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Cation- π Binding of an Alkali Metal Ion by Pendant α,α -Dimethylbenzyl Groups within a Dinuclear Iron(III) Structural Unit

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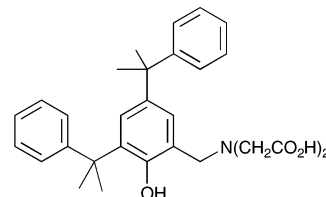
It has been recognized that cation- π interactions between positively charged ions, such as ammonium and alkali metal ions, and unsaturated organic moieties are an important class of noncovalent bond.¹ Evidence is accumulating that the cation- π interaction has a substantial effect on protein structure and function,² but it should also prove to be a useful tool especially in the design and synthesis of novel materials and molecular devices.³ Much of the initial interest in the cation- π interaction was due to the speculation that π -donors such as tyrosine and tryptophan residues were required for the selectivity of the cellular transmembrane potassium channels. A recent crystal structure determination illustrated potassium ion selectivity governed by carbonyl and carboxylate group displacement of coordinated water,⁴ while other structural studies have revealed the presence of hydrophobic regions in potassium channels where aromatic groups may also play a role in potassium ion transport via the cation- π interaction.^{1a}

Indications of the importance of the cation- π interaction were first reported by Kebarle and co-workers⁵ who determined that the strength of the gas-phase interaction between a potassium ion and a benzene molecule was similar to that between a potassium ion and a single water molecule. Subsequently, it was noted that several proteins contain aromatic residues which behave as donors to ammonium cations,⁶ while it was already known that cyclophanes, calixarenes, and related macrocycles could interact with alkali metal cations in aqueous media.^{7,8} Following these observations theoretical calculations revealed that amino acid aromatic residues should interact strongly with sodium and potassium ions.⁹ This suggestion stimulated efforts to characterize more fully the cation- π interaction in view of its potential importance in biological systems. Gas-phase studies have proved especially useful in the analysis of the cation- π interaction given the paucity of solid-state structural data that are currently available regarding this phenomenon. The gas-phase studies are exemplified by the work of Dunbar¹⁰ and Lisy¹¹ and give detailed computational and experimental determinations of cation- π binding energies. Moreover, Gokel and co-workers have demonstrated the effect in X-ray crystallographic studies involving synthetic lariat ether ligands.¹² This work entailed design and preparation of macrocyclic diazopolyethers N-substituted with appropriate unsaturated donor arms. Complexation of these ligands with alkali metal cations enabled the unambiguous observation of the cation- π interaction in the solid state.¹³ Other workers have also noted π -bonding effects in organometallic compounds prepared under stringently anhydrous conditions where the possibility of competition between the cation- π interaction and hydration of the potassium ion is precluded.¹⁴⁻¹⁶

In our work to probe the effect of ligand substitution on the three-dimensional structure of coordination compounds, we have prepared a coordination complex in which a cation- π interaction has an important influence on its solid-state structure. To our knowledge,

it is the first noncyclic system in which a potassium ion is bound by aromatic groups in direct competition with the hydration of said ion.

The ligand **1**, *N*-[3,5-bis(α,α -dimethylbenzyl-2-hydroxy benzyl)] iminodiacetic acid, H₃L, which is a member of the family of *o*-hydroxybenzyl iminodiacetic acid, H₃hda, ligands, was prepared in 80% yield from 2,4-bis-(α,α -dimethylbenzyl)phenol via the Mannich reaction.¹⁷ Complex **2** was prepared by the reaction of ligand **1** (0.08 g/1.7 \times 10⁻⁴ mol) with FeCl₃·6H₂O (0.135 g/5.0 \times 10⁻⁴ mol) in ethanol (95%, 20 mL) in the presence of potassium hydrogen carbonate (0.63 g/6.3 \times 10⁻³ mol). Water (3 mL) was then added to assist the dissolution of the potassium hydrogen carbonate. Thin purple rectangular plates of **2**, K₄[(L)₂(μ -CO₃)₂-Fe^{III}]₂·6H₂O·2EtOH, were grown by slow evaporation of the ethanol solution.



1: *N*-[3,5-bis(α,α -dimethylbenzyl-2-hydroxy benzyl)] iminodiacetic acid.

The X-ray crystallographic analysis¹⁸ of complex **2** (Figure 1) reveals a general motif which we have found with other iron(III) complexes of the *o*-hydroxybenzyl iminodiacetic acid, H₃hda, ligands. Under basic conditions the monomeric unit [Fe(hda)(H₂O)₂] is dimerized through various bridging species, such as oxo, hydroxo, and/or carbonate, giving Fe^{III}₂ units.¹⁹ In **2**, the Fe-N (2.194(6), 2.200(5) Å) and Fe-O (1.915(4)-2.064(4) Å) distances are unexceptional, and the Fe^{III} centers are linked via two carbonate ligands, with an Fe-Fe distance of 4.3723(13) Å. The resulting compounds are found to crystallize in layered or veined structures in which the counterions necessary to balance the charge of the diiron unit are contained within the hydrophilic regions, as for example in K₃[Fe₂(*t*Bu₂hda)(μ -OH)(μ -CO₃)]·3H₂O·EtOH.^{19b} Complex **2** also packs as a layered structure but has the remarkable additional feature of the presence of a π -bound potassium ion which is essentially trapped within the hydrophobic region occupied by the substituent α,α -dimethylbenzyl groups. Clearly such an interaction is not possible for compounds where the substituents on the ring of the ligand are aliphatic groups.

The coordination sphere of K(1) (Figure 1) can be described in terms of a distorted octahedron, comprising the centroids of the phenyl rings, the two phenolate oxygens, and two carbonate oxygen atoms. The K(1)-O bond lengths, 2.613(4)-2.753(4) Å, are typical, while the K(1)-C distances are in the range 3.134(6)-3.342(7) Å. The phenyl-K⁺ interactions are thus rather symmetrical, with K(1) 2.897(3) and 2.930(3) Å above the two phenyl planes. The remaining three K⁺ counterions in **2**, K(2), K(3), and K(4), are coordinated in typical fashion by combinations of carboxylate,

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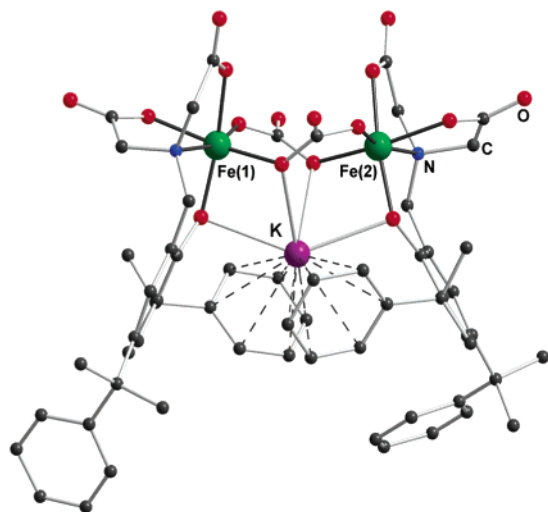


Figure 1. Cation- π binding of potassium ions in complex **2**.

phenolate, and carbonate oxygens, and by the waters and ethanols of crystallization.

The K^+ -phenyl centroid distances in **2** are some of the shortest known for this kind of interaction, and the bond distances and geometry of the cation- π interaction are consistent with calculations made previously by Nicholas,²⁰ Kumpf,²¹ and Caldwell²² for the binding of K^+ ions to free benzene. The observed geometry corresponds most closely with the calculations of the benzene electrostatic potential surface at the MP2/6-311+G* level.²⁰ In the lariat crown ethers of Gokel and co-workers²³ the closest approach of the aromatic group to the K^+ ion varies from 2.97 to 3.57 Å, indicating that the cation- π interaction is quite sensitive to subtle structural changes in the ligating species. Crystal-packing constraints may influence the observed K-C distances in **2** to some extent, but the hydrophobic layer made up of the dimethylbenzyl groups is likely to be quite flexible, and one might therefore expect that the effects of packing constraints would be small.

That the π -bound potassium in **2** is held in the hydrophobic part of the complex is noteworthy. In several studies it has been observed that the cation- π interaction becomes more important in hydrophobic regions of proteins so that aromatic side chains of Phe, Tyr, and Trp become the electron donors where more conventional donors are unavailable.^{2b,d} Thus, the pendant α,α -dimethylbenzyl groups of our ligand represent an electron donor within a hydrophobic environment. The possibility of the presence of a negatively charged phenyl group can be ruled out in the system reported here as was also concluded for the cation- π binding found in organometallic structures.¹⁴⁻¹⁶ Another salient feature of complex **2** is the fact that the interaction of the ligand α,α -dimethylbenzyl groups with the potassium ion immobilizes it in a position close to the iron(III) centers. This enables coordination bonds to form between the phenolate oxygens and the potassium ion effectively bridging the iron and potassium centers. Although there appears to be no particular significance in the bridging between iron(III) ions and potassium ions, it is interesting to speculate about the possibility of immobilizing other alkali or alkaline earth metal ions in the vicinity of transition metal ions since it is known that certain of the groups I and II metal ions behave as cofactors in transition metal-containing enzymes.²⁴

In summary, we have shown that the cation- π interaction between potassium ions and α,α -dimethylbenzyl groups has a strong effect on the solid-state structure of this coordination complex. We have also demonstrated that the cation- π binding of potassium ions is accessible in aqueous media and where the π -donor is nonmacrocylic. Now that we have established a precedent for the cation- π interaction in this system we intend to investigate this phenomenon with particular emphasis on its relevance in biological systems and implications for the field of materials science.

Supporting Information Available: An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (18) **2**: $C_{64}H_{84}Fe_2K_4N_2O_{24}$, $M = 1533.43$, triclinic, $a = 10.0026(6)$ Å, $b = 16.3913(12)$ Å, $c = 21.9296(16)$ Å, $\alpha = 78.662(9)^\circ$, $\beta = 76.825(8)^\circ$, $\gamma = 76.132(8)^\circ$, $V = 3360.2(4)$ Å³, $T = 200(2)$ K, space group P-1, $Z = 2$, $F(000) = 1604$, $D_c = 1.516$ Mg m⁻³, $\mu = 0.761$ mm⁻¹; 20098 data, 12236 unique ($R_{int} = 0.1155$), 877 parameters, $wR_2 = 0.1443$, $S = 0.730$ (all data), $R_1 = 0.0637$ (4672 with $I \geq 2\sigma(I)$).
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