the CE benzo rings is 50% occupied at O2A,C3,C4,O3A and 50% at the O4,C7,C8,O5 position. The disordered sites are related by a center of symmetry. It is fascinating that in one of these two sites (O4,C7,C8,O5), the benzo ring is face-to-face stacked with the Pic^- coordinated to Cs2 with a centroid-centroid separation of 3.723 Å. When in the other position, this ring stacks face-to-face with the C43-C48 benzo group of another CE unit.

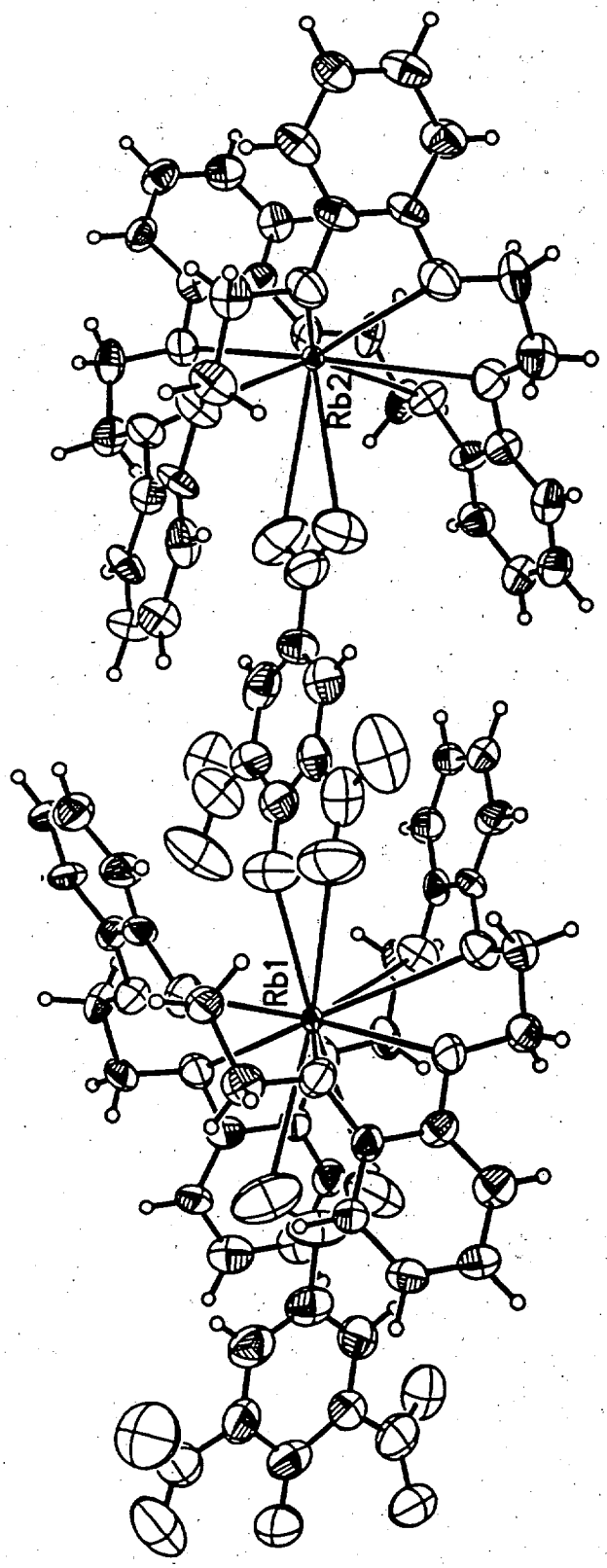

Figure 8S. Crystal Structure of the Complex RbPic-12

Table 15S. Crystal Data and Structure Refinement for the Complex RbPic-12

Compound	RAB57
Color / Shape	yellow / parallelepiped
Empirical formula	$C_{39.25}H_{36.50}Cl_{2.50}N_3O_{15}Rb$
Formula weight	964.31
Temperature	173(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 13.5135(1) Å α = 84.23°
(2042 reflections	b = 16.8163(5) Å β = 81.716(1)°
in full θ range)	c = 19.3287(6) Å γ = 76.921(1)°
Volume	4223.3(2) Å^3
Z	4
Density (calculated)	1.517 Mg/m^3
Absorption coefficient	1.403 mm^{-1}
Diffractometer / scan	Siemens SMART / CCD area detector
Radiation / wavelength	MoKα (graphite monochrom.) / 0.71073 Å
F(000)	1970
Crystal size	0.10 x 0.20 x 0.20 mm
θ range for data collection	1.07 to 27.83°
Index ranges	$-17 \le h \le 17$, $-20 \le k \le 22$, $-21 \le \ell \le 25$
Reflections collected	26659
Independent / observed refls.	18600(R_{int} = 0.0697) / 7364([I>2σ(I)])
Absorption correction	SADABS[1]
Range of relat. transm. factors	0.97 and 0.68
Refinement method	Full-matrix-block least-squares on F^2
Computing	SHELXTL, Ver. 5[2]
Data / restraints / parameters	15425 / 0 / 1122
Goodness-of-fit on F^2	0.971
SHELX-93 weight parameters	0.1241, 0.0000
Final R indices [I>2σ(I)]	R1 = 0.0899, wR2 = 0.2063
R indices (all data)	R1 = 0.2375, wR2 = 0.3110
Extinction coefficient	0.0042(4)
Largest diff. peak and hole	1.938 and -0.687 eÅ^{-3}

Table 16S.Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å x 10^3) for the Complex RbPic-**12**

Atom	x/a	y/b	z/c	U(eq)a
Rb(1)	18(1)	10030(1)	2400(1)	18(1)
Rb(2)	-4918(1)	4907(1)	2664(1)	18(1)
Cl(1)	-1691(4)	13253(3)	-181(2)	121(2)
Cl(2)	6(4)	13672(4)	338(3)	142(2)
Cl(3)	4421(4)	9717(3)	4016(2)	107(2)
Cl(4)	3693(3)	8335(2)	4788(2)	87(1)
Cl(5A)b	-2495(28)	5423(22)	916(18)	100(11)
Cl(6A)b	-1073(17)	5622(14)	1314(12)	51(6)
Cl(5B)b	-2707(16)	4957(13)	608(11)	46(5)
Cl(6B)b	-2535(76)	6406(60)	1207(55)	319(49)
Cl(5C)b	-3068(57)	5574(43)	1203(37)	206(29)
Cl(6C)b	-2422(73)	5718(57)	855(50)	242(44)
Cl(5D)b	-2985(14)	5251(11)	934(10)	33(4)
Cl(6D)b	-1837(72)	5693(59)	966(50)	298(45)
O(1)	-994(5)	11285(4)	3657(4)	47(2)
O(2)	-2257(5)	11253(4)	2609(4)	43(2)
O(3)	-1599(5)	10921(4)	1333(4)	49(2)
O(4)	486(5)	10540(4)	732(4)	48(2)
O(5)	1827(5)	9328(4)	1150(4)	51(2)
O(6)	1490(6)	8166(4)	2280(4)	49(2)
O(7)	817(6)	8537(5)	3538(4)	53(2)
O(8)	407(6)	10100(4)	4046(4)	51(2)
O(9)	-5440(5)	4375(4)	4293(4)	44(2)
O(10)	-3369(5)	4001(4)	3740(4)	44(2)
O(11)	-2643(6)	3678(5)	2476(4)	52(2)
O(12)	-3837(6)	3640(4)	1391(4)	55(2)
O(13)	-5214(6)	4853(4)	983(4)	52(2)
O(14)	-5667(6)	6430(4)	1534(3)	48(2)
O(15)	-6326(5)	6784(4)	2778(4)	42(2)
O(16)	-6757(5)	5625(4)	3884(3)	40(2)
O(17)	-1574(8)	9168(6)	2817(6)	98(3)

O(18)	-2676(11)	9505(7)	4009(6)	130(5)
O(19)	-3335(8)	8601(7)	4616(5)	95(3)
O(20)	-4042(7)	6393(7)	3573(5)	94(4)
O(21)	-3299(9)	6052(7)	2517(7)	107(4)
O(22)	-1109(9)	7621(7)	1213(5)	116(4)
O(23)	-903(9)	8778(7)	1519(6)	113(4)
O(24)	3388(7)	14167(6)	2654(5)	83(3)
O(25)	1933(9)	15065(6)	1945(6)	111(4)
O(26)	1139(9)	14430(8)	1314(7)	134(5)
O(27)	791(9)	11761(7)	1994(5)	109(4)
O(28)	2042(9)	10860(7)	2473(6)	104(4)
O(29)	4278(7)	11970(6)	3683(5)	85(3)
O(30)	4926(7)	12953(6)	3052(5)	89(3)
N(1)	-2916(10)	8849(8)	4044(6)	79(4)
N(2)	-3460(8)	6511(7)	3029(7)	67(3)
N(3)	-1263(9)	8173(9)	1639(6)	73(4)
N(4)	1709(10)	14429(8)	1776(7)	83(4)
N(5)	1619(11)	11582(9)	2270(6)	76(4)
N(6)	4235(9)	12547(8)	3194(6)	71(3)
C(1)	-1853(8)	11928(6)	3502(6)	47(3)
C(2)	-2636(7)	11541(7)	3281(6)	45(3)
C(3)	-2913(8)	10950(6)	2277(6)	38(3)
C(4)	-2559(8)	10758(6)	1574(6)	39(3)
C(5)	-1264(8)	10868(7)	586(6)	46(3)
C(6)	-283(8)	11159(7)	429(6)	54(3)
C(7)	1491(8)	10639(6)	582(5)	38(3)
C(8)	2217(8)	9978(7)	810(5)	40(3)
C(9)	2552(8)	8574(6)	1289(6)	46(3)
C(10)	1925(8)	7955(6)	1586(5)	38(3)
C(11)	890(8)	7666(6)	2651(6)	35(3)
C(12)	522(8)	7873(7)	3355(5)	38(3)
C(13)	654(9)	8674(7)	4272(5)	49(3)
C(14)	1090(8)	9406(6)	4338(5)	46(3)
C(15)	607(8)	10868(7)	4069(5)	40(3)
C(16)	-171(8)	11523(7)	3857(5)	42(3)
C(17)	-47(9)	12319(7)	3847(6)	50(3)
C(18)	839(9)	12461(8)	4070(6)	58(4)
C(19)	1592(10)	11806(8)	4261(6)	58(3)
C(20)	1457(8)	11014(7)	4285(6)	49(3)

C(21)	-3882(8)	10843(6)	2550(6)	45(3)
C(22)	-4488(8)	10544(7)	2163(6)	47(3)
C(23)	-4146(9)	10368(7)	1483(7)	52(3)
C(24)	-3160(9)	10467(7)	1184(7)	54(3)
C(25)	1792(8)	11309(6)	234(5)	41(3)
C(26)	2833(8)	11321(7)	98(6)	45(3)
C(27)	3554(9)	10678(7)	315(6)	51(3)
C(28)	3241(9)	9985(7)	680(5)	52(3)
C(29)	668(8)	7003(7)	2409(6)	47(3)
C(30)	60(8)	6528(7)	2832(7)	55(3)
C(31)	-332(8)	6720(7)	3515(7)	50(3)
C(32)	-78(8)	7393(7)	3766(6)	51(3)
C(33)	-4688(7)	3759(7)	4609(5)	47(3)
C(34)	-3733(8)	4052(7)	4474(5)	51(3)
C(35)	-2407(8)	4170(7)	3504(6)	43(3)
C(36)	-2016(9)	3993(7)	2835(6)	42(3)
C(37)	-2214(9)	3319(7)	1825(6)	56(3)
C(38)	-3031(9)	2967(7)	1604(6)	54(4)
C(39)	-4666(9)	3440(6)	1172(5)	43(3)
C(40)	-5403(9)	4090(7)	950(5)	43(3)
C(41)	-5931(9)	5551(7)	733(6)	51(3)
C(42)	-5538(9)	6291(7)	805(5)	52(3)
C(43)	-5394(10)	7109(6)	1724(6)	47(3)
C(44)	-5752(8)	7317(7)	2424(6)	42(3)
C(45)	-6843(8)	7000(7)	3463(6)	50(3)
C(46)	-7458(8)	6370(6)	3729(5)	48(3)
C(47)	-7178(8)	4970(6)	4199(5)	35(3)
C(48)	-6472(8)	4295(6)	4434(5)	40(3)
C(49)	-6788(9)	3609(7)	4759(5)	46(3)
C(50)	-7829(9)	3607(7)	4884(6)	51(3)
C(51)	-8516(8)	4259(7)	4660(5)	49(3)
C(52)	-8217(8)	4958(7)	4314(6)	45(3)
C(53)	-1849(9)	4511(6)	3911(6)	45(3)
C(54)	-881(9)	4657(7)	3618(7)	55(3)
C(55)	-509(9)	4460(7)	2965(7)	51(3)
C(56)	-1057(8)	4125(7)	2530(6)	52(3)
C(57)	-4772(10)	2642(8)	1160(6)	57(3)
C(58)	-5649(10)	2512(7)	894(6)	61(4)
C(59)	-6384(9)	3155(7)	690(6)	52(3)

C(60)	-6266(10)	3956(7)	706(6)	51(3)
C(61)	-4827(9)	7589(7)	1290(6)	51(3)
C(62)	-4605(9)	8277(7)	1554(6)	47(3)
C(63)	-4968(9)	8466(7)	2226(6)	51(3)
C(64)	-5544(9)	7980(6)	2676(5)	42(3)
C(65)	-2027(10)	8561(8)	2833(8)	67(4)
C(66)	-2719(9)	8383(8)	3463(6)	56(3)
C(67)	-3157(9)	7705(8)	3504(7)	64(4)
C(68)	-2977(9)	7191(7)	2951(6)	47(3)
C(69)	-2362(9)	7341(8)	2346(6)	63(4)
C(70)	-1906(9)	8012(8)	2278(6)	51(3)
C(71)	3020(10)	13579(9)	2547(7)	63(4)
C(72)	2142(9)	13647(8)	2149(7)	62(4)
C(73)	1701(10)	13000(8)	2051(7)	66(4)
C(74)	2095(10)	12242(9)	2332(6)	62(4)
C(75)	2943(9)	12093(8)	2741(6)	58(3)
C(76)	3374(9)	12738(8)	2810(6)	48(3)
C(77)	-665(14)	13774(11)	-383(8)	114(6)
C(78)	4222(11)	9164(8)	4828(7)	73(4)
C(79A)c	-2061(74)	6567(60)	533(54)	178(39)
C(79B)c	-2002(43)	5923(34)	702(29)	75(16)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] 12.5% occupancy; isotropic refinement. [c] 25% occupancy; isotropic refinement.

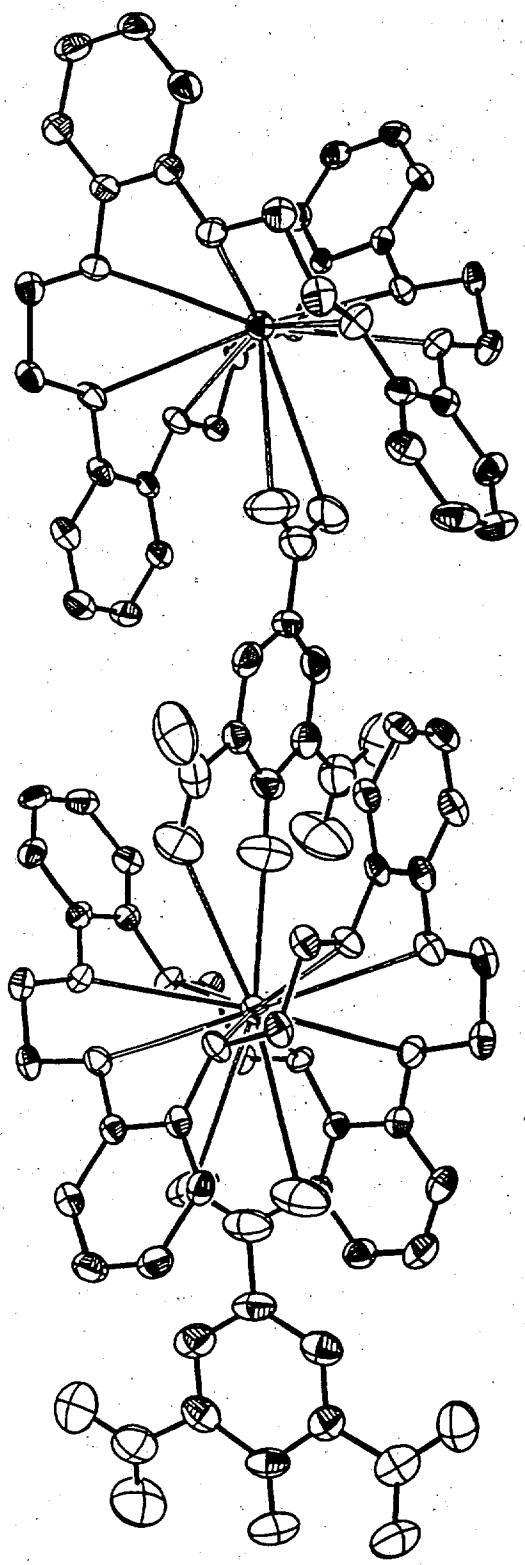

Figure 9S. Crystal Structure of the Complex CsPic-12

Table 17S. Crystal Data and Structure Refinement for the Complex CsPic-12

Compound	RAB56
Color / Shape	yellow / parallelepiped
Empirical formula	$C_{39.25}H_{36.50}Cl_{2.50}CsN_3O_{15}$
Formula weight	1011.75
Temperature	173(2) K
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (8192 reflections in full θ range)	a = 13.5085(2) Å α = 84.283(1)° b = 16.8244(3) Å β = 81.835(1)° c = 19.2714(1) Å γ = 76.771(1)°
Volume	4210.16(10) $Å^3$
Z	4
Density (calculated)	1.596 Mg/m^3
Absorption coefficient	1.111 mm^{-1}
Diffractometer / scan	Siemens SMART / CCD area detector
Radiation / wavelength	MoKα (graphite monochrom.) / 0.71073 Å
F(000)	2042
Crystal size	0.29 x 0.35 x 0.40 mm
θ range for data collection	1.07 to 27.90°
Index ranges	$-17 \le h \le 17$, $-22 \le k \le 14$, $-24 \le \ell \le 23$
Reflections collected	27410
Independent / observed refls.	18483(R_{int} = 0.0228) / 12093([I>2σ(I)])
Absorption correction	SADABS[1]
Range of relat. transm. factors	0.95 and 0.80
Refinement method	Full-matrix-block least-squares on F^2
Computing	SHELXTL, Ver. 5[2]
Data / restraints / parameters	18459 / 0 / 1122
Goodness-of-fit on F^2	1.030
SHELX-93 weight parameters	0.0423, 1.4501
Final R indices [I>2σ(I)]	R1 = 0.0411, wR2 = 0.0873
R indices (all data)	R1 = 0.0792, wR2 = 0.1069
Extinction coefficient	0.00000(7)
Largest diff. peak and hole	0.651 and -0.684 $eÅ^{-3}$

Table 18S. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å x 10^3) for the Complex CsPic-**12**

Atom	x/a	y/b	z/c	U(eq)a
Cs(1)	19(1)	10040(1)	2398(1)	25(1)
Cs(2)	-4918(1)	4918(1)	2653(1)	25(1)
Cl(1)	-1670(1)	13280(1)	-189(1)	96(1)
Cl(2)	42(2)	13680(1)	345(1)	115(1)
Cl(3)	4422(1)	9711(1)	4018(1)	83(1)
Cl(4)	3696(1)	8339(1)	4794(1)	67(1)
Cl(5A)	-2600(13)	5528(10)	1021(9)	96(5)b
Cl(6A)	-1223(16)	5577(12)	1263(11)	143(7)b
Cl(5B)	-2718(8)	4930(7)	619(6)	61(3)b
Cl(6B)	-2574(29)	6310(21)	839(19)	247(14)b
Cl(5C)	-3170(43)	5652(32)	1416(30)	443(28)b
Cl(6C)	-1928(37)	5117(31)	474(27)	365(24)b
Cl(5D)	-2978(11)	5254(9)	922(8)	91(4)b
Cl(6D)	-2145(17)	5616(14)	984(12)	155(7)b
O(1)	-1000(2)	11284(1)	3669(1)	27(1)
O(2)	-2266(2)	11266(1)	2607(1)	24(1)
O(3)	-1605(2)	10942(2)	1324(1)	25(1)
O(4)	486(2)	10543(1)	724(1)	25(1)
O(5)	1827(2)	9322(1)	1142(1)	26(1)
O(6)	1480(2)	8170(1)	2282(1)	26(1)
O(7)	832(2)	8532(2)	3548(1)	29(1)
O(8)	404(2)	10103(2)	4053(1)	32(1)
O(9)	-5448(2)	4387(1)	4301(1)	24(1)
O(10)	-3358(2)	3986(2)	3743(1)	26(1)
O(11)	-2655(2)	3674(2)	2472(1)	28(1)
O(12)	-3844(2)	3646(2)	1380(1)	31(1)
O(13)	-5220(2)	4865(1)	982(1)	28(1)
O(14)	-5674(2)	6439(1)	1525(1)	28(1)
O(15)	-6335(2)	6789(1)	2785(1)	25(1)
O(16)	-6757(2)	5636(1)	3895(1)	23(1)
O(17)	-1595(3)	9155(2)	2822(2)	71(1)

O(18)	-2733(4)	9519(3)	3998(2)	113(2)
O(19)	-3348(3)	8585(2)	4617(2)	75(1)
O(20)	-4047(3)	6398(2)	3561(2)	71(1)
O(21)	-3260(3)	6060(2)	2539(2)	75(1)
O(22)	-1074(3)	7626(2)	1222(2)	79(1)
O(23)	-904(3)	8761(3)	1523(2)	78(1)
O(24)	3361(2)	14168(2)	2681(2)	61(1)
O(25)	1934(3)	15077(2)	1946(2)	82(1)
O(26)	1128(3)	14484(3)	1368(2)	98(2)
O(27)	787(3)	11787(3)	1980(2)	78(1)
O(28)	2024(3)	10907(3)	2444(2)	77(1)
O(29)	4282(2)	11984(2)	3676(2)	62(1)
O(30)	4908(2)	12947(2)	3062(2)	62(1)
N(1)	-2942(3)	8871(3)	4057(2)	55(1)
N(2)	-3461(3)	6512(3)	3038(3)	52(1)
N(3)	-1259(3)	8160(3)	1641(2)	48(1)
N(4)	1712(3)	14470(3)	1805(2)	57(1)
N(5)	1604(4)	11614(3)	2244(2)	58(1)
N(6)	4238(3)	12551(3)	3213(2)	48(1)
C(1)	-1855(3)	11929(2)	3509(2)	27(1)
C(2)	-2645(3)	11540(2)	3298(2)	26(1)
C(3)	-2911(2)	10958(2)	2269(2)	22(1)
C(4)	-2555(2)	10781(2)	1573(2)	24(1)
C(5)	-1275(3)	10886(2)	589(2)	28(1)
C(6)	-285(3)	11162(2)	426(2)	27(1)
C(7)	1480(3)	10638(2)	581(2)	22(1)
C(8)	2221(3)	9962(2)	807(2)	23(1)
C(9)	2543(3)	8574(2)	1292(2)	25(1)
C(10)	1929(3)	7950(2)	1592(2)	26(1)
C(11)	896(2)	7667(2)	2657(2)	23(1)
C(12)	528(3)	7868(2)	3352(2)	26(1)
C(13)	666(3)	8675(2)	4276(2)	34(1)
C(14)	1098(3)	9410(2)	4345(2)	33(1)
C(15)	611(3)	10859(2)	4073(2)	26(1)
C(16)	-167(3)	11516(2)	3858(2)	23(1)
C(17)	-54(3)	12314(2)	3857(2)	30(1)
C(18)	833(3)	12461(3)	4064(2)	36(1)
C(19)	1582(3)	11821(3)	4274(2)	38(1)
C(20)	1480(3)	11010(3)	4281(2)	32(1)

C(21)	-3878(3)	10846(2)	2564(2)	29(1)
C(22)	-4479(3)	10555(2)	2158(2)	33(1)
C(23)	-4118(3)	10367(2)	1480(2)	32(1)
C(24)	-3153(3)	10478(2)	1180(2)	28(1)
C(25)	1782(3)	11317(2)	228(2)	28(1)
C(26)	2827(3)	11322(2)	101(2)	32(1)
C(27)	3549(3)	10668(2)	326(2)	32(1)
C(28)	3247(3)	9983(2)	684(2)	26(1)
C(29)	670(3)	6994(2)	2408(2)	29(1)
C(30)	63(3)	6531(2)	2845(2)	34(1)
C(31)	-308(3)	6735(2)	3521(2)	36(1)
C(32)	-73(3)	7406(2)	3782(2)	32(1)
C(33)	-4699(2)	3765(2)	4614(2)	27(1)
C(34)	-3709(3)	4040(2)	4476(2)	28(1)
C(35)	-2423(2)	4174(2)	3511(2)	23(1)
C(36)	-2033(3)	3995(2)	2821(2)	26(1)
C(37)	-2228(3)	3339(2)	1810(2)	32(1)
C(38)	-3046(3)	2981(2)	1586(2)	33(1)
C(39)	-4669(3)	3445(2)	1160(2)	27(1)
C(40)	-5423(3)	4107(2)	941(2)	25(1)
C(41)	-5940(3)	5568(2)	725(2)	29(1)
C(42)	-5528(3)	6309(2)	795(2)	29(1)
C(43)	-5406(3)	7115(2)	1723(2)	24(1)
C(44)	-5772(2)	7317(2)	2416(2)	21(1)
C(45)	-6835(3)	7008(2)	3466(2)	23(1)
C(46)	-7458(2)	6382(2)	3736(2)	24(1)
C(47)	-7167(2)	4992(2)	4200(2)	20(1)
C(48)	-6447(2)	4300(2)	4427(2)	20(1)
C(49)	-6767(3)	3619(2)	4761(2)	24(1)
C(50)	-7814(3)	3622(2)	4872(2)	31(1)
C(51)	-8523(3)	4294(2)	4651(2)	30(1)
C(52)	-8200(2)	4981(2)	4307(2)	26(1)
C(53)	-1869(3)	4515(2)	3910(2)	30(1)
C(54)	-917(3)	4656(2)	3626(2)	38(1)
C(55)	-519(3)	4464(2)	2955(3)	43(1)
C(56)	-1078(3)	4134(2)	2540(2)	34(1)
C(57)	-4797(3)	2651(2)	1140(2)	34(1)
C(58)	-5670(3)	2518(2)	899(2)	38(1)
C(59)	-6398(3)	3168(3)	680(2)	36(1)

C(60)	-6276(3)	3973(2)	697(2)	30(1)
C(61)	-4825(3)	7595(2)	1290(2)	29(1)
C(62)	-4604(3)	8273(2)	1553(2)	32(1)
C(63)	-4973(3)	8469(2)	2233(2)	33(1)
C(64)	-5557(3)	7986(2)	2669(2)	26(1)
C(65)	-2041(3)	8585(2)	2838(2)	38(1)
C(66)	-2718(3)	8376(3)	3450(2)	38(1)
C(67)	-3168(3)	7711(3)	3511(2)	40(1)
C(68)	-2975(3)	7203(2)	2965(2)	36(1)
C(69)	-2364(3)	7365(2)	2354(2)	37(1)
C(70)	-1921(3)	8027(2)	2284(2)	33(1)
C(71)	3003(3)	13594(3)	2567(2)	40(1)
C(72)	2137(3)	13683(3)	2162(2)	41(1)
C(73)	1715(3)	13047(3)	2056(2)	46(1)
C(74)	2090(3)	12272(3)	2339(2)	42(1)
C(75)	2927(3)	12113(3)	2724(2)	42(1)
C(76)	3363(3)	12744(3)	2816(2)	36(1)
C(77)	-649(6)	13790(4)	-366(4)	105(2)
C(78)	4216(4)	9192(3)	4846(3)	59(1)
C(79A)	-1462(77)	6287(57)	507(52)	385(52)c
C(79B)	-2088(27)	5713(21)	785(19)	116(11)c

[a]U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b]12.5% occupancy; isotropic refinement. [c]25% occupancy; isotropic refinement.

Discussion of the Structures RbPic-TetB24C8 (RbPic-**12**) and CsPic-TetB24C8 (CsPic-**12**)

The complex RbPic-**12** is isostructural with its Cs^+-containing analog. In both of the complexes, the oxygen atoms of TetB24C8 form a symmetric boat-shaped cavity which also provides two major clefts for solvent and/or anion coordination to the metal cations.

The CE conformation is very symmetric. The O-C-C-O torsion angles, starting with O-C1-C2-O, are *+g, s, -g, s, +g, s, -g, s* and all of the C-O-C-C torsion angles are *anti*. The metal ions reside in each of the CE units in nearly identical positions with averages of 3.28(4) Å for the Rb-O distances and 3.29(4) Å for the Cs-O separations. The M-O distances to the CE ring range from 3.316(7) to 3.366(8) Å and 3.224(2) to 3.365(3) Å for M = Rb and Cs, respectively. (Presumably, smaller Na^+ and K^+ ions would require much greater distorsion of this conformation for coordinative saturation.)

The remarkable role of Pic^- in the structures of RbPic-**12** and CsPic-**12** is noteworthy. Opposing benzo substituents of **12** fold over one another to form two large clefts which make the metal ion accesible for further coordination. All of the ring centroid-M-ring centroid angles for the unique clefts in the structures of both of the complexes are approximately 115°. This allows sufficient room for planar Pic^- to coordinate with the metal ion in a bidentate fashion, either through both oxygen atoms of one nitro group or by a phenolate oxygen and an oxygen of an *ortho*-nitro group. Coordination of Pic^- may be assisted by face-to-face stacking with the CE benzo substituents that form the cleft. The Pic^- units bridge the two metal centers in a head-to-tail manner forming infinite coordination polymers. Thus each Pic- is "sandwiched" between four benzo groups from the CEs.

Table 19S. Separation Factors for Competitive Alkali Metal Picrate Extractions from Aqueous Solution[a] into $CHCl_3$[b] by Crown Ethers **1**-**13**

18-membered CEs				21-membered CEs				24-membered CEs			
CE	$\alpha_{K,Na}$	$\alpha_{K,Rb}$	$\alpha_{K,Cs}$	CE	$\alpha_{Cs,Na}$	$\alpha_{Cs,K}$	$\alpha_{Cs,Rb}$	CE	$\alpha_{Cs,Na}$	$\alpha_{Cs,K}$	$\alpha_{Cs,Rb}$
1	66.3	4.00	16.5	**6**	39.2	4.22	1.44	**9**	9.90	3.73	2.61
2	27.0	3.85	8.50	**7**	15.2	2.54	1.01	**10**	9.60	3.47	2.44
3	12.1[c]	4.48[c]	11.0[c]	**8**	31.3[d]	1.48[d]	3.31[d]	**11**	29.0	6.11	2.76
4	43.4	3.20	13.0					**12**	[e]	[e]	[e]
5	84.0	4.00	23.1					**13**	7.48	1.90	1.50

[a]The aqueous solution was 1.00 mM in each of NaPic, KPic, RbPic, and CsPis and contained 5.0 mM of each sulfate as a spike. [b]The $CHCl_3$ solution contained 1.00 mM CE. [c]The value calculated based on the concentrations of alkali metal cations in organic phase after the partial precipitation of complex KPic-**3**. [d]$\alpha_{Rb,M}$ values are given for this CE. [e]The separation factors could not be determined accurately due to co-precipitation of complexes CsPic-**12** and RbPic-**12** in the organic phase.

Table 20S. Separation Factors for Competitive Alkali Metal Iodide Extractions from Aqueous Solution[a] into $CHCl_3$[b] by Crown Ethers **1-13**

18-membered CEs				21-membered CEs				24-membered CEs			
CE	$\alpha_{K,Na}$	$\alpha_{K,Rb}$	$\alpha_{K,Cs}$	CE	$\alpha_{Cs,Na}$	$\alpha_{Cs,K}$	$\alpha_{Cs,Rb}$	CE	$\alpha_{Cs,Na}$	$\alpha_{Cs,K}$	$\alpha_{Cs,Rb}$
1	72.2	2.90	10.2	**6**	45.0	6.01	1.44	**9**	11.6	3.76	2.45
2	17.7	1.89	2.55	**7**	31.0	4.38	1.03	**10**	9.53	3.67	2.42
3	10.5	0.95	0.93	**8**	60.3[c]	2.52[c]	1.42[c]	**11**	9.74	2.44	1.59
4	69.1	8.74	20.0					**12**	[d]	[d]	[d]
5	86.0	3.20	20.0					**13**	11.0	2.00	1.40

[a]The aqueous solution was 0.50 M in each of NaI, KI, RbI, and CsI. [b]The $CHCl_3$ solution contained 10.0 mM CE. [c]$\alpha_{Rb,M}$ values are given for this CE. [d]The separation factors could not be determined accurately due to precipitation of complex CsI-**12** in the organic phase.

Explanation for Linearity of $(\alpha_{M1,M})_X$ *vs.* $(\alpha_{M1,M})_Y$ when Anions of the Extracted Salts Do Not Interact with the Ligand

When two metal salts, M_1X and M_2X, containing the same anion X^- are extracted by the ligand L, the selectivity of L for M_1^+ over M_2^+ is expressed by the formula

$$(\alpha_{M1,M2})_X = D_{M1X}/D_{M2X} .$$

When anion X^- is changed for anion Y^- that has different energy of transfer from aqueous to organic phase than that of X^-, the distribution ratio values, D_{M1Y} and D_{M2Y}, will vary from those of D_{M1X} and D_{M2X} by some quotient. Specifically, $D_{M1Y} = nD_{M1X}$ and $D_{M2Y} = mD_{M2X}$ where $n = m$, unless anion Y^- exhibits an interaction with the ligand that varies from complex M_1LY to M_2LY. Hence, when no specific anion-ligand interaction takes place, the selectivity of L for M_1 over M_2 will be determined as

$$(\alpha_{M1,M2})_Y = D_{M1Y}/D_{M2Y} = nD_{M1X}/nD_{M2X} = D_{M1X}/D_{M2X} = (\alpha_{M1,M2})_X.$$

In other words, anions that are incapable of any specific interaction within the complex *may not* affect the extraction selectivity of the ligand. In such case, the selectivity will be determined only by the relative stability of the complex cations, M_1L^+ and M_2L^+.

For the series of such salts, M_1X, M_2X, M_3X, ..., M_nX and M_1Y, M_2Y, M_3Y, ..., M_nY, with $(\alpha_{M1,M2})_X = (\alpha_{M1,M2})_Y$, $(\alpha_{M1,M3})_X = (\alpha_{M1,M3})_Y$, ..., $(\alpha_{M1,Mn})_X = (\alpha_{M1,Mn})_Y$, the plot of $(\alpha_{M1,M})_X$ *vs.* $(\alpha_{M1,M})_Y$ will be linear with a slope of 1. However, if an anion is capable of interacting with the ligand and this interaction varies with the cation identity, the quotient $n \neq m$ and therefore, the graph of $(\alpha_{M1,M})_X$ *vs.* $(\alpha_{M1,M})_Y$ will deviate from the line with slope of 1.