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Supporting Information

Designer Metallic Acceptor-Containing Halogen Bonds: General Strategies

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Abstract: Being electrostatic interactions in nature, hydrogen bonding (HB) and halogen bonding (XB) are considered to be two parallel worlds. In principle, all the applications that HB has could also be applied to XB. However, there has been no report on a metallic XB acceptor but metal anions have been observed to be good HB acceptors. This missing mosaic piece of XB is because common metal anions are reactive for XB donors. In view of this, we propose two strategies for designing metallic acceptor-containing XB using *ab initio* calculations. The first one is to utilize a metal cluster anion with a high electron detachment energy, such as the superatom, Al_{13}^- as the XB acceptor. The second strategy is to design a ligand passivated/protected metal core while it still can maintain the negative charge; several exotic clusters, such as PtH_5^-, $PtZnH_5^-$ and $PtMgH_5^-$, are utilized as examples. Based on these two strategies, we anticipate that more metallic acceptor-containing XB will be discovered.

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Theoretical Methods

Density functional theory calculations were conducted by applying the PBEPBE[1] and M06-2x[2] functionals using the Gaussian09 software package[3] to determine the geometries of all clusters. All geometries were fully optimized without any geometrical constraints using the 6-311++G (3df, 3pd) basis set[4] for main group elements and the Stuttgart/Dresden (SDD)[5,6] effective core potentials for the transition metals. All the calculated energies were corrected with zero-point energies. Vibrational frequencies were calculated to make sure they are not transition states. Natural population analysis (NPA)[7], as implemented in the Gaussian09 code, was carried out to determine the charge distribution within the complexes. We also mapped the electrostatic potential surfaces (ESP) of all the clusters to visualize the σ-hole and the halogen bonding. The XB strength was calculated using the formula $D_0[CF_3Br\text{-}Y^-] = E[CF_3Br] + E[Y^-] – E[CF_3Br\text{-}Y^-]$ and tabulated in Table 1 and Table S1, where Y^- denotes the XB acceptor.

Results and Discussion

The calculated XB strengths and lengths of all the complexes using the M06-2x functional are tabulated in Table S1. Comparing to those results from the PBEPBE functional in Table 1, the M06-2x functional gives relatively longer bond lengths and weaker bond strengths. However, the binding energy differences between these two methods are around 0.1 eV, which is satisfactory. The two methods used in this manuscript are reliable according to previous works.[8]

Table S1. The XB strength $D_0[CF_3Br\text{-}Y^-]$ (eV) and length (Å) of different systems calculated from the M062x functional.

Species[a]	X-Br^-	X-Al_{13}^-	X-PtH_5^-	X_2-PtH_5^-	X-$PtMgH_5^-$	X-$PtZnH_5^-$
D_0	0.54	0.21	0.42	0.40	0.34	0.38
XB length	3.11	3.57	3.17	3.21	3.27	3.23

[a] CF_3Br is denoted as X for short.

3D coordinates using the PBEPBE functional (Å)

$CF_3Br\text{-}Al_{13}^-$

Al	4.00815600	-1.22170900	1.07968700
Al	2.41121000	0.52598600	2.56271800
Al	1.39225800	-1.95093500	1.73707800
Al	2.40008100	-2.48542400	-0.82273300
Al	4.01515800	-0.33834300	-1.58778600
Al	-0.20394400	-1.52820500	-0.51170800
Al	1.41507000	2.48336200	0.82177300
Al	4.02284700	1.52945200	0.51242600
Al	-0.19682200	0.33665100	1.58501700
Al	2.42167700	1.95125400	-1.73734500
Al	-0.19288000	1.22037500	-1.07692000
Al	1.40242100	-0.52450000	-2.55934600
Al	1.90985200	-0.00009600	0.00034800
C	-5.56947700	-0.00130900	0.00201300
Br	-3.58955600	0.00273400	-0.00447400
F	-6.05391700	-0.90655000	-0.87009000
F	-6.05579300	1.20697900	-0.34235000
F	-6.04748500	-0.30711000	1.22386100

CF_3Br-Br^-

C	-2.22349700	-0.00021200	-0.00006100
F	-2.74228800	0.93839700	0.83933700
F	-2.74118400	-1.19767900	0.39119900
F	-2.73904600	0.25863100	-1.23381200
Br	-0.22387200	0.00033000	0.00126900
Br	2.71940500	-0.00012600	-0.00041600

CF_3Br-PtH_5^-

C	3.08624500	0.00047600	-0.00014300
F	3.59627100	-0.06924900	-1.25725000
F	3.59843400	-1.05227500	0.68895500
F	3.59545600	1.12489900	0.56711900
Br	1.08778300	-0.00149400	0.00053700
Pt	-1.85131200	0.00024000	-0.00009000
H	-1.85898500	1.33383400	-0.93293800
H	-1.85954700	1.29929100	0.98027700
H	-1.85929300	-0.47498400	-1.55658200
H	-1.86060400	-0.53089000	1.53823600
H	-1.86055500	-1.62690500	-0.02927900

CF_3Br-PtH_5^--CF_3Br

C	-4.99167900	-0.00753700	0.00060400
F	-5.48442000	-1.22199900	-0.34008500
F	-5.49591800	0.89026000	-0.87800400
F	-5.49441500	0.30137400	1.21910000
Br	-3.01631800	0.00262700	0.00246300
Pt	-0.00012800	0.00604700	-0.00248800
H	-0.00302900	-1.11771300	1.17433100
H	-0.00283100	0.77611100	1.43043500
H	0.00044500	-1.45930700	-0.70877200
H	0.00033800	1.60777600	-0.29201200
H	0.00262600	0.22322900	-1.61506800
C	4.99143700	-0.00606800	0.00036400
F	5.49188300	0.61824900	-1.09148100
F	5.49462800	0.62607800	1.08643900
F	5.48929200	-1.26554200	0.00538200
Br	3.01644500	-0.00136600	0.00288500

CF_3Br-$PtMgH_5^-$

Pt	1.57146700	-0.00007300	0.00010800
H	1.53572300	-1.04041900	1.24906800
H	1.53524600	0.86791900	1.37460700
H	1.53631500	-1.50949600	-0.60281100
H	1.53596900	1.57547000	-0.40030800
H	1.53673600	0.10711500	-1.62182300
Mg	4.15175600	0.00149500	-0.00266500
C	-3.48972800	0.00078300	-0.00156800
F	-3.99716200	-0.37160900	1.19927900
F	-3.99158600	-0.85306300	-0.92743800
F	-3.99005600	1.22953700	-0.28089000
Br	-1.46651100	-0.00175200	0.00330500

CF_3Br-$PtZnH_5^-$

Pt	1.14622200	0.00043100	-0.00015000
H	1.10472100	1.23987800	1.05267100
H	1.10474000	1.38411300	-0.85445200
H	1.10453600	-0.61698800	1.50436700
H	1.10392200	-0.38445000	-1.58004700
H	1.10432700	-1.62117800	-0.12284700
Zn	3.72139100	-0.00158000	0.00049300
C	-3.87257200	-0.00156000	0.00044400

F	-4.38057700	1.19560600	0.38679400
F	-4.37501300	-0.93625300	0.84567300
F	-4.37887800	-0.26775100	-1.22957000
Br	-1.86067500	0.00278100	-0.00090100

3D coordinates using the M06-2x functional (Å)

CF_3Br-Al_{13}^-

Al	-4.05171300	-0.83898200	-1.37398300
Al	-2.45919500	1.25481100	-2.27741900
Al	-1.45499000	-1.34299100	-2.22649600
Al	-2.44351200	-2.60166700	0.05235900
Al	-4.04745200	-0.78277300	1.41297400
Al	0.14980200	-1.60351600	0.02839500
Al	-1.46367400	2.60200700	-0.05285200
Al	-4.05792400	1.60169600	-0.02881500
Al	0.14126900	0.78375900	-1.41400700
Al	-2.45179800	1.34436900	2.22610500
Al	0.14502100	0.84001800	1.37466000
Al	-1.44734000	-1.25322800	2.27660700
Al	-1.95286800	0.00037900	-0.00031500
C	5.65782500	0.00274200	-0.00201300
Br	3.73103300	-0.00583000	0.00451700
F	6.13993700	-1.18537800	0.33213800
F	6.13197600	0.89170500	0.85871200
F	6.12739400	0.30891000	-1.20304800

CF_3Br-Br^-

C	-2.23646400	-0.00014300	0.00102300
F	-2.73877100	-0.95905500	-0.78090200
F	-2.73910000	1.15676700	-0.43709200
F	-2.73617100	-0.19891600	1.22317800
Br	-0.31021100	0.00051600	-0.00238100
Br	2.80578800	-0.00018200	0.00087300

CF_3Br-PtH_5^-

C	-3.15294500	-0.00079400	-0.00102900
F	-3.64883400	1.08043200	-0.60122100
F	-3.64979200	-0.02339800	1.23510200
F	-3.64522400	-1.06203200	-0.63899200
Br	-1.23271800	0.00220700	0.00219400
Pt	1.93443800	-0.00029300	-0.00029200
H	1.93758000	0.02765500	-1.60358400
H	1.93449800	-1.51623500	-0.52245300
H	1.93624600	1.53336200	-0.46894400
H	1.93113100	-0.96737000	1.27868400
H	1.93182200	0.91797300	1.31448000

CF_3Br-PtH_5^--CF_3Br

C	5.12788200	0.00865700	-0.00455600
F	5.61025900	0.95025100	-0.81139600
F	5.62269600	-1.15545200	-0.41778700
F	5.62239600	0.23909200	1.20921700
Br	3.21081400	-0.00024600	0.00432200
Pt	-0.00003200	-0.00844300	0.00119800
H	-0.00037500	1.45880900	0.64765700
H	0.00005400	-0.16994000	1.59640000
H	-0.00031500	1.06019400	-1.19451300
H	0.00038200	-1.57566100	0.33959100
H	0.00008500	-0.81516700	-1.38468200
C	-5.12787600	0.00887500	-0.00516700
F	-5.61978700	-0.99687000	-0.72445600

F	-5.62492000	-0.10624000	1.22401500
F	-5.61025200	1.13610500	-0.52187300
Br	-3.21083900	0.00005000	0.00542000

CF_3Br-$PtMgH_5^-$

Pt	1.64581300	0.01072800	0.00270300
H	1.60771900	-0.99010800	1.25314700
H	1.63443800	0.89326300	1.33977300
H	1.59527200	-1.48616800	-0.56477700
H	1.63263200	1.55514800	-0.42172600
H	1.60931700	0.08747100	-1.59719300
Mg	4.22906100	-0.04298800	-0.01374400
C	-3.55035700	-0.00107800	-0.00275600
F	-4.04183300	-0.36570300	1.17801400
F	-4.04045600	-0.83710300	-0.91225400
F	-4.02952300	1.20865700	-0.27616900
Br	-1.62551600	-0.01219200	0.00157400

CF_3Br-$PtZnH_5^-$

Pt	-1.19010000	-0.00119100	0.00148900
H	-1.15612000	1.48188900	0.60957500
H	-1.15906500	-0.12278000	1.59951800
H	-1.15547900	1.03452200	-1.22152800
H	-1.16116700	-1.55822200	0.38041200
H	-1.15679700	-0.84413300	-1.36126800
Zn	-3.89317800	0.00304600	-0.00326700
C	3.96280100	0.00250400	-0.00212400
F	4.45247100	0.85105100	0.89829900
F	4.45093000	0.36008600	-1.18714600
F	4.45634300	-1.20088600	0.28054500
Br	2.03992200	-0.00277200	0.00179000

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