A Joint Experimental and Theoretical Study of Cation-π Interactions: Multiple-Decker Sandwich Complexes of Ferrocene with Alkali Metal Ions (Li^+, Na^+, K^+, Rb^+, Cs^+).

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Supplementary Material

X-ray crystallography

Table. Selected crystallographic data.

compound	**2Li$_2$**·(DME)$_2$	**2Na$_2$**·(DME)$_3$	**2K$_2$**·(DME)$_3$
formula	$C_{28}H_{46}B_2FeLi_2N_4O_4$	$C_{32}H_{56}B_2FeN_4Na_2O_6$	$C_{32}H_{56}B_2FeK_2N_4O_6$
f_w	594.04	716.26	748.48
color, shape	orange, block	orange, plate	orange, block
temp (K)	173(2)	173(2)	173(2)
radiation	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å
cryst syst	triclinic	orthorhombic	triclinic
space group	*P*-1	*Pbca*	*P*-1
a (Å)	15.721(5)	15.584(3)	9.8339(16)
b (Å)	16.515(6)	32.374(4)	13.083(2)
c (Å)	21.159(7)	15.4767(16)	16.826(3)
α (deg)	84.86(3)	90	86.743(15)
β (deg)	83.56(3)	90	75.024(13)
γ (deg)	65.71(3)	90	71.342(13)
V (Å^3)	4970(3)	7808.4(19)	1980.6(6)
Z	6	8	2
$D_{calcd.}$ (g cm^{-3})	1.191	1.219	1.255
F(000)	1896	3056	796
μ (mm^{-1})	0.491	0.452	0.634
crystal size (mm^3)	0.16×0.14×0.06	0.42×0.12×0.03	0.23×0.20×0.16
no. of rflns collected	23624	29580	14842
no. of indep rflns (R_{int})	15786 (0.1466)	7280 (0.0954)	7148 (0.0815)
data/restraints/params	15786/504/1051	7280/0/424	7148/0/424
GOOF on F^2	0.840	0.840	0.829
R_1, wR_2 (I>2σ(I))	0.1207, 0.2640	0.0737, 0.1491	0.0529, 0.1107
R_1, wR_2 (all data)	0.3584, 0.3683	0.1884, 0.1917	0.1072, 0.1263
largest diff peak and hole (eÅ^{-3})	0.478, -0.355	0.954, -0.366	0.539, -0.546

Table. continued

compound	**2Rb$_2$**·(DME)$_3$	**2Cs$_2$**·(DME)$_3$	**2Na$_2$**·(THF)$_4$
formula	$C_{32}H_{56}B_2FeN_4O_6Rb_2$	$C_{32}H_{56}B_2Cs_2FeN_4O_6$	$C_{36}H_{58}B_2FeN_4Na_2O_4$
f_w	841.22	936.10	734.31
color, shape	orange, plate	light orange, block	light brown, block
temp (K)	173(2)	173(2)	173(2)
radiation	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å
cryst syst	triclinic	monoclinic	orthorhombic
space group	*P*-1	*C*2/*c*	*Pbcn*
a (Å)	9.8596(18)	9.8708(12)	20.6370(16)
b (Å)	13.136(3)	24.313(3)	11.5631(7)
c (Å)	17.292(4)	17.594(2)	16.2548(10)
α (deg)	85.950(18)	90	90
β (deg)	75.063(16)	103.180(10)	90
γ (deg)	69.938(15)	90	90
V (Å^3)	2032.2(8)	4111.1(9)	3878.8(5)
Z	2	4	4
$D_{calcd.}$ (g cm^{-3})	1.375	1.512	1.257
F(000)	868	1880	1568
μ (mm^{-1})	2.793	2.154	0.453
crystal size (mm^3)	0.36×0.34×0.12	0.19×0.14×0.12	0.42×0.32×0.28
no. of rflns collected	20674	14494	36382
no. of indep rflns (R_{int})	7152 (0.1091)	3941 (0.0755)	3779 (0.0715)
data/restraints/params	7152/0/424	3941/0/214	3779/0/222
GOOF on F^2	1.084	0.815	1.031
R_1, wR_2 (I>2σ(I))	0.1057, 0.2712	0.0345, 0.0582	0.0484, 0.1333
R_1, wR_2 (all data)	0.1571, 0.3005	0.0692, 0.0638	0.0674, 0.1417
largest diff peak and hole (eÅ^{-3})	3.025, -1.338	0.386, -0.652	1.026, -0.430

Table. continued

compound	**2K$_2$**·(THF)$_4$	**2Rb$_2$**·(THF)$_4$
formula	$C_{36}H_{58}B_2FeK_2N_4O_4$	$C_{36}H_{58}B_2FeN_4O_4Rb_2$
f_w	766.53	859.27
color, shape	yellow, plate	orange, needle
temp (K)	173(2)	173(2)
radiation	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	11.0876(19)	11.309(3)
b (Å)	14.624(3)	15.248(5)
c (Å)	12.7422(18)	12.259(4)
α (deg)	90	90
β (deg)	99.159(13)	96.13(3)
γ (deg)	90	90
V (Å^3)	2039.7(6)	2101.9(11)
Z	2	2
$D_{calcd.}$ (g cm^{-3})	1.248	1.358
F(000)	816	888
μ (mm^{-1})	0.614	2.699
crystal size (mm^3)	0.22×0.18×0.12	0.22×0.18×0.12
no. of rflns collected	15298	10870
no. of indep rflns (R_{int})	3732 (0.0828)	3700 (0.1834)
data/restraints/params	3732/0/223	3700/10/223
GOOF on F^2	0.797	0.965
R_1, wR_2 (I>2σ(I))	0.0524, 0.0738	0.0978, 0.1932
R_1, wR_2 (all data)	0.1495, 0.0886	0.2266, 0.2475
largest diff peak and hole (eÅ^{-3})	0.340, -0.257	0.694, -0.932

Geometric parameters of the structurally characterized molecules:

Figure 3: Molecular structure of **2Li$_2$**·(DME)$_2$ (hydrogen atoms omitted for clarity); selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.69(3), B(1)-N(11) = 1.66(2), B(2)-C(21) = 1.64(2), B(2)-N(21) = 1.58(2), Li(1)-N(12) = 2.04(3), Li(2)-N(22) = 1.98(3), Li(1)-O(102) = 1.97(3), Li(1)-O(105) = 1.97(3), Li(2)-O(202) = 2.06(3), Li(2)-O(205) = 1.94(3), Li(1)···COG(1) = 2.26, Li(2)···COG(2) = 2.32; C(11)-B(1)-N(11) = 100.4(15), B(1)-N(11)-N(12) = 123.6(13), N(11)-N(12)-Li(1) = 124.2(11), C(21)-B(2)-N(21) = 108.2(16), B(2)-N(21)-N(22) = 122.3(14), N(21)-N(22)-Li(2) = 123.0(13); C(12)-C(11)-B(1)-N(11) = 98(2), C(11)-B(1)-N(11)-N(12) = 2.7(19), B(1)-N(11)-N(12)-Li(1) = -6(2), C(22)-C(21)-B(2)-N(21) = 81.3(19), C(21)-B(2)-N(21)-N(22) = 4(2), B(2)-N(21)-N(22)-Li(2) = 2(2), C(11)-COG(1)-COG(2)-C(21) = 178.8; C(11)C(12)C(13)C(14)C(15)// C(21)C(22)C(23)C(24)C(25) = 0.5.

Figure 4: Molecular structure of **2Na$_2$**·(DME)$_3$ (hydrogen atoms omitted for clarity); selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.631(9), B(1)-N(11) = 1.617(9), B(2)-C(21) = 1.644(8), B(2)-N(21) = 1.604(9), Na(1)-N(12$^{\#}$) = 2.382(5), Na(1)-N(22) = 2.405(6), Na(1)···COG(1$^{\#}$) = 2.561, Na(1)···COG(2) = 2.590; C(11)-B(1)-N(11) = 105.4(5), B(1)-N(11)-N(12) = 125.5(5), N(11)-N(12)-Na(1*) = 127.2(4), C(21)-B(2)-N(21) = 106.1(5), B(2)-N(21)-N(22) = 124.0(5), N(21)-N(22)-Na(1) = 124.1(4), N(12$^{\#}$)-Na(1)-N(22) = 122.2(2); C(12)-C(11)-B(1)-N(11) = -89.4(7), C(11)-B(1)-N(11)-N(12) = 7.4(8), B(1)-N(11)-N(12)-Na(1*) = -18.0(8), C(22)-C(21)-B(2)-N(21) = 100.0(7), C(21)-B(2)-N(21)-N(22) = -29.5(8), B(2)-N(21)-N(22)-Na(1) = 26.7(8), C(11)-

COG(1)-COG(2)-C(21) = -135.4; C(11)C(12)C(13)C(14)C(15)//C(21)C(22)C(23)C(24)C(25) = 1.2, C(11$^{\#}$)C(12$^{\#}$)C(13$^{\#}$)C(14$^{\#}$)C(15$^{\#}$)//C(21)C(22)C(23)C(24)C(25) = 48.0. Symmetry transformation used to generate equivalent atoms: x - ½, y, -z + ½ (#); x + ½, y, -z + ½ (*).

Figure 5: Molecular structure of **2K$_2$**·(DME)$_3$ (hydrogen atoms omitted for clarity); selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.625(6), B(1)-N(11) = 1.604(6), B(2)-C(21) = 1.623(6), B(2)-N(21) = 1.618(6), K(1)-N(12) = 2.969(3), K(1)-N(22$^{\#}$) = 2.987(4), K(2)-N(22$^{\#}$) = 2.853(3), K(2)-N(12) = 2.929(4), K(1)-O(102) = 2.766(3), K(1)-O(105) = 2.866(3), K(2)-O(202) = 2.768(4), K(2)-O(205) = 2.867(4), K(2)-O(212) = 2.963(4), K(2)-O(215) = 2.768(3), K(1)···COG(1) = 3.228, K(1)···COG(2$^{\#}$) = 3.298; C(11)-B(1)-N(11) = 106.9(3), B(1)-N(11)-N(12) = 122.5(3), N(11)-N(12)-K(1) = 116.1(2), N(11)-N(12)-K(2) = 127.3(3), C(21)-B(2)-N(21) = 106.0(3), B(2)-N(21)-N(22) = 123.0(3), N(21)-N(22)-K(1*) = 93.3(2), N(21)-N(22)-K(2*) = 136.4(2), K(1)-N(12)-K(2) = 90.89(9), K(1*)-N(22)-K(2*) = 92.03(9), N(12)-K(1)-N(22$^{\#}$) = 86.89(9), N(12)-K(2)-N(22$^{\#}$) = 90.19(10); C(12)-C(11)-B(1)-N(11) = 70.5(5), C(11)-B(1)-N(11)-N(12) = 56.8(5), B(1)-N(11)-N(12)-K(1) = -66.0(4), B(1)-N(11)-N(12)-K(2) = 47.3(4), C(22)-C(21)-B(2)-N(21) = 68.0(5), C(21)-B(2)-N(21)-N(22) = 87.3(4), B(2)-N(21)-N(22)-K(1*) = -86.3(3), B(2)-N(21)-N(22)-K(2*) = 10.1(6), C(11)-COG(1)-COG(2)-C(21) = 92.1; C(11)C(12)C(13)C(14)C(15)//C(21)C(22)C(23)C(24)C(25) = 2.7, C(11$^{\#}$)C(12$^{\#}$)C(13$^{\#}$)C(14$^{\#}$)C(15$^{\#}$)//C(21)C(22)C(23)C(24)C(25) = 2.7. Symmetry transformation used to generate equivalent atoms: x – 1, y, z (#); x + 1, y, z (*).

Molecular structure of **2Rb$_2$**·(DME)$_3$ (hydrogen atoms omitted for clarity); selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.623(17), B(1)-N(11) = 1.602(16), B(2)-C(21) = 1.608(19), B(2)-N(21) = 1.613(14), Rb(1)-N(12) = 3.087(11), Rb(1)-N(22*) = 3.130(12), Rb(2)-N(22*) = 2.998(10), Rb(2)-N(12) = 3.050(11), Rb(1)-O(202) = 3.008(11), Rb(1)-O(205) = 2.939(12), Rb(2)-O(102) = 3.043(12), Rb(2)-O(105) = 2.911(13), Rb(2)-O(112) = 2.912(10), Rb(2)-O(115) = 3.018(10), Rb(1)···COG(1) = 3.285, Rb(1)···COG(2*) = 3.265; C(11)-B(1)-N(11) = 107.4(10), B(1)-N(11)-N(12) = 123.4(9), N(11)-N(12)-Rb(1) = 112.9(7), N(11)-N(12)-Rb(2) = 129.1(8), C(21)-B(2)-N(21) = 105.0(9), B(2)-N(21)-N(22) = 124.5(9), N(21)-N(22)-Rb(1$^{\#}$) = 95.0(7), N(21)-N(22)-Rb(2$^{\#}$) = 136.6(7), Rb(1)-N(12)-Rb(2) = 91.4(3), Rb(1$^{\#}$)-N(22)-Rb(2$^{\#}$) = 91.5(3), N(12)-Rb(1)-N(22*) = 87.0(3), N(12)-Rb(2)-N(22*) = 90.1(3); C(12)-C(11)-B(1)-N(11) = 107.3(13), C(11)-B(1)-N(11)-N(12) = -61.2(15), B(1)-N(11)-N(12)-Rb(1) = 68.3(13), B(1)-N(11)-N(12)-Rb(2) = -43.9(15), C(22)-C(21)-B(2)-N(21) = -69.6(13), C(21)-B(2)-N(21)-N(22) = -83.5(13), B(2)-N(21)-N(22)-Rb(1$^{\#}$) = 86.2(11), B(2)-N(21)-N(22)-Rb(2$^{\#}$) = -11.4(18), C(11)-COG(1)-COG(2)-C(21) = -93.2; C(11)C(12)C(13)C(14)C(15)// C(21)C(22)C(23)C(24)C(25) = 2.5, C(11*)C(12*)C(13*)C(14*)C(15*)// C(21)C(22)C(23)C(24)C(25) = 2.5. Symmetry transformation used to generate equivalent atoms: x – 1, y, z (#); x + 1, y, z (*).

Molecular structure of **2Cs$_2$**·(DME)$_3$ (hydrogen atoms omitted for clarity); selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.609(7), B(1)-N(11) = 1.632(5), Cs(1)-N(12) = 3.331(4), Cs(2)-N(12) = 3.101(4), Cs(1)-O(42) = 3.156(4), Cs(2)-O(32) = 3.102(4), Cs(2)-O(35) = 3.146(4), Cs(1)···COG(1) = 3.283; C(11)-B(1)-N(11) = 104.9(3), B(1)-N(11)-N(12) = 121.6(3), N(11)-N(12)-Cs(1) = 89.9(2),

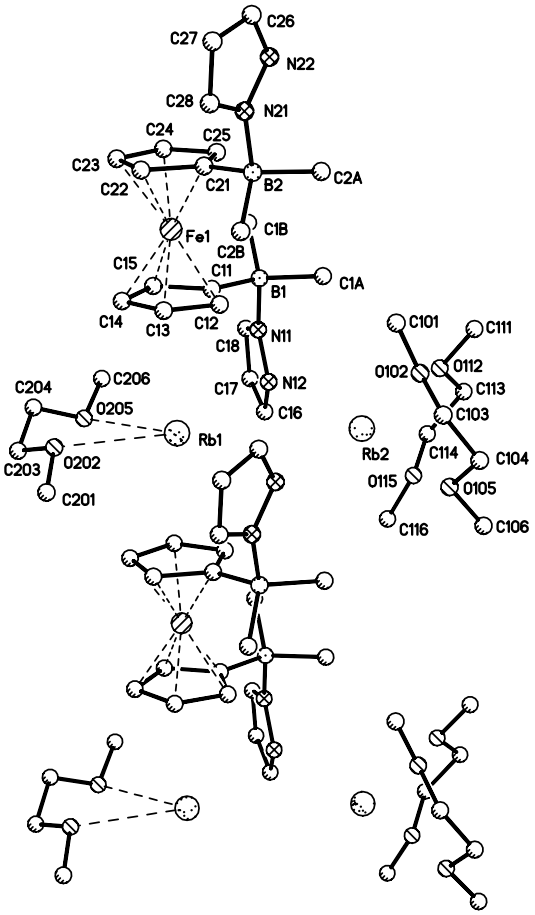
N(11)-N(12)-Cs(2) = 141.9(3), Cs(1)-N(12)-Cs(2) = 97.57(10), N(12)-Cs(1)-N(12*) = 78.85(14), N(12)-Cs(2)-N(12*) = 86.01(15); C(12)-C(11)-B(1)-N(11) = 70.9(5), C(11)-B(1)-N(11)-N(12) = 88.2(5), B(1)-N(11)-N(12)-Cs(1) = -90.3(3), B(1)-N(11)-N(12)-Cs(2) = 12.0(7), C(11)-COG(1)-COG($1^{\#}$)-C($11^{\#}$) = 86.7; C(11)C(12)C(13)C(14)C(15)//C($11^{\#}$)C($12^{\#}$)C($13^{\#}$)C($14^{\#}$)C($15^{\#}$) = 1.7, C(11*)C(12*)C(13*)C(14*)C(15*)//C(11)C(12)C(13)C(14)C(15) = 1.7. Symmetry transformation used to generate equivalent atoms: -x +1, y, -z + $^{3}/_{2}$ (*); -x +2, y, -z + $^{3}/_{2}$ (#).

Figure 6: Molecular structure of **2Na$_2$**·(THF)$_4$ (hydrogen atoms omitted for clarity); selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.612(4), B(1)-N(11) = 1.613(4), Na(1)-N(12) = 2.534(2), Na(1)-N($12^{\#}$) = 2.532(2), Na(1)-O(31) = 2.348(2), Na(1)-O(41) = 2.332(2), Na(1)-C($15^{\#}$) = 2.848(3); C(11)-B(1)-N(11) = 106.2(2), B(1)-N(11)-N(12) = 122.88(19), N(11)-N(12)-Na(1) = 118.75(15), N(11)-N(12)-Na($1^{\#}$) = 112.81(16), Na(1)-N(12)-Na($1^{\#}$) = 86.46(7), N(12)-Na(1)-N($12^{\#}$) = 93.54(7), O(31)-Na(1)-O(41) = 87.51(8); C(12)-C(11)-B(1)-N(11) = -86.1(3), C(11)-B(1)-N(11)-N(12) = -83.9(3), B(1)-N(11)-N(12)-Na(1) = -45.2(3), B(1)-N(11)-N(12)-Na($1^{\#}$) = 53.6(3), C(11)-COG(1)-COG(1*)-C(11*) = -144.8; C(11)C(12)C(13)C(14)C(15)//C(11*)C(12*)C(13*)C(14*)C(15*) = 1.9, C(11)C(12)C(13)C(14)C(15)//C($11^{\#}$)C($12^{\#}$)C($13^{\#}$)C($14^{\#}$)C($15^{\#}$) = 0.0. Symmetry transformation used to generate equivalent atoms: -x + 1, -y + 1, -z + 1(#), -x + 1, y, -z + $^{3}/_{2}$ (*).

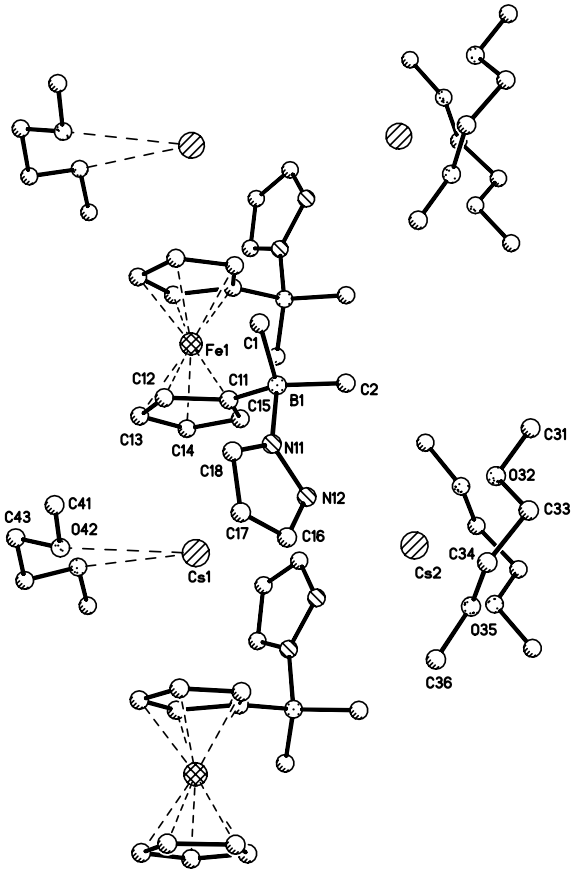
Molecular structure of **2K$_2$**·(THF)$_4$; selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.660(7), B(1)-N(11) = 1.628(7), K(1)-N(12) = 2.863, K(1)-N(12$^{\#}$) = 2.807(4), K(1)-O(31) = 2.700(4), K(1)-O(41) = 2.647(4), K(1)-C(12) = 2.953(4); C(11)-B(1)-N(11) = 103.4(4), B(1)-N(11)-N(12) = 122.1(4), N(11)-N(12)-K(1) = 109.6(3), N(11)-N(12)-K(1$^{\#}$) = 123.2(3), K(1)-N(12)-K(1$^{\#}$) = 96.71(12), N(12)-K(1)-N(12$^{\#}$) = 83.3(2), O(31)-K(1)-O(41) = 84.63(13); C(12)-C(11)-B(1)-N(11) = -111.1(5), C(11)-B(1)-N(11)-N(12) = 79.3(5), B(1)-N(11)-N(12)-K(1) = -59.7, B(1)-N(11)-N(12)-K(1$^{\#}$) = 52.7(5), C(11)-COG(1)-COG(1*)-C(11*) = 180.0; C(11)C(12)C(13)C(14)C(15)// C(11*)C(12*)C(13*)C(14*)C(15*) = 0.0, C(11)C(12)C(13)C(14)C(15)// C(11$^{\#}$)C(12$^{\#}$)C(13$^{\#}$)C(14$^{\#}$)C(15$^{\#}$) = 0.0. Symmetry transformation used to generate equivalent atoms: -x + 1, -y + 1, -z + 1 (#), -x, -y + 1, -z + 1 (*).

Molecular structure of **2Rb$_2$**·(THF)$_4$; selected bond lengths [Å], angles [°], torsion angles [°], and dihedral angles [°]: B(1)-C(11) = 1.69(2), B(1)-N(11) = 1.57(2), Rb(1)-N(12) = 3.090(12), Rb(1)-N(12$^{\#}$) = 2.955(12), Rb(1)-O(31) = 2.865(12), Rb(1)-O(41) = 2.852(13), Rb(1)-C(12) = 3.156(12); C(11)-B(1)-N(11) = 104.3(14), B(1)-N(11)-N(12) = 123.5(16), N(11)-N(12)-Rb(1) = 90.8(8), N(11)-N(12)-Rb(1$^{\#}$) = 134.4(11), Rb(1)-N(12)-Rb(1$^{\#}$) = 99.1(3), N(12)-Rb(1)-N(12$^{\#}$) = 80.9(15), O(31)-Rb(1)-O(41) = 82.1(4); C(12)-C(11)-B(1)-N(11) = -114.6(16), C(11)-B(1)-N(11)-N(12) = 98.0(17), B(1)-N(11)-N(12)-Rb(1) = -80.6(14), B(1)-N(11)-N(12)-Rb(1$^{\#}$) = 23(2), C(11)-COG(1)-COG(1*)-C(11*) = 180.0; C(11)C(12)C(13)C(14)C(15)// C(11*)C(12*)C(13*)C(14*)C(15*) = 0.0, C(11)C(12)C(13)C(14)C(15)// C(11$^{\#}$)C(12$^{\#}$)C(13$^{\#}$)C(14$^{\#}$)C(15$^{\#}$) = 0.0. Symmetry transformation used to generate equivalent atoms: -x + 1, -y + 1, -z + 1 (#), -x, -y + 1, -z + 1 (*).

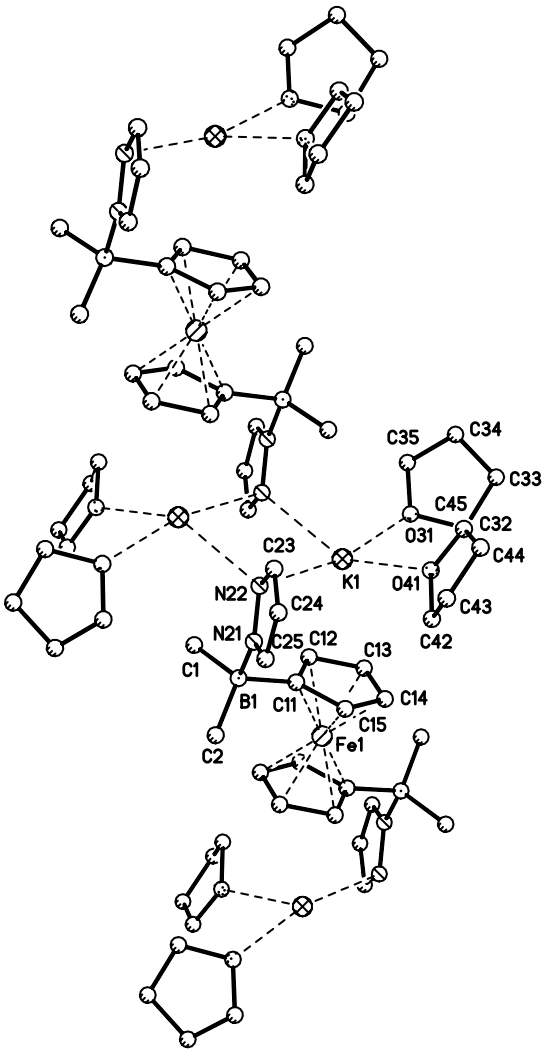
Molecular structure of **2Rb$_2$**·(DME)$_3$ (hydrogen atoms omitted for clarity):



Molecular structure of **2Cs$_2$**·(DME)$_3$ (hydrogen atoms omitted for clarity):



Molecular structure of **2K$_2$**·(THF)$_4$ (hydrogen atoms omitted for clarity):



Molecular structure of **2Rb$_2$**·(THF)$_4$ (hydrogen atoms omitted for clarity):