

# Mechanochemical Synthesis of Non-Solvated Dialkylaluminumyl Anion and XPS Characterization of Al(I) and Al(II) Species

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Dedicated to Professor Rainer Streubel on the occasion of his healthy retirement.

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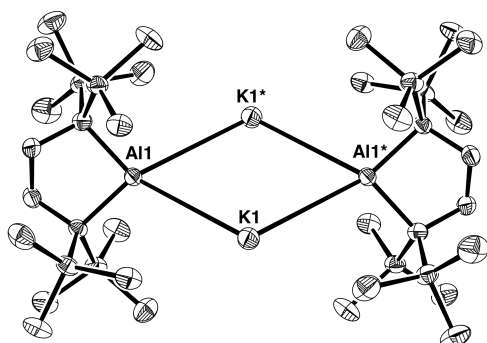
**Abstract:** A non-solvated alkyl-substituted Al(I) anion dimer was synthesized by a reduction of haloalumane precursor using a mechanochemical method. The crystallographic and theoretical analysis revealed its structure and electronic properties. Experimental XPS analysis of the Al(I) anions with reference compounds revealed the lower Al 2p binding energy corresponds to the lower oxidation state of Al species. It should be emphasized that the experimentally obtained XPS binding energies were reproduced by delta SCF calculations and were linearly correlated with NPA charges and 2p orbital energies.

Aluminum (Al) is the most earth-abundant metal and is widely used in industry. Metallic aluminum in zero-oxidation state [Al(0)], obtained through electrolytic reduction of naturally produced stable Al(III) oxide, and alloy are valued as lightweight materials. In molecular chemistry, Al(III) compounds are often used as Lewis acid catalysts, hydride reagents, and alkyl nucleophiles.<sup>[1]</sup> In contrast to the rich chemistry of Al(III) molecules, the molecular chemistry of aluminum in a low oxidation state [Al(II) and Al(I)] has

been developed in the last four decades.<sup>[2]</sup> All reported these molecules can be classified to three classes, radical anion,<sup>[3]</sup> base-stabilized neutral radical,<sup>[4],[5]</sup> and dialumanes.<sup>[6]</sup> The history of the molecular Al(I) chemistry is relatively short because it has grown in the last 25 years.<sup>[7]</sup> There are three different types of Al(I) molecules (Figure 1): (a) a neutral Al compound with one  $\sigma$ -bond, one lone pair of electrons, and two vacant p-orbitals (referred to as alandiyl, alumylene, and aluminylene),<sup>[8]</sup> and its base-stabilized form and oligomers,<sup>[9]</sup> including **A** and (Cp\*Al)<sub>4</sub> as the most widely studied species; (b) dialumene, an Al=Al double bond species;<sup>[6s, 10]</sup> (c) almanyil anion, an anionic Al(I) species having a lone pair of electrons on the Al atom.<sup>[11],[12]</sup> After the first discovery of **B** in 2018,<sup>[11a]</sup> the chemistry of almanyil anion has been rapidly developed in the past few years with a dianionic diamino or (alkyl)(amino) ligand,<sup>[11]</sup> including our latest contribution with a simple and scalable derivative **C**.<sup>[11k, 11l]</sup> In 2020, we also contributed to this chemistry with alkyl-substituted Al(I) anion **D** having a dianionic cyclic-alkylene ligand.<sup>[12]</sup>

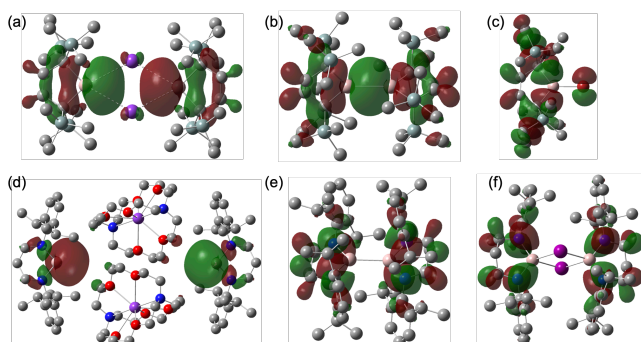


**Scheme 1.** Synthesis of dimeric alumanylpotassium **1** and tetraaminodialumane **5** ( $\text{Si} = \text{SiMe}_3$ , Dip = 2,6- $\text{Pr}_2\text{C}_6\text{H}_3$ ). [a] Yield in parentheses was determined by  $^1\text{H}$  NMR with  $^t\text{Bu}_3\text{C}_6\text{H}_3$  as an internal standard.



**Figure 3.** Molecular structure of **1** with thermal ellipsoids at 50% probability; all hydrogen atoms are omitted for clarity.

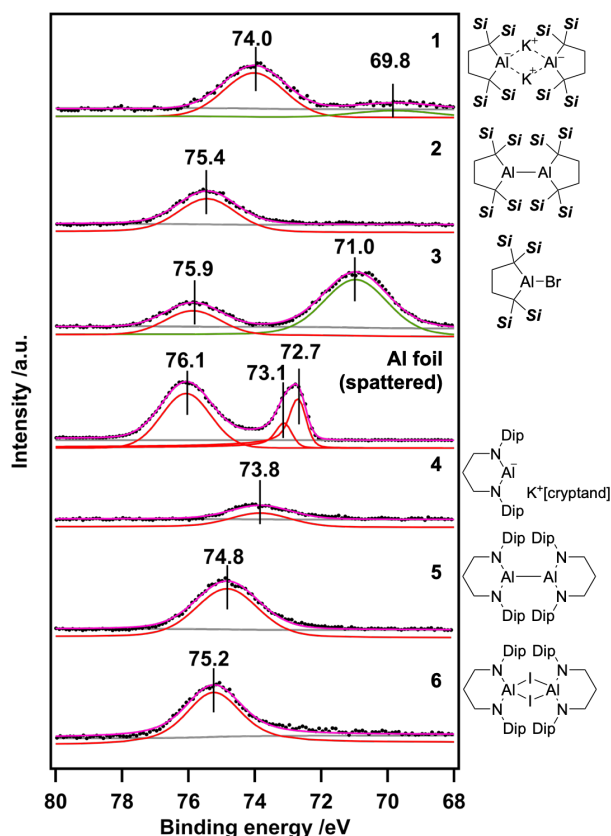
To reveal electronic structure of **1-6**, DFT calculations were performed at the B3LYP/def2svp level of theory (Figure 4). All molecules except for **4** were optimized for their one asymmetric unit obtained by crystallographic analysis, while **4** was optimized for its two asymmetric units to keep the interaction between the anionic aluminum atom and the  $\text{K}^+$ [cryptand] cation. The highest occupied molecular orbital (HOMO) of **1** is differently phased two lone pairs of electrons that are located mainly on the Al atom. The atoms in molecules analysis for **1** showed a polar character of the Al-K bond with a small  $\rho(r)$  value ( $0.010 e/a^3_0$ ) and a positive  $\nabla^2\rho(r)$  value ( $0.021 e/a^5_0$ ). A natural population analysis (NPA) of **1** revealed that Al and K atoms are positively and differently charged (Al: +0.566, K: +0.838). Thus, the Al-K bond in **1** can be considered as a polarized bond between  $\text{Al}^-$  and  $\text{K}^+$ . This characteristics are similar to those observed in the previously reported Al anions.<sup>[11],[12]</sup> Similarly, the anionic parts of **4** possesses a lone-pair character at the Al centers with opposite phases for each Al atom. In contrast to that dialkyldialumane **2** has a significant contribution of the Al-Al bond to HOMO, diaminodialumane **5** exhibits non-bonding N-Al-N character. Bromoalumane **3** shows an antibonding combination between Al-C bond and a lone pair of electrons on the Br atom, while the dimeric iodoalumane **6** has non-bonding N-Al-N character.



**Figure 4.** HOMOs of (a) **1**, (b) **2**, (c) **3**, (d) **4**,<sup>[a]</sup> (e) **5**, and (f) **6** calculated at B3LYP/def2svp level of theory. [a] calculated for two asymmetric units.

It is suggested that the formal oxidation states of the Al atom in the Al anions **1** and **4** are I, those in dialumanes **2** and **5** are II, and those in haloalumanes **3** and **6** are III. To experimentally understand the difference in the Al oxidation states **1-6**, XPS spectra of **1-6** were measured (Figure 5). A single Al 2p XPS peak of Al(I) species, dialkyl-Al anion **1** and diamino-Al anion **4**, was observed at 74.0 eV (**1**) and 73.8 eV (**4**), respectively, which is close to that (73.75 eV) of the reported Al(I)-phosphomolybdate solid<sup>[14]</sup> although it would have uncertainty (see introduction). These values for **1** and **4** were much smaller than that of alumina [75.6 eV: Al(III)]<sup>[22]</sup> and closer to that of aluminum foil [73.1 eV for Al 2p<sub>1/2</sub> and 72.7 eV for Al 2p<sub>3/2</sub>: Al(0)],<sup>[23]</sup> supporting the reduced state of the Al(I) center in **1** and **4**. The Al 2p XPS peaks of **2** and **5** were observed at 75.4 eV (**2**) and 74.8 eV (**5**), respectively, which were larger than those of **1** and **4**, being consistent with that the Al(II) centers of **2** and **5** are electronically more positive than those of **1** and **4**. Similarly, the Al 2p XPS peaks of **3** and **6** exhibited the Al 2p XPS peak at 75.9 eV (**3**) and 75.2 eV (**6**), respectively, which are further increased, reflecting the most electronically positive characters of their Al centers among these Al species **1-6**. The core level of binding energies of **1-6** (for Al 2p and Br 3d states) were calculated by the delta SCF method<sup>[24]</sup> implemented in the OpenMX code.<sup>[25]</sup> The order of calculated binding energies (**1** < **2** < **3**, **4** < **5** < **6**) fit to that of experimentally obtained binding energies as summarized in Table 1. The means absolute error of the calculated binding energies vs. experimental data for **4-6** (0.11 eV) is smaller than that of **1-3** (0.53 eV). The delta SCF calculations could assign other peaks in **1** (KBr impurity, 69.44 eV) and **3** (Br bonded to Al, 70.81 eV) as well as peaks of Al foil [2p<sub>3/2</sub> 72.65 eV, 2p<sub>1/2</sub> 73.16 eV, surface Al<sub>2</sub>O<sub>3</sub> 2p (av.) 76.07 eV]. Thus, it was experimentally and theoretically confirmed that the difference in Al oxidation states of **1-6** reflects binding energies in the XPS analysis, supporting the attribution of formal oxidation states of the Al centers in **1-6**.

The binding energies obtained by experimental XPS analysis were found to be correlated with NPA charges and energy levels of 2p orbitals (Table 1). As the XPS Al 2p binding energies increased, NPA charges increased as **1** < **2** < **3** and **4** < **5** < **6**. This is consistent with the increase of the formal oxidation states for these compounds. Furthermore, the energy levels of 2p-orbitals on the Al atom also increased in the same order. It should be emphasized that these values are linearly correlated with  $R^2 > 0.98$  (Figure 6), although the accurate physical interpretation for this correlation should be studied in the future.

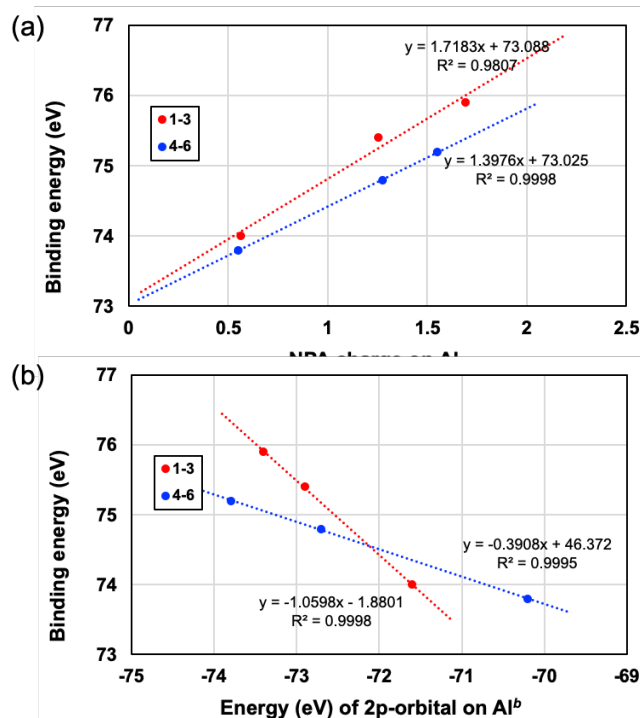


**Figure 5.** Al 2p XPS spectra of **1-6** and Al foil.<sup>[a]</sup> The peaks at 69.8 eV (for **1**) and 71.0 eV (for **3**) can be assigned to Br 3d core-levels of small impurities (KBr) of **1** and the bromide on the Al atom in **3**. [a] Al foil was spattered to remove oxidized film from the surface (the peak at 76.1 eV can be assigned as the aluminum oxide on surface).

**Table 1.** Summary of experimentally obtained binding energy by XPS measurement, calculated binding energy using delta SCF method, calculated NPA charges and energy of 2p orbital on Al atom at the B3LYP/def2svp level of theory.

compound	1	2	3	4	5	6
Binding energy in XPS analysis (eV)	74.0	75.4	75.9	73.8 <sup>[a]</sup>	74.8	75.2
Calculated binding energy (eV) <sup>[b]</sup>	74.14	74.53	75.53	73.97	74.68	75.24
NPA charges on Al	0.566	1.254	1.692	0.552 <sup>[a]</sup>	1.278	1.550
Calculated energy (eV) of 2p orbital on Al <sup>[c]</sup>	-71.6	-72.9	-73.4	-70.2 <sup>[a]</sup>	-72.7	-73.8

[a] calculated for two asymmetric units, [b] averaged values from those of 2p<sub>3/2</sub> and 2p<sub>1/2</sub> states with consideration of degeneracy, [c] calculated as an average of core 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> orbitals from NBO analysis.



**Figure 6.** Linear relationship between the observed binding energy of **1-6** in XPS analysis and (a) NPA charge on the Al atom, or (b) the energy levels of the calculated 2p-orbitals of Al atom.

In conclusion, we reported the synthesis of dialkylaluminumpotassium dimer **1** with ball-milling reduction. A combination of the X-ray structural analysis and DFT calculations revealed the electronic structure of **1** with a contribution of lone-pair and vacant 3p-orbital on the Al(I) center. Experimental and theoretical XPS analysis of Al anions, dialumanes, and haloalumanes revealed their different Al 2p binding energies, depending on the difference in the oxidation states. The experimentally observed XPS binding energies were also found to be linearly correlated with calculated NPA charges and 2p energy levels of the Al atom, which fairly supported the attribution of Al formal oxidation states. These findings would open new ways to investigate unusual oxidation states of main group element chemistry and a reference dataset for Al(I) and Al(II) species for XPS analysis.

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[26]-[49]</sup>

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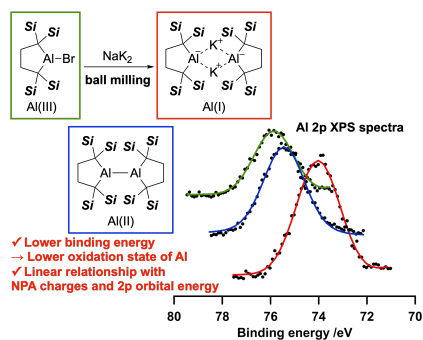
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## Entry for the Table of Contents



A non-solvated alkyl-substituted Al(I) anion dimer was synthesized by a reduction of haloalumane precursor using a mechanochemical method. The crystallographic and theoretical analysis revealed its structure and electronic properties. Experimental XPS analysis of the Al(I) anions with reference compounds revealed the lower Al 2p binding energy corresponds to the lower oxidation state of Al species. It should be emphasized that the experimentally obtained XPS binding energies were reproduced by delta SCF calculations and were linearly correlated with NPA charges and 2p orbital energies.