Synthesis and structure of (2-hydroxy-2'-carboxy-5-methylazobenzoate)-potassium (I)

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The salt K(Hazc).1.5H₂O has been isolated by reacting H₂azc (where H₂azc = 2-hydroxy-2'-carboxy-5-methylazobenzene) with KOH. X-ray structure determination has revealed the presence of an infinite structure in which the potassium ions are bridged by carboxylic, phenolic and water oxygen atoms but not coordinated to the azo function. One water molecule is also hydrogen-bonded to a carboxyl oxygen function. The potassium ion has a coordination sphere K07 formed by carboxyl, aquo and phenolic oxygen atoms. Its geometry is irregular with three K-O bonds in the range 2.672(3)-2.762(3) Å and the remaining four in the range 2.921(3)-3.157(3) Å. The significant deviation in K-O bond distances (0.2 Å) is attributed to the hydrogen-bonding with some oxygen atoms. The bridging water molecules are of two types: one occupying a general position and the other sitting on a crystallographic two-fold axis. Crystal data are: crystal system, monoclinic; space group C2/c; a = 35.423(1) Å, b = 4.462(2) Å, c = 18.181(7) Å, β = 95.48(3); V = 2861(2) Å³; Z = 8; R = 4.41%, Rw = 4.56%.

The tridentate ligand, 2-hydroxy-2'-carboxy-5-methyl-azobenzene (H₂azc) (I), has been found to bind manganese¹ utilising all the three coordinating sites viz, carboxylic oxygen, phenolic oxygen and azo nitrogen. Unfortunately, single crystals could not be grown in spite of our best attempts. This prompted us to examine the binding of this ligand to a more hard metal, potassium² and its X-ray structure is reported here.

Materials and Methods

The ligand 2-hydroxy-2'-carboxy-5-methylazobenzene (H₂azc) was prepared by a reported procedure³. All other chemicals and solvents were of AR grade and used as obtained.

Preparation of complex

To a methanolic solution (20 ml) of H₂azc (0.45 g, 1.76 mmol) was added 0.10 g (1.78 mmol) of KOH. The resulting solution was stirred in air for 1 h. Upon slow evaporation of the solvent in air, red crystals were obtained. It was collected by filtration and dried in vacuo yield: 0.40 g (71%). [Found: C, 52.21; H, 4.18; N, 8.88; Reqd. for C₁₄H₁₄N₂O₄.K0₅: C, 52.32; H, 4.36; N, 8.72%].

X-ray structure determination

A red prismatic single crystal of K(Hazc).1.5H₂O (0.48 x 0.30 x 0.13 mm³) grown by slow evaporation of a methanolic solution was used. The unit cell parameters of K(Hazc).1.5H₂O were determined by least-squares fit of 22 reflections selected from a rotation photograph (2θ ranges, 5-22°). Data were collected by the ω-scan method in the 2θ range 2-55° on a Nicolet R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction during ~32 h of exposure to X-rays. Data were corrected for Lorentz polarisation effects. Systematic absences led to the identification of the space group as Cc or C2/c. The structure was successfully solved in C2/c. Among the 3778 reflections collected, 3277 were unique and 1428 satisfying I > 3σ(I) were used for structure solution.
Results and Discussion

The aerial reaction of an equimolar mixture of H₂azc with KOH in methanol afforded a red crystalline complex of composition K(Hazc).1.5H₂O. X-ray work revealed that the crystals belong to the space group C2/c with eight formula units in the unit cell. There are no discrete molecules in the three-dimensional lattice in which potassium ions are bridged by water molecules as well as by phenolic oxygen atoms. A fragment of the lattice is shown in Figs 1 and 2 and a view of potassium and oxygen network in the lattice of the molecule is presented in Fig. 3. Selected bond distances and angles are listed in Table 3.

We first consider Fig. 2 in which the organic ligand...
Table 3—Selected bond lengths (Å) and bond angles (°) with esd’s in parenthesis

<table>
<thead>
<tr>
<th>Bond Length/Angle</th>
<th>K(1)-O(2)</th>
<th>K(1)-O(1w)</th>
<th>K(1)-O(2w)</th>
<th>K(1)-O(1a)</th>
<th>K(1)-O(3a)</th>
<th>N(1)-N(2)</th>
<th>O(1)-C(1)</th>
<th>O(2)-C(14)</th>
<th>O(3)-C(14)</th>
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<tr>
<td></td>
<td>2.921(3)</td>
<td>2.688(3)</td>
<td>2.762(3)</td>
<td>3.103(3)</td>
<td>3.084(3)</td>
<td>1.283(4)</td>
<td>1.317(5)</td>
<td>1.250(4)</td>
<td>1.253(5)</td>
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<td>O(2)-K(1)-O(1w)</td>
<td>76.4(1)</td>
<td>87.5(1)</td>
<td>81.6(1)</td>
<td>119.1(1)</td>
<td>138.8(1)</td>
<td>131.1(1)</td>
<td>147.6(1)</td>
<td>116.5(1)</td>
<td>152.6(1)</td>
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<tr>
<td>O(1w)-K(1)-O(2w)</td>
<td>81.6(1)</td>
<td>119.1(1)</td>
<td>79.0(1)</td>
<td>72.6(1)</td>
<td>147.6(1)</td>
<td>133.1(1)</td>
<td>116.5(1)</td>
<td>138.8(1)</td>
<td>133.1(1)</td>
</tr>
<tr>
<td>O(1w)-K(1)-O(3a)</td>
<td>75.3(1)</td>
<td>58.6(1)</td>
<td>88.5(1)</td>
<td>139.0(1)</td>
<td>138.8(1)</td>
<td>133.1(1)</td>
<td>116.5(1)</td>
<td>133.1(1)</td>
<td>119.1(1)</td>
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<td>O(1)-K(1)-O(1wa)</td>
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<td>54.6(1)</td>
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<td>101.0(1)</td>
<td>139.0(1)</td>
<td>101.0(1)</td>
<td>119.1(1)</td>
<td>119.1(1)</td>
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<tr>
<td>O(1a)-K(1)-O(1wa)</td>
<td>68.5(1)</td>
<td>141.2(1)</td>
<td>68.5(1)</td>
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<tr>
<td>O(3a)-K(1)-O(1wa)</td>
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Fig. 3—A view of the network of potassium and oxygen atoms in K(Hazc).1.5H₂O lattice.

gand appears in detail. The ligand is non-planar. There is a dihedral angle of 16.6° between the two benzene rings and a dihedral angle of 26.8° between the carboxyl group and the benzene ring to which it is attached.

The carboxyl group acts as a bridge between two potassium atoms, K(1) and K(1a), related by a two-fold axis. The two C–O distances, C(14)–O(2), 1.250(4) Å and C(14)–O(3), 1.253(5) Å are nearly equal. However, the K(1)–O(2) length, 2.921(3) Å is significantly longer than the K(1a)–O(3) length, 2.672(3) Å. This is understandable since O(2) is also hydrogen-bonded to O(1w) as can be seen in Fig. 1. There is no corresponding hydrogen-bonding in the case of O(3).
Each phenolic oxygen, O(1), which is believed to be in the undissociated OH form acts as a bridge between two potassium ions, (Fig. 1), the K−O bonds being relatively weak, 3.103(3) and 3.157(3) Å.

There are two kinds of water molecules in the lattice. One of these, O(1w), occupies a general position while the other, O(2w) sits on a crystallographic two-fold axis. This explains the stoichiometry K[Hzc].1.5H₂O for the formula unit. The water molecules act as bridges between different pairs of potassium ions. Additionally, O(1w) is hydrogen-bonded to a carboxyl oxygen atom O(2) (O(1w)...O(2), 2.842 Å).

In effect, an infinite network of potassium and oxygen molecules results (Fig. 3) where each potassium ion is relatively strongly coordinated (K−O distances in the range 2.672(3)−2.762(3) Å) to carboxyl oxygen O(3), O(1w) and O(2w) and is relatively weakly coordinated (2.921(3)−3.157(3) Å) to carboxyl oxygen O(2), phenolic oxygen O(1), a second phenolic oxygen O(1) and a second O(1w). The seven coordinated KO₆ geometry is of an irregular kind. Neither of the corresponding manganese complexes of the types Mn[Hzc]₂ nor KMn[Hzc]₂.4H₂O afforded X-ray quality single crystals and hence crystal structures of these complexes could not be done. However, from the structures known for other similar type of complexes, it becomes evident that manganese is coordinated to both phenolic and carboxylic oxygen atoms as well as to the azo function. In case of potassium complex discussed here, the metal is not coordinated to the azo function.

In conclusion, the structural determination of K[Hzc].1.5H₂O has revealed the presence of an infinite structure based on binding of potassium ions by carboxylic, phenolic and aquo bridges and on hydrogen bonding. The potassium ion is not coordinated to the azo function but is bonded to carboxyl, aquo and phenolic oxygen atoms, the coordination sphere being KO₆ of irregular geometry.

The supplementary data on anisotropic thermal parameters, complete bond distances and angles, H-atoms coordinates and tables of observed and calculated structure factors are available from the authors on request.

Acknowledgement
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References