Alkali-metal Complexes. Part 8.[1] Crystal Structures of Potassium Quinolin-8-olate–Quinolin-8-ol(1/1) and –Quinolin-8-ol(1/2)

By **David L. Hughes** and **Mary R. Truter,*** Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts AL5 2JQ

The crystal structures of the complexes K(quin)·Hquin (1) and K(quin)·2Hquin (2) (Hquin = quinolin-8-ol) have been determined. Crystals of (1) are monoclinic, with a = 6.375(3), b = 12.616(3), c = 19.366(4) Å, β = 90.76(4)°, Z = 4, and space group $P2_1/c$; full-matrix least-squares refinement with isotropic vibration parameters for the hydrogen atoms has given an R factor of 0.076 5 for 1 302 reflections. The structure consists of centrosymmetrical dimers in which each potassium ion is six-co-ordinated by a chelating anion and by two chelated neutral molecules, the oxygen and nitrogen atoms of the last molecules being shared with the other potassium ion in the dimer. The dimers are held in chains along the a axis by centrosymmetric pairs of short, but not symmetric, O–H ··· O hydrogen bonds (O–H 0.92, H ··· O 1.52, and O ··· O 2.430 Å). Complex (2) is triclinic, with a = 7.601(4), b = 11.803(3), c = 14.108(3) Å, α = 70.42(1), β = 104.51(3), γ = 104.27(3)°, Z = 2, and space group $P\bar{1}$. Least-squares refinement with isotropic vibration parameters for hydrogen and anisotropic vibration parameters for the other atoms has led to R = 0.068 3 for 1 935 observations. In the centrosymmetrical dimeric molecules each potassium ion is seven-co-ordinate approximately in a pentagonal bipyramid. The equatorial plane is formed by two nearly parallel neutral chelating molecules and by the nitrogen atom of the chelating anion, the oxygen atom of which forms one apex of the pentagonal bipyramid. The other apex is occupied by a nitrogen atom of a neutral ligand in the other half of the dimer. Both of the hydrogen atoms on the chelating neutral molecules of one potassium ion are directed towards the same anionic oxygen in a neighbouring molecule across a centre of symmetry (O ··· O 2.599 and 2.566 Å). Thus, alternate centres of symmetry along the a axis relate (*i*) the co-ordination dimers, and (*ii*) two pairs of hydrogen bonds. Because the neutral molecules are approximately parallel these contacts are reinforced by stacking effects.

IT was reported in Part 1[2] that the salts formed by alkali metals with quinolin-8-ol (Hquin), namely M(quin), can form adducts with additional molecules of Hquin having the general formula M(quin)·n Hquin (n = 1 for Na, Li, or K; 2 for K, Rb, or Cs). Preliminary X-ray measurements showed that the complexes with n = 2 were isomorphous. From i.r. spectra Banerjee *et al.*[2] suggested that the structures in the solids were probably analogous to that of the pyridine solvate of the silver complex[3] with n = 1, with the cations co-ordinated by chelate entities and strong hydrogen bonds between adjacent molecules. It was clear that there were diagnostic differences between the two potassium complexes, but it was not possible to interpret them or to predict the co-ordination number and stereochemistry round the potassium.

We have now determined the crystal structures of potassium complexes with n = 1 (1) and n = 2 (2). Figure 1 shows the numbering adopted for the quinolin-8-ol molecule.

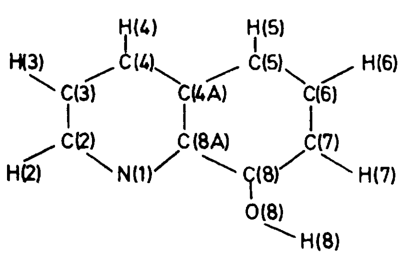

FIGURE 1 Numbering scheme for quinolin-8-ol. Neutral molecules have atoms designated as X(n) or X′(n) and the anions as X*(n)

EXPERIMENTAL

Potassium Quinolin-8-*olate–Quinolin*-8-*ol* (1/1), (1).—Crystals of (1), *en masse*, appear very pale yellow; individually, they are colourless and transparent, and have the shape of prisms with much variation in cross-section. A single crystal (0.31 × 0.17 × 0.14 mm) was wedged and sealed in a capillary tube. The space group and preliminary cell dimensions were derived from photographs, and accurate dimensions were obtained from the centring of 25 reflections in the range 2θ 19—36° on a four-circle diffractometer.

Crystal data. $C_{18}H_{13}KN_2O_2$, M = 328.4, Monoclinic, a = 6.375(3), b = 12.616(3), c = 19.366(4) Å, β = 90.76(4)°, U = 1 557.4 Å^3, D_m = 1.39 (by flotation), Z = 4, D_c = 1.400 g cm^{-3}, $F(000)$ = 680, μ(Mo-K_α) = 3.5 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å (1 Å = 10^{-10} m), space group $P2_1/c$, uniquely determined.

Diffraction intensities were measured on a card-controlled Picker diffractometer, using zirconium-filtered Mo-radiation. 1 451 Independent reflections, with $2\theta \leqslant 40°$, were measured in the 2θ—ω scan mode at a 2θ scan speed of 0.5° min^{-1}. Background measurements (b_1 and b_2) were made for 25 s before and after each scan. For each reflection, the peak net intensity, I, and its standard deviation, σ_I, were calculated from $I = T - [(b_1 + b_2)t_s/50]$ and $\sigma_I^2 = T + [(b_1 + b_2)t_s^2/2\,500]$, where T is the total scan count measured in the scan time t_s in s. The net intensities of two reflections, measured every 40 reflections, were found to increase slightly over the period of measurement, and the intensity data were scaled accordingly. Lorenz and polarisation factors were applied, but no absorption correction was made. Structure amplitudes and $|E|$ values were derived.

The E statistics confirmed a centrosymmetric structure. The suite of direct-methods programs described in ref. 1 was used to determine the structure. The multisolution program MULSA assigned values to all 111 reflections with $|E| \geqslant 1.8$ in one of the sets of phases, and this set was extended to the 160 reflections with $|E| \geqslant 1.6$ in SAP4B. All the non-hydrogen atoms were outstanding in an E map phased by these reflections. Refinement of parameters with isotropic temperature factors was rapid. Hydrogen-atom co-ordinates [except for H(8)] were then calculated and included in the refinement, and all non-hydrogen atoms were allowed to refine anisotropically. Co-ordinates for H(8) were located in a difference-Fourier map and also allowed to refine. Scattering factors for hydrogen were taken from ref. 4, those for K^+, C, N, and O from ref. 5. In the final stages of full-matrix least-squares refinement, 1 302 reflections (all those with a net intensity greater than zero) were used, and were weighted by the method of Sheldrick in his program SHELX,[6] with a final weighting scheme $w = 0.169\,2/(\sigma_F^2 + 0.003\,768F^2)$. The final values for R and R' were 0.076 5 and 0.085 9. The final atomic co-ordinates are in Table 1.

TABLE 1

Atomic co-ordinates (fractional $\times 10^4$) for complex (1) with standard deviations in parentheses

Atom	x	y	z
K	3 359(3)	4 542(1)	−650(1)
N(1)	3 724(11)	6 776(5)	−225(3)
C(2)	2 191(14)	7 335(8)	43(5)
C(3)	2 027(16)	8 409(7)	−10(5)
C(4)	3 491(14)	8 963(7)	−348(4)
C(4A)	5 202(12)	8 432(6)	−662(4)
C(5)	6 771(14)	8 950(7)	−1 039(4)
C(6)	8 330(15)	8 353(7)	−1 320(5)
C(7)	8 430(13)	7 243(6)	−1 246(4)
C(8)	6 910(12)	6 717(6)	−875(4)
C(8A)	5 213(11)	7 313(6)	−585(4)
O(8)	6 937(9)	5 675(4)	−773(3)
N*(1)	1 771(10)	2 715(5)	−1 308(3)
C*(2)	2 759(14)	1 810(7)	−1 330(4)
C*(3)	2 126(19)	915(8)	−1 708(5)
C*(4)	360(17)	999(7)	−2 080(4)
C*(4A)	−842(13)	1 950(7)	−2 078(4)
C*(5)	−2 729(15)	2 080(8)	−2 453(5)
C*(6)	−3 757(15)	3 011(8)	−2 423(5)
C*(7)	−2 998(13)	3 852(8)	−2 034(4)
C*(8)	−1 147(11)	3 778(6)	−1 654(4)
C*(8A)	−36(11)	2 794(6)	−1 688(4)
O*(8)	−349(7)	4 585(4)	−1 284(3)
H(2)	1 261(118)	6 849(60)	238(39)
H(3)	1 077(162)	8 836(84)	167(55)
H(4)	3 553(107)	9 719(64)	−461(37)
H(5)	6 804(108)	9 719(65)	−1 068(36)
H(6)	9 304(99)	8 692(50)	−1 615(32)
H(7)	9 517(104)	6 772(56)	−1 409(35)
H(8)	8 087(160)	5 338(84)	−954(52)
H*(2)	4 003(89)	1 745(40)	−1 062(28)
H*(3)	2 834(130)	417(63)	−1 681(45)
H*(4)	−181(110)	429(58)	−2 333(39)
H*(5)	−3 381(95)	1 528(53)	−2 732(32)
H*(6)	−5 035(106)	3 131(47)	−2 645(31)
H*(7)	−3 696(96)	4 530(48)	−2 010(30)

Potassium Quinolin-8-*olate–Quinolin*-8-*ol* (1/2), (2).—Small colourless crystals are easily chipped off large pale yellow clumps of (2). Single crystals are elongated clear plates; they are slightly air-sensitive, so for analysis the crystal selected (0.25 × 0.17 × 0.19 mm) was sealed in a capillary tube. *X*-Ray photographs showed the crystals to be triclinic and gave preliminary cell dimensions. Accurate dimensions were obtained by refinement of the settings of 25 reflections, with 2θ in the range 16—28°, centred on a diffractometer.

Crystal data. $C_{27}H_{20}KN_3O_3$, $M = 473.6$, Triclinic, $a = 7.601(4)$, $b = 11.803(3)$, $c = 14.108(3)$ Å, $\alpha = 70.42(1)$, $\beta = 104.51(3)$, $\gamma = 104.27(3)°$, $U = 1\,136.1$ Å^3, $D_m = 1.37$ (flotation), $Z = 2$, $D_c = 1.384$ g cm^{-3}, $F(000) = 492$, μ(Mo-K_α) = 2.6 cm^{-1}, space group $P\bar{1}$, from the structure analysis.

The measurement and processing of the diffraction intensities was as for complex (1). Correction was made for the slight reduction in the intensities of the two control reflections. Of 2 123 independent reflections with $2\theta \leqslant 40°$, 1 935 had a net intensity greater than zero. The E statistics suggested the centrosymmetric space group $P\bar{1}$.

The IBM 1130 direct-methods suite of programs failed to produce a solution for (2); reflections with high $|E|$ values were found to have $|l| = 0$—3 or 6—12, and triplet links between the two groups were weak. However, the automatic direct-methods routine EEES in the program SHELX, using a starting set of 15 reflections (three of fixed phase to define the origin, and 12 whose signs were systematically alternated) showed the correct solution in an E map from the phase set with the third-highest Parachor value.

TABLE 2

Atomic co-ordinates (fractional $\times 10^4$) for complex (2) with standard deviations in parentheses

Atom	x	y	z
K	7 570(2)	4 856(1)	903(1)
N(1)	6 264(6)	6 948(4)	−653(4)
C(2)	6 002(8)	7 863(8)	−381(7)
C(3)	6 028(9)	9 066(7)	−1 027(8)
C(4)	6 315(9)	9 331(7)	−1 978(8)
C(4A)	6 604(7)	8 410(6)	−2 323(5)
C(5)	6 893(9)	8 619(8)	−3 328(6)
C(6)	7 153(9)	7 694(9)	−3 590(6)
C(7)	7 182(8)	6 530(7)	−2 899(5)
C(8)	6 894(7)	6 295(6)	−1 934(5)
C(8A)	6 577(6)	7 235(5)	−1 612(4)
O(8)	6 861(7)	5 176(4)	−1 237(3)
N′(1)	8 144(5)	2 507(4)	2 337(3)
C′(2)	7 932(8)	2 194(7)	3 292(5)
C′(3)	7 997(8)	1 033(7)	3 980(5)
C′(4)	8 252(8)	136(6)	3 685(5)
C′(4A)	8 465(7)	400(5)	2 653(4)
C′(5)	8 682(8)	−494(6)	2 266(6)
C′(6)	8 882(8)	−194(7)	1 284(7)
C′(7)	8 883(8)	1 008(7)	644(6)
C′(8)	8 665(6)	1 892(5)	992(4)
C′(8A)	8 433(6)	1 603(5)	2 021(4)
O′(8)	8 655(6)	3 076(4)	430(4)
N*(1)	8 527(7)	5 783(4)	2 656(3)
C*(2)	7 381(10)	5 602(6)	3 272(6)
C*(3)	7 836(11)	5 935(6)	4 173(5)
C*(4)	9 558(11)	6 459(6)	4 446(5)
C*(4A)	10 882(8)	6 708(5)	3 833(4)
C*(5)	12 733(9)	7 265(5)	4 081(5)
C*(6)	13 894(10)	7 453(6)	3 441(6)
C*(7)	13 347(9)	7 105(5)	2 549(5)
C*(8)	11 584(8)	6 528(5)	2 277(4)
C*(8A)	10 304(7)	6 339(4)	2 937(4)
O*(8)	11 038(5)	6 116(3)	1 462(3)
H(2)	5 811(72)	7 643(51)	216(41)
H(3)	5 831(77)	9 642(60)	−710(45)
H(4)	6 369(95)	10 105(73)	−2 413(57)
H(5)	6 920(72)	9 473(59)	−3 768(45)
H(6)	7 320(84)	7 832(61)	−4 240(53)
H(7)	7 345(57)	5 913(41)	−3 138(33)
H(8)	7 411(60)	4 832(42)	−1 346(35)
H′(2)	7 518(51)	2 706(36)	3 425(29)
H′(3)	7 920(53)	896(38)	4 603(36)
H′(4)	8 371(75)	−790(61)	4 127(45)
H′(5)	8 818(68)	−1 302(54)	2 717(41)
H′(6)	9 032(79)	−760(59)	981(47)
H′(7)	8 986(57)	1 131(40)	25(35)
H′(8)	8 663(56)	3 111(39)	−56(31)
H*(2)	6 279(77)	5 247(49)	3 025(42)
H*(3)	6 807(65)	5 733(42)	4 535(37)
H*(4)	9 977(63)	6 733(41)	4 938(36)
H*(5)	13 062(88)	7 568(62)	4 668(52)
H*(6)	15 069(69)	7 880(43)	3 563(34)
H*(7)	14 174(71)	7 201(46)	2 157(39)

Least-squares refinement of the atomic parameters followed a course similar to that for (1) except that the quin and Hquin ligands were refined in sequence, in three blocks; the potassium ion was included in each block. The two hydroxyl hydrogen atoms, H(8) and H′(8), were again located in a difference map and allowed to refine independently. For the 1 935 reflections used in the refinement, convergence was reached at $R = 0.068\ 3$ and $R' = 0.089\ 3$, using the Sheldrick weighting procedure which refined to $w = 0.176\ 7/(\sigma_F^2 + 0.006\ 932F^2)$. Final atomic co-ordinates are in Table 2.

TABLE 3

Bond lengths (Å) and angles (°) (those involving H are excluded) in the ligand molecules

	Complex (1)		Complex (2)		
	Hquin	quin *	Hquin	Hquin′	quin *
N(1)–C(2)	1.317(10)	1.305(9)	1.333(12)	1.313(9)	1.312(11)
C(2)–C(3)	1.364(12)	1.401(12)	1.405(11)	1.393(10)	1.392(12)
C(3)–C(4)	1.343(12)	1.333(12)	1.333(16)	1.330(13)	1.324(10)
C(4)–C(4A)	1.423(10)	1.423(11)	1.411(14)	1.425(10)	1.402(11)
C(4A)–C(5)	1.407(10)	1.407(11)	1.420(11)	1.399(12)	1.409(8)
C(4A)–C(8A)	1.420(10)	1.399(10)	1.412(8)	1.404(7)	1.407(8)
C(5)–C(6)	1.366(11)	1.346(12)	1.335(16)	1.348(13)	1.346(12)
C(6)–C(7)	1.409(11)	1.386(11)	1.395(11)	1.404(10)	1.387(11)
C(7)–C(8)	1.383(10)	1.386(10)	1.357(10)	1.351(12)	1.370(8)
C(8)–C(8A)	1.438(10)	1.431(9)	1.423(11)	1.421(8)	1.439(9)
C(8A)–N(1)	1.365(9)	1.362(9)	1.347(8)	1.367(9)	1.372(7)
C(8)–O(8)	1.330(8)	1.342(8)	1.355(7)	1.357(7)	1.330(7)
C(2)–H(2)	0.94(7)	0.95(5)	0.83(6)	0.83(5)	0.88(5)
C(3)–H(3)	0.88(10)	0.78(7)	0.99(8)	0.85(5)	0.98(5)
C(4)–H(4)	0.98(8)	0.93(7)	0.91(7)	1.07(6)	0.82(5)
C(5)–H(5)	0.97(8)	0.97(7)	0.99(6)	0.97(6)	0.96(8)
C(6)–H(6)	0.95(6)	0.93(6)	0.91(8)	0.95(8)	0.92(5)
C(7)–H(7)	0.97(7)	0.96(6)	0.94(6)	0.86(5)	0.90(6)
O(8)–H(8)	0.92(11)		0.72(6)	0.68(5)	
C(2)–N(1)–C(8A)	117.4(7)	116.8(7)	115.8(5)	116.0(5)	116.6(6)
N(1)–C(2)–C(3)	124.0(9)	125.9(9)	124.1(9)	124.6(8)	125.0(6)
C(2)–C(3)–C(4)	120.1(10)	117.0(10)	119.3(10)	120.5(7)	118.1(8)
C(3)–C(4)–C(4A)	120.3(9)	121.0(9)	120.0(7)	118.2(6)	121.3(7)
C(4)–C(4A)–C(5)	123.9(8)	123.6(9)	123.2(7)	122.2(6)	123.9(6)
C(4)–C(4A)–C(8A)	115.2(8)	116.7(8)	116.4(7)	117.5(7)	116.8(5)
C(5)–C(4A)–C(8A)	120.9(8)	119.6(8)	120.4(8)	120.3(6)	119.3(6)
C(4A)–C(5)–C(6)	118.5(8)	119.6(9)	119.2(7)	119.8(6)	119.0(7)
C(5)–C(6)–C(7)	122.6(9)	121.6(9)	121.9(8)	120.8(9)	122.6(6)
C(6)–C(7)–C(8)	119.9(9)	121.7(8)	120.5(9)	120.9(8)	121.5(7)
C(7)–C(8)–C(8A)	119.2(7)	116.9(8)	120.5(6)	119.7(5)	117.1(6)
C(7)–C(8)–O(8)	122.9(7)	123.1(7)	123.2(7)	124.9(6)	123.2(6)
C(8A)–C(8)–O(8)	117.9(8)	119.9(6)	116.4(6)	115.4(6)	119.7(5)
N(1)–C(8A)–C(4A)	123.0(7)	122.5(7)	124.4(7)	123.2(5)	122.2(6)
N(1)–C(8A)–C(8)	118.2(7)	117.0(7)	118.0(5)	118.2(5)	117.3(5)
C(4A)–C(8A)–C(8)	118.8(7)	120.4(7)	117.6(6)	118.6(6)	120.5(5)

Lists of measured and calculated structure factors and temperature factors for both complexes are in Supplementary Publication No. SUP 22400 (23 pp.).*

Computing.—The programs SHELX [6] and ORTEP [7] (for the diagrams) were run on the ICL 4/70 computer at this Station. Our Department's IBM 1130 computer and the *X*-RAY ARC [8] library of programs were used for all other calculations.

RESULTS

Quinolin-8-ol is extremely versatile; it can form compounds (*i*) as a neutral molecule, (*ii*) by transfer of H(8) to N(1) as a zwitterion, or (*iii*), by loss of H(8), as an anion. These potassium complexes are the first having two forms present in the same crystal in which the hydrogen atoms on the oxygen atoms have been located unequivocally so distinguishing the anionic and neutral entities. Table 3 shows the bond lengths and angles in the ligand molecules. Angles involving the aromatic hydrogen atoms have standard deviations ranging from 3 to 7° in (1) and 3 to 6° in (2), and so are not quoted.

Description of the Structure of Complex (1).—As shown in Figure 2, complex (1) contains dimeric molecules in which each potassium ion is six-co-ordinate. The cationic charge is neutralised by a chelating anion and both the oxygen and the nitrogen atom of the quinolin-8-ol molecule are shared by two centrosymmetrically related potassium ions. Table 4 gives the distances and angles involving potassium and also those relevant to hydrogen bonding.

The dimeric molecules are held by centrosymmetrical pairs of strong O–H · · · O* hydrogen bonds in columns along the *a* (needle) axis of the crystal. Figure 2 is a projection down this axis. Most of the short contacts in Table 5, relations I—IV, are within the columns; between columns, H*(6) is directed towards the centre of an aromatic ring of the neutral ligand in relation X, and H*(4) has short contacts with the anionic ligand of the same molecule. Along the *b* axis, there are short interactions between H(4) and C(4^{V}) and C*(3^{VI}).

Within the dimer, the ligands are inclined such that H*(2) is directed towards the centre of a ring of the neutral ligand (relation I) with H*(2) · · · C and · · · N distances in the range 3.26—3.43 Å. Table 6 shows that both ligands are planar (deviations for the aromatic hydrogen atoms are less than the standard deviations and are not shown), and that their normals are inclined at 69°. The angles between the normal to the anion [plane (2)] and the entities in relation X are 65.5° to the neutral and 38.0° to the anionic

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

ligands. There are no parallel adjacent pairs of ligands, and hence no stacking of aromatic rings, in this crystal.

Description of the Structure of Complex (2).—As shown in Figure 3 the potassium ion is surrounded by three chelating ligands at distances given in Table 7; the two neutral ones are nearly parallel (Table 6) with their planes *ca.* 1.2 Å apart, while the anionic one is approximately normal to these. In addition a seventh contact is made by dimerisation about the centre of symmetry at ½, ½, 0 to give a K···N(1$^{\mathrm{I}}$) distance of 3.175 Å. The seven-co-ordination thus achieved round potassium is approximately a pentagonal bipyramid with the neutral ligands and the nitrogen of the anion forming the equatorial plane [plane (6) in Table 6]; O*(8) is one apex and N(1$^{\mathrm{I}}$) the other. Both of the hydrogen atoms of the neutral ligands H(8) and H′(8) are hydrogen-bonded to the same anionic oxygen O*(8$^{\mathrm{II}}$) in the molecule related by a centre of symmetry at 1, ½, 0 (Figure 3).

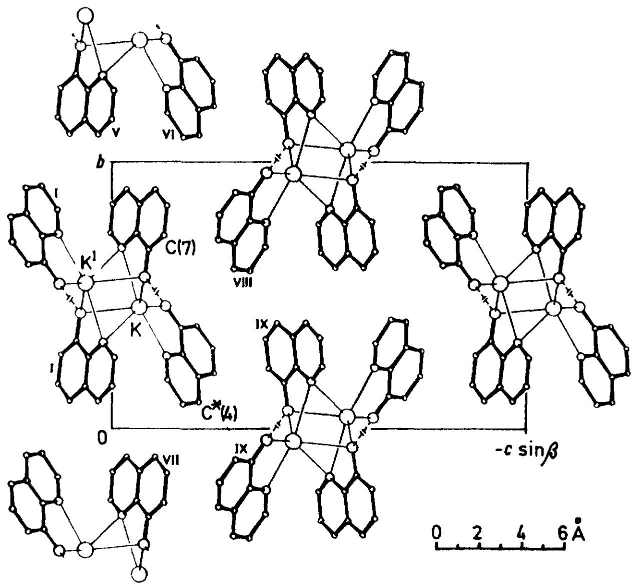

FIGURE 2 Projection of the structure of complex (1) down the *a* axis. For clarity, hydrogen atoms have been omitted. Roman numeral superscripts refer to the following equivalent positions relative to the co-ordinates of the crystal chemical unit in Table 1 at x, y, z:

I	$1 - x, 1 - y, -z$	VII	$x, y - 1, z$
II	$x + 1, y, z$	VIII	$1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$
III	$x - 1, y, z$	IX	$1 - x, -\frac{1}{2} + y, -\frac{1}{2} - z$
IV	$-x, 1 - y, -z$	X	$-x, -\frac{1}{2} + y, -\frac{1}{2} - z$
V	$1 - x, 2 - y, -z$	XI	$-x, \frac{1}{2} + y, -\frac{1}{2} - z$
VI	$x, y + 1, z$		

Relation I forms the co-ordination dimer, III and IV give the dimeric molecule one unit cell further away from the reader and the hydrogen-bonding pairs about 0, ½, 0, with O(8$^{\mathrm{III}}$)–H(8$^{\mathrm{III}}$) as donor to O*(8) and O(8$^{\mathrm{I}}$)–H(8$^{\mathrm{I}}$) as donor to O*(8$^{\mathrm{IV}}$): II gives the crystal chemical unit nearer the reader and one of the two hydrogen bonds about 1, ½, 0; VIII and IX are nearer the reader than XI and X respectively

The packing diagram (Figure 4) shows the view looking down the *a* axis on columns of co-ordination dimers which are hydrogen-bonded to molecules in the next cells above and below the plane of the paper. As can be seen from Table 8, most of the short contacts in the structure correspond to the symmetry operations given by I and II and are subsidiary to the main potassium–nitrogen or

TABLE 4

Distances (Å) and angles (°) involving potassium or hydrogen bonding in complex (1)

K···K$^{\mathrm{I}}$	3.452(3)		
K–N(1)	2.945(6)		
K–O(8)	2.705(6)	K–O*(8)	2.649(5)
K–N*(1)	2.815(6)	K–O(8$^{\mathrm{I}}$)	2.779(6)
		K–N(1$^{\mathrm{I}}$)	3.002(7)
O(8)–H(8)	0.92(10)		
H(8)···O*(8$^{\mathrm{II}}$)	1.52(10)		
O(8)···O*(8$^{\mathrm{II}}$), O*(8)···O(8$^{\mathrm{III}}$)		2.430(7)	

Angles (°) subtended at potassium (standard deviations 0.2°):

	N(1)	O(8)	N*(1)	O*(8)	N(1$^{\mathrm{I}}$)
O(8)	57.0				
N*(1)	159.5	133.7			
O*(8)	100.2	134.2	59.6		
N(1$^{\mathrm{I}}$)	109.0	80.0	91.1	144.6	
O(8$^{\mathrm{I}}$)	79.8	102.0	109.9	112.9	55.6

Angles (°) subtended at O(8):

	K	K$^{\mathrm{I}}$	C(8)	O*(8$^{\mathrm{II}}$)
K$^{\mathrm{I}}$	78.0(2)			
C(8)	121.8(5)	104.1(4)		
O*(8$^{\mathrm{II}}$)	110.0(2)	114.0(2)	120.5(5)	
H(8)	118(6)	113(6)	114(6)	8(6)

Angles (°) subtended at O*(8)

	K	C*(8)	O(8$^{\mathrm{III}}$)
C*(8)	124.2(4)		
O(8$^{\mathrm{III}}$)	117.3(2)	112.3(4)	
H(8$^{\mathrm{III}}$)	114(6)	117(6)	5(4)

Angles (°) subtended at N(1):

	K	K$^{\mathrm{I}}$	C(8A)
K$^{\mathrm{I}}$	71.0(1)		
C(8A)	112.7(5)	97.7(4)	
C(2)	124.5(5)	122.1(5)	117.4(7)

Other angles (°):

C*(8A)–N*(1)–K	118.8(5)
C*(2)–N*(1)–K	124.1(5)
O(8)–H(8)···O*(8$^{\mathrm{II}}$)	167(10)

TABLE 5

Intermolecular distances (Å) in complex (1), ⩽3.50 Å excluding hydrogen atoms and 3.1 Å for hydrogen to carbon, nitrogen, or oxygen

a	b	a···b$_i$ or b···a$_j$	*i*	*j*
C(2)	C(7)	3.44	III	II
C(2)	C*(8)	3.49	IV	IV
C(2)	C*(8A)	3.49	IV	IV
C(3)	C(6)	3.44	III	II
C(7)	O*(8)	3.44	II	III
C(8)	O*(8)	3.31	II	III
O(8)	C*(7)	3.36	II	III
O(8)	C*(8)	3.19	II	III
C*(2)	C*(6)	3.44	II	III
H(2)	N*(1)	2.91	IV	IV
H(2)	C*(8)	2.86	IV	IV
H(2)	C*(8A)	2.96	IV	IV
H(2)	O*(8)	2.78	IV	IV
H(4)	C(4)	2.95	V	V
H(4)	C*(3)	2.98	VI	VII
H(7)	O*(8)	2.77	II	III
H(7)	C*(4)	3.09	VIII	IX
H(7)	C*(4A)	3.07	VIII	IX
H(7)	C*(5)	3.05	VIII	IX
H(8)	C*(7)	2.89	II	III
H(8)	C*(8)	2.44	II	III
H*(4)	C*(8)	2.99	X	XI
H*(4)	O*(8)	2.91	X	XI
H*(6)	C(5)	2.95	X	XI
H*(6)	C(6)	2.90	X	XI
H*(7)	O(8)	2.82	III	II

hydrogen-bonding contacts. Because the planes of the neutral ligands are nearly parallel, these operations lead to stacking of aromatic rings. The perpendicular distances between these planes are 3.3 and 3.5 Å about $x = \frac{1}{2}$ and 1 respectively.

TABLE 6

Equations of planes in the form $lX' + mY' + nZ' + d = 0$ where X', Y', and Z' are co-ordinates (Å) referred to orthogonal axes which are related to the fractional co-ordinates x, y, z along the crystallographic axes by the transformations $X' = xa + yb\cos\gamma + zc\cos\beta$, $Y' = yb\sin\gamma - zc\cos\alpha^*\sin\beta$, and $Z' = zc\sin\alpha^*\sin\beta$. Distances (Å) from the planes are in square brackets, those of atoms excluded from calculation of the plane are italicised

In complex (1)

Plane (1):

$$-0.5283X' - 0.1045Y' - 0.8425Z' + 1.7834 = 0$$

[N(1) 0.000(6), C(2) 0.009(9), C(3) 0.008(9), C(4) −0.012(9), C(4A) −0.010(7), C(5) 0.003(9), C(6) 0.012(9), C(7) 0.004(8), C(8) −C.015(8), C(8A) 0.009(7), *O*(*8*) *−0.051*(*5*), *H*(*8*) *−0.1*(*1*), $O^*(8^{II})$ *0.005*(*5*), *K 1.105*(*2*), K^I *−2.225*(*2*)]

Plane (2):

$$0.5229X' + 0.3267Y' - 0.7872Z' - 3.7211 = 0$$

[N*(1) 0.001(6), C*(2) −0.009(9), C*(3) −0.009(10), C*(4) 0.009(9), C*(4A) −0.002(8), C*(5) 0.000(9), C*(6) −0.006(9), C*(7) −0.003(8), C*(8) −0.002(7), C*(8A) 0.014(7), $O^*(8)$ *0.026*(*5*), $H(8^{III})$ *−0.7*(*1*), $O(8^{III})$ *−1.214*(*5*), *K 0.271*(*2*)]

Angles between the normals to planes (1) and (2): 69.3°

In complex (2)

Plane (3):

$$-0.8844X' - 0.3396Y' - 0.3199Z' + 4.9788 = 0$$

[N(1) 0.014(5), C(2) 0.004(8), C(3) −0.015(8), C(4) −0.014(8), C(4A) −0.005(6), C(5) 0.015(8), C(6) 0.025(8), C(7) −0.009(7), C(8) −0.016(6), C(8A) −0.004(5), *O*(*8*) *−0.015*(*5*), *H*(*8*) *−0.31*(*5*), $O^*(8^{II})$ *−1.204*(*5*), *K −0.964*(*1*), K^I *2.888*(*1*)]

Plane (4):

$$-0.8992X' - 0.3346Y' - 0.2816Z' + 6.3130 = 0$$

[N′(1) 0.014(4), C′(2) 0.022(7), C′(3) −0.008(7), C′(4) −0.020(6), C′(4A) −0.008(6), C′(5) 0.023(7), C′(6) 0.030(7), C′(7) 0.001(7), C′(8) −0.021(5), C′(8A) −0.016(5), *O′*(*8*) *−0.055*(*5*), *H′*(*8*) *0.03*(*4*), $O^*(8^{II})$ *−0.015*(*5*), *H′*(*2*) *0.22*(*4*), *K 0.385*(*1*)]

Plane (5):

$$-0.3646X' + 0.7794Y' - 0.5093Z' - 2.8017 = 0$$

[N*(1) 0.003(5), C*(2) 0.001(7), C*(3) 0.003(7), C*(4) −0.013(7), C*(4A) 0.007(6), C*(5) −0.006(7), C*(6) 0.004(7), C*(7) 0.011(7), C*(8) −0.015(6), C*(8A) 0.002(5), $O^*(8)$ *−0.090*(*4*), $O(8^{II})$ *−1.911*(*4*), $H(8^{II})$ *−1.44*(*4*), $O'(8^{II})$ *1.059*(*4*), $H'(8^{II})$ *0.92*(*4*), *K − 0.259*(*1*)]

Plane (6):

$$0.9190X' + 0.3908Y' - 0.0518Z' - 6.0188 = 0$$

[N(1) −0.241(5), O(8) −0.003(5), N′(1) −0.433(4), O′(8) 0.478(5), N*(1) 0.347(6), *K −0.073*(*1*), $O^*(8)$ *2.444*(*4*), $N(1^I)$ *−3.015*(*5*)]

Angles (°) between normals to the planes:

(3) and (4)	2.4	(3) and (6)	158.3
(3) and (5)	77.3	(4) and (6)	160.5
(4) and (5)	77.9	(5) and (6)	90.1

Angles between normal to plane (6) and K–N(1^I) and K–O*(8) bonds: 22 and 24° respectively

Between the *a*-axis columns there is a small effect of meshing of hydrogen atom H(5′) into an anionic ring; H(4) has short interactions with another anion. There are no intermolecular hydrogen contacts less than 2.5 Å. Although H′(2) appears significantly out of plane (4) of Table 6 it does not have any unusual contacts.

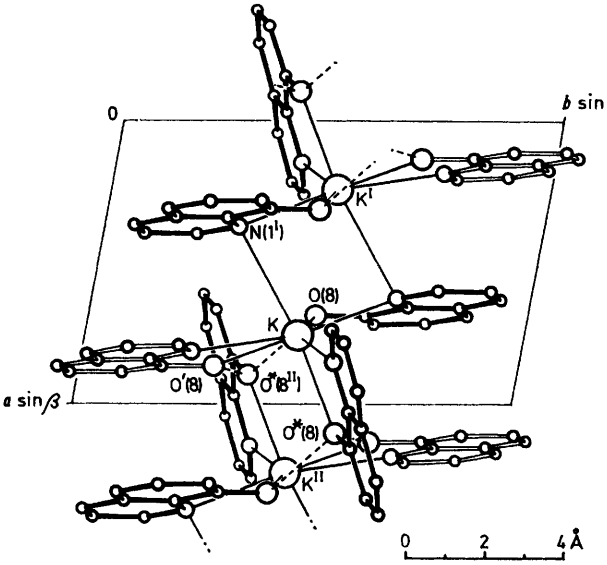

FIGURE 3 Structure of complex (2) projected down the crystallographic *c* axis. The primed ligand is shown with open bonds, the other two with solid bonds. Roman numeral superscripts refer to the following equivalent positions relative to the co-ordinates of the crystal chemical unit in Table 2 at *x*, *y*, *z*:

I	$1 - x, 1 - y, -z$	IV	$2 - x, 2 - y, -z$
II	$2 - x, 1 - y, -z$	V	$x, y - 1, z$
III	$2 - x, 1 - y, 1 - z$	VI	$x, y + 1, z$

Hydrogen atoms are omitted for clarity. Broken lines indicate hydrogen bonds, *e.g.* from O(8) and O′(8) to O*(8^{II})

DISCUSSION

Dimensions of the Ligands.—The versatility of the ligand may result from the relative constancy of dimensions. In Table 3 there are only very small differences between the corresponding bond lengths for neutral and anionic ligands. Around C(8), from the effects of the lower electropositivity of the hydroxyl group in comparison with the anionic oxygen, we should find[9] shorter ring bonds, a longer C–O bond, and a widening of the C(7)–C(8)–C(8A) angle in the neutral molecules. The dimensions in complex (2) tend towards these features, but in both complexes the only significant distinction between the anion and neutral ligand is in the ring angle at C(8). A survey of the literature carried out with the aid of the files of the Cambridge Crystallographic Data Centre[10] yielded six independent values of the C–O distance in neutral molecules, six in zwitterions, and 44 in chelated anions. The mean values were 1.364, 1.352, and 1.328 Å, with standard deviations of ±0.006, ±0.014, and ±0.003 Å respectively; the C–O lengths in complex (2) are in agreement with this pattern, but those in (1) appear anomalous. For comparison, the mean[11] of many aromatic C–OH bonds is 1.36 ± 0.01 Å, a distance which, coupled with the observation that the hydrogen atom is coplanar with the aromatic rings, suggests some π-bond character for the C–O bond.

The mean values for the aromatic carbon–carbon bonds are 1.386 Å in each of the three ligands of complex (2), 1.395 and 1.390 Å for the two of complex (1). Their distribution is as expected from simple considerations of Kekule's resonance structures or the more sophisticated treatment for the quinoline system.[12]

Intermolecular Interactions.—Where neutral quinolin-8-ol molecules are present in crystals, hydrogen bonding is invariably found. If no metal is present, H(8) lies in the plane of the molecule and at *ca.* 2.3 Å from N(1); this may be regarded as an internal hydrogen bond but, in addition, there are intermolecular hydrogen bonds O–H · · · N such that pairs of symmetry-related molecules are held as hydrogen-bonded dimers. This is found in crystals of the unsubstituted free molecule,[13] in 5,7-dibromoquinolin-8-ol,[14] and the isomorphous 5-chloro-7-iodoquinolin-8-ol [14] and in the molecular complexes with 2,3,5,6-tetrachloro-*p*-benzoquinone (2 : 1) [15] and 1,3,5-trinitrobenzene (1 : 1).[16]

TABLE 7

Distances (Å) and angles (°) involving potassium or hydrogen bonding in complex (2)

K–N(1)	2.895(4)	K–N*(1)	2.893(5)
K–O(8)	2.840(5)	K–O*(8)	2.756(3)
K–N′(1)	2.894(4)	K–N(1$^{\text{I}}$)	3.174(4)
K–O′(8)	2.758(6)		
O(8)–H(8)	0.72(6)	O′(8)–H′(8)	0.68(5)
O(8) · · · O*(8$^{\text{II}}$)	2.599(6)	O′(8) · · · O*(8$^{\text{II}}$)	2.566(6)
H(8) · · · O*(8$^{\text{II}}$)	1.88(4)	H′(8) · · · O*(8$^{\text{II}}$)	1.93(5)
K · · · K$^{\text{I}}$	4.117	K · · · K$^{\text{II}}$	4.876

Angles (°) subtended at potassium (standard deviation 0.1—0.2°):

	N(1)	O(8)	N′(1)	O′(8)	N*(1)	O*(8)
O(8)	55.2					
N′(1)	168.5	120.2				
O′(8)	122.4	67.5	55.9			
N*(1)	99.4	152.4	86.7	134.3		
O*(8)	95.1	109.3	96.3	97.7	57.7	
N(1$^{\text{I}}$)	94.7	79.3	73.8	79.9	117.1	169.6

Angles (°) subtended at O(8):

	K	C(8)	O*(8$^{\text{II}}$)
C(8)	122.2(4)		
O*(8$^{\text{II}}$)	104.4(2)	113.7(4)	
H(8)	109(4)	110(4)	5(4)

Angles (°) subtended at O′(8):

	K	C′(8)	O*(8$^{\text{II}}$)
C′(8)	127.8(4)		
O*(8$^{\text{II}}$)	107.7(2)	123.2(4)	
H′(8)	122(4)	107(4)	17(4)

Angles (°) subtended at O*(8):

	K	C*(8)	O(8$^{\text{II}}$)	O′(8$^{\text{II}}$)	H(8$^{\text{II}}$)
C*(8)	125.3(3)				
O(8$^{\text{II}}$)	101.5(2)	116.5(4)			
O′(8$^{\text{II}}$)	88.9(2)	136.9(4)	74.1(2)		
H(8$^{\text{II}}$)	102(1)	115(1)	2(1)	76(1)	
H′(8$^{\text{II}}$)	93(1)	131(1)	78(1)	6(1)	80(2)

Angles (°) subtended at N(1):

	K	K$^{\text{I}}$	C(8A)
K$^{\text{I}}$	85.3(1)		
C(8A)	119.7(4)	98.2(3)	
C(2)	119.8(4)	108.2(4)	115.8(5)

Other angles (°):

K–N′(1)–C′(2)	122.5(5)
K–N′(1)–C′(8A)	121.1(3)
O′(8)–H′(8) · · · O*(8$^{\text{II}}$)	157(5)
K–N*(1)–C*(2)	123.2(4)
K–N*(1)–C*(8A)	119.9(4)
O(8)–H(8) · · · O*(8$^{\text{II}}$)	173(5)

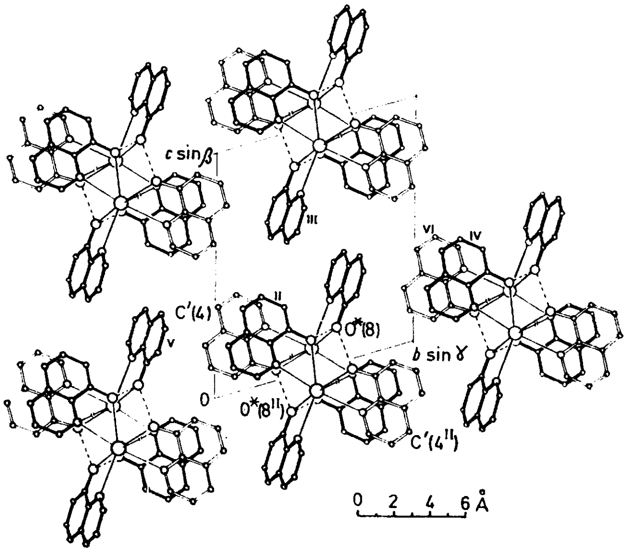

FIGURE 4 Structure of complex (2) projected down the crystallographic *a* axis with the ligands distinguished as in Figure 3. The molecules within the limits x = 0.5—1.5 are shown so that the hydrogen bonds (broken lines) are included, while the K–N(1$^{\text{I}}$) type contacts forming the dimeric molecules are out of this unit cell and shown as interrupted bonds

Of the ions reported to give complexes containing neutral quinolin-8-ol ligands, those of K^+, Rb^+, and Cs^+ are the largest; the next largest is silver with Ag^+–O (ionic) distances normally *ca.* 2.5 Å. Smaller ions are U$^{\text{VI}}$,[17-20] Th$^{\text{IV}}$, and Sc$^{\text{III}}$,[21] with M–O in the range 2.2—2.4 Å; the complex [UO_2(quin)$_2$(Hquin)] was found, both in the unsolvated crystalline form [17] and in a technically more amenable chloroform solvate,[18] to have the two anions chelated and the third molecule in a zwitterion form and unidentate through the phenolate

TABLE 8

Intermolecular distances in complex (2), $\leqslant$ 3.50 Å excluding hydrogen atoms and $\leqslant$ 3.0 Å for hydrogen to carbon, nitrogen, or oxygen

a	b	a · · · b$_i$ or b · · · a$_j$	*i*	*j* (if different from *i*)
C(2)	C′(8)	3.50	I	
C(2)	O′(8)	3.43	I	
C(3)	C′(8)	3.47	I	
C(3)	C′(8A)	3.34	I	
C(4)	C′(8A)	3.50	I	
C(4A)	C′(2)	3.37	I	
C(5)	C′(4A)	3.43	II	
C(7)	N′(1)	3.43	II	
C(7)	O*(8)	3.49	II	
C(8)	O*(8)	3.38	II	
C(8A)	C′(8)	3.48	II	
O(8)	C*(8)	3.41	II	
C′(8)	O*(8)	3.50	II	
C*(4)	C*(4)	3.43	III	
H(4)	C*(6)	2.79	IV	
H(7)	C*(8)	2.96	II	
H(8)	C*(8)	2.72	II	
H′(5)	C*(4)	3.00	V	VI
H′(5)	C*(4A)	2.93	V	VI
H′(8)	C*(8)	2.98	II	
H*(2)	C(7)	2.94	I	

oxygen, while the NH^+ entity formed a hydrogen bond with the oxygen atom of one of the chelated ligands. The hydrogen atom was not located by X-ray methods, but the existence of an NH bond was shown by the i.r. spectrum[19] and that of the positive charge on the nitrogen by X-ray photoelectron spectroscopy.[20]

Smaller cations, such as titanium, were studied by Frazer and Goffer[22] who interpreted the i.r. spectra as indicating that the neutral molecule was unidentate through the oxygen atom taking part in hydrogen bonding similar to that of the uncomplexed molecule.

Only for the silver complex [Ag(quin)(Hquin)] (pyridine solvate)[3] is the hydrogen bonding comparable with that found in the present work, *i.e.* with the hydrogen away from the nitrogen atom, and the hydrogen bonding of the form O–H $\cdots$ O, not O–H $\cdots$ N. In the silver complex, the metal is four-co-ordinated by a chelating anion and a neutral molecule, the monomeric units being held by single O $\cdots$ O bonds, 2.457 Å in chains in the crystal; a difference of 0.05 Å in the Ag–O bonds was taken as evidence for distinct O–H $\cdots$ O rather than symmetrical hydrogen bonds.

In the potassium complexes the hydrogen bonding is strong, judged both by the individual length and by the effect of symmetry in providing double [in (1)] or quadruple [in (2)] bridging. Although the O $\cdots$ O distance (2.430 Å) in (1) is ' very short ' the hydrogen atom was unequivocally located on O(8) so the bond is not symmetrical; a strong but unsymmetrical hydrogen bond is consistent with the i.r. spectrum[2] which showed no OH stretching frequency or the anomalous effect characteristic of symmetrical hydrogen bonds. This aspect of the i.r. spectrum was similar for (2) where the O $\cdots$ O distances are also short (2.599 and 2.566 Å) with angles of 157° at H(8) and 173° and H'(8). If allowance is made for the apparent shortening of an O–H bond, measured by X-ray methods,[23] from the value of 0.97 Å obtained by neutron diffraction, positions for H(8) and H'(8) can be calculated and H $\cdots$ O hydrogen-bond distances deduced; these are H(8) $\cdots$ $O^*(8^{II})$ 1.48 Å in (1), and H(8) $\cdots$ $O^*(8^{II})$ and H'(8) $\cdots$ $O^*(8^{II})$ 1.64 and 1.66 Å in (2).

In complex (2), but not in (1), another solid-state effect characteristic of the quinolin-8-ol ring system is manifest: the close stacking of parallel planes. This is found in the molecular complexes of quinolin-8-ol mentioned above, and in the bis-chelated metal complexes with planar orientation, *e.g.* palladium(II)[24] and copper(II)[25] complexes both of which can also form charge-transfer complexes such as those with 2,3,5,6-tetrachloro-*p*-benzoquinone[26] and 1,2,4,5-tetracyanobenzene.[27] This stacking is the only type of intermolecular contact in the palladium(II) complex, but both the α and β forms of $[Cu(quin)_2]$ have centrosymmetrical $Cu(\mu\text{-}O)_2Cu$ bridges normal to the quinolinolate planes. An indication that the stacking effect may be important is that the arrangement of ligands may distort to produce it, *e.g.* in tris(phenanthrene-9,10-quinone)molybdenum[28] one of the ligands is bent about the O $\cdots$ O line to make two ligands parallel. In all cases the separations between the planes of the ligands are 3.2—3.3 Å; individual atom–atom distances are in the range 3.0—3.5 Å.

Both potassium complexes exist only in the solid state, the neutral ligands being lost in solution and even from the solid; the vapour is fungicidal[29] and the density is difficult to determine because it suddenly increases as the additional ligand molecules are lost. The rubidium and caesium complexes which are isomorphous with (2) behave in the same way, and we will now consider whether any structural features offer an explanation.

In both potassium complexes all the ligand molecules chelate, some of the donor atoms of the neutral molecules are shared, and the hydroxyl hydrogen atoms take part in intermolecular hydrogen bonding. Complex (2) shows no significant difference between the K–O distances to one neutral molecule (O') and to the anion (O*) in agreement with the finding from the averages in many structures[30] that alkali-metal cation–oxygen distances do not vary systematically with the formal charge on the oxygen atom. It therefore does not appear that the neutral molecules are more loosely bound. The closer the potassium ion is to the plane of the chelate ring the shorter are the K–X distances; this is consistent with favourable interaction with the lone pairs of electrons on trigonally hybridised atoms.

In Figure 5 the resemblance between the dimeric molecules of (1) and (2) is shown. The potassium–oxygen and –nitrogen distances have average values of 2.785 and 2.984 Å in (2) and 2.744 and 2.921 Å in (1). The ratio of the differences is 1.02 : 1 for both types of bond, in agreement with the formula given by Wells[31] for the variation in radius with co-ordination number; radius for seven co-ordination : radius for six-co-ordination = 1.020 : 1.

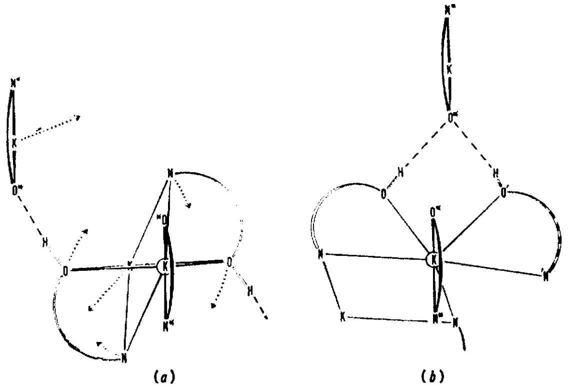

FIGURE 5 Comparison of the structures of complexes (1) and (2), both shown in projection down the normal to the N*(1) $\cdots$ O*(8) vector passing through that vector and K. The small circle represents a centre of symmetry. In (*a*) the arrangement in (1) is shown, with arrows suggesting the direction of movement to give (2), shown in (*b*)

We thank Dr. J. D. Owen for assistance with computing, and the Royal Society for some equipment.

[8/1086 *Received, 9th June,* 1978]

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