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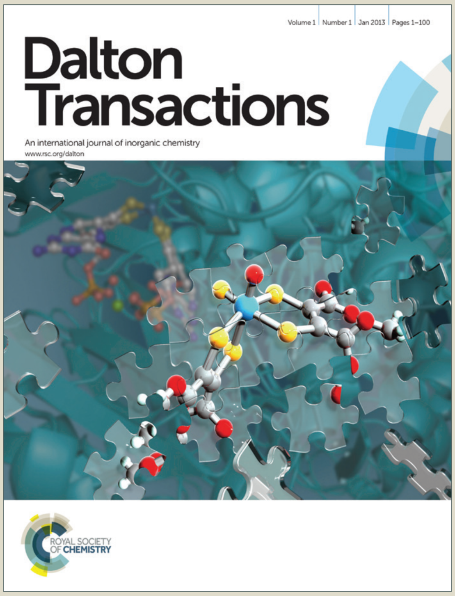

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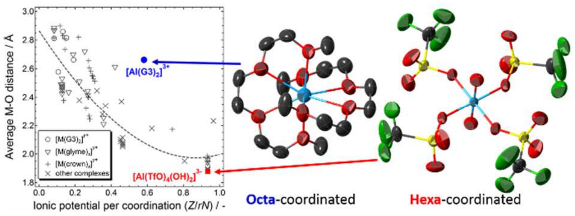
Graphical Abstract

A novel aluminum-based homometallic double complex salt incorporating octa-coordinated cationic and hexa-coordinated anionic complexes were characterized for the first time.



Key Word: Aluminum complex, homometallic double complex salt, crystal structure, coordination chemistry

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Extraordinary Aluminum Coordination in a Novel Homometallic Double Complex Salt†

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We have characterized a novel aluminum-based homometallic double complex salt, incorporating discrete octa-coordinated cationic $[Al(G3)_2]^{3+}$ and hexa-coordinated anionic $[Al(TfO)_4(OH)_2]^{3-}$ complexes (G3 = triglyme, TfO = trifluoromethanesulfonate). X-ray crystallogaphy, Raman spectra, and DFT calculations demonstrate extraordinaty weak Al^{3+} coordination in $[Al(G3)_2]^{3+}$.

Double complex salts (DCSs), where both cationic and anionic constituents are composed of complex ions, are a promising class for various developments within the field of material sciences. Owing to their designable diversity and remarkable properties arising from the intrinsic nature of constituents, many attempts have been made to prepare a wide variety of DCSs for very different application targets; drugs, catalysts, stimuli-response materials, and analytical reagents.[1] So far, however, only a few examples of DCSs containing Li^+, Na^+, and Al^{3+} ions have been reported, probably due to their poor double-complexation ability.[2] Recently Li- and Na-based monometallic complexes with different glymes have attracted attention as promising electrolytes for highly efficient electrochemical energy storage, Li-ion and Na-ion secondary batteries, much owing to outstanding properties, such as high ionic conductivity and excellent electrochemical stability.[3] The same chemistry could be applicable also to aluminum-based materials, to promote even further enhanced electrochemical energy storage systems *e.g.* secondary Al-batteries. Furthermore, moving from monometallic to bimetallic complexes (such as DCSs) can contribute to further improve the overall electrochemical activity, as both cationic and anionic mobile species can be active, which might be needed to accomplish functional Al electrolytes.

DCSs can in general be subdivided into two groups based on the metal constituents; homometallic and heterometallic DCSs. Many homometallic DCSs incorporate metal cations complexed by ether-based ligands and the counteranions as metal cations coordinated by anions.[2b,4] On the other hand, in heterometallic DCSs, both cations and anions are less limited to involving ether-based ligands.[2a,5] In stark contrast to these in general structurally very diverse DCSs, all aluminum-based DCSs ever reported incorporate the same tetrahedral alkylhaloaluminate $[AlR_nX_{4-n}]^-$ complex unit (n ≤ 4, R and X denote alkyl group and halogen atom, respectively),[6] with to the best of our knowledge only a few exceptions; the homometallic $[Al(DMSO)_6][Al(NCS)_6]$[2d] and the heterometallic $[Al(L^1)_2][Li(L^2)_2]$ (where L^1 and L^2 indicate bis(*N*,*N*'-di-*t*-butylethylenediamido) and bis(tetramethylethylenediamino), respectively).[2a] This clearly indicates alkylhaloaluminate-free aluminum-based DCSs to be quite rare.

In general, the Al^{3+} ion preferentially adopts tetra- and/or hexa-coordination in the crystalline state, irrespective of if it results in cationic or anionic Al-complexes. An octa-coordinated Al^{3+} ion has been found in a single case; in an $[Al(BH_4)_4]^-$ anionic complex,[7] where eight hydrogen atoms from four BH_4^- units are arranged in a distorted tetrahedral configuration, balanced by non-metallic organic cations (hence classified as conventional monometallic complex salts). An octa-coordinated Al^{3+} *cationic* complex has, however, never been reported. In this article, we report on the first ever aluminum-based homometallic DCS (DCS **1**). Furthermore, DCS **1** incorporates both a unique octa-coordinated Al^{3+} cationic complex and a hexa-coordinated Al^{3+} anionic complex.

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Single crystals of DCS **1** were isolated from a solution of aluminum trifluoromethanesulfonate ($Al[TfO]_3$) dissolved in triglyme (G3), after one month of storage at ambient temperature. DCS **1** crystallizes with one quarter of the molecular entities in the asymmetric unit, while the remaining fragments are generated by symmetry operation. The crystal structure[8] of DCS **1** incorporates two discrete ionic species; the $[Al(G3)_2]^{3+}$ cation and the $[Al(TfO)_4(OH)_2]^{3-}$ anion, as shown in Fig. 1. Additional G3 solvent molecules, with four different disordered arrangements (Fig. S1 and S2 in ESI), are co-crystallized with the ionic species. As all experiments, sample preparation and X-ray diffraction measurements, were performed under a dry inert atmosphere, the origin of the OH groups in the anionic complex is unclear at present. A highly characteristic Al^{3+} coordination was found in the $[Al(G3)_2]^{3+}$ cation, where a single Al^{3+} ion is surrounded by two G3 molecules in a meridional fashion and all eight ether oxygen atoms of the two G3 molecules coordinate to the Al^{3+} ion, thereby forming a distorted dodecahedral octa-coordinated cationic complex. The coordination environment of this octa-coordinated Al^{3+} ion is hence completely different from that of the only other known octa-coordinated Al complex, the $[Al(BH_4)_4]^-$ anion.[7] This kind of meridional coordination is also found in various systems involving metal ions complexed with two equivalent glyme molecules, G*n*.[3e,9] Furthermore, the preferential coordination of ions is known as one of the determining factors for solvate structures. Although Al^{3+} potentially forms tetra-coordinated ions, the common example being the tetrahedral alkyl-haloaluminate $[AlR_nX_{4-n}]^-$ anions,[6] a single G3 molecule cannot wrap around the Al^{3+} ion to create tetrahedral coordination due to conformational restrictions, even if it has four ether oxygen atoms available. Moreover, G3 possesses relatively strong solvation ability compared to the $[TfO]^-$ anion, as demonstrated for the Li salt-glyme systems.[10] This combination of both conformational and solvation nature of G3 likely causes the very special arrangement that we here find in the $[Al(G3)_2]^{3+}$ cation. In contrast, the surrounding of the Al^{3+} ion in the $[Al(TfO)_4(OH)_2]^{3-}$ anion is a very typical octahedron; the Al^{3+} ion is coordinated by four oxygen atoms from four different $[TfO]^-$ anions arranged in a plane and two oxygen atoms from two different OH^- groups located at the remaining vertices, resulting in a hexa-coordinated anionic complex. An analogous octahedral configuration was observed in the $[AlCl_2(THF)_4][AlCl_4]$ crystal.[6c] On the basis of the Cambridge Crystallographic Data Centre (CCDC), $[Al(urea)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$, $[Al(DMSO)_6]^{3+}$, and $[Al(NCS)_6]^{3-}$, are complex ions with similar octahedral configurations.[2d,11]

In the DCS **1** crystal, the $[Al(G3)_2]^{3+}$ cations and the $[Al(TfO)_4(OH)_2]^{3-}$ anions are arranged individually along the *c*-axis, and the $[Al(TfO)_4(OH)_2]^{3-}$ anions and the G3 molecules are alternately stacked through hydrogen-bonding between G3 ether oxygen atoms and OH^- hydrogen atoms with four different disordered arrangements (each site occupancy = 0.25, Fig 2). The very long distances between the Al nuclei of the cationic and anionic complexes strongly suggest extremely weak interionic interactions, due to their highly crowded surroundings. In contrast to these large separations between the cationic and anionic complexes, the (O–)H···O distances between the $[Al(TfO)_4(OH)_2]^{3-}$ anions and the G3 molecules are in the range 1.919–1.927 Å, indicating relatively strong hydrogen bonding. Alternating stacking and this strong interaction result in the disorder of the ether oxygen atoms of the G3 molecules.

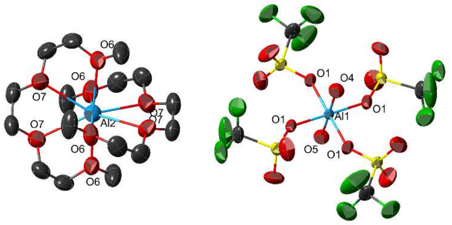

Fig. 1 Configurations of the $[Al(G3)_2]^{3+}$ cation (left) and the $[Al(TfO)_4(OH)_2]^{3-}$ anion (right) in the crystal of DCS **1** as thermal ellipsoid models. Hydrogen atoms and the labels of non-coordinating atoms are omitted for clarity. Thermal ellipsoids were set at 50% probability. Light blue, Al; red, O; gray, C; yellow, S; green, F. Selected bond lengths [Å]: Al1–O1 1.8769(17), Al1–O4 1.874(4), Al1–O5 1.873(4), Al2–O6 2.512(2), Al2–O7 2.739(3).

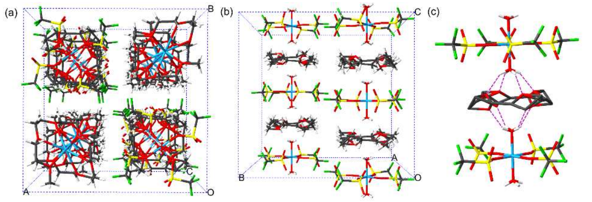

Fig. 2 (a) Packing diagram of DCS **1** along the *c*-axis in perspective view; (b) arrangement of the anionic complex $[Al(TfO)_4(OH)_2]^{3-}$ and the G3 molecules in the crystal; (c) hydrogen-bonding schematic between $[Al(TfO)_4(OH)_2]^{3-}$ and G3. In (c) hydrogen atoms of G3 were omitted for clarity and hydrogen bonds are indicated by dotted lines. Light blue, Al; red, O; gray, C; white, H; yellow, S; green, F.

The most striking feature of DCS **1** is the metal–oxygen (M–O) distances, especially in the $[Al(G3)_2]^{3+}$ cations. For typical ether-based complexes, the Al–O distances lie in the range 1.92–2.26 Å.[2f,6] Strongly polarizable and/or small anionic ligands, such as H_2O, DMSO, and acetylacetonate, can provide structurally favorable octahedral coordination, resulting in rather much shorter Al–O distances, *ca.* 1.86–1.91 Å.[11,12] In the case of DCS **1**, the Al–O distances of the octahedral anionic complex $[Al(TfO)_4(OH)_2]^{3-}$ are 1.873–1.874 Å, implying preferential Al^{3+} coordination and ligation via interionic (coulombic) interactions. On the other hand, the distances in the $[Al(G3)_2]^{3+}$ cation deviate strongly from those anticipated on the basis of previous reports; they are as long as 2.512 and 2.739 Å despite involving the small and trivalent Al^{3+} ion as the central atom – and thus a quite extraordinary coordination.

In general, quite short M–O distances will be found among the cases incorporating small and multivalent metal ions, owing to the strong interaction induced by strong electric fields. The oxygen coordination of various metal ions is well characterized in crystal structures, and the M–O distances in different complexes are likely to follow the above inclination. Hence, with a clear exception for the $[Al(G3)_2]^{3+}$ cation, a roughly linear relationship between the average M–O distances and ionic radii of the central metal ions is expected and indeed observed, irrespective of the metal species, ligand structure, and ligation manner, as shown in Fig. 3(a).[4,9,13,14] The ionic radius (*r*) changes depending the coordination number for the same metal ion. The radius of the octa-coordinated Al^{3+} ion and some other cases were estimated by extrapolation based on the correlation between ionic radius and coordination number.[15] Also various meridionally coordinated $[M(G3)_2]^{y+}$ complexes involving different metal ions as central atoms exhibit a similar relationship. The latter observation further emphasizes the special coordination of the Al^{3+} ion in the $[Al(G3)_2]^{3+}$ cation. It is well known that the valence and the coordination number of metal ions strongly impact on the strength of their electric field effects toward each single ligation. Altogether, the electric field effects dominate the M–O interactions, thus the ionic radius *r* should be normalized by the ionic potential, to further rationalize the coordination in $[Al(G3)_2]^{3+}$.

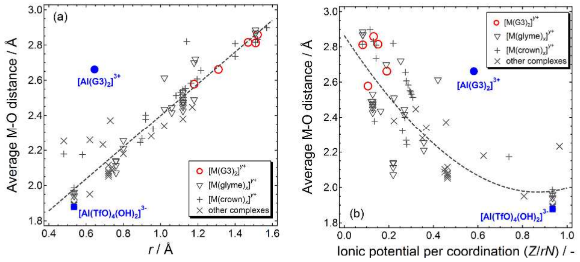

Fig. 3 (a) Relationship between average metal–oxygen (M–O) distances and ionic radii of coordinated metal ions (*r*) in different complexes; (b) Variation of average M–O distances of various complexes with the ionic potential per single coordination. The dotted lines are guide to the eye only. "Other complexes" indicate the complexes involving any M–O coordination.

Fig. 3(b) shows the variation of M–O distances in different complexes with ionic potential per coordination number *Z*/*rN*, where *Z* and *N* are valence and coordination number of coordinated metal ions in each complex, respectively. In accordance with literature data on *N*-methylacetamide complexes with alkali and alkaline earth metals,[13] Fig. 3(b) reveals a relation between M–O distances and *Z*/*rN*, with the one exception – that of [Al(G3)$_2$]$^{3+}$. The quite large Al–O separations in the [Al(G3)$_2$]$^{3+}$ cation, despite the relatively large ionic potential, imply extraordinary weak coordination of the G3 molecules towards the Al^{3+} ions. Steric hindrance around the small and therefore highly crowded Al^{3+} ion is a likely reason.

The complexation of Al[TfO]$_3$ with G3 can also be detected and qualified by analyzing the effects on the intra- and intermolecular vibrational modes of each constituent. Indeed, DCS **1** provides a characteristic Raman spectrum; although no bands for pure G3 or pure Al[TfO]$_3$ are discernible in the range 865–890 cm^{-1}, an intense band is clearly observed at 872 cm^{-1} (Fig. S3a). This vibrational mode is readily assigned to a combination of CH$_2$ rocking, *r*(CH$_2$), and CO stretching, *v*(CO), modes of G3 in the [Al(G3)$_2$]$^{3+}$ cation, based on previous studies of complexation of metal ions with glymes.[3] In addition, by comparison with a pure G3 spectrum, with many bands arising from many different conformers overlapping severely in the range 800-860 cm^{-1}, as deciphered in detailed for various G*n* molecules,[16] the band located at 850 cm^{-1} is assignable to similar intramolecular vibrations of non-coordinating G3 solvent molecules within DCS **1** (Fig. 2 and Fig. S1). Also the [TfO]$^-$ anion coordination in the anionic complex [Al(TfO)$_4$(OH)$_2$]$^{3-}$ can be characterized based on the Raman spectrum. The Raman active symmetric SO$_3$ stretching mode is known to be sensitive to the coordination manner of [TfO]$^-$ anions and to lie in the spectral range 1100–1000 cm^{-1}.[17] As expected, the DCS **1** and the parent Al[TfO]$_3$ salt provide completely different spectra; a single intense peak at 1057 cm^{-1} with a small shoulder in the former and two sharp peaks located at 1068 and 1046 cm^{-1} in the latter (Fig. S3b). Based on comparisons with the crystal structures of various homoleptic aluminum salts[12,18] and the Raman spectra of M^{y+}[TfO]$_y$ salts,[17a,19] three [TfO]$^-$ anions are likely to coordinate to a single Al^{3+} cation bidentately, thereby constructing a hexa-coordinated octahedron in the Al[TfO]$_3$ salt. In DCS **1**, four [TfO]$^-$ anions coordinate to a single Al^{3+} cation monodentately (Fig. 1). The loss of the split band feature when moving from the pure Al[TfO]$_3$ salt to DCS **1** can thus be explained by a change in the site symmetry and the correlated motions of the [TfO]$^-$ anions.

As a final measure of the (relative) interaction strengths within the cationic and the anionic parts of DCS **1**, we apply DFT calculations on the discrete complex units; [Al(G3)$_2$]$^{3+}$ and [Al(TfO)$_4$(OH)$_2$]$^{3-}$. The interaction energies reveal much stronger interactions within the anionic [Al(TfO)$_4$(OH)$_2$]$^{3-}$, (*ca.* −9300 kJmol^{-1}) than within the cationic [Al(G3)$_2$]$^{3+}$ (*ca.* −3100 kJmol^{-1}) – thus *ca.* only 1/3 as strongly bound Al^{3+} in the latter. While this measure, based on simply removing the central Al^{3+} cation, likely suffers from a significant basis set superposition error (BSSE) in the former complex (due to the artificial construction of a −6 charged feature), a second measure based on a reference system consisting of the energies of the separate building blocks optimized separately confirms Al^{3+} to be much more weakly coordinated in the cationic complex (*ca.* 60%, *ca.* −3200 kJmol^{-1} and *ca.* −5200 kJmol^{-1}, respectively).

In all, the obtained crystal structure of DCS **1** and the various characterization methods applied together demonstrate the unique and remarkably weak coordination of G3 molecules to Al^{3+} ion to form the [Al(G3)$_2$]$^{3+}$ cation. Furthermore, by analogy with glyme-based monometallic molten complex electrolytes, wherein the desolvation process largely determines the charge transfer reaction of M/M^{y+} at the metal | electrolyte interface,[20] the moderate ion-dipole interaction arising from the extraordinary Al^{3+} coordination infers some promise of electrochemical activity, opening up possibilities for novel aluminum conducting electrolytes with the active species being cationic. The electrochemical studies are in progress and will be reported in the forthcoming paper.

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