Deciphering the chemical bonding in anionic thallium clusters

Supporting Information

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1. Hypothetical KTl Model Structure with O_h Tl_6 Clusters

The hypothetical KTl model structure with regular octahedral $[Tl_6]^{6-}$ was obtained through a restricted structural optimization upon KTl with quantum mechanics calculations. During the optimization, the lattice parameters were adopted from experimental values[1] and kept fixed. The coordinates of Tl atoms were adjusted so that they are restricted to form regular octahedra. The positions of K atoms, the size and orientation of the regular $[Tl_6]^{6-}$ octahedra were optimized. The resulting regular octahedral $[Tl_6]^{6-}$ clusters have the closest Tl-Tl distance at 3.24 Å. This value is sensible because it is close to the Tl-Tl distances, 3.230(1) Å and 3.200(1) Å, of the nearly regular octahedral $[Tl_6]^{6-}$ clusters in Cs_4Tl_2O.[2] Details of the model structure is listed and compared with the experimental structure in Table S1.

Table S1. Comparison between the experimental KTl structure[1] and the hypothetical KTl model structure with O_h $[Tl_6]^{6-}$ clusters.

Cmce, *a* = 15.329(4) Å, *b* = 15.069(4) Å, *c* = 8.137(2) Å							
		experimental			hypothetical		
		x	y	z	x	y	z
K1	8*e*	1/4	0.2205(6)	1/4	1/4	0.2250	1/4
K2	8*d*	-0.1774(6)	0	0	-0.1881	0	0
K3	8*f*	0	0.2002(5)	-0.0751(9)	0	0.2043	0.9057
Tl1	16*g*	0.11306(8)	0.39558(6)	0.0689(1)	0.1056	0.3976	0.0602
Tl2	8*f*	0	0.5438(1)	0.2193(1)	0	0.5460	0.2682

2. Pictorial Demonstration of the Correspondence between Orbitals/Spinors

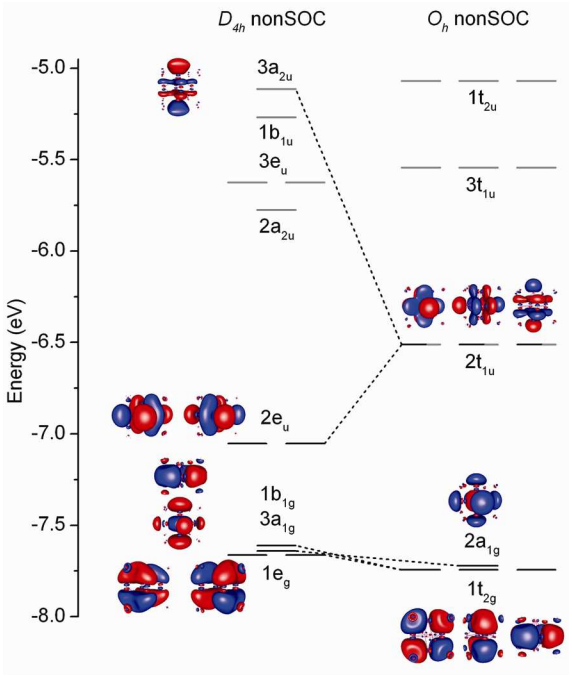

Figure S1. The correspondences between the MOs of O_h and D_{4h} $[K_8Tl_6]^{2+}$.

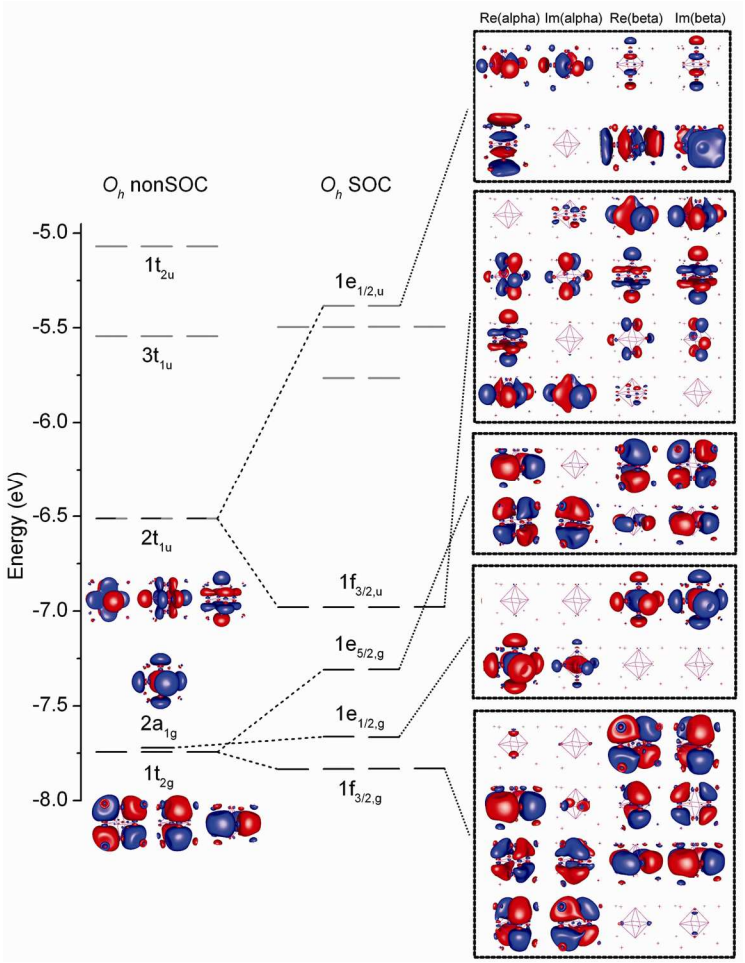

Figure S2. The correspondence between the nonSOC MOs and the SOC spinors of O_h $[K_8Tl_6]^{2+}$.

When carrying out calculations with spin-orbit coupling (SOC), many quantum mechanics computation packages, e.g. TURBOMOLE,[3] have to abandon symmetry at all. All molecules are treated as C_1* (the double group of C_1). So the computation packages do not give the irreducible representation (irrep) symbols of the spinors. To figure them out, we can firstly plot out the sketches of spinors with TURBOMOLE. Unlike a molecular orbital (MO), which can be shown with 1 sketch, each spinor has 4 sketches corresponding to the real and imaginary parts of the

two complex components of the spinor.[4] By comparing the sketches of spinors with those of MOs (from nonSOC calculations), we can see their topological correspondence (Figure S2).

Then, with group theory,[5] we can deduce that the vector irrep T_{2g} will derive into a two-dimensional $E_{5/2,g}$ and a four-dimensional $F_{3/2,g}$ spinor irreps: $T_{2g} \otimes E_{1/2,g} = E_{5/2,g} \oplus F_{3/2,g}$, where $E_{1/2,g}$ is the irrep spanned by the elementary spinor (α, β). Likewise, $A_{1g} \otimes E_{1/2,g} = E_{1/2,g}$, and $T_{1u} \otimes E_{1/2,g} = E_{1/2,u} \oplus F_{3/2,u}$. So the irrep symbols of the spinors can be assigned.

3. $Na_2K_{21}Tl_{19}$

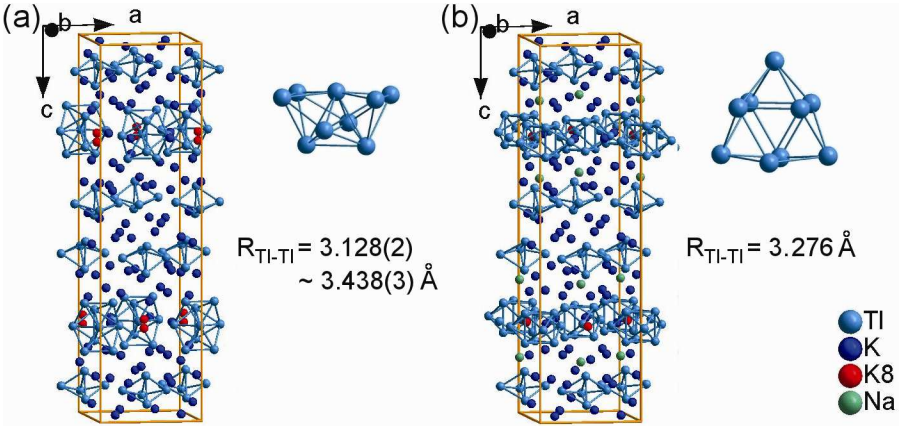

Figure S3. The unit cell and the geometry of the $[Tl_9]^{9-}$ cluster in (a) experimental $Na_2K_{21}Tl_{19}$ with C_{2v} $[Tl_9]^{9-}$ and (b) hypothetical $Na_2K_{21}Tl_{19}$ with D_{3h} $[Tl_9]^{9-}$.

Table S2. Comparison between the experimental $Na_2K_{21}Tl_{19}$ structure[6] and the hypothetical $Na_2K_{21}Tl_{19}$ model structure with D_{3h} $[Tl_9]^{9-}$ clusters.

Cmcm, *a* = 11.345(2) Å, *b* = 13.807(3) Å, *c* = 41.832(8) Å							
		experimental			hypothetical		
		x	y	z	x	y	z
Na1	8*f*	0	-0.035(1)	0.3669(6)	0	-0.0420	0.3531
K1	8*g*	0.1947(9)	0.4608(8)	1/4	0.1486	0.4326	1/4
K2	8*f*	0	0.411(1)	0.4610(4)	0	0.4090	0.4604
K3	16*h*	0.1741(6)	0.1341(6)	0.4849(3)	0.1719	0.1340	0.4865
K4	16*h*	0.2869(7)	0.0587(6)	0.3991(3)	0.2740	0.0484	0.4009
K5	16*h*	-0.2307(7)	-0.1776(7)	0.3323(3)	-0.2169	-0.2144	0.3284
K6	8*f*	0	0.237(1)	0.3840(4)	0	0.2261	0.3832
K7	8*f*	0	0.583(1)	0.1837(5)	0	0.5076	0.1658
K8[a]	8*f*	0	-0.172(2)	0.2618(6)	0	0.6368	1/4
Tl1	8*f*	0	0.2855(1)	0.29086(6)	0	0.2430	0.2892
Tl2	4*c*	0	0.0695(2)	1/4	0	0.8698	1/4
Tl3	8*g*	-0.2719(1)	-0.2908(1)	1/4	-0.2510	-0.2759	1/4
Tl4	16*h*	0.1420(1)	0.0875(1)	0.31380(4)	0.1444	0.0375	0.2892
Tl5	8*f*	0	-0.3015(2)	0.45911(6)	0	-0.3022	0.4606
Tl6	8*f*	0	-0.0610(1)	0.44117(6)	0	-0.0608	0.4348
Tl7	8*f*	0	-0.2529(2)	0.38520(6)	0	-0.2643	0.3848
Tl8	16*h*	0.2838(1)	0.3140(1)	0.42526(4)	0.2778	0.3036	0.4248

[a]K8 (8*f*) site (red in Figure S3) is half occupied (occupancy 0.500(1)). In computational model structures, this site was adjusted to a fully occupied 4*c* site by change the z coordinate to 1/4.

$Na_2K_{21}Tl_{19}$ has two sorts of Tl clusters coexisting in its structure.[6] For every formula unit, there are two $[Tl_5]^{7-}$ and one $[Tl_9]^{9-}$ which has a symmetry of C_{2v} and can be viewed as a 4-capped trigonal bipyramid (Figure S3(a)). To satisfy Wade-Mingos rules, the formal charges of the clusters should be $[Tl_5]^{7-}$ and $[Tl_9]^{9-}$ so they require $2 \times 7 + 11 = 25$ electrons, however, the cations can only afford 23 valence electrons. So $Na_2K_{21}Tl_{19}$ is also formally "hypoelectronic". The electron deficiency was attributed by the authors solely to $[Tl_9]^{9-}$ so the formal charges were assigned as $[Tl_5]^{7-}$ and $[Tl_9]^{9-}$. The reason is that $[Tl_5]^{7-}$ has the trigonal bipyramidal geometry which is in accordance with the Wade-Mingos closo structure while the C_{2v} structure of $[Tl_9]^{9-}$ (Figure S3(a)) differs significantly from the closo structure, i.e. a tricapped trigonal prism (Figure S3(b)).

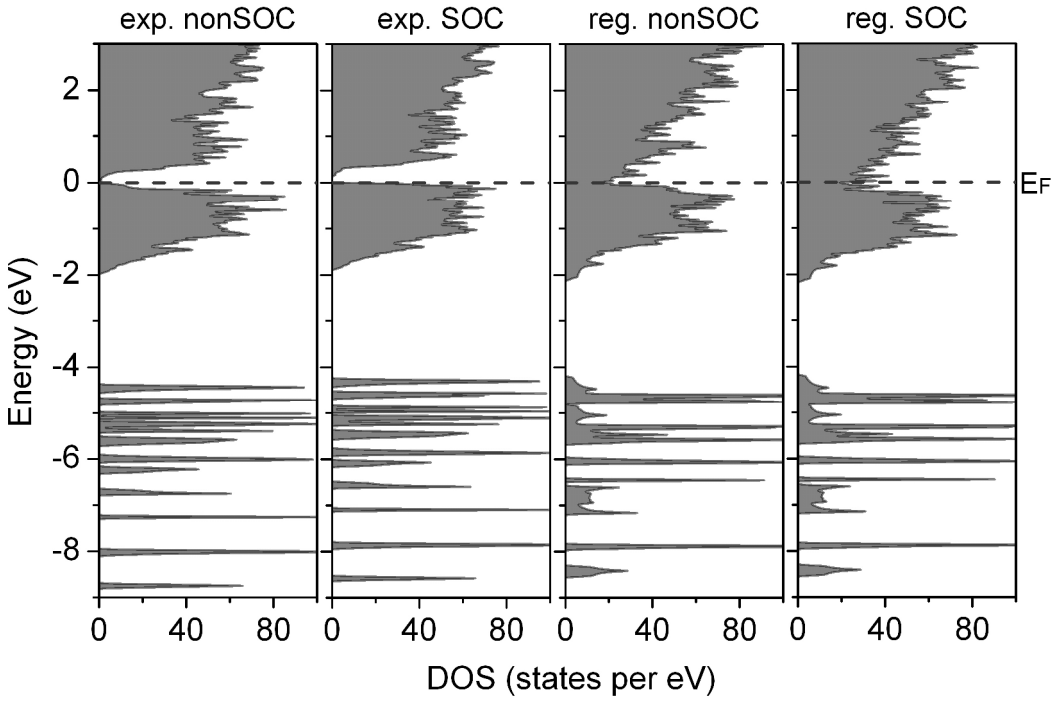

Figure S4. The nonSOC and SOC DOS curves of experimental (with C_{2v} $[Tl_9]^{9-}$ clusters) and hypothetical (with regular D_{3h} $[Tl_9]^{9-}$ clusters) $Na_2K_{21}Tl_{19}$.

However, band structure calculations reveal that, just like KTl, the formally "hypoelectronic" $Na_2K_{21}Tl_{19}$ is actually electron exact – E_F falls into a gap in the DOS curves for both SOC and nonSOC cases (Figure S4). This closed shell electron configuration can be experimentally confirmed by the diamagnetism of $Na_2K_{21}Tl_{19}$.[6] And it can be understood as the result of JT distortion of the $[Tl_9]^{9-}$ clusters from the Wade-Mingos closo structure (D_{3h}) to the experimental C_{2v} geometry.

We built a hypothetical $Na_2K_{21}Tl_{19}$ model structure with the regular D_{3h} tricapped trigonal prism $[Tl_9]^{9-}$ clusters. The details are in Figure S3 and Table S2. It was built in a way similar to how we built the hypothetical KTl with regular O_h Tl_6 clusters. DOS curves of this hypothetical structure from both nonSOC and SOC calculations (Figure S4) afford no gap at E_F. So evidently, band gap opens only when the $[Tl_9]^{9-}$ clusters distort from D_{3h} to C_{2v}. Here, SOC does not have a significant effect. JT is the only cause that alleviates the formal "hypoelectronicity".

4. WIEN2k calculations

Computational parameters of the band structure calculations with the WIEN2k program package[7] are summarized in Table S3.

Table S3. Computational parameters of WIEN2k calculations.

	Cs_4Tl_2O	Cs_8Tl_8O	$Cs_{18}Tl_8O_6$	$Na_2K_{21}Tl_{19}$	$K_{10}Tl_7$	Na_2Tl	$Na_{14}K_6Tl_{18}Mg$
R_{mt}							
Tl	2.95	2.90	2.90	2.90	3.00	3.00	3.05
Cs	2.70	2.70	2.70	-	-	-	-
K	-	-	-	2.80	3.00	-	2.80
Na	-	-	-	2.70	-	2.80	2.80
Mg	-	-	-	-	-	-	2.70
O	2.50	2.70	2.70	-	-	-	-
$R_{mt}K_{max}$	7.0	7.0	7.0	6.0	6.0	6.0	7.0
R0							
Tl	1.0E-4	1.0E-4	5.0E-6	5.0E-6	5.0E-6	5.0E-6	5.0E-6
Cs	1.0E-4	1.0E-4	1.0E-4	-	-	-	-
K	-	-	-	5.0E-5	1.0E-5	-	5.0E-5
Na	-	-	-	5.0E-5	-	1.0E-4	1.0E-4
Mg	-	-	-	-	-	-	1.0E-4
O	1.0E-4	1.0E-4	1.0E-4	-	-	-	-
core-val. separation	-6.0 Ry	-6.0 Ry	-6.0 Ry	-5.0 Ry	-5.0 Ry	-5.0 Ry	-5.0 Ry
add. LO							
Tl	l=0,2	l=0,(1),2	l=2	l=2	l=2	l=2	l=2
Cs	l=0,1,2	l=0,1,2	l=0,2	-	-	-	-
K	-	-	-	l=0,1	l=0,1	-	l=0,1
Na	-	-	-	l=0,1	-	l=0,1	l=0,1
Mg	-	-	-	-	-	-	l=1
O	l=0,1	l=0,1	l=0	-	-	-	-
k-points							
shift	yes	yes	yes	yes	yes	yes	yes
inequiv.	231	371	119	49	132	144	119

Reference:

(1) Dong, Z. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1993,** *115* (24), 11299-11303.

(2) Saltykov, V.; Nuss, J.; Wedig, U.; Jansen, M. *Z. Anorg. Allg. Chem.* **2011,** *637* (3-4), 357-361.

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(4) Armbruster, M. K.; Weigend, F.; van Wuellen, C.; Klopper, W. *Phys. Chem. Chem. Phys.* **2008,** *10* (13), 1748-1756.

(5) Altmann, S. L.; Herzig, P., *Point-group theory tables*. Clarendon Press; Oxford University Press: Oxford New York, 1994.

(6) Dong, Z. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1994,** *116* (8), 3429-3435.