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### Molecular Topology in Crystals of a Potassium(I) Complex with [Z-5-(2-Chlorobenzylidene)-4-Oxoimidazolin-2-YL]-3-Amino-Propanoate

A. Mrozek<sup>a</sup>; J. Karolak-Wojciechowska<sup>a</sup>; R. Czyłkowski<sup>a</sup>; K. Kieć-Kononowicz<sup>b</sup>

<sup>a</sup> Institute of General and Ecological Chemistry, Technical University, Poland <sup>b</sup> Department of Chemical Technology of Drugs, Collegium Medicum of Jagiellonian University, Poland

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# MOLECULAR TOPOLOGY IN CRYSTALS OF A POTASSIUM(I) COMPLEX WITH [Z-5-(2-CHLOROBENZYLIDENE)-4- OXOIMIDAZOLIN-2-YL]-3-AMINO-PROPANOATE

A. MROZEK<sup>a,\*</sup>, J. KAROLAK-WOJCIECHOWSKA<sup>a</sup>,  
R. CZYŁKOWSKI<sup>a</sup> and K. KIEĆ-KONONOWICZ<sup>b</sup>

<sup>a</sup>*Institute of General and Ecological Chemistry, Technical University,  
90-924, Łódź Żwirki 36, Poland;*

<sup>b</sup>*Department of Chemical Technology of Drugs, Collegium Medicum of Jagiellonian University,  
30-688 Kraków, Medyczna 9, Poland*

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In a complex with [Z-5-(2-chlorobenzylidene)-4-oxoimidazolin-2-yl]-3-amino-propanoate acid (APAC), potassium ion adopts distorted square-bipyramidal (4 + 2) coordination. All donor atoms are oxygens; four of them originate from carboxylate groups of APAC, while the remaining ones are water oxygens. The equatorial plane of coordination polyhedron is composed of two carboxylate oxygens (with K–O distances of 2.769 and 2.806 Å) and two water oxygens (with K–O distances of 2.722 and 2.749 Å). Two axial K–O bonds (2.663 and 2.664 Å), involving the remaining carboxylate O atoms, complete the sixfold coordination of the K atom. Coordination polyhedra are condensed in two ways. The distance between two potassium pairs are significantly different, 4.224 and 3.801 Å. APAC molecules are held together by a network of hydrogen bonds and create a gap along the *[ab]* plane with molecular ribbons of potassium ions and water molecules inside. Due to the potassium alignment of aliphatic chains in two neighbouring, crystalgraphically independent APAC molecules, small cavities are created, which form small channels along the *b* axis with the remaining water molecule.

*Keywords:*  $\beta$ -Alanine; Potassium complex; Polymeric structure; X-ray structure analysis

## INTRODUCTION

In previous studies arylidene-imidazoline-4-one amino acids have been studied from the viewpoint of their binding to ionotropic (iGluRs) [1] and/or metabotropic (iGluRs) receptors [2]. From information based on a model of ligand-receptor interactions with iGluRs [3] it was postulated that the presence of COO<sup>−</sup> groups was indispensable for binding [4,5]. For this reason, we focus our attention on interactions between arylidene-imidazoline-4-one amino acids and metals (mainly potassium and calcium).

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\*Corresponding author. E-mail: agmrozek@mail.p.lodz.pl

As a first example, we have made an interesting 6-coordinated potassium polymeric complex with *o*-Cl-benzylidene-imidazoline-4-one  $\beta$ -alanine and water molecules.

Potassium appears in numerous structures as a central atom in coordination compounds and organic salts. We found over 1200 structures in the Cambridge Structural Database [6] with a potassium atom, though only 118 of them were complexes of six-coordinate potassium with six oxygen donor atoms. In more than half of them (58%) potassium adopts a planar coordination, whilst in the remaining structures square-bipyramidal coordination is observed with K–O bond distances ranging from 2.33 to 3.32 Å. It should be noted that no structure containing potassium with amino acids was found. As the one example of a potassium complex with carboxylate oxygen donor atoms, the structure of hexa(3,5-dicarboxypyridine)-potassium tetrabromoaurate (III) can be mentioned [7]. In this structure, potassium is surrounded by equivalent oxygen atoms to form a regular octahedron with rather short K–O distances of 2.56 Å. We were unable to find any polymeric potassium complex in the CSD, although numerous papers on coordination polymers are to hand [8–10].

## EXPERIMENTAL

Potassium [*Z*-5-(2-chlorobenzylidene)-4-oxoimidazolin-2-yl]-3-aminopropanoate (AP AC) was obtained by a method described in the literature [11]. Suspension of 3-amino-propanoic acid (4.8 g, 0.054 mol) and potassium *tert*-butanolate (4.2 g, 0.036 mol) in 500 ml of anhydrous ethanol was stirred at room temperature for 0.5 h. Then *Z*-5-(2-chlorobenzylidene)-2-methylthioimidazolin-4-one (7.5 g, 0.0297 mol) was added and the reaction mixture was refluxed for 4 h and the solvent then removed *in vacuo*. The solid obtained was recrystallised from ethanol to give deep yellow crystals. Yield 75%. TLC:  $R_f$  (chloroform-isopropanol-25% aq. ammonia – 9:11:2) = 0.15;  $^1\text{H-NMR}$  (300 MHz; DMSO-*d*<sub>6</sub>):  $\delta$  = 2.48 (t,  $J$  = 1.8 Hz, 2H,  $\text{CH}_2\text{COOH}$ ), 3.54 (br s, 2H,  $\text{HN-CH}_2$ ), 6.48 (s, 1H,  $\text{ArCH=}$ ), 7.18 (dt,  $J$  = 1.4 Hz,  $J$  = 7.6 Hz, 1H, 4'-H), 7.32 (t,  $J$  = 7.6 Hz, 1H, 5'-H), 7.41 (d,  $J$  = 7.9 Hz, 1H, 3'-H), 8.73 (br s, 1H,  $\text{NHCH}_2$ ), 8.85 (br s, 1H, 6'-H); FTIR (KBr):  $\nu$  = 3319, 3062 (NH, OH), 2958 (CH), 1705 (C=O), 1667 ( $\text{ArCH=}$ ), 1623, 1508, 1405, 1198, 1035, 767, 694  $\text{cm}^{-1}$ .

X-ray analysis was carried out using a single crystal of dimensions  $0.3 \times 0.1 \times 0.06$  mm obtained by slow evaporation from ethanol solution. All measurements were performed using a Kuma4 CCD  $\kappa$ -axis diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation at room temperature. The crystal was positioned 62 mm from the KM4-CCD camera; 496 frames were measured at  $1.5^\circ$  intervals with a counting time of 25 s. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. Some 13954 reflections were measured, of which 6977 were considered as observed using the criterion  $I > 2\sigma(I)$ . Data reduction and analysis were carried out with Kuma Diffraction (Wrocław) programs [14].

The structure was solved by direct methods [12] and refined using SHELXL 93 [13]. The full-matrix least-squares refinement was based on  $F^2$  and used anisotropic temperature factors for all non-H-atoms; positions of all H-atoms, except H112 and H-atoms from water molecules, were found in electron density maps and refined in riding mode with isotropic displacement parameters 1.5 times the respective  $U_{\text{eq}}$  values for the parent atoms. Refinement converged to  $R = 0.0692$ ,  $wR = 0.0710$

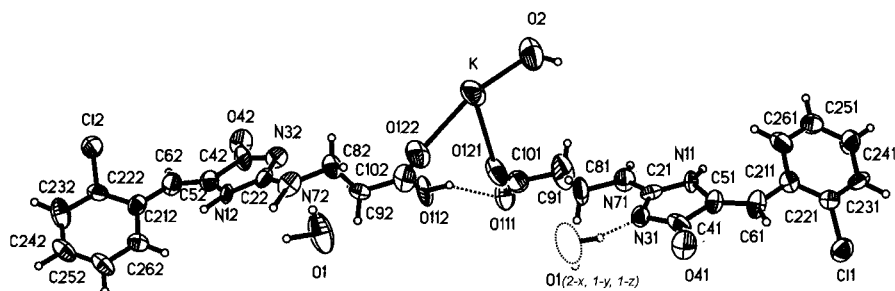


FIGURE 1 An ORTEP drawing of the crystallographically independent unit with atom numbering. The non-hydrogen atoms are shown with 50% probability ellipsoids.

TABLE I Crystal data and structure refinement details

Chemical formula	$C_{13}H_{12}ClN_3O_3 \cdot C_{13}H_{11}ClN_3O_3^- \cdot K^+ \cdot 2H_2O$
Formula weight	661.54
Temperature	293 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.527(2)$ Å $b = 7.555(2)$ Å $c = 28.018(6)$ Å $\alpha = 82.27(3)^\circ$ $\beta = 80.92(3)^\circ$ $\gamma = 68.42(3)^\circ$
Volume	$1458.0(6)$ Å <sup>3</sup>
Z	4
Density (calculated)	$1.507$ g/cm <sup>3</sup>
$\mu$ (MoK $\alpha$ )	$0.425$ mm <sup>-1</sup>
$F(000)$	684
Crystal size	$0.3 \times 0.1 \times 0.06$ mm
$\Theta$ Range for data collection	$3.32$ to $28.78^\circ$
Index ranges	$-9 \leq h \leq 10$ , $-10 \leq k \leq 10$ , $0 \leq l \leq 36$
Reflections collected	13954
Independent reflections	6977 [ $R(\text{int}) = 0.1603$ ]
Method of structure solution	direct method
Method of structure refinement	full-matrix least squares on $F^2$
No. of parameters refined	3.89
Goodness-of-fit on $F^2$	0.821
Final $R1$ [ $I > 2\sigma(I)$ ]	0.0692
Final $wR2$ index	0.0710
Largest diff. peak and hole	$0.325$ and $-0.226$ e/Å <sup>3</sup>
Extinction coefficient	$0.0003(8)$

(with  $w = 1/[\sigma^2(F_0^2)]$ , empirical extinction correction coefficient  $g = 0.0003(8)$ , data/restraints/parameters = 6977/0/389,  $S = 0.821$ ;  $\Delta\rho_{\min} = 0.226$  eÅ<sup>-3</sup>,  $\Delta\rho_{\max} = 0.325$  eÅ<sup>-3</sup>. Atomic scattering factors were obtained from SHELXL [13].

The molecular geometry of the structure is presented in Fig. 1. Crystal data and structure refinement details are gathered in Table I, final atomic coordinates and equivalent isotropic displacement factors in Table II, and selected geometrical details in Table III. Listings of the observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors.

TABLE II Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement ( $\text{\AA}^2 \times 10^3$ ) for **1**.  $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$
C11	7876(1)	8391(1)	600(1)	55(1)
N11	5627(3)	5858(3)	2346(1)	28(1)
C21	6368(4)	5128(5)	2757(1)	45(1)
N31	7637(4)	5844(4)	2869(1)	42(1)
O41	8782(4)	8121(4)	2430(1)	63(1)
C41	7794(5)	7167(5)	2474(1)	49(1)
C51	6522(5)	7112(5)	2105(1)	44(1)
C61	6408(5)	8055(5)	1666(1)	48(1)
N71	5842(4)	3765(4)	3040(1)	50(1)
C81	6647(6)	2927(6)	3499(1)	63(1)
C91	5731(7)	1560(7)	3713(2)	94(2)
C101	6465(6)	562(8)	4206(2)	70(1)
O111	7098(4)	-1170(4)	4274(1)	73(1)
O121	6277(4)	1702(4)	4517(1)	70(1)
C211	5110(5)	8108(4)	1322(1)	37(1)
C221	5654(5)	8330(5)	825(1)	44(1)
C231	4508(5)	8243(6)	491(1)	52(1)
C241	2720(5)	8052(6)	645(1)	59(1)
C251	2160(5)	8001(6)	1142(1)	67(1)
C261	3314(5)	7941(5)	1474(1)	52(1)
C12	7885(1)	-3670(2)	9327(1)	62(1)
N12	9257(4)	-621(4)	7561(1)	35(1)
C22	8270(5)	19(5)	7183(1)	42(1)
N32	7127(4)	-997(4)	7120(1)	43(1)
C42	7327(5)	-2253(5)	7524(1)	47(1)
O42	6470(4)	-3426(4)	7618(1)	60(1)
C52	8689(5)	-2016(5)	7826(1)	47(1)
C62	9077(5)	-3047(5)	8265(1)	49(1)
N72	8476(4)	1397(4)	6866(1)	49(1)
C82	7389(5)	2079(5)	6439(1)	45(1)
C92	8228(5)	698(6)	6044(1)	55(1)
C102	7322(6)	1548(7)	5575(1)	57(1)
O112	7666(4)	203(4)	5284(1)	67(1)
O122	6245(4)	3176(4)	5511(1)	65(1)
C212	10341(5)	-2939(5)	8577(1)	41(1)
C222	10019(4)	-3309(5)	9077(1)	41(1)
C232	11269(6)	-3335(5)	9408(1)	60(1)
C242	12956(5)	-3135(5)	9220(1)	52(1)
C252	13332(5)	-2685(5)	8728(1)	50(1)
C262	12092(4)	-2597(4)	8419(1)	37(1)
K	2977(1)	4020(2)	5059(1)	81(1)
O1	10595(5)	3982(5)	6359(1)	97(1)
O2	498(5)	3804(5)	4479(1)	95(1)

## DISCUSSION

The complex has a polymeric structure. Crystals contain molecular ribbons of potassium ions bridged by oxygen atoms from APAC molecules carboxylate groups and water molecules. In the independent unit five chemical species have been identified (Fig.1). Each APAC molecule consists of two aromatic rings, phenyl and 1,2-imidazole. Dihedral angles between these rings are similar in both molecules,  $37.3(2)$  and  $36.5(2)^\circ$ , respectively. The APAC ligands **1** and **2** differ in two important points. First, the carboxylate group in **1** is ionic with the negative charge located

TABLE III Selected bond distances (Å) and angles (°)

<i>a. The ligand molecules:</i>					
Molecule 1		Molecule 2			
O111–C101	1.216(6)	O112–C102	1.313(4)		
O121–C101	1.262(6)	O112–H112	0.85		
C51–C61–C211–C261	29.7(5)	O122–C102	1.207(5)		
N71–C81–C91–C101	180.0(9)	C52–C62–C212–C262	43.6(6)		
		N72–C82–C92–C102	–170.8(3)		
<i>b. Hydrogen bonds:</i>					
N71–H71...O42 <sup>IV</sup>	2.820(4)	133.76	O1–H12W...N31 <sup>V</sup>	2.753(5)	164.45
N72–H72...O41 <sup>V</sup>	3.212(4)	141.90	N72–H72...O1	3.033(5)	113.76
N11–H11...O42 <sup>IV</sup>	2.812(4)	138.23	O2–H22W...O1 <sup>I</sup>	2.744(4)	141.46
N12–H12...O41 <sup>V</sup>	2.797(4)	136.23	O2–H21W...O112 <sup>IV</sup>	2.861(5)	136.94
O112–H112...O121	2.487(4)	177.50			
<i>c. Potassium ion environment:</i>					
K–O2	2.722(3)	O2–K–O2 <sup>III</sup>	78.93(9)	O122 <sup>I</sup> –K–O111 <sup>II</sup>	166.65(9)
K–O2 <sup>III</sup>	2.749(4)	O122–K–O121	68.28(9)	O122 <sup>I</sup> –K–O2	93.47(9)
K–O122	2.769(3)	O2–K–O121	94.47(9)	O122 <sup>I</sup> –K–O2 <sup>III</sup>	97.88(9)
K–O121	2.806(3)	O2 <sup>III</sup> –K–O122	118.18(9)	O122 <sup>I</sup> –K–O122	91.20(8)
K–O122 <sup>I</sup>	2.663(3)	O2–K–O122	161.45(9)	O122 <sup>I</sup> –K–O121	83.02(9)
K–O111 <sup>II</sup>	2.664(3)	O2 <sup>III</sup> –K–O121	173.38(9)	O111 <sup>II</sup> –K–O2	99.6(1)
				O111 <sup>II</sup> –K–O2 <sup>III</sup>	87.54(9)
				O111 <sup>II</sup> –K–O122	75.51(9)
				O111 <sup>II</sup> –K–O121	93.01(9)
<i>d. The bridging system:</i>					
K–K <sup>I</sup>	3.801(2)	K–K <sup>III</sup>	139.36(6)		
K–K <sup>III</sup>	4.224(2)	K–O2–K <sup>III</sup>	101.1(1)		
		K–O122–K <sup>I</sup>	88.79(9)		

Symmetry codes: <sup>I</sup>– $x+1, -y+1, -z+1$ ; <sup>II</sup>– $x+1, -y, -z+1$ ; <sup>III</sup>– $x, -y+1, -z+1$ ; <sup>IV</sup>1– $x, -y, 1-z$ ; <sup>V</sup>2– $x, 1-y, 1-z$ .

mainly on O121. The length of respective C–O bonds and absence of the hydrogen confirm it explicitly (Table III). In contrast, hydrogen is bonded to O112 in the carboxylate group of molecule **2**. Secondly, the conformations of aliphatic  $\beta$ -alanine chains in both molecules vary significantly (see Table III). This is well illustrated by the torsion angles N71–C81–C91–C101 and N72–C82–C92–C102, 180 and  $-170.8^\circ$ , respectively, in both molecules. Consequently, chains are oppositely oriented in both molecules.

The sequence of two APAC molecules (Fig. 1) is repeated by symmetry operations. In the crystal, this results in separation of hydrophobic and hydrophilic sections. Thus, the hydrophobic aromatic rings form a stack down the  $b$  axis with a distance of about 4.2 Å (see Fig. 2). In addition, due to the opposing alignment of aliphatic chains in two neighbouring and stacked APAC molecules, small cavities are formed (Fig. 2) along the  $b$  axis with a water molecule inside (represented by oxygen O1 in Figs. 1 and 2). In this region, all hydrophilic carboxylate groups face each other and create a gap, almost parallel to the  $ab$  plane, in which the molecular ribbon of potassium ions and water molecules (represented by O2 oxygen in Figs. 1 and 2) is located (Fig. 2).

Hydrogen bonds in the crystal can be divided into two groups, according to their role in the crystal structure. We identify H-bonds joining ligand molecules and H-bonds involving water molecules. First, stacked columns of APAC molecules are joined in two ways. One hydrogen bond links the columns across the gap *via* the carboxylate oxygens, O112–H112...O121 (Figs. 1 and 2 and Table III). Then, each of two carbonyl

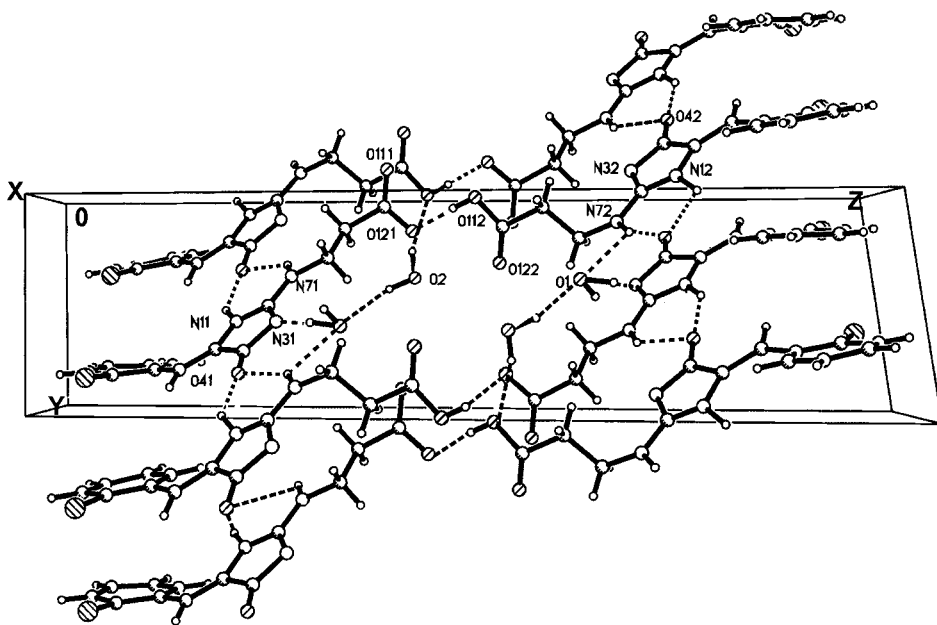


FIGURE 2 Stacking and H-bond network projection down the  $a$  axis. Potassium (I) ions are omitted for clarity.

oxygens, O41 and O42, forms two bifurcated H-bonds anchoring two NH groups (both from the same molecule). Both APAC molecules are joined with the first water molecule in the crystal. Moreover, two H-bonds, one with N31 from the ionised ligands ( $O1-H12W \cdots N31^V$ ) and the other with N72 from the unionised ligands ( $O1 \cdots H72-N72$ ), are observed (Table III). At the same time, O1 is linked to the second water molecule ( $O2^I-H22W \cdots O1$  in Table III). The last bond bridges the potassium ribbon and cyclic parts of APAC molecules. Water molecules located in the gap are connected to carboxylate oxygen atom  $O112^{IV}$  ( $O2-H21W \cdots O112$ ).

The potassium coordination sphere consists of six oxygens and one (O121) of them possesses a negative charge (Fig. 3). Hence, the potassium atom adopts a distorted square-bipyramidal coordination (4 + 2). The four basal equatorial bonds are formed by two carboxylate oxygens (O121; O122) with K–O bond distances of 2.769(3) and 2.806(3) Å, respectively, and two water oxygens (O2;  $O2^{III}$ ) with bond distances of 2.722(3) and 2.749(4) Å respectively (see Table III). O–K–O angles in this plane vary from 68.28(9) to 118.18(9)°. Axial donor atoms are two carboxylate oxygens,  $O111^{II}$  and  $O122^I$ , with contact distances of 2.664(3) and 2.663(3) Å, respectively, while the  $O111^{II}-K-O122^I$  angle equals 166.65(9)°.

This coordination bipyramids are condensed in two ways, at edges of equatorial planes ( $O2 \cdots O2^{III}$  3.498 Å) and the longer bipiramid edge ( $O122 \cdots O122^I$  3.875 Å; Fig. 3). Condensed polyhedra are arranged along  $a$  (Fig. 4). The K–K<sup>III</sup> distance from bipyramids condensed by the shorter edge equals 4.224(2) Å. Thus, when the polyhedra are connected *via* the longer edge, the K–K<sup>I</sup> distance is equal to 3.801(2) Å.

In the ionised APAC molecule, there are two oxygens that take part in coordination spheres. In the crystal, these oxygens contribute to the coordination spheres of potassium ions in two neighbouring ribbons, creating inter-ribbon bridges down the  $y$  axis.

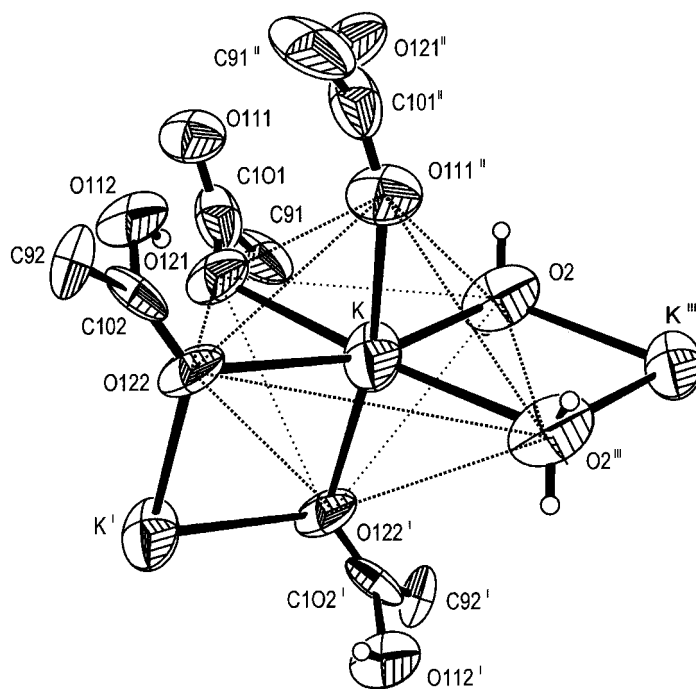


FIGURE 3 Fragment of the polymeric structure of 1. Displacement ellipsoids are drawn at the 50% probability level.

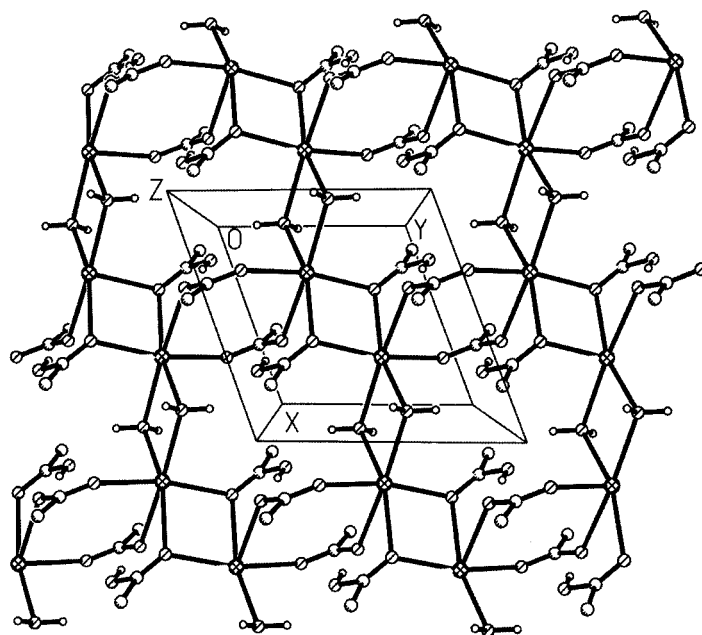


FIGURE 4 Potassium(I) network down the *c* axis. APAC molecules are represented only by  $\alpha$ -carbon atoms and carboxylate groups.



## CONCLUDING REMARKS

The structure of the polymeric potassium complex initiates a new class of compounds. In fact, in the CSD [6] no structure of a potassium complex with amino acids or polymeric potassium complexes was found. This prompts us to further research the synthesis and X-ray study of other related metal complexes of amino acid derivatives of interest. The results seem to be particularly appropriate for describing the iono-(iGluRs) [1] and metabotropic (iGluRs) receptor [2] binding properties for arylidene-imidazoline-4-one amino acids.

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