Coordination Complexes of Groups 1 and 2. Potassium *O,O′*-Catecholdiacetate

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Abstract: Potassium chloride and catecholdiacetate form a 1:2 potassium, catecholdiacetate complex. The crystals are monoclinic with $a = 23.650$ (5) Å, $b = 11.889$ (2) Å, $c = 7.857$ (2) Å, $\beta = 106.61$ (3)°, $Z = 8$, and space group $C2/c$. The crystal structure has been determined by tangent and cosine direct phasing methods and refined by block diagonal least squares to a final R of 0.029 on 1635 observed diffractometer data. The complex cation has crystallographic symmetry 2 with the potassium lying between a pair of twofold related ligand molecules. The coordinating atoms are the ether and carboxyl oxygens from one crystallographic asymmetric unit and a carboxyl oxygen from a symmetry related unit. This pentagonal group is then transformed by a crystallographic rotation axis, containing the potassium atom, to give a ten-coordinated unit. The geometry of the coordination can be described as an irregular pentagonal antiprism. The K–O distances range between 2.75 and 2.92 Å. The potassium cation lies 1.55 Å from the least-squares plane of a pentagonal group of oxygens. A hydrogen atom located on a crystallographic inversion center is shared between two catecholdiacetate ligands.

In the course of work on coordination complexes of group 1 and 2 cations,[3,4] it has been determined that catecholdiacetic acid ($CDAH_2$) forms a crystalline precipitate with potassium but not with lithium, sodium, caesium, or ammonium. This was a rather unusual result since all the known precipitimetric reagents for potassium also precipitate ammonium, caesium, and rubidium.[5]

The potassium complex salt is a white, crystalline solid (mp 253–255°; ir (BKr, μm) 3.0–4.5 (m), 5.5–6.0 (s), 6.62 (m), 6.95 (m), 7.5 (s), 7.9–8.5 (m), 8.85 (m), 9.5 (m), 12.3 (w), 13.7 (s)) whose elemental analysis proved correct (within 0.2% of the calculated value for C and H) for $CDAHK{\cdot}CDAH_2$. Thus, the actual stoichiometry of the reaction of $CDAH_2$ and potassium chloride is:

$$2CDAH_2 + KCl \rightleftharpoons CDAHK{\cdot}CDAH_2 + HCl \qquad (1)$$

Equation 1 is precisely the reverse of a reaction organic chemists perform routinely during purification of carboxylic acids;[6] i.e., protonation of a carboxylate salt by a strong, inorganic acid. Although reaction would normally proceed far to the left (pK_{a_1} of $CDAH_2$[7] = 2.4, pK_a of HCl < 1), it is "driven" to the right by precipitation of the catecholdiacetate complex. Presumably the reason for the higher potassium precipitimetric selectivity of $CDAH_2$ over $NaBPh_4$ rests on two main structural features: (1) size and (2) coordination.[8] It has been accepted for some time[5] that the factor responsible for the precipitation of potassium by tetraphenylboron, cobaltinitrite, chloroplatinate, and perchlorate is the size of the anion. Large anions do not fit well into the water structure.[9] Also, larger anions fit better in a potassium salt crystal lattice. In addition to size, (a property it shares with the above anions), $CDAH{\cdot}CDAH_2$ contains 12 oxygen atoms of which eight are available for coordination with the cation. The most recent review on crystal structure determination of coordination complexes of group 1 ions[10] leads to the inference that in most of the known structures of its coordination[8] complexes, potassium is surrounded by oxygen atoms at the corners of a regular figure; i.e., a cube for the nonactin complex[11] and an octahedron for the valinomycin complex[12] and a pentagonal antiprism in the crystal structure of the 1:2 complex of potassium iodide and 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (benzo-19-crown-5).[13]

In order to verify the above conjectures, the X-ray crystal structure determination of the $CDAHK{\cdot}CDAH_2$ complex salt was undertaken.

Experimental Section

Crystals of potassium *O,O′*-catecholdiacetate were obtained from an aqueous solution of this compound by slow temperature reduction of the heated solution. The crystals in the form of thin plates were stable in air and did not deteriorate in an X-ray beam. The crystal density was found by flotation methods using a mixture of bromoform and benzene. Lattice parameters and intensities were measured on a Nonius CAD-4 automatic diffractometer using graphite monochromated Cu Kα radiation. The space group, C_2/c, was determined from systematic absences and intensity statistics. The unit cell dimensions were obtained from a least-squares calculation of 32 observed 2θ measurements with $\theta \geq 30°$ using Cu Kα radiation. The crystal data are given in Table 1. The cell volume and crystal system indicated that the asymmetric unit of the crystal contained half a complex unit, CDAH plus ½H and ½K. The two *O,O′*-catecholdiacetate ligands of the complex are symmetry related and the potassium ion and one of the hydrogen atoms are on special positions in the lattice (inversion centers).

Reflections with $\theta < 70°$ were measured using the standard θ–2θ scanning technique with multiple passes through each reflection. Three check reflections were measured once per hour and served to monitor crystal and instrument stability. There was no significant change in the intensity of these reflections. A total of 2022 independent reflections were measured. A reflection is considered to be observed if $I \geq 3\sigma(I)$. Of the total, 387 reflections failed to meet this condition and were considered to be unobserved. Lorentz and polarization factors were applied to the raw intensities. No correction was made for absorption or extinction.

Structure Determination and Refinement. Three origin fixing reflections were assigned phases, three sigma one phases with $|E| \geq 2.5$ were accepted, and four reflections were treated as twofold ambiguities. The $|E|$ data set was then hand phased using the restriction that new phases were accepted only if the calculated cosine triples[14] were larger than 0.85 and the associated A values were larger than 3.5. Cosine quartets[15] were employed to confirm the estimates of phase as obtained from cosine triples. The value of a quartet was determined if the B value was greater than 1.0 and the cross E's involved in the estimate were all greater than 2.0 or all less than 0.5. These conditions specified the cosine to be +1 or −1, respectively. Using these procedures the 126 largest $|E$'s$|$ were phased. Based upon these phases, an E synthesis was calculated, and the structure was immediately revealed.

The structure was initially refined with individual isotropic thermal parameters using a block-diagonal least-squares technique. The weighting scheme was $w = 1/\sigma^2(F^2)$. The X-ray atomic scattering factors for all atoms were from the International Tables for X-ray Crystallography (1972). The R factor, after four cycles of refinement, was 0.12. By converting to individual anisotropic temperature factors followed by three additional cycles of refinement, the R factor was reduced to 0.075. A difference synthesis using

Table I. Crystal Data for Potassium *O,O'*-Catecholdiacetate

Formula	$KC_{20}H_{19}O_{12}$
Mol wt	489.1 daltons molecule^{-1}
Space group	C_2/c
a	23.650 (5) Å
b	11.889 (2) Å
c	7.857 (2) Å
β	106.61 (3)°
Z	8
ρ_{calcd}	1.53
ρ_{obsd}	1.55
R	0.026
R_w	0.034

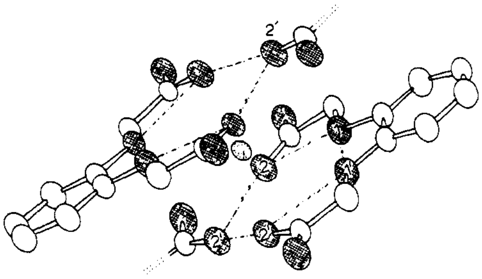

Figure 1. Potassium *O,O'*-catecholdiacetate (1:2) complex illustrating this sandwiching of the potassium ion between symmetry (C_2) related pentagons of oxygen atoms.

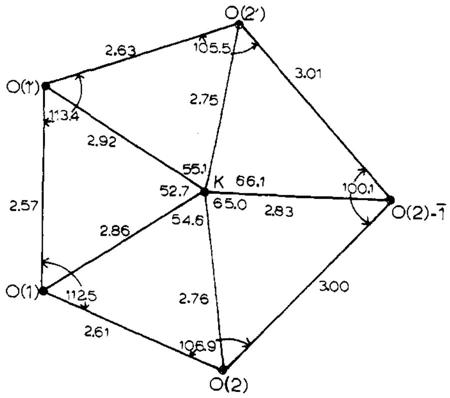

Figure 2. Geometry of the pentagon of oxygen atoms coordinated to the potassium ion.

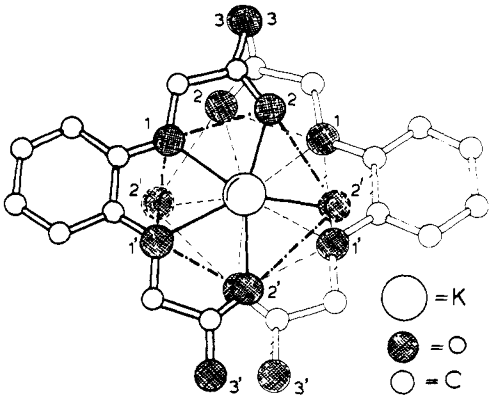

Figure 3. A projection of the potassium *O,O'*-catecholdiacetate complex perpendicular to the plane of the pentagonal oxygen illustrating the antiprism orientations of the two pentagons.

these refined nonhydrogen parameters revealed the correct hydrogen positions. Positional and individual isotropic thermal parameters for all hydrogens and positional anisotropic thermal parameters for nonhydrogen atoms were refined for two additional cycles by block diagonal least squares. The final R factor was 0.029 and the standard deviation of an observation of unit weight was 1.53. This final result was obtained with the sigma weighting scheme above and with the exclusion of the 2,0,2 reflection which appears to be strongly affected by secondary extinction.

The final fractional coordinates and anisotropic thermal parameters for the nonhydrogen atoms are given in Table II. The refined fractional coordinates for the hydrogen atoms are given in Table III. (Observed and calculated structure factors can be obtained from the authors upon request.)

Potassium Coordination

The potassium lies on a crystallographic twofold axis, and around this cation are ten oxygen atoms whose geometry describes an irregular pentagonal antiprismatic polygon. The coordinating atoms are the ether and carboxyl oxygens from one crystallographic asymmetric unit and the carboxyl oxygen O(2) transformed via the crystallographic inversion center at (0,0,0) or ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$). These five oxygens, which form an irregular pentagon, are transformed by the twofold rotor at ($\frac{1}{2}$,y,$\frac{1}{4}$) to give the full coordination. Since the O(2) oxygen is doubly coordinated to the potassium, it is not surprising that the O(2)-C(8) bond is somewhat distorted relative to the O(2')-C(8') bond. The potassium-ether oxygen distances average 2.88 Å while the analogous distance for the carboxyl oxygens is 2.78 Å. The independent pentagonal group of coordinating atoms is approximately planar with a root-mean-square deviation of 0.67 Å from the least-squares plane through those atoms. The distance of the cation from this plane is 1.55 Å. The O-O-O contact angles range from 100.1 to 113.4° with an average value of 107.8°. The oxygen-oxygen contact distances for one asymmetric unit are about 2.6 Å while contact distances across asymmetric units are about 3.0 Å. This difference in oxygen-oxygen distance makes the pentagonal geometry only approximate. This type of coordination where four binding oxygens form a ten-coordinated structure is very uncommon. The crystal structure of the 1:2 complex between potassium iodide and the catechol derived macrocyclic ether benzo-15-crown-5[13] is the only other crystallographically verified example of pentagonal antiprismatic coordination to potassium currently in the literature. There are five independent oxygens which form the unique polygon in the crown ether structure. The full coordination is established via an inversion center on which the potassium is located. The oxygen-oxygen contacts of this compound range between 2.52 and 2.87 Å. The K-O contacts are in the interval 2.78-2.96 Å. The coordination in this sturcture is somewhat more symmetric due to more uniform O-O contact distances.

Figure 1 shows the complete structure of potassium *O,O'*-catecholdiacetate. Two complete asymmetric units and the C(8) carboxyl unit from two other asymmetric units are required to complete the coordination. Figure 2 shows the geometry of the independent coordinating pentagon as viewed along the normal of the least-squares plane through the five oxygens. The figure shows contact distances and angles for the independent coordinating unit. Figure 3 shows two catecholdiacetate ligands and the potassium; the view is the same as in Figure 2.

Anion Geometry

Bond distances and angles of the catecholdiacetate ligand are given in Figures 4 and 5. Standard deviations in the distances, as obtained from the refinement procedure, are about 0.003 Å. If this standard deviation is assumed to be correct, one could then conclude that the differences in the bond distances of the benzo group were significant. Two X-ray crystallographic determinations of the structure of

Table II. Positional and Thermal Parameters for the Nonhydrogen Atoms of Potassium *O,O'*-Catecholdiacetate[a]

Atom	*X/A*	*Y/B*	*Z/C*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K	0.50000 (–)	0.39066 (4)	0.25000 (–)	0.0283 (2)	0.0210 (2)	0.0358 (2)	0.0000 (0)	0.0144 (2)	0.0000 (–)
O(1)	0.38396 (5)	0.48526 (9)	0.16638 (17)	0.0345 (7)	0.0222 (6)	0.0589 (8)	0.0020 (5)	0.0251 (6)	0.0040 (6)
O(1')	0.38771 (5)	0.27089 (10)	0.13221 (19)	0.0384 (7)	0.0220 (6)	0.0674 (9)	–0.0020 (5)	0.0285 (7)	–0.0063 (6)
O(2)	0.46308 (6)	0.58907 (10)	0.05155 (19)	0.0493 (8)	0.0286 (7)	0.0577 (8)	0.0063 (6)	0.0341 (7)	0.0051 (6)
O(2')	0.48037 (6)	0.20104 (10)	0.03881 (20)	0.0490 (8)	0.0280 (7)	0.0657 (9)	–0.0093 (6)	0.0345 (7)	–0.0086 (6)
O(3)	0.43193 (6)	0.75941 (10)	0.10465 (19)	0.0499 (8)	0.0235 (7)	0.0660 (9)	–0.0022 (6)	0.0303 (7)	0.0001 (6)
O(3')	0.45198 (7)	0.02279 (12)	0.02307 (27)	0.0593 (10)	0.0254 (8)	0.1316 (15)	–0.0038 (7)	0.0536 (10)	–0.0151 (9)
C(1)	0.33897 (7)	0.42708 (15)	0.20483 (23)	0.0295 (9)	0.0295 (10)	0.0360 (9)	–0.0015 (7)	0.0124 (7)	0.0035 (7)
C(2)	0.34134 (7)	0.31015 (16)	0.18555 (24)	0.0306 (10)	0.0336 (11)	0.0408 (10)	–0.0009 (7)	0.0155 (8)	–0.0015 (8)
C(3)	0.29801 (9)	0.24435 (17)	0.22154 (32)	0.0462 (12)	0.0312 (11)	0.0800 (15)	–0.0118 (9)	0.0304 (11)	–0.0090 (11)
C(4)	0.25272 (10)	0.29409 (18)	0.27489 (35)	0.0419 (12)	0.0480 (12)	0.0817 (16)	–0.0154 (10)	0.0369 (11)	–0.0088 (12)
C(5)	0.25077 (9)	0.40807 (17)	0.29356 (30)	0.0382 (11)	0.0439 (11)	0.0618 (13)	–0.0034 (9)	0.0266 (10)	–0.0024 (10)
C(6)	0.29424 (8)	0.47473 (16)	0.25943 (27)	0.0401 (11)	0.0326 (11)	0.0543 (11)	0.0036 (8)	0.0213 (9)	0.0033 (9)
C(7)	0.38394 (8)	0.60471 (14)	0.18192 (26)	0.0404 (11)	0.0246 (9)	0.0480 (10)	0.0019 (8)	0.0204 (8)	–0.0007 (8)
C(7')	0.39296 (8)	0.15148 (15)	0.11367 (28)	0.0388 (11)	0.0225 (10)	0.0625 (12)	–0.0057 (8)	0.0213 (9)	–0.0058 (9)
C(8)	0.43103 (8)	0.64817 (15)	0.10597 (23)	0.0350 (10)	0.0248 (9)	0.0363 (9)	0.0011 (8)	0.0114 (8)	0.0026 (7)
C(8')	0.44673 (8)	0.12654 (14)	0.05317 (25)	0.0387 (10)	0.0234 (9)	0.0463 (10)	–0.0025 (7)	0.0156 (8)	–0.0046 (8)

[a] Anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^3c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{31}h,la^*c^*)]$.

Table III. Atomic Positional Parameters for the Hydrogen Atoms of Potassium *O,O'*-Catecholdiacetate

	X/A	*Y/B*	*Z/C*
H(3)	0.303	0.170	0.218
H(4)	0.224	0.245	0.295
H(5)	0.219	0.444	0.336
H(6)	0.296	0.554	0.278
H(7a)	0.391	0.627	0.300
H(7b)	0.345	0.636	0.110
H(7'a)	0.399	0.111	0.227
H(7'b)	0.356	0.117	0.032
H(03)	0.465	0.786	0.060
H(03')	0.501	0.001	0.001

Range SD(*X*)	0.001–0.002	Av SD(*X*)	0.001
Range SD(*Y*)	0.001–0.003	Av SD(*Y*)	0.002
Range SD(*Z*)	0.001–0.004	Av SD(*Z*)	0.003
Range BISO[a]	0.947–6.173	Av BISO	2.289
Range SD (BISO)	0.413–1.076	Av SD (BISO)	0.541

[a] BISO = isotropic thermal factor.

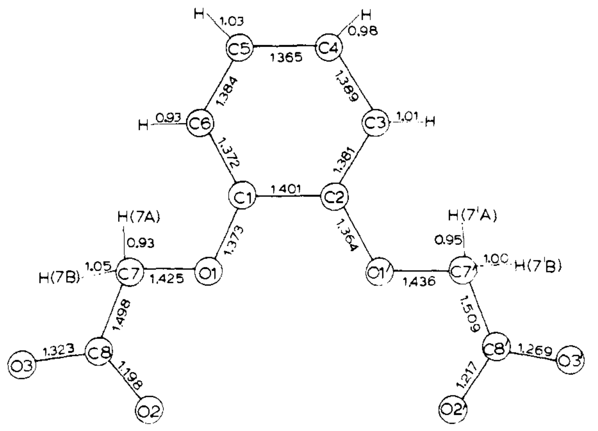

Figure 4. Bond distances in the *O,O'*-catecholdiacetate ligand (σ = 0.006 Å).

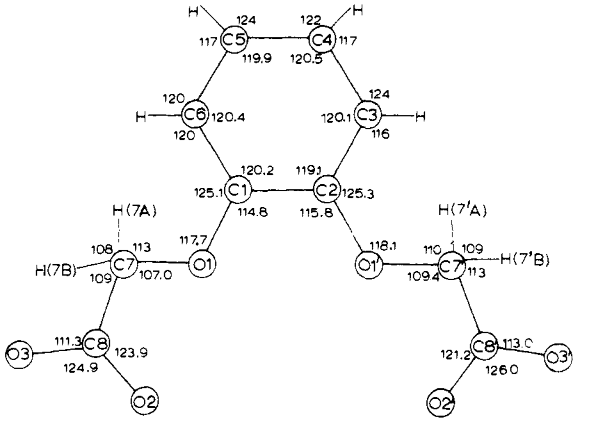

Figure 5. Valency angles in the *O,O'*-catecholdiacetate ligand (σ = 0.6°).

catechol[16,17] show no such differences. Also no significant differences in these bond lengths occur in the potassium iodide complex with benzo-15-crown-5.[13] Based upon these examples and the fact that there is no chemically reasonable explanation for assuming such differences, it is believed that a reasonable average estimate for the standard deviations in the bond distances is approximately 0.006 Å.

Unlike the catechol structures, which show no distortion in sp^2 symmetry around the C(1) and C(2) carbons, this structure and structures of macrocyclic ethers derived from catechol show considerable distortion around these atoms. Since catecholdiacetate is not a closed ring compound the explanation for this distortion is not as simple as for the others. Perfect sp^2 symmetry of C(2) and C(3) would alter the relative orientation of the acetate substituents in such a way as to expand the pentagon significantly increasing the distance between the O(2) and O(2') atoms within each ligand. Presumably the net result is that the coordination is not as stable as in the observed conformation.

Differences in the bond distances around the C(8) and C(8') carbons are directly related to molecular packing in the crystal and to the preservation of electrical neutrality (see hydrogen bonding). The catechol diacetate ligand is nearly planar with the largest deviation from a least-squares plane through the benzo group being 0.35 Å; see Table IV.

Crystal Packing and Hydrogen Bonding

The catecholdiacetate ligands lie in planes parallel to the *b* axis and the *ac* diagonal (Figure 6). Two intermolecular hydrogen bonds in the structure (Table V) connect molecules within these layers. O(3) of molecule A is hydrogen bonded to O(2') of an inversion related molecule B, and O(3') of molecule A is hydrogen bonded to an inversion related O(3') on molecule B'. The hydrogen atom of the later bond is that residing on an inversion center. Molecules B and B' are related by translation along the *b* axis. Thus there is formed an infinite double ribbon of catecholdiacetate molecules running parallel to the *b* axis. Ribbons adja-

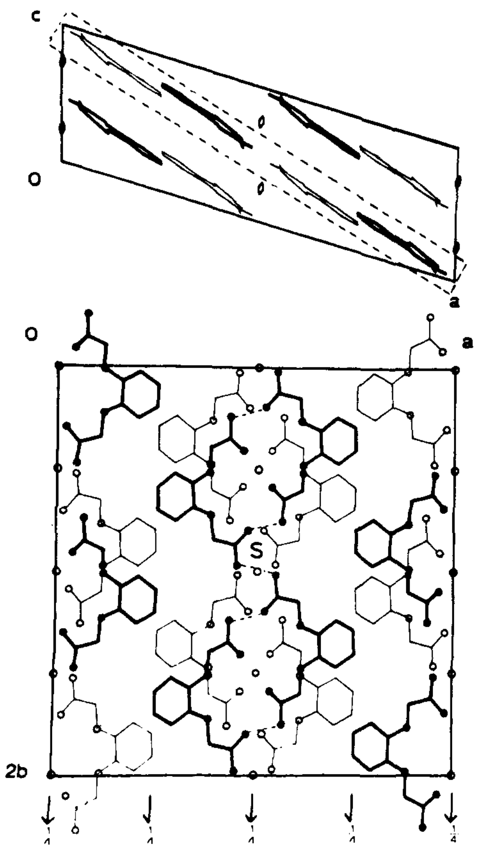

Figure 6. Molecular packing in crystals of potassium *O,O′*-catecholdiacetate (1:2). The dark molecules in the {001} projection correspond to the layers in the dotted outline in the {010} projection. Hydrogen bonds in the central strand of dark molecules are also illustrated. The symmetric hydrogen bond is in the center of the 001 projection (s).

Table IV. Least-Squares Plane through Benzo Group (Equation of plane: $0.2867X - 0.0801Y + 0.9546Z = 3.232$)

Atom	Deviation[a]	Atom	Deviation[a]
C(1)	-0.003	O(2)	-0.320
C(2)	-0.001	O(2′)	0.086
C(3)	0.004	O(3)	-0.347
C(4)	-0.002	O(3′)	-0.038
C(5)	-0.002	C(7)	-0.019
C(6)	0.005	C(7′)	0.031
O(1)	-0.006	O(98)	-0.238
O(1′)	0.002	C(8′)	0.023

[a] Deviation from least-squares plane (A).

cent in the *c* direction are held together in infinite sheets by the potassium ions. These sheets are perpendicular to the *a* axis and have benzene rings on their surfaces. The contacts between adjacent sheets are normal van der Waals forces. Although the hydrogen bonds are of the same length they differ in that the one between inversion related O(3′) molecules must be a symmetric hydrogen bond. Either the hydrogen must reside at the inversion center or be disordered on either side of this point in order to preserve the crystal symmetry. Electron density maps indicate that the former condition is in fact the case.

Table V. Hydrogen Bonding in Potassium *O,O′*-Catecholdiacetate

X–H···Y	X–H (A)	H···Y (A)	X···Y (A)	∠X–H···Y (deg)
O(3)–H(03)···O(2′)	0.986	1.721	2.690	166.5
O(3′)–H(O3′)···O(3′)	1.230	1.230	2.660	180.0

Thus, the net effect of potassium ions and hydrogen bonds is to produce a two-dimensional polymer. We suggest that it is this polymeric crystalline structure which is responsible for the relative water insolubility and that a slight change in cation size (e.g., Na, smaller; Cs, larger) would weaken the hydrogen bonds, ultimately rendering the material water soluble.

The participation of four ligands in the tenfold coordination of each potassium ion is in sharp contrast to the coordination observed in valinomycin. The doughnut shaped valinomycin molecule surrounds the potassium ion providing sixfold coordination in solid and solution. However, *O,O′*-catecholdiacetate complex does resemble the sandwich complexes of enniatin proposed by Ovchinnikov on the basis of spectral analysis.[18] A sandwich complex of potassium *O,O′*-catecholdiacetate could be envisioned in solution that would resemble the complex shown in Figure 1, with water molecules replacing the 2′ oxygens.

Acknowledgments. The authors wish to express their appreciation to Dr. Herbert Hauptman for his enthusiastic support and contribution to the solution of the structure and to acknowledge the technical assistance of Miss P. Strong and Miss M. Tugac. This research was supported in part by U.S. Public Health Grant No. GM 19684-02.

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