The cyclo-Sb_6 Ring in the $[Sb_6(RuCp^*)_2]^{2-}$ Ion

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The cyclo-Sb_6 Ring in the $[Sb_6(RuCp^*)_2]^{2-}$ Ion

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The $[Sb_6(RuCp^*)_2]^{2-}$ (1) anion represents the first example of a Zintl cluster with a boat-like cyclo-Sb_6 subunit and the first ruthenium polyantimonide complex. The anion is dynamic in solution and fragments in the gas phase. Structural parameters and DFT calculations suggest the possibility of Sb=Sb double bond character.

The chemistry of the polyantimonides (i.e. the $[Sb_x]^{n-}$ ions) is quite rich due to their propensity for disproportionation processes and facile structural rearrangements.[1] The polyantimonides are far more likely to undergo cluster growth and disproportionation reactions with transition metals relative to their lighter polyphosphide congeners.[2] For example, $[E_7ML_n]^{3-}$ (M= transition metal, L=ligand) and $[E_{14}M_n]^{x-}$ are known for E = P, As, and Sb,[3,4] but Sb_7^{3-} also disproportionates in reactions with transition metal precursors to give new polyanions, such as $[Sb_8]^{8-}$ in the $[MSb_8]^{n-}$ ions [5] and the neutral Sb_{20} dodecahedron in the $[Sb@M@Sb_{20}]^{n-}$ icosahedral clusters, that have no phosphorus analogs.[6] While the cluster chemistry stemming from reactions of *elemental* phosphorus is quite rich, the complexes derived from the $[P_x]^{n-}$ Zintl ion precursors are dominated by the P_7^{3-} ion and its derivatives.[1,2]

Within the class of transition metal polyantimonides containing naked Sb_x subunits, there are a number of structural motifs that have been identified. These include cyclic units of Sb_3,[7] Sb_4,[8] Sb_5,[9] Sb_7,[10] Sb_8 [11] and larger catenated ring structures.[12] However, to our knowledge, naked Sb_6 units and their transition metal derivatives remain unknown despite the plethora of cyclo-P_6 [13] and, to a lesser extent, cyclo-As_6 subunits [14] known in the literature. These include a D_{2h} planar cyclo $[P_6]^{4-}$ units known in solid-state compounds [15] and a chair conformer of an $[As_6]^{4-}$ ring isolated from a reaction of Rb_4As_6 with $AsPh_3$ in liquid ammonia.[16] The only structurally characterized Sb_6 rings reported in the literature are the cyclo-Ar_6Sb_6 (Ar= *o*-Tol, *m*-Tol) stibanes [17] and the $[(Ph_3P)_4Sb_6]^{4+}$ bicyclic cation.[18] We describe here the synthesis, structure and dynamic behaviour of a the $[Sb_6(RuCp^*)_2]^{2-}$ anion (**Fig. 1**) from the reaction of a highly reduced K_3Sb intermetallic precursor and Ru(COD)Cp*Cl (COD=1,5-cyclooctadiene, Cp* =1,2,3,4,5-pentamethylcyclo-pentadienyl). To our knowledge, the $[Sb_6(RuCp^*)_2]^{2-}$ anion is the first Ru polyantimonide and contains the first structurally characterized boat-like cyclo-Sb_6 ring reported to date. The $[K(18\text{-crown-}6)Sb_6]^-$ anion has been observed in the gas phase,[19] but its structure is unknown.

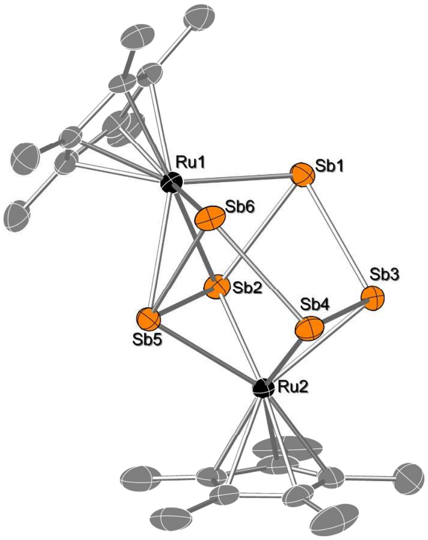

Fig. 1 X-ray structure of $[Sb_6Ru_2(Cp^*)_2]^{2-}$ ion drawn with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond distances(Å): Sb1-Sb2 2.7878(2), Sb1-Sb3 2.8371(3), Sb2-Sb5 2.9538(2), Sb3-Sb4 2.7324(2), Sb4-Sb6 2.8519(3), Sb5-Sb6 2.7886(3), Ru1-Sb6 2.6848(3), Ru1-Sb1 2.6872(3), Ru1-Sb2 2.7634(3), Ru1-Sb5 2.7903(3), Ru2-Sb2 2.6969(3), Ru2-Sb3 2.7093(3), Ru2-Sb4 2.7094(3), Ru2-Sb5 2.7175(3).

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Electronic Supplementary Information (ESI) available: Full experimental details, crystallographic data, NMR (^1H and ^{13}C) spectra, and LDI-TOF mass spectra. CCDC 1859496-1859497. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

Table 1. Sb-Sb bond lengths in polystibnide anions (Å)

Sb_n	$[Sb_4]^{2-}$ [8]	$[Sb_5]^{5-}$ [9]	$[Sb_7]^{3-}$ [10]	$[Sb_8]^{8-}$ [11]	$[Sb_{10}]^{2-}$ [19]	$[Sb_{11}]^{3-}$ [12]
Sb-Sb	2.749(1)– 2.751(1)	2.8059(10) – 2.9103(10)	2.711(4) –2.906(2)	2.847(2) –2.872(3)A	2.673(2) –2.851(3)	2.716(4) –2.853(4)
Sb-Sb (av.)	2.750	2.849	2.820	2.861	2.743	2.803
Δ(range)	0.002	0.1044	0.195	0.025	0.178	0.137

Δ: the differences between longest Sb-Sb contacts and the shortest Sb-Sb contacts.

Ethylenediamine (en) solutions containing 2,2,2-crypt and extracts of "K_3Sb" react with toluene solutions of transition-metal complex [Ru(COD)Cp*Cl] (COD=1,5-cyclooctadiene) at 60-65°C for 2.5h to give the $[Sb_6(RuCp^*)_2]^{2-}$ anion (**1**). Dark red prismatic crystals of the $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]$•2tol (tol= toluene) salt have been isolated in 30% yield (based on K_3Sb) after *ca.* one week at room temperature. The use of a precursor with nominal composition "K_5Sb_4" also gives **1** but in a relatively lower yield. The salt has been characterized by single crystal X-ray diffraction, ^1H and ^{13}C NMR spectroscopy, energy dispersive X-ray analysis (EDX) and laser desorption-ionization time-of-flight mass spectrometry (LDI-TOF MS). Layering a deuterated pyridine solution of $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]$•2tol with toluene yielded large, dark red block-like crystals $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]$•tol•py, which has an identical form of **1** but a different solvate structure. In this paper, only the bis toluene solvate structure is described.

The $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]$•2tol salt is triclinic, space group *P-1*, and contains one $[Sb_6(RuCp^*)_2]^{2-}$ anion, two $[K([2.2.2]crypt)]^+$ cations, and two toluene solvent molecules (one is highly disordered) in the lattice. The $[Sb_6(RuCp^*)_2]^{2-}$ anion, **1**, (**Fig. 1**) has virtual C_s point symmetry defined by the mirror plane passing through Ru1, Ru2 and the mid-point of the Sb3-Sb4 bond. The Sb_6 polyantimonide can be viewed as a boat-like cyclo-Sb_6 structure that is η^4-coordinated to each of the two RuCp* transition metal fragments. However, the two RuCp* units coordinate to different parts of the Sb_6 ring and are structurally inequivalent. The structure of **1** can also be viewed as a distorted Sb_6 trigonal prism with two of the three square faces capped by two Ru(Cp*) fragments.

The Sb-Sb bonds in $[Sb_6(RuCp^*)_2]^{2-}$ fall in the range 2.7324(2)- 2.9538(2) Å (av. 2.83 Å), which are typical of 2-center, 2-electron single bonds in these types of compounds (**Table 1**). Although the longest Sb-Sb bond in $[Sb_6(RuCp^*)_2]^{2-}$ (Sb2-Sb5 2.9538(2)Å) is slightly longer than typical homoatomic Sb-Sb single bonds, it is significantly shorter than the secondary Sb-Sb bonds observed in $[Sb_7Cr(CO)_3]^{3-}$(3.331(4) Å)[3a] and $[Sb@Pd_{12}@Sb_{20}]^{3/4-}$(3.11 Å).[6] The Sb2…Sb3 and Sb4…Sb5 separations are around 3.4 Å and may have some secondary boning interactions but, to a first approximation, they can be considered non-bonding. The other Sb-Sb separations are all greater than 3.9 Å. As a consequence, the Sb atoms are all two-connected (excluding Ru interactions) and can be viewed as Sb^- centers from an 8-N Zintl type analysis. From this perspective, the compound comprises a cyclo-$[Sb_6]^{6-}$ ring captured by two $[Ru(Cp^*)]^{2+}$ fragments.

In an alternative resonance form, the short Sb3-Sb4 contact of 2.7324(2) Å could be viewed as having Sb=Sb double bond character. As such, the ring can be viewed as $[Sb_6]^{4-}$ ring coordinated to two $[Ru(Cp^*)]^+$ fragments. The presence of a single π-bond in the $[Sb_6]^{4-}$ ring is consistent with a simple Lewis model and is similar to the ELF analyses of $[P_6]^{4-}$.[16] However, this model is in contrast to the delocalized π-bonding structure observed in naked $[As_6]^{4-}$ containing two π-bonds that involve lone-pair participation.[16] DFT calculations (see below) and comparisons to known di-stibenes (e.g. Bbt-Sb=Sb-Bbt; $d_{Sb=Sb}$ = 2.7037(6) Å, Bbt = 2,6-bis[bis(trimethylsilyl) methyl]-4-[tris(trimethylsilyl)methyl]phenyl)[20] support the single π-bond model in **1** but the bonding in a naked $[Sb_6]^{4-}$ ring remains unknown.

The Ru-Sb contacts in **1** are in the range 2.6848(3)-2.7903(3) Å (av. 2.72 Å), and are slightly longer than the typical Ru-Sb single bond distances found in organometallic complexes containing Cp*Ru-Sb fragments. For example, the antimony complexes $\{Cp^*Ru[Sb(C_{36}H_{60}N_3O_6)_3]_3\}^+[CF_3SO_3]^-$(2.581-2.597 Å, av. 2.591 Å),[21] tri-isopropylstibane ruthenium complexes $[Cp^*RuCl_2(Sb^iPr_3)]$(2.613(3)Å) and $[Cp^*(Sb^iPr_3)Ru(\mu\text{-}Cl)_2RuCp^*]$ (2.656(7) Å),[22] have slightly shorter average Ru-Sb distances.

The $[Sb_6(RuCp^*)_2]^{2-}$ ion can also be viewed as a distorted deltahedral cluster derived from a mono-capped square anti-prism. According to Wade's Rules,[23] an Sb atom donates three electrons and a [Ru(Cp*)] fragment donates one electron to cluster bonding. In this description, the $[Sb_6(RuCp^*)_2]^{2-}$ ion is an *aracho* 8-vertex deltahedral cluster (2n + 6 electrons, where n = 8) with 22 skeletal bonding electrons [(6 ×3)Sb + 1×2(Cp*Ru) +2(charge)]. Transformation of electron-precise group 15 polyanions into electron-deficient polyhedral structures by introducing electron-deficient vertices has been demonstrated in the formation of the *nido* 10-vertex polyhedral cluster $[Sb_7Ni_3(CO)_3]^{3-}$ from the reaction of the electron-precise $[Sb_7]^{3-}$ with $Ni(CO)_2(PPh_3)_2$.[24]

The ^1H and ^{13}C NMR spectra of **1** were recorded from

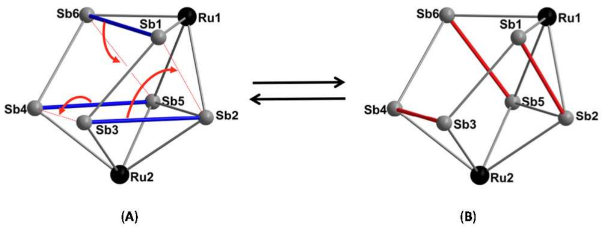

Fig. 2 Proposed dynamic behaviour of $[Sb_6(RuCp^*)_2]^{2-}$ anion in solution (Cp* groups omitted for clarity). The dotted red lines represent non-bonding separations (> 3.36 Å) that are converted to Sb-Sb bonds (2.7 - 2.8 Å) during the exchange process. Both drawing A and B use the atomic labelling scheme shown in **Fig. 1**.

deuterated pyridine solutions of the $[K([2.2.2]crypt)]_2$-$[Sb_6(RuCp^*)_2]$•2tol salt and are shown is Figures S4 and S5, respectively. The ^1H NMR spectrum of **1** (Figure S4), contains only one singlet at 2.45 ppm for the methyl protons of Cp* ligands along with the associated peaks for the solvate molecules and the cryptands. Similarly, the ^{13}C NMR spectra (Figure S5), show two resonances, at 15.33 and 83.68 ppm, assigned to the methyl carbons and the ring carbons of the Cp* ligands, respectively, along with peaks for the solvates and cryptands. Because the RuCp* groups are inequivalent in the solid state structures of **1**, these data indicate that the cluster is dynamic in solution with an exchange process that makes the two Ru(Cp*) groups equivalent on the NMR time scale. A proposed exchange mechanism is shown in **Fig. 2** that involves electronic reorganization of three Sb-Sb bonds along a vibrational mode of the molecule. This exchange process renders both RuCp* groups equivalent and is akin to the accepted dynamic exchange processes in the related $[E_9]^{4-}$ ions (E = Sn, Pb).[25] Although the fluxionality of Zintl anions in solution has been well established, especially for heavier polyanions of spin-active group 14 elements and the polyphosphides, the corresponding dynamic properties for heavier polypnictides arsenic, antimony, and bismuth have been less investigated due to the lack of I=1/2 nuclei for these elements.

LDI-TOF MS data were collected from the $[K([2.2.2]crypt)]_2[Sb_6(RuCp^*)_2]$•2tol salt in the negative-ion mode by loading crystals of the salt directly onto carbon tape and by depositing the complex on the sample plates from pyridine solutions. Both deposition methods gave similar spectra and are shown in Figure S6-S9. As is common for mass spectral analyses of Zintl type compounds, usually only anions with the charge of -1 are observed. While the $[Sb_6(RuCp^*)_2]^{2-}$ parent anion was not observed, the $[Sb_6Ru_2Cp^*]^-$ (**1** – Cp*) and $[Sb_6Ru_2]^-$ (**1** – 2Cp*) ions were observed at m/z = 1068.4 and m/z = 933.2, respectively (see Figure S6). In addition, a series of naked $[Ru_xSb_y]^-$ binary anions such as $[Sb_yRu]^-$,(y=4-9), $[Sb_yRu_2]^-$ (y=3-12), and Cp* coordinated Ru-Sb clusters such as $[Sb_yRu_2(Cp^*)]^-$ (y=3-8) and $[Sb_yRu(Cp^*)]^-$ (y= 3,4 and 9) were also observed (see Figure S6).

B3LYP density-functional calculations (DFT) were performed using the Lanl2dz basis set on **1** with the crystallographic data as the initial structural model. The methyl groups of the Cp* ligands were replaced by H atoms. As expected, the calculated bond distances in the Sb_6Ru_2 core of the optimized ion $[Sb_6(RuCp)_2]^{2-}$ are slightly longer (av. 0.08 Å) than the experimental values (see Table S3). The lone pair/π-bonding character can be observed in three of the frontier occupied molecular orbitals (Figure S2) showing Sb3-Sb4 π-interactions in the HOMO, HOMO-4 and HOMO-5.

In summary, the $[Sb_6(RuCp^*)_2]^{2-}$ anion, **1**, was synthesized from a solution reaction between a $[Sb_x]^{n-}$ Zintl ion precursor and a Cp*Ru(**II**) precursor. The complex has a distorted Sb_6 ring and displays facile dynamic exchange in solution. DFT calculation suggests some π-bonding between Sb3 and Sb4, consistent with a $[Sb_6]^{4-}$ ring description. The gas phase chemistry shows Cp* deficient derivatives of the parent ion as well as series of $[Ru_xSb_y]^-$ binary anions.

Conflicts of interest

There are no conflicts to declare.

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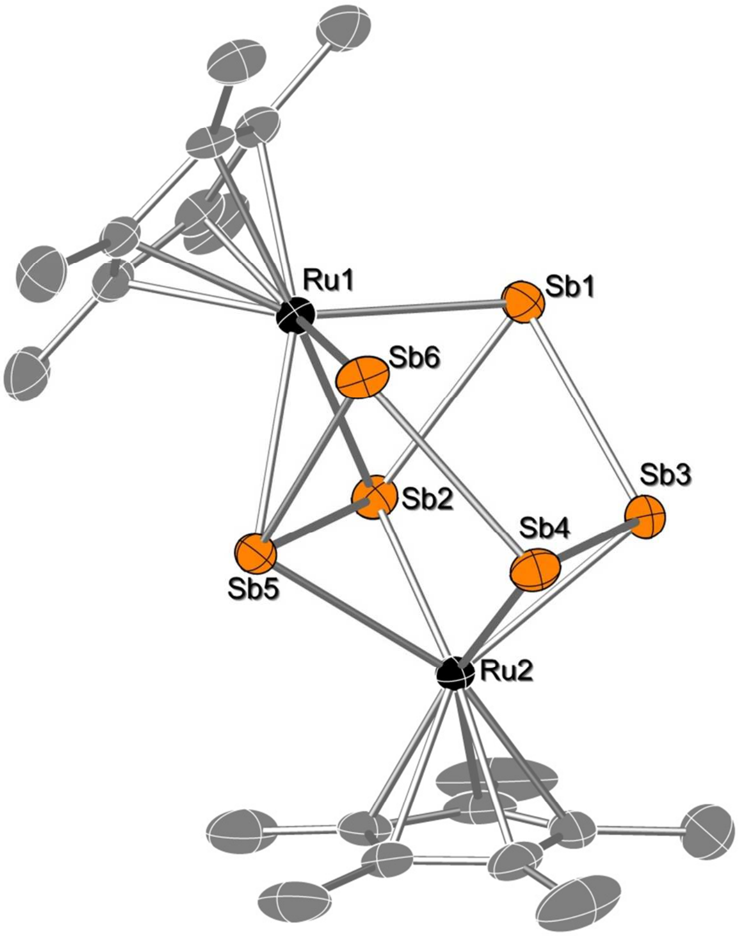

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