longer one to O(4) with angle 108°. Brown's treatment gives acceptor strengths of 0.34 and 0.08 respectively for the O(10) and O(4) atoms so that there is 0.58 bond valence for O(18)–H(18). This bonding reinforces the electrostatic attraction between the picrate anions and the complex cations, so that there are neutral columns parallel to the *a* axis, held on alternate centres of symmetry by K–O(17) bridges and by H(45) carboxylic acid hydrogen bonds.

The *a* axis is the needle axis of the crystal. The pleochroism is consistent with the nearly parallel benzene rings, Table IV, planes (i) (vii) and (viii) which are stacked approximately along the crystallographic [201] axis, Figure 4, with angles between their normals and the *a* axis of 42°, 45° and 47°. The picrate ions have many contacts to the centrosymmetrically related ones at 0, 0, ½ (relation II) on one side, and to the benzene ring $C(35^{III})$–$C(40^{III})$ on the other (a reinforcement of the carboxylate bridge). The C(35)–C(40) benzene ring lies between the picrate III and the C(22)–C(27) benzene ring within the dimeric cation I, Table III. For the C(22)–C(27) ring the contacts to a centrosymmetrically related molecule by relation VII are in the range 3.6 to 3.8 Å, so the packing along the *b* axis is loose.

In the picrate ion, the large angle of twist, 56.1°, of the *ortho* nitro group not involved in hydrogen bonding is not uncommon, for example in serotonin picrate [13] there is similar hydrogen bonding strongly to the phenolate oxygen and weakly to one *ortho* nitro group oxygen atom while the other *ortho* nitro group is twisted 53° out of the plane of the benzene ring. The corresponding value in thallium picrate is 41° [14].

The antibiotic monensin has recently been shown by spectroscopic and potentiometric methods [15] and by crystal structure analysis of the sodium bromide derivative [3] to form metal complexes in the acid form, the intramolecular hydrogen bonding being similar to that in the complex silver salt [1a] and in the hydrated acid [2c].

In the acid salt of potassium with *o, o'*-catecholdiacetic acid [$COOHCH_2OC_6H_4OCH_2OCOOK$] [$C_6H_4(OCH_2COOH)_2$] [16] there are two features analogous to those in the present structure, a centrosymmetrical



bridge (K–O 2.76 and 2.83 Å) with the oxygen not acting as an acceptor for a hydrogen bond, and K–O contact 2.75 Å to a carboxylate oxygen which is an acceptor of a hydrogen bond O···H 1.72 Å. Important differences are that the potassium ion is 10-coordinate and that, as the two catecholdiacetate molecules are symmetry related, the second carboxylate hydrogen bond corresponds to an equal sharing of this atom between two oxygen atoms, *i.e.* a stronger hydrogen bond O···H···O.

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