Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPLEMENTARY INFORMATION

Ab initio and DFT analysis of the low-lying electronic states of metal dihalides: Quantum chemical calculations on the neutral BrMCl (M=Cu, Ag, Au)

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Table S1. Electronic configuration and Mullliken charge distribution obtained for AgClBr at the HF level with different basis sets and ECPs.

Basis set Label	Electronic configuration (^{2}A')	Mulliken Charge		
		Br	Ag	Cl
ANO-RCC	$(3p_zCl)^2(4d\pi)^2\ (4d\pi)^2\ (4d\sigma)^2(3p_yCl)^2(4p_zBr)^2\ (4p_yBr)^1$ $(3p_xCl)^2\ (4d\pi)^2\ (4d\pi)^2\ (4p_xBr)^2$	0.16	0.59	-0.75
ANO-DK3	$(4d\sigma)^2(4d\pi)^2\ (4d\pi)^2\ (4p_zBr)^2\ (3p_zCl)^2(3p_yCl)^2(4p_yBr)^1$ $(4d\pi)^2\ (4d\pi)^2\ (4p_xBr)^2(3p_xCl)^2$	-0.21	0.66	-0.45
ANO-DK3-u	$(4d\sigma)^2(4d\pi)^2\ (4d\pi)^2\ (4p_zBr)^2\ (3p_zCl)^2(3p_yCl)^2(4p_yBr)^1$ $(4d\pi)^2\ (4d\pi)^2\ (4p_xBr)^2(3p_xCl)^2$	-0.12	0.58	-0.46
17e-CG-AIMP	$(4d\sigma)^2(4d\pi)^2(4d\pi)^2(4p_zBr)^2\ (3p_zCl)^2(3p_yCl)^2(4p_yBr)^1$ $(4d\pi)^2\ (4d\pi)^2\ (4p_xBr)^2\ (3p_xCl)^2$	0.04	0.37	-0.41
17e-CG-AIMP-u	$(4d\pi)^2\ (4d\pi)^2\ (4d\sigma)^2\ (3p_yCl)^2\ (4p_zBr)^2(4p_yBr)^2\ (3p_zCl)^1$ $(4d\pi)^2\ (4d\pi)^2\ (3p_xCl)^2\ (4p_xBr)^2$	-0.39	0.77	-0.38
19e-NP-AIMP	$(4d\pi)^2\ (4d\sigma)^2\ (4d\pi)^2\ (4p_yBr)^2\ (3p_zCl)^2(3p_yCl)^2\ (4p_zBr)^1$ $(4d\pi)^2\ (4d\pi)^2\ (4p_xBr)^2\ (3p_xCl)^2$	0.03	0.47	-0.5
19e-MWB	$(3p_zCl)^2\ (4d\pi)^2\ (4d\pi)^2\ (d\sigma)^2(3p_yCl)^2\ (4p_zBr)^2\ (4p_yBr)^1$ $(4d\pi)^2\ (4d\pi)^2\ (3p_xCl)^2\ (4p_xBr)^2$	-0.06	1.07	-1.01
19e-LANL2DZ	$(4d\pi)^2\ (d\sigma Cl)^2\ (4d\pi)^2\ (3p_yCl)^2\ (4p_zBr)^2(4p_yBr)^2\ (3p_zCl)^1$ $(4d\pi)^2\ (4d\pi)^2\ (3p_xCl)^2\ (4p_xBr)^2$	-0.53	1.12	-0.59
17e-NR-AIMP	$(4d\sigma)^2\ (4d\pi)^2\ (4d\pi)^2\ (4p_zBr)^2\ (3p_zCl)^2(3p_yCl)^2\ (4p_yBr)^1$ $(4d\pi)^2\ (4d\pi)^2\ (4p_xBr)^2\ (3p_xCl)^2$	0.07	0.36	-0.43
17e-NR-AIMP-u	$(4d\pi)^2\ (4d\pi)^2\ (4d\sigma)^2\ (3p_yCl)^2\ (4p_zBr)^2(4p_yBr)^2\ (3p_zCl)^1$ $(4d\pi)^2\ (4d\pi)^2\ (3p_xCl)^2\ (4p_xBr)^2$	-0.35	0.71	-0.36

Table S2. Orbital contribution to the total mulliken charge and spin (in parenthesis) beard by the metal from ADF calculations (B3LYP/TZVP) for copper (n=4), silver (n=5) and gold (n=6)

	Cu	Ag	Au
ns	0.37 (-0.01)	0.48 (-0.02)	0.14 (-0.01)
(n-1)d	0.47 (0.45)	0.27 (0.17)	0.59 (0.29)
np	-0.37 (-0.02)	-0.21 (-0.02)	-0.24 (-0.02)
Total	0.47 (0.42)	0.54 (0.13)	0.48 (0.27)

Table S3. Relativistic orbital energies for copper (n=4), silver (n=5) and gold (n=6) in atomic units.

	Cu	Ag	Au
$ns_{1/2}$	-0.245	-0.237	-0.292
$(n-1)d_{3/2}$	-0.488	-0.526	-0.494
$(n-1)d_{5/2}$	-0.474	-0.501	-0.429

Table S4. CASPT2 Mulliken charge distribution of ClCuBr and ClAgBr neutral molecules at the degeneracy of the ground state by CASPT2 level of theory.

	M	Cl	Br
Cu	28.1	17.6	35.4
Ag	46.4	17.5	35.1
Au	78.5	17.3	35.2