J. Am. Chem. Soc. **1989**, *111*, 5707-5708

Alkali-Metal-Anion Dimers and Chains in Alkalide Structures

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Received January 12, 1989

Abstract: The alkali-metal anions in three alkalide structures, K$^+$(C222)K$^-$ (I), Rb$^+$(C222)Rb$^-$ (II), and Rb$^+$(18C6)Rb$^-$ (III) form unusual alkali-metal-anion dimers (I and II) or chains (III). The anion–anion distances in the dimers and chains are at least 1 Å shorter than the nominal diameters of the anions as determined from other alkalide structures. Possible interactions between the anions in these structures are discussed.

Since the first alkalide, Na$^+$(C222)Na$^-$, was synthesized and its crystal structure determined in 1974[1,2] more than 30 alkalides have been synthesized and characterized by optical spectroscopy, chemical analysis, solid-state NMR, and other techniques.[3] Thus we now have a great deal of information about these negative alkali-metal ions (Na$^-$, K$^-$, Rb$^-$, and Cs$^-$) both in solution and in the solid state. These anions have closed ns^2 shells and therefore are expected to have spherical shapes and nondirectional interactions with their surroundings. They should, however, be very polarizable because of their large sizes. One would expect these anions to be separated from each other in their structures by the positively charged counterions. Indeed, this is often the case. We report here, however, the crystal structures of three alkalides, K$^+$(C222)K$^-$ (I), Rb$^+$(C222)Rb$^-$ (II), and Rb$^+$(18C6)Rb$^-$ (III), in which the anions (K$^-$ or Rb$^-$) form either dimers or chains with anion–anion distances much shorter than the nominal diameters of the anions.

The crystalline compounds were synthesized by the usual procedures described elsewhere.[4] The recrystallization procedure and the techniques for handling, examining, and mounting crystals have also been reported.[5] Data were collected with a Nicolet P3F diffractometer with Mo Kα radiation and a graphite crystal monochromator.

The compounds I and II are isostructural as expected. The crystallographic data for these structures are given in Table I. Figures 1 and 2 show the ORTEP stereo packing diagrams for I and II, respectively. Complete data for these two compounds and the third (III) can be found in the Supplementary Material.

Table I. Crystallographic and Refinement Data for K$^+$(C222)K$^-$ (I) and Rb$^+$(C222)Rb$^-$ (II)

	I	II
space group	$P\bar{1}$	$P\bar{1}$
cell params		
a, Å	12.300 (5)	12.418 (4)
b, Å	12.421 (6)	12.419 (3)
c, Å	11.474 (6)	11.582 (3)
α, deg	106.55 (4)	106.36 (2)
β, deg	92.68 (4)	91.46 (3)
γ, deg	62.02 (3)	62.38 (2)
V, Å^3	1476.0 (11)	1506.8 (7)
Z	2	2
crystal dimens, mm	0.30 × 0.45 × 1.00	0.25 × 0.30 × 0.40
scan type	θ–2θ	θ–2θ
maximum 2θ	45°	45°
temp, K	211 (3)	218 (3)
no. of reflctns collected	4136	5210
no. of unique reflctns	3895	3970
no. of reflctns used in refinmnt with $F_o^2 > 3.0\sigma(F_o^2)$	2700	1671
R	0.033	0.061
R_w	0.032	0.069
high peak in final diff map, e/Å^3	0.14 (2)	0.84 (9)

The complexed cations K$^+$(C222) and Rb$^+$(C222) are similar to those in the ordinary salts K$^+$(C222)I$^-$[6] and Rb$^+$(C222)SCN$^-$.[7] The average M–O distances are 2.83 (3) Å in I and 2.96 (6) Å in II compared with 2.79 (1) Å in K$^+$(C222)I$^-$ and 2.91 (2) Å in Rb$^+$(C222)SCN$^-$.

Table II. Estimated Diameters (in Å) of Alkali-Metal Anions from Structures of Alkalides and Alkali Metals

compounds	$r_{\mathrm{M^-(min)}}$[a]	$r_{\mathrm{M^-(av)}}$[b]	d_{atom}[c]	$r_{\mathrm{M^+}}$	$r_{\mathrm{M^-}}$[d]
Na metal[e]			3.72	.95	2.77
K$^+$(C222)Na$^-$	2.55	2.73 (14)			
Cs$^+$(18C6)$_2$Na$^-$	2.34	2.64 (16)			
Rb$^+$(15C5)$_2$Na$^-$	2.60	2.89 (16)			
K$^+$(HMHCY)Na$^-$	2.48	2.77 (10)			
Cs$^+$(HMHCY)Na$^-$	2.35	2.79 (8)			
K metal[e]			4.63	1.33	3.30
K$^+$(C222)K$^-$	2.94	3.12 (10)			
Cs$^+$(15C5)$_2$K$^-$	2.77	3.14 (16)			
Rb metal[f]			4.85	1.48	3.37
Rb$^+$(C222)Rb$^-$	3.00	3.21 (14)			
Rb$^+$(18C6)Rb$^-$	2.99	3.23 (9)			
Rb$^+$(15C5)$_2$Rb$^-$	2.64	3.06 (16)			
Cs metal[f]			5.27	1.67	3.60
Cs$^+$(C222)Cs$^-$	3.17	3.50 (15)			
Cs$^+$(18C6)$_2$Cs$^-$	3.09	3.46 (15)			

[a] $r_{\mathrm{M^-(min)}}$ is equal to the distance between an anion and its nearest hydrogen minus the van der Waals radius of hydrogen, 1.2 Å. [b] $r_{\mathrm{M^-(av)}}$ is the average radius over the nearest hydrogen atoms. The numbers in brackets are the numbers of hydrogen atoms for averaging. [c] d_{atom} is the interatomic distance in metal. [d] $r_{\mathrm{M^-}}$ is equal to d_{atom} minus $r_{\mathrm{M^+}}$. [e] Reference 11. [f] Reference 10.

The most striking feature in these two structures is that the anions occur in pairs with unusually short distances between the anions. The distances between adjacent anions in a pair are 4.90 Å in I and 5.13 Å in II. The next nearest anion is 7.95 Å away in I and 8.61 Å in II. The interionic distances in the anion pairs are much shorter than expected from the presumed sizes of the anions. Alkali-metal-anion sizes can be estimated from the crystal structures of alkalides by making the assumption that the alkali-metal anions are in contact with their surrounding atoms. In fact, all of the closest neighbors are hydrogen atoms. We take 1.2 Å as the van der Waals radius of a hydrogen atom. Table II shows the "minimum" and "effective" radii of alkali-metal anions as calculated from the crystal structures. The sizes of alkali-metal anions can also be estimated from the crystal structures of the alkali metals with the assumption that the sum of the radii of an alkali-metal cation and its anion is equal to the interatomic distance in the metal.[8] Table II shows the interatomic

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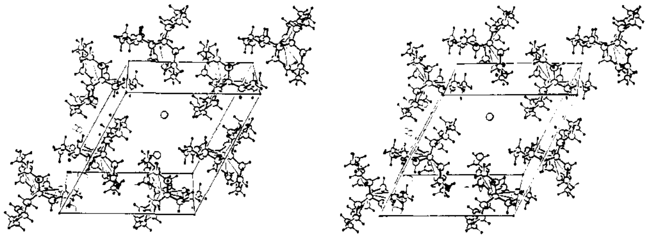

Figure 1. ORTEP stereo packing diagram of $K^+(C222)K^-$.

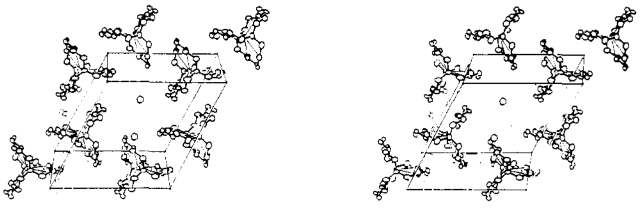

Figure 2. ORTEP stereo packing diagram of $Rb^+(C222)Rb^-$.

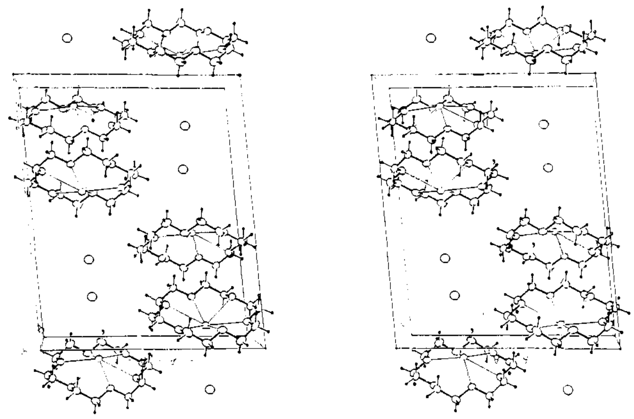

Figure 3. ORTEP stereo packing diagram of $Rb^+(18C6)Rb^-$.

distances in the metals and the calculated radii of alkali-metal anions based on the assumption described above.

Table II shows that the minimum radius of the anion K^- is 2.8–2.9 Å, while the effective radius (from the average over the nearest hydrogens) is 3.1 Å. However, the shortest K^-–K^- distance in $K^+(C222)K^-$ is only 4.90 Å, nearly 1 Å shorter than the minimum diameter of K^- and 1.3 Å shorter than its effective diameter. The structure of $Rb^+(C222)Rb^-$ shows the same feature.

The crystallographic data for the third compound $Rb^+(18C6)Rb^-$ are listed in Table III, while Figure 3 shows the ORTEP stereo packing diagram. Since Rb^+ ($r = 1.48$ Å) is larger than the hole size of the crown ether ($r = 1.4$ Å), the Rb^+ cation lies 0.93 Å above the plane of the 6 oxygens. As a result, Rb^+ is coordinated by six ether oxygens on one side and is essentially in contact with the anion Rb^- on the other.

An unusual structure in III is the nearly one-dimensional chain along the *b* direction with Rb^-–Rb^- distances of only 5.13 Å, the same as that of the Rb^-–Rb^- pairs in II. The chains zigzag in the *b*–*c* plane with a displacement of 1.5 Å in the *c* direction.

What is the nature of the interactions in these dimers and chains? Neutral alkali atom dimers and other clusters have been studied by a variety of spectroscopies and theoretical calculations.[9] The dissociation energies of neutral dimers (X_2 or XY) are in the range of 0.5–1.0 eV and the bond lengths are from 0.3 to 0.7 Å shorter than the interatomic distances in the metals. Since these dimers have bond orders of unity, these results are not unexpected.

Table III. Crystallographic and Refinement Data for $Rb^+(18C6)Rb^-$ (III)

space group	$P2_1/n$
cell params	$a = 14.852$ (4), $b = 8.614$ (2), $c = 18.075$ (4) Å, $\beta = 95.26°$, $V = 2302.7$ (8) Å^3, $Z = 4$
crystal dimens, mm	0.20 × 0.26 × 0.70
scan type	θ–2θ
maximum 2θ	50°
temp, K	200 (3)
no. of reflctns collectd	4557
no. of unique reflctns	4077
no. of reflctns used in refinmnt with $F_o^2 > 3.0\sigma(F_o^2)$	1631
R	0.044
R_w	0.046
high peak in final diff map, e/Å^3	0.45 (7)

Alkali-metal anions have a closed ns^2 shell, so it is unlikely that there is any net bonding between these s orbitals. However, both potassium and rubidium have empty d orbitals that could be involved in bonding. The expense of exciting electrons from the $s\sigma$ antibonding orbital to a *d* orbital might be compensated by the bonding that results, contributing to the stability of dimers or chains. We have reported previously[5] the structure of $Cs^+(C222)Cs^-$ in which the Cs^- anions form zigzag chains along the *b* direction with Cs^-–Cs^- distances of 6.38 Å, ~0.6 Å shorter than the "effective" contact distance for a pair of Cs^- ions (7.0 Å). Another point in favor of *d*-orbital involvement is that although we have determined the structures of seven sodides, none shows any dimers or chains of Na^- ions. [In the series of C222-complexed alkalides, neither $Na^+(C222)Na^-$ nor $K^+(C222)Na^-$ has a dimer or chain structure; all sodide anions are isolated from each other.] This can be explained by the fact that sodium does not have low-lying *d* orbitals and the 3*p* orbitals are too high in energy to contribute to bonding.

An alternative explanation that also involves *d*-orbital character is substantial distortion of K^-, Rb^-, and Cs^- from spherical shape because of their extremely large polarizabilities. According to this picture, effective closest packing of the ions can only be achieved by distortion of the anions, leading to unusually close anion–anion contacts. If this explanation is correct, the lack of sodide dimers results simply from the smaller size of Na^-.

Conventional MAS–NMR experiments on the crystalline compounds I, II, and $Cs^+(C222)Cs^-$ have failed to detect the anions, although the MAS–NMR of compounds with isolated alkali-metal anions give strong peaks for the anions.[12,13] The spectrum of K^- from I obtained recently by the spin-echo NMR technique shows that the K^- anions in I are highly perturbed.[14] This is consistent with its unusual structure.

Acknowledgment. This research was supported by U.S. National Science Foundation Solid-State Chemistry Grant No. DMR 87-14751 and the Michigan State University Center for Fundamental Materials Research. The X-ray diffractometer system was provided by NSF Grant CHE-84-03823.

Supplementary Material Available: Tables of data collection and refinement summaries, positional parameters, thermal parameters, bond distances and angles, and torsion angles and drawings of single molecule for I–III (40 pages); tables of observed and calculated structure factors (61 pages). Ordering information is given on any current masthead page.

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