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Sorin-Claudiu Roşca, Hanieh Roueindeji, Vincent Dorcet, Thierry Roisnel,
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1 Article

2 $K^{\cdots}C_{\pi}$ and $K^{\cdots}F$ Non-Covalent Interactions in π - 3 Functionalized Potassium Fluoroalkoxides

4 Sorin-Claudiu Roșca, Hanieh Roueindeji, Vincent Dorcet, Thierry Roisnel, Jean-François
5 Carpentier * and Yann Sarazin *

6 * Correspondence: yann.sarazin@univ-rennes1.fr; Tel.: +33-223-233-019

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9 **Abstract:** Secondary interactions stabilize coordinatively demanding complexes of *s*-block metals.
10 The structures of potassium fluoroalkoxides that, in addition to intra- and intermolecular $K^{\cdots}F$
11 contacts, also exhibit $K^{\cdots}C_{\pi}$ interactions with tethered π ligands, are reported. A potassium-arene,
12 a rare potassium-alkyne and a potassium-olefin complexes have been prepared by deprotonation
13 of functionalized α,α -bis(trifluoromethyl)alcohols with $KN(SiMe_2R)_2$. They all feature a cuboid K_4O_4
14 core with μ^3 -bridging *O* atoms, and multiple stabilizing $K^{\cdots}F$ contacts in the range 2.71–3.37 Å. The
15 potassium-arene complex shows η^2 , η^3 and η^6 $K^{\cdots}C_{\pi}(\text{arene})$ interactions in the range 3.35–3.47 Å.
16 The potassium-alkyne and potassium-olefin compounds are stabilized by η^2 interactions with the
17 unsaturated carbon-carbon bond, in the range 3.17–3.49 Å and 3.15–3.19 Å, respectively. Comparison
18 with the parent complex devoid of flanking π ligand illustrates the role of $K^{\cdots}C_{\pi}$ interactions.

19 **Keywords:** alkoxide ligands; potassium complexes; secondary interactions; potassium-fluorine
20 contacts; potassium- C_{π} interactions; π ligands

22 1. Introduction

23 Complexes of the electropositive alkali and alkalino-earth metals are characterized by ionic
24 bonding between the cation and the ligands and co-ligands. In addition to regular (weakly) bonding
25 interactions in, for instance, amido or alkoxo salts of these elements, there has been a growing
26 awareness in the past 10–15 years that non-covalent interactions can help towards the stabilization of
27 these species, especially as the size and coordinative demand of the metal increase upon descending
28 groups 1 or 2. The concept of so-called secondary interactions, which are essentially weak donor-
29 acceptor interactions between the cation and charge-neutral C_{π} , halide, H, etc. atom or group of
30 atoms, was highlighted in a landmark article by Ruhlandt-Senge and co-workers in 2010 [1]. This and
31 other groups have in particular prepared many a compound of alkali metals (M) featuring one or
32 more $M^{\cdots}F$ [2–6] and, perhaps more prominently, $M^{\cdots}C_{\pi}(\text{arene})$ [4,7] intramolecular interactions. Of
33 note, the importance of $M^{\cdots}C_{\pi}(\text{arene})$ in biological structures, supramolecular assemblies, and
34 catalytic and ion transportation processes has long been established [8–14]. Many such complexes
35 have been structurally characterized; there are nearly 300 referenced X-ray structures to date in the
36 Cambridge Structural Database (CSD) for η^6 -coordinated $K^{\cdots}C_{\pi}(\text{arene})$ compounds alone.

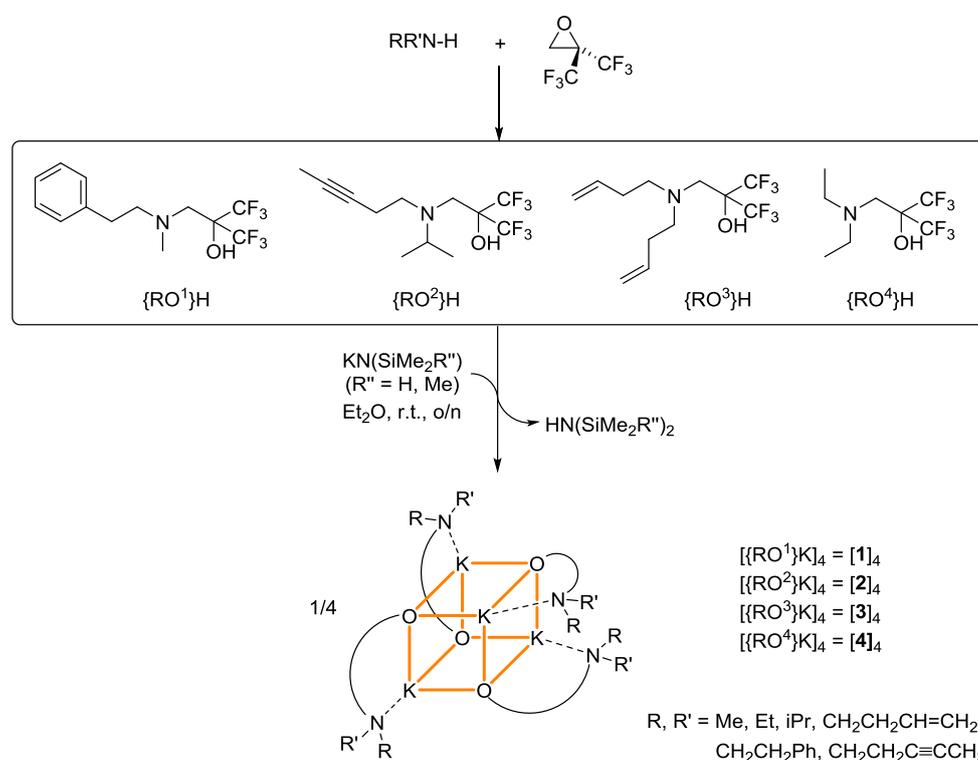
37 As part of our program aimed at implementing the large alkaline earths (Ae = Ca, Sr, Ba) in
38 molecular catalysis, we prepared some time ago several heteroleptic amido-Ae aryloxides and
39 fluoroalkoxides stabilized by secondary interactions, in particular intramolecular $Ae^{2+}\cdots F$ contacts and
40 $\beta\text{-Si-H}\cdots Ae^{2+}$ agostic distortions when using the $N(SiMe_2H)^-$ amido co-ligand [15–18]. More recently,
41 we have prepared Ae-olefin and Ae-alkyne fluoroalkoxo complexes that both exhibit strong
42 intramolecular $Ae^{2+}\cdots C_{\pi}$ in the solid state and in solution [19–20]. We have also shown that *multiple*
43 $Ae^{2+}\cdots F$, $\beta\text{-Si-H}\cdots Ae^{2+}$ and $Ae^{2+}\cdots C_{\pi}$ secondary interactions could be combined within the same
44 molecular structure to yield electron-deficient, yet stable Ae complexes.

45 In the course of this work, we have prepared and structurally characterized several unusual
 46 homometallic potassium fluoroalkoxides that display intramolecular $K^{\cdots}C_{\pi}(\text{arene})$, $K^{\cdots}C_{\pi}(\text{olefin})$
 47 and $K^{\cdots}C_{\pi}(\text{alkyne})$ interactions with tethered π ligands. K^+ -arene complexes are indeed well-known.
 48 However, structurally authenticated $K^+(\eta^2\text{-alkyne})$ complexes (13 structures in the CSD at the time
 49 of writing) are mostly limited to heterobimetallic acetylides such as $[(C_5HMe_4)_2Ti(\eta^1-C\equiv C-SiMe_3)_2]^-$
 50 $[K]^+$ [21] or $\{[(Me_3\text{-tacn})Cr(C\equiv CH)_3]_2K\}^+[CF_3SO_3]^-$ bearing a *N*-methyl-substituted triazacyclonane
 51 ligand ($Me_3\text{Tacn}$) [22]. The sole example of homometallic complex is the polymeric
 52 $\{[(C_5Me_4)_2SiMe_2C\equiv CPh]K\cdot THF\}_\infty$ [23]. $K^+(\eta^2\text{-olefin})$ complexes are more common (46 examples in the
 53 CSD), with representative examples including $[Sn\{(Me_3Si)CHCH=CH(SiMe_3)\}_3][K\cdot THF]^+$ [24],
 54 $[Zn\{(Me_3Si)CHCH=CH(SiMe_3)\}_3][K]^+$ [25], $[Zn(CH_2SiMe_3)(TMP)(CH=CH_2)][K\cdot PTMEDA]^+$ [26], or
 55 the rare homometallic $[KC_{60}(THF)_5]\cdot 2THF$ fulleride [27].

56 In this context, the structural motifs of several polymetallic potassium fluoroalkoxides
 57 displaying strong intramolecular interactions with pendant olefin, alkyne or arene are discussed in
 58 the followings. The structure of the parent complex where the ligand is devoid of dangling π group
 59 is also presented for comparison.

60 2. Results

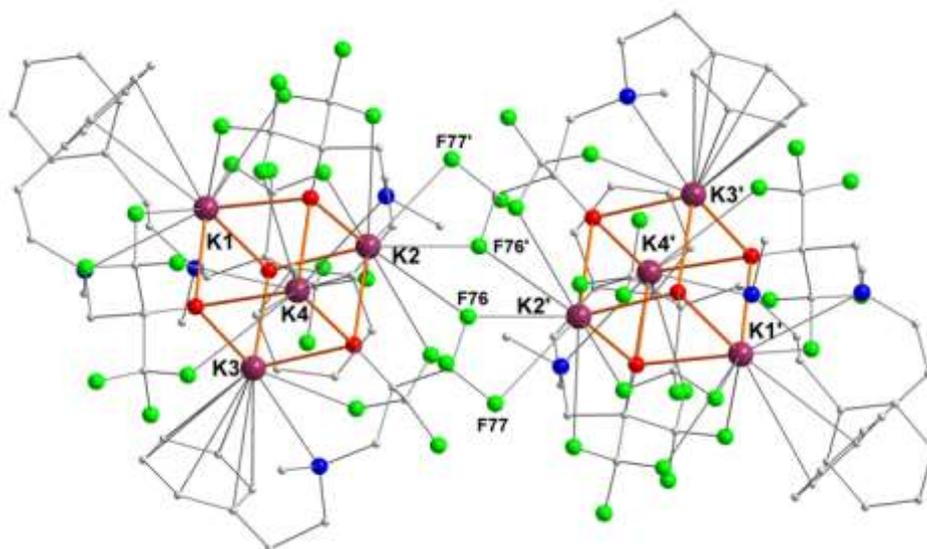
61 The fluoroalcohols $\{RO^x\}H$ - $\{RO^x\}H$ bearing two strongly electron-withdrawing CF_3 groups in α
 62 position to the hydroxyl can be prepared in high yield by treatment of 2,2-bis(trifluoromethyl)oxirane
 63 with the appropriate amine in Et_2O [16,20]. They were reacted with an equimolar amount of the
 64 potassium precursors $[KN(SiMe_2R'')]_2$ or $[KN(SiMe_2H)]_2$ to afford the corresponding potassium
 65 fluoroalkoxides in 33-85% isolated (non-optimized) yields (Scheme 1). The resulting compounds
 66 $\{RO^x\}K_4$ were obtained as colorless, analytically pure solids ($x = 1$, [1]₄; $x = 2$, [2]₄; $x = 3$, [3]₄; $x = 4$,
 67 [4]₄). They all crystallized as tetranuclear complexes in a K_4O_4 cubane arrangement (*vide infra*). Their
 68 composition was established by X-ray crystallography and was corroborated by NMR spectroscopy.
 69 Their purity was confirmed by combustion analyses. All complexes are soluble in common organic
 70 solvents, including aliphatic hydrocarbons.



71 **Scheme 1.** Fluoroalcohols used in this study, with a synthetic scheme for the preparation of the
 72 tetranuclear potassium fluoroalkoxides $[\{RO^x\}K]_4$ [1]₄-[5]₄. A representation of the cuboid structures of
 73 these complexes is given; $K^{\cdots}F$ and $K^{\cdots}C_{\pi}$ secondary interactions not displayed.

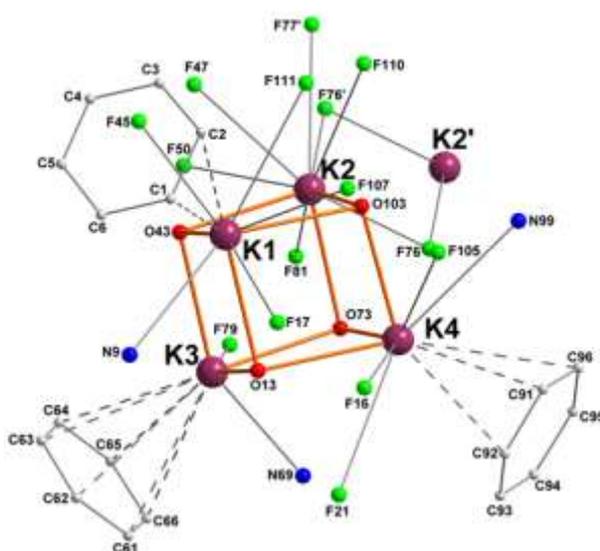
74 2.1. Potassium-arene complex $[\{RO^1\}K]_4$ ($[1]_4$)

75 The compound $[\{RO^1\}K]$ crystallized as the distorted cubane $[\{RO^1\}K]_4$ ($[1]_4$), a multinuclear
 76 structure typical of potassium alkoxides (Figure 1) [18, 28-30]. Two K_4O_4 cuboid motifs are associated
 77 through bridging $K \cdots F$ interactions to generate a centro-symmetric macromolecular edifice containing
 78 eight potassium ions. The distances to the bridging fluorine atoms $K2-F76'$ (2.963(1) Å), $K2-F76$
 79 (3.171(1) Å) and $K2-F77'$ (3.279(2) Å) are well below the sum of van der Waals radii for potassium
 80 (2.75 Å) and fluorine (1.47 Å), testifying to substantial interactions. They are also below the accepted
 81 distance for significant $K-F$ interactions (*ca.* 3.40 Å) [31].



82 **Figure 1.** Representation of the molecular solid-state structure of the potassium-arene complex
 83 $[\{RO^1\}K]_4$ ($[1]_4$). Color code: purple, K; green, F; blue, N; red, O; grey, C. H atoms omitted for clarity.

84 A simplified view of the coordination pattern in $[1]_4$ is depicted in Figure 2. In each of the two
 85 identical cubanes, each potassium atom is coordinated by three oxygen atoms in μ^3 -positions, with
 86 characteristic d_{K-O} bond distances in the range 2.611(2)-2.825(2) Å.



87 **Figure 2.** Simplified representation of the molecular solid-state structure of complex $[\{RO^1\}K]_4$ ($[1]_4$).
 88 Color code: purple, K; green, F; blue, N; red, O; grey, C. Hydrogen atoms are omitted for clarity. Only
 89 the heteroatoms and aryl substituents interacting with potassium are depicted.

90 The nitrogen atoms N9, N69 and N99 are bound to K1, K3 and K4, respectively; there is not any
 91 nitrogen atom coordinated to K2. In addition, each metal ion is stabilized by multiple K⁺⋯F contacts:
 92 K1, K2, K3 and K4 are respectively involved in four, seven, one and three such interactions. They
 93 range from very strong ($d_{K-F} = 2.806(1)$ Å for K3) to mild ($d_{K-F} = 3.324(2)$ Å for K4) [31]. Another
 94 prominent feature of this complex is the presence of K⁺⋯C_π(arene) intramolecular interactions with
 95 three capping aromatic rings from the tethered side-arms of the ligands. Hence, K1, K3 and K4 show
 96 respectively η^2 , η^6 and η^3 π -interactions with the aromatic substituents. Such K⁺⋯C_π(arene) contacts,
 97 all below 3.48 Å, are not uncommon for potassium [4,9,11,13]. A summary of relevant metric
 98 parameters for [1]₄ is given in Table 1.

99 **Table 1.** Key metric parameters in the potassium-arene complex [{RO¹}K]₄ ([1]₄).

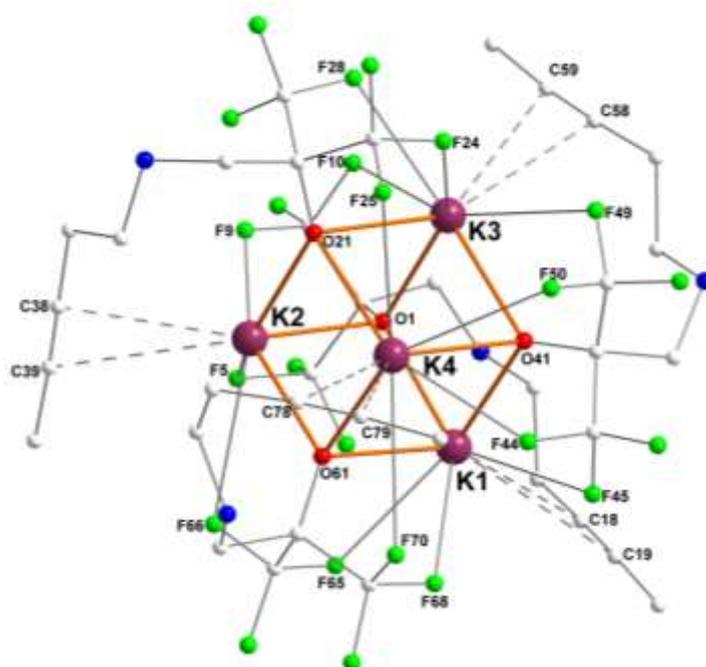
K _i	K _i –O (Å)	K _i –N (Å)	K _i ⋯F (Å)	K _i ⋯C _π (arene) (Å)
K1	O13 = 2.6600(16)	N9 = 3.174(2)	F17 = 2.8804(16)	C1 = 3.4177(30)
	O43 = 2.7493(15)		F45 = 2.8507(15)	C2 = 3.4631(33)
	O103 = 2.7989(15)		F107 = 2.9548(17)	
			F111 = 3.2131(16)	
K2	O43 = 2.6856(15)	n/a	F47 = 2.9987(15)	n/a
	O73 = 2.6927(15)		F50 = 2.8312(14)	
	O103 = 2.6136(15)		F76 = 3.1711(14)	
			F76' = 2.9632(14)	
			F77' = 3.2792(16)	
			F81 = 3.0715(15)	
			F110 = 3.0715(15)	
K3	O13 = 2.6301(15)	N69 = 3.1033(19)	F79 = 2.8062(13)	C61 = 3.4535(24)
	O43 = 2.7087(15)			C62 = 3.4738(25)
	O73 = 2.6869(14)			C63 = 3.4296(25)
				C64 = 3.3749(24)
				C65 = 3.3688(24)
C66 = 3.413(2)				
K4	O13 = 2.8254(15)	N99 = 3.159(2)	F16 = 3.0642(17)	C91 = 3.3482(25)
	O73 = 2.7305(13)			C92 = 3.4120(33)
	O103 = 2.6112(16)			F105 = 3.0760(17)

100 NMR spectroscopy did not provide information regarding the structure of [1]₄ in solution. Its ¹H
 101 NMR spectrum in [D₆]benzene features broad resonances. In the ¹⁹F NMR spectrum, a unique, sharp
 102 singlet is detected at –76.34 ppm, indicating that all CF₃ groups are equivalent on the NMR time-
 103 scale; there was no indication for the persistence of K⁺⋯F interactions in solution. ¹H DOSY NMR
 104 measurements proved erratic, hence provided limited help in assessing the nuclearity of the complex
 105 in solution; they were however consistent with the existence of a multinuclear species.

106 2.2. Potassium-alkyne complex [{RO²}K]₄ ([2]₄)

107 The potassium fluoroalkoxide [{RO²}K] bearing a dangling alkynyl side-arm recrystallized from
 108 pentane as the tetranuclear [{RO²}K]₄ ([2]₄) showing also a K₄O₄ cuboid arrangement (Figure 3).
 109 Besides the presence of multiple K⁺⋯F interactions (three or four per potassium), one of its main
 110 characteristic is the presence of η^2 -K⁺⋯C_π(alkyne) interactions, in the range 3.131(3)–3.495(3) Å.
 111 Remarkably, none of the nitrogen atoms of the ligand backbones coordinates onto a potassium center

112 ($d_{K-N} > 3.832(2)$ Å, and generally over 4.5 Å), thus highlighting the key contributions of $K^+ \cdots F$ and
 113 $K^+ \cdots C_{\pi}(\text{alkyne})$ secondary interactions in this complex. Of interest, $[2]_4$ is a rare example of non-
 114 acetylide potassium-alkyne complex, the sole other occurrence being $[\{(C_5Me_4)_2SiMe_2C \equiv CPh\}K \cdot THF]_{\infty}$
 115 [23]. However, the $K^+ \cdots C_{\pi}(\text{alkyne})$ interatomic distances in $[2]_4$ (in the range 3.131(3)–3.495(3) Å, see
 116 Table 2) are for most of them much shorter than in this latter compound (3.406 and 3.470 Å). On the
 117 other hand, they are much longer than in $K^+ \cdots C_{\pi}(\text{acetylide})$ compounds, where it often approximates
 118 2.95–3.10 Å [21,22,32].



119 **Figure 3.** Representation of the molecular solid-state structure of the potassium-alkyne complex
 120 $[\{RO^2\}K]_4$ ($[2]_4$). Color code: purple, K; green, F; blue, N; red, O; grey, C. H atoms omitted for clarity.

121 **Table 2.** Key metric parameters in the potassium-alkyne complex $[\{RO^2\}K]_4$ ($[2]_4$).

K_i	K_i-O (Å)	$K_i \cdots F$ (Å)	$K_i \cdots C_{\pi}(\text{alkyne})$ (Å)
K1	O1 = 2.6880(14)	F45 = 3.2152(14)	C18 = 3.172(2)
	O41 = 2.6298(13)	F65 = 2.8043(14)	C19 = 3.427(2)
	O61 = 2.7262(14)	F68 = 2.7585(14)	
K2	O1 = 2.7275(14)	F5 = 2.9529(14)	C38 = 3.213(2)
	O21 = 2.7106(13)	F9 = 2.7144(14)	C39 = 3.341(2)
	O61 = 2.6296(14)	F66 = 3.1664(16)	
K3	O1 = 2.6628(14)	F10 = 3.1002(16)	C58 = 3.278(2)
	O21 = 2.7979(14)	F24 = 2.7792(14)	C59 = 3.495(3)
	O41 = 2.6794(14)	F28 = 2.8195(15)	
		F49 = 3.3239(13)	
K4	O21 = 2.6876(14)	F25 = 2.9942(16)	C78 = 3.131(3)
	O41 = 2.8169(14)	F44 = 2.6820(13)	C79 = 3.216(4)
	O61 = 2.6401(14)	F50 = 2.9804(14)	
		F70 = 3.3078(15)	

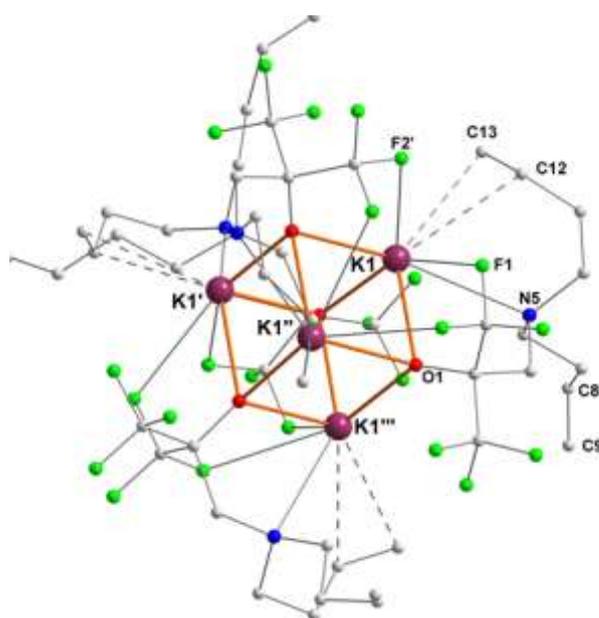
122 Relevant metric parameters for $[2]_4$ are collated in Table 2. Examination of the $K_i \cdots C_{\pi}(\text{alkyne})$
 123 distances shows large discrepancies, with $K4-C78$ and $K1-C18$ being as short as 3.131(3) and 3.172(2)
 124 Å, respectively, whereas $K3-C59$ reaches 3.495(3) Å. One should note that for each potassium, the
 125 distance to the “internal” $C_{\pi}(\text{alkyne})$ atom is systematically much shorter than that to the “external”
 126 one (internal and external $C_{\pi}(\text{alkyne})$ atoms are respectively in γ and δ positions to the nitrogen
 127 atom), hence indicating a dissymmetric binding mode for the alkyne. As seen for $[1]_4$, the intensity of
 128 $K^+ \cdots F$ interactions also varies largely in $[2]_4$, in the range 2.682(1)–3.324(1) Å. The $C=C$ bond lengths in
 129 $[2]_4$, in the region 1.153(5)–1.7179(4) Å, are unexceptional and are typical of non-coordinated ($-CX_2$)–
 130 $C \equiv C-CH_3$ fragments.

131 The solution NMR data (recorded in $[D_6]$ benzene) for $[2]_4$ did not inform us about the nuclearity
 132 of the complex in solution. A sharp singlet is observed at -77.32 ppm in the ^{19}F NMR spectrum, and
 133 the resonances at 78.15 ($C \equiv C-CH_3$) and 76.98 ($C \equiv C-CH_3$) ppm in the $^{13}C\{^1H\}$ NMR spectrum did not
 134 provide useful information about the potential coordination/dissociation of the alkyne in solution.

135 2.3. Potassium-alkene complex $[(RO^3)K]_4$ ($[3]_4$)

136 The potassium-alkene complex $[(RO^3)K]$ also crystallized as the tetranuclear cubane $[(RO^3)K]_4$
 137 ($[3]_4$) in the tetragonal space group $P-42_1c$ (Figure 4). The four potassium centers are therefore
 138 symmetrically equivalent. Each exhibits η^2 -coordination of an olefin and two $K^+ \cdots F$ intramolecular
 139 interactions ($K1-F1 = 3.062(2)$ Å, $K1-F2' = 2.928(2)$ Å). For each ligand, only one of the olefin is
 140 coordinated to potassium ($K1-C12 = 3.192(4)$ and $K1-C13 = 3.148(4)$ Å), whereas the second olefinic
 141 tether (corresponding to C8 and C9) is remote from the metal ion. The two $K^+ \cdots C_{\pi}(\text{alkene})$ distances
 142 in $[3]_4$ are very comparable. They are in the range of those measured in
 143 $[Sn\{(Me_3Si)CHCH=CH(SiMe_3)\}_3][K \cdot THF]^+$ (3.065(8) and 3.164(8) Å) [24], in the fulleride
 144 $[KC_{60}(THF)_5] \cdot 2THF$ (3.204(1) and 3.356(1) Å) [27], in $[Zn\{(Me_3Si)CHCH=CH(SiMe_3)\}_3][K]^+$ (2.942(3)–
 145 3.283(3) Å) [25], or in $[Zn(CH_2SiMe_3)(TMP)(CH=CH_2)][K \cdot PTMEDA]^+$ (2.985(4) and 3.167(3) Å) [26],
 146 although the K^+ -olefin interaction was much more dissymmetric in these complexes. The main metric
 147 parameters for $[3]_4$ are summarized in Table 3.

148 The ^{19}F NMR spectrum of $[3]_4$ displays a sharp singlet at -75.86 ppm for all CF_3 groups. The 1H
 149 and especially $^{13}C\{^1H\}$ spectra ($\delta_{13C} = 137.70$ and 116.01 ppm for the $C_{\pi}(\text{alkene})$ atoms) did not show
 150 differences between the two types of olefins, coordinated and dissociated; this suggests that they
 151 either exchange very fast on the NMR time-scale, or that the tetranuclear arrangement is disrupted
 152 in $[D_6]$ benzene.



153 **Figure 4.** Representation of the molecular solid-state structure of the potassium-alkene complex
 154 $[(RO^3)K]_4$ ($[3]_4$). Color code: purple, K; green, F; blue, N; red, O; grey, C. H atoms omitted for clarity.

155

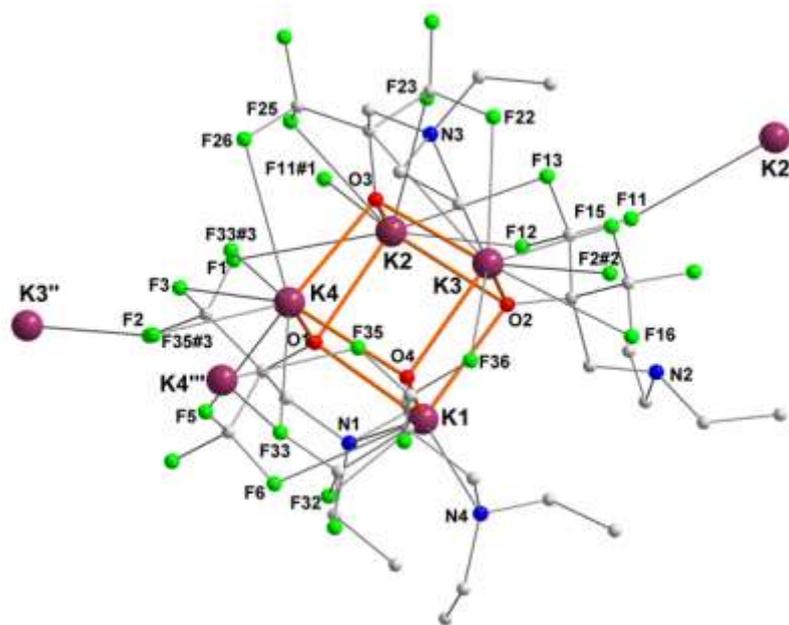
Table 3. Key metric parameters in the potassium-alkene complex $[\{RO^3\}K]_4$ ($[3]_4$).

K1–O (Å)	K1–N (Å)	K1...F (Å)	K1...C π (alkene) (Å)
O1 = 2.635(2)	N5 = 3.031(3)	F1 = 3.062(2)	C12 = 3.192(4)
O1' = 2.625(2)		F2' = 2.928(2)	C13 = 3.148(4)
O1'' = 2.765(2)			

156 Since one of the two tethered olefins in the ligand $\{RO^3\}^-$ is not directly involved in the
 157 coordination sphere of K^+ , we prepared a related proteo-ligand $\{RO^5\}H$ having only one dangling
 158 olefinic group, and where the other one is replaced by an isopropyl group. This new ligand led to the
 159 clean preparation of a compound of composition $[\{RO^5\}K]_n$ according to NMR spectroscopy and
 160 elemental analysis; however, all attempts to grow X-ray quality crystals proved unsuccessful, and we
 161 could not obtain useful information in the solid state.

162 2.4. Potassium complex $[\{RO^4\}K]_4$ ($[4]_4$)

163 The potassium complex $\{RO^4\}K$, where the ancillary ligand is devoid of π ligand, crystallized at
 164 the tetranuclear $[\{RO^4\}K]_4$ ($[4]_4$) with a distorted K_4O_4 cuboid core (Figure 5). Each potassium is
 165 involved in several intermolecular (e.g. K2–F11^{#2}, K2–F33^{#3}, K3–F32^{#1}, K4–F35^{#4}, K2'–F11, K3'–F2,
 166 K4'''–F35) and intramolecular $K^+\cdots F$ interactions, leading to the formation of infinite two-dimensional
 167 layer coordination polymers. In addition to the array of $K^+\cdots F$ contacts, all potassium centers are
 168 coordinated by three μ^3 -bridging oxygen atoms. K1 and K3 are also coordinated by a nitrogen atom
 169 (N4 and N3, respectively), but K2 and K4 are not. As a result and to compensate for an otherwise
 170 overwhelming electron deficiency, K2 and K4 exhibit six $K^+\cdots F$ interactions each. This is more than
 171 for K1 and K3, which respectively feature two and five interactions.



172 **Figure 5.** Representation of the molecular solid-state structure of the potassium complex $[\{RO^4\}K]_4$
 173 ($[4]_4$). Only the main component of disordered ethyl groups are depicted. Color code: purple, K; green,
 174 F; blue, N; red, O; grey, C. H atoms omitted for clarity.

175 Table 4 displays the key metric parameters in $[4]_4$. All $K^+–O$ bond lengths are in the same range,
 176 2.586(2)–2.767(2) Å. The $K^+–N$ bond is weaker for K3 (K3–N3 = 3.162(2) Å) than for K1 (K1–N4 =
 177 2.974(2) Å), which explains the greater number of $K^+\cdots F$ contacts for the former.

178 There is a unique sharp singlet at -76.38 ppm for all CF_3 groups in the ^{19}F NMR spectrum of $[\mathbf{4}]_4$,
 179 and its ^1H NMR spectrum features only three resonances at 2.70 (s), 2.56 (q) and 0.82 (t) ppm. We
 180 could not obtain reliable information as to the nuclearity of the complex in solution.

181 **Table 4.** Key metric parameters in the potassium complex $[\{\text{RO}^i\}\text{K}]_4$ ($[\mathbf{4}]_4$).

K_i	$\text{K}_i\text{-O}$ (Å)	$\text{K}_i\text{-N}$ (Å)	$\text{K}_i\cdots\text{F}$ (Å)
K1	O1 = 2.5862(16)	N4 = 2.9742(19)	F6 = 3.0859(17)
	O2 = 2.7289(16)		F32 = 3.1388(15)
	O4 = 2.6800(16)		
K2	O1 = 2.6237(16)		F1 = 3.2086(18)
	O2 = 2.7311(16)		F11 ^{#1} = 3.132(2)
	O3 = 2.7092(16)		F12 = 3.0195(19)
			F13 = 3.128(2)
			F23 = 2.7488(16)
		F25 = 2.9952(17)	
K3	O2 = 2.7675(16)	N3 = 3.162(2)	F2 ^{#2} = 2.8409(15)
	O3 = 2.5884(16)		F15 = 2.8113(17)
	O4 = 2.6698(16)		F16 = 3.314(2)
			F22 = 2.9606(18)
		F36 = 3.376(2)	
K4	O1 = 2.6872(16)		F3 = 3.1502(17)
	O3 = 2.5936(16)		F5 = 2.9039(17)
	O4 = 2.7204(16)		F26 = 3.2365(19)
			F33 = 3.0363(16)
			F33 ^{#3} = 3.1629(16)
		F35 ^{#3} = 2.9690(15)	
K2'	1	1	F11 = 3.132(2)
K3''	1	1	F2 = 2.8408(15)
K4'''	1	1	F33 = 3.1629(16)
			F35 = 2.9690(15)

¹ Only the intermolecular $\text{K}^+\text{-F}$ contacts are given.

182

183 3. Discussion

184 Compared to the polymeric $[\mathbf{4}]_4$ where electron depletion at the potassium centers is
 185 compensated solely by a large number of $\text{K}^+\cdots\text{F}$ intramolecular and intermolecular interactions,
 186 resulting in the formation of two-dimensional networks, the presence of π ligands in $[\mathbf{1}]_4$ (arene), $[\mathbf{2}]_4$
 187 (alkyne) and $[\mathbf{3}]_4$ (alkene) profoundly influences the coordination pattern of these compounds. A
 188 comparison of the structural and metric parameters for these complexes shows that as the number of
 189 $\text{K}^+\cdots\text{C}\pi$ interactions increases, one generally observes a lowering of the number or the strength of $\text{K}^+\cdots\text{F}$
 190 contacts. This is perhaps best epitomized in the structure of the arene complex $[\mathbf{1}]_4$, where the four
 191 potassium centers display different coordination environments.

Beyond structural considerations, this work shows that other than the well-known $K^+ \cdots C_{\pi}(\text{arene})$ interaction, alkenes and alkynes efficiently provide stabilization to potassium alkoxides. The potassium-alkyne complex described here is the only one of this type. This is in line with the recent account of the utilization of π ligands in alkaline earth chemistry [19,20]. In an attempt to extend the range of potential π ligands for *s*-block metals, we have also prepared a ligand possessing a dangling *allene* moiety. However, we have so far been unable to grow X-ray quality crystals for the resulting potassium complex. One should note that independently of the mode of coordination (η^2 , η^3 or η^6) of the arene in [1]₄, the $K^+ \cdots C_{\pi}(\text{arene})$ distances are considerably longer than the distances to the coordinated alkyne and alkene in complexes [2]₂ and [3]₂. DFT computations would be very useful to probe the respective intensities of the interactions between the π ligands and the potassium ions in these complexes, but they are precluded owing to the structural complexity of these polynuclear species, and because we have no reliable information about their structures in solution. For the same reason, bond valence sum analysis, which can be a convenient way to analyze the bonding pattern for a given complex [33], was also rendered prohibitively complicated.

We found no indication by NMR spectroscopy, especially $^{13}\text{C}\{^1\text{H}\}$ NMR, of any degree of covalence in the interaction between K^+ and the three different types of π ligands. Instead, this interaction is thought to be purely electrostatic, as seen for alkaline earths [19], and it occurs without any detectable polarization of the carbon-carbon unsaturated bonds [34].

The present results constitute further support in favor of Ruhlandt-Senge's statement that secondary interactions are a key tool to satisfy coordinative demands of electropositive elements and eventually yield stable and unusual molecular compounds [1]. The interactions $K^+ \cdots C_{\pi}$ and $K^+ \cdots F$ described here complement other non-covalent interactions reported before, such as agostic $\beta\text{-Si-H} \cdots K^+$ distortions seen in $[\text{KN}(\text{SiMe}_2\text{H})_2]_{\infty}$ [15]. These (and other related) potassium fluoroalkoxides are convenient synthetic precursors for the introduction of the ligands onto other metals, such as alkaline earths or lanthanides, *via* salt metathesis reactions. We are continuing our efforts in this field, and are seeking to combine these types of interactions to yield stable alkali and alkaline earths compounds. One route we are currently investigating is the use of enantiomerically pure chiral fluoroalkoxides to direct the formation of specific architectures.

4. Materials and Methods

4.1. General protocols

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; $\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 5$ ppm). $\text{HN}(\text{SiMe}_3)_2$ (abcr) and $\text{HN}(\text{SiMe}_2\text{H})_2$ (abcr) were dried over CaH_2 and distilled prior to use. The compounds $[\text{KN}(\text{SiMe}_3)_2]$ and $[\text{K}(\text{N}(\text{SiMe}_2\text{H})_2)]$ were prepared following literature protocols [15]. The proteo-ligands $\{\text{RO}^1\}\text{H}$ - $\{\text{RO}^3\}\text{H}$ were obtained as described earlier [16,20]. The new $\{\text{RO}^4\}\text{H}$ was obtained following the same protocols, using HNEt_2 as starting material; see the Supporting Information for detail. 2,2-Bis(trifluoromethyl)oxirane was purchased from Synquest Laboratories and used as received. Solvents (THF, Et_2O , CH_2Cl_2 , pentane and toluene) were purified and dried (water contents all below 10 ppm) over columns alumina (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl prior to use. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw-vacuum cycles.

NMR spectra were recorded on Bruker AM-400 and AM-500 spectrometers. All ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts were determined using residual signals of the deuterated solvents and were calibrated vs. SiMe_4 . Assignment of the resonances was carried out using 1D (^1H , $^{13}\text{C}\{^1\text{H}\}$) and 2D (COSY, HMBC, HMQC) NMR experiments. Coupling constants are given in Hertz. $^{19}\text{F}\{^1\text{H}\}$ chemical shifts were determined by external reference to an aqueous solution of NaBF_4 .

Elemental analyses performed on a Carlo Erba 1108 Elemental Analyzer at the London Metropolitan University by Stephen Boyer were the average of two independent measurements.

The November 2016 CSD database was used for the searches of XRD structures.

242 4.2. Synthesis of complex $[\{RO^1\}K]_4$ ($[1]_4$)

243 KN(SiMe₃)₂ (0.06 g, 0.33 mmol) was added with a bent finger to a solution of {RO¹}H (0.10 g, 0.33
244 mmol) in Et₂O (10 mL). The reaction mixture was stirred at room temperature overnight. Volatiles
245 were removed *in vacuo* to afford a sticky solid. Stripping with pentane (3 × 3 mL) afforded the title
246 compound as a white solid (0.080 g, 69%). The compound was recrystallized from a concentrated
247 pentane solution at -30 °C. ¹H NMR (500.13 MHz, [D₆]benzene, 298 K): δ 7.21-7.14 (m, 2H, *m*-C₆H₅),
248 7.12-7.08 (overlapping m, 3H, *p*-C₆H₅ and *o*-C₆H₅), 2.66-2.60 (br m, 2H, NCH₂CH₂), 2.56-2.52
249 (overlapping m, 4H, CH₂C(CF₃)₂ and NCH₂CH₂), 2.18 (s, 3H, NCH₃) ppm. ¹³C{¹H} NMR (125.73 MHz,
250 [D₆]benzene, 298 K): δ 140.22, 129.06, 128.30, 126.69 (all C₆H₅), 127.62 (q, ¹J_{C-F} = 294.2 Hz, CF₃), 81.24
251 (hept, ²J_{C-F} = 22.6 Hz, C(CF₃)₂), 63.64 (NCH₂CH₂), 60.61 (CH₂C(CF₃)₂), 45.33 (NCH₃), 34.06 (NCH₂CH₂)
252 ppm. ¹⁹F{¹H} NMR (376.49 MHz, [D₆]benzene, 298 K): δ -76.34 (s, 6F, CF₃) ppm. Elemental analysis
253 for C₁₃H₁₄F₆KNO (353.35 g·mol⁻¹): calc. C 44.2%, H 4.0%, N 4.0%; found C 44.3 %, H 3.8 %, N 3.9 %.

254 4.3. Synthesis of complex $[\{RO^2\}K]_4$ ($[2]_4$)

255 KN(SiMe₃)₂ (0.08 g, 0.44 mmol) was added in solid portions with a bent finger to a solution of
256 {RO²}H (0.13 g, 0.44 mmol) in Et₂O (10 mL). The reaction mixture was stirred at room temperature
257 overnight. Volatiles were removed under vacuum and the resulting oil was stripped with pentane (3
258 × 3 mL) to afford the title compound as a colorless solid. The compound was recrystallized from a
259 concentrated pentane solution at -30 °C. Yield 50 mg (33%). ¹H NMR (400.13 MHz, [D₆]benzene, 298
260 K): δ 2.92 (hept, 1H, ³J_{H-H} = 6.8 Hz, CH(CH₃)₂), 2.80 (t, 2H, ³J_{H-H} = 6.5 Hz, NCH₂CH₂), 2.71 (s, 2H,
261 CH₂C(CF₃)₂), 2.39 (m, 2H, NCH₂CH₂), 1.60 (t, 3H, ²J_{H-H} = 2.3 Hz, C≡C-CH₃), 0.92 (d, 6H, ³J_{H-H} = 6.5 Hz,
262 CH(CH₃)₂) ppm. ¹³C{¹H} NMR (100.63 MHz, [D₆]benzene, 298 K): δ 127.81 (q, ¹J_{C-F} = 294.8 Hz, CF₃),
263 81.97 (hept, ²J_{C-F} = 22.1 Hz, C(CF₃)₂), 78.19 (C≡C-CH₃), 76.94 (C≡C-CH₃), 57.54 (CH₂C(CF₃)₂), 51.91
264 (CH(CH₃)₂), 51.63 (NCH₂CH₂), 19.51 (NCH₂CH₂), 18.26 (CH(CH₃)₂), 3.06 (C≡C-CH₃) ppm. ¹⁹F{¹H}
265 NMR (376.47 MHz, [D₆]benzene, 298 K): -77.32 (s, 6F, CF₃) ppm. Elemental analysis for C₁₂H₁₆F₆KNO
266 (343.35 g·mol⁻¹): calc. C 42.0%, H 4.7%, N 4.1%; found C 42.0%, H 4.4%, N 4.1%.

267 4.4. Synthesis of complex $[\{RO^3\}K]_4$ ($[3]_4$)

268 KN(SiMe₂H)₂ (0.11 g, 0.65 mmol) was added in solid portions with a bent finger to a solution of
269 {RO³}H (0.21 g, 0.67 mmol) in Et₂O (10 mL). The reaction mixture was stirred at room temperature
270 overnight. Volatiles were removed under vacuum and the resulting oil was stripped with pentane (3
271 × 4 mL) to afford the title compound as a colorless oil. In a matter of days, the oil crystallized and the
272 title compound was isolated as off-white crystals. Yield (161 mg, 72%). ¹H NMR (400.13 MHz,
273 [D₆]benzene, 298 K): δ 5.79 (ddt, 2H, ³J_{H-H} (*trans*) = 17.4 Hz, ³J_{H-H} (*cis*) = 9.9 Hz, ³J_{H-H} = 6.7 Hz, CH=CH₂),
274 5.13-5.01 (m, 4H, CH=CH₂), 2.76 (s, 2H, CH₂C(CF₃)₂), 2.62 (t, 4H, ³J_{H-H} = 6.4 Hz, NCH₂CH₂), 2.06 (q, ³J_{H-}
275 _H = 6.4 Hz, 4H, NCHCH₂) ppm. ¹³C{¹H} NMR (100.63 MHz, [D₆]benzene, 298 K): δ 137.70 (CH=CH₂),
276 127.78 (q, ¹J_{C-F} = 295.3 Hz, CF₃), 116.01 (CH=CH₂), 81.58 (hept, ²J_{C-F} = 22.4 Hz, C(CF₃)₂), 61.03
277 (CH₂C(CF₃)₂), 53.12 (NCH₂CH₂), 29.79 (NCH₂CH₂) ppm. ¹⁹F{¹H} NMR (376.49 MHz, [D₆]benzene, 298
278 K): δ -75.86 (s, 6F, CF₃) ppm. Elemental analysis for C₁₂H₁₆F₆KNO (343.35 g·mol⁻¹): calc. C 42.0%, H
279 4.7%, N 4.1%; found C 42.1%, H 4.6%, N 4.2%.

280 4.5. Synthesis of complex $[\{RO^4\}K]_4$ ($[4]_4$)

281 KN(SiMe₂H)₂ (0.16 g, 0.80 mmol) was added with a bent finger to a solution of {RO⁴}H (0.20 mg,
282 0.80 mmol) in Et₂O (10 mL). The reaction mixture was stirred overnight at room temperature. The
283 volatiles were removed *in vacuo* to yield $[\{RO^4\}K]_4$ as a colorless solid (0.20 g, 85%). X-ray quality
284 crystals were obtained from a concentrated pentane solution at -30 °C. ¹H NMR (400.16 MHz,
285 [D₆]benzene, 298 K): δ 2.70 (s, 2H, CH₂C(CF₃)₂), 2.56 (q, 4H, ³J_{H-H} = 6.9 Hz, NCH₂CH₃), 0.82 (t, 6H, ³J_{H-H}
286 = 7.0 Hz, NCH₂CH₃) ppm. ¹³C{¹H} NMR (100.62 MHz, [D₆]benzene, 298 K): δ 129.30 (q, ¹J_{C-F} = 295.3 Hz,
287 CF₃), 81.91 (hept, ²J_{C-F} = 22.8 Hz, C(CF₃)₂), 58.97 (CH₂C(CF₃)₂), 47.36 (NCH₂CH₃), 10.01 (NCH₂CH₃) ppm.
288 ¹⁹F{¹H} NMR (376.49 MHz, [D₆]benzene, 298 K): δ -76.38 (s, 6F, CF₃) ppm. Elemental analysis for
289 C₈H₁₂F₆KNO (291.28 g·mol⁻¹): calc. C 33.0%, H 4.1%, N 4.8%; found C 32.9%, H 4.0%, N 4.9%.

290 4.6. X-ray diffraction crystallography

291 X-ray diffraction data were collected at 150 K using a Bruker APEX CCD diffractometer with
 292 graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). A combination ω and Φ scans was carried
 293 out to obtain at least a unique data set. The crystal structures were solved by direct methods, and
 294 remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares
 295 based on F2 (programs SIR97 and SHELXL-97) [35,36]. Carbon-, oxygen-, and nitrogen- bound
 296 hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The
 297 hydrogen atom contributions were calculated, but not refined. All non-hydrogen atoms were refined
 298 with anisotropic displacement parameters. The locations of the largest peaks in the final difference
 299 Fourier map calculation as well as the magnitude of the residual electron densities were of no
 300 chemical significance. The crystallographic data for all compounds are available as CIF files from the
 301 Cambridge Crystallographic Database Centre (CCDC numbers 1530195-1530198). A summary of
 302 crystallographic data is given in Table 5.

303 **Table 5.** Summary of crystallographic data for [1]₄–[4]₄.

	[(RO¹)K]₄ ([1]₄)	[(RO²)K]₄ ([2]₄)	[(RO³)K]₄ ([3]₄)	[(RO⁴)K]₄ ([4]₄)
Formula	C ₁₀₄ H ₁₁₂ F ₄₈ K ₈ N ₈ O ₈	C ₄₈ H ₆₄ F ₂₄ K ₄ N ₄ O ₄	C ₄₈ H ₆₄ F ₂₄ K ₄ N ₄ O ₄	C ₃₂ H ₄₈ F ₂₄ K ₄ N ₄ O ₄
CCDC	1530195	1530196	1530197	1530198
Mol. wt.	2826.82	1373.43	1373.43	1165.14
Crystal system	monoclinic	triclinic	tetragonal	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> -4 2 ₁ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	14.2195(4)	13.9764(4)	13.5114(14)	18.9136(8)
<i>b</i> (Å)	11.8504(4)	14.1787(4)	13.511	10.7740(5)
<i>c</i> (Å)	39.8155(13)	16.1077(4)	17.556(3)	24.7556(9)
α (°)	90	84.8310(10)	90	90
β (°)	97.5260(10)	81.5600(10)	90	108.265(2)
γ (°)	90	80.1870(10)	90	90
<i>V</i> (Å ³)	6651.4(4)	3104.31(15)	3205.0(6)	4790.4(4)
<i>Z</i>	2	2	8	4
Density (g/cm ³)	1.411	1.469	1.423	1.616
Abs. coeff., (mm ⁻¹)	0.378	0.402	0.389	0.505
<i>F</i> (000)	2880	1408	1408	2368
Crystal size, mm	0.51×0.23×0.15	0.490×0.410×0.280	0.39×0.27×0.10	0.410×0.150×0.120
θ range, deg	2.92 to 27.48	2.922 to 27.521	3.02 to 27.50	2.953 to 27.483
	-18< <i>h</i> <18	-18< <i>h</i> <18	-17< <i>h</i> <13	-24< <i>h</i> <24
Limiting indices	-15< <i>k</i> <12	-17< <i>k</i> <18	-17< <i>k</i> <17	-13< <i>k</i> <13
	-51< <i>l</i> <51	-19< <i>l</i> <20	-22< <i>l</i> <18	-32< <i>l</i> <31
<i>R</i> (int)	0.055	0.0318	0.0886	0.0550
Reflections collected	59233	35803	17470	57371
Reflec. Unique [<i>I</i> >2 σ]	15220	14178	3501	10958
Completeness to θ (%)	99.8	99.3	99.6	99.8
Data/restraints/param.	15220/0/797	14178/0/759	3501/0/191	10958/4/668
Goodness-of-fit	0.989	1.010	0.963	1.056
<i>R</i> ₁ [<i>I</i> >2 σ] (all data)	0.0453 (0.0797)	0.0418 (0.0625)	0.0466 (0.1014)	0.0402 (0.0681)
<i>wR</i> ₂ [<i>I</i> >2 σ] (all data)	0.1054 (0.1185)	0.0989 (0.1101)	0.0794 (0.0942)	0.0968 (0.1166)
Largest diff. e-Å ⁻³	0.27 & -0.301	0.901 & -0.894	0.234 & -0.222	0.844 & -0.667

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308 Dorcet and Thierry Roisnel carried out the X-ray crystal structure determinations and the interpretation of the
309 crystal data; Sorin-Claudiu Roşca, Hanieh Roueindeji, Jean-François Carpentier and Yann Sarazin analyzed the
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