SUPPLEMENTARY INFORMATION

FOR

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Selective Modification of the Metal Coordination Environment in Heavy Alkaline-earth Iodide Complexes

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Table 1. Comparison of selected structural parameters of neutral calcium diiodides $[(L)_nCaI_2]$ and cationic monoiodides $[(L)_nCaI]I$

Entry	Complex	C.N.	Ca–I (Å)[a]	H^xCaI[b]	Ref.
1	$[CaI_2(18\text{-crown-6})]$	8	3.034	68.85	[1]
2	$[CaI(dme)_3]I$	6	3.053	58.45	[2]
3	$[CaI_2(hmteta)]$	6	3.057	58.46	[1]
4	$[CaI(thf)_5]BPh_4$	6	3.066	61.27	[3]
5	$[CaI_2(thp)_4]$	6	3.077	59.26	[1]
6	$[CaI_2(bipy)_2]$	6	3.078	58.31	[4]
7	$[CaI(diglyme)_2]I$	6	3.096	54.92	[5]
8	$[CaI_2(thf)_4]$	6	3.104	58.54	[6]
9	$[CaI_2(thf)_4]$	6	3.106	58.76	[7]
10	$[CaI[OC(C_6H_5)_2CH_2C_6H_4\text{-Cl-4}(thf)]$	6	3.109	59.44	[7]
11	$[CaI_2(Et_2O)_4]$	6	3.114	53.09	[1]
12	$[CaI_2(diglyme)(dme)]$	7	3.114	56.74	[8]
13	$[CaI_2([18]aneO_2S_4)]$	8	3.117	53.15	[9]
14	$[CaI_2(diglyme)(thf)_2]$	7	3.119	57.30	[1]
15	$[CaI(dme)_3]I$	7	3.121	58.45	[10]
16	$[CaI(diglyme)_2]I$	7	3.121	56.74	[11]
17	$[CaI_2([15]aneO_3S_2)]$	7	3.128	57.52	[9]
18	$[CaI_2(tmeda)_2]$	6	3.129	54.70	[1]
19	$[CaI_2(dme)_2(thf)]$	7	3.134	54.92	[12]
20	$[CaI(thf)_2\{CH(Me_3SiNPPh_2)_2\}]$	5	3.135	54.13	[13]
21	$[CaI_2([18]aneO_4Se_2)]$	8	3.174	56.84	[9]
22	$[CaI(OPPr_3)_5]I$	6	3.267	43.60	this work

a) average value; b) average value of both hemispheres H^x-CaI-1 and H^x-CaI-2

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Table 2. Crystal data and Crystal Data and Summary of X-ray Data Collection for $CaI_2(OPPh_3)_4$

Empirical formula	$C_{72}H_{60}CaI_2O_4P_4$	
Formula weight	1406.96	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 24.075(5) Å	α = 90°
	b = 14.215(3) Å	β = 113.59(3)°
	c = 20.814(4) Å	γ = 90°
	Volume	6528(2) Å^3
Z	4	
Density (calculated)	1.432 Mg/m^3	
Absorption coefficient	1.188 mm^{-1}	
F(000)	2840	
Theta range for data collection	1.70 to 25.00°	
Index ranges	$-28 \le h \le 18$, $0 \le k \le 16$, $0 \le l \le 24$	
Reflections collected	4312	
Independent reflections	4312 [*R*(int) = 0.0000]	
Observed reflections	1789	
Completeness to theta = 25.00°	74.9%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4312 / 390 / 197	
Goodness-of-fit on F^2	1.052	
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0708$, $wR^2 = 0.1374$	
R indices (all data)	$R1 = 0.1967$, $wR^2 = 0.1792$	
Largest diff. peak and hole	0.979 and -0.543 e$^-$ Å^{-3}	

Table 3. Fractional Coordinates and Isotropic Thermal Parameters for $CaI_2(OPPh_3)_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

	x	*y*	*z*	U_{eq}
Ca1	5000	3495(2)	2500	35(1)
I1	5632(1)	3448(1)	4164(1)	52(1)
O1	4757(7)	1992(10)	2658(8)	40(5)
P1	4790(3)	981(4)	2887(3)	35(2)
O2	5910(7)	2938(10)	2493(8)	37(4)
P2	6415(2)	2733(3)	2251(3)	32(2)
O3	5393(6)	4988(10)	2608(8)	41(5)
P3	5505(3)	6015(4)	2755(3)	37(2)
O4	4125(7)	4039(11)	2433(8)	34(4)
P4	3481(3)	4235(4)	2292(3)	34(2)
C1	4485(3)	872(8)	3544(3)	48(3)
C2	4495(6)	10(8)	3863(6)	48(3)
C3	4258(7)	-69(10)	4370(7)	57(6)
C4	4011(6)	715(12)	4558(6)	77(9)
C5	4001(7)	1577(10)	4238(7)	69(8)
C6	4238(6)	1656(8)	3731(6)	48(3)
C7	5563(4)	569(5)	3220(6)	51(3)
C8	5960(5)	834(9)	3890(6)	51(3)
C9	6558(5)	523(11)	4155(6)	51(3)
C10	6757(4)	-53(9)	3751(7)	64(8)
C11	6360(5)	-318(10)	3082(7)	44(7)
C12	5763(5)	-7(9)	2816(6)	51(3)
C13	4356(3)	290(7)	2124(5)	51(3)
C14	4208(6)	-640(8)	2191(6)	51(3)
C15	3872(7)	-1162(7)	1597(8)	65(9)
C16	3686(5)	-755(10)	936(6)	59(8)
C17	3834(6)	175(10)	870(5)	51(3)
C18	4169(6)	697(8)	1464(6)	51(3)
C19	7137(4)	2691(4)	2983(5)	34(5)
C20	7667(5)	2682(9)	2867(5)	48(3)
C21	8227(4)	2650(11)	3432(7)	48(3)
C22	8257(4)	2626(9)	4113(6)	48(3)

Table 3: (cont.)

	x	y	z	U_{eq}
C23	7727(6)	2635(11)	4229(5)	48(3)
C24	7167(4)	2667(9)	3664(6)	48(3)
C25	6251(5)	1644(5)	1763(4)	20(5)
C26	5653(5)	1429(8)	1335(6)	48(3)
C27	5518(5)	594(9)	955(7)	48(3)
C28	5980(7)	-25(6)	1004(6)	57(6)
C29	6578(6)	191(7)	1432(8)	48(7)
C30	6713(5)	1026(7)	1812(6)	32(6)
C31	6459(4)	3642(6)	1665(5)	24(5)
C32	6794(5)	4447(7)	1952(5)	41(3)
C33	6837(7)	5159(7)	1516(7)	56(8)
C34	6545(6)	5065(8)	793(7)	49(4)
C35	6210(6)	4260(10)	505(5)	49(4)
C36	6167(5)	3549(7)	941(5)	42(6)
C37	6285(3)	6256(8)	3317(4)	28(6)
C38	6665(5)	5511(7)	3650(7)	45(4)
C39	7268(5)	5682(11)	4086(7)	49(7)
C40	7490(4)	6597(12)	4187(6)	67(5)
C41	7109(6)	7341(9)	3854(8)	67(5)
C42	6507(5)	7171(7)	3419(7)	59(8)
C43	5339(2)	6626(7)	1939(4)	33(6)
C44	5343(5)	6117(7)	1371(5)	40(4)
C45	5217(6)	6564(9)	734(5)	35(4)
C46	5087(5)	7521(9)	666(5)	38(5)
C47	5084(6)	8031(7)	1234(6)	38(4)
C48	5209(5)	7583(7)	1871(5)	37(5)
C49	5055(4)	6460(4)	3202(5)	36(6)
C50	5305(4)	6529(9)	3929(5)	40(4)
C51	4959(6)	6872(10)	4275(5)	35(4)
C52	4362(6)	7146(8)	3894(7)	38(5)
C53	4112(4)	7077(10)	3167(7)	38(4)
C54	4459(5)	6734(8)	2821(5)	37(5)
C55	2976(4)	3331(6)	1764(4)	34(6)
C56	2415(5)	3556(7)	1244(6)	48(3)

Table 3: (cont.)

	x	y	z	U_{eq}
C57	2035(5)	2847(10)	846(6)	48(3)
C58	2218(6)	1912(8)	968(6)	48(3)
C59	2779(6)	1687(6)	1489(7)	48(3)
C60	3159(5)	2397(7)	1887(6)	34(5)
C61	3400(5)	4317(4)	3115(4)	41(3)
C62	2841(5)	4181(9)	3150(5)	41(3)
C63	2790(6)	4248(10)	3791(7)	45(7)
C64	3298(7)	4451(9)	4396(5)	49(4)
C65	3857(6)	4587(11)	4361(5)	49(4)
C66	3908(5)	4520(9)	3720(6)	47(7)
C67	3182(3)	5282(5)	1780(5)	49(7)
C68	3314(6)	5452(8)	1198(6)	45(4)
C69	3089(7)	6253(9)	795(6)	71(9)
C70	2733(6)	6884(7)	972(7)	67(5)
C71	2601(6)	6713(7)	1554(7)	37(6)
C72	2826(6)	5912(7)	1958(6)	42(6)